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THE RAYLEIGH AND RAMAN SCATTERING

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TRANSLATOR'S NOTE

A comprehensive account is given of the Raman effect of isolated systems, atoms, and molecules. The first three chapters introduce the subject adequately and reduce to a minimum the necessity for a prior knowledge of radiation theory.

Conventional physical notations have been followed. The footnotes, along with the references, have been placed at the end of each chapter because they are often lengthy in the original German edition.

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THE RAYLEIGH SCATTERING AND RAMAN EFFECT[1]

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PART I
GENERAL THEORY

Chapter 1. Introduction

When radiation passes through matter, aside from that reflected and refracted, weak randomly scattered radiation will appear. The blue of the sky represents such scattered radiation. It manifests itself in the laboratory by the resonance-fluorescence of dilute gases and by the blue opalescence of gases near their critical points (or near the critical mix point of partially soluble liquids). Under ordinary conditions the scattering effects are readily detected in pure liquids but the purification of the liquids and the thorough removal of dust particles require considerable care. In 1869 Lallemand discovered the scattering of liquids and concluded that this property is characteristic of the liquid.[2] However, his studies did not achieve the necessary recognition since the liquids he used were not trusted to be free of dust.[3] In 1913, Martin rediscovered the scattering in liquids.[4] At that time, his research was extended to investigation of the blue color of the sky and of the critical opalescence. The studies in both fields proceeded independently for many years.

Originally, the color of the sky was attributed to particles suspended in air. This view which originated with Leonardo da Vinci,[5] together with the assumptions about the nature of the particles (dust, water droplets, ice crystals), form the basis of the investigations by Newton, Clansius, Brucke, and Tyndall and of the early studies by Lord Rayleigh. In 1873 Maxwell[6] concluded from Rayleigh's work that the molecules themselves constitute the scattering particles and believed that the scattering radiation may facilitate the identification of molecules. Twenty-six years later, Lord Rayleigh[7] revived these ideas. With the aid of these assumptions and by using an estimated value for the transparency of air, he demonstrated that the Loschmidt number agreed to within an order of magnitude with values known at that time. He also attempted to explain the polarization of the radiation from the sky in terms of the anisotropy of the gas molecules. Later experiments on atmospheric extinctions substantiated Lord Rayleigh's suppositions and were used to re-evaluate the Loschmidt number.

The electron theories of dispersion of Lorentz and Planck lead to the same relations between refractive index and scattering radiation as Rayleigh's theory; in addition, the dependence of the refractive index on the molecular eigenfrequencies was properly expressed. This made it possible to recognize the principles underlying resonance-fluorescence which was discovered by Wood[8] in 1905. In 1910 a series of important questions was settled in a classic paper by Lorentz.[9] At the same time, Smoluchowski,[10] starting from apparently different premises, presented an explanation of the critical opalescence. He considered density fluctuations, rather than molecules, as the scattering centers, invoking the increasing fluctuations near the critical point to explain the opalescence. Einstein[11] treated this problem quantitatively, while others generalized and proved it experimentally. Today we know that critical opalescence may be interpreted by a generalization of Rayleigh's theory. The difference between "molecular theory" and "fluctuation theory" is a formal one only.

In 1915, Cabannes[12] demonstrated scattering of light by gases. Soon thereafter, Smoluchowski[13] and Strutt[14] (the present Lord Rayleigh) reported analogous results, and, in addition, Strutt was able to account for the partial polarization of the scattered radiation. The systematic experimental and theoretical investigations in this field had their inception with these finds.

At the time when Maxwell concluded that the radiation from the sky was of molecular origin, Lommel assumed the anharmonic oscillator as a model for the scattering molecule.[15] Starting with the elastic light theory, he developed the complete mathematical theory of scattered radiation. Aside from the scattering of the unshifted frequency (Lommel called it "isochromatic fluorescence" and associated it with the observations made by Lallemand), summation and difference tones occur between the incident frequency and the eigenfrequency. Lommel discussed these terms with respect to resonance and different incident frequencies.

In the later Lorentz electron theory, which was applied to the dispersion problems, these terms do not appear. They vanish because of the assumption of quasi-elastic forces. For this reason the scattering theory no longer received any attention, except for a few general remarks on optic vibrations by Lord Rayleigh. In 1923, Smekal, using light quantum considerations, discussed the effect of a light quantum of any frequency on atomic transitions conserving the energy by means of light quanta.[16] If the final state is above the initial state, the frequency of the scattered radiation is lower ($\nu - \Delta E/h$) than that of the incident radiation, and higher ($\nu + \Delta E/h$) in the reverse case.

Stimulated by Smekal's studies, Kramers and Heisenberg showed classically the development of the modified scattered radiation.[17] By transferring the corresponding classical wave theory, they derived the quantum theoretical scattering formula. The importance of this investigation far surpasses the particular problem dealt with, since it became the starting point of the modern quantum mechanics. The results remains completely valid in the modern theory. In his radiation theory, Dirac gave the most conclusive derivation.[18]

In 1906, the resonance phenomenon of the modified scattered radiation of iodine vapor (incident frequency identical with absorption frequency) was observed by Wood.[19] Partially analogous observations were performed by Fuchtbauer and Wood, while studying the optical excitation of mercury vapor. These observations were interpreted differently before the advent of the modern quantum theory. Hence, the observations of the modified scattering for any given incident frequency, carried out by Raman in the course of systematic investigations of light scattering of liquids, were of great importance.[20] At practically the same time, Landsberg and Mandelstam[21] made similar observations by studying the light scattering of crystals.[22] More than 500 studies deal with this phenomenon.[23]

REFERENCES AND FOOTNOTES

1. The following discussion deals with the quantum theory of light scattering and its application to isolated systems such as atoms and molecules. The problems of molecular interaction associated with the application of the theory to aggregate systems, i.e., gases, liquids, and crystals, are not presented. Even within the narrow scope of the present discussion no effort for completeness has been made. Questions that are already treated in detail in available texts (see Cabannes, La diffusion moléculaire de la lumière; Kohlrausch, Der Smekal-Raman Effekt) are discussed only when the new approach resulted in significant progress. Experimental techniques are described in the above texts.

   The author wishes to thank R. Baer, A. Langseth, J. Rud Nielsen and F. Rasetti for the spectra reproduced in Figs. 5, 14, and 17.
2. A. Lallemand, Compt. rend. 69, 190, 283, 918, 1294 (1869); J. phys. et radium 5, 329 (1876).
3. Lallemand's contention that the scattering of a series of saturated hydrocarbons increases with increasing refractive index indicates that he observed a genuine molecular scattering.
4. W. H. Martin, Trans. Roy. Soc. Can. 7, 219 (1913).
5. Leonardo da Vinci, Trattato della Pittura.
6. Lord Rayleigh, Phil. Mag. 47, 375 (1899). Coll. papers IV, p. 397.
7. Lord Rayleigh, ibid.
8. R. W. Wood, Phil. Mag. 10, 513 (1905).
9. H. A. Lorentz, Proc. Amsterdam 13, 42 (1910).
10. M. V. Smoluchowski, Ann. Physik 25, 208 (1908).
11. A. Einstein, Ann. Physik 33, 1275 (1910).
12. J. Cabannes, Compt. rend. 160, 62 (1915).
13. M. V. Smoluchowski, Bull. Ac. Soc. Cracovie (1916), 218.
14. R. J. Strutt, Proc. Roy. Soc. (London) 94, 453, 95, 155 (1918).
15. E. Lommel, Poggendorffs Ann. 143, 26 (1871), Wiedemanns Ann. 3, 251 (1878).
16. A. Smekal, Naturwiss. 11, 873 (1923).
17. H. A. Kramers and W. Heisenberg, Z. Phys. 31, 681 (1925).
18. P. A. M. Dirac, Proc. Roy. Soc. (London) 114, 710 (1927).
19. W. R. Wood, Phys. Z. 9, 450 (1908)
20. C. V. Raman, Indian J. Phys. 2, 387 (1928); C. V. Raman and U. S. Krishnan, Nature 121, 501 (1928).

21. G. Landsberg and L. Mandelstam, Naturwiss. 16, 57, 772 (1928).

22. Cabannes reported (Compt. rend. 186, 1201 (1928); Y. Rocard, ibid. 1107) some earlier experiments involving optical vibrations of gases in connection with Raman's communication. However, these experiments yielded negative results because of insufficient intensity.

23. The present remarks do not warrant a complete literature survey; they merely emphasize the highlights in the development. A summary of numerous theoretical studies can be found in the dissertation by Rocard (Ann. phys. 10, 116 (1928).

The bibliography given by Cabannes in La Diffusion Moléculaire de la Lumière, Paris, (1929) and by Kohlrausch in Der Smekal-Raman Effekt, Berlin, (1931) should be consulted.

Chapter 2. The Quantum Theory of Scattering Phenomena. Corpuscular and and Wave Concepts.

In the preceding chapter, the corpuscular and wave concepts were used to describe the same phenomenon; the clarification of the relationship between the two constitutes one of the main achievements of the modern quantum theory. According to Bohr and Heisenberg the description of each phenomenon may be given in terms of the corpuscular or wave concept.[1] Each of these concepts of space-time description--initially mutually exclusive--is useful only to a limited extent, the applicability of either being determined by the uncertainty principle. On the other hand, a complete description of the processes is possible by means of either concept, but when this is done each will lose part of its descriptive nature. With regard to the theory of radiation this implies the following:

1. Wave Concept: The field quantities satisfying Maxwell's equations are "probability amplitudes," the square of whose absolute quantity gives the probability of finding a light quantum in a given time-space region.

2. Corpuscular Concept: Light quanta obey the Bose-Einstein, rather than the Boltzmann, statistics. Knowledge of the presence of a particle (light quantum) in a cell of phase space increases the probability of finding a second one there. This situation, which can hardly be illustrated classically, gives rise to induced emission.

These relations are expressed formally by Dirac, who proved that a system of particles obeying the Bose-Einstein statistics is equivalent to a wave field.[2]

The scattering phenomena to be discussed presently can be understood by the use of classical wave theory. However, quantum mechanics must be invoked in order to correlate the scattering of the atoms and molecules with their structure and energy levels.[3] The progress in the field of scattering phenomena achieved by the quantum theory consists mainly--aside from clarifying the main principles discussed above--in the basic change in our concept of the structure of the scattering atoms and molecules, rather than in any altered description of the scattering process.

REFERENCES AND FOOTNOTES

1. N. Bohr, Atomtheoric and Naturbeschreibung, Berlin (1931); W. Heisenberg, "Die physikalishen Prinzipien der Quantumtheorie," Leipzig (1930).

2. P. A. M. Dirac, Quantum Mechanics, Oxford (1930).

3. For the special case of quantum transitions between vibrational states of heavy particles (nuclei) having constant electronic energy, the classical treatment (wave theory for radiation, and corpuscular theory for molecules) may be applied to another problem. The quantum theoretical transition frequencies of an oscillator are directly related to the classical eigenfrequencies and often, the uncertainty relations are of less importance because of the large mass of the nuclei. Many results concerning the molecular structure can be deduced classically, such as the selection rules, for instance. Quantum theory alters drastically the temperature function. The advantage of the quantum-mechanical method lies in its increased simplicity and in the fact that the significance of the results and the range of their validity may now be recognized. See Chapters 14 and 25. Phenomena which are greatly affected by the electronic configuration elude the classical approach. The polarization of the scattered rays, as far as they are not determined by the selection rules, can be treated quantum mechanically only.

Chapter 3. Correspondence Theory of the Scattering Phenomenon[1]

The correspondence principle leads to a simple derivation of the scattering formula. The radiation of a material system is given classically by the time-dependence of an electric moment. The variation of the eigenfunction resulting from an incident wave is determined, and the matrix elements of the electric moments are formed. Then using the correspondence principle the expression for the radiation is calculated. The theoretical justification for the application of quantum theory to matter and classical theory to radiation has been derived by Dirac and Heisenberg.[2, 3]

We now proceed with the calculations, given a system of particles and the time-dependent Schrödinger equation:[4]

$$(H_0 + (\hbar/i)\,\partial/\partial t)\Psi^{(0)}(q,t) = 0$$

$$(H_0^* - (\hbar/i)\,\partial/\partial t)\Psi^{(0)*}(q,t) = 0. \tag{3.1}$$

The energy operator H is given by the classical Hamiltonian when the momenta are replaced by $-(\hbar/i)\,\partial/\partial q$; q refers to the coordinates. The general solution is

$$\Psi^{(0)} = \sum_r a_r \psi_r \exp(-iE_r t/\hbar), \tag{3.2}$$

where a_r is an arbitrary constant; the ψ_r are no longer time-dependent but represent the solution of the time-independent Schrödinger equation by substituting Eq. (3.2) into (3.1); E_r denotes the energy of state r. If the system is in state k, the solution is

$$\Psi_k^{(0)} = \psi_k \exp(-iE_k t/\hbar). \tag{3.2a}$$

Let a light wave fall into this system such that its wavelength is large compared with the dimensions of the system and that its frequency is different from the eigenfrequencies of the system.[5] The electronic vector is

$$E = A^* \exp(2\pi i \nu t) + A \exp(-2\pi i \nu t). \tag{3.3}$$

A is a complex vector and A^* its complex conjugate. Equation (3.3) includes any polarization condition; for linearly polarized light:

$$A_y = A_z = 0 \qquad A_x = (1/2)\, E \exp(i\phi)$$

and

$$E_y = E_z = 0 \qquad E_x = E \cos(2\pi\nu t - \phi).$$

For circularly polarized light:

$$A_x = iA_y = (1/2) E \exp(i\phi), \quad A_z = 0$$

$\left\{ \begin{array}{l} A_y = -\frac{i}{2} E e^{i\phi} \\ A_y^* = \frac{i}{2} E e^{-i\phi} \end{array} \right.$

$$E_x = E\cos(2\pi\nu t - \phi), \quad E_y = E \sin(2\pi\nu t - \phi), \quad E_z = 0.$$

The system is perturbed by the external field E; the additional energy H is - (ME), where $M = \sum_j e_j r_j$ (e_j is the charge, r_j the position vector of the j-th particle). The Schrödinger equation of the perturbed system is now

$$(H_0 - (ME) + (\hbar/i)\, \partial/\partial t)\Psi(q,t) = 0$$

$$(H_0^* - (ME) - (\hbar/i)\, \partial/\partial t)\Psi^*(q,t) = 0. \tag{3.4}$$

Let us consider the case where the unperturbed system exists in state k, and choose as solution of Eq. (3.4)

$$\Psi_k = \Psi_k^{(0)} + \Psi_k^{(1)}. \tag{3.5}$$

Then, from Eqs. (3.4) and (3.1),[6]

[illegible]

$$(H_0 + \hbar\partial/i\partial t)\Psi_k^{(1)} = (EM)\Psi_k^{(0)}$$

see note p.9'

$$(H_0^* - \hbar\partial/i\partial t)\Psi_k^{(1)*} = (EM)\Psi_k^{(0)*}. \tag{3.6}$$

As solution of Eq. (3.6) we use

$$\Psi_k^{(1)} = \psi_k^+ \exp(-i/\hbar\,(E_k + h\nu)t) + \psi_k^- \exp(-i/\hbar(E_k - h\nu)t) \tag{3.7}$$

which, along with Eqs. (3.2a) and (3.3), yields Eq. (3.6). Equating the

see note p.9'

coefficients of equal time-dependence gives

$$\begin{aligned}
&H_0\psi_k^{+} - (E_k + h\nu)\psi_k^{+} = (AM)\psi_k;\\
&H_0\psi_k^{-} - (E_k - h\nu)\psi_k^{-} = (A^{*}M)\psi_k;\\
&H_0^{*}(\psi_k^{+})^{*} - (E_k + h\nu)(\psi_k^{+})^{*} = (A^{*}M)\psi_k^{*};\\
&H_0^{*}(\psi_k^{-})^{*} - (E_k - h\nu)(\psi_k^{-})^{*} = (AM)\psi_k^{*}.
\end{aligned} \tag{3.8}$$

The right side of the equations may be expanded in terms of the unperturbed eigenfunctions ψ_r:

$$\begin{aligned}
&(AM)\psi_k = \sum_r (AM_{kr})\psi_r\\
&(AM)\psi_k^{*} = \sum_r (AM_{rk})\psi_r^{*}, \text{ where}\\
&M_{kr} = \int \psi_r^{*} M\psi_k \, d\tau.
\end{aligned} \tag{3.9}$$

Let us consider now the time-independent Schrödinger equation

$$H_0\psi_r = E_r\psi_r, \quad H_0\psi_r^{*} = E_r\psi_r^{*}.$$

Then from Eqs. (3.8) and (3.9) the following expressions for $\psi_k^{\pm}$ are obtained in terms of the unperturbed eigenfunctions:

$$\begin{aligned}
&\psi_k^{+} = \sum_r \frac{(AM_{kr})}{E_r - E_k - h\nu}\,\psi_r && \psi_k^{-} = \sum_r \frac{(A^{*}M_{kr})}{E_r - E_k + h\nu}\,\psi_r\\
&(\psi_k^{+})^{*} = \sum_r \frac{(A^{*}M_{rk})}{E_r - E_k - h\nu}\,\psi_r^{*} && (\psi_k^{-})^{*} = \sum_r \frac{(AM_{kr})}{E_r - E_k + h\nu}\,\psi_r^{*}.
\end{aligned} \tag{3.9a}$$

The solution of Eq. (3.6) according to (3.7), is then given by

$$\Psi_k^{(1)} = 1/h \sum_r \psi_r \left[\frac{(AM_{kr})}{\nu_{rk} - \nu} \exp\left(- i/\hbar\, (E_k + h\nu)t\right) + \frac{(A^{*}M_{kr})}{\nu_{rk} + \nu} \exp\left(- i/\hbar\, (E_k - h\nu)t\right) \right]$$

$$\psi_k^{(1)*} = 1/h \sum_r \psi_r^* \left[\frac{(A^* M_{kr})}{\nu_{rk} - \nu} \exp\left(i/\hbar(E_k + h\nu)t\right) + \frac{(AM_{kr})}{\nu_{rk} + \nu} \exp\left(i/\hbar(E_k - h\nu)t\right) \right] \qquad (3.10)$$

Equation (3.10) represents the perturbation of the eigenfunction by the external field.

We now formulate the moment of the perturbed state k, since we are interested in the emitted radiation from a classical dipole with the same time-dependence.[7]

$$\begin{aligned} \int (\psi_k^{(0)} + \psi_k^{(1)})^* M(\psi_k^{(0)} + \psi_k^{(1)}) d\tau = M_{kk} \\ + 1/h \sum_r \left[\frac{(AM_{kr})M_{rk}}{\nu_{rk} - \nu} + \frac{M_{kr}(AM_{rk})}{\nu_{rk} + \nu} \right] \exp(-\ 2\pi i\nu t) \\ + 1/h \sum_r \left[\frac{(A^* M_{kr})M_{rk}}{\nu_{rk} + \nu} + \frac{M_{kr}(A^* M_{rk})}{\nu_{rk} - \nu} \right] \exp(2\pi i\nu t). \end{aligned} \qquad (3.11)$$

The first part of (3.11) is time-independent and not associated with radiation; it represents the permanent dipole moment of the state k. The second part has the form

$$\begin{aligned} M_{kk}^{(1)} = C_{kk} \exp(-\ 2\pi i\nu t) + C_{kk}^* \exp(2\pi i\nu t), \text{ where} \\ C_{kk} = 1/h \sum_r \left(\frac{(AM_{kr})M_{rk}}{\nu_{rk} - \nu} + \frac{M_{kr}(AM_{rk})}{\nu_{rk} + \nu} \right). \end{aligned} \qquad (3.12)$$

This second part, Eq. (3.12), is real and its time-dependence is the same as that of the incident radiation. It represents the scattered radiation of the same frequency, and is referred to as the "coherent radiation."

The classical radiation associated with the moment (3.12) is:[8]

$$I = \frac{2\overline{\ddot{M}^2}}{3c^3} = \frac{64\pi^4\nu^4}{3c^3} \left| C_{kk} \right|^2. \qquad (3.13)$$

Equation (3.13) represents the intensity scattered per second.

Next we wish to know the radiation corresponding to the transition from state k to state n. Neglecting the squared expressions in E,

$$\begin{aligned}\int(\Psi_n^{(0)} + \Psi_n^{(1)})^* M(\Psi_k^{(0)} + \Psi_k^{(1)})d\tau &= M_{kn}\exp(-2\pi i\nu_{kn}t)\\ &+ 1/h\sum_r\left[\frac{(AM_{kr})M_{rn}}{\nu_{rk}-\nu} + \frac{M_{kr}(AM_{rn})}{\nu_{rn}+\nu}\right]\exp\left(-2\pi i(\nu_{kn}+\nu)t\right) \qquad (3.14)\\ &+ 1/h\sum_r\left[\frac{(A^*M_{kr})M_{rn}}{\nu_{rk}+\nu} + \frac{M_{kr}(A^*M_{rn})}{\nu_{rn}-\nu}\right]\exp\left(-2\pi i(\nu_{kn}-\nu)t\right).\end{aligned}$$

The individual members of (3.14) are complex, in contrast to those in (3.11); in order to relate them to the classical radiation of a real dipole, an additional expression is necessary. This may be formulated according to Klein in the following manner:[9] the radiation corresponding to the component $M_{\ell m}\exp(-2\pi i\nu_{\ell m}t)$ of the electric moment with initial state ℓ is zero when $\nu_{\ell m} < 0$; when $\nu_{\ell m} > 0$ it is equal to the classically radiated intensity associated with the quantity:

$$M_{\ell m}\exp(-2\pi i\nu_{\ell m}t) + M_{\ell m}^*\exp(2\pi i\nu_{\ell m}t).$$

When these conditions are applied to Eq. (3.14), it may be seen that the first term represents the spontaneous emission ν_{kn} associated with the transition k → n, while the second term corresponds to a scattering of frequency $(\nu_{kn} + \nu)$; this occurs only when $(\nu_{kn} + \nu) > 0$ and $E_n < E_k + h\nu$. The energy of the final state E_n may be larger or smaller than that of the initial state E_k. In the first case, the scattered light is of larger wavelength, and in the second case, it is of shorter wavelength (Stokes and anti-Stokes scattering). When k and n represent different quantum levels but $E_k = E_n$ (degeneracy), the emitted scattering is unshifted, differing from that given by (3.11) and (3.13) in its coherence properties and polarization. It will be discussed further in the ensuing chapters.

The third term in (3.14) leads to radiation when $\nu_{kn} - \nu > 0$, and $E_n < E_k - h\nu$; therefore, the initial state must be an excited level. It describes an induced emission of two quanta $(\nu_{kn} - \nu)$ and ν to a lower level n. In addition, there exists a spontaneous transition probability not covered by the present theory. The significance of these processes will be clarified in subsequent discussions.

If we now consider the evaluation of the intensity with the aid of Klein's procedure, then, by limiting ourselves to the scattering radiation (second term):

$$I_{kn} = \frac{64\pi^4}{3c^3} (\nu + \nu_{kn})^4 \left| C_{kn} \right|^2 , \quad \text{where} \tag{3.15}$$

$$C_{kn} = 1/h \sum_r \left[\frac{(AM_{kr})M_{rn}}{\nu_{rk} - \nu} + \frac{M_{kr}(AM_{rn})}{\nu_{rn} + \nu} \right] .$$

For k = n, Eq. (3.15) transforms into (3.13).

The intensity of radiation of a particular polarization and direction of propagation, rather than that of the total scattered radiation, is expressed by the classical formula for the intensity of the dipole radiation

$$I_{kn}(q) = \frac{c}{4\pi} \frac{16\pi^4}{\lambda'^4 r^2} \overline{\left| (Mq) \right|^2} = \frac{c}{4\pi} \frac{32\pi^4}{\lambda'^4 r^2} \left| (C_{kn} q) \right|^2 , \tag{3.16}$$

where q is a unit vector in the direction of polarization along which the scattering is observed, r the distance between the scattering system and a distant observer, and λ' the emitted wavelength ($\lambda' = \frac{c}{\nu + \nu_{kn}}$).

In the case of degeneracy, the total radiation intensity of a given frequency is obtained by summing over all degenerate initial and final states. Equations (3.12), (3.13), and (3.15) have been derived by Kramers and Heisenberg before the advent of quantum mechanics.[10] The quantum-mechanical derivation was given by Born, Heisenberg, and Jordan,[11] while the present derivation[12] is based upon a perturbation calculation of the Schrödinger treatment.[13]

A discussion on the scattering formula will be presented in Chapter 5.

REFERENCES AND FOOTNOTES

1. In this and subsequent chapters only a slight knowledge of quantum mechanics is assumed. The reader not interested in the derivation of the scattering formula can omit it since the results are recounted in Chapter 5.

2. P. A. M. Dirac, Quantum Mechanics, Oxford (1930).

3. W. Heisenberg, Ann. Physik 9, 338 (1931).

4. Refer to the article by V. Laue and to the introduction of the article by Kronig.

5. This assumption, which we retain throughout the present article, restricts the validity of the results to visible and ultraviolet radiation; x-ray scattering will not be discussed here.

6. On the right side of Eq. (3.6) the quantity $(EM)\psi_k^{(1)}$ is omitted as being too small and of second-order.

7. The terms which correspond to the integral $\int \psi_k^{(2)*} M\psi_k^{(1)} d\tau$ are omitted in (3.11); they are proportional to the square of the incident field strength.

8. See texts on Electrodynamics or Sommerfeld, Atomic Structure and Spectral Lines, Vol. I, appendix.

9. O. Klein, Z. Physik 41, 407 (1927).

10. Kramers and Heisenberg, l. c.

11. M. Born, W. Heisenberg, P. Jordan, Z. Physik 35, 557 (1925).

12. O. Klein, l. c.

13. E. Schrödinger, Ann. Physik 81, 109 (1926). In this paper Schrödinger obtained a different result from the above by starting with his original interpretation of the eigenfunction as a charge density. Here, displaced scattering occurs only when the unperturbed state is taken as $(\psi_k^{(0)} + \psi_n^{(0)})$, that is, when both levels k and n are excited. However, by following the above treatment, it is seen that scattering occurs as soon as state k is excited regardless of the population of the final state n. Experiments confirm the latter theory, which is essentially a statistical one.

Chapter 4. Dirac's Scattering Theory[1]

The theory of scattered radiation outlined above suffices for most cases. There, however, the relation between electric moment and scattering was merely hypothesized, but in Dirac's method this hypothesis is replaced by a quantum theoretical treatment of the radiation field. Previously we treated the system of particles (molecules) in an external field; now the molecule and the radiation field should form a single system[2] whose Hamiltonian is made up of the energy of the molecule H_m, of the radiation H_s, and of the interaction energy H', i.e.,

$$H = H_M + H_s + H'.$$

The unperturbed system consists of

$$H_0 = H_M + H_s,$$

where the interaction energy is considered to be the perturbation.

To determine H_s, we imagine the radiation to be enclosed in a cavity (空洞) with walls having specular reflecting surfaces, so that the radiation field may be thought of as comprised of standing waves, i.e., eigenvibrations;[3]

$$E = \sum_s E_s = \sqrt{\frac{8\pi}{V}} \sum_s e_s \dot{q}_s(t) \sin \Gamma_s,$$

$$\Gamma_s = \frac{2\pi\nu_s}{c} (k_s r) + \delta_s, \tag{4.1}$$

where e_s is a unit vector in the direction of the field; q_s, its amplitude; ν_s, the frequency; k_s, the propagation vector; r, the position vector; c, the velocity of light; δ_s, an arbitrary phase; and V, the volume of the cavity. By comparison with the classical expression for the energy density, one obtains for the energy

$$H_s = 1/2 \sum_s \left[\dot{q}_s^2 + 4\pi^2 \nu_s^2 q_s^2\right]. \tag{4.2}$$

Equation (4.2) represents the energy of a system of oscillators with frequency ν_s and mass 1. For each plane wave (eigenvibration) there exists such an oscillator. For a large cavity, the number of eigenvibrations of a particular polarization direction j, within the frequency range ν and $\nu + d\nu$ and solid angle $d\omega$, i. e.,

Dirac § 62 58(34)

$$dN_j = \nu^2/c^3 \, V d\nu d\omega, \tag{4. 3}$$

which, when integrating over the coordinates and polarization direction, yields

$$dZ = \frac{8\pi\nu^2}{c^3} \, V d\nu. \tag{4. 3a}$$

As in the previous chapter, the interaction energy between radiation and molecule is again given by

$$H' = -(EM). \tag{4. 4}$$

The Schrödinger equation of the unperturbed system (molecule plus radiation) is

$$(H_0 - E)\psi = 0$$

$$H_0 = H_M + 1/2 \sum_s (\dot{q}_s{}^2 + 4\pi^2 \nu_s{}^2 q_s{}^2).$$

The eigenvalues are the sum of the energies of the molecule and cavity while the eigenfunctions are products.

$$\begin{aligned} E_{nS} &= E_n + \sum_s (n_s + 1/2) h\nu_s \\ \psi_{nS} &= \psi_n \prod^{s} u_{n_s}. \end{aligned} \tag{4. 5}$$

The state of the radiation field is determined by the quantum numbers n_s, which indicate the number of light quanta that occupy the individual eigenvibrations. The eigenfunctions u_{n_s} are harmonic oscillator functions.[4]

Let us consider, next, any given state of the radiation field, S_0, and state k of the molecule. As long as the energy is the sum of that of the molecule and the cavity, the system remains in its given state. When H' is included, however, transitions to other states S, n take place. If we develop the eigenfunction in terms of the unperturbed system

$$\psi = \sum_{nS} a_{nS}(t)\psi_{nS} \exp(-iE_{nS}t/\hbar),$$

(for $t = 0$, $a_{kS_0} = 1$; for all others, $a = 0$), then the perturbation theory gives, in first-order approximation,

$$a_{nS}^{(1)} = (H')_{nS}^{kS_0} \frac{1 - \exp\left(2\pi i(\nu_{nk} + \nu_{SS_0})t\right)}{2(\nu_{nk} + \nu_{SS_0})}$$

$$(H')_{nS}^{kS_0} = \int \psi^*_{nS} H' \psi_{kS_0} d\tau, \qquad (4.6a)$$

and, in second-order approximation,

$$a_{nS}^{(2)} = \sum_{rS'} \frac{(H')_{rS'}^{kS_0}(H')_{nS}^{rS'}}{2(\nu_{rk} + \nu_{S'S_0})} \left[\frac{1 - \exp\left(2\pi i(\nu_{nr} + \nu_{SS'})t\right)}{2(\nu_{nr} + \nu_{SS'})} - \frac{1 - \exp\left(2\pi i(\nu_{nk} + \nu_{SS_0})t\right)}{2(\nu_{nk} + \nu_{SS_0})}\right] \qquad (4.6b)$$

Upon substituting the value for H' given by Eqs. (4.4) and (4.1), the first-order approximation yields processes for which the atom changes its quantum state and for which the population number of a cavity oscillator changes by +1 or -1. These processes correspond to emission and absorption of a light quantum. To obtain the scattering radiation, we must consider the second-order approximation. Since H', according to Eqs. (4.4) and (4.1), is linear in q_s and since the selection rules for the harmonic oscillator are $\Delta n_s = \pm 1$, one can see by inspection of the form of Eq. (4.6b) that only those transitions are possible for which two cavity oscillators change by ± 1, while the molecule may change, or remain in the same state. If we consider, first, the state of the cavity, then we can distinguish four cases. The indices α and β denote both of the eigenvibrations that undergo a change in state.

1. $n'_\alpha = n_\alpha + 1$, $n'_\beta = n_\beta + 1$ $h\nu_\alpha$ and $h\nu_\beta$ appear (double-emission)
2. $n'_\alpha = n_\alpha - 1$, $n'_\beta = n_\beta - 1$ $h\nu_\alpha$ and $h\nu_\beta$ disappear (double-absorption)
3. $n'_\alpha = n_\alpha - 1$, $n'_\beta = n_\beta + 1$ $(h\nu_\alpha, h\nu_\beta)$ disappears and
4. $n'_\alpha = n_\alpha + 1$, $n'_\beta = n_\beta - 1$ $(h\nu_\beta, h\nu_\alpha)$ appears (scattering).

The first two processes occur in the correspondence theory. They are not treated further here as they were studied in detail by M. Göppert-Mayer.[5]

If we limit ourselves to the third process (the fourth does not yield any new data), we obtain the quantity $\left| a_{nS}^{(2)} \right|^2$. We shall employ Eq. (4.6), along with the matrix elements shown in (4.4), (4.1), and (4.5) and the following values for the coordinate matrices of the oscillator:

$$q_{n_s, n_s+1} = \sqrt{\frac{(n_s + 1)h}{8\pi^2 \nu_s}} \exp(2\pi i \nu_s t); \quad \dot{q}_{n_s, n_s+1} = i\sqrt{\frac{(n_s + 1)h\nu_s}{2}} \exp(2\pi i \nu_s t)$$

$$q_{n_s, n_s-1} = \sqrt{\frac{n_s h}{8\pi^2 \nu_s}} \exp(-2\pi i \nu_s t); \quad \dot{q}_{n_s, n_s-1} = i\sqrt{\frac{n_s h\nu_s}{2}} \exp(-2\pi i \nu_s t).$$

$\left| a_{nS}^{(2)} \right|^2$ gives the probability of finding, at time t, the molecule in state k and the cavity in state S $(n_1, n_2 \ldots n_\alpha - 1 \ldots n_\beta + 1 \ldots n_j)$, when at t = 0 they were at n and S_0 $(n_2, n_1 \ldots n_\alpha \ldots n_\beta \ldots n_j)$, respectively.(6)

$$\left| a_{nS}^{(2)} \right|^2 = \frac{64\pi^2}{V^2} n_\alpha (n_\beta + 1)\nu_a \nu_\beta \sin^2 \Gamma_a \sin^2 \Gamma_\beta \left| S_{kn}^{a\beta} \right|^2 \frac{\sin^2 \pi(\nu_{kn} + \nu_a - \nu_\beta)t}{(\nu_{kn} + \nu_a - \nu_\beta)^2}$$

$$S_{kn}^{\alpha\beta} = 1/h \sum_r \left[\frac{(e_\alpha M_{kr})(e_\beta M_{rn})}{\nu_{rk} - \nu_\alpha} + \frac{(e_\beta M_{kr})(e_a M_{rn})}{\nu_{rn} + \nu_\alpha} \right] . \qquad (4.7)$$

To obtain the probability of the scattering of an incident spectral line of frequency ν_1, Eq. (4.7) was summed over all final states S and over all eigenvibrations α that occur in the incident radiation.

Let us carry through the first summation, replacing it by integration over dω and emitted frequencies dν. When we consider the number of vibrations per solid angle, the frequency range as given by Eq. (4.3), and the density $\rho_{j'}(\nu', \omega')d\nu' d\omega'$ of the radiation of a given polarization, direction, and frequency existing in the cavity, where $\rho_{j'}(\nu', \omega')d\nu' d\omega' = \sum_\beta^{\Delta\nu' \Delta\omega'} n_\beta h\nu_\beta / V$, then we have

$$\sum_S \left| a_{nS}^{(2)} \right|^2 = \frac{64\pi^2}{Vh} n_a \nu_a \sin^2 \Gamma_a \overline{\sin^2 \Gamma_\beta} \sum_{j'} \int\int \left(\rho_{j'}(\nu', \omega') + \frac{h\nu'^3}{c^3}\right)$$

$$\left| S_{kn}^{a, k'j'} \right|^2 \frac{\sin^2 \pi(\nu_{kn} + \nu_\alpha - \nu')t}{(\nu_{kn} + \nu_\alpha - \nu')^2} d\nu' d\omega'.$$

For $S_{kn}^{a\beta}$, ν_β is replaced by the continuous frequency ν', and the quantity e_β by the unit vector $e_{k'j'}$, which assumes the direction of the electric vector of the scattered wave. This is now a continuous function of the solid angle. $e_{k'j'}$ is perpendicular to the direction of propagation k' and is fixed by the state of polarization $j'(j' = 1, 2)$. We indicate this by $S_{kn}^{a, k'j'}$. For large time intervals, the factor $\sin^2 \pi(\nu_{kn} + \nu_a - \nu')t/(\nu_{kn} + \nu_a - \nu')^2$ has a sharp maximum at $\nu' = (\nu_{kn} + \nu_a)$. Therefore, only frequencies in the immediate vicinity of the quantity ν' contribute appreciably to the value of the integral. The remaining terms we can consider as constant over ν', thereby giving the expression

$$\int_{-\infty}^{\overset{\nu_{kn}+\nu_a}{\cancel{\infty}}} \frac{\sin^2 \pi(\nu_{kn} + \nu_a - \nu')t}{(\nu_{kn} + \nu_a - \nu')^2} \, d\nu' = \pi^2 t.$$

The limits of integration are not essential; they may extend from $-\infty$ to $+\infty$, because of the sharp maximum. The quantity $\overline{\sin^2 \Gamma_\beta}$ is evaluated over all eigenvibrations. Since the phases δ_β contained in Γ_β (see Eq. (4.1)) are independent, $\overline{\sin^2 \Gamma_\beta} = 1/2$ and

$$\sum_S \left| a_{nS}^{(2)} \right|^2 = \frac{32\pi^4 t}{Vh} n_a \nu_a \sin^2 \Gamma_\alpha \sum_{j'} \int \left[\rho_{j'}(\nu', \omega') + \frac{h\nu'^3}{c^3} \right] \left| S_{kn}^{a, k'j'} \right|^2 d\omega'. \tag{4.8}$$

If we integrate Eq. (4.8) over the eigenvibrations represented in the incident frequency ν, then

$$\rho_j(\nu, \omega) d\nu d\omega = \sum_a^{\Delta\nu, \Delta\omega} \frac{n_a h \nu_a}{V},$$

and finally,

$$W_{kn}(\nu, \nu') = \frac{16\pi^4}{h^2} \sum_{jj'} \int\int\int \rho_j(\nu, \omega) \left[\frac{h\nu'^3}{c^3} + \rho_{j'}(\nu', \omega') \right] \left| S_{kn}^{kj, k'j'} \right|^2 d\nu d\omega d\omega'. \tag{4.9}$$

W_{kn} gives the probability per unit time for the transition of the molecule from state k to state n under the influence of the radiation, and for a quantum $h\nu$ of undetermined direction and polarization to be scattered, i. e., $h\nu \rightarrow h\nu' = h(\nu + \nu_{kn})$. This probability is increased, as shown in Eq. (4.9), when radiation of frequency $(\nu + \nu_{kn})$ already exists (induced emission). We will now discuss two special cases of Eq. (4.9).

First, we assume that $\rho_{j'}(\nu', \omega') = 0$ and that the molecule is affected by a plane monochromatic wave of the form (3.3). Then,

$$\iint \sum_j \rho_j(\nu, \omega) d\nu d\omega = \frac{\overline{E}^2}{4\pi} = \frac{|A|^2}{2\pi},$$

and Eq. (4.9) becomes

$$W_{kn}(\nu; \nu + \nu_{kn}) = \frac{16\pi^4(\nu + \nu_{kn})^3}{hc^3} \cdot \frac{|A|^2}{2\pi} \cdot \int 1/h^2 \sum_{j'} \left| \sum_r \left[\frac{(e_0 M_{kr})(e_{k'j'} M_{rn})}{\nu_{rk} - \nu} + \frac{(e_{k'j'} M_{kr})(e_0 M_{rn})}{\nu_{rn} + \nu} \right] \right|^2 d\omega'. \tag{4.9a}$$

Vector e_0 is a unit vector in the direction of the incident electric vector.

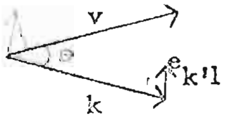

Figure 1

The integral may be written as follows:

$$\int \sum_{j'} \left| (e_{k'j'} V) \right|^2 d\omega',$$

where V is a vector. If we choose both polarization components so that $e_{k'1}$ is in the plane formed by k and V and $e_{k'2}$ is perpendicular to it, then

$$\int \sum_j \left| (e_{k'j'} V) \right|^2 d\omega' = 2\pi \int_0^\pi \left| (e_{k'1} V) \right|^2 \sin\theta d\theta = 2\pi \int_0^\pi |V|^2 \sin^3\theta d\theta = \frac{8\pi}{3} |V|^2$$

and

$$W_{kn}(\nu, \nu + \nu_{kn}) = \frac{64\pi^4(\nu + \nu_{kn})^3}{3hc^3} \cdot \frac{|A|^2}{h^2} \left| \sum_r \left[\frac{(e_0 M_{kr}) M_{rn}}{\nu_{rk} - \nu} + \frac{M_{kr}(e_0 M_{rn})}{\nu_{rn} + \nu} \right] \right|^2. \tag{4.10}$$

The scattering intensity is

$$I_{kn} = h(\nu + \nu_{kn}) W_{kn}. \tag{4.10a}$$

Expression (4.10a), however, represents the intensity emitted by a classical dipole of moment $C_{kn}\exp\left(-2\pi i(\nu+\nu_{kn})t\right)+C^{*}_{kn}\exp\left(2\pi i(\nu+\nu_{kn})t\right)$, where

$$C_{kn}=1/h\sum_{r}\left[\frac{(AM_{kr})M_{rn}}{\nu_{rk}-\nu}+\frac{M_{kr}(AM_{rn})}{\nu_{rn}+\nu}\right].$$

This is in agreement with the result given by the correspondence theory (Eqs. (3.12) and (3.15)).

One can see from Eq. (4.9a) that the directional distribution of the radiation is the same as that of the classical dipole (Eq. (3.16)). The result obtained by the correspondence theory, according to which the calculated transitions occur only when $\nu'=(\nu+\nu_{kn})>0$, follows as a consequence of the positive oscillator frequency, ν'.

As a second application of Eq. (4.9), we consider the case where $\rho_{j'}(\nu,\omega)$ and $\rho_{j'}(\nu',\omega')$ are different from zero but independent of j,ω and j',ω', respectively (spatially isotropic radiation). Then,

$$\rho(\nu)=\sum_{j}\int\rho_{j}(\nu,\omega)\,d\omega=8\pi\rho_{j}(\nu,\omega),$$

$$\rho(\nu')=8\pi\rho_{j'}(\nu',\omega').$$

$\rho(\nu)$ is to differ from zero within a short interval $\Delta\nu$ and $\int\rho(\nu)d\nu=\rho(\nu)\Delta\nu$. The integration over $d\omega$, $d\omega'$ yields

$$W_{kn}(\nu,\nu')=\bar{\rho}(\nu)\left[\frac{8\pi h\nu'^{3}}{c^{3}}+\rho(\nu')\right]\Phi_{kn}(\nu)\Delta\nu, \tag{4.11}$$

$$\Phi_{kn}(\nu)=\frac{16\pi^{4}}{3h^{2}}\,1/h^{2}\sum_{x}\sum_{x'}\left|\sum_{r}\left[\frac{(M_{x})_{kr}(M_{x'})_{rn}}{\nu_{rk}-\nu}+\frac{(M_{x'})_{kr}(M_{x})_{rn}}{\nu_{rn}+\nu}\right]\right|^{2}.$$

This can also be rewritten as follows:

$$W_{kn}(\nu,\nu')=\bar{\rho}(\nu')\Delta\nu\left(C_{kn}+D_{kn}\rho(\nu')\right), \tag{4.11a}$$

$$\frac{C_{kn}}{D_{kn}}=\frac{8\pi h\nu'^{3}}{c^{3}}. \tag{4.11b}$$

The scattering probability consists of two parts. One is proportional to the radiation density of the incident frequency, and the other is proportional to the product of the radiation density of the incident and emitted frequencies.

The quantities C_{kn} and D_{kn} correspond to the Einstein coefficients A_{kn} and B_{kn} for spontaneous and induced emission and their relations are the same (see Eq. (4.11b)). The form of Eq. (4.11a) is important for the discussion of thermal equilibrium. It was originally deduced by Pauli, from equilibrium considerations for free electrons.[6,7] In the present derivation, the form of the equation is already apparent in the initial expression (4.7), where the scattering probability is proportional to the product $n_\alpha(n_\beta + 1)$. This result, based on the oscillator matrices, can also be derived from the Bose-Einstein statistics.

Equation (4.11a) suggests that the scattering phenomenon consists of an independent sequence of absorption and emission processes.[7,8] However, this is not correct, as was shown by Placzek on the basis of equilibrium considerations, and by Weiskopf, by means of Dirac's theory.[8,9,10]

REFERENCES AND FOOTNOTES

1. P. A. M. Dirac, Proc. Roy. Soc. (London) A114, 710 (1927); E. Amaldi, Lincei Rend. 9, 876 (1929); M. Göppert-Mayer, Ann. Physik 9, 273 (1931). A detailed discussion of the Dirac radiation theory and its application to other problems besides the one treated here is given by E. Fermi, Rev. Mod. Phys. 4, 87 (1932).

2. Another treatment of the radiation theory was described by Heisenberg, Ann. Physik 9, 338 (1931).

3. See E. Fermi, l. c.

4. Von Laue, Volume VI, Part I of this handbook.

5. M. Göppert-Mayer, l. c.

6. Several terms are neglected here which would lead to energies of forbidden transitions and which originate in the idealized perturbation treatment where the interaction energy between radiation and matter is taken into account at time t = 0.

7. W. Pauli, Z. Physik 18, 272 (1923).

8. A. Einstein and P. Ehrenfest, Z. Physik 19, 301 (1923); A. Smekal, ibid. 32, 241 (1925), 34, 81 (1925).

9. G. Placzek, Z. Physik 38, 585 (1929).

10. V. Weisskopf, Ann. Physik 9, 23 (1931).

Chapter 5. The General Scattering Equation

On the basis of the results of the two preceding chapters, we shall now deduce the salient properties of scattered radiation.

(a) Coherence Properties. The terms represented in Eqs. (3.12) and (3.15) differ basically in their coherence properties. We must remember that ψ_r, belonging to a definite state r (solution of the time-independent Schrödinger equation), is associated with an arbitrary, undetermined phase factor $\exp(i\delta_r)$. (If ψ_r satisfies the Schrödinger equation, then $\psi_r \exp(i\delta_r)$ does also.) The phase factor of M_{kr} is, therefore, $\exp i(\delta_k - \delta_r)$, and the perturbed moment $M_{kn}^{(1)}$ has, according to Eq. (3.14), the phase factor $\exp i(\delta_k - \delta_n)$. According to Eq. (3.11), the phase factor will disappear for $k = n$.

Let us examine the radiation scattered from various scattering centers. Then, for $k = n$, interference will occur and the total intensity will depend upon the orientation of the scattering centers. Therefore, we call this scattering, Eq. (3.12), "coherent." For $k \neq n$, interference cannot occur because the phase factor varies arbitrarily for different scattering centers. The intensities are additive, and the total intensity will be independent of the orientation of the scattering centers, but, ceteris paribus, proportional to the number of centers per unit volume. It should be mentioned that the unshifted (Rayleigh) scattering of degenerate states consists of a coherent and an incoherent part. The latter corresponds to transitions between the various degenerate states. Only the first part (coherent) contributes to the dispersion, it depends upon the interference of radiation from the individual scattering centers.[1]

(b) The Scattering Tensor and the Static Field. According to Eqs. (3.3), (3.12) and (3.15), there is a tensor relation between the complex amplitudes A of the incident radiation and the induced moment C_{kn}. Let ρ and σ denote the cartesian coordinates x, y, z. Then,

$$(C_\rho)_{kn} = \sum_\sigma (c_{\rho\sigma})_{kn} A_\sigma, \tag{5.1}$$

$$(c_{\rho\sigma})_{kn} = 1/h \sum_r \left[\frac{(M_\sigma)_{kr}(M_\rho)_{rn}}{\nu_{rk} - \nu} + \frac{(M_\rho)_{kr}(M_\sigma)_{rn}}{\nu_{rn} + \nu} \right]. \tag{5.2}$$

The quantity $(c_{\rho\sigma})_{kn}$ represents a complex and unsymmetric tensor. A discussion of the properties of the scattered radiation must necessarily involve this tensor.

For the coherent scattering (k = n),

$$(c_{\rho\sigma})_{kk} = 1/h \sum_r \left[\frac{(M_\sigma)_{kr}(M_\rho)_{rk}}{\nu_{rk} - \nu} + \frac{(M_\rho)_{kr}(M_\sigma)_{rk}}{\nu_{rk} + \nu} \right], \qquad (5.2a)$$

and, according to Eq. (3.12),

$$(M_\rho)_{kk}^{(1)} = \sum_\sigma \left[(c_{\rho\sigma})_{kk} A_\sigma \exp(-2\pi i \nu t) + (c_{\rho\sigma})^*_{kk} A^*_\sigma \exp(2\pi i \nu t) \right]. \qquad (5.3)$$

Since $(M_\sigma)_{kr} = (M_\sigma)^*_{rk}$, $(c_{\rho\sigma})_{kk} = (c_{\sigma\rho})^*_{kk}$. The ~~polarizability~~ scattering tensor becomes symmetric for real values of $(c_{\rho\sigma})_{kk}$, which occurs, as may be seen from (5.2a) for the static case ($\nu = 0$). In addition, for real values of $(c_{\rho\sigma})_{kk}$, according to Eq. (3.3),

$$(M_\rho)_{kk}^{(1)} = \sum_\sigma (c_{\rho\sigma})_{kk} \cdot E_\sigma. \qquad (5.3a)$$

The real quantity $(c_{\rho\sigma})_{kk}$ is called "the polarizability $\underline{a}_{\rho\sigma}^{(k)}$ of the state k."[2] The polarizability is, therefore, a symmetric tensor. If $(c_{\rho\sigma})_{kk}$ remains real for $\nu \neq 0$, then the relation (5.3a) applies to a frequency-dependent polarizability. This is true whenever the energy operator H is real since then the eigenfunction and the matrix element of the electric moment can be written in real form. The energy operator is real in the absence of external magnetic fields and upon neglect of spins.

Moreover, it can be shown that $(c_{\rho\sigma})_{kk}$ is also real for a complex energy operator, provided the given state is not degenerate. For degenerate states and for a complex energy operator, this holds only for the average value, defined by (5.2b).[3]

For the (shifted and nonshifted) incoherent scattered radiation, the scattering tensor remains unsymmetric,[4] as may be seen from Eq. (5.1). When $\nu = 0$, the scattering formula gives the effect of an external electric field on the spontaneous transition probability k → n. Since different selection rules apply for scattering and spontaneous emission, forbidden lines may then appear whose intensities are given by Eq. (3.1), with $\nu = 0$ (see Chapter 13).

(c) The Scattering Tensor and the Effective Cross Section. To obtain the relation between the scattering tensor and the scattering intensity, one can express the quantity A in terms of the incident intensity I_0:

$$A = |A|\, e$$

$$I_0 = (c/2\pi)\, |A|^2.$$

From Eqs. (5.1) and (3.16), one obtains

$$I_{kn}(q) = \frac{16\pi^4}{\lambda'^4 r^2} \left| \sum_{\rho\sigma} (c_{\rho\sigma})_{kn} q_\rho e_\sigma \right|^2 I_0. \tag{5.4}$$

For the case that only the σ component of the incident light differs from zero and that the scattering is observed along the direction of polarization, ρ,

$$I_{kn}(\rho) = \frac{16\pi^4}{\lambda'^4 r^2} \left| (c_{\rho\sigma})_{kn} \right|^2 I_0. \tag{5.4a}$$

When Eq. (3.15) is combined with this, the total energy scattered per unit time becomes

$$\begin{aligned} I_{kn} &= Q_{kn} \cdot I_0, \\ Q_{kn} &= \frac{2^7 \pi^5}{3\lambda'^4} \sum_\rho \left| \sum_\sigma (c_{\rho\sigma})_{kn} e_\sigma \right|^2. \end{aligned} \tag{5.5}$$

The quantity Q_{kn} has the dimensions of an area (I_0 = incident intensity = energy per unit time and unit area); we call it "the effective cross section for light," or "the scattering cross section associated with the transition k → n." A completely absorbing area with the same cross section, perpendicular to the direction of the incident ray, would absorb the same amount of energy--apart from reflections.

As may be seen from (5.5), the scattering cross section depends on the polarization of the incident light. If it contains the σ component only, (5.5) becomes

$$Q_{kn} = \frac{2^7 \pi^5}{3\lambda'^4} \sum_\rho \left| (c_{\rho\sigma})_{kn} \right|^2. \tag{5.5a}$$

For the degenerate case, the scattering cross section associated with the transition k → n is

$$Q_{kn} = 1/g_k \sum_{ss'} Q_{ns'}^{\ ks}. \tag{5.5b}$$

The sum extends over all degenerate initial states s and final states s'; g_k denotes the statistical weight of the initial state.

If one averages the intensities over all directions of propagation and polarization of the incident light (it is always assumed to be a plane-wave in a given direction of propagation), or, which is equivalent, over all orientations of the scattering systems, assuming a fixed direction and polarization of the incident light, then (5. 5) becomes:

$$\overline{Q}_{kn} = \frac{2^7 \pi^5}{3\lambda'^4} \; 1/3 \; \overline{\sum_{\rho}} \; \overline{\sum_{\sigma}} \left| (c_{\rho\sigma})_{kn} \right|^2 . \tag{5.5c}$$

This average quantity differs from the effective cross section for isotropic incident light, $Q_{kn}^{\ iso}$, which is

$$Q_{kn}^{\ iso} = \frac{2^7 \pi^5}{3\lambda'^4} \overline{\sum_{\rho}} \, \overline{\sum_{\sigma}} \left| (c_{\rho\sigma})_{kn} \right|^2 , \tag{5.5d}$$

thereby agreeing with Eq. (4.11). Thus,

$$Q_{kn}^{\ iso} = 3 \, \overline{Q}_{kn} . \tag{5.6}$$

By the definition of (5. 5b), the averaging shown in (5. 5c) is unnecessary for a random system since no preferred orientation is specified. The effective cross section for unidirectional irradiation is independent of the state of polarization of the incident wave, and is 1/3 the value of the cross section for isotropic radiation.

(d) Frequency Dependence. The frequency dependence of the shifted and unshifted scattering is determined by two factors: 1. by $(\nu + \nu_{kn})^4$ and ν^4, respectively; in the correspondence theory, this factor arises in the emission of radiation from the transition of the induced moment. 2. by the denominator in Eqs. (3.12) and (5. 2). Three characteristic cases of the scattered intensity must be distinguished:

1. The incident frequency, ν, is small compared with the transition frequencies occurring in the scattering formula. If the frequency dependence in the denominator is neglected, the intensity is proportional to $(\nu + \nu_{kn})^4$ and ν^4, respectively.

2. The incident frequency is close to an absorption band ν_{rk}, so that the effect of a single term predominates. The scattering intensity will vary as $\nu^4/(\nu_{rk} - \nu)^2$ and as $(\nu + \nu_{kn})^4/(\nu_{rk} - \nu)^2$ for the unshifted and the shifted radiation, respectively. The same holds for the unshifted frequency when $r < k$, where $\nu_{rk} (\nu_{rk} = - \nu_{kr})$ is an emission frequency. Then resonance occurs because of the second term in (5.2a). For the shifted scattering, Eq. (5.2), resonance occurs when, in the second term, $r < n$, i.e., when the incident frequency is close to an emission frequency, ν_{nr}, of the final state. At the resonance frequency itself, the scattering becomes infinite as indicated by (5.2) and (5.2a). In this case, these expressions no longer hold as damping effects were neglected in their derivations, but it has definitely been established that the intensity reaches a maximum in the vicinity of an absorption band. An extension of these equations to the resonance case will be discussed in Chapter 7.

3. The incident frequency is large compared with the transition frequencies occurring in the scattering formula: the intensity of the coherent scattering will be independent of the frequency and the quantities $(c_{\rho\sigma})_{kk}$ for $\rho \neq \sigma$ will vanish. The intensity of the shifted scattering, as well as the incoherent part of the unshifted scattering, approaches zero.

This may be proved in the following manner. According to Eqs. (5.2) and (5.2a), we may write

$$\lim_{\nu \to \infty} \left| (c_{\rho\rho})_{kk} \right|^2 = \frac{4}{h^2 \nu^4} \left| \sum_r \nu_{rk} \left| (M_\rho)_{kr} \right|^2 \right|^2 ,$$

$$\lim_{\substack{\nu \to \infty \\ \rho \neq \sigma}} \left| (c_{\rho\sigma})_{kk} \right|^2 = \frac{1}{h^2 \nu^4} \left| \sum_r \left\{ \nu_{rk} \left[(M_\sigma)_{kr} (M_\rho)_{rk} + (M_\rho)_{kr} (M_\sigma)_{rk} \right] + \nu \left[(M_\sigma)_{kr} (M_\rho)_{rk} - (M_\rho)_{kr} (M_\sigma)_{rk} \right] \right\} \right|^2 \qquad (5.7)$$

$$\lim_{\nu \to \infty} \left| (c_{\rho\sigma})_{kn} \right|^2 = \frac{1}{h^2 \nu^4} \left| \sum_r \left\{ \nu_{rk} \, (M_\sigma)_{kr} (M_\rho)_{rn} + \nu_{rn} (M_\rho)_{kr} (M_\sigma)_{rn} + \nu \left[(M_\sigma)_{kr} (M_\rho)_{rn} - (M_\rho)_{kr} (M_\sigma)_{rn} \right] \right\} \right|^2 .$$

To evaluate these expressions, we make use of the commutation rules

$$q_s p_{s'} - p_{s'} q_s = \hbar/i \; \delta_{s'}{}^{s} ,$$
$$q_s q_{s'} - q_{s'} q_s = 0, \qquad (5.8)$$

where q_s and p_s represent, respectively, the coordinate and momentum of the s degree of freedom; p_s is replaced by $\hbar/i\ \partial/\partial q_s$. Then, we set

$$p_s^{kr} = 2\pi i \mu \nu_{rk} q_s^{kr}, \tag{5.9}$$

$$\sum_r \nu_{rk} \left| q_s^{kr} \right|^2 = \frac{h}{8\pi^2 \mu},$$

$$\sum_r \nu_{rk} q_s^{kr} q_{s'}^{rn} + \nu_{rn} q_{s'}^{kr} q_s^{rn} = 0, \tag{5.10}$$

$$\sum_r q_s^{kr} q_{s'}^{rn} - q_{s'}^{kr} q_s^{rn} = 0.$$

If we put $M = \sum_j e_j r_j$, the last two sums vanish and the first one will be different from zero. Therefore,

$$\lim_{\nu \to \infty} \left| (c'_{\rho\rho'})_{kk} \right|^2 = 1/\nu^4 \sum_j \left(\frac{e_j^2}{4\pi^2 \mu_j} \right)^2. \tag{5.11}$$

The factor ν^4 in the denominator cancels because the same term occurs in the factor relating the transition moment to the radiation. The physical significance of these results will be dealt with in Chapter 10.

In the intermediate region the frequency dependence is more complex, it becomes a function of the transition frequencies and of the magnitude of the transition amplitudes M_{kr}, M_{rk}. Each special case can be discussed in the light of Eqs. (5.2a). Closely related to the frequency dependence is the behavior of the intensities of the Stokes and anti-Stokes lines, I_{kn}/I_{nk}. See Chapters 8 and 25.

(c) The Intermediate States. According to (5.2) and (5.2a), the intensity and polarization of the scattered radiation are determined by the transition frequencies (absorption and emission) ν_{rk} and the transition amplitudes M_{kr} and M_{rn}. The transition probabilities for spontaneous emission (or absorption) are given by the squares of $|M_{kr}|$ and $|M_{rn}|$. It is important that the scattering formula contain the transition amplitudes rather than the transition probabilities. Thereby, terms that belong to different intermediate states r can reinforce, weaken, or cancel each other (interference of the probabilities). Some examples will be cited later.

Since the quantities M_{kr}, M_{rn} in (5.2) occur as products, only those states contribute to the sum over r for which the transition probabilities from r to k and n are different from zero, that is, the states must combine with the initial as well as with final states. It is immaterial whether or not the intermediate state r can be reached energetically from the initial state by absorption of the incident frequency $h\nu$. The only condition that the incident frequency must fulfill is that stated in Chapter 3: $h\nu > E_n - E_k$, which is always fulfilled in the case of anti-Stokes scattering. For Stokes scattering, the energy of the incident light quanta must be sufficient to reach the final state, as shown in Fig. 2. Similarly, state r may be energetically above$^{(1)}$, below$^{(2)}$, or between$^{(3)}$ the initial and final states.

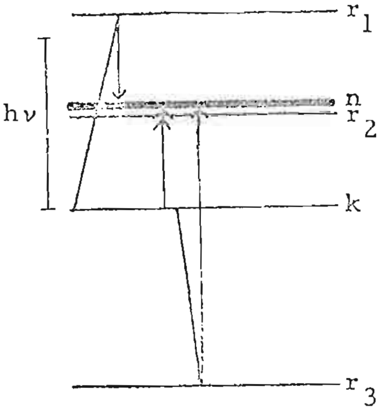

Figure 2

Intermediate state for the transition k → n

It is difficult to understand why the scattering of a system that is in state k is affected by "unoccupied" states r. It should be remembered that "the system is in state k" refers to the unperturbed system, while its reactions towards external perturbations (in the present case, the incident light) must be determined quantum mechanically by specifying the eigenvalues and eigenfunctions of all states.

(f) Selection Rules. According to the preceding analysis two states k and n combine in the Raman effect when there is a state that can combine with k and n in absorption or emission. This is the so-called "third common level rule." The quantity M_{kn}, which determines the spontaneous transition probability between the two states, does not appear in the scattering formula. There is no correlation between the intensities and selection rules of a spontaneously emitted (or absorbed) line and those of a Raman line.

If the selection rules for spontaneous emission are known, by applying the "third common level rule," the selection rules for the Raman effect can be deduced partially. One cannot derive the complete set of selection rules, since the existence of a common level is a necessary but not sufficient condition for a transition to be permitted. As was mentioned earlier, the various terms in the sum over r may cancel out resulting in zero intensity. Due to the frequency factor in the denominator, this can occur only when the same frequency belongs to several transitions, that is, when a degeneracy exists.[6]

There is a simple method which permits the derivation of all the selection rules. Forbidden transitions are usually predicated upon the symmetry properties of the system. They give rise to the fact that the Hamiltonian is invariant under certain coordinate transformations, the so-called symmetry operations (e.g., reflection, rotation, etc.).[7] Therefore, the transformation properties of the scattering formula must be investigated. The characteristic quantity $(c_{\rho\sigma})_{kn}$ given in (5.2) transforms like the matrix element of a tensor component $\int \psi_n^* c_{\rho\sigma} \psi_k \, d\tau$.

This is proved in the following way: For the scattering amplitude c_{kn} (Eq. (3.15)), it follows from Eqs. (3.14) and (3.7) that

$$(C_\rho)_{kn} = \int \psi_n^* M_\rho \psi_k^+ d\tau + \int \psi_n^{-*} M_\rho \psi_k d\tau .$$

According to (3.8), the quantities defined in (3.7) and (3.9a) transform as follows:

ψ_k^+ as $(AM)\psi_k$, and

ψ_n^{-*} as $(AM)\psi_n^*$.

$(C_\rho)_{kn}$ as $\int \psi_n^* M_\rho (AM)\psi_k d\tau$, and

$(c_{\sigma\rho})_{kn}$ as $\int \psi_n^* M_\rho (A_\sigma M)\psi_k d\tau$.

$(A_\sigma M)$ transforms as the σ components of a vector, and $M_\rho (A_\sigma M)$ as the product of two vector components, i.e., as a tensor component. The notation, $(c_{\rho\sigma})_{kn}$, introduced at the beginning has thereby been justified.

If the given system possesses any symmetry, the terms separate into different types. They differ from one another by the transformations of the symmetry operations for the eigenfunction. When a center of symmetry exists, there will be even and odd terms. For an inversion, the even functions remain invariant, while the odd ones change in sign. The matrix element $(f_{\lambda})_{kn} = \int \psi_n^* f_{\lambda} \psi_k d\tau$[8] can be different from zero only when, for a given symmetry operations, the quantity $\psi_n^* f_{\lambda} \psi_k$ remains invariant.[9] Since the classes of the eigenfunctions and the transformation rules are well-known for all the possible symmetries,[10] the selection rules for spontaneous emission (dipole radiation) can be determined immediately, provided f is replaced by a vector, the electric moment. The selection rules for the Raman effect can be obtained upon replacing the vector by a tensor. This rule has the advantage in that the selections rules are obtained by examining only the properties of the initial and final states. The intermediate states need not be considered.

As an example, we select a system with a center of symmetry. Upon inversion, all vector components change sign. Therefore, for a transition to occur in spontaneous emission, $\psi_k \psi_n^*$ must also change its sign. Even with odd, or odd with even, terms will combine. This rule is known in atomic spectra (the nucleus forms the center of symmetry) as Laport's rule. For the Raman effect, it is necessary to consider a tensor. Since a tensor itself possesses a center of symmetry, inversions leave its components invariant and $\psi_k \psi_n^*$ must retain its sign. This accounts for the fact that in the Raman effect even terms combine with even, and odd with odd, and that a centrosymmetric system cannot have the same transitions in the absorption spectrum as in the Raman effect. This is the so-called "mutual exclusion rule:" Transitions which are permitted in absorption are forbidden in the Raman effect, and vice versa. For all practical purposes, it is essential to investigate whether there is real or accidental degeneracy between the even and odd terms. If degeneracy does exist, there will be absorption, and Raman bands will be present which possess the same, or almost the same, frequencies, but which are associated with different transitions. This kind of degeneracy cannot arise from the symmetry, but rather, from the dynamics of the system as can easily be verified. For instance, a purely Coulombic force field (H atom) can cause such a degeneracy. A series of important applications of the mutual exclusion rule will be cited later.

So that the remaining selection rules may be deduced, it is expedient to separate the scattering tensor into an isotropic, a symmetric, and an antisymmetric part:

$$(c_{\rho\sigma})_{kn} = (c^{0}\delta_{\sigma}{}^{\rho} + c_{\rho\sigma}{}^{s} + c_{\rho\sigma}{}^{a})_{kn} \tag{5.12}$$

$$(c^{0})_{kn} = 1/3\ (c_{xx} + c_{yy} + c_{zz})_{kn} = 1/3h \sum_{r} \frac{\nu_{rk} + \nu_{rn}}{(\nu_{rk} - \nu)(\nu_{rn} + \nu)} \left[\sum_{\sigma} (M_{\sigma})_{kr}(M_{\sigma})_{rn}\right]$$

$$(c_{\rho\sigma}{}^{s})_{kn} = 1/2\ (c_{\rho\sigma} + c_{\sigma\rho})_{kn} - (c^{0})_{kn}\delta_{\sigma}{}^{\rho}$$

$$= 1/2h \sum_{r} \frac{\nu_{rk} + \nu_{rn}}{(\nu_{rk} - \nu)(\nu_{rn} + \nu)} \left[(M_{\sigma})_{kr}(M_{\rho})_{rn} + (M_{\rho})_{kr}(M_{\sigma})_{rn}\right] - (c^{0})_{kn}\delta_{\sigma}{}^{\rho}$$

$$(c_{\rho\sigma}{}^{a})_{kn} = 1/2\ (c_{\rho\sigma} - c_{\sigma\rho})_{kn} \tag{5.13}$$

$$= \frac{2\nu + \nu_{kn}}{2h} \sum_{r} \frac{1}{(\nu_{rk} - \nu)(\nu_{rn} + \nu)} \left[(M_{\sigma})_{kr}(M_{\rho})_{rn} - (M_{\rho})_{kr}(M_{\sigma})_{rn}\right] .$$

The isotropic part is a scalar quantity, which remains invariant under all symmetry operations. $\psi_n^{*}\psi_k$ must likewise remain invariant, but this is possible merely for terms of the same species. The sum of the diagonal elements of a tensor is called its "trace." $(c^{0})_{kn}$ of the scattering is called "the trace scattering," for which the selection rule permits the combination of terms of the same species only.

The second part represents a symmetric tensor with zero trace. The matrix elements of such a quantity determine the quadrupole radiation.[11] Hence, the selection rules for this part are identical with those of the quadrupole radiation, and is referred to as "the quadrupole scattering."[12]

The third part represents an antisymmetric, or axial, vector. It gives rise to scattering that is analogous to that of a magnetic dipole. We designate this part as "the magnetic dipole scattering." The selection rules are the same as those for the spontaneous magnetic dipole radiation of an atom or molecule, provided the selection rules are determined by the symmetry, rather than by the accidental magnetic properties of the axial vector.[13] There is a difference, however, in that the diagonal elements of the matrix (not of the tensor!) do not correspond to radiation, since the quantum state is unchanged. They represent the permanent magnetic moment of the particular level, and, in the present case, refer to the coherent scattering k = n.

As may be seen from (5.12), the frequency dependence of the trace and quadrupole scattering is the same. For small frequencies, that of the magnetic dipole scattering, however, is different; it drops off faster because of the factor $(2\nu + \nu_{kn})$ in the numerator. The relative frequency dependence of the three quantities is determined by the quantities of the individual transitions $r \rightarrow k$, $r \rightarrow n$ inside the square brackets of (5.12). Since this is different for c^{0}, c^{s}, and c^{a}, the behavior of these quantities depends appreciably on the frequency.[14]

Finally, the scattering intensity is given by

$$\left|(c_{\rho\sigma})_{kn}\right|^{2} = \left|\delta_{\sigma}^{\rho}(c^{0})_{kn} + (c_{\rho\sigma}^{s})_{kn} + (c_{\rho\sigma}^{a})_{kn}\right|^{2},$$

indicating that the amplitudes rather than the intensities of the three contributions of the scattered radiation are additive.[14] In principle, the sum could vanish because of interference. However, this could arise accidentally rather than as a result of any existing symmetry. The components of one part do not transform into those of another part due to the distinct symmetry properties of the three parts of the tensor. If the scattering system is freely rotating in space, the interference terms cancel out (see next chapter) and the intensity of the scattered radiation consists of the sum of the three parts. For coherent scattering one obtains, according to (5.13),

$$(c^{q})_{kk} = \alpha_{(k)}^{(0)} = 2/3h \sum_{r}\left[\frac{\nu_{rk}}{\nu_{rk}^{2} - \nu^{2}} \sum_{\sigma}\left|(M_{\sigma})_{kr}\right|^{2}\right]$$

$$(c_{\rho\sigma}^{s})_{kk} = (\alpha_{\rho\sigma}^{(s)})_{(k)} = 1/h \sum_{r} \frac{\nu_{rk}}{\nu_{rk}^{2} - \nu^{2}}\left[(M_{\sigma})_{kr}(M_{\rho})_{rk} + (M_{\sigma})_{kr}^{*}(M_{\rho})_{rk}^{*}\right] - (c^{0})_{kk} \qquad (5.14)$$

$$(c_{\rho\sigma}^{a})_{kk} = \nu/h \sum_{r} \frac{1}{\nu_{rk}^{2} - \nu^{2}}\left[(M_{\sigma})_{kr}(M_{\rho})_{rk} - (M_{\sigma})_{kr}^{*}(M_{\rho})_{rk}^{*}\right].$$

In coherent scattering, there is always a contribution from the trace scattering present since equivalent terms combine. The trace and symmetric parts are real, whereas the antisymmetric one is imaginary. The latter vanishes, as was stated above in part (b) for (1) real eigenfunctions, $\left[(M_{\sigma})_{kr} = (M_{\sigma})_{kr}^{*}\right]$, and (2) for $\nu = 0$, as evidenced by Eq. (5.13) and from thermodynamic considerations. For $\nu = 0$, Eq. (5.13) shows that the antisymmetric parts of the incoherent part of the unshifted radiation vanishes.

REFERENCES AND FOOTNOTES

1. For random systems, only part of the coherent scattering contributes to the dispersion (see page

2. If state k has a g_k degeneracy, then (5.2) is summed over the states s

$$a_{\rho\sigma}^{(k)} = 1/g_k \sum_s (c_{\rho\sigma})_{ks}^{ks}. \qquad (5.2b)$$

3. E. Teller, unpublished.

4. Later we shall introduce a few important examples for which it is symmetric.

5. Here the incident intensity is defined by the radiation density divided by the velocity of light: $I_0 = \frac{\int \rho(\nu) d\nu}{c}$.

6. Another example is the harmonic oscillator (see Chapter 9).

7. The basic ideas of the symmetry concept will be presented in Chapter 17.

8. f may denote either a vector or a tensor of any order, and f_λ any component.

9. For degenerate states, additional information is required; the matrix element $(f_\lambda)_{nl}^{ks}$ differs from zero only when $\sum_{sl} \sum_{\mu} a_{\mu sl} \; \psi_{nl}^{*} f_{\mu} \psi_{ks}$ is invariant with respect to symmetry operations and when $a_{\mu sl} \neq 0$ for $\mu = \lambda$.

10. H. Bethe, Ann. Physik **3**, 133 (1929).

11. E. Segre, Nuovo cimento **8**, 2 (1931); A. Rabinowicz and J. Blaton, Ergeb. exakt. Naturwiss. **11**, 176 (1932).

12. The part of the scattered radiation of the induced dipole moment that behaves like spontaneous quadrupole radiation should not be confused with the scattering from the induced quadrupole moment. The latter occurs only when the atomic displacement can no longer be neglected in relation to the wavelength of the light vector. This radiation is generally too weak to be observed, although it could be detected under resonance conditions. Here the incident frequency would have to be near transition frequencies permitted in the spontaneous quadrupole rather than dipole radiation. The theory has been developed for the unshifted radiation only. See E. Segre, l. c.; J. Blaton, Z. Physik **74**, 418 (1932).

13. B. H. C. Brinkman, Diss. Utrecht (1932).

14. Since for $\rho = \sigma$, $c_{\rho\sigma}^{a} = 0$, and for $\rho \neq \sigma$, $c^{0} = 0$, two out of three quantities contribute to each component. This result depends on the particular selection of the cartesian tensor components and is valid for these only.

Chapter 6. The Scattering Equation for Random Systems

The results derived in the preceding chapter are of a general nature. They apply to crystals (insofar as the systems examined are small compared with the wavelength), or to atoms, and molecules in any external field. For random atoms or molecules, such as gases in the absence of any external field, the above expressions simplify considerably.

We shall consider next the general properties of such a system. As a result of random orientation, the total angular momentum is an integral part of the classical equation of motion. There is a corresponding quantum number which is a measure of the total angular momentum. The eigenvalues of its square are $\hbar^2 J(J+1)$.[1]

Each state J is (2J + 1) degenerate (directional quantization). Consider a weak magnetic field; then, for each J there are (2J + 1) values of m, where, for the vector model, m is the projection of the total angular momentum onto the field direction. Since there is no preferred orientation in space, all physical properties of the system must be independent of the direction of the field. The same holds for the intensity of the scattered radiation, which, according to Eqs. (5.5a) and (5.5b), may be expressed by

$$\frac{1}{(2J+1)} \sum_{m} \sum_{m'} \left| (c_{\rho\sigma})_{nm'}^{km} \right|^2 . \qquad (6.1)$$

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The summation extends over the magnetic initial and final states, m and m' respectively; k and n refer to all non-magnetic quantum numbers of the initial and final states. The factor 1/2J + 1 arises from the fact that the expression must be divided by the spatial degeneracy of the initial state. The probability of finding an atom of state J in a magnetic state m is 1/(2J + 1).[2] Equation (6.1) remains unchanged when averaged over all orientations of the magnetic field. Averaging and summing are interchangeable. If the summation is carried out over m', followed by averaging, the result will be independent of the second index m.[3] Hence, in (6.1), one can replace one of the summations by averaging over all orientations of the magnetic field and by multiplying by the degree of spatial degeneracy:

$\overline{m'}$, $\overline{m}$ を固定しておいて 全方向に対して平均

$$\frac{1}{2J+1} \sum_{m} \sum_{m'} \left| (c_{\rho\sigma})_{nm'}^{km} \right|^2 = \sum_{m'} \overline{\left| (c_{\rho\sigma})_{n\overline{m}'}^{k\overline{m}} \right|^2} , \qquad (6.2)$$

where m, m' are the magnetic quantum numbers for any fixed direction of the magnetic field, $\bar{m}$, $\bar{m}'$ are those for a field direction different from the original one and extend over all orientations. The quantity $\left|(c_{\rho\sigma})_{n\bar{m}'}^{k\bar{m}}\right|^2$ changes with the orientation ~~is now changed~~, and one must average over all its values. This can be done by expressing $\left|(c_{\rho\sigma})_{n\bar{m}'}^{k\bar{m}}\right|^2$ in terms of the tensor components in a coordinate system whose z axis coincides with the magnetic field.

$$(c_{\rho\sigma})_{n\bar{m}'}^{k\bar{m}} = \sum_{\bar{\rho}} \sum_{\bar{\sigma}} (c_{\bar{\rho}\bar{\sigma}})_{n\bar{m}'}^{k\bar{m}} \cos\bar{\rho}\rho \cos\bar{\sigma}\sigma. \tag{6.3}$$

direction cosines

The quantities $(c_{\bar{\rho}\bar{\sigma}})_{n\bar{m}'}^{k\bar{m}}$ are no longer dependent upon the direction of the magnetic field, and hence, $(6.\overset{3}{2})$ must be averaged over the products of the direction cosines. Provided $c_{\rho\sigma}$ is separated into the three parts defined above, upon averaging Eq. $(6.\underset{3}{2})$, the terms containing products of different parts vanish, and

$$\sum_{m}\sum_{m'}\left|(c_{\rho\sigma})_{nm'}^{km}\right|^2 = \delta_\sigma^\rho \sum_{m}\sum_{m'}\left|(c_{\rho\sigma}^{0})_{nm'}^{km}\right|^2 + \sum_{m}\sum_{m'}\left|(c_{\rho\sigma}^{s})_{nm'}^{km}\right|^2 + \sum_{m}\sum_{m'}\left|(c_{\rho\sigma}^{a})_{nm'}^{km}\right|^2. \tag{6.4}$$

The scattered radiation of random systems consists of three independent parts, whose intensities are additive: trace, quadrupole, and dipole scattering.

So that the treatment may be simplified, we shall introduce circular coordinates: z, $(x + iy)/2$, and $(x - iy)/\sqrt{2}$, which are denoted by 0, +1, and -1, respectively. Here the selection rules for m assume a simple form. The following are the relationships between the circular and cartesian vector and tensor components.

$$\begin{aligned} M_0 &= Mz \\ M_1 &= 1/\sqrt{2}(M_x + iMy) \\ M_{-1} &= 1/\sqrt{2}(M_x - iMx) \end{aligned} \tag{6.5a}$$

$$\begin{aligned} c_{11} &= 1/2(c_{xx} - c_{yy}) + i/2(c_{xy} + c_{yx}) \\ c_{-1-1} &= 1/2(c_{xx} - c_{yy}) - i/2(c_{xy} + c_{yx}) \\ c_{-11} &= 1/2(c_{xx} + c_{yy}) + i/2(c_{xy} - c_{yx}) \\ c_{1-1} &= 1/2(c_{xx} + c_{yy}) - i/2(c_{xy} - c_{yx}) \end{aligned} \tag{6.5b}$$

$$c_{10} = 1/\sqrt{2}(c_{xz} + ic_{yz})$$
$$c_{01} = 1/\sqrt{2}(c_{zx} + ic_{zy})$$
$$c_{-10} = 1/\sqrt{2}(c_{xz} - ic_{yz})$$
$$c_{0-1} = 1/\sqrt{2}(c_{zx} - ic_{zy})$$
$$c_{00} = c_{zz}.$$

In circular coordinates, the invariant quantity c^0 becomes

$$c^0 = 1/3(c_{xx} + c_{yy} + c_{zz}) = 1/3(c_{00} + c_{1-1} + c_{-11}); \tag{6.5c}$$

Since the tensor relation between two vectors is[4]

$$C_\lambda = \sum_\mu c_{\lambda\mu} A_{-\mu}, = \sum_\mu c_{\lambda-\mu} A_\mu \tag{6.5d}$$

The three terms in Eq. (5.12) are given by:

$$c_{\lambda\mu} = c^0 \delta_{-\mu}^{\lambda} + c_{\lambda\mu}^{s} + c_{\lambda\mu}^{a},$$
$$c_{\lambda\mu}^{s} = 1/2(c_{\lambda\mu} + c_{\mu\lambda}) - c^0 \delta_{-\mu}^{\lambda}, \qquad C_{00}^{s} = C_{00} - \tfrac{1}{3}(C_{00} + C_{1-1} + C_{-11}) = \tfrac{1}{3}(2C_{00} - C_{1-1} - C_{-11}) \tag{6.5e}$$
$$c_{\lambda\mu}^{a} = 1/2(c_{\lambda\mu} - c_{\mu\lambda}).$$

The circular tensor components have the following significance: for linearly polarized incident radiation the matrix element c_{00} denotes the parallel component of the vector amplitude of the scattering moment. Perpendicular to it, c_{10} and c_{-10} describe the left and right circularly polarized components, respectively. Correspondingly, the quantities $c_{\lambda\mu}$ determine the relations for circularly polarized incident radiation. In general, the matrix element $c_{\lambda\mu}$ refers to the λ component of the scattering amplitude when the polarization of the incident light is $-\mu$. The minus sign is determined by Eq. (6.5d). Equations (6.2) and (6.4) remain unaltered in the new coordinates.

Upon rotation around the z(0)-axis, the quantities M_λ and $c_{\lambda\mu}$ are multiplied by exp $(i\lambda\phi)$ and by exp $(i(\lambda + \mu)\phi)$, respectively. The angular dependence of the eigenfunction is given by exp $(im\phi)$ and the product $\psi_{nm'}^{*}\psi_{km}$ is multiplied by exp $(i(m - m')\phi)$; hence the following selection rules apply to m:

Absorption: $(M_\lambda)_{nm'}^{km} \neq 0$ for $m' - m = \lambda$, (6.6a)

Raman effect: $(c_{\lambda\mu})_{nm'}^{km} \neq 0$ for $m' - m = \lambda + \mu$. (6.6b)

The scattering cross section of randomly oriented systems is, as was stated in (5.5b) and (5.5c),

$$\overline{Q}_{kn} = \frac{2^7 \pi^5}{9\lambda'^4} G_{kn},$$

$$G_{kn} = \frac{1}{2J+1} \sum_m \sum_{m'} \sum_\lambda \sum_\mu \left| (c_{\lambda\mu})_{nm'}^{km} \right|^2. \qquad (6.7)$$

This expression can be simplified in various ways. If we use the selection rules (6.6b) and note that G_{kn} is invariant and no longer needs to be averaged, we obtain, from Eq. (6.2)

$$G_{kn} = \sum_\lambda \sum_\mu \left| (c_{\lambda\mu})_{n\lambda+\mu}^{k0} \right|^2. \qquad (6.7a)$$

The quantity $\overline{m}$ in (6.2) was arbitrarily set equal to zero. Expression (6.7) may be modified further by assuming that each component of the incident light yields the same scattering cross section regardless of its polarization. Therefore,

$$G_{kn} = 3 \sum_m \sum_{\cancel{\lambda}\mu} \left| (c_{0\mu})_{nm+\mu}^{km} \right|^2. \qquad (6.7b)$$

In general, it is possible to reduce the four sums in (6.7) to two, but in most instances expression (6.7a) is most suitable.

According to (6.4), the scattering cross section for random systems is comprised of a sum of three separate cross sections:

$$G_{kn} = G_{kn}^0 + G_{kn}^s + G_{kn}^a. \qquad (6.8)$$

1. Trace Scattering. According to (6.5c) and (6.5e), trace scattering occurs only when the components $\lambda + \mu = 0$ and $m = 0$.

$$(c^0)_{nm}{}^{km} = 1/3 \sum_{\lambda} (c_{\lambda-\lambda})_{nm}{}^{km}$$

$$(c^0)_{nm}{}^{km} = (1/3h) \sum_{r} \frac{\nu_{rk} + \nu_{rn}}{(\nu_{rk} - \nu)(\nu_{rn} + \nu)} \sum_{\lambda} (M_{\lambda})_{rm+\lambda}^{km} (M_{-\lambda})_{nm}{}^{rm+\lambda}. \quad (6.9)$$

The summation over $\overline{m}$ in Eq. (6.2) vanishes because of the selection rule $\Delta m = 0$. Since c^0 is a scalar quantity (independent of direction), the summation over all orientations of the magnetic field may also be neglected, and, for $\overline{m} = 0$,

$$\frac{1}{2J+1} \sum_{m} \left|(c^0)_{nm}{}^{km}\right|^2 = \left|(c^0)_{n0}{}^{k0}\right|^2. \quad (6.10)$$

With the aid of (6.5e) and (6.7), the scattering cross section for the trace scattering may be represented by

$$\begin{aligned} Q_{kn}{}^0 &= \frac{2^7 \pi^5}{9\lambda'^4} G_{kn}{}^0 \\ G_{kn}{}^0 &= 3\left|(c^0)_{n0}{}^{k0}\right|^2. \end{aligned} \quad (6.11)$$

The selection rule for J is readily obtained since for the trace scattering only terms of the same symmetry species combine. Because the Hamiltonian of a system randomly oriented in space is invariant, the eigenfunctions separate into a series of species in such a way that there is a symmetry type for each J. Therefore, terms with different J belong to different species and the selection rule $\Delta J = 0$ applies. For linearly polarized incident light, $(c_{00})_{nm'}{}^{km} \neq 0$ and the scattered radiation associated with a dipole parallel to the electric vector will be linearly polarized in the plane of the incident electric field and the direction of observation. The angular dependence of the intensity is analogous to Eq. (3.16):

$$I(\theta) = \frac{3}{8\pi} Q_{kn} \sin^2 \theta. \quad (6.12a)$$

For unpolarized incident light (for instance, by considering the radiation to be due to two mutually perpendicular, independently vibrating dipoles),

$$I(\phi) = \frac{3}{8\pi} \frac{Q_{kn}}{2} (1 + \cos^2 \phi), \quad (6.12b)$$

where ϕ is the angle between the directions of propagation and observation. Scattering that is observed at right angles to the incident light is also linearly polarized, the degree of polarization being

$$\rho_n(\phi) = I_\perp / I_\parallel = \cos^2 \phi. \tag{6.12c}$$

Scattering observed along the direction of propagation is not polarized, as is expected from symmetry considerations.

For circularly polarized incident light, the directional distribution and the degree of depolarization are identical with those for unpolarized light. If the scattered radiation is separated along circular coordinates, then for right circularly polarized incident light ($\mu = -1$), the trace scattering will contain only $c_{-11} \neq 0$. Hence for right circularly polarized incident light and observation in the direction of propagation, $\phi = 0$, the scattering becomes right circularly polarized, whereas for $\phi = \pi$, the scattering becomes left circularly polarized. Upon observing it in any of the intermediate directions, both components are present. The ratio of left to right circularly polarized components is

$$P(\phi) = \tan^4 \phi/2. \tag{6.12d}$$

2. Quadrupole Scattering. Since none of the tensor components vanish, $\Delta m = 0, \pm 1, \pm 2$; the transitions ± 2 occur for circularly polarized light because only then $|\lambda + \mu| > 1$. The selection rules for J are the same as those for the quadrupole radiation: $\Delta J = 0, \pm 1, \pm 2$. The intensity vanishes for the transitions in J: $0 \rightarrow 0$, $0 \rightleftarrows 1$, $1/2 \rightarrow 1/2$.

The tensor component will assume the following form:

$$(c_{\lambda\mu}{}^{s})^{km}_{nm+\lambda+\mu} = 1/2h \sum_r \frac{\nu_{rk} + \nu_{rn}}{(\nu_{rk} - \nu)(\nu_{rn} + \nu)} \Big[(M_\mu)^{km}_{r,m+\mu} (M_\lambda)^{r,m+\mu}_{n,m+\lambda+\mu} + (M_\lambda)^{km}_{r,m+\underset{\lambda}{\cancel{\mu}}} (M_\mu)^{r,m+\lambda}_{n,m+\lambda+\mu} \Big] - (c^{(0)})^{km}_{nm} \delta^{\lambda}_{-\mu}. \tag{6.13}$$

The result of averaging expression (6. 3) in accordance with (6. 2) yields

$$\frac{1}{2J+1}\sum_{m}\left|(c_{00}{}^{s})_{nm}^{km}\right|^{2} = 2/15\, G_{kn}{}^{s}$$ $\frac{4}{30}$

$$\frac{1}{2J+1}\sum_{m}\left|(c_{01}{}^{s})_{nm+1}^{km}\right|^{2} = \frac{1}{2J+1}\sum\left|(c^{s}_{0-1})_{nm-1}^{km}\right|^{2} = 1/10\, G_{kn}{}^{s}$$ $\frac{12}{30}$

$$\frac{1}{2J+1}\sum_{m}\left|(c^{s}_{1-1})_{nm}^{km}\right|^{2} = 1/30\, G_{kn}{}^{s} \qquad (6.14)$$ $\frac{3}{30}$

$$\frac{1}{2J+1}\sum_{m}\left|(c_{11}{}^{s})_{nm+2}^{km}\right|^{2} = \frac{1}{2J+1}\sum\left|(c^{s}_{-1-1})_{nm-2}^{km}\right|^{2} = 1/5\, G_{kn}{}^{s}$$ $\frac{12}{30}$

$$G_{kn}{}^{s} = \sum_{\lambda\mu}\left|(c_{\lambda\mu}{}^{s})_{n,\,\lambda+\mu}^{k0}\right|^{2}. \leftarrow G_{kn}^{s} = \frac{1}{2J+1}\sum_{m}\sum_{m'}\sum_{\lambda}\sum_{\mu}\left|(c_{\lambda\mu}^{s})_{nm'}^{km}\right|^{2} \qquad (6.14a)$$

Equation (6.14) determines the degree of polarization. For linearly polarized incident light, the depolarization factor of light scattered perpendicularly to the incident vector becomes

$$\rho = \frac{\sum_{m}\left|(C_1)_{nm+1}^{km}\right|^{2}}{\sum_{m}\left|(C_0)_{nm}^{km}\right|^{2}} = \frac{\sum_{m}\left|(c_{10}{}^{s})_{nm+1}^{km}\right|^{2}}{\sum_{m}\left|(c_{00}{}^{s})_{nm}^{km}\right|^{2}} = 3/4. \qquad (6.15a)$$

Equations (6.14) and (3.16) indicate that for any arbitrary direction of observation

$$I(\theta) = 3/8\pi\,(6+\sin^{2}\theta)\,\frac{Q_{kn}{}^{s}}{10}, \quad \text{and } \rho(\theta) = \frac{3}{3+\sin^{2}\theta}. \qquad (6.15b)$$

Correspondingly, for unpolarized light,

$$\rho_n = 6/7$$

$$I(\phi) = 3/8\pi\,(13+\cos^{2}\phi)\,\frac{Q_{kn}{}^{s}}{20} \qquad (6.15c)$$

$$\rho_n(\phi) = \frac{6+\cos^{2}\phi}{7}.$$

Since $\left|(c_{11})^{km}_{nm+2}\right|^2 \neq 0$ for circularly polarized incident light and observation along the direction of propagation ($\phi = 0$), the scattered radiation will also contain a left circularly polarized component when the incident light is right circularly polarized, and vice versa. The reversal coefficient (ratio of intensity of component polarized in the same sense to that polarized in a reverse sense) is, according to (6.14),

$$P = \frac{\sum\limits_{mm'} \left|(C_1)_{nm'}^{km}\right|^2}{\sum\limits_{mm'} \left|(C_{-1})_{nm'}^{km}\right|^2} = \frac{\sum\limits_{m} \left|(c_{11}{}^{s})_{nm+2}^{km}\right|^2}{\sum\limits_{m} \left|(c_{-11}{}^{s})_{nm}^{km}\right|^2} = 6. \qquad (6.15d)$$

According to (3.11) and (3.16) the reversal coefficient may simply be written as:

$$P(\phi) = \frac{13 + \cos^2\phi + 10\cos\phi}{13 + \cos^2\phi - 10\cos\phi}. \qquad (6.15e)$$

3. Magnetic Dipole Scattering. There are non-zero components only when $\lambda \neq \mu$. Therefore, for linearly polarized incident light, $\Delta m = \pm 1$, and for circularly polarized light, $\Delta m = 0$. The selection rules for J are the same as for spontaneous dipole radiation: $\Delta J = 0, \pm 1$, where the transition $0 \rightarrow 0$ is forbidden.

$$(c_{\lambda\mu}{}^{a})_{nm+\lambda+\mu}^{km} = \frac{2\nu + \nu_{kn}}{2h} \sum_{r} (\nu_{rk} - \nu)^{-1}(\nu_{rn} + \nu)^{-1}$$
$$\left[(M_\mu)_{r,\,m+\mu}^{km}(M_\lambda)_{n,\,m+\lambda+\mu}^{r,\,m+\lambda} - (M_\lambda)_{r,\,m+\lambda}^{km}(M_\mu)_{n,\,m+\lambda,\,\mu}^{r,\,m+\lambda}\right]. \qquad (6.16)$$

Upon averaging, according to Eq. (6.2), we have

$$\frac{1}{2J+1}\sum_{m}\left|(c_{01}{}^{a})_{nm+1}^{km}\right|^2 = \frac{1}{2J+1}\sum_{m}\left|(c^{a}_{0-1})_{nm-1}^{km}\right|^2$$
$$= \frac{1}{2J+1}\sum_{m}\left|(c^{a}_{1-1})_{nm}^{km}\right|^2 = 1/6\; G_{kn}{}^{a}. \qquad (6.17)$$

$$\frac{1}{2J+1}\sum_{m}\left|(c_{\lambda\mu}{}^{a})_{nm+1}^{km}\right|^2 = \frac{1}{2J+1}\sum_{m}\left|(c_{\mu\lambda}{}^{a})_{nm+1}^{km}\right|^2$$

$$G_{kn}{}^{a} = \sum_{\lambda\mu}\left|(c_{\lambda\mu}{}^{a})_{n\lambda+\mu}^{k0}\right|^2. \qquad (6.17a)$$

Since the components c_{00} and c_{11} do not occur, the depolarization factor for linearly polarized, and the reversal factor for circularly polarized, incident light are

$$\rho = \infty$$

$$P = 0. \qquad (6.18a)$$

According to Eq. (6.17) and the dipole formula, the angular functions for linearly polarized and unpolarized incident light are as follows:

$$I(\theta) = 3/8\pi\,(1 + \cos^2\theta)\,\frac{Q_{kn}^{\ a}}{2}$$

$$\rho(\theta) = \frac{1}{\cos^2\theta}$$

$$I(\phi) = 3/8\pi\,(2 + \sin^2\phi)\,\frac{Q_{kn}^{\ a}}{4} \qquad (6.18b)$$

$$\rho_n(\phi) = 1 + \sin^2\phi.$$

$\rho_n = 2$, when the scattering is observed at right angles to the incident radiation.

As for the isotropic scattering, the reversal factor is different from zero for circularly polarized incident light, provided ϕ is neither 0 nor π. However, the angular dependence varies slightly since the components c_{1-1} and c_{0-1} are different from those for the isotropic scattering. Here,

$$P(\phi) = \frac{1 - \cos^4\phi/2}{1 - \sin^4\phi/2}\,. \qquad (6.18c)$$

Equations (11) to (13) describe completely the behavior of the scattered radiation for any particular type of incident light. The scattered radiation is determined by the three quantities $G_{kn}^{\ 0}$, $G_{kn}^{\ s}$, $G_{kn}^{\ a}$, which are, according to (6.7), proportional to the cross sections of the isotropic quadrupole and magnetic dipole scattering.

For linearly polarized incident light and observation at right angles to it, the depolarization factor may be written, according to (6.11), (6.14), (6.15a), and (6.17):

$$\rho = \frac{3G_{kn}^{\ s} + 5G_{kn}^{\ a}}{10G_{kn}^{\ 0} + 4G_{kn}^{\ s}}\,. \qquad (6.19)$$

In the following treatment these conditions are assumed, whereas for circularly polarized light P is given for $\phi = 0$. The reversal coefficient for circularly polarized incident light, is

$$P = \frac{6G_{kn}{}^{s}}{10G_{kn}{}^{0} + G_{kn}{}^{s} + 5G_{kn}{}^{a}} . \tag{6.20}$$

$G^0 = 1$ $G^a = 2$ $P = 0$
$G^s = 5$ $G^a = 1$ $\frac{30}{10}$ $P = 3$

In general, for unpolarized incident light,

$$\rho_n = \frac{2\rho}{1 + \rho} . \tag{6.21}$$

The three quantities $G_{kn}{}^{0}$, $G_{kn}{}^{s}$, and $G_{kn}{}^{a}$ may be found experimentally for each Raman line by measuring P and ρ. Thereby their ratio can be evaluated, and by measuring the intensities, the absolute values are obtained. If one of the three quantities G disappears as a result of the selection rules, then either $P = 0$ (for zero quadrupole scattering) or P and ρ are related according to Eqs. (6.19) and (6.20): for zero isotropic scattering,

$$P^{(s,a)} = \frac{3}{2\rho - 1} ; \tag{6.22a}$$

and for zero magnetic dipole scattering,

$$P^{(0,s)} = \frac{2\rho}{1 - \rho} . \tag{6.22b}$$

The angular function of the total intensity of a scattered line is given by (6.12), (6.15), and (6.18), or directly by Eq. (3.16) for linearly polarized incident light:

$$I(\theta) = 3/8\pi \frac{Q_{kn}}{1 + 2\rho} \left[1 + \rho - (1 - \rho) \cos^2 \theta \right] . \tag{6.23a}$$

For natural or circularly polarized light:

$$I(\phi) = 3/8\pi \frac{Q_{kn}}{2 + \rho_n} \left[1 + \rho_n + (1 - \rho_n) \cos^2 \phi \right] . \tag{6.23b}$$

The angular dependence of the total intensity is determined by means of the depolarization factor (with $\phi = 90^\circ$), and the total intensity of a Raman line scattered in any direction is given by two constants, the depolarization factor and the absolute intensity at $\theta = 90^\circ$, for instance. In order to evaluate the three constants $G_{kn}{}^{0}$, $G_{kn}{}^{s}$, $G_{kn}{}^{a}$, it is necessary to measure P.

According to (6.23), the scattered intensity for linearly polarized incident light will be:

$$I(\pi/2) = 3/8\pi\, Q_{kn} \frac{1 + \rho}{1 + 2\rho}, \tag{6.24a}$$

and for unpolarized for circularly polarized incident light:

$$I_n(\pi/2) = 3/8\pi\, Q_{kn} \frac{1 + \rho_n}{2 + \rho_n}, \tag{6.24b}$$

so that (6.23) may be replaced by

$$\begin{aligned} I(\theta) &= I(\pi/2)\left[1 - \frac{1 - \rho}{1 + \rho} \cos^2 \theta\right], \\ I(\phi) &= I(\pi/2)\left[1 + \frac{1 - \rho_n}{1 + \rho_n} \cos^2 \phi\right]. \end{aligned} \tag{6.25}$$

Finally, the expressions for the angular dependence of ρ and P of the total scattering may be deduced from (6.12), (6.15), and (6.18), or directly from (3.16), as follows:

$$\begin{aligned} &\rho(\theta) = \frac{\rho}{1 - (1 - \rho) \cos^2 \theta}, \quad \rho_n(\phi) = 1 - (1 - \rho_n) \sin^2 \phi \\ &P(\phi) = \frac{1 + (\rho_n - 1)/2 \sin^2 \phi - (1 - P)/(1 + P) \cos \phi}{1 + (\rho_n - 1)/2 \sin^2 \phi + (1 - P)/(1 + P) \cos \phi} \end{aligned} \tag{6.26}$$

The most important properties of the scattering are summarized in Table I. The columns show the selection rules for m and J, the values of ρ, ρ_n, and P, and the angular functions for ordinary and linearly polarized incident radiation. Figure 3 demonstrates the angular dependence for unpolarized light. The isotropic scattering reaches a maximum along the direction of the incident light, and the magnetic dipole scattering perpendicular to it. The quadrupole scattering is independent of direction, except for a slight predominance of the direction of incident radiation. In any event, the intensity distribution is symmetrical about $\pi/2$, unless the wavelength is no longer large compared with the dimensions of the atoms.

Table I. Selection rules, depolarization factor, and angular dependence of the three parts of the scattering radiation

Type of Scattering	$\triangle m$	$\triangle J$	Transitions Forbidden in J	ρ	ρ_n	P	I	I_n
Isotropic	0	0	—	0	0	1	$\sin^2 \theta$	$1 + \cos^2 \phi$
Quadrupole	$0, \pm 1, \pm 2$	$0, \pm 1, \pm 2$	$0 \rightarrow 0, 0 \rightleftarrows 1, \frac{1}{2} \rightarrow \frac{1}{2}$	$\frac{3}{4}$	$\frac{6}{7}$	6	$1 + \frac{\sin^2 \theta}{6}$	$1 + \frac{\cos^2 \phi}{13}$
Magnetic dipole	$0, \pm 1$	$0, \pm 1$	$0 \rightarrow 0$	∞	2	0	$1 + \cos^2 \theta$	$1 + \frac{\sin^2 \phi}{2}$

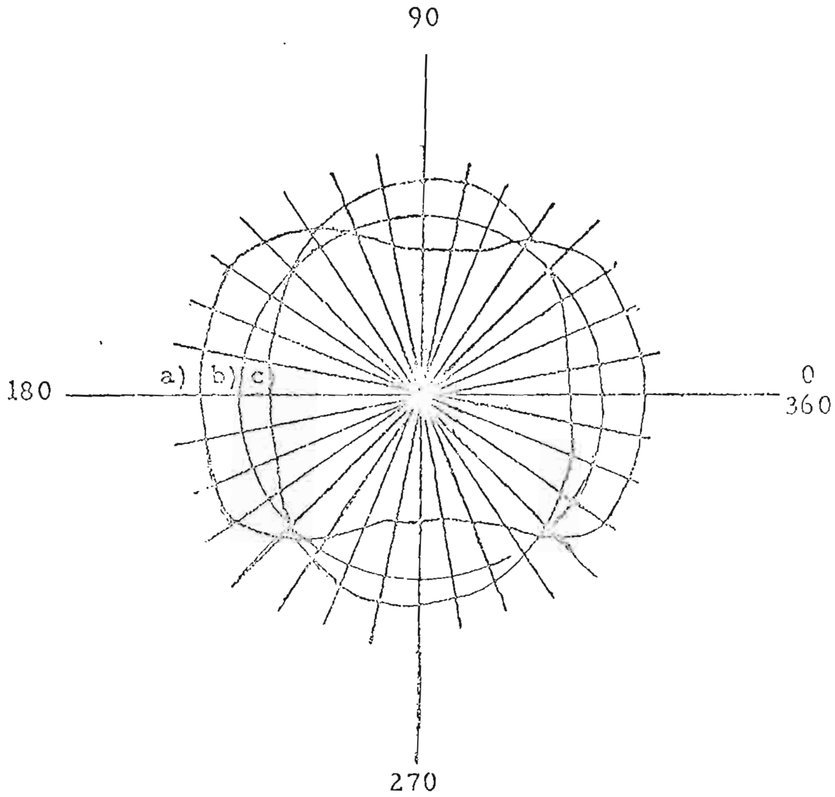

Figure 3. Angular dependence of the scattered light intensity for unpolarized incident light.

a) Isotropic scattering

b) Quadrupole scattering

c) Magnetic dipole scattering

The expressions (6.11), (6.14a), and (6.17a) must be solved for G. The matrix element $(M_\lambda)_{n,\,m+\lambda}^{km}$ of the λ component of the electric moment may be written in the form:

$$(M_\lambda)_{v'J'm+\lambda}^{vJm} = b_{v'J'}^{\;vJ}\; g_{J'm+\lambda}^{Jm}, \tag{6.27}$$

where v denotes all the quantum numbers except J and m; $b_{v'J'}^{\;vJ}$ is independent of m and the direction; $g_{J'm'}^{Jm}$ is a simple function of J and m, and is the same for random systems. The formulas may be found in text books on quantum theory.[5] If Eq. (6.27) is substituted into the expressions for the tensor components, and applied in Eqs. (6.14a) and (6.17a), the quantities G become functions of $b_{v'J'}^{\;vJ}$ which are independent of direction. For instance, for the trace scattering,

$$\left[G^0\right]_{v'J'}^{\;vJ} = \frac{(2J+1)}{3h^2}\left|d_{JJ}\cdot J(J+1) + d_{JJ+1}\,(J+1)(2J+3) + d_{JJ-1}\cdot J(2J-1)\right|^2 \tag{6.28}$$

where

$$d_{JJ'} = \sum_{v''}\frac{\left|b_{v''J''}^{vJ}\right|^2\left(\nu_{vJ}^{v''J''} + \nu_{v'J'}^{v''J''}\right)}{\left(\nu_{vJ}^{v''J''} - \nu\right)\left(\nu_{v'J'}^{v''J''} + \nu\right)}.$$

<u>Undisplaced Scattered Radiation.</u> For the undisplaced radiation, further simplifications are possible. Let us introduce the oscillator strength

$$f_{kr} = \frac{8\pi^2\mu\nu_{rk}}{3e^2h}\sum_\lambda \left|(M_\lambda)_{r\lambda}^{k0}\right|^2. \tag{6.29}$$

This quantity relates the average absorption associated with the transition k → r (in particular, for $\nu_{kr} > 0$, induced emission) and the absorption (induced emission) of a classical oscillator having the charge and mass of an electron and frequency $|\nu_{kr}|$. According to Eqs. (6.29), (6.9), and (6.11), we obtain for the scattered radiation

$$G_{kk}^{\;0} = 3\left(\frac{e^2}{4\pi^2\mu}\right)^2\left|\sum_r \frac{f_{kr}}{\nu_{rk}^2 - \nu^2}\right|^2. \tag{6.30}$$

If r > k (absorption frequency), $f_{rk} > 0$; if r < k (emission frequency) ν_{rk} is negative and $f_{kr} < 0$ (negative dispersion).

There is a simple relation between unshifted isotropic scattering and polarizability of the state k. According to (5.2b):

$$(\alpha_{\lambda\mu})_{(k)} = \left(\frac{1}{2J+1}\right)\sum_{m}(c_{\lambda\mu})_{km}^{\ \ km} = \frac{1}{2J+1}\sum_{m}(c_{\lambda-\lambda})_{km}^{\ \ km}\delta_{\mu}^{\ \lambda}.$$

If $c_{\lambda-\lambda}$ is separated into isotropic, quadrupole, and magnetic dipole contributions, the last two vanish when summed over m:

$$\sum_{m}(c^{s}_{\lambda-\lambda} + c^{a}_{\lambda-\lambda})_{km}^{\ \ km} = 0,$$

and

$$(a_{\lambda-\lambda})_{(k)} = \frac{1}{2J+1}\sum_{m}(a_{\lambda-\lambda})_{km}^{\ \ km} = (c^{(0)})_{k0}^{\ \ k0} = (\alpha^{(0)})_{(k)}; \qquad (6.31)$$

expressing the istropy of the tensor. Hence, from (6.31) and (6.11), it follows that

$$\left|(\alpha^{0})_{(k)}\right|^{2} = 1/3\ G_{kk}^{\ \ 0}. \qquad (6.32)$$

Also, the quadrupole and magnetic dipole contributions of the unshifted scattered radiation may be represented in terms of the oscillator strengths, with the aid of Eq. (6.29). Expressions which require that the intermediate states be distinguished on the basis of ΔJ are not reproduced here.

REFERENCES AND FOOTNOTES

1. See Kronig, Chapter 2 of this Handbook.

2. Selective excitation of the magnetic state is not being discussed as it is contingent upon external perturbations which would destroy the free orientation.

3. The proof is furnished by G. Placzek and E. Teller, Z. Physik 81, 209 (1933).

4. λ and μ denote circular, and ρ and σ are cartesian coordinates.

5. See Weyl, Group Theory and Quantum Mechanics.

Chapter 7. Resonance Processes

When the incident frequency coincides with the eigenfrequency, the scattering amplitude can become infinite in some instances. Radiation damping, which, in quantum mechanics, arises from the finite lifetime of the stationary states, was neglected in the derivations given in Chapters 3 and 4. If this damping is taken into account,[1] for freely rotating systems, Eq. (5.1) will be replaced by

$$(c_{\lambda\mu})^{km}_{nm+\lambda+\mu} = 1/h \sum_{r} \left[\frac{(M_{\mu})^{km}_{rm+\mu} (M_{\lambda})^{rm+\mu}_{nm+\lambda+\mu}}{\nu_{rk} - \nu - i\gamma_r} \quad \frac{(M_{\lambda})^{km}_{rm+\lambda} (M_{\mu})^{rm+\lambda}_{nm+\lambda+\mu}}{\nu_{rn} + \nu + i\gamma_r} \right] . \tag{7.1}$$

The damping constant γ_r is defined by

$$4\pi\gamma_r = 1/\tau_r = \frac{64\pi^4}{3c^3 h} \sum_{r''} \nu^3_{rr''} \sum_{\lambda} \left| (M_{\lambda})^{r0}_{r''\lambda} \right|^2 .$$

$\hbar\gamma = \frac{\hbar}{4\pi\tau}$

$\gamma' = \frac{\hbar}{4\pi\tau}$

The summation extends over the levels r'', which are lower than r; τ_r denotes the lifetime of the state r. As it is the same for the magnetic sublevels of r, the damping constant γ_r will be independent of m.

Provided $\left| \nu_{rk} - \nu \right| \gg \gamma_r$ and $\left| \nu_{rn} + \nu \right| \gg \gamma_r$, damping may be neglected and Eq. (7.1) transforms into the usual scattering formula. Near the region of resonance, the damping factor becomes appreciable, as may be seen from Eq. (7.1).[2]

We shall now discuss the possible resonance processes:

1. Undisplaced Scattering ($E_k = E_n$). Resonance may occur for all transition frequencies of the states considered above. The only terms in (7.1) giving rise to resonance are the first and second terms, for absorption ($\nu_{rk} > 0$) and emission frequencies ($\nu_{rk} < 0$), respectively.

2. Displaced Scattering. The first term gives rise to resonance when $\nu = \nu_{rk}$, and the second term, when $\nu = -\nu_{rn}$. Since ν and $\nu + \nu_{kn}$ (incident and emitted radiation) are always positive, the former (the latter) situation occurs when $E_r > E_k$ and $E_r > E_n$ ($E_r < E_k$ and $E_r < E_n$). Therefore, resonance never occurs when the energy of the intermediate state r lies between that of the initial and final states. On the other hand, resonance occurs when the incident frequency is the same as the absorption frequency of the initial state or the emission frequency of the final state. In other words, the emitted frequency must coincide with the absorption frequency of the final state or with the emission frequency of the initial state.

The last case, which can be readily visualized by reference to Fig. 2 will require further consideration. It appears paradoxical that an atom in state k, irradiated with an emission frequency n, which is not a transition frequency of k, should scatter very strongly, and that for continuous irradiation an absorption line appears in the transmitted light which does not correspond to any absorption frequency of k. Since there is a spontaneous transition from state k to r_3, it is not permissible to choose ψ_k as the unperturbed eigenfunction. Rather, a finite probability exists for the atom to be in a state r. Hence the appearance of an absorption line ν_{nr_3} (absorption frequency of state r_3) can be explained by assuming that the initial state is a linear combination of ψ_k and ψ_{r_3}.[3]

Near resonance, the degree of depolarization of the scattered radiation can be readily calculated because the ratio of the three terms of the scattering which according to Eq. (6.22) determines the polarization, becomes a universal quantity depending only on the total angular momentum J of the initial, resonance and final states.[4] As example, we choose the depolarization of the undisplaced scattering of a state with total angular momentum J near resonance of a transition $\Delta J = 0$ (see Chapter 25, b). According to Eqs. (6.11), (6.14), (6.17), (6.19), and (6.28),

$$\rho = 1/2 \frac{2J(J+1)+1}{3J(J+1)-1}. \tag{7.2}$$

The scattering cross section near resonance may be obtained from (1). If, from the resonance state r, only the transition to the initial state k is possible, then the scattered radiation will not be displaced. The cross section, according to (7.1) and (6.7), becomes

$$Q_{kk}(\nu = \nu_{rk}) = \lambda^2/2\pi \;\; g_r/g_k. \tag{7.3}$$

The cross section will be of the order of the square of the resonance frequency; it is independent of the f-value of the transition k → r. The greatest value of the cross section will be obtained for $J_k = 0$, $J_r = 1$, where here $g_r/g_k = 3/1 = 3$ and

$$Q_{kk} = 3/2\pi \;\; \lambda^2. \tag{7.3a}$$

If transitions from the resonance level r to other states are possible, displaced resonance radiation will appear also. In that case the individual scattering cross sections G_{kn}, as well as the total cross section $\sum_{n} G_{kn}$, depends upon the f-value of the transitions k → r. The total cross section is usually smaller than (7.3).

The depolarization in the resonance region is very sensitive to external perturbations, as may be seen from Eq. (7.1). To first-order approximation, an external field causes a splitting of the directional degenerate states. This is not important outside the region of resonance, but in its immediate vicinity slight displacements of the transition frequencies become apparent since the denominator of the scattering formula is small. Those terms in the scattering formula that are subject to interference because of exact directional degeneracy will occur now and will give rise to a change in polarization in such a way that the field will always cause an increase in the depolarization. If the external field (e.g., magnetic field) is parallel to the electric vector of the incident radiation (perpendicular to a plane, for circular polarization), the polarization of the scattered radiation remains unchanged to a first-order approximation. Oppenheimer and Weisskopf supplied the proof for this rule which was annunciated by Heisenberg before the advent of the modern quantum theory.[5, 6]

Aside from a depolarization effect, the magnetic field causes a rotation of the plane of maximum polarization, which rotation is proportional to the field strength and vanishes abruptly outside the region of resonance. This is shown also by the complexity of the damping term in the scattering formula.

Effects of the external field on the polarization of resonance radiation was studied experimentally for the undisplaced scattering (resonance fluorescence). The same observations are expected to occur for the displaced resonance radiation. Most likely, investigations of the vapor state of thallium could be carried out without great difficulties.

Resonance radiation has been dealt with in the article by Hanle in this Handbook, by Pringsheim,[8] and by Weisskopf. A few special cases are treated in Chapters 12, 13, and 25.

REFERENCES AND FOOTNOTES

① V. Weisskopf, Ann. Physik 9, 23 (1931).

2. In an additional paper, Weisskopf (Physik, to appear in 1933) showed that Eq. (7.1) is applicable in the above form when the lifetimes of the initial and final states are large compared with the lifetime of the intermediate state. This holds only if the initial and final states correspond to the ground state or meta-stable states, or, for molecules, to vibrational and rotational states of the electronic ground state. This paper should be referred to in connection with the discussion of subsequent examples.

3. A treatment of this case by Kramers and Heisenberg, using pre-quantum theory, should be replaced by the above.

④ This has no significance when as a result of special force fields, terms having different J values are degenerate, (examples: H-atom; three dimensional harmonic oscillator); Eq. (7.2) is not applicable.

5. Oppenheimer, Z. Physik 43, 27 (1927); Weisskopf, l. c.

6. W. Heisenberg, Z. Physik 31, 617 (1925). Heisenberg used the opposite approach in that he calculated the intensity and polarization of fluorescence in the above-defined magnetic field and from that deduced the value of these quantities for fluorescence in the absence of a magnetic field.

7. Compare with the investigations on Hg by E. F. Richter, Ann. Physik 7, 293 (1931).

8. P. Pringsheim, Fluorescence and Phosphorescence, Berlin, (1928).

Chapter 8. Scattering Processes and Thermal Equilibrium

The expressions derived in Chapter 4 for the scattering probability assure thermal equilibrium. They satisfy the requirements that Planck's energy distribution of the radiation cavity and the Boltzmann distribution (corresponding to the same temperature) of atoms in stationary states will not be altered in the course of the scattering processes. This may be demonstrated in the following manner. According to Eq. (4.9), the number of occurrences for a scattering process involving a light quantum of polarization j, within the frequency range ν and $\nu + d\nu$ and solid angle $d\omega$, to go over into ν' and $\nu' + d\nu'$, $d\omega'$ and j', and for an atom to go from state k to n,[1] is given by

$$dZ_{kn} = N_k W_{kn} d\nu d\nu' d\omega d\omega' \delta_{\nu+\nu_{kn}}^{\nu'}$$

$$dZ_{kn} = N_k \rho_j(\nu, \omega)\left(\frac{h\nu'^3}{c^3} + \rho_{j'}(\nu', \omega')\right) \Phi_{kn}(\nu, \nu', k_j, k_{j'}) d\nu d\nu' d\omega d\omega' \delta_{\nu+\nu_{kn}}^{\nu'} \tag{8.1}$$

$$\Phi_{kn} = \frac{16\pi^4}{h^2} \left| \sum_\rho \sum_\sigma \left[c_{\rho\sigma}(\nu)\right]_{kn} e_\rho e_\sigma \right|^2.$$

Since from Eq. (5.$\overset{2}{1}$)

$$\left[c_{\rho\sigma}(\nu)\right]_{kn} = \left[c_{\sigma\rho}(\nu + \nu_{kn})\right]_{nk}^*, \tag{8.2}$$

$$\Phi_{kn}(\nu, \nu', k_j, k'_{j'}) = \Phi_{nk}(\nu', \nu, k_j{}', k_j), \text{ where} \tag{8.3}$$

$$\nu' = \nu + \nu_{kn}.$$

If transitions occur between degenerate states, Eq. (8.3) will apply separately to the individual transitions of the quantities $\Phi_{ns'}^{ks}$ corresponding to different sub-states. If we set, as in Eq. (5.2b),

$$W_{kn} = 1/g_k \sum_{ss'} W_{ns'}^{ks}, \qquad \Phi_{kn} = 1/g_k \sum_{ss'} \Phi_{ns'}^{ks},$$

then instead of (8.3) we have

$$g_k \Phi_{kn} (\nu, \nu', k_j, k'_{j'}) = g_n \Phi_{nk} (\nu', \nu, k_{j'}, k_j). \tag{8.4}$$

Upon substituting the Boltzmann distribution and Planck's relation in place of N_k and $\rho_j(\nu, \omega)$ into (8.1),

$$N_k = \frac{g_k \exp(-E_k/kT)}{\sum g_n \exp(-E_n/kT)} \quad \text{and} \quad \rho_j(\nu, \omega) = \frac{h\nu^3}{c^3} \; \frac{1}{\exp(h\nu/kT) - 1}. \tag{8.5}$$

It may be seen from Eq. (8.4) that the process defined in (8.1) occurs as often as its inverse. The inverse of (8.1) arises from the exchange of the initial and final states of the atoms, and from the exchange of the incident and emitted quanta. The equality of the probability of inverse processes is usually sufficient to assure thermal equilibrium.[2]

Alternatively, if one equates the number of occurrences of inverse processes (principle of microscopic reversibility or detailed balancing), Eq. (8.4) may be deduced. This identity--which is sufficient but not necessary for the attainment of thermal equilibrium--is based on the Hermitian, i.e., quasi-Hermitian, character of the quantum mechanical matrices, which is expressed by (8.2). The Eqs. (8.3) and (8.4) follow directly from (8.2).[3]

The intensity relations between Stokes and anti-Stokes lines, and the frequency-dependence of the intensity of these two lines are correlated in Eq. (8.3).[4] If we introduce the previously defined scattering cross section, Q_{kn}, which is associated with Φ_{kn} in the following manner:

$$Q_{kn}(\nu k_j) = \frac{h\nu'}{c\rho_j(\nu, \omega)} \sum \int W_{kn} d\omega' = \frac{h^2 \nu'^4}{c^4} \sum_{j'} \int \Phi_{kn}(\nu, k_j, \nu', k_{j'}) d\omega', \tag{8.6}$$

and make use of (8.4) and (8.6), then we obtain

$$\nu^4 g_k Q_{kn}(\nu, k_j) = \nu'^4 g_n Q_{nk}(\nu', k_{j'}). \tag{8.7}$$

Upon averaging over all values of k_j or $k_{j'}$, as in Chapter 6,

$$\nu^4 g_k Q_{kn}(\nu) = \nu'^4 g_n Q_{nk}(\nu'). \tag{8.7a}$$

For systems randomly oriented in space, it is not necessary to average; hence

$$\frac{g_k Q_{kn}(\nu)}{g_n Q_{nk}(\nu + \nu_{kn})} = \frac{(\nu + \nu_{kn})^4}{\nu^4}. \tag{8.8}$$

Equation (8.8) applies also separately to trace, quadrupole, and magnetic dipole scattering. Thereby, the intensity and polarization for each direction is fixed. The depolarization factor is now

$$\rho(k \rightarrow n, \nu) = \rho(n \rightarrow k, \nu + \nu_{kn}). \tag{8.9}$$

The intensity of the line k → n excited by ν along any direction is determined by the intensity along the same direction of the line n → k excited by $\nu + \nu_{kn}$. If we express the ratio of the population of states in terms of the Boltzmann distribution,

$$\frac{N_k}{N_n} = \frac{g_k}{g_n} \exp(-h\nu_{kn}/kT),$$

the statistical weights cancel, and

$$I_{kn}(\nu) = I_{nk}(\nu + \nu_{kn}) \left(\frac{\nu + \nu_{kn}}{\nu}\right)^4 \exp(-h\nu_{kn}/kT) \quad \text{and}$$
$$\frac{I_{kn}(\nu)}{I_{nk}(\nu)} = \frac{I_{nk}(\nu + \nu_{kn})}{I_{nk}(\nu)} \cdot \left(\frac{\nu + \nu_{kn}}{\nu}\right)^4 \exp(-h\nu_{kn}/kT). \tag{8.10}$$

The intensity ratio of the Stokes to the anti-Stokes line is quite different depending upon the frequency function in the interval ν and $\nu + \nu_{kn}$. Two borderline cases may be cited.

We assume that the frequency dependence of the scattering moment (i. e., the tensor $c_{\rho\sigma}$) may be neglected within this region. For instance, this holds for molecules when ν is far from any resonance region. The frequency dependence of the intensity will be given by the factor ν'^4 (ν' refers to the emitted frequency), and Eq. (8.10) gives

$$\frac{I_{kn}}{I_{nk}} = \left(\frac{\nu + \nu_{kn}}{\nu - \nu_{kn}}\right)^4 \exp(-h\nu_{kn}/kT). \tag{8.10a}$$

In contrast, resonance modifies the Stokes and anti-Stokes lines differently. If $E_r > E_k > E_n$ (E_r is the intermediate state), then resonance will occur at $\nu \approx \nu_{rk}$ for the anti-Stokes line ($\nu + \nu_{kn}$) (transition k → n), and at $\nu \approx \nu_{rn}$ for the Stokes line ($\nu - \nu_{kn}$). Therefore, the first factor in (8.10) becomes very small when $\nu \approx \nu_{rn}$ and very large when $\nu \approx \nu_{rk}$. In the latter case, for each temperature at which the state k is fairly well populated, the anti-Stokes line will be more intense than the Stokes line, by an order of magnitude. The well-studied resonance spectrum of I_2 vapor constitutes such an example.

Similarly, in the intermediate region between that given by Rayleigh's laws on one hand, and resonance on the other, the intensity ratio of the Stokes and anti-Stokes lines is a function of frequency and temperature as shown in Eq. (8.10).

REFERENCES AND FOOTNOTES

1. In Chapter 4, the probability is given in integral form, while the differential form is used here. It is written symmetrical in ν and ν' by means of the operator $\delta^{\nu'}_{\nu+\nu_{kn}}$ which defines the energy of the system.

2. For example, B. R. H. Fowler, Statistical Mechanics.

3. Ornstein and Kramers, Z. Physik 42, 481 (1927); Pauli, Sommerfield commemoration issue.

4. Rossi, Rend. Linc. 9, 319 (1929); Placzek, Z. Physik 58, 585 (1929); Ornstein and Rekveld, in a paper on the same subject (Z. Physik 57, 539 (1929), used an incorrect expression for the frequency function but corrected it later (Z. Physik 68, 257 (1933)).

5. A completely analogous relation may be obtained for the cross sections of collisions of the first and second kind, Klein and Rosseland, Z. Physik 4, 46 (1927). If we denote the energy of the incident electron by η, then

$$\eta^3 g_k Q_{kn}(\eta) = (\eta + \eta_{kn})^3 g_n Q_{nk} (\eta + \eta_{kn}). \qquad (8.8a)$$

The difference in the exponents of η in (8.8a) and (8.8) is due to relativistic mechanics applicable to light quanta. This relation can be written in a form that is valid for both types of processes if the effective cross section is defined in terms of the number of particles rather than the energy. For the newly-defined cross sections S_{kn},

$$\frac{g_k S_{kn}(\lambda)}{g_n S_{nk}(\lambda')} = \frac{\lambda^2}{\lambda'^2}, \qquad (8.8b)$$

where λ refers to the de Broglie wavelength and

$$1/\lambda' = 1/\lambda + 1/\lambda_{kn}.$$

PART II

THE SCATTERED RADIATION OF ISOLATED SYSTEMS

A. LIMITING CASES

Chapter 9. The Harmonic Oscillator

We shall discuss the behavior of a one-dimensional oscillator, fixed in the x direction, and a particle of charge e and mass μ to be acted upon by a potential

$$V = k/2 \ x^2. \tag{9.1}$$

The energy states are characterized by the quantum number v:[1]

$$E_v = (v + 1/2)h\nu_0, \ \nu_0 = 1/2\pi \sqrt{k/\mu}. \tag{9.2a}$$

The selection rule is $\Delta v = \pm 1$, (9.2b)

and the matrix elements of the electric moments become

$$(M_x)^v_{v+1} = e\sqrt{\frac{(v+1)h}{8\pi^2\mu\nu_0}}$$

$$(M_x)^v_{v-1} = e\sqrt{\frac{vh}{8\pi^2\mu\nu_0}} \tag{9.2c}$$

$$(M_y)^v_{v'} = (M_z)^v_{v'} = 0.$$

To calculate the unshifted scattered radiation, we examine Eqs. (5.2c) and (5.13). Upon summing over the two intermediate states (v + 1) and (v - 1), we obtain, for the trace scattering,

$$(c^0)_{vv} = a_v^{(0)} = 1/3 \ \frac{e^2}{4\pi^2\mu} \cdot \frac{1}{\nu_0^2 - \nu^2}, \tag{9.3a}$$

and for the quadrupole scattering,

$$\begin{aligned}
(c_{xx}{}^{(s)})_{vv} &= (a_{xx}{}^{(s)})_v = 2a_v{}^{(0)} \\
(c_{yy}{}^{(s)})_{vv} &= (a_{yy}{}^{(s)})_v = -a_v{}^{(0)} \\
(c_{zz}{}^{(s)})_{vv} &= (a_{zz}{}^{(s)})_v = -a_v{}^{(0)} \\
(c_{\rho\sigma}{}^{(s)})_{vv} &= 0, \quad \rho \neq \sigma;
\end{aligned} \tag{9.3b}$$

the magnetic dipole scattering vanishes.

For incident radiation polarized along the x direction, the scattering moment becomes

$$(M_x{}^{(1)})_{vv} = \left[(a_v{}^{(0)}) + (a_{xx}{}^{(s)})_v\right] E_x = \frac{e^2}{4\pi^2 \mu} \cdot \frac{E_x}{\nu_0{}^2 - \nu^2} . \tag{9.4}$$

According to Eq. (9.3), the scattered radiation of the harmonic oscillator is independent of the quantum state, and its intensity has the classical value. Now, the significance of the quantity f in Chapter 6 becomes clearer. As may be seen from Eqs. (5.3) and (5.14), the amplitude of the coherent scattering can be written as a sum of oscillator amplitudes. The f-value associated with a given transition represents the ratio of oscillator amplitude to scattering amplitude of an oscillator with charge and mass of an electron.

To calculate the shifted scattering radiation, we substitute (9.2) into Eq. (5.1). Only transitions $v \rightarrow v \pm 2$ with intermediate levels $v + 1$ and $v - 1$ have to be considered, because of the third common-level rule and the selection rule $\Delta v \pm 1$. Since $(M_y)^v_{v'}$ and $(M_z)^v_{v'}$ become zero, only the component $(c_{xx})^v_{v\pm 2}$ does not vanish and

$$(c_{xx})^v_{v\pm 2} = \frac{e^2(v \pm 1)}{8\pi^2 \mu \nu_0} \left(\frac{1}{\pm\nu_0 - \nu} + \frac{1}{\mp\nu_0 + \nu} \right) = 0 \tag{9.5}$$

Because both terms in the Kramers-Heisenberg formula cancel each other out, there is no displaced scattered radiation associated with a harmonic oscillator. However, the frequencies and transition amplitudes appearing in the two terms are different for an anharmonic oscillator. They do not completely compensate each other, with the result that displaced scattered radiation will appear. Nonetheless, it may not be concluded that molecules give rise to displaced scattered radiation for anharmonic nuclear vibrations only and that the intensities of the Raman lines are a direct function of the anharmonicity. These statements apply merely to that part of the scattered radiation that arises from nuclear scattering, while the essential part of the radiation scattered by molecules is due to electronic scattering.

In the classical theory one obtains the scattered radiation of the oscillator by starting with the expression for forced vibration

$$\mu\ddot{x} + kx = eE_x, \tag{9.6}$$

which gives the result shown in Eq. (9.4). When anharmonic forces are introduced, terms appear in the solution of (6) that correspond to the displaced scattered radiation. Lommel pointed out these relations earlier.[2]

The three-dimensional isotropic harmonic oscillator behaves analogously; it represents a system freely oriented in space. The displaced scattered radiation vanishes, but the undisplaced radiation consists of the trace scattering. The scattering cross section

$$\Omega^{(0)} = 8\pi/3 \left(\frac{e^2}{\mu c^2} \cdot \frac{\nu^2}{\nu_0^2 - \nu^2}\right)^2, \tag{9.7}$$

is independent of the quantum state,

REFERENCES AND FOOTNOTES

1. See the article by von Laue.
2. References in Chapter I.

Chapter 10. The Free Electron

The eigenfunction of the free electron extends over the whole space. Since our formulas are valid for scattering systems whose dimensions are small compared with the wavelength, they are not applicable directly in this case. By neglecting the frequency changes of the scattering (Compton effect), one can consider, instead of a free electron, an electron in a force field that restricts the displacement of the scattering system to a region small in relation to the wavelength. The binding energy should also remain small compared with the energy $h\nu$ of the incident light quantum, and it should not affect the intensity.[1] The type of force field is not important, but the latter condition requires that the eigenfrequencies of the system be small relative to the incident frequency. For this case, the scattering formula has been discussed in Chapter 5, and it has been shown that the incoherent scattered radiation and the components $c_{\rho\sigma}$ $(\rho \neq \sigma)$ of the scattering tensor for the coherent scattering vanish. For $c_{\rho\rho}$ we obtain, using Eq. (5.11) for the special case of a one-electron system,

$$\left| (c_{\rho\rho})_{kk} \right|^2 = 1/\nu^4 \left(\frac{e^2}{4\pi^2 \mu} \right)^2 . \tag{10.1}$$

The scattered radiation consists of trace scattering only, and the scattering cross section becomes

$$Q = 8\pi/3 \cdot \frac{e^4}{\mu^2 c^4} . \tag{10.2}$$

This expression was originally derived by J. J. Thompson; it can be obtained from Eq. (9.7) by putting k = 0. It should be remembered that the scattering intensity of the free electron is independent of the incident frequency, a fact that is important for astrophysical applications.

The expression (5.11) can now be interpreted in terms of Eqs. (10.1) and (10.2). The scattering intensity for large frequencies of any system becomes equal to the square of the sum of the scattering amplitudes of its particles, which are assumed to be free. From this and Eq. (10.2), the principle evolved that the quantum theoretical scattering intensity of a bound electron, in the limit of large frequencies, goes over into the classical scattering intensity of the free electron. This principle was already postulated before the introduction of modern quantum theory, but it gained further significance with the discovery of the fundamental laws of quantum mechanics.[2]

If $h\nu/(\mu c^2)$ is no longer small compared with 1, the conditions for the force field cannot be met simultaneously. Retardation and relativistic effects become appreciable; these considerations lead to the Compton effect and to deviations from (10.1) and (10.2). See the Klein-Nishina formula.[3]

REFERENCES AND FOOTNOTES

1. The harmonic oscillator illustrates that both conditions can be met simultaneously. If we equate the displacement of the system to the zero-point amplitude of the oscillator in a given force field, the first condition is

$$\sqrt{\frac{h}{8\pi^2 \mu \nu_0}} << \lambda, \qquad \nu_0 \gg \nu \frac{h\nu}{\mu c^2}$$

and the second condition is $\nu_0 << \nu$. As long as $h\nu << \mu c^2$, both conditions are compatible.

2. H. A. Kramers, Physica 5, 369 (1925).

3. See Beck, Chapter 33.

B. ATOMS

Chapter 11. Energy Levels and Selections Rules

The atomic energy levels are characterized in the following manner. If the electronic interactions are neglected, each electron will be associated with an angular moment $l_j \cdot \hbar/2$ and a spin moment $s_j \hbar = 1/2 \cdot \hbar$. If interaction is taken into consideration, these vectors can combine in several ways, depending upon the coupling relations. The simplest combination is known as the Russel-Saunders coupling. Here the orbital angular moments of the individual electrons yield a resultant orbital angular momentum L, and the spins, a resultant spin moment S. The vectors L and S combine to give the total angular momentum J, where J can assume the values

$$L + S,\ L + S - 1,\ \ldots,\ |L - S|.$$

In the usual Russel-Saunders notation, the values of the quantum number L are described by the letters S, P, D, F, for L = 0, 1, 2, 3, respectively. In addition, the left index designates the multiplicity 2S + 1, and the right index the total angular momentum J. ${}^4P_{1/2}$ denotes a term of $S = 3/2$, $L = 1$, and $J = 1/2$.[1]

The following selection rules apply to emission and absorption (dipole radiation). Strictly: $\Delta J = 0, \pm 1$, and to a good approximation: $\Delta L = \pm 1$; for weak spin-orbital interaction: $\Delta S = 0$.

In addition to the rules for J transitions, the following rules exist for scattered radiation: $\Delta L = 0, \pm 2$(2) and, as for emission, $\Delta S = 0$ for weak spin-orbital interaction.

According to Chapter 6, the rule of alternating states applies, independent of LS coupling: In emission even terms combine with odd, and odd with even; for scattered radiation, even terms combine with even and odd terms with odd.

REFERENCES AND FOOTNOTES

1. For atoms possessing a valence electron, this description is usually accompanied by another numeral, denoting the value of the main quantum number.

2. In the absence of spin-orbital coupling the trace, and magnetic dipole scattering for the transitions $\Delta L = \pm 2$ will have zero intensity.

Chapter 12. Undisplaced Scattered Radiation

According to Table I, quadrupole, and magnetic dipole radiation vanish for the transitions $J = 0 \rightarrow J = 0$, so that the scattering will be linearly polarized. The rare gases having a ^1S ground state are representative examples.

Table II presents the depolarization factors for natural incident light reported by Lord Rayleigh,[1] Cabannes and his students,[2] and Partharasathy.[3]

Table II. Depolarization factors of the scattered radiation of rare gases.

	ρ_n		
Helium	< 0.065(1)	< 0.03(3)	
Neon	< 0.01(2)		
Argon	0.0046(1)	0.0055(2)	0.0056(3)
Krypton	0.0055(2)		
Xenon	0.0055(2)		

An upper limit was established for the depolarization factor of He and Ne, while finite values of the order of a half per cent were observed for the remaining rare gases. It is doubtful whether the deviation from zero is real,[4] particularly since Stuart[5] reported that the values of 0.0077,(6) 0.0050,(7) and 0.062(8) for CCl_4 obtained by the same method as that for the rare gases, are irreconcilable with his measurements of the Kerr effect. His experiments yielded a maximum value of 0.0015 (see Chapter 24).

The scattering cross sections of the rare-gas atoms depend upon the polarizability according to Eq. (6.31) since they involve only isotropic scattering and may be expressed in terms of the refractive index. The statistical polarizability of rare gases was calculated by Kirkwood.[9]

The rare gases are the only atoms giving rise to scattered radiation outside the region of resonance. Since the atoms of other elements exist as dilute gases, i.e., vapors, the intensity will not be strong enough to be observed except in the resonance region.[10] The unshifted resonance radiation was observed for the following vapors:[11]

Ground state $^1S_0$: Mg, Zn, Cd;

$^2S_{1/2}$: Li, Na, K, Hg, Au;

$^4S_{3/2}$: As, Sb, Bi;

$^3P_0$: Pb;

$^2P_{1/2}$: Tl.

The scattered radiation is usually depolarized if the ground state of the atom differs from a ^1S state. This is also true for S states of higher multiplicity, such as for the ^2S ground state ($J = 1/2$) of the alkali metals.

As may be seen from Table I, the quadrupole scattering is forbidden for the transition J 1/2 → 1/2, while the magnetic dipole scattering is not. The depolarization factor is now computed for the case where the incident frequency is close to the frequency of the first doublet of the main series (the D lines for Na), corresponding to a transition $^2P_{3/2} \rightarrow {}^2S_{1/2}$ or $^2P_{1/2} \rightarrow {}^2S_{1/2}$ (see Fig. 4).

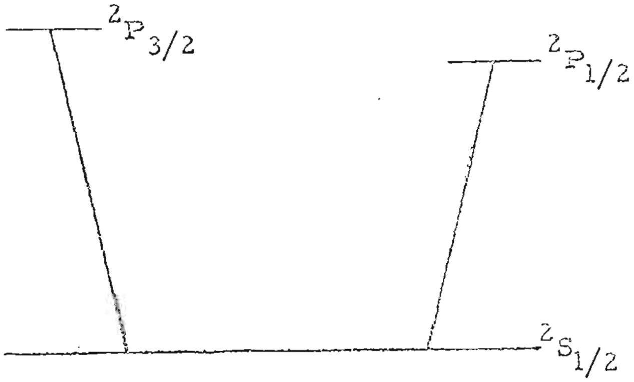

Fig. 4. Ground term and first excited terms of the alkali metals.

The difference between incident and resonance frequency should be small, so that the summation must include only the two intermediate states in the scattering formula, as shown in Fig. 4. However, the frequency interval has to be appreciable compared with the multiplet splitting. Then, following Eqs. (6.9), (6.16), (6.19), and (6.27), the depolarization factor becomes:

$$\rho = \frac{1}{4}\,\frac{\left|\dfrac{2\left|b_{S_{1/2}}^{P_{1/2}}\right|^2}{\nu_{S_{1/2}}^{P_{1/2}}-\nu} - \dfrac{\left|b_{S_{1/2}}^{P_{3/2}}\right|^2}{\nu_{S_{1/2}}^{P_{3/2}}-\nu}\right|^2}{\left|\dfrac{\left|b_{S_{1/2}}^{P_{1/2}\cancel{-\nu}}\right|^2}{\nu_{S_{1/2}}^{P_{1/2}}-\nu} + \dfrac{\left|b_{S_{1/2}}^{P_{3/2}}\right|^2}{\nu_{S_{1/2}}^{P_{3/2}}-\nu}\right|} = \frac{1}{4}\,\frac{\left|2-\dfrac{I_{3/2}}{I_{1/2}}\,\dfrac{\nu_{S_{1/2}}^{P_{1/2}}-\nu}{\nu_{S_{1/2}}^{P_{3/2}}-\nu}\right|}{\left|1+\dfrac{I_{3/2}}{I_{1/2}}\,\dfrac{\nu_{S_{1/2}}^{P_{1/2}}-\nu}{\nu_{S_{1/2}}^{P_{3/2}}-\nu}\right|} \tag{12.1}$$

where b is defined by (6.27), and the intensity of the two lines of the doublet is given by

$$\frac{I_{3/2}}{I_{1/2}} = \frac{\left|b_{S_{1/2}}^{P_{3/2}}\right|^2}{\left|b_{S_{1/2}}^{P_{1/2}}\right|^2}\,.$$

The intensity ratio has, to a first approximation, a value of 2 (neglecting spin-orbital interaction). If this value is substituted into Eq. (12.1), the numerator (magnetic dipole scattering) vanishes by cancellation of the two terms, and therefore $\rho = 0$ far from the region of resonance (if the interval between the incident frequency and the resonance region is large compared with the multiplet splitting). Upon approaching the resonance region, the terms will no longer cancel each other out when the distance is not large compared with the multiplet splitting, and the difference in the resonance denominator of the two terms must then be taken into account. At the two regions of resonance, the depolarization factor is obtained by considering the first (second) term only. Hence, the resonance radiation of the line ${}^2P_{1/2} \to {}^2S_{1/2}$ (the D_1 line of Na) will be unpolarized, with $\rho = 1$. For the line ${}^2P_{3/2} \to {}^2S_{1/2}$ (the D_2 line of Na), $\rho = 1/4$.[12]

For higher doublets of the main series of heavier alkali metals, the spin-orbit interaction becomes appreciable. The intensity relations substituted into (12.1), and corrected according to Fermi, results in depolarized scattered radiation beyond the region of resonance.[13] The depolarization factor of the resonance radiation itself is altered for molecules whose nuclei possess a magnetic moment.[14]

This change arises in the following manner: analogous to the vectorial combination of S and L giving the total angular momentum J thereby resulting in the multiplicity of the energy levels of the alkali metals (see Chapter 11), the nuclear spin combines with the angular momentum J to give the total angular momentum (usually denoted by F), which causes the hyperfine structure of the terms and spectral lines (see article by Beck). Since, according to Chapter 7, the depolarization factor of the resonance radiation is determined by the initial, intermediate, and final states, the components of the hyperfine structure of a line in the resonance fluorescence exhibit different depolarization. This, in turn, changes the depolarization factor of the total line. As an example, we shall consider the 2537-A Hg line. The scattered radiation will be completely polarized for the $^1S_0$ ground term provided the nuclear spins are neglected. According to Schüler and Keyston,[15] the 200-Hg isotope (69.9%) has zero nuclear spin, the 199-Hg isotope (16.4%) has a spin of 1/2, and the 201-Hg isotope (13.7%), a spin of 3/2. The hyperfine structure components of the even isotope are completely polarized, but for the two components of the isotope 199, the polarization is the same as that discussed above for the Na D doublets. The $^3P_1$ term splits into two terms with F = 1/2 and F = 3/2; these two components correspond to transitions of the total angular momentum $3/2 \rightarrow 1/2$ and $1/2 \rightarrow 1/2$, as in the case of the Na D lines.

The actual situation is more complex since the hyperfine structure components of several isotopes overlap. In view of this, the observed depolarization factors for the five components of the 2537-A Hg line[16] are those shown in Table III.

Table III. Depolarization factors of the hyperfine structure components of the 2537-A Hg line.

Component	ρ (%)
21.5	28.3
11.5	0
0	0
-10.4	8.2
-25.4	32.1
Total Line	8.3

In addition, the depolarization factors depend upon the intensity distribution within the exciting line. The data in Table III refer to a broad line having a homogeneous intensity distribution.

The various sets of experiments of data are in fair agreement. Ellett and McNair[17] demonstrated that the three center components are almost completely polarized and the total line was found to have a depolarization of 7.5-11.7%.[18]

If the distance from the resonance region becomes large compared with the hyperfine structure splitting, the effects due to nuclear spin vanish, analogous to the multiplet splitting, discussed above.

The investigations of the polarization of resonance radiation may prove to be a valuable tool for nuclear-spin determinations, particularly for systems having several isotopes. This method could complement the direct spectroscopic investigations of nuclear spins; however, an exact knowledge of the spectral composition of the effective incident light is indispensable.[19]

REFERENCES AND FOOTNOTES

1. Lord Rayleigh, Proc. Roy. Soc. (London) 98, 57 (1920).

2. J. Cabannes, Compt. rend. 171, 852 (1920); J. phys. et radium 4, 276 (1923); La Diffusion Moléculaire de la Lumière, Paris, (1929). J. Cabannes and J. Granier, J. phys. et radium 4, 429 (1923); J. Cabannes and A. Lepape, Compt. rend. 179, 325 (1924).

3. S. Partharasathy, Indian J. Phys. 7, 163 (1932).

4. Rough calculations indicate that the interaction of atoms (measured at atmospheric pressure) cannot produce depolarizations of this order of magnitude.

5. H. A. Stuart, Ergeb. exakt. Naturwiss. 10, 159 (1931).

6. J. Cabannes and J. Granier, Compt. rend. 192, 885 (1926).

7. R. Rao, Indian J. Phys. 2, 61 (1927).

8. S. Partharasathy, ibid. 7, 163 (1932).

9. Kirkwood, Z. Phys. 33, 52 (1932); compare Hassé, Proc. Cambridge Phil. Soc. 26, 542 (1930); Slater and Kirkwood, Phys. Rev. 37, 632 (1931) (He); Podolski, Proc. Nat. Ac. Ad. Washington 14, 253 (1928); Podolski and Rojansky, Phys. Rev. 34, 1367 (1929), for displaced and undisplaced scattered radiation of atomic hydrogen.

10. See the bibliography in Pringsheim, "Fluoreszenz und Phosphoreszenz;" Kapuscinski, Bull. int. Ac. Ad. Pol (A) 284 (1929); (Ag), J. Rud Nielsen and Wright, J. Opt. Soc. Am. 20, 27 (1930) (K).

11. Instead of forming the invariants, one can, because of the low J values, start with the total scattering tensor and sum over the magnetic levels directly.

12. See below, concerning the changes caused by nuclear spins.

13. E. Fermi, Z. Phys. 59, 680 (1930).

14. A. Ellett, Phys. Rev. 35, 588 (1930).

15. Schüler and Keyston, Z. Phys. 72, 423 (1931).

16. Mitchell, Phys. Rev. 40, 964 (1932).

17. Ellett and McNair, Phys. Rev. 31, 180 (1928).

18. V. Keussler, Ann. Phys. 82, 793 (1927); Olson, Phys. Rev. 32, 443 (1928); Larrick and Heydenburg, Phys. Rev. 39, 289 (1932).

19. The discrepancy between the conclusions about the nuclear spin of Na, reached by Heydenburg-Larrick-Ellett (Phys. Rev. 40, 1041 (1932)) on the basis of polarization measurements of the sodium D_2 line, and those from intensity variations of the Na_2 bands may be attributed to an inadequate knowledge of these relationships.

Chapter 13. Displaced Scattered Radiation

Displaced scattered radiation of atoms has been observed in the resonance region only. A typical case is that of thallium (see Fig. 5). The ground state is a 2 ^2P level; its doublet splitting amounts to 7800 cm^{-1}. The 2 $^2P_{3/2}$ level is metastable, and the transition 2 $^2P_{1/2} \rightarrow$ 2 $^2P_{3/2}$ can occur as quadrupole and magnetic dipole scattering. Trace scattering is not permitted, since $\Delta J \neq 0$; hence, $\rho \geq 3/4$, regardless of the incident frequency. As is shown in Fig. 5, resonance occurs for the incident wavelengths 3776 A (intermediate state 2 $^2S_{1/2}$) and 2768 A (intermediate state 2 $^2D_{3/2}$). Terenin[1] confirmed the prediction of the displaced line in both instances. According to equations analogous to (7.2), ρ should be equal to unity (unpolarized line), and equal to 7 for the two wavelengths respectively.[2] The former result agrees with the findings of Terenin; there are no polarization measurements available for the 2768 A line.

At room temperature, the 2 $^2P_{3/2}$ level is sparsely populated and therefore ineffective which accounts for the fact that the 5350 and 3539 A excitations do not give rise to resonance scattering. Orthman and Pringsheim demonstrated the existence of the anti-Stokes line at elevated temperature.[3]

The occurrence of lines in an electric field, forbidden in spontaneous emission, can be considered as a borderline case of the displaced scattered radiation, as was stated in Chapter 5. Pauli was the first to compute the intensity of the forbidden Hg lines, which becomes discernible by means of an external electric field.[4] In place of an external field, fields (gaseous discharge) originating in the light source itself can be effective, although forbidden lines observed in a discharge cannot be interpreted readily since they can arise from forced dipole transitions or from spontaneous quadrupole transitions. Regarding the selection rules, all transitions that are possible in spontaneous quadrupole scattering can be produced by external fields (quadrupole scattering). However, the reverse does not hold because of the isotropic and magnetic dipole scattering. For instance, the transitions J: $0 \rightarrow 0$ and $1/2 \rightarrow 1/2$ are forbidden in quadrupole radiation and scattering, but do occur in isotropic scattering. In such instances we deal with forced dipole radiation exclusively; in others, one can differentiate by investigating the intensity relations of the multiplet components,[5] the decrease in intensity within the series,[6] and the Zeeman effects.[7]

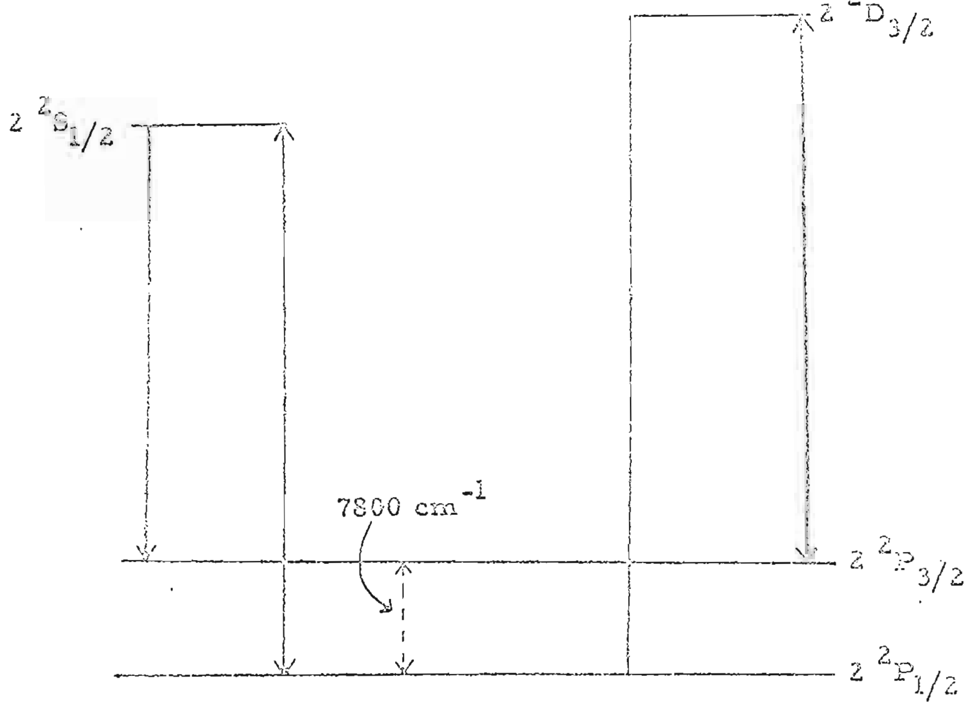

Fig. 5. Energy levels of thallium. The vertical lines represent the following transitions:

$2\ ^2S_{1/2} \rightarrow 2\ ^2P_{1/2}$	3776 A;
$2\ ^2S_{1/2} \rightarrow 2\ ^2P_{3/2}$	5350 A;
$2\ ^2D_{3/2} \rightarrow 2\ ^2P_{1/2}$	2768 A;
$2\ ^2D_{3/2} \rightarrow 2\ ^2P_{3/2}$	3529 A.

REFERENCES AND FOOTNOTES

1. A. Teremin, Z. Physik 31, 36 (1925); 37 98 (1926).
2. If a nuclear spin exists, the depolarization factor is altered as for undisplaced resonance radiation, and so it can be computed analogously.
3. Pringsheim, "Fluorescence and Phosphorescence."
4. W. Pauli, Math. phys. Mitt, Dän. Gesell, Wiss. 7, No. 3 (1925).
5. S. Sambursky, Z. Physik. 68, 774 (1931).
6. S. Sambursky, Z. Physik. 76, 132 (1932).
7. Ittmann and Brinkman, Naturwiss. 19, 292 (1931); compare Segré and Bakker, Z. Physik. 72, 724 (1931).

C. MOLECULES

Chapter 14. The Polarizability Theory[1]

The scattering formulas for molecules may be evaluated in the same manner as those for atoms. The summations are carried out by substituting the transition amplitudes and frequencies into Eqs. (5.1), (6.9), (6.13), and (6.16). This is an involved operation because of the complexity of the molecular energy levels. Due to our meager knowledge of the excited states, it can be carried out for special cases only. The general result can be derived in a direct manner.

The molecular scattering mechanism will be considered next. If we treat light scattering by electrons in a given electronic state, the energy changes occurring in the process must involve the nuclei whose quantum numbers are the only ones that change. (Nuclear scattering may be neglected due to the heavy mass of the nuclei.)

The possibility of energy transfer from incident radiation to the nuclei, or *vice versa*, is *predicated upon* the coupling between nuclear and electronic motions. This process constitutes the Raman effect of molecules. So that the scattered radiation may be computed, the scattering molecules are first assumed to possess fixed nuclei; subsequently, the scattering is modified by the nuclear motions. A molecule in a given non-degenerate electronic state and with fixed nuclei can give rise to undisplaced, coherent scattered radiation[2] whose intensity is determined by the tensor $(c_{\rho\sigma})_{kk} = (a_{\rho\sigma})_{(k)}$ according to Eqs. (5.2a) and (5.4a). This tensor is real and symmetric for a non-degenerate state, as shown in the following discussion.

Since the eigenfunctions and the energy levels of the molecule with rigid nuclei depend on the orientation of the nuclei, it follows from Eq. (5.14) that the polarizability $a_{(k)}$ will also depend upon the nuclear orientation. We shall assume that the scattering intensity of a molecule with non-rigid nuclei is as strong for each given configuration as the scattering intensity of a rigid molecule having the same nuclear configuration. This assumption and its limits will now be proved.

To obtain the undisplaced scattering radiation for a given state s (vibration and rotation state), the scattering moment must be averaged over all nuclear configurations possible in this state. Since the probability of a configuration in the nuclear state s and electron ground state (k) is given by $\mu_s \mu_s^*$,[3]

$$(M^{(1)})_s^{\,s} = \bar{\alpha}_{(k)}^{(s)}\, E = E \int u_s^{*}(q)\alpha_k(q)u_s(q)dq = (\alpha_{(k)})_s^{\,s}\, E, \qquad (14.1)$$

where u and $\alpha_{(k)}$ denote the nuclear eigenfunction and the polarizability, respectively, of the electronic ground state. The displaced scattered radiation may be evaluated by starting with the "Zwischen" solution of the Schrödinger equation $(u_s + u_{s'})$ taking only the transitions from the ground state s into account:

$$(M^{(1)})_{s'}^{\,s} = E \int u_s^{*}(q)\alpha_{(k)}u_{s'}(q)dq = (\alpha_{(k)})_{s'}^{\,s}\, E. \qquad (14.2)$$

The scattering intensity associated with the transition s → s' may be determined by the matrix elements of the polarizability. The splitting up of the polarizability is classically analogous to the formation of the matrix elements. The polarizability, being time-dependent because of the change in q, will be expanded into time-dependent Fourier components. These combine with the incident wave and give rise to displaced and undisplaced scattered radiation.

To clarify the above statement, consider the eigenfunction of a molecule, written in the following manner--compare with the article by Kronig--:

$$\psi_{ns}(\xi, q) = \phi_n(\xi, q)u_{ns}(q), \qquad (14.3)$$

where q, ξ refer to the nuclear and electronic coordinates, respectively; and s, n to the nuclear and electronic quantum numbers, respectively.[4] $\phi_n(\xi, q)$ represents the solution of the Schrödinger equation for rigid particles; it contains the nuclear coordinates q as parameters. The energy E_{ns} is obtained when the eigenvalue $E_n(q)$ of the Schrödinger equation for rigid nuclei is substituted as potential energy into the Schrödinger equation for non-rigid nuclei:

$$E_{ns} = E_n(0) + W_{ns}. \qquad (14.4)$$

$E_n(0)$ is the eigenvalue for the nuclei in the equilibrium configuration. According to Eqs. (3.7) and (3.10), the eigenfunction of the electronic ground state (E_0) for rigid nuclei, when perturbed by the incident light, becomes:

$$\Phi_0 = \Phi_0(0) + \Phi_0(1)$$

$$\Phi_0 = \phi_0 \exp\left[- i/\hbar\, E_0(q)t\right] + \phi_0^{+} \exp\left[-i/\hbar(E_0(q) + h\nu)t\right] + \phi_0^{-} \exp\left[- i/\hbar(E_0(q) - h\nu)t\right], \tag{14.5a}$$

where, from Eq. (3.9a),

$$\begin{aligned} \phi_0^{+}(q, \xi) &= 1/h \sum_n{}' \frac{(AM_n^{\;0})}{\nu_0^{\;n} - \nu}\, \phi_n(q, \xi) \\ \phi_0^{-}(q, \xi) &= 1/h \sum_n{}' \frac{(A^{*}M_n^{\;0})}{\nu_0^{\;n} + \nu}\, \phi_n(q, \xi); \end{aligned} \tag{14.5b}$$

for non-rigid nuclei:

$$\Psi_{0s} = \Psi_{0s}^{(0)} + \Psi_{0s}^{(1)} = \exp\left[- i/\hbar\, E_0(0)t\right]\Big\{\psi_{0s} \exp\left[- i/\hbar\, W_{0s}t\right] + \psi_{0s}^{+} \exp\left[- i/\hbar(W_{0s} + h\nu)t\right] + \psi_{0s}^{-} \exp\left[- i/\hbar(W_{0s} - h\nu)t\right]\Big\} \tag{14.6a}$$

$$\begin{aligned} \psi_{0s}^{+} &= 1/h \sum_n \sum_{s''}{}' \frac{(A\ M_{ns''}^{\;0s})}{\nu_{0s}^{\;ns''} - \nu}\, \phi_n u_{ns''}, \\ \psi_{0s}^{-} &= 1/h \sum_n \sum_{s''}{}' \frac{(A^{*}M_{ns''}^{\;0s})}{\nu_{0s}^{\;ns''} + \nu}\, \phi_n u_{ns''}. \end{aligned} \tag{14.6b}$$

As long as the incident frequency is far from any resonance region and $(\nu_0^{\;n} - \nu)$ is large compared with the splitting and shift of the electronic level, this splitting and shift due to nuclear vibrations can be neglected in Eq. (14.6) and $\nu_{ns''}^{\;0s}$ may be replaced by $\nu_0^{\;n}(q)$.

In addition, if ν is large compared with the nuclear frequencies of the electronic ground state, the term with the intermediate level n = 0 (infrared term) in the sum (14.6b), in contrast to that in (14.5b) may be neglected, and (14.6b) becomes[5]

$$\psi_{0s}^{\;+} = 1/h \sum_n{}' \frac{\sum_{s''} (AM_{ns''}^{\;0s}) u_{ns''}}{\nu_0^{\;n} - \nu} \phi_n = 1/h \sum_n{}' \frac{AM_n^{\;0}(q)}{\nu_0^{\;n} - \nu} u_{0s} \phi_n$$

$$\psi_{0s}^{\;+} = \phi_0^{\;+} u_{0s} , \tag{14.7}$$

$$\psi_{0s}^{\;-} = 1/h \sum_n{}' \frac{(A^* M_n^{\;0}(q))}{\nu_0^{\;n} + \nu} u_{0s} \phi_n = \phi_0^{\;-} u_{0s} .$$

Hence, from Eqs. (14.5a) and (14.6a),

$$\Psi_{0s}(\xi, q) = \overline{\Phi}_{0s}(\xi, q) u_{0s} \exp\,(- i/\hbar\ W_{0s} t). \tag{14.8}$$

Only the electronic part of the eigenfunction will be modified provided ν and $\nu_0^{\;n} - \nu$ are large compared with the nuclear frequencies. The perturbations are the same for each configuration q as for a rigid system of particles.

Analogous to Eq. (3.14), we express the quantity associated with emission from 0, s → 0, s' by

$$\iint \Psi_{0s'}^{\;*}(\xi, q) M \Psi_{0s}(\xi, q) d\xi dq$$

which, together with (14.7) and (14.8), transforms into

$$\iint \Psi_{0s'}(\xi, q) M \Psi_{0s}(\xi, q) d\xi dq$$

$$\begin{aligned} &= \int_{dq} u_{0s'}^{\;*} u_{0s} \int_{d\xi} M \Big\{ \phi_0^{\;*} \phi_0 \exp\left[- 2\pi i \nu_{s'}^{\;s} t\right] + (\phi_0^{\;*} \phi_0^{\;+} + \phi_0^{\;-*} \phi_0) \\ &\quad \times \exp\left(- 2\pi i(\nu_{s'}^{\;s} + \nu)t\right) + (\phi_0^{\;*} \phi_0^{\;-} + \phi_0^{\;+*} \phi_0) \exp\left(- 2\pi i(\nu_{s'}^{\;s} - \nu)t\right)\Big\} d\xi dq \end{aligned} \tag{14.9}$$

$$\begin{aligned} &= \int u_{0s'}^{\;*}(q) M_0^{\;0}(q) u_{0s}(q) dq \exp\,(- 2\pi i \nu_{s'}^{\;s} t) + \int u_{0s'}^{\;*}(q) C_0^{\;0}(q) u_{0s}(q) dq \\ &\quad \times \exp\left(- 2\pi i(\nu_{s'}^{\;s} + \nu)t\right) + \int u_{0s'}^{\;*}(q) C_0^{\;0}(q) u_{0s}(q) dq \exp\left(- 2\pi i(\nu_{s'}^{\;s} - \nu)t\right). \end{aligned}$$

As in Eq. (3.14), the first term represents spontaneous emission; it is determined by the permanent moment M_0, which is a function of the nuclear configuration. The second term represents the scattered radiation, and is determined by the scattering amplitude defined by Eq. (3.12), that is, by the induced moment of the rigid molecule, which, in turn, is a function of the nuclear configuration. The third term represents, as in (14.14), the double emission; it occurs when $\nu < \nu_{s'}^{s}$. In the present treatment, it is assumed by $\nu \gg \nu_{s'}^{s}$ thus making this term insignificant.

Upon replacing the scattering amplitude (employing Eq. (5.1)) by the scattering tensor, we obtain

$$
\begin{aligned}
(c_{\rho\sigma})_{0s'}^{0s} &= \int u_{0s'}^{*}(q)(c_{\rho\sigma})_{0}^{0}(q)u_{0s}(q)dq \\
&= \int u_{0s'}^{*}(q)\alpha_{\rho\sigma}(q)\psi_{0s}(q)dq = (\alpha_{\rho\sigma})_{s'}^{s}.
\end{aligned}
\tag{14.10}
$$

Since $\alpha_{\rho\sigma}$ is a symmetric tensor, its matrix elements are also symmetric tensors. For systems in non-degenerate electronic states and far from resonance, the scattering tensor for the displaced scattered radiation is also symmetric. The magnetic dipole scattering disappears, a fact that can be verified by direct application of Eq. (5.13) or Eq. (6.12).

The separation of the tensor represented by Eq. (5.12) results in the following terms:

$$
\begin{aligned}
&(c^{(0)})_{0s'}^{0s} = (\alpha^{0})_{s'}^{s} \\
&(c_{\rho\sigma}^{(s)})_{0s'}^{0s} = (\alpha_{\rho\sigma})_{s'}^{s} \\
&(c_{\rho\sigma}^{(a)})_{0s'}^{0s} = 0.
\end{aligned}
\tag{14.11}
$$

The trace scattering and the quadrupole scattering are functions of the isotropic and anisotropic part of the polarizability, respectively, and both depend upon the nuclear configuration. The upper limit of the depolarization factor is 3/4 (6/7) because of the disappearing magnetic dipole scattering, as seen in Table I. Nearer the resonance region, these considerations become invalid. In general, magnetic dipole scattering will then occur, causing an increase in the depolarization and under certain conditions resulting in new lines.

In the following treatment, we assumed a non-degenerate electronic ground state without specifying the excited electronic state. If multiplet splitting should arise, the derivation still remains valid, since we can neglect this splitting just the same as the larger one caused by nuclear displacements.

For degenerate electronic states two possible cases can be differentiated. If the degenerate levels can undergo mutual transitions during the scattering process, the undisplaced scattering of the rigid molecules contains an incoherent part corresponding to these transitions. The functional dependence on the nuclear displacements must be taken into consideration in the same manner as that associated with the coherent part, but different selection rules will now apply.

For small spin-orbital interaction, the spin part of the electronic eigenfunction can be separated, provided the degeneracy is due to spin alone. States with different spin quantum numbers do not combine which accounts for the absence of incoherent scattering radiation and for the fact that the above results retain their validity. An example is given by the electronic ground state of 0_2 $(^3\Sigma)$. A more complex situation arises when, aside from spin, orbital degeneracy exists, which is associated with large multiplet splitting.

The assumptions made in the polarizability theory are summarized again, as follows:

1. Electronic ground states that are not appreciably degenerate.
2. $\nu \gg \nu_k$, $(\nu_e - \nu) \gg \nu_k$.

As was indicated above, the theory can readily be extended to molecules that do not fulfill the first conditions. However, the second condition is more significant. Scattering phenomena not covered by the polarizability theory are treated in Chapter 25.

REFERENCES AND FOOTNOTES

1. G. Placzek, Z. 70, 84 (1931); Leipzig Lectures, (1931) p. 71; F. Rasetti, Leipzig Lectures, (1931) p. 59. The present article reviews these lectures, while discussing several topics in greater detail. Earlier investigations that concern diatomic molecules are those by van Vleck, Proc. Nat. Acad. Am. 15, 754, (1929), and Manneback (Z. Physik 62, 224 (1930)). The classical borderline case (a diatomic molecule consisting of polarizable ions) was treated by Cabannes, Trans. Farad. Soc. 25, 813 (1929), and J. Cabannes and Y. Rocard, J. Phys. et radium 10, 52 (1929).

2. Displaced scattered radiation that is associated with electronic transitions when the molecule exists in its electronic ground state occurs only when $\nu > \nu_e$ (ν_e corresponds to the lowest electronic frequency); however, in the subsequent discussion it is assumed that $\nu << \nu_e$.

3. This is not strictly correct, since the eigenfunction perturbed by the incident wave ought to be examined.

4. It is presumed that the notation n will not be mistaken for that used ordinarily to indicate the final state.

5. In order to transform (14.6), the quantity $AM_n^{\;0}(q)u_{0s}(q)$ is being derived in terms of $u_{ns''}$:

$$\left[AM_n^{\;0}(q)\right]u_{0s}(\psi) = \sum_{S''}{}' B_{ns''}^{\;\;0s} u_{ns''}(q).$$

Multiplication by $u_{ns''}$, and integration over q yields because of the orthogonality of $u_{ns''}$:

$$B_{ns''}^{\;\;0s} = AM_{ns''}^{\;\;0s},$$

and

$$\sum_{S''}{}' (AM_{ns''}^{\;\;0s})u_{ns''} = \left[AM_n^{\;0}(q)\right]u_{0s}.$$

Chapter 15. Application of the Polarizability Theory

In contrast to the properties of the general scattering tensor, the matrix elements of the polarizability are Hermitian, as may be seen from Eq. (12.10):

$$(\alpha_{\lambda\mu})_{s'}^{s} = (\alpha_{-\lambda-\mu})_{s'}^{s*}. \qquad (15.1)$$

The notation for the indices is determined by the complex description for the tensor components (Eq. (6.5)); also note the selection rules for m.

The intensity ratio of the Stokes and anti-Stokes lines are given essentially by the population of the states, so that

$$\frac{I_a}{I_{st}} = \frac{(\nu + \nu_{s'}^{s})^4}{(\nu - \nu_{s'}^{s})^4} \exp\left(-h\nu_{s'}^{s}/kT\right). \qquad (15.2)$$

If the assumptions of the polarizability theory regarding the incident frequency no longer apply, deviations from (15.2) become considerable. Hence, appropriate measurements of I_a/I_{st} may serve as proof of the polarizability theory. The limits can easily be predicted according to Chapter 11, provided the main ultraviolet absorption bands are known.

In addition to the frequency dependence of the scattering intensity, given by $(\nu + \nu_{s'}^{s})^4$, that of the polarizability must also be considered. However, the latter is small within the range of validity of the polarizability theory, and may be neglected within a frequency range comparable with the vibrational frequencies. The experimental part will be discussed in Chapter 25.

The scattering intensity and polarization for each transition s → s' is given by two constants since the magnetic dipole scattering vanishes. Hence, in accordance with Table I, $\rho \leq 3/4$ ($\rho_n \leq 6/7$), and from Eq. (6.22b)

$$P = \frac{2\rho}{1-\rho} = \frac{\rho_n}{1-\rho_n}, \qquad (15.3)$$

where P is the reversal coefficient for circularly incident light.[1] The sense of the circular polarization is reversed for all the lines for which $\rho > 1/3$ ($\rho_n > 1/2$). Such reversal was observed by Hanle and Bär in a series of scattering lines of liquids.[2, 3]

Figure 6 shows a reproduction of benzaldehyde by R. Bär. The strongly depolarized lines show a strong reversal of the circular polarization (see the line 615 cm^{-1}). A quantitative verification of Eq. (15.3) has not yet been carried out. Since P varies between 0 and 6, while ρ varies between 0 and 3/4, measurements of P will yield more accurate ratios of isotropic-to-quadrupole scattering than will measurements of ρ.

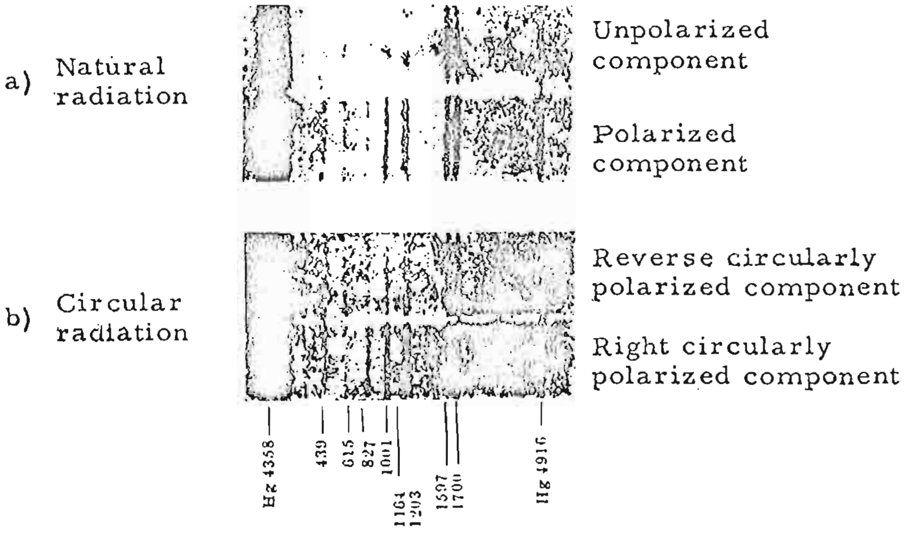

Fig. 6. Raman spectrum of benzaldehyde with natural and circular radiation. (According to R. Bär)

To obtain further information on the intensity, we separate nuclear eigenfunctions into rotational and vibrational eigenfunctions:[4]

$$u_s = U_v(x)\theta_{rm}(\theta). \qquad (15.4)$$

U_v depends on the relative coordinates of the nuclei, and θ on the orientation of the molecule, that is, on the Eulerian angles θ; v and r refer to the vibrational and rotational quantum numbers, respectively.

The isotropic part of the polarizability does not depend on the orientation of the molecule, and therefore the matrix elements vanish for transitions whose rotational quantum numbers change.[5] We obtain

$$(a^0)_{v'r'm'}{}^{vrm} = (a^0)_{v'}{}^{v}\,\delta_{r'm'}{}^{rm} \qquad (15.5a)$$

and, according to Eq. (6.11)

$$(G^0)_{v'r}{}^{vr} = 3\left|(a^0)_{v'}{}^{v}\right|^2. \qquad (15.5b)$$

Trace scattering occurs for pure vibrational transitions only; the intensity is not a function of the rotational state.

To compute the quadrupole scattering, the polarizability components $(a_{\lambda\mu}{}^{s})$, given in terms of coordinates fixed in space, must be expressed in terms of coordinates fixed in the molecule, $a_{\lambda'\mu'}{}^{s}$:

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$$a_{\lambda\mu}{}^{s} = \sum_{\lambda'\mu'} a_{\lambda'\mu'}{}^{s} D_{-\lambda'\lambda} D_{-\mu'\mu} \cdot \tag{15.6}$$

$D_{\lambda'\mu'}$, $D_{\mu'\mu}$ denote direction cosines; the negative sign of the first indices arises from the use of circular coordinates introduced in Chapter 6.

The quantities fixed in the molecule $a_{\lambda'\mu'}{}^{(s)}$ are independent of orientation, while the direction cosines are independent of the internal coordinates, so that

$$(a_{\lambda\mu}{}^{(s)})_{v'r'm'}{}^{vrm} = \sum_{\lambda'\mu'} (a_{\lambda'\mu'}{}^{s})_{v'}{}^{v} (D_{-\lambda'\mu} D_{-\mu'\mu})_{r'm+\lambda+u}{}^{rm} \delta_{m+\lambda+u}{}^{m'} \cdot \tag{15.7}$$

At the same time, the selection rule $(m' - m) = \lambda + \mu$ is obeyed.

By modifying Eq. (15.7) and introducing $\left[G^{s}\right]_{v'r'}{}^{vr}$ (defined in Eqs. (6.14), (6.7), and (6.8)), we obtain the following sum rule:

$$\sum_{r'} \left[G^{s}\right]_{v'r'}{}^{vr} = \sum_{\lambda'\mu'} \left|(a_{\lambda'\mu'}{}^{s})_{v'}{}^{v}\right|^{2} . \tag{15.8}$$

This means that the sum of the scattering intensities of the quadrupole scattering, associated with the vibration-rotation transitions v, r → v'r', is independent of r. The sum on the right side is invariant. It represents the total intensity of the quadrupole scattering v → v' of a randomly-oriented molecule upon complete circular irradiation. The quantity $3\left|(a^{0})_{v'}{}^{v}\right|^{2}$ has the same significance as in (15.5b). The summation is equally valid for the trace scattering, and hence, for the total scattering. Here the summation extends over r only.

Upon complete irradiation of the system, the total intensity associated with transitions from a given rotational state of a vibrational level v to all the rotational states associated with the vibrational level v' is independent of the rotational energy. It is equal to the scattering intensity of the line v → v' of a molecule randomly oriented in space.

The same rule holds regardless of the polarization of the incident light and for each component of the scattered radiation. In this case, however, the orientation of the space-fixed molecule is no longer arbitrary; it is necessary to average over all orientations.

Proof: Instead of G, the absolute values of the square of each tensor component must be summed over m. They differ from G by a constant factor for the transitions r → r'. Trace and quadrupole scatterings require a different factor which is obtained by averaging over all orientations in space, as in Eqs. (6.11) and (6.14), instead of summing over the magnetic quantum levels.

Next, we wish to sum over the final states r', as well as over the initial states r. Since the first sum is independent of r, the second sum merely multiplies the right side of Eqs. (15.5b) and (15.8) by the sum over the population indices of all states r, which is equal to the total number of molecules in state v. The total intensity of the rotation-vibration band v → v' is independent of the extent of excitation of the rotational levels. It becomes equal to the scattering intensity which is associated with the transition v → v' of a non-rotating molecule, fixed in space, and averaged over its spatial orientation.

Employing the expressions

$$3\left|(\alpha^0)^v_{v'}\right|^2 = \left[G^0\right]^v_{v'},$$
$$\sum_{\lambda'\mu'} \left|(\alpha_{\lambda'\mu'}{}^s)^v_{v'}\right|^2 = \left[G^s\right]^v_{v'} . \qquad (15.9)$$

We can determine the intensity and polarization of the scattered radiation v → v' by these two constants, following the formulas (6.7), (6.8), (6.19) to (6.26), and $\left[G^a\right]^v_{v'} = 0$.

In most instances, the rotational structure is not resolved, and a single spectral line v → v' will appear whose intensity and polarization are given by Eq. (15.9).

In place of the quantities in Eq. (15.9) we can introduce the two invariants, the linear average value $a^v_{v'}$ and the anisotropic part $\left[\gamma\right]^v_{v'}$:

$$a^v_{v'} = (\alpha^0)^v_{v'}; \; \left(\left[\gamma\right]^v_{v'}\right)^2 = 3/2 \left[G^s\right]^v_{v'}. \qquad (15.10)$$

Denoting the three diagonal components of the tensor $(\alpha)^v_{v'}$ by c_x, c_y, and c_z, we have

$$\left(\left[\gamma\right]^v_{v'}\right)^2 = 1/4 \sum_{i,k} \left|(c_i - c_k)\right|^2, \qquad (15.10a)$$

whereupon the depolarization factor becomes, according to Eq. (6.19),

$$\rho = \frac{3\left[G^s\right]^v_{v'}}{10\left[G^0\right]^v_{v'} + 4\left[G^s\right]^v_{v'}} = \frac{3\left(\left[\gamma\right]^v_{v'}\right)^2}{45\left(a^v_{v'}\right)^2 + 4\left(\left[\gamma\right]^v_{v'}\right)^2} . \qquad (15.11)$$

The average value $a^v_{v'}$ is linearly invariant and equal to the matrix element of the average value of α. In contrast to this, there is no simple relation between the anisotropic part of the tensor $(\alpha)^v_{v'}$ and that of α.

REFERENCES AND FOOTNOTES

1. Placzek, Leipzig Lectures (1931) p. 71; Cabannes, J. phys. et radium 2, 381 (1931).

2. W. Hanle, Physik. Z. 32, 556 (1931); Ann. Physik 11, 885 (1931); 15, 345 (1932).

3. R. Bär, Helv. Phys. Acta 4, 130 (1931); Z. Physik 79, 455 (1932).

4. The index 0 referring to the electronic ground state has henceforth been omitted.

5. In Chapter 6 it has been demonstrated that the trace scattering becomes zero for transitions involving changes in J or m.

6. This has been proved by Placzek and Teller, Z. Physik. 81, 209 (1933).

Chapter 16. Rayleigh Scattering and the Vibrational Raman Effect

To calculate the two constants (introduced in the previous chapter) that determine the intensity and polarization of the line v → v', a knowledge of the vibrational eigenfunction and of the polarizability is required. The latter quantity, which is a function of the molecular coordinates, is generally not known and has not yet been computed satisfactorily although an approximate knowledge of the vibrational eigenfunction is sufficient for most quantitative predictions. It may be written, in first approximation, as a product of harmonic oscillator eigenfunctions, each of which depends on a normal coordinate of a single eigenvibration:[1]

$$U_v = \psi_{v_1}(q_1)\psi_{v_2}(q_2) \cdots \psi_{v_{3N-6}}(q_{3N-6}). \tag{16.1}$$

The vibrational energy is then

$$W_v = \sum_j^{3N-6} (v_j + 1/2)h\nu_j. \tag{16.2}$$

We shall now derive the polarizability in terms of the normal coordinates, starting with the equilibrium position[2]

$$a(q) = a_0 + \sum_j \left(\frac{\partial a}{\partial q_j}\right)_0 q_j + 1/2 \sum_{jk} \left(\frac{\partial^2 a}{\partial q_j \partial q_k}\right) q_j q_k + 1/6 \sum_{jk\ell} \frac{\partial^3 a}{\partial q_j \partial q_k \partial q_\ell} q_j q_k q_\ell. \tag{16.3}$$

The matrix elements are formed with the aid of (16.1). According to the selection rules for the coordinate matrices of the harmonic oscillator, the n^{th} term will be different from zero for transitions involving n, n - 2, n - 4, vibrational quanta. If the series is terminated at the linear term, only undisplaced scattered radiation and vibrational transitions of n = ± 1 will be obtained, and scattered lines of frequency $(\nu \pm \nu_j)$ fundamentals will result. For the Rayleigh scattering,

$$(a)_v^{\ v} = a_0 + 1/2 \sum_j (v_j + 1) \left(\frac{\partial^2 a}{\partial q_j^2}\right)_0 b_j^2, \tag{16.4a}$$

where the zero-point amplitude of the normal vibration j is designated by b_j,[3]

$$b_j = \left(\frac{h}{8\pi^2 \nu_j}\right)^{1/2}. \tag{16.5}$$

The term in the sum of (16.4a) gives the difference between the polarizability of the molecule in the equilibrium position and that in the excited vibrational state of the molecule.

For the vibrational transitions, where [v] refers to the unchanged quantum numbers, we obtain

$$\begin{aligned}
(a)^{[v]v_j}_{[v]v_j+1} &= (v_j+1)^{1/2}\Big[\left(\frac{\partial a}{\partial q_j}\right)_0 b_j + 1/6(v_j+1)\left(\frac{\partial^3 a}{\partial q_j^3}\right)_0 b_j^{\,3} + 1/6\sum_{k\neq j}\left(\frac{\partial^3 a}{\partial q_j \partial q_k^2}\right) b_j b_k^{\,2} + . \\
(a)^{[v]v_j}_{[v]v_j+2} &= 1/2\Big((v_j+1)(v_j+2)\Big)^{1/2}\left(\frac{\partial^2 a}{\partial q_j^2}\right)_0 b_j^{\,2} + \dots \\
(a)^{[v]v_j}_{[v]v_j+3} &= 1/6\Big((v_j+1)(v_j+2)(v_j+3)\Big)^{1/2}\frac{\partial^3 a}{\partial q_j^3} b_j^{\,3} + \dots \\
(a)^{[v]v_j,\,v_k}_{[v]v_j+1,\ v_k+1} &= 1/2\Big((v_j+1)(v_k+1)\Big)^{1/2}\left(\frac{\partial^2 a}{\partial q_j \partial q_k}\right)_0 b_j b_k + \dots
\end{aligned} \tag{16.4b}$$

For a transition involving n vibrational quanta, the expansion starts with the n^{th} term. Since the zero-point amplitudes are small quantities,[4] the intensities associated with the lines v → v' decreases the larger the number of vibrational quanta involved in the transition, as in the case of the infrared spectrum. Provided some coefficients assume particularly large or small values, the sequence in the expansion of the polarizability can be altered; this occurs, for instance, whenever some coefficients disappear because of symmetry.

For all practical purposes, it is sufficient to examine the transitions $v \to v$ and $v_j \to v_j \pm 1$ (Rayleigh scattering and fundamentals), since the overtones and combination tones are rarely intense enough to be observed. The eigenfunction (16.1) must be modified when anharmonicity is taken into account, since it affects the intensity of the overtones. However, Eq. (16.4) remains valid in that even derivatives of a apply to undisplaced lines and odd overtones, whereas odd derivatives apply to fundamentals and even overtones.

The polarizability, α, summed over the states v will yield the intensity. The intensity of the undisplaced scattering is, to a first approximation (when the square term in (16.4a) is neglected), independent of v and, therefore, of the temperature. The average intensity per molecule for the undisplaced scattering is now:[5]

$$I(\nu) = I_p \sum_v \frac{N_v}{N} Q_v{}^v = \frac{2^7\pi^5}{9\lambda^4} \frac{\sum\limits_v \exp(-E_v/kT)\left\{\left[G^0\right]_v{}^v + \left[G^s\right]_v{}^v\right\}}{\sum\limits_v \exp(-E_v/kT)} I_p \quad (16.6a)$$

$$I(\nu) = \frac{2^7\pi^5}{9\lambda^4}\,(3\alpha_0{}^{(0)2} + 2/3\,\gamma_0{}^2)I_p,$$

where I_p is the incident intensity. For the Stokes vibrational line,

$$I(\nu - \nu_j) = \frac{2^7\pi^5}{9\lambda'^4} \frac{\sum\limits_{v_j} \exp(-E_{v_j}/kT)\left\{\left[G^0\right]_{[v]v_j+1}^{[v]v_j} + \left[G^s\right]_{v_j+1}^{v_j}\right\}}{\sum\limits_{v_j} \exp(-E_{v_j}/kT)} I_p$$

$$= \frac{2^7\pi^5}{9\lambda'^4} \frac{\sum\limits_{v_j} (v_j + 1)\exp(-(v_j + 1/2)h\nu_j/kT)}{\sum\limits_{v_j} \exp(-(v_j + 1/2)h\nu_j/kT)} (3a_{1j}{}^2 + 2/3\,\gamma_{1j}{}^2)I_p \quad (16.6b)$$

$$= \frac{2^7\pi^5}{9\lambda'^4} \frac{(3a_{1j}{}^2 + 2/3\,\gamma_{1j}{}^2)I_p}{1 - \exp(-h\nu_j/kT)},$$

and for the anti-Stokes line,

$$I(\nu + \nu_j) = \frac{2^7\pi^5}{9\lambda'^4}\,(3a_{1j}{}^2 + 2/3\,\gamma_{1j}{}^2)I_p\left[-1 + \exp(h\nu_j/kT)\right]^{-1} \quad (16.6c)$$

where a_{1j} and γ_{1j} are, respectively, the average and anisotropic parts of the tensor $(\partial\alpha/\partial q_j)_0$. The latter quantity is usually different from $(\partial\gamma/\partial q_j)_0$ since the construction of the (quadratic) invariant γ_{1j} and differentiation are not interchangeable.

Equations (16.6b, c) show that the intensities of the Stokes and anti-Stokes lines increase with temperature. This may be ascribed to the fact that the higher vibrational levels scatter more because of greater nuclear amplitudes (16.4b). If the vibration is anharmonic, the frequencies ν^{vj}_{vj+1} will depend upon v and, in addition to the rotational structure, the line will show a further broadening or fine structure. The quantities $a^{(0)}$ and γ involved in the depolarization factor of the Rayleigh scattering are not independent functions since the three principal values of the polarizability must be positive:

$$a^{(0)2} \geq \gamma^2/9.$$

According to Eq. (5.11), $\rho \leq 1/3$ and $P \leq 1$ for the Rayleigh line, thus indicating no reversal of the circular polarization. An analogous relation does not exist for the invariant quantities of the tensor associated with the displaced scattered radiation. As the polarizability can increase or decrease for a vibration, the principal values of the tensor derivatives may assume different signs. Other properties, particularly the derivation of the selection rules, require a knowledge of the symmetry character of the molecular vibrations.

REFERENCES AND FOOTNOTES

1. See Krönig, Chapter 6, concerning the definition of normal coordinates.

2. The derivation is valid for each component; the index $\lambda\mu$ is omitted to simplify the expression.

3. Equation (16.4) is valid provided the normal coordinates are normalized so that the kinetic energy may be written in the form:

$$T = 1/2 \sum_j b_j \dot{q}_j^2 .$$

The quantities q_j and b_j have the dimension $\ell\sqrt{m}$. Occasionally, pure lengths are chosen as normal coordinates (e.g., the displacement of one of the vibrating atoms) by assigning to each normal vibration a reduced mass, μ_j, and by proceeding from the normalization $T = 1/2 \sum_j \mu_j \dot{q}_j^2$. The zero-point amplitude, b_j', associated with the vibration j, is also a length:

$$b_j' = \frac{b_j}{\sqrt{\mu_j}} . \tag{16.5a}$$

Since the selection of the reduced mass is not arbitrary, the former type of normalization is applied throughout the text.

4. The displacements of the atoms from equilibrium, corresponding to the quantities b_j, are small relative to the interatomic distances.

5. Since the molecules are assumed to be randomly distributed (ideal gas), the intensities are additive also for the coherent scattered radiation.

Chapter 17. Fundamental Concepts of the Symmetry Theory[1]

A three-dimensional configuration is said to be symmetric if there are linear, orthogonal coordinate transformations which leave its properties unchanged. These transformations are the so-called symmetry operations, and the geometric representation is comprised of symmetry elements. The symmetry operations have group character, i.e., the successive application of two symmetry operations yields again a symmetry operation. Only those operations are considered that leave a point in space (which must not necessarily lie inside the molecule) invariant. They are described as point symmetry operations; the corresponding elements are described as point symmetry elements, and the group of the point symmetry operation, as point group.

The point symmetry operations include inversion,[2] mirror reflection, rotation, and rotation followed by reflection.[3] The corresponding symmetry elements are the center of symmetry, the plane, the rotation, and rotation-reflection axes. According to Schoenflies, they are described by the letters i, σ, C_p, and S_p, respectively.[4] The possible point groups may be obtained by combining these symmetry elements, and are limited merely by the relations existing between the symmetry operations. A few simple relations are the following:

$$(S_p)^2 = C_{p/2}$$

$$(S_p)^{p/2} = \begin{cases} C_2 & \text{for } p/2 \text{ even} \\ i & \text{for } p/2 \text{ odd} \end{cases}$$

$$C_2\sigma_h = \sigma_h \cdot C_2 = i \quad (\sigma_h \text{ is a plane perpendicular to } C_2).$$

$$C_2 \cdot i = i \cdot C_2 = \sigma_h$$

$$i \cdot \sigma_h = \sigma_h \cdot i = C_2.$$

The point groups are summarized below, along with the Schoenflies description and their symmetry elements. For a systematic construction, which may be carried out along different principles, texts devoted to this particular topic should be consulted.

1.	C_p	p-fold axis; the operations involve p rotations of an angle $2\pi/p$ about the axis.
2.	S_p	(for even p only) p-fold rotation-reflection axis; the operations are the p-rotation-reflections (rotation of an angle $2\pi/p$, followed by a reflection in a plane perpendicular to this axis). S_p implies $C_{p/2}$ as well as C_2 and i when p/2 is even and odd, respectively.
3.	C_{pv}	p-fold axis C_p and p planes of symmetry, σ_v, going through it at mutual angles of $2\pi/p$.
4.	D_p	Dihedral group. C_p and a twofold axis perpendicular to it require (p - 1) additional twofold axes. They intersect each other and C_p at mutual angles of $2\pi/p$.
5.	C_{ph}	C_p and a plane σ_h perpendicular to it. When p is even, there are also the elements i and S_p.
6.	D_{pd}	$= S_{2p}$. If, in addition to D_p, there is a vertical plane which bisects the angle between the two axes, (p - 1) additional planes exist. There is a rotation-reflection elements, S_{2p}, as well as C_2 and i for even and odd p, respectively.
7.	D_{ph}	If, in addition to C_{pv}, there is a plane σ_h perpendicular to the axis, then p twofold axes are formed by the lines of intersection of the planes σ_v and σ_h. When p is even, i and S_p are also present.

Special Cases:

a.	C_1	No symmetry.
b.	$C_s = C_{1h}$	Reflection plane.
c.	$S_2 = i$	Center of symmetry.
d.	$V = D_2$	Fourfold group. Three mutually perpendicular twofold axes (two of which require the third).
e.	$V_h = D_{2h}$	V and a center of symmetry. Three planes going through these axes.
f.	$V_d = D_{2d}$	V and a vertical plane that bisects the angle between the two axes. Another such plane and a fourfold S_4 axis are required.

8 - 12. Cubic groups:

These may be visualized most easily by means of a cube whose planes are intersected at the center by the three twofold axes of the fourfold group ($V = D_2$).

8.	T	Tetrahedral group. If, to a fourfold group, a threefold axis is added in a spatial cube-diagonal, then three additional threefold axes are generated in the remaining cube-diagonals.
9.	T_d	One of the twofold axes of T becomes a fourfold rotation-reflection axes. The same will also hold for the two remaining twofold axes. Six planes are generated by any two of the cube-diagonals.
10.	O	Octahedral groups. One of the twofold axes of T as well as the other two are transformed into fourfold axes. This generates six additional twofold axes which connect the center of adjacent cube edges.
11.	T_h	T and a center of symmetry. There are now three planes through the twofold axes.
12.	O_h	O and a center of symmetry in the center of the cube determines the remaining cubic symmetry elements.

13 - 14. Icosahedral group.

13.	I	Simple icosahedral group. The group of the spatial rotation of the icosahedron or of the pentagon dodecahedron. It contains six fivefold, 10 threefold, and 15 twofold axes.
14.	I_h	Complete icosahedron. It contains an additional center of symmetry.

The number of operations, including the identity operation, denotes the order of the group as follows:

p for C_p, S_p
2p for C_{pv}, D_p, C_{ph}
4p for D_{ph}, D_{pv}
12 for T
24 for T_d, O, T_h
60 for I
120 for I_h.

If a point group contains all the symmetry elements of another group, the latter is called the subgroup of the former. For instance, C_4 contains the subgroup C_2; C_{4h} contains C_{2h}, i, and C_{1h}.

Applications of symmetry considerations usually assume that the molecular symmetry is given by the symmetry of the positions of the atoms. The total Hamiltonian of the molecule is invariant with respect to the symmetry operations that transform the atoms into each other. The symmetry of a molecule may be established by considering the nuclei that cannot be transformed into each other, and generating the remaining points by applying the symmetry operations of the group. Each point generates (z - 1) additional points when z is the order of the group. In the general case, there are z points of each type. A special case exists when there are points that lie on symmetry elements. Aside from the identity, there are additional symmetry operations that transform these points into themselves. The group of these operations is called "the eigensymmetry" of these points. It can be considered as the symmetry of the force field when the point is part of the molecule and is always a subgroup of the molecular symmetry. The position of a point having an eigensymmetry is described as a special point position; its order (the number of equivalent points) is no longer equal to that of the molecular symmetry group, but is equal to the ratio of that order to the order of the particular group.

Not every subgroup of the molecular symmetry is an eigensymmetry; for instance, C_4 cannot have points of C_2 eigensymmetry. If a point lies on an axis, then it has the C_4 symmetry. In case of crystals, the existence of glide planes and screw axes obviates this restriction.

We shall treat the CCl_4 molecule as an example. The molecular symmetry is T_d; the Cl atoms lie on the threefold axes through which vertical planes run. Their eigensymmetry is C_{3v}, and the order of the point group is $24/6 = 4$. The eigensymmetry of the C atom in the center of the tetrahedron is T_d, and it is transformed into itself by all the symmetry operations.

The application of symmetry considerations to crystals requires an extension as well as a restriction. The extension involves operations that do not leave any point in space unchanged (translation, screw, and glide operations). The translations require an infinite repetition of the symmetry elements in periodic order, but this is not possible for all the symmetry elements. Hence, the number of point groups occurring in crystals is reduced to 32; these are:

C_p and C_{ph} for $p = 1, 2, 3, 4, 6$

C_{pv}, D_p, D_{ph} for $p = 2, 3, 4, 6$

S_p for $p = 2, 4, 6$

D_{pd} for $p = 2, 3$

and the five cubic groups. The symmetry groups constitute the Schoenflies point groups or crystal classes, which, together with the translations, form the 230 space groups.

REFERENCES AND FOOTNOTES

1. The following treatment describes in a condensed form the basic concepts and the notation required for further symmetry considerations. For detailed discussions on the subject, articles by P. P. Ewald (Handbuch der Physik (Geiger-(Scheel), Vol. 24), Schoenflies (Theory of the Crystal Structure, Berlin (1923)), and Niggli (Geometrische Kristallographie des Diskuntinuums, Leipzig (1919)) have to be consulted.

2. Reflection at the center (inversion).

3. Rotation, followed by reflection in a plane perpendicular to the axis of rotation.

4. The index p denotes a p-fold axis. Symbolically, symmetry elements and symmetry operations are not distinguishable, e.g., C_p may describe a p-fold axis or a rotation of an angle $2\pi/p$.

Chapter 18. The Vibrational Raman Effect and Molecular Symmetry.

1. Symmetry Properties of the Normal Modes of Vibration.[1]

To study the effect of molecular symmetry on the normal modes of vibration, one must set up the vibrational Hamiltonian. In terms of the normal coordinates, q,

$$H = T + V = 1/2 \sum_j \dot{q}_j^{\,2} + 1/2 \sum_j \omega_j^{\,2} q_j^{\,2}, \qquad \omega_j = 2\pi\nu_j. \tag{18.1}$$

Since the q's are linear combinations of the position coordinates of the nuclei, the symmetry operations represent linear orthogonal transformations of the normal coordinates. By definition, the kinetic energy in (18.1) is invariant with respect to these transformations, so that only the potential energy has to be investigated. The latter must remain invariant with respect to the symmetry operations contained in the symmetry group of the molecule. Hence, the normal coordinates of a symmetric molecule is separated into a number of species, which differ from each other by their transformations under the symmetry operations.

These normal coordinates are identical with the classes of eigenfunctions introduced in Chapter 5. The possible transformation laws for the normal coordinates and vibrational eigenfunctions are the same.

All of the symmetry groups possess one type of vibration whose normal coordinates are invariant with respect to all symmetry operations. During these vibrations the symmetry of the molecule is retained. This type is called "totally symmetric." The groups that contain two operations only[2] (these are σ, i, and C_2) have two types of vibrations. The normal coordinates of one are invariant with respect to the symmetry operations, while those of the other alter their signs. In the first case the vibrational configuration remains unchanged under the symmetry operations, but in the latter case the displacements of all points are reversed. Figure 7 shows an example for a reflection plane.

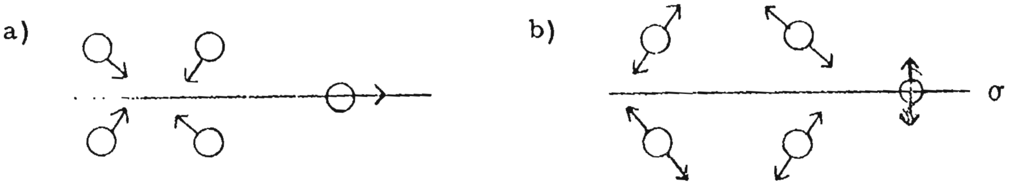


Fig. 7. Eigenvibrations of a system having a plane of symmetry.
a) symmetric vibration, b) antisymmetric vibration

For groups that do not have axes higher than twofold the vibrations may be either symmetric or antisymmetric with respect to each symmetry operation. Here the number of species is identical with that of the symmetry operations.

Systems containing axes with $p > 2$ are more complex. There are normal coordinates which, upon rotation by multiples of $2\pi/p$, transform into each other, and the corresponding vibrations are degenerate. Systems having axial symmetry are doubly degenerate; the degeneracy of cubic systems is two- and threefold, and that of icosahedral systems is fivefold.

The types of vibrations belonging to group C_p may be described by an integer ℓ, defined only modulus p. $\ell = 0$ and $\ell = p/2$ (p even) correspond to the totally symmetric and antisymmetric types, respectively. For the remaining values of ℓ, the vibrations are degenerate. If, upon rotation by $2\pi/p$, the degenerate normal coordinates ξ, η are combined into $\xi \pm i\eta$, this quantity is multiplied by $\exp(-2\pi i\ell/p)$:

$$C_p(\xi + i\eta) = (\xi + i\eta) \exp(-2\pi i\ell/p). \qquad (18.2)$$

Since the choice of the sign of η is arbitrary but that of ℓ is not, vibrations with ℓ and $-\ell$ are identical. Hence, there are $p/2$ and $p/2 - 1$ vibrations for p even and odd, respectively. Other groups will be given in subsequent tables.

2. Selection Rules.[3]

The symmetry types of the normal modes of vibration are distinguished by their selection rules.

Reference to the general discussion in Chapter 5 will be useful in arriving at the selection rules. According to the results given in Chapter 14, the matrix elements $(\alpha_{\lambda\mu})_{v'}^{v}$ may be investigated, instead of the transformation properties of the total eigenfunction and of the general tensor $c_{\lambda\mu}$. The transformation properties are essentially those of the vibrational eigenfunction and the symmetric tensor $\alpha_{\lambda\mu}$. The matrix element differs from zero only when $U_v \alpha_{\lambda\mu} U_{v'}$ remains invariant with respect to all operations of the symmetry of the molecule.[4] Let us consider as example the groups that contain only one symmetry element (C_h, C_2, C_i). Here the normal coordinates and the vibrational eigenfunctions separate into two classes: symmetric and antisymmetric (temporarily described by + and -, respectively).

The invariance of $U_v \alpha_{\lambda\mu} U_{v'}$ requires that $\alpha_{\lambda\mu}$ must remain invariant or change its sign under the symmetry operation, depending on whether U_v and $U_{v'}$ belong to the same class or to a different one. Because the components of α are invariant to an inversion, only terms belonging to the same class combine in the Raman effect for systems having a C_i symmetry. In case of absorption (infrared), the tensor α is replaced by the vector M, and only terms belonging to different classes combine. Analogous results have been derived in Chapter 5 for the total eigenfunction. For group C_h, the reflection of the tensor must be investigated. Choosing the z axis perpendicular to the plane of reflection, we see that the components $\lambda + \mu = 0, \pm 2$ remain invariant to a reflection, while the components $\lambda + \mu = \pm 1$ change signs.[5] When the tensor is expressed in terms of cartesian rather than circular coordinates, α_{xx}, α_{yy}, α_{zz}, α_{xy} belong to the former, and α_{xx}, α_{yz} to the latter, class. Therefore, for the Raman transitions $+ \rightleftarrows -$, the selection rule $\lambda + \mu = \pm 1$ applies, and for the transitions $\pm \rightarrow \mp$, the rule $\lambda + \mu = 0, \pm 2$ applies. In absorption, the selection rules $\lambda = \pm 1 (M_z = 0)$ and $\lambda = 0 (M_x = M_y = 0)$ pertain to the transitions $+ \rightarrow -$ and $\pm \rightarrow \pm$, respectively. These are also the selection rules for C_2, because a tensor transforms, with respect to a reflection in a plane perpendicular to this axis; a vector behaves in an opposite way. If the z axis is selected as the axis of rotation, then in the Raman effect the selection rules are the same as for the reflection plane, whereas they are different in absorption.

In addition, it is necessary to identify the class to which the eigenfunction of a given energy state whose quantum numbers are specified belongs. According to (16.1), the vibrational eigenfunction can be approximated by the product of the eigenfunctions of harmonic oscillators (the so-called Hermitian polynomials), each of which depends on one normal coordinate. The eigenfunctions of a symmetric vibration remain invariant under the symmetry operation (independent of the quantum number), since their argument (the normal coordinate) does not change. For antisymmetric vibrations, the normal coordinates change signs. The Hermitian polynomials are even or odd functions of the argument, depending on the even or odd character of the vibrational quantum number. In the former case, the eigenfunctions of the antisymmetric vibrations remain invariant also, while in the latter, the signs are changed. The total vibrational eigenfunction is symmetric (antisymmetric) if the sum of the quantum numbers of the antisymmetric vibrations are even (odd).[6]

From the above, the selection rules for any vibrations transition can now be derived. For example, for C_i only those transitions are permitted in the Raman effect (infrared) for which the sum of the quanta of the antisymmetric vibrations is even (odd).[7] Fundamentals and overtones of symmetric vibrations can occur in the Raman effect, but those of antisymmetric vibrations are forbidden. The selection rules for C_2 and C_h permit all the vibrations to appear in the Raman effect. Individual components of the scattering tensor vanish, a fact that becomes noticeable in the polarization (see below) and in the rotational structure of the Raman lines (see Chapter 21), particularly in the case of crystals.

The selection rules for more complex systems may be obtained in an analogous manner.[8] The rules apply rigorously and are not contingent upon assumptions of harmonic forces. If the vibrations are strongly anharmonic, Eq. (16.1) no longer holds for the vibrational eigenfunction. It was used only in establishing the class of the eigenfunction which cannot be altered by anharmonicity and coupling. If the anharmonicity increases to the extent that it is no longer meaningful to differentiate between fundamentals and overtones and to describe energy levels in terms of vibrational quantum numbers, states belonging to different species can still be distinguished, and the selection rules for these transitions remain valid.

Aside from these rigorous rules, there are approximate ones which are of practical importance; they may be obtained from the polarizability derivatives, but are affected by anharmonicity and by the higher-order terms in the expansion. The rule derived in the preceding chapter falls into this category. Here, the intensities of the overtones and combination tones vanish for harmonic forces and rapid convergence of the expression (16. 3). Similarly, for vibrations of systems containing symmetry axes with $p > 2$, the coefficient $(\partial \alpha / \partial q_j)_0$ may disappear, while some higher coefficients in (16.14b) do not; then the intensity of the fundamental is only approximately zero. In practice, this approximation proved to be adequate in the analyses of molecules investigated up to the present time.

From the selection rules, important predictions can be made concerning the polarizabilities of the vibrational Raman lines. According to (15.11) and (15. 3), they are determined by the relative values of the trace and quadrupole scatterings (anisotropic). If one of the two terms of the scattered radiation vanishes, the depolarization factor and reversal coefficient have fixed values (see Table I, Chapter 6). The rules for the trace scattering may be expressed in a general form, in contrast to those for the quadrupole scattering, which vary from group to group. For the fundamental modes of vibration, the following holds:

The trace scattering is forbidden for non-totally symmetric vibrations, but it is permitted for totally symmetric vibrations. This rule applies rigorously to vibrations that are antisymmetric with respect to at least one element of symmetry, but only approximately to degenerate vibrations that do not possess this property.

Proof: a) According to Chapter 6, only combinations of states belonging to the same species give rise to trace scattering. Energy levels that differ by 1 (in general, by an odd integer) in the quantum number, of a single antisymmetric vibrations, belong to different species. This results from the above discussed property of the Hermitian polynomials.

b) The approximate validity for other cases may be derived as follows: The average value of the polarizability is

$$a = 1/3 \sum_{\lambda} \alpha_{\lambda-\lambda} ,$$

whose matrix element determines the intensity of the trace scattering; in the series expansion, only the linear terms are retained:

$$a = a_0 + \sum_{j} \left(\frac{\partial a}{\partial q_j}\right)_0 q_j. \tag{18.5}$$

Under a symmetry operation, the normal coordinate transforms into a linear combination of its degenerate normal coordinates;

$$S_n \cdot q_j = \sum_{r} c_{jr}{}^{(n)} q_r. \tag{18.6}$$

The index n refers to the symmetry operation, and the summation is carried out over all the normal modes of vibration. If q_j and q_r are not degenerate, $c_{jr} = 0$; particularly, if the vibration j is not degenerate, $c_{jr} = 0$ when $j \neq r$ and c_{jj} can be either + or -.

The coefficients c_{jr} form an orthogonal system for a given n, and we have

$$\sum_{n} c_{jr}{}^{(n)} = 0 \tag{18.7}$$

for the non-totally symmetric vibrations.[9] For the totally symmetric vibrations, we have $c_{jr} = \delta_r^j$.

Since the scalar quantity a is invariant with respect to symmetry operations, it follows from Eqs. (18.5) and (18.6) that

$$\sum_j \left(\frac{\partial a}{\partial q_j}\right)_0 q_j = \sum_j \sum_r c_{jr}^{(n)} q_r \left(\frac{\partial a}{\partial q_j}\right)_0, \tag{18.8}$$

which may be written in the form:

$$\sum_r q_r \left[\sum_j \left(\frac{\partial a}{\partial q_j}\right)_0 c_{jr}^{(n)} - \left(\frac{\partial a}{\partial q_r}\right)_0\right] = 0. \tag{18.8a}$$

Since Eq. (18.8) must be identical for all values of q,

$$\left(\frac{\partial a}{\partial q_r}\right)_0 = \sum_j \left(\frac{\partial a}{\partial q_j}\right)_0 c_{jr}^{(n)}. \tag{18.9}$$

Upon summing over the symmetry operations n of the point group, we see that the right side of (18.9) becomes zero for the non-totally symmetric q's because of (18.7) and therefore we obtain

$$\left(\frac{\partial a}{\partial q_r}\right)_0 = 0. \tag{18.10}$$

The coefficient that determines the intensity of the isotropic scattering vanishes, as a first approximation, and the polarization of the lines associated with fundamentals of non-totally symmetric vibrations is the same as that of the quadrupole scattering, i.e., $\rho = 3/4$, $\rho_n = 6/7$, $P = 6$.

Because Raman lines associated with isotropic scattering are usually stronger than those that are not, a qualitative rule may be deduced: The fundamentals of the totally symmetric vibrations give rise to the most intense Raman lines. For the totally symmetric fundamentals and overtone vibrations of cubic systems, the quadrupole scattering vanishes. The same holds for the quadrupole term of the unshifted scattered radiation, but if degenerate vibrations are excited in the initial state, this will be only approximately correct.

Proof: If the initial state is the ground state or one in which only non-degenerate vibrations are excited, the total vibrational eigenfunction for the initial and final states must have at least tetrahedral symmetry (see Table IX).

For the product $U_v \alpha U_{v'}$ to be invariant, α must also possess tetrahedral symmetry. In that case, a tensor is reduced to a scalar, and the isotropic part will remain.

If non-totally symmetric vibrations are excited, the above statement no longer applies strictly. To prove this, we must refer to the derivation of the polarizability. It can be shown that the first coefficient (α_0, for the unshifted scattered radiation; $(\partial\alpha/\partial q_j)_0$, for the fundamental; $(\partial^n\alpha/\partial q_j^n)_0$, for the (n - 1)th overtone) has cubic symmetry (isotropic), while the higher terms, as for as degenerate normal coordinates occur, will be anisotropic.[10] This effect may be thought of as a distortion of the molecule by the vibration, and may usually be neglected.[11] Therefore, for molecules having cubic symmetry, the Rayleigh lines, and the Raman lines associated with the fundamental and overtones of totally symmetric vibrations, have

$$\rho = \rho_n = 0, \ P = 0.$$

Tables IV - IX show the types of vibration and selection rules for the fundamentals in a form that is useful for crystals also. The non-crystallographic point groups will be mentioned below. The point groups are arranged according to crystal systems. Each table contains one crystal system, and each row corresponds to one type of vibration. The columns are separated into three parts (I, II, and III). Part I contains the symbols describing the types of vibration for the point groups (crystal classes) of the crystal system. Additional details will be presented later. Part II contains the characters for each type of vibration of the highest symmetric (holohedral) point group. It gives the transformation laws of the normal coordinates for the symmetry elements of the group, and for others which are listed in parentheses. This information may be derived from the preceding discussion, but has been tabulated here for ready reference. The signs + and - denote symmetric and antisymmetric, respectively. The remaining signs refer to degenerate normal coordinates. With respect to each symmetry operation and ordinary space coordinates, the three degenerate normal coordinates of the threefold-degenerate vibrations of the cubic system transform with or without a change in sign, indicated by - K or + K, respectively. For the doubly-degenerate vibrations, the information refers to the linear combination $q = \xi + i\eta$ ($q^* = \xi - i\eta$). Here $e^{\pm 1}$ implies that $\xi + i\eta$ is to be multiplied by exp ($-2\pi i/3$), and exp ($2\pi i/3$). The symbol * refers to the complex

Tables IV - IX of Chapter 18 were inadvertently omitted.

Tables IV - IX present symmetry species and selection rules for the following point groups: triclinic, monoclinic, rhombic, tetragonal, hexagonal, rhombahedral (included in Table VII), and cubic.

Table IV. Symmetry types and selection rules — triclinic point group

C_i	C_1		i	Raman	Infrared
g	A	R	+		v
u	A	T	-	v	
		x	-		
		y	-		
		z	-		

Table V. Monoclinic point group

	C_{2h}	C_2	C_s		C_2	(σ_h)	i	Raman	Infrared
	A_g	A	A'	R_z	+	+	+	$c_{xz} = c_{yz} = 0$	v
	A_u	A	A''	T_z	+	-	-	v	$M_\perp = 0$
	B_g	B	A''	$R_x R_y$	-	-	+	$c_{ii} = c_{xy} = 0$	v
	B_u	B	A'	$T_x T_y$	-	+	-	v	$M_z = 0$
C_2	.	.		x	-	+	-		
σ_h	.		.	y	-	+	-		
i	.			z	+	-	-		

Table VI. Rhombic point group

	V_h	V	C_{2v}		$C_2^{(z)}$	$C_2^{(y)}$	σ_h	i	Raman	Infrared
	A_{1g}	A_1	A_1		+	+	+	+	$c_{ik} = 0$	v
	A_{1u}	A_1	A_2		+	+	-	-	v	v
	B_{1g}	B_1	A_2	R_z	+	-	-	+	$c_{xy} \neq 0$	v
	B_{1u}	B_1	A_1	T_z	+	-	+	-	v	$M_z \neq 0$
	B_{2g}	B_2	B_1	R_y	-	+	+	+	$c_{xz} \neq 0$	v
	B_{2u}	B_2	B_2	T_y	-	+	-	-	v	$M_y \neq 0$
	B_{3g}	B_3	B_2	R_x	-	-	-	+	$c_{yz} \neq 0$	v
	B_{3u}	B_3	B_1	T_x	-	-	+	-	v	$M_x \neq 0$
$C_2^{(z)}$	.	.	.	x	-	-	+	-		
$C_2^{(y)}$	.	.		y	-	+	-	-		
σ_y	.		.	z	+	-	+	-		
i	.									

Table VII. Tetragonal point group

	D_{4h}	D_4	C_{4v}	C_{4h}	C_4	V_D	S_4		C_4	(S_4)	(σ_v^y)	C_2^y	i	Raman	Infrared
	A_{1g}	A_1	A_1	A_g	A	A_1	A		+	+	+	+	+	$c_{xx}=c_{yy}:c_{ik}=0$	v
	A_{1u}	A_1	A_2	A_u	A	B_1	B		+	-	-	+	-	v	v
	A_{2g}	A_2	A_2	A_g	A	A_2	A	R_z	+	+	-	-	+	v	v
	A_{2u}	A_2	A_1	A_u	A	B_2	B	T_z	+	-	+	-	-	v	$M_\perp = 0$
	B_{1g}	B_1	B_1	B_g	B	B_1	B		-	-	+	+	+	$c_{xx}=-c_{yy}\neq 0$	v
	B_{1u}	B_1	B_2	B_u	B	A_1	A		-	+	-	+	-	v	v
	B_{2g}	B_2	B_2	B_g	B	B_2	B		-	-	-	-	+	$c_{xy}\neq 0$	v
	B_{2u}	B_2	B_1	B_u	B	A_2	A		-	+	+	-	-	v	v
	E_g	E	E	$\underline{E}_g$	$\underline{E}$	E	$\underline{E}$	$R_\perp$	$\mp i$	$\pm i$	*	-*	+	$c_{ii}=c_{xy}=0:$ $\lvert c_{xz}\rvert=\lvert c_{yz}\rvert$	v
	E_u	E	E	$\underline{E}_u$	$\underline{E}$	E	$\underline{E}$	$T_\perp$	$\mp i$	$\pm i$	*	-*	-	v	$M_z = 0$
C_4	.	.	.	.	.			z	+	-	+	-	-		
S_4	.			.		.	.	x+iy	-i	-i	*	-*	-		
$\sigma_v^{(y)}$	.		.					x-iy	i	i	*	-*	-		
$C_2^{(y)}$	.	.				.									
i	.			.											

Table VIII. Hexagonal point group

	D_{6h}	D_6	C_{6v}	C_{6h}	C_6	D_{3h}	C_{3h}	D_{3d}	D_3	C_{3v}	S_6	C_3		C_3	$C_2^{(z)}$	$C_2^{(y)}$	σ_h	$\sigma_v^{(y)}$	i	Raman	Infrared
	A_{1g}	A_1	A_1	A_g	A	A_1'	A'	A_{1g}	A_1	A_1	A_g	A		+	+	+	+	+	+	$c_{xx}=c_{yy}; c_{ik}=0$	v
	A_{1u}	A_1	A_2	A_u	A	A_1''	A''	A_{1u}	A_1	A_2	A_u	A		+	+	+	-	-	-		v
	A_{2g}	A_2	A_2	A_g	A	A_2'	A'	A_{2g}	A_2	A_2	A_g	A	R_z	+	+	-	+	-	+	v	v
	A_{2u}	A_2	A_1	A_u	A	A_2''	A''	A_{2u}	A_2	A_1	A_u	A	T_z	+	+	-	-	+	-	v	$M_\perp=0$
	B_{1g}	B_1	B_1	B_g	B	A_1''	A''	A_{1g}	A_1	A_1	A_g	A		+	-	+	-	+	+	v	v
	B_{1u}	B_1	B_2	B_u	B	A_1'	A'	A_{1u}	A_1	A_2	A_u	A		+	-	+	+	-	-	v	v
	B_{2g}	B_2	B_2	B_g	B	A_2''	A''	A_{2g}	A_2	A_2	A_g	A		+	-	-	-	-	+	v	v
	B_{2u}	B_2	B_1	B_u	B	A_2'	A'	A_{2u}	A_2	A_1	A_u	A		+	-	-	+	+	-	v	v
	E_g^+	E^+	E^+	$\underline{E}_g^+$	$\underline{E}^+$	E'	$\underline{E}'$	E_g	E	E	$\underline{E}_g$	$\underline{E}$		$e^{\mp 1}$	+	-*	+	-*	+	$c_{zi}=0; c_{xx}=-c_{yy};$ $\lvert c_{xy}\rvert=\lvert c_{xx}\rvert$	v
	E_u^+	E^+	E^+	$\underline{E}_u^+$	$\underline{E}^+$	E''	$\underline{E}''$	E_u	E	E	$\underline{E}_u$	$\underline{E}$		$e^{\mp 1}$	+	-*	-	*	-	v	v
	E_g^-	E^-	E^-	$\underline{E}_g^+$	$\underline{E}^-$	E''	$\underline{E}''$	E_g	E	E	$\underline{E}_g$	$\underline{E}$	$R_\perp$	$e^{\mp 1}$	-	-*	-	-*	+	$c_{ii}=c_{xy}=0;$ $\lvert c_{xz}\rvert=\lvert c_{yz}\rvert$	v
	E_u^-	E^-	E^-	$\underline{E}_u^+$	$\underline{E}^-$	E'	$\underline{E}'$	E_u	E	E	$\underline{E}_u$	$\underline{E}$	$T_\perp$	$e^{\mp 1}$	-	-*	+	*	-	v	$M_z=0$
C_3	·	·	·	·	·	·	·	·	·	·	·	·	z	+	+	-	-	+	-		
$C_2^{(z)}$	·	·	·	·	·								x+iy	e^{-1}	-	-*	+	*	-		
$C_2^{(y)}$	·	·				·		·	·				x-iy	e^{1}	-	-*	+	*	-		
σ_h	·			·		·	·														
σ_v^y	·		·					·		·											
i	·			·				·			·										

Table VIIIa. Rhombohedral point group (included in Table VII)

D_{3d}	D_3	C_{3v}	S_6	C_3		C_3	$C_2^{(y)}$	$\sigma_v^{(y)}$	i	Raman	Infrared
A_{1g}	A_1	A_1	A_g	A		+	+	+	+	$c_{xx}=c_{yy}; c_{ik}=0$	v
A_{1u}	A_1	A_2	A_u	A		+	+	-	-	v	v
A_{2g}	A_2	A_2	A_g	A	R_z	+	-	-	+	v	v
A_{2u}	A_2	A_1	A_u	A	T_z	+	-	+	-	v	$M_\perp=0$
E_g	E	E	$\underline{E}_g$	$\underline{E}$	$R_\perp$	$e^{\mp 1}$	-*	-*	+	$c_{zz}=0, c_{xx}=-c_{yy}$; $\lvert c_{xz}\rvert=\lvert c_{yz}\rvert, \lvert c_{xy}\rvert=\lvert c_{xx}\rvert$	v
E_u	E	E	$\underline{E}_u$	$\underline{E}$	$T_\perp$	$e^{\mp 1}$	-*	*	-	v	$M_z=0$
					z	+	-	+	-		
					x+iy	e^{-1}	-*	-*	-		
					x-iy	e^{+1}	-*	-*	-		

Table IX. Cubic point group

	O_h	T_h	O	T_d	T		(C_2^z)	C_2^y	C_3	(S_4)	C_4	i	Raman	Infrared
	A_{1g}	A_g	A_1	A_1	A		+	+	+	+	+	+	$c_{xx}=c_{yy}=c_{zz}; c_{ik}=0$	v
	A_{1u}	A_u	A_1	A_2	A		+	+	+	-	+	-	v	v
	A_{2g}	A_g	A_2	A_2	A		+	+	+	-	-	+	v	v
	A_{2u}	A_u	A_2	A_1	A		+	+	+	+	-	-	v	v
	E_g	$\underline{E}_g$	E	E	$\underline{E}$		+	+	$e^{\mp 1}$	*	*	+	$c_{xx}+c_{yy}+c_{zz}=0; c_{ik}=0$ $\lvert c_{xx}\rvert=\lvert c_{yy}\rvert=\lvert c_{zz}\rvert$	v
	E_u	$\underline{E}_u$	E	E	$\underline{E}$		+	+	$e^{\mp 1}$	-*	*	-	v	v
	F_{1g}	F_g	F_1	F_1	F	R	K	K	K	-K	K	+	v	v
	F_{1u}	F_u	F_1	F_2	F	T	K	K	K	K	K	-	v	$\lvert M_x\rvert=\lvert M_y\rvert=\lvert M_z\rvert$
	F_{2g}	F_g	F_2	F_2	F		K	K	K	K	-K	+	$c_{ii}=0; \lvert c_{xy}\rvert=\lvert c_{yz}\rvert=\lvert c_{zx}\rvert$	v
	F_{2u}	F_u	F_2	F_1	F		K	K	K	-K	-K	-	v	v
C_2^z	.	.	.	.	.	x	-x	-x	y	y	y	-x		
C_2^y	.	.	.	.	.	y	-y	y	z	-x	-x	-y		
C_3	.	.	.	.	.	z	z	-z	x	-z	z	-z		
S_4	.			.										
C_4	.		.											
i	.	.												

conjugate normal coordinate, and $-^{*}$ to the same coordinate with its sign changed. The sign of * is arbitrary, but if it is given for one symmetry operation, it will be fixed for all the others.[12] An example may be cited: If, in Table VII, the column $C_2^{(y)}$ is designated by *, then in the $\sigma_v^{(y)}$ column the E vibrations symmetric and antisymmetric to i are denoted by * and $-^{*}$, respectively, because of $\sigma_v^{(y)} = iC_2^{(y)}$. The description for the symmetry elements is summarized in Chapter 17. If a unique axis is present, it is selected as the z axis, and the planes are characterized by an index giving the direction perpendicular to it.

The first column of Part II gives the type of vibration to which the zero frequencies, the translations, and rotations belong. The transformation laws for the ordinary space coordinates are shown below. Part III lists the selection rules for the fundamentals in the Raman effect and in the infrared absorption; v denotes a forbidden vibration. The selection rules for the components of the tensor (vector) associated with the fundamentals are of importance for the rotational structure and for crystals.

For the nonholohedral point groups, the vibration types and selection rules are obtained by considering only those symmetry elements that occur in the particular group. These are designated by points in the lower section of Part I. Several vibration types of the holohedral point group will coincide, but those components occur that are permitted in at least one of the coinciding holohedral types. In Part I the vibration types of the holohedral class are correlated with those of the hemihedral one. For each holohedral type, the symbol of the vibration type into which it is transformed in the hemihedral groups is given.

As example, the selection rules for S_4 are presented. Table VII, column S_4 lists the symbols A, B, E, several times. The selection rules for A are: $c_{ii} = c_{xy} = 0$, v, v, v; for B: $c_{xx} = -c_{yy} \neq 0$, $c_{xy} \neq 0$; for E: $c_{ii} = c_{xy} = 0$, $c_{xx} = c_{yz}$, v. Hence, for S_4, we have

A $c_{xx} = c_{yy}$, $c_{ik} = 0$

B $c_{xx} = -c_{yy}$, $c_{zi} = 0$

E $c_{ii} = c_{xy} = 0$, $c_{xz} = c_{yz}$.

The transformation laws of the three vibration types are obtained by considering, in Table VII, Part II, only the columns that correspond to the symmetry elements of S_4, which in this case is S_4. For more complicated systems, the symmetry elements must be obtained from the point groups in the columns at the lower left.

The symbols are chosen so that the characteristic symmetry elements stand out clearly. Symmetry with respect to a unique axis is indicated by A; for groups that do not have such an axis (V_1, V_h, and the cubic groups),[13] it refers to symmetry with respect to the three mutually-perpendicular twofold axes. Antisymmetry with respect to a unique axis (for V and V_h, antisymmetry with respect to two of the three twofold axes) is indicated by B, and E and F represent two- and threefold degeneracy, respectively. Symmetry and antisymmetry with regard to the remaining symmetry elements are designated as follows:

g, u refer to a center of symmetry, i

' " refer to σ (in case of several planes, the one perpendicular to the unique axis is chosen).

\+ - refer to $C_2^{(z)}$ (necessary in case of degenerate vibrations).

If there is another symmetry element present, another index is added. In particular, σ will distinguish between the remaining independent symmetry element.

The vibrations denoted by g(u) are forbidden in the infrared (Raman effect). A symmary of these rules is presented at the end of this chapter. So that the selection rules can be applied to molecules, it is necessary to investigate the distribution of the vibrations of a given molecule among the various symmetry types and the number of vibrations of each type. This number is determined by the eigensymmetry of the specific point groups.

Let us consider a molecule belonging to group C_s. There are points that assume a general position and those that lie in the plane (C_s). Since the number of vibrations is independent of the force field, the vibrations may be thought of in such a way that only equivalent points move and the others remain at rest. Equivalent points refer to nuclei that are transformed into each other by symmetry operations; molecules of C_s symmetry have general sets of nuclei, which consist of two points each, and sets of points that involve one nucleus each. If we consider a general set and assume the displacement of one nucleus, then the displacement of the equivalent nucleus follows. The vibrations are thereby established from the transformation laws of the different types of vibration. For the symmetric ones, the displacements are reflected, while for the antisymmetric ones, in addition, the sign must be changed (see Fig. 7). Since the first point has three degrees of freedom, each general set of nuclei contributes three vibrations of each type. The sets of points of C_s consist of one point each, lying in the plane. This point moves in the plane and perpendicular to it, for symmetric and antisymmetric vibrations, respectively. Hence, it has two degrees of freedom in the plane and one degree of freedom perpendicular to the plane, and each set contributes two vibrations to the symmetric type and one vibration to the antisymmetric type. The total number of vibrations obtained in this manner does include the translations and rotations which have to be subtracted eventually.

The following generalization applies to groups that do not contain degenerate vibrations (triclinic, monoclinic, and rhombic systems).

In a system of symmetry G, the number of vibrations of each set of points of symmetry g which contributes to each type G_j is equal to the number of independent linear combinations of the space coordinates (x, y, z). These transform, with respect to the operations of g, in the same manner as do the normal coordinates of G_j. In the preceding tables, the transformation laws for the space coordinates are always given below those for vibrations.

Example: Ethylene, C_2H_4, (Fig. 9) has the symmetry V_h (Table VI). The H atoms lie in the plane of symmetry (xz plane) and have the symmetry $C_s(\sigma_y)$; the C atoms also lie on the twofold axis, and their symmetry is $C_{2v}^{(z)}$. Let the z axis be the figure axis, and let the xz plane be the plane of the molecule; then for C_s the symmetry element is σ_y, and for C_{2v}, we have $C_2^{(z)}$ and σ_y.[14] The σ_y column of Table VI shows a plus sign for x and z, and a minus sign for y. Therefore, the H atoms contribute two vibrations to the +, and one vibration to the - types. For the C atoms, the two columns $C_2^{(z)}$ and σ_y have to be considered.

Since the contributions of the translations and rotations are included in the tables (in the first column of Part II), they must eventually be subtracted, and the following results are obtained:

V_h	C_{1h}	$C_{2v}^{(z)}$	T and R	Result
A_g	2	1		3
A_u	1	0		1
B_{1g}	1	0	1	0
B_{1u}	2	1	1	2
B_{2g}	2	1	1	2
B_{2u}	1	1	1	1
B_{3g}	1	1	1	1
B_{3u}	2	1	1	2

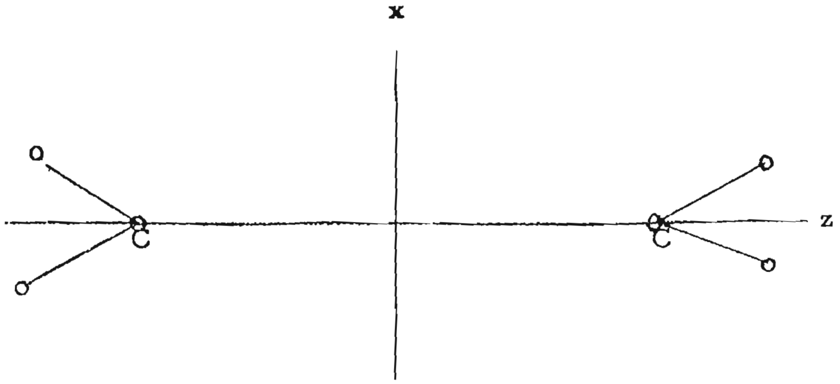


Fig. 9

Two kinds of degenerate vibrations must be distinguished before the above rule can be extended to groups containing degenerate vibrations.[15] For one kind, it is possible to select the normal coordinates in such a manner that they do not transform into each other under the symmetry operations, while for the other kind this is no longer possible.[16] The vibrations of C_p and C_{ph} belong to the former, and those of C_{pv} and D_p to the latter kind. The first are called "separable degenerate," and the latter "inseparable degenerate." This distinction arises from the fact--not proven here--that for the separable-degenerate vibrations the dynamics of a general set of nuclei is determined uniquely by the displacements of f points (f degree of degeneracy) and the type of vibration, whereas for the inseparable-degenerate vibrations f possibilities remain. Hence, the following addendum applies:

If the type G_j is separable degenerate, the above number must be divided by the degeneracy. If the eigensymmetry g contains inseparable-degenerate types of vibration, the space coordinates that transform like the degenerate normal coordinates of this vibration type should be counted as one.

For instance, each general set of nuclei contributes to a separable-degenerate type of vibration 3 and to an inseparable-degenerate type 3f vibrations. The separable-degenerate types of vibration (these are the twofold-degenerate types of the groups C_p, C_{ph}, S_p, T, and T_h) are underlined in the above tables.

Examples:

1. NH_3 having pyramidal symmetry, C_{3v}. The types of vibration as listed in Tables VIII or VIIIa are:

C_{3v}	C_3	σ_v	R and T
A_1	+	+	T_z
A_2	+	-	R_z
E	$e^{\pm 1}$	*	$T_\perp$, $R_\perp$
z	+	+	
x + iy	e^{-1}	*	
x - iy	e^{+1}	*	

Symmetry for H: $C_s(\sigma_v)$; for N: C_{3v}. If we consider the N atom (G = g) and remember that the sign of * is arbitrary, there will be $1A_1$, $0A_2$, and 1E vibrations (since E is inseparable degenerate, x + iy and x - iy count as one coordinate).

For the H atom, the σ_v column must be examined. Since the symbol * can be represented as linear combination of + and -, there will be $2A_1$, $1A_2$, and 3 E vibrations. Upon subtracting the rotational and translational modes, we obtain:

	C_{3v}	σ_i	T and R	Result
A_1	1	2	1	2
A_2	0	1	1	0
E	1	3	2	2

2. Planar benzene (Fig. 10), assuming D_{6h} symmetry. The eigensymmetry for the C and H atoms is C_{2v}. (The extent to which this symmetry corresponds to the actual molecule is not discussed here.)

The columns $C_2^{(y)}$ and $\sigma_v^{(y)}$ of Table VII are employed here, so that the transformation law of the coordinates becomes:

	$C_2^{(y)}$	$\sigma_v^{(y)}$
y	+	+
x	-	+
z	-	-

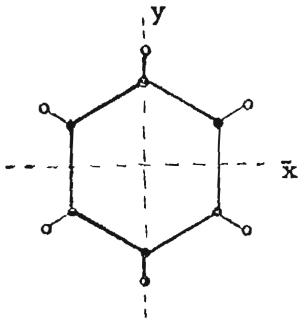


Fig. 10

The results may now be summarized as follows:

D_{6h}	C_{3v}	T and R	Result
A_{1g}	1		2
A_{1u}	0		0
A_{2g}	1	1	1
A_{2u}	1	1	1
B_{1g}	0		0
B_{1u}	1		2
B_{2g}	1		2
B_{2u}	1		2
E^+_g	2		4
E^+_u	1		2
E^-_g	1	1	1
E^-_u	2	1	3

3. Octahedral molecule XY_6. ($SbCl_6$ presumably belongs to this symmetry group.[17] Symmetry 0_h. Symmetry for X: 0_h; for Y: C_{4v}:

a) 0_h: According to Table VIII, the transformations of the coordinates accord with those of the normal coordinates for F_{1u} only. The point 0_h contributes one vibration to this type. Since F_{1u} is inseparable degenerate, the three coordinates are counted as one.

b) C_{4v}: The symmetry elements are C_4 and σ_y. The transformations for σ_y are not given explicitly; they may be derived from $C_2^{(y)}$ and i by the relation $\sigma_y = i \cdot C_2^{(y)}$. The following results are then obtained:

O_h	C_4	σ_y	C_{4v}	O_h	T and R	Results
A_{1g}	+	+	1			1
A_{1u}	+	-	0			0
A_{2g}	-	+	0			0
A_{2u}	-	-	0			0
E_g	*	+	1			1
E_u	*	-	0			0
F_{1g}	+ -i i	- * *	1		1	0
F_{1u}	+ -i i	+ * *	2	1	1	2
F_{2g}	- i -i	- * *	1			1
F_{2u}	- i -i	+ * *	1			1
z	+	+				
x + iy	-i	*				
x - iy	+i	*				

Because the E vibration of C_{4v} is inseparable degenerate and the coordinates x + iy and x - iy transform like the normal coordinates, x ± iy are counted as one. By adding the vibration F_{1u} due to X, and subtracting the rotations and translations belonging to F_{1g} and F_{1u}, we obtain

$$\Gamma = 1A_{1g} + 1\,E_g + 2F_{1u} + 1F_{2g} + 1F_{2u}.$$

A simpler method may be employed for examples 1 and 3 when the vibrations contributed by the totally symmetric point group are subtracted as translations. They may be omitted initially, so that only the rotational degrees of freedom need to be subtracted at the end.

No distinction is made in the tables between the rigorous and the approximate selection rules as this is not of practical importance. It is sufficient to know that the rules apply strictly when at least one of the states for a given transition is nondegenerate, for example, when one of the two states is the ground state. The rules are always valid for the point groups that do not possess any degenerate vibrations (triclinic, monoclinic, and rhombic systems).

In addition, the selection rules for the over- and combination tones may be deduced from the given tables. The characters of the particular species are multiplied and the row having the characters of the resulting products gives the new symmetry species. A different procedure applicable to degenerate species has been outlined by Placzek and Tisza. The selection rules for the Raman effect and the infrared spectrum are correlated in the above tables. For systems containing a center of symmetry, the mutual exclusion rule applies. This rule was derived in Chapter 5 and holds also for the group 0. In the remaining groups, transitions occur that are permitted in the Raman effect as well as in the infrared spectrum but complete agreement between the selection rules exists for the C_{3v} group only.[18]

The preceding tables have to be supplemented by the non-crystallographic point groups, by the axial groups for arbitrary values of p, and by the icosahedral group, because these can be realized for molecules also. The most important results are presented here, but details may be found in the papers by Placzek and Tisza.

The transformation law for the vibration types of C_p was stated at the beginning of this chapter: upon rotation by $2\pi/p$, the normal coordinates are multiplied by $\exp(-2\pi i\ell/p)$, where the degenerate normal coordinates are combined linearly to give $q = \xi + i\eta$. The symmetry type is determined by the integer ℓ; for $\ell = 0, p/2$, the vibrations are nondegenerate (symmetric and antisymmetric). The degenerate vibrations may be described by a linear combination of one-dimensional oscillators (in the normal coordinate space): these are assigned a main quantum number v_j and an azimuthal quantum number s_j. The energy depends on v_j only, and $s_j = v_j \ldots - v_j$ giving even (odd) values for even (odd) values of v_j. If an azimuthal quantum number is formally introduced for the nondegenerate vibrations by putting $s_j = v_j$, then the selection rule is given by:

$$\lambda + \mu = zp - \sum_j \ell_j (s_j' - s_j), \qquad \ell + zp \leftrightarrow \ell^{*} \tag{18.11}$$

where z is an arbitrary number. For even (odd) transitions in v_j, $s_j' - s_j$ is even (odd).

The selection rule for the fundamental ($\Delta v_j = \delta_r^{\,j}$) of the r vibration, where the initial state is identical with the vibrational ground state, is $s_j = 0$, $s_j' = 0$; for $j \neq r$, $s_j' = \pm 1$. Since ℓ is defined only module p^{*}, we have

$$\lambda + \mu = \pm \ell. \tag{18.12}$$

The fundamentals occur only for the vibrations with $\ell = 0, 1, 2$, because $\lambda + \mu \leq 2$.[19] If the initial state is different from the ground state, then Eq. (18.12) is approximately correct.[20]

The general rules may be derived for the more complicated axial groups C_{ph}, C_{pv}, D_p, D_{ph}. For S_p, Eq. (18.12) is replaced by

$$\lambda + \mu = \frac{\pm \ell}{1 + p/2}.$$

Linear molecules are of particular importance. They belong to the group $D_{\infty v}$ and $C_{\infty v}$, depending on the presence of a center of symmetry. For these groups there is an infinite number of types of vibrations. Since linear molecules possess at least $C_{\infty v}$ symmetry, the possible types of vibration reduce to those given in Table X. For types A and B, the nuclei vibrate parallel and perpendicular to the axis, respectively.

Finally, the results that are most commonly used and that have been dealt with in this discussion are summarized in Table X.

Table X

The Types of Vibration for Linear Molecules.

$D_{\infty h}$	$C_{\infty v}$	C_{∞}	σ_v	i	Raman Effect	Infrared
A_g	A	+	+	+	$c_{xx} = c_{yy}$, $c_{ik} = 0$	v
A_u	A	+	+	-	v	$M_{\perp} = 0$
E_g	E	$e^{\mp i\phi}$	*	+	$c_{xz} = c_{yz} = 0$	v
E_u	E	$e^{\mp i\phi}$	*	-	v	$M_z = 0$
	z	+	+	-		
	x + iy	$e^{-i\phi}$	*	-		
	x + iy	$e^{i\phi}$	*	-		

1. Polarization Rule:

a) Raman lines associated with non-totally symmetric fundamentals have a depolarization factor $\rho = 3/4$, $\rho = 6/7$, and $P = 6$.

b) The depolarization factor of Raman lines due to totally symmetric vibrations is zero for molecules of cubic symmetry. For noncubic molecules, ρ is not determined by symmetry and may vary between zero and 3/4. Therefore, in the first case $\rho = \rho_n = P = 0$, and in the latter case $0 \leq \rho_n \leq 6/7$; $0 \leq P \leq 6$.

c) The depolarization factor of the Rayleigh scattering is zero for molecules having cubic symmetry. For the other molecules it is independent of the symmetry of the system.

$$0 \leq \rho \leq 1/3, \qquad 0 \leq \rho_n \leq 1/2, \qquad 0 \leq P \leq 1.$$

2. Selection Rules:

In the Raman effect the following fundamentals are forbidden:

a) In general: vibrations that are antisymmetric with respect to a center of symmetry.

b) Tetragonal system: vibrations not totally symmetric with respect to the fourfold axis.

c) Hexagonal system: nondegenerate vibrations, except for the totally symmetric ones.

d) Cubic system: nondegenerate vibrations, with the exception of the totally symmetric ones; the threefold-degenerate vibrations, except for one type.

The remaining vibrations are permitted.[22]

3. Intensity Rules:

a) Over- and combination tones are rather weak in the Raman effect.

b) The most intense lines usually correspond to the fundamental modes of vibration.

4. The Number of Normal Modes of Vibration:

For a given molecule the number of vibrations of each species is given by the symmetry of the individual points and is derived by the rules outlined in this chapter.

REFERENCES AND FOOTNOTES

1. Brester, Krystallsymmetry and Reststrahlen (Diss. Utrecht (1923); Placzek, Leipzig Lectures (1931)), p. 71 Group-theoretical treatment: Wigner, Göttinger Nachrichten 1930, p. 133.
2. one of which is the identity.
3. Placzek, Leipzig Lectures (1931), p. 71; Cabannes, Ann. phys. 18, 285 (1932); Group-theoretical treatment: Tisza, Z. Physik 32, 285 (1932); Placzek, Z. Physik (to appear toward the end of 1933).
4. See Reference 11, Chapter 5 concerning the degenerate states.
5. Tensor components transform as the products of the coordinates, which appear as their indices.
6. For groups containing several elements of symmetry (except an axis with $p > 2$) the above rule applies to each symmetry element separately. The symmetry type of the eigenfunction is determined by the transformation properties under the operations of the group.
7. If additional elements, aside from the center of symmetry, exist, the exclusion is vlid; the number of permitted transitions can be further restricted.
8. The following procedure for deriving the selection rules is more complicated, but permits a simple correlation with the classical case (the limiting case of high vibrational quantum numbers):

We start with a molecule in equilibrium position (Fig. 8, I); the polarizability is invariant with respect to the operations S of the symmetry group of the molecule:

$$S(\alpha_{\lambda\mu})_0 = (\alpha_{\lambda\mu})_0. \tag{18.3}$$

Equations (18.3) require that some components $(\alpha_{\lambda\mu})_0$ vanish. For instance, the polarizability ellipsoid will become a rotation ellipsoid about the axis, provided an axis of higher than twofold symmetry exists.

For arbitrary displacements of the nuclei (Fig. 8, II), the symmetry is destroyed. The position of the nuclei and the polarizability are altered by a symmetry operation (Fig. 8, III). The results obtained are the same, whether the symmetry operations are applied to the displacements (to the polarizability of the distorted configuration) or to the polarizability of II directly. In both instances, configuration III is generated.

If the displacements of the molecule are denoted by the normal coordinates $q_1, q_2 \ldots q_n$,

$$S_{\phi}\alpha_{\lambda\mu}(q_1, q_2 \ldots q_n) = \alpha_{\lambda\mu}(S \cdot q_1, S \cdot q_2 \ldots S \cdot q_n) \qquad (18.4)$$

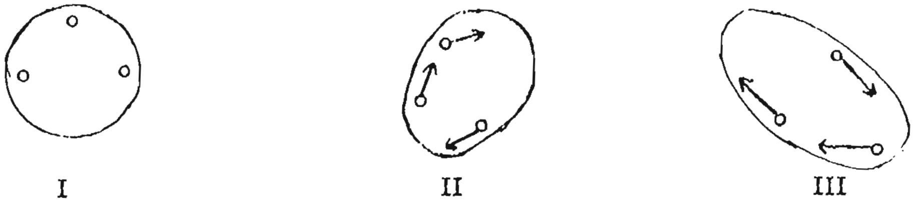

I II III

Fig. 8. Symmetry properties of displacements, and polarizability of a distorted molecule.

Equation (18.4) causes a series of tensor components to vanish when, classically, the Fourier component or, quantum mechanically, the matrix element of $\alpha_{\lambda\mu}$ is formed. This results in the above selection rules. For example, let us take the reflection plane. Denoting q_s and q_a as the symmetric and antisymmetric normal coordinates, respectively, we see that Eq. (18.4) becomes

$$\alpha_{\lambda\mu}(q_s, q_a) = \alpha_{\lambda\mu}(q_s, -q_a) \text{ for } \lambda + \mu = 0, \pm 2 \qquad (18.4a)$$

$$\alpha_{\lambda\mu}(q_s, q_a) = -\alpha_{\lambda\mu}(q_s, -q_a) \text{ for } \lambda + \mu = \pm 1. \qquad (18.4b)$$

Each normal coordinate is classically a simple periodic function of the time, with a period equal to the vibration frequency. In the Fourier expansion of (18.4), the term corresponding to this period (fundamental) vanishes for the antisymmetric vibrations. The relation $\lambda + \mu = 0, \pm 2$ applies to the former, and $\lambda + \mu = + 1$ to the latter; this is in accord with the above result and has the following significance: For the symmetric vibrations, the polarizability remains symmetric with respect to the plane, leaving two principal axes of the polarizability ellipsoid in the plane. For the antisymmetric vibrations, the ellipsoid vibrates out of the plane. The identical result is obtained when the matrix element of (18.4a) is formed and when the above-discussed properties of the Hermitian polynomials are taken into account.

9. This may be illustrated in the following manner: Let us consider a molecule of a given symmetry and assign arbitrary displacements to the nuclei, thereby destroying the original symmetry. When the operations of the molecular symmetry are applied consecutively to the distorted molecule, and the displacements are added, the resultant should have the original symmetry. The displacements can therefore be represented by the totally symmetric normal coordinates only. If the original displacement is chosen so that it corresponds to a non-totally symmetric vibration, containing no totally symmetric component, the displacements will be zero under the proper symmetry operations:

$$\sum_n c_{jr}^{(n)} = 0.$$

10. We may proceed for instance, by writing out relation (18.4) for all the operations of the tetrahedron with the derivation of the polarizability expression.

11. The intensity of the quadrupole (anisotropic) term of the undisplaced scattered radiation is a maximum (for a high population of the excited degenerate states) and is of the same order of magnitude as the intensity of the first overtones of the degenerate vibrations.

12. This arises from the fact that the two degenerate normal coordinates described by ξ and η were not identified. Therefore, it is equally possible to employ the coordinate $q' = iq$, instead of $q = \xi + i\eta$. If Sq is equal to q^*, we have

$$Sq' = iSq = iq^* = -(q')^*.$$

13. in addition, C_S; symbol A is used as basis for the indices ' and ".

14. In more complicated cases, the required symmetry elements should be indicated at the lower left corner of the tables.

15. G. Placzek, Z. Physik (to appear in 1933).

16. Expressed differently: In the first case, the linear transformations corresponding to the symmetry operations can be made to coincide with the principal axes, but this cannot be done in the latter case. From the group-theoretical point of view, only the latter case is an "essential" degeneracy.

17. O. Redlich, Naturwiss. 20, 365 (1932).

18. For groups for which transitions are permitted, in the infrared spectrum and in the Raman effect: C_{1h}, C_2, and C_3.

19. As was shown initially, the sign of ℓ is not significant here.

20. It applies strictly if at least one of the two states is degenerate.

21. The term exp ($\mp i\phi$) implies that, upon rotation about any angle ϕ, the expression $\xi + i\eta$ is to be multiplied by exp-($i\phi$), and $\xi - i\eta$ by exp ($i\phi$).

22. This summary applies to the crystallographic point groups only. As was shown above, there are further exclusions for non-crystallographic groups.

Chapter 19. Simple Vibrational Spectra

Some representative vibrational spectra are discussed, by using experimental data of liquid samples. The theory of free molecules applies to these cases in first approximation only; some modifications are presented in Chapter 20.

1. The XY_3 Molecule.

Two symmetry groups will be considered: the pyramidal C_{3v} and the plane D_{3h} symmetries. The C_{3v} group has two totally symmetric eigenfrequencies, A_1 and two degenerate ones, E. Both are permitted in the infrared and Raman. The D_{3h} has one totally symmetric A' vibration (X does not move while the Y_3 triangle expands symmetrically) which is infrared inactive, one A" vibration antisymmetric with respect to the plane of the molecule (X moves along the axis, and the three Y particles move in the opposite direction perpendicular to the plane and symmetric with respect to the trigonal axis), which is Raman inactive, and two E' vibrations, degenerate with respect to the plane, which are Raman and infrared active.[1] Consequently, a C_{3v} molecule should have four Raman lines, and a D_{3h} should have three strong lines of which two are expected to be completely depolarized, with $\rho = 6/7$ in both cases.

The data of a series of trihalides possessing four Raman lines are summarized in Table XI.[2] The depolarization factors have been observed by Cabannes and Rousset.[3]

Table XI

Depolarization Factor of the Raman Lines of Some Trihalides.

PBr_3		PCl_3		$AsCl_3$	
ν, cm^{-1}	ρ_n	ν, cm^{-1}	ρ_n	ν, cm^{-1}	ρ_n
116	0.86[4]	190	0.86	158	0.86
162	0.185	258	0.28	194	0.42
380	0.28	484	0.86	370	0.86
400	0.86	511	0.16	405	0.08

Assignments on the basis of analogies must be made with great care (a rearrangement of frequencies is observed for PCl_3 and PBr_3). For instance, in the case of PCl_3 the highest frequency is totally symmetric, while for PBr_3 it is degenerate.

The ions NO_3^- and $CO_3^=$ are planar, as was deduced from experiments. Solutions of nitrate salts show three Raman lines, a strong one at 1049 cm^{-1} and two weak ones at 720 and 1360 cm^{-1}.[5] The depolarization factor of the first two lines was determined;[6] the 1049-cm^{-1} line was found to be polarized and the 720-cm^{-1} line depolarized. Therefore, the 1049-cm^{-1} line is ascribed to the totally symmetric vibrations, and the other two lines to the degenerate vibrations. A strong band, observed near 830 cm^{-1} in the infrared but not in the Raman spectrum, may be due to the antisymmetric vibration forbidden in the Raman effect. The $CO_3^=$ ion exhibits similar spectra, but in solution only one strong line at 1065 cm^{-1} has been noted. Because the depolarization factor was found to be 0.2,[7] it may be attributed to the totally symmetric vibration.[8]

These conclusions are reached on the basis of Raman spectra of the carbonate and nitrate crystals which show, aside from permitted ground-state frequencies, the first overtone of a vibration whose fundamental is forbidden. These results accord with investigations by Schaefer, who reported extensive infrared data on crystals prior to the discovery of the Raman effect.

2. The Molecule XY_3Z (X and Z along the symmetry axis) Having C_{3v} Symmetry.

According to Table VIIIa, three totally symmetric A vibrations and three degenerate E vibrations are permitted in the Raman effect and infrared spectrum. Many carbon compounds belong to this group (CH_3 - X, CCl_3 - X, etc.) as well as $POCl_3$ as may be concluded from its Raman spectrum.[9]

Table XII

Depolarization Factor of the Raman Lines of $CHCl_3$.

ν, cm^{-1}	259	364	664	756	1214	3016
ρ_n	0.87	0.19	0.07	0.86	0.87	0.20

The spectrum of $CHCl_3$ can be cited as an example.[10] Six lines are observed.[11] The depolarization factors in Table XII show that the lines at 364, 664, and 3016 cm^{-1} may be ascribed to the totally symmetric vibrations, and those at 259, 756, and 1214 cm^{-1} to the degenerate ones. The data obtained by means of circularly polarized incident light are in good agreement.[12] The first three lines are polarized in the same sense, and the last three in the opposite sense.

3. The Molecule XY_4.

Three configurations must be considered: the tetrahedral, pyramidal, and planar.[13] We have the following classification of the eigenvibrations:

a) Tetrahedral Model, T_d

Type	Z	Raman, ρ_n	Infrared
A_1	1	0	v
E	1	6/7	v
F_2	2	6/7	
	5	4	2

b) Pyramidal Model, C_{4v}

Type	Z	Raman, ρ_n	Infrared
A_1	2		$M_\perp = 0$
B_1	2	6/7	v
B_2	1	6/7	v
E	2	6/7	$M_z = 0$
	7	7	3

c) Planar Model, D_{4h}

Type	Z	Raman, ρ_n	Infrared
A_{1g}	1		v
A_{2u}	1	v	$M_{\perp} = 0$
B_{1g}	1	6/7	
B_{2g}	1	6/7	
B_{2u}	1	v	
E_u	2	v	$M_z = 0$
	7	3	3

The T_d model has four Raman lines, of which one will have $\rho_n = 0$ and three will have $\rho_n = 6/7$. The C_{4v} molecule shows seven lines, of which five will have $\rho_n = 6/7$, and the D_{4h} model has three Raman lines, two of which have $\rho_n = 6/7$. For T_d the totally symmetric type is permitted in the infrared spectrum, but for C_{4v} it is forbidden, and for D_{4h} the mutual exclusion rule applies.

The majority of molecules investigated possess tetrahedral symmetry.[14] The spectra of the tetrachlorides XCl_4 (X = C, Si, Ti, Sn) consist of four lines,[15] of which three have $\rho = 6/7$, while the strongest line (totally symmetric) has a value of ρ_n close to 0.05.[16] Cabannes and Rousset attributed the deviation from zero to an isotope effect. From known chlorine isotope distributions ($Cl_{35} : Cl_{37} = 3.185 : 1$),[17] it is assumed that 66.2% of the molecules XCl_4 contain different isotopes:

XCl_4^{35}	33.5%
$XCl_3^{35}Cl^{37}$	42.2%
$XCl_2^{35}Cl_2^{37}$	19.8%
$XCl^{35}Cl_3^{37}$	4.2%
XCl_4^{37}	0.3%

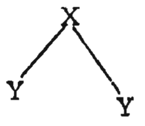
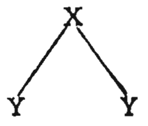
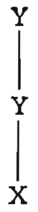
The symmetry of the mixed chloride is no longer tetrahedral, a fact that explains the depolarized totally symmetric Raman line.[18] In addition, Langseth showed a splitting of the line (see also Chapter 22 and Reference 10 of Chapter 23). To ascertain whether the total depolarization of 5% entails an isotope effect, one should investigate the tetraiodo compound, which cannot show any isotope effect.

4. The Molecule XY_2.

If the Y atoms are equivalent, two models are possible: the equilateral triangle, C_{2v}, and the linear structure, $D_{\infty h}$. For nonequivalent Y atoms, a C_S (scalene) or a $C_{\infty v}$ (linear Y-Y-X) structure is possible. The types of vibrations are described in Table XIII.

Table XIII

Normal Vibrations of the Molecules XY_2.

C_s		C_{2v}		$C_{\infty v}$		$D_{\infty h}$	
 X Y Y		 X Y Y		 Y Y X		 Y X Y	
A	3	A_1	2	A_1	2	A_{1g}	1
		B_1	1	E	1	A_{1u}	1
						E_u	1

For all the molecules, with the exception of the $D_{\infty h}$, the vibrations are Raman and infrared active. The C_{2v} and $C_{\infty v}$ molecules have one frequency with a depolarization factor of 6/7. Both exhibit the same vibrational spectrum; however, the rotational structures of their infrared bands and Raman lines are distinct. The $D_{\infty h}$ molecule has two vibrations which are antisymmetric with respect to the center of symmetry and consequently Raman inactive.

a) SO_2. The Raman spectrum of this molecule has three lines: 1340, 1146, and 526 cm^{-1}. The depolarization measurements by Cabannes and Rousset indicate that the depolarization factor of the 1340-cm^{-1} line has a value of 6/7.[19] This observation would lead to an equilateral triangular model. This structure confirms the one reported by Mecke[21] and by Placzek, but differs from earlier ones.[22] The asymmetric linear model has already been excluded on the basis of its chemical behavior.

b) N_2O. Plyler and Barker demonstrated, on the basis of the rotational structure of the infrared bands, that this molecule has a $C_{\infty v}$ symmetry, N-N-O.[23] The linear structure was deduced from the rotational levels and the asymmetry was deduced from the absence of alternating intensities. Plyler and Barker observed the fundamental frequencies at 2224.1, 1285.4, and 589.1 cm^{-1}, the latter corresponding to our E-type vibration.

In the Raman spectrum the fundamentals occur at 2223.2 and 1286.5 cm^{-1}.[24] After exposing the sample for 14 days, weak lines associated with overtones were observed which accord with Plyler and Barker's observations rather than with the permitted fundamental of the degenerate mode.[25,26]

The N_2O molecule illustrates very well that symmetry considerations cannot be applied rigorously to the determinations of molecular structure. It is important to note that some molecular configuration can give rise to an approximate symmetry which can decide the structure of the spectrum. The only Raman line observed for N_2O by Dickinson-Dillon-Rassetti[27] was believed to be a confirmation of the symmetric model N-O-N by Placzek.[28] This had also been deduced by Snow from infrared studies, absence of any dipole moment, and the approximate magnitude of the frequencies.[29] Because N and O possess very similar masses and electron configurations, even the asymmetric configuration is expected to have a small dipole moment. The normal modes of vibration and the derivatives of the polarizability components will be symmetric and antisymmetric with respect to a (fictitious) center of symmetry, thereby reducing the intensity of two out of three fundamental frequencies. Additional infrared and Raman studies proved that the asymmetric structure is the correct one. It has not yet been established whether the absence of the degenerate vibration is caused solely by the pseudosymmetry, or whether there are other contributing factors.[30]

c) CO_2, CS_2. These molecules are linearly symmetric. However, their Raman spectra indicate complicating features which will be elaborated on in the next chapter.

5. The Linear Molecule X_2Y_2

The $D_{\infty h}$ symmetry group gives rise to two A_g vibrations, one A_u, one E_g, and one E_u. The mutual exclusion rule applies because of the existence of a center of symmetry.

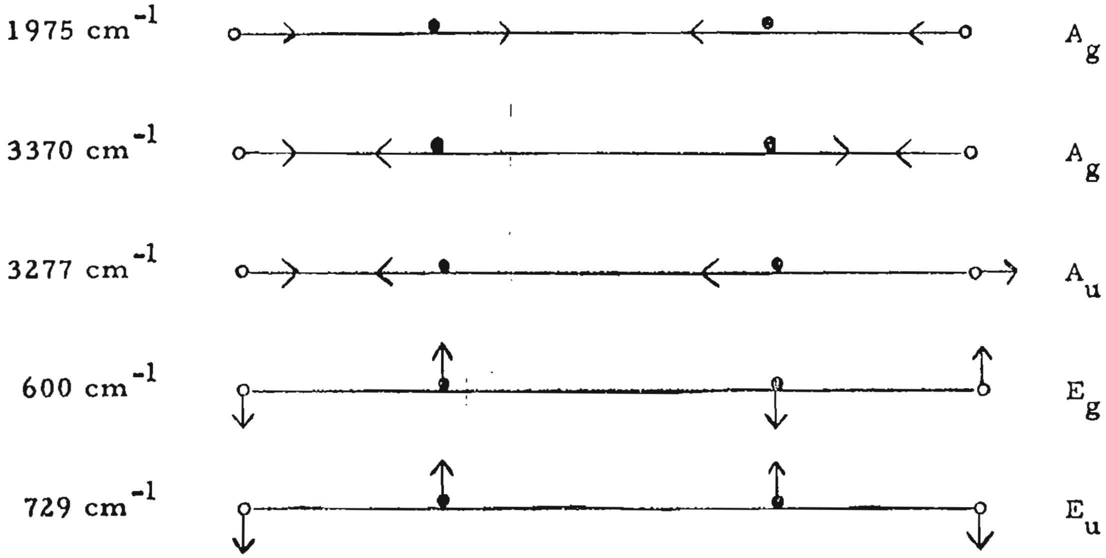


Fig. 11. The normal modes of vibration of acetylene, C_2H_2.

The acetylene molecule belongs to this group. Figure 11 represents the fundamental frequencies and assignments, as given by Mecke from infrared and Raman spectra.[31] The totally symmetric frequencies 1974 and 3372 cm^{-1} appear in the Raman spectrum, while the E_g frequency near 600 cm^{-1} was not detected.[32] These observations lead to the conclusion that the polarizability of C_2H_2 is not greatly influenced by the transverse displacements involved in the stretching vibrations (see Chapter 24).

6. Cis-Trans Isomers.

At times, qualitative observations may lead to structure determinations; the cis-trans isomers $C_2X_2Y_2$ may be cited as such an example (see Fig. 12).

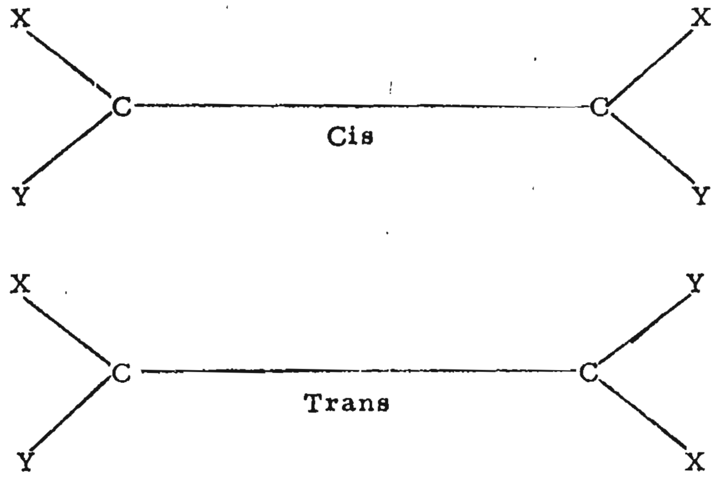


Fig. 12. Cis-trans isomers of the molecule $C_2X_2Y_2$.

The lower frequencies are particularly sensitive to the geometric configuration of the molecules. Distinguishing between the two isomers on the basis of their spectra, however, is rather intricate, even when all the frequencies are known, as the latter depend greatly on the characteristic force field. An analysis of the molecular symmetry yields the following information: the isomer has the C_{2h} symmetry, thereby permitting all frequencies to appear in the Raman spectrum. The trans isomer has the C_{2v} symmetry, with a center of symmetry. One-half of the vibrations are antisymmetric, making the fundamental frequencies inactive in the Raman effect. Hence, the cis isomer will show a richer spectrum than the trans isomer. Kohlrausch and his co-workers arrived at these conclusions independent of theory, on the basis of extensive experiments.[33] They adjudged this method of identification as powerful as the measurements of dipole moments. Chemical means do not always permit unequivocal differentiation between two isomers.

The complete assignments of the spectra of simple cis-trans isomers (CH_2Cl_2, CH_2Br_2) have not yet been achieved. A knowledge of the depolarization measurements would materially aid in these assignments.

REFERENCES AND FOOTNOTES

1. The relevant discussion by Placzek (Leipzig Lectures (1931) p. 71) contains errors which are corrected in the English edition.

2. Some weak lines for PCl_3, reported by Daure (Ann. phys. 12, 375 (1929)) have not been found by Nisi (Japan J. Phys. 6, 1 (1930)) and Trumpy, (Z. Physik 68, 675 (1931)). They may have been caused by $POCl_3$ impurities.

3. J. Cabannes and A. Rousset, Compt. rend. 194, 707 (1931).

4. Cabannes and Rousset report for the particular vibration: $\rho_n = 6/7 = 0.86$, making it difficult to estimate the accuracy of this value. However, it may be deduced from the investigation by Simons (Comm. phys-math. Soc. Scient. Fenn. 6, 13 (1932)). He gives values of ρ_n which are between 0.84 and 0.90 for a series of non-totally symmetric vibrations of several molecules.

5. Literature cited by Kohlrausch in Der Smekal - Raman Effekt.

6. P. Grassmann, Z. Physik 77, 616 (1932).

7. Cabannes, Rousset, loc. cit.

8. From the Raman spectrum of the carbonate crystal, the two degenerate frequencies are determined to be 714 and 1438 cm^{-1}. The frequency antisymmetric with respect to the plane is found, from the ultraviolet spectrum, to be 870 cm^{-1}. It can be seen that the force field of the two ions $CO_3^=$ and NO_3^- is very similar.

9. Cabannes and Rousset, Compt. rend. 194, 707 (1932).

10. L. Simons, Comm. phys.-math.-Soc. Scient. Fenn. 6, 13 (1932).

11. Dabadghao (Indian J. Phys. 5, 207 (1930)) reports two additional weak lines in the spectrum of chloroform and in that of bromoform, at 1445 and 3072 cm^{-1}; but they are disputed by Kohlrausch (Der Smekal - Raman Effekt).

12. W. Hanle, Ann. Phys. 11, 885 (1931).

13. Additional less likely models, such as a linear structure or a configuration of symmetry V_d, will not be discussed here. The symmetry V_d arises from a square by having its edges displaced out of the plane in opposite directions. The reader interested in these structures can perform the analysis on basis of the given tables.

14. Such a conclusion cannot be reached by merely counting the number of lines. Occasionally, lines corresponding to permitted fundamentals may be too weak to be discerned, or overtones may appear in the spectrum. Therefore, polarization measurements are necessary, and, if possible, a comparison with the infrared spectrum and an investigation of the rotational structure should be carried out.

15. See Chapter 20 concerning the molecule CCl_4.

16. Cabannes and Rousset, Compt. rend. 194, 79 (1932).

17. A. Elliot, Nature 126, 133 (1930).

18. As the potential energy is unaffected by the isotope effect, it retains the original tetrahedral symmetry. The anisotropy arises from the kinetic energy. As a result of the different masses, dissimilar isotopes have different amplitudes for the totally symmetric vibrations.

19. S. Bhagavantam, Indian J. Phys. 5, 35 (1930); R. G. Dickinson and S. S. West, Phys. Rev. 35, 1126 (1929).

20. Cabannes and Rousset, loc. cit.

21. R. Mecke, Z. Physik 64, 173 (1930).

22. G. Placzek, Leipzig Lectures (1931), p. 71.

23. Watson and Parker, Phys. Rev. 37, 1484 (1931); Bayley - Cassie - Angus, Proc. Roy. Soc. (London) 180, 192 (1930).

24. Plyler and Barker, Phys. Rev. 38, 1827 (1931); Barker, Phys. Rev. 41, 368 (1932).

25. A. Langseth and J. Rud Nielsen, Nature 130, 92 (1932).

26. See Fig. 15.

27. Dickinson-Dillon-Rasetti, Phys. Rev. 34, 582 (1929).

28. G. Placzek, Leipzig Lectures (1931), p. 71.

29. C. P. Snow, Proc. Roy. Soc. (London) 128, 294 (1930).

30. In the case of C_2H_2, a degenerate vibration is removed. See below.

31. R. Mecke, Z. Physik. Chem. 17, 1 (1932).

32. E. Segré, Linc. Rend. 12, 226 (1930); Daure and Kastler, Compt. rend. 192, 1721 (1931); S. Bhagavantam, Indian J. Phys. 6, 319 (1932).

33. A. Dadieu, A. Pongratz, and K. W. F. Kohlrausch, Wiener Akademieberichte (IIa) 140, 353, 647 (1931).

Chapter 20. Vibrational Spectra of Perturbed Systems

Anharmonicity in molecular vibrations gives rise to a shift of the vibrational level as calculated for a harmonic force field, and a mixing of the eigenfunctions. These effects are computed with the aid of the perturbation theory. The modified terms and eigenfunctions may be derived from the matrix elements of the perturbation energy (this is given here by the higher terms in the potential energy expression) and from the frequencies of the unperturbed system.[1] The calculations can be simplified by making use of the fact that "only terms of the same symmetry type can perturb each other."

Proof: Energy shifts and mixing of eigenfunctions are both determined by the matrix elements of the perturbation energy which has the symmetry of the molecular system. The matrix elements of such a quantity are different from zero for terms of the same species, as was demonstrated in Chapter 5 in the derivation of the selection rules for the trace scattering.

The terms of each species can be treated separately since only these eigenfunctions mix. Additional limiting conditions arise in the first approximation of the perturbation energy. If the cubic terms in the potential-energy expression are considered, terms differing by not more than three vibrational quantum numbers (distributed over 1, 2, or 3 normal vibrations) will perturb each other. In the scattering spectrum, this perturbation causes a shift of the frequencies compared with those calculated by Eq. (16.2), and a change in the intensities. In order to perform the computations the matrix elements of the polarizability are formed with the aid of the perturbed eigenfunctions.

The perturbed eigenfunctions are linear combinations of the unperturbed oscillator eigenfunctions:

$$\left[\psi\right]_{v} = \sum_{v'} c_{vv'}\psi_{v'} \, . \tag{20.1}$$

The coefficients $c_{vv'}$ can be evaluated using perturbation theory and will become zero for all the states belonging to different symmetry types:

$$\left[\alpha\right]_{v'}^{v} = \sum_{v''} \sum_{v'''} c_{vv''}\, c_{v'v'''}^{*} (\alpha)_{v'''}^{v''} \, , \tag{20.2}$$

where $\left[\alpha\right]_{v'}^{v}$ and $(\alpha)_{v'}^{v}$ denote the perturbed and unperturbed matrix elements, respectively. If the diagonal terms c_{vv} are large compared with the off-diagonal ones, which is generally true, then Eq. (20.2) may be written:

$$[a]_{v'}{}^{v} = c_{vv}c_{v'v'}{}^{*}(a)_{v'}{}^{v} + c_{vv}\sideset{}{'}\sum_{\substack{v'' \\ v''\neq v'}} c_{v'v''}{}^{*}(a)_{v''}{}^{v} + c_{v'v'}{}^{*}\sideset{}{'}\sum_{\substack{v'' \\ v''\neq v}} c_{vv''}(a)_{v'}{}^{v''}. \tag{20.3}$$

According to (20.3), the intensity of a (permitted) overtone or combination tone v → v' changes when the perturbed eigenfunction $[\psi]_v$ contains the eigenfunction of a term that differs by 1 from the term v in the quantum number of a single normal vibration.[2] Then, a matrix element corresponding to a fundamental will occur in expression (20.3). It is usually larger than the matrix element associated with the overtone or the combination tone. The intensity can change markedly when the ground state eigenfunction is contained to a small extent, only in $\psi_{v'}$. For normal anharmonicity, its effect upon the intensities of the combinations and overtones is of the same order of magnitude as the effect of the nonlinearity of the polarizability which was considered in Chapter 16.

Term shifts and mixing of eigenfunctions attain importance whenever terms are accidentally so close that their spacing is of the order of magnitude of the coupling energy (matrix element of the perturbation energy), as in the case of adjacent vibrational frequencies. Fermi was the first to interpret the spectrum of CO_2 on this bases.[3] The same phenomenon occurs in other molecules also and has its classical counterpart in the coupling of a set of oscillators of comparable frequencies.

To calculate the perturbation effect, we choose the unperturbed system as the one having similar frequencies and to which the rules of the perturbation theory of degenerate systems are applied. Term shifts are given by the eigenvalues of the matrix $(H^{(1)})_{v'}{}^{v}$, where $H^{(1)}$ is the perturbation energy. The eigenfunctions are linear combinations whose coefficients are those of the linear equations with the determinant $(H^{(1)})_{v'}{}^{v}$. The case of two nondegenerate vibrational frequencies of a molecule for which the condition $\nu_v \approx 2\nu_2$ is fulfilled may serve as an example.

If we set $\nu_1 + 2\nu_2 = S$ and $\nu_1 - 2\nu_2 = \Delta$, the vibrational Hamiltonian for the harmonic oscillator becomes, upon neglecting other vibrations:

$$H' = 1/2\left[\dot{q}_1{}^2 + \dot{q}_2{}^2 + 4\pi^2(\nu_1{}^2 q_1{}^2 + \nu_2{}^2 q_2{}^2)\right]$$

$$H = 1/2\left[\dot{q}_1{}^2 + \dot{q}_2{}^2 + \pi^2 S^2(q_1{}^2 + q_2{}^2/4)\right] + \pi^2 S\Delta(q_1{}^2 - q_2{}^2/4) + \frac{\pi^2\Delta^2}{2}(q_1{}^2 + q_2{}^2/4). \tag{20.4}$$

The Δ part independent of H is taken as the unperturbed Hamiltonian. The eigenvalues are

$$W_n^{(0)} = (H^{(0)})_n^{\ n} = hS/4\ (n + 3/2),\quad n = 2V_1 + V_2. \tag{20.5}$$

Each level is $n(\frac{n+2}{2})$ and $n(\frac{n+1}{2})$-fold degenerate, for n even and odd, respectively. Provided only the cubic terms in the potential energy expression are retained, the perturbation energy is confined to the term $\beta_{12}q_1q_2^{\ 2}$. The remaining cubic terms do not contain matrix elements of coupled quasi-degenerate terms. In addition, the terms in (20.4) that contain the quantity Δ must be retained; the Δ^2 part may be omitted since $\Delta << S$. Hence,

$$H^{(1)} = \pi^2 S\Delta(q_1^{\ 2} - q_2^{\ 2}/4) + \beta_{12}q_1q_2^{\ 2}. \tag{20.6}$$

The perturbation may now be calculated with the aid of (20.6) for n = 2 (quasi-degeneracy of the term $V_1 = 0$, $V_2 = 2$ with $V_1 = 1$, $V_2 = 0$). The matrix elements of $H^{(1)}$ are derived from the well-known oscillator matrices. The matrix will have the following form:[4]

$$h \begin{vmatrix} \frac{\Delta}{2}(-1 + 1/4) & P\sqrt{2} \\ P\sqrt{2} & \frac{\Delta}{2}(1 + 1/4) \end{vmatrix}, \tag{20.7}$$

where $P = \beta_{12}/4\pi^3\sqrt{h/S^3}$, and the eigenvalues are given by

$$\frac{W_2^{(1)}}{h} = \Delta/8 \pm \sqrt{\Delta^2/4 + 2P^2}\ . \tag{20.8}$$

From (20.5) and (20.6), the total energy becomes

$$\frac{W_2}{h} = S/2 \pm \sqrt{\Delta^2/4 + 2P^2}\ ; \tag{20.9}$$

if we subtract the zero-point energy by letting the zero-point energy be the ground state, the eigenfunctions are, according to (20.4) and (20.5):

$$\left[\psi\right]_{01} = 1/\sqrt{2x}\left\{\sqrt{x + |\Delta|}\,\psi_{10} \pm \sqrt{x - |\Delta|}\,\psi_{02}\right\}$$

$$\left[\psi\right]_{02} = 1/\sqrt{2x}\left\{\sqrt{x - |\Delta|}\,\psi_{10} \mp \sqrt{x + |\Delta|}\,\psi_{02}\right\} \qquad (20.10)$$

$$x = \sqrt{\Delta^2 + 8P^2}.$$

The minus or plus signs apply when P and Δ have the same or different signs, respectively. The mixing of the eigenfunctions is a function of the relative values of the frequency difference $|\Delta| = \nu_1 - 2\nu_2$ and the term splitting x, where x depends on the ratio of Δ to the interaction energy $P\sqrt{2}$.

When $\Delta^2 << P^2$ (quasi-degeneracy), it follows from (20.9) that the energy is

$$\frac{W_2}{h} = S/2 \pm P\sqrt{2}\,(1 + \Delta^2/16P^2), \qquad (20.9a)$$

where both perturbed eigenfunctions contain almost equal parts of ψ_{01} and ψ_{02}. If $\Delta = 0$, this is correct, and the assignments of the quantum numbers V_1, V_2 to the perturbed eigenfunctions will be of more formal significance:

$$\left[\psi\right] = 1/\sqrt{2}\left[\psi_{10} \pm \psi_{02}\right]. \qquad (20.10a)$$

When $\Delta^2 \gg P^2$, the energy becomes

$$\frac{W_2}{h} = S/2 \pm \Delta/2\,(1 + 4P^2/\Delta^2) = \begin{cases} \nu_1 + 2P^2/\Delta \\ 2\nu_2 - 2P^2/\Delta \end{cases} \qquad (20.9b)$$

where the eigenfunctions are given by $(\psi)_{10}$ and $(\psi)_{02}$. The result is identical with the one obtained from the usual perturbation calculation without taking account of the commensurability.[5] It should be noted that perturbation effects of terms with different n values can attain the same order of magnitude.

We shall now investigate the perturbations on the Raman spectrum, particularly on the transition from the ground states $V_1 = 0$, $V_2 = 0$ to the two perturbed levels. The transition is permitted in the Raman effect whenever a mutual perturbation of the two levels exists. The perturbation term

$\beta_{12}q_1q_2^{\,2}$ does not vanish when q_1 is totally symmetric and totally symmetric vibrations are always permitted in the ground state. Likewise, $V_1 = 0$, $V_2 = 0 \rightarrow V_1 = 0$, $V_2 = 2$ is permitted, as both terms belong to the same symmetry class.[6]

From Eqs. (20.5), (20.10) and (16.4b), it follows that:

$$\left[\alpha\right]_{10}^{00} = 1/\sqrt{2x}\left\{\sqrt{x+|\Delta|}\,(\alpha)_{10}^{00} \pm \sqrt{x-|\Delta|}\,(\alpha)_{02}^{00}\right\}$$

$$\left[\alpha\right]_{02}^{00} = 1/\sqrt{2x}\left\{\sqrt{x-|\Delta|}\,(\alpha)_{10}^{00} \mp \sqrt{x+|\Delta|}\,(\alpha)_{02}^{00}\right\} \qquad (20.11)$$

$$\left[\alpha\right]_{10}^{00} = \left(\frac{\partial\alpha}{\partial q_1}\right)_0 b_1\,; \qquad \left[\alpha\right]_{02}^{00} = \left(\frac{\partial^2\alpha}{\partial q_2^{\,2}}\right)_0 b_2^{\,2}\sqrt{2}\,.$$

where b designates the zero-point amplitude (see (16.5)). The intensity ratio (denoting $(\alpha)_{10}^{00}$ and $(\alpha)_{02}^{00}$ by α_1 and α_2, respectively) is given by

$$\frac{\left|\left[\alpha\right]_{02}^{00}\right|^2}{\left|\left[\alpha\right]_{01}^{00}\right|^2} = \frac{\left|\left(\sqrt{x-|\Delta|}\,\alpha_1 \mp \sqrt{x+|\Delta|}\,\alpha_2\right)\right|^2}{\left|\left(\sqrt{x+|\Delta|}\,\alpha_1 \pm \sqrt{x-|\Delta|}\,\alpha_2\right)\right|^2}\,. \qquad (20.12)$$

Equation (20.12) represents the intensity ratio when α_1 and α_2 have the same relative anisotropy, a condition that must not generally be fulfilled. If α_1 and α_2 have distinct anisotropies, invariants must be formed in order to evaluate the intensity and polarization. For the sake of simplicity, the first assumption is initially maintained but discarded later. We shall consider the magnitude of (20.12) for different values of $|\Delta|$.

For $\Delta^2 \gg P^2$ $(x \approx |\Delta|)$, Eq. (20.12) transforms into $|\alpha_2|^2/|\alpha_1|^2$ (unperturbed intensity ratio) which is of the order of 1 : 100.

If we let ν_1 and $2\nu_2$ approach each other more closely (decrease in $|\Delta|$), but retain the same interaction energy P, the intensity ratio can become larger or smaller. The former holds when $P\Delta$ and $\alpha_1\alpha_2$ possess the same sign, and the latter when they have different signs. In the record instance the intensity of the overtone vanishes when the ratio of the excitation strength of the two eigenfunctions $\left(\frac{x-|\Delta|}{x+|\Delta|}\right)$ equals the unperturbed intensity ratio and then increases again. Near the quasi-degeneracy the intensities attain the same order of magnitude, and from Eq. (20.12) for $\Delta = 0$, the intensity ratio becomes

$$I = \frac{\left|\alpha_1 - \alpha_2\right|^2}{\left|\alpha_1 + \alpha_2\right|^2} \approx \frac{\alpha_1 - 2\alpha_2}{\alpha_1 + 2\alpha_2} \, . \tag{20.13}$$

Here, both eigenfunctions contribute equally to the perturbed states, so that the difference between fundamental and overtone loses its significance. In (20.13) the denominator refers to the line of greater (smaller) frequency for the case $P > 0$ ($P < 0$).

The sum of the intensities of both lines is independent of Δ, and equal to the unperturbed intensity, which is almost completely concentrated in the fundamental. The perturbation causes a different distribution of the intensity in the two lines. The contribution of the two unperturbed levels in the perturbed state to the scattering intensity is not proportional to their excitation because the interference of the probabilities plays an important role.[7]

The preceding discussion is also correct when α_1 and α_2 possess a different relative anisotropy. Both lines will no longer have the same depolarization factor, and the invariant quantities of the perturbed lines must be derived if intensity and polarization ratios are to be computed. Representing the trace and the square of the anisotropy of α_1 and α_2 by a_1, a_2 and γ_1^2, γ_2^2, respectively, we obtain:

$$[a]_{10}^{00} = c_1 a_1 + c_2 a_2; \; [\gamma^2]_{10}^{00} = c_1^2 \gamma_1^2 + c_2^2 \gamma_2^2 + 2c_1 c_2 \, 3/2 \sum_{\rho\sigma} (\alpha_{\rho\sigma}^{s})_1 (\alpha_{\rho\sigma}^{s})_2;$$

$$[a]_{02}^{00} = -c_2 a_1 + c_1 a_2; [\gamma^2]_{02}^{00} = c_2^2 \gamma_1^2 + c_1^2 \gamma_2^2 - 2c_1 c_2 \, 3/2 \sum_{\rho\sigma} (\alpha_{\rho\sigma}^{s})_1 (\alpha_{\rho\sigma}^{s})_2;$$

$$c_1 = \sqrt{\frac{x + |\Delta|}{2x}}, \qquad c_2 = \begin{cases} \sqrt{\dfrac{x - |\Delta|}{2x}} & \text{for } P\Delta > 0 \\ -\sqrt{\dfrac{x - |\Delta|}{2x}} & \text{for } P\Delta < 0. \end{cases} \tag{20.14}$$

With the aid of the expressions presented in Chapter 16 and (20.14), the intensity and polarization can be computed.

Analogous perturbation effects occur where the following relation exists between three frequencies:

$$\nu_1 + \nu_2 \approx \nu_3,$$

if the transformation rule of the ν_3 vibration type is the same as for the product of ν_1 and ν_2. All other commensuration relations (e.g., $\nu_1 \approx n\nu_2$ for $n > 2$) lead to similar effects upon retention of higher-than-cubic terms in the potential energy expression. In these cases, the perturbations will be rather weak.

1. CO_2.

Figure 13 describes the normal modes of vibration of the linear molecule. Only the totally symmetric vibration ν_1 can occur as fundamental in the Raman effect. ν_2 and ν_3 are antisymmetric with respect to the center of symmetry, and hence, are forbidden.

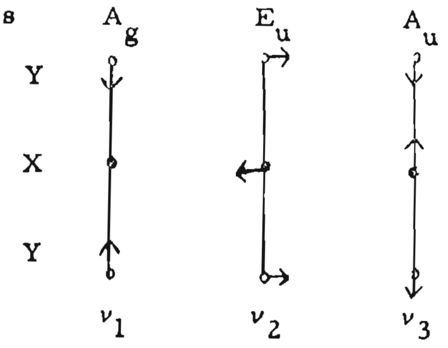


Fig. 13. Normal modes of vibration of the linear molecule XY_2.

The spectrum of CO_2, shown in Fig. 14, consists of two strong lines, each accompanied by a weak satellite. According to Fermi, we assume that the relation $\nu_1 \approx 2\nu_2$ is applicable. However, the hereby-induced perturbations differ from the one discussed above since ν_2 is a degenerate vibration.

If we disregard ν_3, the terms are characterized by the quantum numbers V_1, V_2, and s. The azimuthal quantum numbers run from V_2 to $-V_2$, and give rise to even (odd) values for even (odd) V_2. For the harmonic oscillator, the energy is independent of s:

$$W^0_{V_1V_2} = h\left[\nu_1(V_1 + 1/2) + \nu_2(V_2 + 1)\right], \qquad (20.15)$$

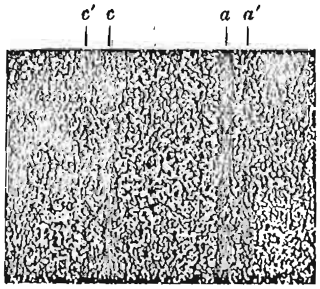


Fig. 14. Raman spectrum of CO_2 (Langseth and Nielsen).

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with a degeneracy of $(V_2 + 1)$. As a result of anharmonicity, terms with different s values split, but the degeneracy between + s and - s is determined by the symmetry and remains unaltered.

Letting $\nu_1 + 2\nu_2 = S$, $\nu_1 - 2\nu_2 = \Delta$, $2V_1 + V_2 = n$, then according to (20.15) we obtain

$$W_n^{(0)} = S/4\,(2V_1 + V_2 + 2) = S/4\,(n + 2), \qquad (20.16)$$

and the perturbation energy will be

$$H^{(1)} = \pi^2 S\Delta(q^2 - r^2/4) + \beta q r^2, \qquad (20.17)$$

where q is the normal coordinate associated with ν_1. The two degenerate normal coordinates are described as in Chapter 17 by $\xi + i\eta = r \exp(i\phi)$.

The eigenfunctions contain ϕ in the form of $\exp(is\phi)$. Since terms with different s values belong to different symmetry types, only terms with identical s can perturb each other. For the case $n = 2$ ($V_1 = 1$, $V_2 = 0$, $s = 0$ and $V_1 = 0$, $V_2 = 2$, $s = 0, \pm 2$), perturbation with $s = 0$ has to be examined. From the following expressions:

$$(r^2)_{V_2 s}^{V_2 s} = \frac{h(V_2 + 1)}{\pi^2 S} \quad (r^2)_{V_2 - 2, s}^{V_2 s} = \frac{h}{2\pi^2 S}\sqrt{V_2^2 - s^2},$$

$$(r^2)_{V_2 + 2, s}^{V_2 s} = \frac{h}{2\pi^2 S}\sqrt{(V_2 + 2)^2 - s^2},$$

we obtain, for the matrix elements of $H^{(1)}$:

$$H^{(1)} = \Delta/4\,(2V_1 - V_2), \quad (H^{(1)})_{V_1+1, V_2-2, s}^{V_1 V_2 s} = P\sqrt{(V_1 + 1)(V_2^2 - s^2)}$$

$$(20.18)$$

$$(H^{(1)})_{V_1-1, V_2+2, s}^{V_1, V_2, s} = P\sqrt{V_1\left[(V_2 + 2)^2 - s^2\right]}.$$

For n = 2, this becomes

$$\begin{vmatrix} \Delta/2 & 2P \\ 2P & -\Delta/2 \end{vmatrix}$$

having the eigenvalues

$$\frac{W_2^{(1)}}{h} = \pm \sqrt{\Delta^2/4 + 4P^2} \qquad (20.19)$$

A comparison with (20.8) indicates that the splitting here is larger than that for the nondegenerate frequency ν_2. The total energy for the term n = 2 is, according to (20.16) and (20.19), upon subtracting the zero-point energy,

$$\frac{W_2}{h} = S/2 + \begin{cases} +\frac{x_2}{2} \\ -\frac{\Delta}{2} \\ -\frac{x_2}{2} \end{cases}, \qquad x_2 = \sqrt{\Delta^2 + 16P^2}. \qquad (20.20)$$

The middle term $2\nu_2$ constitutes the unperturbed term s = ± 2. In a similar manner, the splitting of the term n = 3 may be obtained. These are the six terms $0\ 3_{\pm 3}$, $0\ 3_{\pm 1}$, ${}^{1}{}_{\pm 1}$.[8] As the matrix elements of the perturbation theory are quadratic in s, by combining terms with the same s value, we obtain from (20.18) the perturbation matrix for both terms of s = + 1 and those of s = - 1; this matrix is

$$\begin{vmatrix} \Delta/4 & 2P\sqrt{2} \\ 2P\sqrt{2} & -3\Delta/4 \end{vmatrix}, \qquad (20.21)$$

having the eigenvalues

$$\frac{W_3^{(1)}}{h} = -\frac{\Delta}{4} \pm \sqrt{\Delta^2/4 + 8P^2}, \tag{20.22}$$

and the total energy less zero-point energy is

$$\frac{W_3}{h} = \frac{3S - \Delta}{4} \begin{cases} \frac{x_3}{2} \\ -\frac{\Delta}{2} \\ -\frac{x_3}{2} \end{cases}, \qquad x_3 = \sqrt{\Delta^2 + 32P^2}. \tag{20.23}$$

The middle term $\frac{3S - 3\Delta}{4} = 3\nu_2$ corresponds to the unperturbed term with $s = \pm 3$. As may be seen from (20.22), if $x_3 > x_2$, the splitting increases with increasing excitation.

If the proper splitting factor (x_2 or x_3) is substituted for x, the eigenfunction given in (20.10) remains valid, as well as the expressions (20.11) and (20.14) for the intensity and polarization of the Raman lines.

Figure 15 represents the energy levels for CO_2. Let us investigate the possible Raman transitions. Three lines are possible from the ground state to the states n = 2. The center line, which has not yet been observed, is supposed to be as strong as an unperturbed overtone.[9] The two other lines have the frequencies

$$a = \frac{S + x_2}{2}, \qquad c = \frac{S - x_2}{2}, \tag{20.24}$$

where x_2 denotes the splitting; these may be identified with the two strong lines in Fig. 14. With x_2 in place of x, the intensities and polarization are expressed by (20.11), (20.12), (20.13), and (20.14).

As the state 01_1 is slightly excited at room temperature ($\nu_1 = 677.5$ cm^{-1}), transitions to n = 3 are possible, giving rise to three lines. The center one corresponds to the unperturbed overtone, but has not been observed. The frequencies of the adjacent lines are:

$$a' = \frac{S + x_3}{2}, \qquad c' = \frac{S - x_3}{2}. \tag{20.25}$$

The two lines are the weak satellites adjacent to the main lines in Fig. 14. P and Δ may be determined from the ratio of the splittings. This ratio is

$$\frac{x_3}{x_2} = \sqrt{\frac{\Delta^2 + 32P^2}{\Delta^2 + 16P^2}}\ ; \tag{20.26}$$

for $\Delta = 0$ (complete degeneracy), we have

$$\frac{x_3}{x_2} = \sqrt{2}, \text{ and } x_2 = 4P. \tag{20.27}$$

The observed and calculated ratios are in fair agreement. Table XIV summarizes the measured frequencies.

$$\frac{x_3}{x_2} = 144.2/102.8 = 1.405.$$

Hence, $\nu_1 \approx 2\nu_2$ is almost exact, and from (20.27) we obtain

$$P = 25.7 \text{ cm}^{-1}.$$

Fermi obtained $P = 28 \text{ cm}^{-1}$ by using an estimated value for the anharmonicity constant. This agreement is far superior to that expected from the approximations involved, and may partly be fortuitous, as was stated by Fermi.

For $\Delta = 0$, we have

$$\nu_2 = \$/4 = \frac{a + c}{4} = \frac{a' + c'}{4} = 668.5 \text{ cm}^{-1}\ ;$$

the direct measurement of ν_2 in the infrared (transition $00_0 \rightarrow 01_1$) leads to a value of 667.5 cm^{-1}. The agreement is perfect. Also, the higher terms, which are known from infrared studies, may be represented by $\Delta = 0$.[10]

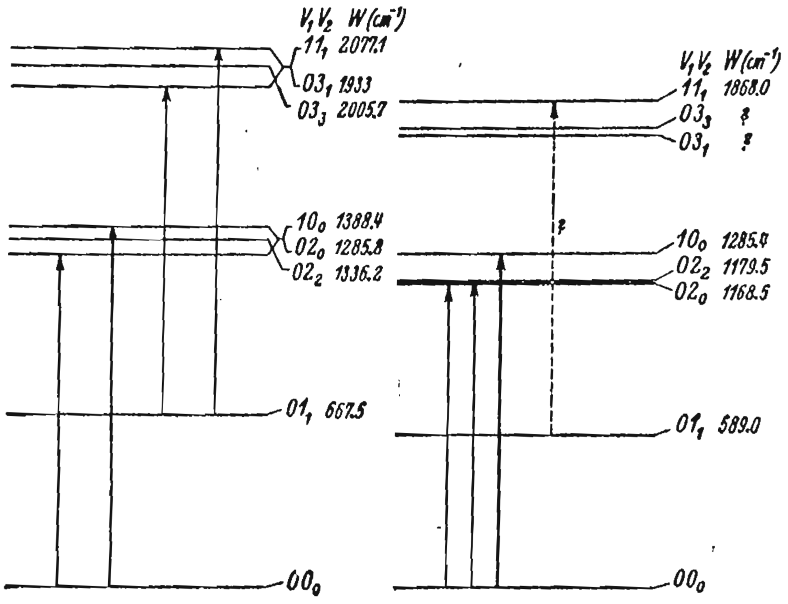
Dennison assumes the values

$$P = 25.6\ \text{cm}^{-1} \text{ and } \Delta = +\ 4.2\ \text{cm}^{-1},$$

with little certainty in the value for Δ.[11]

Exact intensity and polarization measurements would be of great value; it has merely been reported that line a is more intense than line c.[12] This does not lead to definite conclusions as the value for Δ is uncertain due to the interference effect mentioned above. If the complete set of intensity and polarization data were known for the four lines a, c, a', and c', the tensors α_1 and α_2, as well as the value for Δ, could be estimated.

For comparison, the lowest terms of N_2O and its Raman lines measured by Langseth and Nielsen are presented in Fig. 15. (The broken line indicates a doubtful Raman line.) For this molecule, ν_1 and $2\nu_2$ are sufficiently close to cause a mutual perturbation. The term 02_0 is lowered by 11 cm^{-1} with respect to 02_2, through the perturbation of 10_0. The perturbation effects are smaller than those for CO_2 because of the larger value of Δ. A knowledge of the positions of the terms 03_3 and 03_1 would be important for the evaluation of P and Δ.



a) CO_2 b) N_2O

Fig. 15. Energy levels of CO_2 and N_2O.

2. CS_2.

The Raman spectrum of CS_2 resembles that of CO_2. It consists of the two strong lines 655.0 and 796.3 cm^{-1}, which as in the case of CO_2, are accompanied by two weak satellites, 642.6 and 810.9 cm^{-1}.[13]

By assigning these lines to ν_1 and $2\nu_2$ (assuming linear symmetry), Placzek showed that the infrared spectrum can be interpreted on the basis of the fundamentals $\nu_1 = 655$, $\nu_2 = 400$, $\nu_3 = 1522$ cm^{-1}.[14]

The fundamental $\nu_2 = 396.8$ cm^{-1} was observed in the infrared by Dennison and Wright.[15] Since this frequency is almost half that of the Raman line $2\nu_2$ (796.3 cm^{-1}), Dennison concluded that resonance between the terms 10_0 and 02_0 is nonexistent, and obtained $\Delta = -1367$ and $|P| = 7.0$. The perturbation effect of the remaining terms entering into the second-order approximation should be of the same order of magnitude. The high intensity of the overtone 796.3 cm^{-1} appears to contradict this, however. Pienkowski measured an intensity ratio of 1 : 3.1.[16] If the corresponding Fermi interaction energy is calculated (by neglecting a_2), values are obtained that do not accord with the experimental ones.

Another approach comprising the weak satellites can be attempted. According to measurements by Mesnage, the weak lines are almost symmetrical with respect to the center of gravity of the two strong lines ($a' = 642.6$ cm^{-1}, $c' = 810.9$ cm^{-1}).[17] This demonstrates that the mutual perturbation of the respective levels (10_0 and 02_0; 11_1 and 13_1) is large in relation to the effect of the remaining states. From this premise and from the given term splittings we obtain $x_2 = 140.8$, $x_3 = 168.3$, and

$$\Delta = -106, \qquad |P| = 33, \tag{20.28}$$

resulting in $\nu_2 = 389.5$ cm^{-1}. The difference between the calculated and observed frequency appears to be small, particularly since the Raman spectrum was measured for the liquid and the infrared ν_2 frequency for the gaseous state.

The values presented in (20.28) yield an intensity ratio of 1 : 7 when the original Fermi expression is employed. With the aid of (20.9) the observed ratio 1 : 3.1 is obtained, provided the value of $|a_2|/|a_1|$ is 0.15. This corresponds to a ratio of the intensity of the overtone to that of the fundamental of 1 : 40, which may well be possible although high.

Evidently, the observed position of the levels can be correlated with the measured ratio of the intensities. The assumption made by Pienkowski that both lines possess identical depolarization factors can be understood only if the tensors α_1 and α_2 possess approximately equal relative anisotropy and if their mixing does not alter the depolarization factor. From the selection rules, it follows that the two tensors are axially symmetric but that they can have distinct anisotropies. Verification of this interpretation of the spectrum requires a completion of the Raman and infrared measurements.

The results obtained by Bhagavantam on the Raman spectrum of liquid carbon bisulfide should be included.[18] He detected two weak lines at 400 and 1500 cm^{-1}, and identified them with the frequencies ν_2 and ν_3. These are forbidden in the free molecule because they are antisymmetric with respect to the center of symmetry of the molecule. Should these results prove correct, then the lines would be caused by the effect of adjacent molecules destroying the molecular symmetry. Similar cases have been observed in crystals. Further studies should assist in the elucidation of the effect of internal fields.

3. Methane, Methyl Compounds, CCl_4.

Another series of spectra can also be more easily interpreted by means of perturbation effects. The most important example is that of methane. The infrared and Raman spectra can be analyzed on the basis of a tetrahedral model. The normal frequencies are

$$\nu_1 = 2915, \ \nu_2 = 1522, \ \nu_3 = 1304, \text{ and } \nu_4 \approx 3020 \text{ cm}^{-1},$$

where ν_1 is totally symmetric, ν_2 doubly degenerate, and ν_3, ν_4 triply degenerate. The Raman spectrum contains the strong line 2914.8 cm^{-1} (ν_1), the moderately intense line 3022.1 cm^{-1} (ν_3), which occurs in the infrared also, and the weak line 2071.5 cm^{-1}.[19] The latter corresponds to the overtone $2\nu_2$ which is intensified because of the proximity of ν_1. Its symmetry condition is fulfilled but will not be proved here. The line ν_2 has not been observed.

A similar observation was made for many methyl derivatives: Compounds that permit the separate treatment of the methyl-group vibrations[20] give rise to two totally symmetric and two degenerate normal vibrations

(A_1 : ν_1', ν_2' and E : ν_3', ν_4'), if the pyramidal structure is assumed. The first occur near 2960 cm^{-1} and between 1200 - 1400 cm^{-1}, while the latter are near 1450 and 3050 cm^{-1}. Hence, we have $\nu_1' \approx 2\nu_3'$.[21] Methyl halides and other methyl compounds show an additional line near 2860 cm^{-1}, which is ascribed to the overtone $2\nu_3'$ being intensified by the adjacent ν_1'. The fact that the 2860 cm^{-1} vibration gives rise to a parallel band in the infrared and that it has the expected polarization as measured by Simons[22] confirms this assignment.

The spectrum of CCl_4 will be discussed briefly. On the basis of its Raman and infrared spectra, the molecule has the tetrahedral structure of the methyl halides described in Chapter 19. From infrared and polarization data the following fundamentals are obtained (the description of the frequencies agrees with that for methane): $\nu_1 = 459$, $\nu_2 = 219$, $\nu_3 = 314$, and $\nu_4 \approx 773$ cm^{-1}. The frequencies are observed in the Raman effect. In contrast to other tetrahalides, two lines of equal intensity occur (758 and 789 cm^{-1}) near ν_4 which indicate an accurate relation $\nu_1 + \nu_3 = \nu_4$. When the term splitting and the intensity distribution are calculated, a complex intensity distribution rather than a doublet is obtained without the assumption of a particular value for $(\partial^2\alpha/\partial q_1 \partial q_3)_0$.[23, 24] As a result of the low values of the frequencies, a series of excited states which are occupied to a considerable extent at room temperature should be taken into account.

In addition, the Raman spectrum exhibits a faint broad line at 1540 cm^{-1}, ascribed to $2\nu_4$. The depolarization factor $\rho < 6/7$ substantiates this assignment.[25] In contrast to the fundamental, isotropic scattering is permitted for the overtone. The theoretical treatment of its splitting process is more complex than that of ν_4 and has not yet been carried out.[26, 24]

To summarize: A qualitative understanding has been reached of a series of spectra by considering perturbation effects suggested by Fermi's explanation of the CO_2 spectrum. If the quantitative aspects of the theory are to be proved, further investigations are required.

4. Existence of Several Equilibrium Configurations. NH_3.

A peculiarity of the energy levels of NH_3 is due to the fact that, according to quantum mechanics, a particle can penetrate a potential barrier when its energy is not sufficient to overcome the height of the potential. NH_3 has the structure of a flat pyramid, and there are two equally-permitted equilibrium positions (above and below the plane of the H atoms) for the N atom.

As a consequence, Hund showed that all vibrational levels split into two.[27] This splitting increases with increasing vibrational energy, and when measured in terms of vibrational numbers it can be considered as the period of oscillation, i.e., as the time during which change in the equilibrium position occurs. Only the two totally symmetric of the four normal vibrations were observed in the Raman effect of the gas:[28] $\nu_1 = 3334\ cm^{-1}$ and $\nu_2 = 949\ cm^{-1}$.[29] The latter is a doublet, 933.8 and 964.3 cm^{-1} (see Fig. 18). The selection rules will be used in the interpretation of the spectrum. Aside from the symmetry elements of the pyramidal molecule (c_{3v} symmetry), the plane of the three H atoms is taken as the plane of symmetry for the two equally-permitted equilibrium positions. With respect to this plane, each vibrational level splits into a symmetric (α) and antisymmetric (β) term, where the β term is usually the higher one. The selection rules for the combinations of the split terms are those of the D_{3h} group.

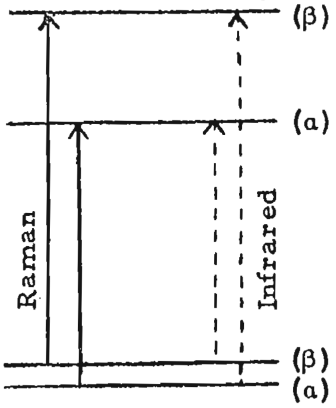


Fig. 16. Vibrational spectrum of NH_3.

According to Table VIII, totally symmetric vibrations permitted in the Raman effect involve transitions $\alpha \rightleftarrows \alpha$, or $\beta \rightleftarrows \beta$, while in the infrared transitions occur between $\alpha \rightleftarrows \beta$. Both spectra are expected to display doublets for the transitions from the ground state to the first excited state (compare Fig. 16) so that the following holds:

$$\Delta_{\text{Raman}} = \Delta_0 - \Delta_1$$
$$\Delta_{\text{IR}} = \Delta_0 + \Delta_1 . \tag{20.29}$$

The vibrational form of ν_1 practically leaves the N atom in its rest position, but it participates in the ν_2 vibration. This would lead to a splitting of the vibrational levels which is little affected by the quantum number V_1 but increases with increasing value of V_2. The N atom gets closer to the potential barrier height for higher excitations of ν_2. The ν_1 frequency is not split in the Raman effect, but it is split by about 1.6 cm^{-1} in the infrared, according to Dennison and Hardy,[30] giving

$$\Delta_0 \approx \Delta_1^{(\nu_1)} = 1 \text{ cm}^{-1} . \tag{20.30}$$

The splitting of ν_2 is considerably larger; it amounts to 33 cm^{-1} in the infrared and 30.5 cm^{-1} in the Raman effect. The agreement between (20.30) and the difference of these two values, $2\Delta_1$, is better than expected from the accuracy of the experiments.

From the observed splitting, the period of oscillation is estimated to be 3×10^{-10} sec in the ground state and 10^{-11} sec in the first excited state of ν_2. For discussions on the shape of the potential barrier, papers by Dennison and Uhlenbeck, Fermi, Rosen, and Morse should be consulted.[31]

Spectra of other molecules should also demonstrate the existence of several equilibrium positions. It would be of interest to investigate molecules having hindered rotation. They might be treated in an analogous manner.

5. Benzene.

A remarkable feature of the spectrum of benzene is the occurrence of a series of identical frequencies in the Raman and infrared spectra. According to the mutual exclusion rule, this can take place only provided the dynamics of the system causes an approximate or complete degeneracy between even and odd terms.

It is possible that the coincidence of both lines at 3000 cm^{-1}, associated with the H atom, can be explained in this manner. If there is a weak interaction between the H atoms, the vibrations of the individual atoms will be symmetric and antisymmetric with respect to the center and of comparable magnitude. However, the lower frequencies can hardly be explained in this fashion. An alternative would mean that the benzene molecule does not possess a center of symmetry or that the breakdown of the selection rules is caused by the fields of the adjacent molecules. The latter is unlikely, since there is, for example, a strong band in the infrared spectrum corresponding to the intense line 1178 cm^{-1} of the Raman scattering. An investigation of the Raman spectrum of benzene in the gaseous state and an extension of the infrared spectrum towards longer wavelengths would be of great import in the elucidation of this problem. The strong line at 992 cm^{-1} may be ascribed to the totally symmetric vibration of the ring, on the basis of polarization measurements.[32]

REFERENCES AND FOOTNOTES

1. See texts on Quantum Theory, for instance: A. Sommerfeld, Atombau and Spektrallinien, Wellenmechanik Supplement.

2. The variation in the intensity does not imply an increase, it may actually result in a decrease, if the coefficients c_{vv} and $c_{vv'}$ have different signs.

3. E. Fermi, Z. Physik 71, 250 (1931); D. M. Dennison, Phys. Rev. 41, 304 (1932).

4. The general case leads to a matrix of order $(n + 2)/2$ and $(n + 1)/2$ for even and odd n, respectively. When the quasi-degenerate states are arranged in order of increasing V_1, the matrix assumes the form

$$h\begin{vmatrix} C_{00} & C_{01} & 0 & 0 & 0 & ---------- & 0 \\ C_{10} & C_{11} & C_{12} & 0 & 0 & ---------- & 0 \\ 0 & C_{21} & C_{22} & C_{23} & 0 & ---------- & 0 \\ 0 & 0 & C_{32} & C_{33} & C_{34} & ---------- & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{\frac{n+\left\{\begin{smallmatrix}1\\2\end{smallmatrix}\right.}{2}\ \frac{n+\left\{\begin{smallmatrix}1\\2\end{smallmatrix}\right.}{2}} & \end{vmatrix}$$

$$hC_{V_1V_1} = (H^{(1)})^{V_1V_2}_{V_1V_2} = h\Delta/4\ (4V_1 - n + 1/2).$$

$$hC_{V_1,V_1-1} = hC_{V_1-1,V_1} = (H^{(1)})^{V_1V_2}_{V_1-1,V_1+2} = hP\sqrt{V_1(n - 2V_1 + 1)(n - 2V_1 + 2)}\ .$$

Only the diagonal terms and the adjacent ones are different from zero. The eigenvalues of this matrix for $n > 3$ must be evaluated numerically.

5. D. M. Dennison, loc. cit.

6. Instead of examining the perturbation term, the following argument may be advanced: State $V_1 = 0$, $V_2 = 2$ is totally symmetric for the nondegenerate types of vibration. Therefore, perturbation can occur only when $V_1 = 1$, $V_2 = 0$ is also totally symmetric. A term for which only one quantum of a single vibration is excited is of the same species as the vibration type of the eigenvibration; therefore q_1 must be totally symmetric.

7. Fermi (loc. cit.) assumed that the intensity is proportional to the excitation strength of the state 1, 0, that is a_2 is equal to 0. The intensity of the unperturbed overtone can be neglected compared with that of the fundamental,

i.e., $|a_2|^2/|a_1|^2$. However, the a_2/a_1 cannot be neglected as it is associated with the interference of the probabilities. For instance, when the intensity of the unperturbed overtone is 1/100 of that of the fundamental for $\Delta = 0$ the intensity will be changed by 50%, through a_2 according to Eq. (20.13).

8. Conforming to the notation introduced by Dennison, the quantum number S is written as lower index of V_2.

9. Trace scattering is not permitted for this line since it involves a transition between different species ($s = 0$, $s = \pm 2$), giving a depolarization factor of 6/7.

10. Martin and Barker, Phys. Rev. 41, 291 (1931).

11. Term shifts, compared with $\Delta = 0$, are of the order of 0.1 cm^{-1}.

12. Dickinson-Dillon-Rasetti, l.c.; Langseth and J. R. Nielsen, loc. cit. The latter authors report quantitative measurements.

13. P. L. Mesnage, J. phys. et radium 2, 403 (1931).

14. G. Placzek, Z. Physik 70, 84 (1931).

15. Dennison and Wright, Phys. Rev. 38, 2077 (1931).

16. Pienkowski, Acta Phys. Pol. 1, 87 (1932).

17. Mesnage, loc. cit.

18. Bhagagantam, Phys. Rev. 39, 1029 (1932); Indian J. Phys. 5, 59 (1930).

19. Dickinson-Dillon-Rasetti, loc. cit.

20. The conditions were stipulated by Bartholome and Teller, Z. phys. Chem. (B) 19, 366 (1933).

21. This relation corresponds to the relation $\nu_1 \approx 2\nu_2$ for methane, because in going from CH_4 to CH_3X we have $\nu_1 \rightarrow \nu_1'$, $\nu_2 \rightarrow \nu_3'$.

22. Simons, loc. cit.

23. Placzek and Teller, unpublished; experimental data on intensities and width have been reported by Ornstein and Went, Proc. Amsterdam 35, 1024 (1932).

24. See Reference 2 of Conclusion.

25. Placzek and van Wijk, Z. Physik 67, 582 (1931).

26. Langseth (Z. Physik 72, 350 (1931)) reports a doublet ν_4 for CBr_4, for which the relation $\nu_4 \approx \nu_1 + \nu_3$ does not exist. In contrast, Dadieu and Kohlrausch (Montash. Chem. 57, 492 (1931)) describe the same frequency as a broad singlet. This issue requires further clarification. The author cannot agree with Schaefer (Cl. Schaefer, Z. Physik 60, 586 (1930); Cl. Schaeffer and R. Kern, Z. Physik 78, 609 (1932)), who believes that the splitting in CCl_4 and CBr_4 arises from the anisotropy of the C atom.

27. F. Hund, Z. Physik 43, 805 (1927).

28. Dickinson-Dillon-Rasetti, loc. cit.; Amaldi and Placzek, Z. Physik 81, 259 (1933).

29. One of the degenerate frequencies was found near 1630 cm^{-1} in the infrared spectrum and was likewise detected in the Raman spectrum of liquid ammonia. The other frequency has not been established accurately, but it is expected to occur near ν_1.

30. D. M. Dennison and T. D. Hardy, Phys. Rev. 39, 938 (1932).

31. Dennison and Uhlenbeck, Phys. Rev. 41, 313 (1932); Fermi, Rend. Lincei 16, 179 (1932); Rosen and Morse, Phys. Rev. 42, 410 (1932).

32. G. Placzek, Leipzig Lectures (1931) p. 71; J. Weiler, Z. Physik 72, 206 (1931). The attempt made by Weiler to explain the low depolarization factor (0.07) of the line 992 cm^{-1} in terms of symmetry considerations is based on insufficient evidence. For noncubic systems, the symmetry causes the depolarization factor of totally symmetric vibrations to be within the limits 0 and 6/7. The exact value is a function of the normal coordinates. There is no satisfactory theory available to predict this.

33. J. Cabannes, Trans. Farad. Soc. 25, 813 (1929); G. Placzek and W. R. van Wijk, Z. Phys. 67, 582 (1931); L. Simons, loc. cit.; W. Hanle, Ann. Physik 15, 345 (1932).

Chapter 21. Rotational Structure

In Chapter 15 it was shown that the total intensity of the rotation-vibration band v → v' and the rotation band v → v is independent of the degree of excitation of the rotational levels. It is equal to the scattering intensity associated with the transition v → v' and v → v of the nonrotating molecule fixed in space and averaged over its spatial orientation. Up to now we have examined the total intensity; in order to obtain the distribution among the individual rotational lines, we must express the matrix element of the polarizability in terms of coordinates fixed in space rather than fixed in the molecule. For this purpose the expressions (15.5) and (15.7) must be evaluated. In Chapter 15 it was emphasized that the isotropic part of the polarizability is independent of the orientation of the molecule and that the matrix elements for the transitions involving a change in the rotational quantum numbers will vanish. Hence, the trace scattering associated with a vibrational transition does not include rotational lines. Its intensity, which according to (15.15b) is independent of the rotational levels, will be concentrated in the pure vibrational line, the Q branch. The polarization of the rotational lines is identical with that of the quadrupole scattering ($\rho = 3/4$, $\rho_n = 6/7$, $P = 6$). This also applies to the Q branch when the trace scattering is forbidden for the particular vibrational transition; the fundamentals of the non-totally symmetric vibrations fall into this category.

The intensity distribution of the quadrupole scattering may be computed by means of Eq. (15.17). Results of such a calculation can also be obtained from the qualitative examination of the rotational structure: In the Fourier expansion of α, the coefficient associated with the frequency $\nu_{r'}{}^{r}$ constitutes the classical counterpart of the matrix element $(\alpha)_{r'}{}^{r}$. So that α may be expanded for the pure rotational Raman effect, the polarizability components α_{ik} are expressed in terms of a space-fixed coordinate system by $\alpha_{i'k'}$ which are fixed in the molecule:[1]

$$\alpha_{ik} = \sum_{i'k'} \alpha_{i'k'} \cos i'i \cos k'k,$$

where $\alpha_{i'k'}$ is independent of the rotational level and of the molecular orientation. If the molecule rotates, the direction cosines become functions of time, and the rotational frequencies will occur in the Fourier expansion of α_{ik}. The expansion is particularly simple in the case of the symmetric rotor since the direction cosines may be given by the Eulerian angles

θ, ϕ, and χ. θ is time independent, while ϕ and χ are linear functions of time:

$$\phi = \nu_\phi t, \ \chi = \nu_\chi t.$$

The direction cosines depend linearly on the spherical functions of ϕ and χ, and the frequencies $n_1\nu_\phi + n_2\nu_\chi$ in (15.2) occur for $|n_1| \leq 2$, $|n_2| \leq 2$, resulting in a rotational spectrum with 25 branches $\nu + n_1\nu_\phi + n_2\nu_\chi$.

If the polarizability is a symmetric tensor whose axis coincides with the figure-axis, it is independent of the azimuth about the figure-axis, χ. Since the rotational frequency about this axis vanishes in the Fourier expansion, the rotational spectrum will consist of the five branches ν, $\nu \pm \nu_\phi$, $\nu \pm 2\nu_\phi$. For zero angular momentum about the figure-axis (as for diatomic and linear molecules[2]), the total angular momentum is perpendicular to the figure-axis and the polarizability ellipsoid assumes the same position after half a rotational frequency. Consequently, the rotational frequencies do not occur in the Fourier expansion of α, and the rotation spectrum has only the branches ν and $\nu \pm 2\nu_\phi$. For isotropic polarizability, α is independent of orientation, leaving a ν branch in the spectrum without any rotational structure.

The rotation-vibration spectrum may be treated similarly upon replacing the polarizability component $\alpha_{i'k'}$ by the Fourier component $\beta_{i'k'}$ associated with the vibrational frequency. The rotational structure for totally symmetric vibrations (i.e., vibrations that do not alter the symmetry of the molecule) is the same as that of the unshifted line. For the remaining vibrations, the symmetry of $\beta_{i'k'}$ is reduced. Hence, Raman lines of isotropic molecules can exhibit rotational structure. The simple frequency ν_ϕ occurs in the rotation-vibration spectrum of linear molecules, and $2\nu_\phi$, the double rotation frequency about the figure-axis, is involved in that of axially symmetric molecules.

The evaluation of (15.7) for the symmetric rotor whose energy levels are given by (see the first chapter of this volume by Krönig)

$$W_{JK} = B\left[J(J+1) + \beta K^2\right]; \qquad B = \frac{h^2}{8\pi^2 A}, \ \beta = (A/C - 1), \tag{21.1}$$

yields[3]

$$\left[G^s\right]^{VJK}_{V'J'K'} = b^{JK}_{J'K'} \sum_{\lambda'\mu'} \left|(\alpha_{\lambda'\mu'}{}^{s})_{V'}{}^{V}\right|^2 \delta^{K'-K}_{\lambda'+\mu'}, \tag{21.2}$$

where C and A represent, respectively, the moments of inertia about the figure-axis and about an axis perpendicular to it. The quantity number of the angular momentum about the figure-axis K can assume the values from J to - J. The quantity $G^{S}\,{}^{VJK}_{V'J'K'}$ is that introduced in Chapter 6 for the intensity of the quadrupole scattering,[4] and $b^{JK}_{J'K'}$ is a function of J and K, as outlined in Table XV.

The quantities $b^{JK}_{J'K'}$ obey the relations

$$b^{JK}_{J'K'} = b^{J,-K}_{J',-K'}\,, \tag{21.3a}$$

$$(2J+1)b^{JK}_{J'K'} = (2J'+1)b^{J'K'}_{JK}\,, \tag{21.3b}$$

$$\sum_{J'} b^{JK}_{J'K'} = 1 \tag{21.3c}$$

$$\sum_{K'} b^{J,K}_{J',K+\Delta K} = 1/5\,(2J'+1) \qquad \text{(for a fixed } \Delta K). \tag{21.3d}$$

The selection rules for J are

$$J = 0,\ \pm 1,\ \pm 2.$$

The sum in (21.2) extends over those components for which

$$\lambda' + \mu' = K' - K. \tag{21.4}$$

For $\Delta K = \pm 2$, this involves one component $a_{11}(a_{-1-1})$; for $\Delta K = \pm 1$, two identical components a_{01} and a_{10} (a_{0-1} and a_{-10}); for $\Delta K = 0$, three components, which are related by $a^{(s)}_{1-1} = a^{(s)}_{-11}$, $a_{00} + 2a_{1-1} = 0$. The selection rule for K is

$$\Delta K = 0,\ \pm 1,\ \pm 2. \tag{21.5}$$

For any ΔJ, the transition probability for $J \rightarrow J'$, $K \rightarrow K'$ depends, according to (21.2) and (21.4), on one component of the tensor $(a^{(s)})^{V}_{V'}$, fixed in the molecule.[5] In the event that this component vanishes because of the vibrational selection rules, the rotational branch is absent. The resolved rotational structure furnishes information on the symmetry of the vibration associated with a particular band.

Table XV

The Intensity Factors $b^{JK}_{J'K'}$ for the Rotation Spectrum (Placzek and Teller)

K' \ J'	J	$J+1$	$J+2$
K	$\dfrac{\left[J(J+1) - 3K^2\right]^2}{J(J+1)(2J-1)(2J+3)}$	$\dfrac{3K^2\left[(J+1)^2 - K^2\right]}{J(J+1)(J+2)(2J+1)}$	$\dfrac{3\left[(J+1)^2 - K^2\right]\left[(J+2)^2 - K^2\right]}{2(J+1)(J+2)(2J+1)(2J+3)}$
$K + 1$	$\dfrac{3(2K+1)^2(J-K)(J+K+1)}{2J(J+1)(2J-1)(2J+3)}$	$\dfrac{(J-2K)^2(J+K+1)(J+K+2)}{2J(J+1)(J+2)(2J+1)}$	$\dfrac{\left[(J+1)^2 - K^2\right](J+K+2)(J+K+3)}{(J+1)(J+2)(2J+1)(2J+3)}$
$K - 1$	$\dfrac{3(2K-1)^2(J+K)(J-K+2)}{2J(J+1)(2J-1)(2J+3)}$	$\dfrac{(J+2K)^2(J-K+1)(J-K+2)}{2J(J+1)(J+2)(2J+1)}$	$\dfrac{\left[(J+1)^2 - K^2\right](J-K+2)(J-K+3)}{(J+1)(J+2)(2J+1)(2J+3)}$
$K + 2$	$\dfrac{3\left[J^2 - (K+1)^2\right]\left[(J+1)^2 - (K+1)^2\right]}{2J(J+1)(2J-1)(2J+3)}$	$\dfrac{\left[(J+1)^2 - (K+1)^2\right](J+K+1)(J+K+3)}{2J(J+1)(J+2)(2J+1)}$	$\dfrac{(J+K+1)(J+K+2)(J+K+3)(J+K+4)}{4(J+1)(J+2)(2J+1)(2J+1)}$
$K - 2$	$\dfrac{3\left[J^2 - (K-1)^2\right]\left[(J+1)^2 - (K-1)^2\right]}{2J(J+1)(2J-1)(2J+3)}$	$\dfrac{\left[(J+1)^2 - (K-1)^2\right](J-K+1)(J-K+3)}{2J(J+1)(J+2)(2J+1)}$	$\dfrac{(J-K+1)(J-K+2)(J-K+3)(J-K+4)}{4(J+1)(J+2)(2J+1)(2J+3)}$

For instance, the polarizability ellipsoid of axially-symmetric molecules is symmetric with respect to the figure axis ($\lambda' + \mu' = 0$), and $\Delta K = 0$ applies to the unshifted scattered radiation as well as to the totally symmetric vibration bands. The spectrum consists of five branches of the following frequencies:[6]

$$\begin{aligned}
\nu^{J}_{J+2} &= -(4J+6)\,B/h, && \text{S - branch}\\
\nu^{J}_{J-2} &= (4J-2)\,B/h, && \text{O - branch}\\
\nu^{J}_{J+1} &= -2(J+1)\,B/h, && \text{R - branch}\\
\nu^{J}_{J-1} &= 2J\cdot B/h && \text{P - branch}\\
\nu^{J}_{J} &= 0 && \text{Q - branch}
\end{aligned} \tag{21.6}$$

Introducing the anisotropy γ through the relation $\gamma = \alpha_{00} - \alpha_{-11} = 3/2\, \alpha_{00}{}^{s}$, which is applicable to the rotation ellipsoid, one derives the expression

$$\left[G^{s}\right]^{VJK}_{V'J'K'} = b^{JK}_{J'K'}\; 2/3\, \left|(\gamma)^{V}_{V'}\right|^{2}. \tag{21.7}$$

According to (18.11), we have

$$K' - K = zp - \sum_{j} \ell_j (s'_j - s_j), \tag{21.8}$$

and from (18.12), for the fundamentals, we have

$$\Delta K = \pm\, \ell. \tag{21.8a}$$

For $\ell = 1$: the rotational spectrum consists of ten branches, whose frequencies are obtained by adding

$$B\beta/h\,(2K+1) \text{ and } -B\beta/h\,(2K-1). \tag{21.9}$$

For $\ell = 2$: $\Delta K = \pm\, 2$, and the frequencies to be added to (21.6) are

$$4B\beta/h\,(K+1) \text{ and } -4B\beta/h\,(K-1). \tag{21.10}$$

To determine the intensities from (21.2), we must include the population of the rotational levels. The intensity of a rotational line may be expressed as a fraction of the intensity of the quadrupole scattering v → v', i.e.,

$$\frac{I^{VJK}_{V'J'K'}}{I^{V}_{V'}} = \frac{(2J+1)\exp(-W_{JK}/kT)}{S(T)} \cdot \frac{b^{JK}_{J'K'} \sum\limits_{\lambda'\mu'} \left|(a_{\lambda'\mu'}{}^{s})^{V}_{V'}\right|^{2} \delta^{\lambda'+\mu'}_{K'-K}}{\sum\limits_{\lambda'\mu'} \left|(a_{\lambda'\mu'}{}^{s})^{V}_{V'}\right|^{2}} . \qquad (21.11)$$

Here, S(T) represents the partition function of the rotor. For molecules containing identical nuclei there enters still another factor correcting for a change of weight of state JK due to nuclear spin.[7] For diatomic molecules, this factor is (see the article by Krönig and Beck)

$$i(2i+1) \text{ for } J^{\text{even}}_{\text{odd}} \text{ and } \substack{\text{Fermi}\\ \text{Bose}} \text{ statistics,}$$

$$(i+1)(2i+1) \text{ for } J^{\text{even}}_{\text{odd}} \text{ and } \substack{\text{Bose}\\ \text{Fermi}} \text{ statistics,}$$

where i denotes the nuclear spin.[8] The factors for the most important cases of polyatomic molecules are summarized by Dennison,[9] and by Placzek and Teller.[10]

If nonzero components exist for only one value of $\lambda' + \mu'$ because of the vibrational selection rule, both sums in (21.11) become identical, and the intensity distribution in the rotation spectrum will be determined by the universal constant $b^{JK}_{J'K'}$, and by the rotational energy (moment of inertia). This has been observed in the case of the fundamentals of molecules having p-fold symmetry with $p > 3$. Molecules with $p = 3$ assume a special role. Since ℓ is defined only module p and since the sign of ℓ is immaterial, the components $\lambda' + \mu' = 1$, as well as $\lambda' + \mu' = 2$, differ from zero for the degenerate vibrations ($\ell = 1$). Therefore, the quotient in (21.11) is different from 1. Branches with $\Delta K = 1$ and $\Delta K = 2$ occur whose intensity is a function of the absolute value of the square of the corresponding tensor components fixed in the molecule.

The values of the frequencies (21.9) and (21.10) and the complete rotational spectrum will be modified by the vibration-rotation interaction. As the degenerate vibrations usually possess an angular momentum, the states having such excited vibrations are associated with an angular momentum of the form $\sum_t{}' \xi_t s_t$. The prime over the summation sign means that summation is to be taken over the degenerate vibrations only. ζ_t is a constant characteristic of the normal mode t, and therefore depends on the vibrational force field. When the summation is carried out over the vibrations of the same symmetry type, then we obtain

$$\left|\zeta_t\right| \leq 1 \quad \text{and} \quad \sum_t{}'' \zeta_t = 1.$$

When the degenerate vibration is the only one of a given type, we have

$$\left|\zeta_t\right| = 1.$$

The angular momentum of the pure rotation about the figure axis is

$$L = K - \sum_t{}' \zeta_t s_t. \tag{21.12}$$

The energy can be separated formally into vibrational and rotational contributions. For the latter, K must be replaced by L, and we have

$$E = E_{rot} + E_{vib} = B\left[J(J+1) + \beta L^2\right] + \sum_t h\nu_t(V_t + 1/2). \tag{21.13}$$

In the expressions for the intensity, K is not to be replaced by L. They remain unchanged, because only the total angular momentum and its components are involved in the derivation. The selection rules apply to K, but the frequencies are determined by L, which alters the appearance of the spectrum when $\ell \neq 0$. According to (21.12), L is not an integer; it depends largely on the values of ζ_t, and may be derived for specific cases from (21.12) and (21.13).

If we limit ourselves to bands associated with fundamentals originating from the ground state, it can be shown that the interaction between vibrations and rotations results only in an apparent change of the moment of inertia. Equation (21.13) gives the frequency of the transition from the ground state to $V_t = 1$, $s_t = 1$

$$\nu^{VJK}_{V'J'K'} = B/h\left[J'(J'+1) - J(J+1) + \beta(K' \mp \zeta_t)^2 - \beta K^2\right] + \nu_t.$$

Because of Eq. (21.8), we have

for the transition s_t: $0 \rightarrow 1$ $K' = K + \ell_t$;

for the transition s_t: $0 \rightarrow -1$ $K' = K - \ell_t$.

In place of (21.9) and (21.10) one obtains, respectively,

$$B\beta/h\left[(2K+1) - 2(K+1)\zeta_t + \zeta_t^2\right] \quad \text{and} \quad -B\beta/h\left[(2K-1) - 2(K-1)\zeta_t - \zeta_t^2\right], \tag{21.9a}$$

and $4B\beta/h\left[(K+1) - 1/2(K+2)\zeta_t + 1/4\,\zeta_t^2\right]$ and

$$4B\beta/h\left[(K-1) - 1/2(K-2)\zeta_t - 1/4\,\zeta_t^2\right]. \tag{21.10a}$$

For the line interval, we have

$\Delta\nu = 2B\beta/h\,(1 - \zeta_t)$ for the bands $K \rightarrow K \pm 1$,

$\Delta\nu = 4B\beta/h\,(1 - \zeta_t/2)$ for the bands $K \rightarrow K \pm 2$.

These expressions show that without correction the resulting values of β do not yield the actual moments of inertia. It may be determined from the Raman spectrum for the case $p = 3$, since branches with $\Delta K = 1$ and $\Delta K = 2$ occur for the same vibration. Then, one obtains two equations with two unknowns, and both β and ζ_t can be evaluated.

In some instances ζ_t may be deduced from symmetry considerations. For a spherical rotor a comparison with the infrared spectra is advantageous.[11] The moment of inertia of methane has been evaluated in this manner.

The linear molecule represents a special case of the symmetric rotor. The moment of inertia about the axis is zero, giving $L = 0$, and the angular momentum about the axis is equal to the angular momentum of the vibration:[12]

$$K = \sum_t{}' s_t. \tag{21.14}$$

Only vibrations with $\ell = 0$ and $\ell = 1$ are present (see Table X). For the former, we have $\lambda' + \mu' = 0$, and for the latter, $\lambda' + \mu' = 1$, resulting in $\Delta K = 0$ and $\Delta K = 1$ for the two fundamentals, respectively.

If the molecule exists in the ground vibrational state (or, in general, in a state in which degenerate vibrations are not excited), then according to (21.14) we have K = 0, and according to (21.11) and Table XV for the rotational structure of the Rayleigh line and for the totally symmetric bands ($\ell = 0$) we have:

$$\frac{I^{VJ}_{V'J'}}{I^{V}_{V'}} = \frac{b^{J0}_{J'0}(2J+1)g_J \exp(-BJ(J+1)/kT)}{S(T)} \tag{21.15}$$

$$b^{J0}_{J0} = \frac{J(J+1)}{(2J-1)(2J+3)},$$

$$b^{J0}_{J\pm 1,0} = 0,$$

$$b^{J0}_{J+2,0} = 3/2\,\frac{(J+1)(J+2)}{(2J+1)(2J+3)}, \tag{21.15a}$$

$$b^{J0}_{J-2,0} = 3/2\,\frac{\overset{(J-1)J}{J\cancel{(J+1)}}}{(2J+1)(2J-1)}.$$

The P and R branches vanish, as was illustrated earlier. However, they do occur when degenerate vibrations are excited in the initial state. The same is true for the fundamentals of the bands $\ell = 1$:

$$\frac{I^{VJ}_{V'J'}}{I^{V}_{V'}} = b^{J0}_{J'1}(2J+1)g_J\,\frac{\exp(-BJ(J+1)/kT)}{S(T)} \tag{21.16}$$

$$b^{J0}_{J1} = 3/2\,\frac{1}{(2J-1)(2J+3)}, \qquad b^{J0}_{J+1,1} = 1/2\,\frac{J}{2J+1}, \tag{21.16a}$$

$$b^{J0}_{J+2,1} = \frac{(J+1)(J+3)}{(2J+1)(2J+3)}.$$

The Q branch is extremely weak since b^{J0}_{J1} approaches zero as J^{-2} goes to zero. Two cases may be distinguished for the overtones of these bands: when $\Delta s = 0$, the bands possess the same structure as those of the totally symmetric vibrations, and Eqs. (21.15) and (21.15a) are applicable. When Δs has the value 2, then ΔK is equal to 2 and the intensity distribution is a function of $b^{J0}_{J'2}$. Equations (21.15) and (21.15a) are also valid for diatomic molecules.[13]

Spherical-top molecules have three identical moments of inertia. The rotational energy is independent of K:

$$W_{rot} = BJ(J+1)\,. \tag{21.17}$$

The frequencies belonging to different transitions K → K', but to the same transition J → J', coincide. Therefore, the transition probabilities must be summed over K and K'. From Eqs. (21.2) and (21.3), the following is obtained:

$$\sum_{K} \sum_{K'} \left[G^{s}\right]^{VJK}_{V'J'K'} = 1/5(2J'+1) \sum_{\lambda'\mu'} \left|a_{\lambda'\mu'}^{(s)}\right|^{2} = 2/15(2J'+1)\left[\gamma^{2}\right]^{V}_{V'} . \tag{21.18}$$

The transition probability is independent of the rotational quantum numbers except for the factor 2J' + 1. This can also be demonstrated in a different manner.[14]

The quantity $\left[\gamma^{2}\right]^{V}_{V'}$ vanishes for the Rayleigh line and for the totally symmetric vibrational lines due to the spherical symmetry of a, and there will be no rotational structure. The remaining lines possess rotational structure, and from (21.18) and (21.16), we obtain

$$\frac{I^{VJ}_{V'J'}}{I^{V}_{V'}} = 1/5 \, \frac{(2J+1)(2J'+1)\exp\left(-BJ(J+1)/kT\right)}{S(T)} . \tag{21.19}$$

The interaction between vibration and rotation may be treated like that for the symmetric rotor. For a detailed treatment of the spherical and asymmetrical rotors, papers by Placzek and Teller should be consulted.

A number of experimental data will now be presented. The rotational structure of the Rayleigh line was resolved for several diatomic molecules, such as H_2,[15] N_2,[16] O_2,[16] HCl,[17] and CO,[18] and for the polyatomic molecules CO_2,[19] and NH_3.[20] The rotational structure of the vibrational lines was resolved for H_2,[15] CH_4,[22] and NH_3 (in aqueous solution).[23] In all cases except for NH_3, the experiments were conducted on the gases.

Figure 17 shows the rotational Raman spectrum of N_2 reported by Rasetti. The distinct alternation of intensity is due to the nuclear spin of the N atom, and accounts for the fact that levels with even and odd J values have different weights. The present example indicates that the even rotational levels have the higher weight. Figure 17 demonstrates that the line interval between the strong rotation lines is larger than that between the first strong line and the exciting line. From (21.6) it follows that the frequency ν^{J}_{J-2} is equal to 2B/h (2J - 1). For even values of J, the frequency of the first line, ν^{2}_{0}, is 6B/h, which is smaller than the line interval 8B

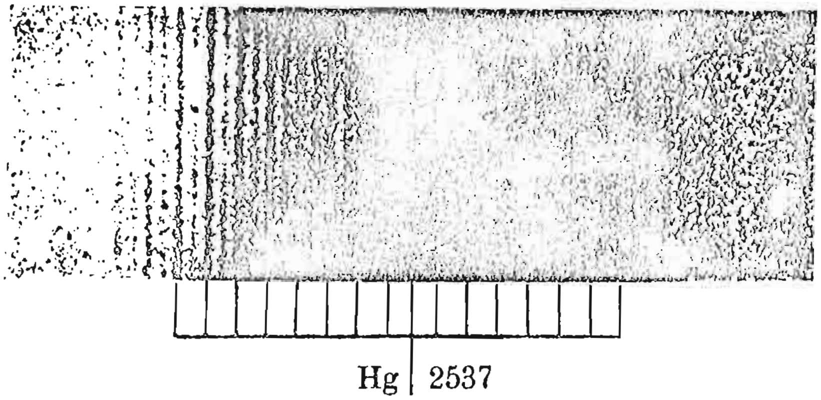


Fig. 17. Rotational Raman spectrum of nitrogen (per F. Rasetti).

but larger than that for odd values, ν_1^3 equals 10B/h. Since N_2 has even J's, the strong lines correspond to transitions between even values for J. Nitrogen obeys the Bose-Einstein statistics because of its even values of J and Σ_g^+ electronic ground state. The significance of this in nuclear physics has been discussed by Beck. The measurements by Rasetti made it possible to determine more accurately the moments of inertia and the interatomic distance of N_2 in the electronic ground state. This had not been accomplished earlier because the homopolar nitrogen molecule is infrared inactive. The electronic transitions arising from the ground state have not been analyzed due to their unfavorable location in the far-infrared. In a similar manner, the Raman spectrum of O_2 conformed to the Bose-Einstein statistics and nuclear spin of zero.

Bhagavantam investigated the intensity of the spectrum of H_2;[24] only his quantitative results obtained by means of optical density measurements will be discussed: 1) the intensity of a series of rotational lines; 2) the intensity of the perpendicular components of the rotational line V = 0, J = 1 → V = 0, J = 3, and of the Q branch V = 0 → V = 0, J → J (unshifted line); 3) the intensity of the perpendicular component V = 0, J = 1 → V = 1, J = 1. For the vibrational line 0 → 1, the lines of the Q branch do not overlap exactly; they may be resolved due to the vibration-rotation interaction. Table XVI summarizes the measured intensities (in arbitrary units) of the rotational lines for the vibrational transition 0 → 0. For comparison, values at 30 °C

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were calculated by means of (21.15) and (21.15a), having recourse to the weight factor for spin 1/2 and the Fermi statistics (odd rotational levels in the ratio 3 : 1). The first line was used as fiduciary point.

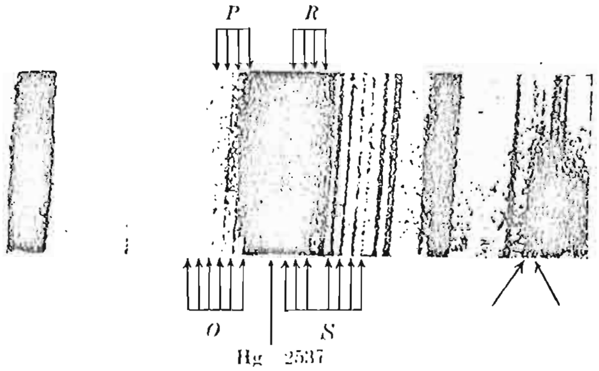

Fig. 18. Raman spectrum rotations of NH_3 (per Amaldi and Placzek). The two arrows at the right show the vibration doublet 933.8, 964.3, whose splitting is caused by the two possible equilibrium positions of the N-atom (see Chap. 20, Sec. 4).

The observed and calculated values agree fairly well. However, Bhagavantam reported to have observed discrepancies between the theory and his experimental results of 2) and 3), accepting them in confirmation of the theory of "photo spin" advanced by Raman and Bhagavantam.[25] Actually, the disparity is largely due to the error in applying the uncorrected formulae of Manneback. The inconsistencies will be further discussed below. Raman and Bhagavantam's theory stipulates that classically, as well as quantum mechanically, the selection rules for the scattering process are independent of the rotation of the scattering molecules. The particle concept of the scattering process of collision between spinning photon and molecule would require such a dependence. Hence, the classical and quantum theories of the scattered radiation must be modified. The applicability of the "photon spin" concept is limited by the uncertainty principle, but the results are implied in quantum mechanics. Raman and Bhagavantam's error originates already in the classical theory. If the incident light is separated into right and left circularly-polarized components (This corresponds to the right and left photon spins of the particle concept.), it can be shown that for the components of the example chosen by Raman and Bhagavantam the selection rules depend classically on the rotation of the molecule. Hence, the modification of the scattering theory suggested by the Indian authors is unjustifiable.

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Table XVI

Intensities of the Rotation Spectrum of H_2 (Bhagavantam).

J	J'	Observed	Calculated
0	2	0.67	0.67
2	0	0.13	0.12
1	3	2.0	2.1
3	1	0.13	0.12
2	4	0.30	0.32
4	2	-	0.006
3	5	0.21	0.23
4	6	-	0.010

A comparison between the results of Bhagavantam and those obtained with the correct expressions (21.15) and (21.15a) indicates a discrepancy smaller by a factor of two in the latter instance. Since the polarized trace scattering does not contribute to the scattering components, the total scattering intensity is given by (21.15) and (21.15a) as

$$\frac{I_{\perp}(V:0\rightarrow 0,\ J:1\rightarrow 3)}{I_{Q\perp}(V:0\rightarrow 0)} = \frac{9g_J b^{10}_{30}\exp(-2B/kT)}{\sum_J (2J+1)g_J b^{J0}_{J0}\exp\left(-BJ(J+1)/kT\right)} = 1.22 \qquad (21.19a)$$

$$g_J = \begin{matrix} 1 & \text{for J even} \\ 3 & \text{for J odd,} \end{matrix}$$

and for the vibrational line, we have

$$\frac{I_{\perp}(V:0\rightarrow 1,\ J:1\rightarrow 3)}{I_{\perp}(V:0\rightarrow 1,\ J:1\rightarrow 1)} = \frac{b^{10}_{30}}{b^{10}_{10}} = 3/2 = 1.5. \qquad (21.19b)$$

Bhagavantam obtained numerical values of 0.43 and 0.65 for (21.19a) and (21.15b), respectively, and, consequently, a higher relative intensity of the Q branch than predicted from theory. The various sources of error (for example, the incomplete elimination of the more intense parallel component) account for the intensity of the Q branch. On the microdensitometer trace, the lines V : 0 → 1, J : 1 → 1 and V : 0 → 1, J : 2 → 2 are not resolved, resulting in incorrect intensity values. An independent check of these difficult measurements would be of considerable interest. It has also been reported that the spectrum of liquid H_2 exhibits rotational structure.[26]

Houston and Lewis succeeded in resolving the rotational structure of the Rayleigh line of CO_2. In accord with the selection rules, branches with $\Delta J = 0, \pm 2$ exist (the odd rotational levels are absent because the oxygen nucleus has zero spin).[27] The moment of inertia was computed from the line interval, and the position of the most intense line agrees with the calculated one. This applies likewise to the data published by Rasetti. The rotational structure of the vibrational lines in CO_2 and N_2O was investigated by Langseth and J. R. Nielsen.

The spectrum of CO_2 shows two strong lines and two satellites (see Fig. 14), both having unresolved O and S branches. The same observation was made for the corresponding lines ($00_0 \rightarrow 10_0$ and $00_0 \rightarrow 02_0$) of N_2O. In addition, very weak lines occur which Langseth and Nielsen interpreted as rotation branches of the overtone $00_0 \rightarrow 02_0$. The Q branch in the CO_2 spectrum is missing, although it is predicted from the intensity expressions ($\Delta K = 2$); it is observed in N_2O. There is no obvious reason for this behavior because the relative intensities of the branches for CO_2 and N_2O are identical; thus, some doubt remains as to the assignment of these weak lines.

A study of the rotational structure of the degenerate vibrations in H_2O and C_2H_2 would be of interest, as the intensity expressions predict a weak Q branch. The two fundamentals have not yet been detected in the Raman effect.

Figure 18 presents the rotational Raman spectrum of NH_3.[28] An alternation of intensities is observed, as in the case of N_2, but here it is not a result of nuclear spin. The nonlinear NH_3 molecule has O and S, as well as P and R branches. Each second line of the latter coincides with a line of the O and S branches, thereby increasing their intensity. In addition, line intensities of the P and R branches fall off faster than those of the O and S branches. The lines $\Delta J = 1$ originate (see (21.6)) from higher-excited, and therefore less-populated, rotational levels than do the adjacent ones with $\Delta J = 2$. The complexity of the spectrum and the positions of the strongest lines are in qualitative agreement with the intensity distribution calculated according to (21.14) by summing over K. The rotational structure of the totally symmetric vibrational line 3333 cm^{-1} was investigated in aqueous solution by Langseth,[29] and by Williams and Hollander.[30] Langseth observed several lines, forbidden by the selection rules ($\Delta K \neq 0$), but not detected by Hollander and Williams.

In the spectrum of methane, Dickinson-Dillon-Rasetti examined a series of rotation-vibration lines associated with the threefold-degenerate frequency 3020 cm^{-1}. The angular momentum of the vibration and the moment of inertia may be deduced by comparing the line interval with that in the infrared band. One obtains[31]

$$\zeta = 0.07 \text{ and } A = 5.3 \times 10^{-40}.$$

The totally symmetric vibrational line and the Rayleigh line do not possess rotational structure because of the cubic symmetry. Bhagavantam[32] furnished additional evidence for the Rayleigh line.

The Structure of the Unresolved Bands.

The rotational structure of heavy molecules cannot be resolved. On either side of the Rayleigh and Raman lines depolarized wings are noted. From evaluations of the intensity expressions for the Rayleigh line, it has been shown for the bands $\Delta K = 0$, that the line shape depends on the relative magnitude of the moments of inertia.[33]

The P(R) and S(O) branches do not give rise to separate maxima, but to a single maximum which, for $C/A > 0.2$ and for $C/A < 0.05$, appears as a sharp line and becomes broad for intermediate values.[34]

If B/kt and $B\beta/kt$ are each much smaller than 1, a symmetric line results (classical limiting case). When $(B/kt)^{1/2}$ is no longer small compared with 1, the intensities of the R and S branches increase at the expense of those of the P and O branches, while the intensity of the Q branch remains invariant. The latter changes only when B/kt can no longer be neglected.

The contribution of the Q branch to the total quadrupole scattering is given by the following expression, provided B/kt is much smaller than 1:

$$F_Q = 1/8\left[(2 + 21/\beta + 27/\beta^2) - (12/\beta + 27/\beta^2)(1 + \beta)^{1/2}\,\frac{\text{arc sinh}\,\beta^{1/2}}{\beta^{1/2}}\right]. \tag{21.20}$$

This quantity is plotted in Fig. 19 as a function of the ratio of the moments of inertia $C/A = 1/(1 + \beta)$. For the rotor, F_Q has a value of 0.25, decreases rapidly with increasing C/A, goes through a minimum (0.169) for C/A = 0.3, assumes a value of 0.20 for the spherical rotor, and increases to 0.254 for a planar structure (C/A = 2).

The trace scattering contributes to the intensity of the Q branch, but it does not contribute to the remaining branches. Consequently, the depolarization factor $\rho_n(Q)$ of the Q branch is lower than that of the total line (band) ρ_n. One obtains

$$\rho_n(Q) = \frac{F_Q \rho_n}{1 - 7/6\,(1 - F_Q)\rho_n} .$$

Raman and his co-workers attempted a comparative study between $\rho_n(Q)$ and ρ_n, assuming that $\rho_n(Q)$ could be deduced from polarization measurements made by using narrow spectroscopic slits.[35] For linear molecules, they reported a smaller decrease in the depolarization factor than would be expected from a value of 1/4 for F_Q, and concluded that the theory should be modified by including the photon spin. A value of 1/4 for F_Q is calculated from Manneback's theory of diatomic molecules. The question concerning the contribution of the remaining rotational branches to the Q branch while using the given narrow spectral slit widths has not been discussed by these authors. Moreover, the data do not constitute quantitative measurements because the exposure times varied widely.

A quantitative procedure for the comparison between $\rho_n(Q)$ and ρ_n could prove to be a worthwhile project. Sources of error, such as the dependence of instrument polarization on the spectral slit width, would have to be taken into account.[36] Then, it might be possible to estimate the moments of inertia even when the rotational structure could otherwise not be resolved.

Among the studies on the rotational broadening of scattered lines are those by Weiler[37] and Trumpy;[38] the measurements were performed on liquids. This makes a comparison with theory rather tenuous because the premises of the theory applicable to free molecules break down. Aside from other factors causing line broadening, hindering of free rotation may induce changes in the intensity distribution of Raman lines; further experiments are required to clarify this point. The studies on liquids disclose a line broadening which is more extensive than that of free molecules.

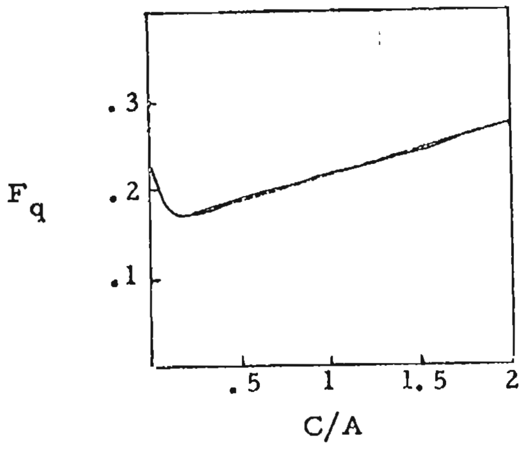

Fig. 19. Contribution of the Q branch to the total intensity of the quadrupole (anisotropic) scattering.

REFERENCES AND FOOTNOTES

1. Primed and unprimed coordinates refer to a body-fixed and space-fixed coordinate system, respectively. These designators cannot be mistaken for primed quantum numbers denoting the final state.

2. An angular momentum due to the electrons exists only for a degenerate electronic state (II-, Δ-state). However, these cases have been excluded from the start.

3. Placzek and Teller, Z. Physik 81, 209 (1933). This article should be consulted for more details. Diatomic molecules were treated classically by Cabannes and Rocard (J. phys. et radium 10, 52 (1929)), by S. Bhagavantam (Indian J. Phys. 6, 331 (1931)), and quantum theoretically by Manneback (Z. Physik 62, 224 (1930); 65, 574 (1930)). Houston, Phys. Rev. 41, 263 (1932); Condon, Phys. Rev. 41, 759 (1932), presents a correlation with the statistical case.

4. This constant, defined by Placzek and Teller, differs by a factor (2J + 1).

5. These relations exist between the components with the same $\lambda' + \mu'$.

6. The vibrational frequency must be added to the vibrational bands.

7. This factor is included in the partition function.

8. These statements apply when the electronic eigenfunctions are symmetric with respect to the symmetry operations, and when the rotations in space are equivalent. It applies to the states Σ_g^+ and Σ_u^-.

9. D. M. Dennison, Rev. Mod. Phys. 3, 280 (1931).

10. Placzek and Teller, loc. cit.

11. No additional data are given in this instance. The selection rules are

$\ell = 0 : \Delta K = 0$ (∥ - bands),
$\ell = 1 : \Delta K = 1$ (⊥ - bands).

The vibrations $\ell = 2$ are forbidden, and the bands $\ell = 1$ have the same line intervals as in the Raman effect.

12. It can be shown that for the linear molecule the quantities ξ in (21.11) become unity.

13. The expressions given by Manneback (Z. Physik 62, 224; 65, 574 (1930)) are identical with (21.15a) except for the Q branch. This expression was inadvertently omitted, according to private communication from Manneback.

14. Placzek and Teller, loc. cit.

15. F. Rasetti, Phys. Rev. 34, 367 (1929); S. Bhagavantam, Indian J. Phys. 6, 319 (1931).

16. F. Rasetti, loc. cit.; Proc. Nat. Acad. Am. 15, 515 (1929); Z. Physik 61, 298 (1930).

17. R. W. Wood, Phil. Mag. 7, 744 (1929); R. W. Wood and G. H. Dieke, Phys. Rev. 35, 1355 (1930).

18. E. Amaldi, Z. Physik 79, 192 (1932).

19. Houston and Lewis, Proc. Nat. Acad. Am. 17, 229 (1931).

20. Amaldi and Placzek, Z. Physik 81, 259 (1933).

21. A preliminary note by C. M. Lewis (Phys. Rev. 41, 389 (1932)) describes a series of other gases.

22. Dickinson-Dillon-Rasetti, Phys. Rev. 34, 582 (1929).

23. A. Langseth, Z. Physik 77, 60 (1932); Hollander and Williams, Phys. Rev. 42, 378 (1932).

24. S. Bhagavantam, Indian J. Phys. 7, 107 (1932).

25. C. V. Raman and S. Bhagavantam, Indian J. Phys. 6, 353 (1931).

26. I. C. McLennan and I. H. McLeod, Nature 123, 160 (1929); Trans. Roy. Soc. Can. III/3, 22, 413 (1928); 23, 19 (1929); McLennan, Smith, and Wilhelm, ibid. 23, 247, 249 (1929).

27. From the fact that the missing rotational levels are the odd ones it is concluded that the electronic ground state of CO_2 is either Σ_g^+ or Σ_u^-. (See Footnote 8).

28. Amaldi and Placzek, Z. Physik 81, 259 (1933).

29. A. Langseth, Z. Physik 77, 60 (1932).

30. Williams and Hollander, Phys. Rev. 42, 378 (1932).

31. Placzek and Teller, loc. cit.; Teller and Tisza, Z. Physik 73, 791 (1932).

32. S. Bhagavantam, Nature 130, 740 (1932); C. M. Lewis, Phys. Rev. 41, 389 (1932).

33. Placzek and Teller, loc. cit.

34. The exact discussion is rather complex. One must refer to the figures in the paper by Placzek and Teller. There, the dependence of the line shape and separation of the maxima on β has been examined.

35. C. V. Raman and S. Bhagavantam, loc. cit.; C. V. Raman and S. Venkatesvaran, Nature 128, 870 (1931).

36. Placzek and Van Wijk, Z. Physik 67, 582 (1931).

37. J. Weiler, Z. Physik 68, 782 (1931).

38. B. Trumpy, Kgl. Norske Viskens-Selsk. Forh. 5 No. 16 and 47 (1932).

Chapter 22. Fine Structure of the Scattered Radiation.

Aside from the rotations of molecules and intermolecular effects, there are other factors that contribute to the fine structure of the lines.

For instance, anharmonicity may cause frequency shifts of the vibrational Raman lines. If a large number of molecules are in the excited state at the temperature of the experiment, the corresponding transition frequencies do not coincide and a splitting occurs. This is well demonstrated by high-molecular-weight compounds at room temperature ($kT = 200\ \mathrm{cm}^{-1}$). Also, a broadening of the Raman lines has been observed for molecules having a number of low frequencies. An abnormally large splitting of the weak components of the CO_2 doublets has been observed.

In the case of structurally-similar weakly-coupled groups, the existence of many closely spaced frequencies gives rise to analogous effects. The fine structure of the spectrum of the hydrocarbons near $3000\ \mathrm{cm}^{-1}$ (the H atoms contribute largely to these vibrations) may be explained on this basis.

Partially-free-rotating groups may also cause a broadening of Raman lines. The vibrational frequencies of the molecules can undergo changes, depending upon the orientation of the rotating groups. Bartholome and Teller presumed that the large widths (10%) of the spectral bands of chain molecules observed by Collines[1] are the result of such a mechanism.

Isotope effects may also be reflected in structural changes of the lines. For diatomic molecules, the isotopic displacements are determined by mass differences; for polyatomic molecules, the relations are more complex. In case of symmetric molecules, aside from frequency shifts, removal of degeneracies may take place due to a reduction in symmetry. Langseth noticed a fine structure in CCl_4 and attributed it to an isotopic effect.[2] According to Gerlach, a weak component of the 992-cm^{-1} line in benzene may also be ascribed to an isotopic shift (a benzene ring containing a C_{13} atom).[3]

In doubtful cases isotope and anharmonicity splittings could be distinguished by means of temperature studies of the intensities of the fine-structure components. In addition, the Doppler effect may be mentioned as a cause for line broadening, but, in contrast to the previous factors, Doppler broadening is a function of the angle of observation. For the half-width of the Rayleigh line, we have

$$\delta = \nu_0\, 2 \sin \theta/2\, (2kT/mc^2 \ln 2)^{1/2}. \qquad (22.1)$$

The same expression applies to the Raman line, provided the Raman frequency is small compred with ν.

REFERENCES AND FOOTNOTES

1. Collins, Phys. Rev. 40, 829 (1932).
2. A. Langseth, Z. Physik 72, 350 (1931).
3. W. Gerlach, Ber. Bayr. Akad. Wiss. 39 (1932).

Chapter 23. Scattering Spectra and Intermolecular Force Field.

A great number of papers on Raman spectra deal with interatomic forces and their dependence on chemical substitution. Because this problem is concerned with the theory of molecular structure and only indirectly with the theory of scattered radiation, it will not be discussed in great detail. A thorough treatment may be found in the book by Kohlrausch;[1] among the publications that have appeared since that time are those by Mecke,[2] Urey and Bradley,[3] Redlich and co-workers,[4] and Bartholome and Teller.[5]

A brief outline is presented here. The force field of the molecule in its equilibrium position is expressed in terms of the coefficients in the potential-energy expression

$$V = 1/2 \sum_{rs} \sum_{ik} a_{ik}^{rs} x_i^r x_k^s, \tag{23.1}$$

where x_i^r is the i^{th} component of the displacement of the r^{th} atom from its equilibrium position. The coefficients are not independent; rather, they are related by

$$a_{ik}^{rs} = a_{ki}^{sr}.$$

This results in $3n(3n+1)/2$ independent constants, where n refers to the number of atoms in the molecule. In the absence of an external field, the number of constants is reduced to $(3n - 6)(3n - 5)/2$ which is further reduced by any existing symmetry. The relations between the quantities a_{ik}^{rs} and the frequencies are obtained by introducing normal coordinates. Equation (23.1) takes the form

$$V = 1/2 \sum_j 4\pi^2 \nu_j^2 q_j^2.$$

Since, generally, there will be $(3n - 6)$ frequencies, the force field cannot be determined from the frequencies alone; $(3n - 6)(3n - 7)/2$ coefficients will remain undetermined.

The selection of the normal coordinate depends on the type of vibration, and the relative displacement of the atoms depends on the force field. If, for a given symmetry type, there exists only one vibration, then it is possible to establish the form of the vibration from its symmetry. By means of the frequencies, the force field can be established for those molecules only that possess a single vibration of a given vibration type. The CO_2 molecule is one of the few of such examples. One can attempt a comparison between observed and calculated frequencies, provided several force fields are assumed.[7] If improbable forces (such as interactions between distant atoms) are ignored, the observed frequencies may be computed in different ways. Therefore, any conclusions must be treated cautiously.

The same is true for assignments of frequencies to specific groups or bonds. Many frequencies are altered but slightly by different chemical substituents, although this may be due to the fact that vibrations of different symmetry types do not interact, or due to specific dynamic conditions.[8] These exist in some molecules while others may show a mixing of vibrations accompanied by frequency shifts. Hence, these shifts cannot always be interpreted as the result of changes in the force field.

The investigations of force constants can be carried out experimentally by means of the fine structure of the vibrational lines in the Raman and infrared spectra, making use of isotope effects and rotational structure of the vibration bands. The isotopic shift of a vibration line is proportional to the contribution of the isotopes to the total kinetic energy of the vibration.[9] Hence, the relative amplitudes of the atoms for specific vibrations can be determined, and the vibration type for the known frequencies gives the remaining potential constants in Eq. (23.1). A closer examination of the isotope effect can yield interesting results. Particularly, if sufficient quantities of the recently discovered H_2 isotope were available, isotopically-substituted molecules could be prepared and used to great advantage.

Furthermore, the interaction between vibration and rotation is a function of the interatomic force field. The characteristic quantities, ξ_t, can be derived from the rotational fine structure, yielding additional data. By means of this method, a calculation of the force field has been successfully carried out for the molecule CH_4.[10]

The coefficients a_{ik}^{rs}, which determine the potential-energy distribution, are associated with energy changes accompanying changes in the interatomic distances. Hence, they characterize the stiffness of the bonding, rather than the bonding energy, the latter being obtained from the dissociation energy.[11] The force constants give an indication of the nature of the chemical bonding. A purely polar bond gives rise to a central force field, while large ionic polarizabilities lead to deviations from such a force field. In contrast, homopolar bonds imply directional forces. The relation between force field and the nature of bonding constitutes one of the many unsolved problems of quantum chemistry.

REFERENCES AND FOOTNOTES

1. Kohlrausch, Der Smekal-Raman Effekt (Berlin (1931)).

2. R. Mecke, Leipzig Lectures (1931), 23; Z. phys. Chem. (B) 16, 409, 421; 17, 1 (1932).

3. Urey and Bradley, Phys. Rev. 38, 1969 (1931).

4. Redlich, Kurz, and Rosenfeld, Z. phys. Chem. (B) 19, 231 (1932).

5. Bartholome and Teller, Z. phys. Chem. (B) 19, 366 (1932); W. F. Kohlrausch, ibid. 20, 217 (1933).

6. This may be seen by introducing into (23.1), in place of x_i^r which fixes the position of the atoms, the (3n - 6) displacements of the atoms in a coordinate system fixed in the molecule and the six displacements of this coordinate system with respect to a system fixed in space. As the potential energy is independent of the latter, the above number of independent coefficients may be obtained.

7. Since vibrations of different types of symmetry do not interact, normal coordinates can be introduced separately for each symmetry type, thereby simplifying the computations considerably. The observed frequencies must be classified according to symmetry species as well as possible.

8. Illustrative examples of organic chain molecules are given by Bartholome and Teller (loc. cit.).

9. Salant and Rosenthal, Phys. Rev. 42, 812 (1932), and Footnote 10.

10. The theory correlating the quantities ξ_t with the force field, and the general theory of the isotope effect of polyatomic molecules, will be discussed in a forthcoming article by Teller.

11. For the diatomic molecule, the shape of Franck's potential curve is given by the force constant (vibrational frequency of the ground state), and the height of the horizontal part of this curve is determined by the bond energy. A function of the stiffness of the bond, which takes into account differences in interatomic distances, has been derived by Mecke (Leipzig Lectures (1931), p. 23).

Chapter 24. Experimental Results and the Polarizability Tensor.[1]

The theory outlined above demonstrates that the scattering properties of a molecule are characterized by the polarizability tensor and its derivatives in terms of the normal coordinates.

A specific knowledge of these tensors is not essential for the derivation of selection rules, polarization rules, and rotational structure. These properties can be derived from the symmetry of the system, and from a qualitative inspection the low intensities of the overtones can be predicted. However, symmetry considerations are inadequate for a theoretical understanding of the absolute intensity, for intensity distributions in the vibrational and Rayleigh lines, as well as for the depolarization factors of the Rayleigh and totally symmetric Raman lines of noncubic molecules. These problems require rigorous calculations involving the polarizability tensor, a task that has not yet been accomplished. Yet these tensors can be estimated empirically with the aid of intensity and polarization measurements.[2] A few experimental results are summarized here, and utilized in tensors calculations. Also, an attempt is being made to offer a theoretical interpretation.

1. Experimental Data.

The majority of these studies concerns the depolarization of the Rayleigh line.[3] Table XVII presents the depolarization factors of the Rayleigh lines of several molecules. The measurements on gases were performed with instruments of insufficient spectral resolution. Although the vibrational Raman lines were observed, their intensities were too faint to exert a marked influence on the value of ρ_n.

The first three columns show results obtained by Cabannes,[4] Rao,[5] and Partharasathy,[6] which are believed to be the most accurate ones available at this time. Cabannes[7] published a summary and a discussion of additional measurements.

The fourth column lists the most probable values for the depolarization factors; the original data given by Cabannes were slightly changed in view of the later data by Partharasathy, and question marks are affixed wherever major discrepancies appear.

One should consult the examples cited in the tables of Chapter 19 to obtain an estimate of the magnitude of the depolarization factors for totally symmetric vibrations. The contribution of the vibrational Raman effect to the total has been largely investigated for gaseous systems and is essentially

Table XVII

Depolarization (100 ρ_n) of the Total Scattering of Some Molecules in the Gaseous State.

	Cabannes	Rao	Partharasathy	Most Probable Values
N_2	3.75	3.57	3.55	3.6
O_2	6.45	6.42	6.50	6.5
Cl_2	-	4.37	4.07	4.2
H_2	2.2	2.74	2.57	2.6
HCl	-	0.66	0.71	0.7
HBr	-	-	0.84	0.8
HI	-	-	1.27	1.3
CO	1.7	-	1.30	1.5
CO_2	9.8	9.7	9.72	9.7
CS_2	-	11.1	-	11.1
N_2O	12.2	12.0	12.47	12.5
SO_2	-	4.1	3.11	3.6 (?)
H_2O	-	1.99	-	2.0
H_2S	-	-	0.93	0.9
NH_3	-	1.31	0.98	1.1 (?)
CCl_4	0.77	0.50	0.62	?
CH_4	1.5	-	1.12	?
C_2H_6	1.6	-	1.30	1.4 (?)
C_2H_4	-	-	2.92	2.9
C_2H_2	-	-	4.52	-
C_6H_6	4.20	4.2	-	4.45

of qualitative nature.[8] Studies on diatomic and triatomic molecules reveal that the Raman line intensity is of the order of a few thousands of the total radiation.[9] Similar results have been recorded for liquids, whose contribution is considerably higher than that of gases.[10,11] The coherent part of the Rayleigh scattering is reduced by interference effects of the molecular scattering. Liquid data may be converted to comparable gas data by substituting the empirical relation between the scattering intensities of gases and liquids in the expression for the total scattering. The vibrational-line intensities are assumed to be proportional to the density, although the intensity distribution in the vibrational spectrum has not been investigated sufficiently.[12] Most papers are concerned with intensity relations between Stokes and anti-Stokes lines (see Chapter 25), while accurate relative intensities of vibrational lines are lacking. Values reported by Dawe and Carrelli, and West show wide discrepancies which can be attributed to inconsistent measurements of the variable line widths.

Measurements of absolute intensities could aid in the determination of the absolute scattering cross sections and tensors.[13] However, more accuracy may be attained by calculating average polarizabilities from refractive indices.

2. Principal Axes and Numerical Values of the Polarizability Tensor.

We shall discuss next the calculation of the principal axes of the tensor α and $(\partial^n\alpha/\partial q^n)$, from the depolarization factors of the Rayleigh and totally symmetric Raman lines, respectively. Only axially-symmetric systems will be considered, so that the orientation of the axes is determined by the symmetry relation $c_x = - c_y$.

According to (15.10) and (15.10a), we have

$$\gamma^2 = (\alpha_z - \alpha_x)^2$$

$$a = 1/3\ (\alpha_z + 2\alpha_x).$$

If the principal values of the tensors α and $(\partial\alpha/\partial q)$ are described by c_z and $c_x = c_y$, then, for the Rayleigh and Raman lines, it follows from (15.11) that

$$\rho_n = \frac{(1 - c_x/c_z)^2}{2 + c_x/c_z + 9/2\ (c_x/c_z)^2}\ . \qquad (24.1a)$$

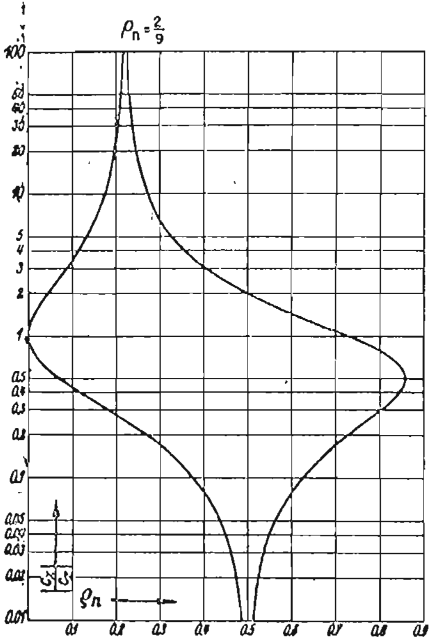

Fig. 20. Depolarization factor plotted against the ratio of tensor components for axial symmetry.

Figure 20 shows a plot of the ratio of the principal axes versus the depolarization factor; the quantity c_x/c_y is plotted on a logarithmic scale along the ordinate. The left curve corresponds to positive, the right to negative values of c_x/c_y. For the Rayleigh line we are restricted to the left curve since the diagonal elements of the tensor are necessarily positive ($\rho_n < 1/2$). There are two possible values of c_x/c_y for each one of the depolarization factors. One value is obtained for ρ_n greater than 2/9 of a Rayleigh line as the right curve is absent. The polarizability ellipsoid will be an oblate rotation ellipsoid.

If the depolarization factor of a Raman line is close to 2/9 or 1/2, an unequivocal assignment is possible. One ratio will yield a value that is excluded on physical grounds. If ρ_n is smaller than 2/9, the polarizability for the particular vibration changes along both principal directions in the same sense; if ρ_n is greater than 1/2, the principal values change in the opposite sense. The former is observed for the totally symmetric vibration 992 cm^{-1} of benzene ($\rho_n = 0.07$), both possibilities exist for the intermediate values of ρ_n.

The depolarization factor is insensitive to small deviations from isotropy, as may be seen from Fig. 20. A 1% depolarization may correspond to a 30% difference in the values of the principal tensor components. On the other hand, isotropic molecules may exhibit an apparent anisotropy due to impurities or incomplete correction for converging incident light.

The approximate relation between the depolarization of the Rayleigh line and the Kerr constant[14] may be used in deducing ambiguous cases. For gases of moderate density ($n - 1 << 1$), the Kerr constant (see definition in the paper by Debye-Sack, Eq. (140)) is

$$K_e = 3\pi N(\Theta_1 + \Theta_2), \tag{24.1}$$

where N refers to the number of molecules per cubic centimeter. According to Eq. (136) of Debye-Sack, Θ_1 and Θ_2 are given by the following expressions:

$$\Theta_1 = \frac{-1}{45\,kT}\left[(a_1 - a_2)(\beta_{11} - \beta_{22}) + (a_2 - a_3)(\beta_{22} - \beta_{33}) + (a_3 - a_1)(\beta_{33} - \beta_{11})\right]$$

$$(24.2)$$

$$\Theta_2 = \frac{1}{45\,k^2T^2}\left[(a_1 - a_2)(\mu_1^2 - \mu_2^2) + (a_2 - a_3)(\mu_2^2 - \mu_3^2) + (a_3 - a_1)(\mu_3^2 - \mu_1^2)\right],$$

where μ_i denotes the components of the dipole moment, a_i the diagonal elements of the optical polarizability tensor, and β_{ii} the components of the statistical polarizability tensor in the directions of a_i. The directions of the principal axes of the two tensors coincide when the molecule possesses rhombic or higher symmetry. If dispersion is neglected and β_{ii} is equal to a_i, according to (24.2), (15.10a), and (15.11), we obtain

$$\Theta_1 = \frac{2\gamma^2}{45\,kT} = \frac{2a^2}{kT}\,\frac{\rho_n}{6 - 7\rho_n}. \tag{24.3}$$

Expressing the mean value of the polarizability in terms of the refractive index $(n - 1) = 2\pi Na$, we obtain,

$$\Theta_1 = \frac{(n - 1)^2}{2kT\pi^2N^2}\,\frac{\rho_n}{6 - 7\rho_n}. \tag{24.3a}$$

For nonpolar compounds having $\Theta_2 = 0$, the following expression holds:

$$K_e = \frac{3}{2\pi kT}\,\frac{(n-1)^2}{N}\,\frac{\rho_n}{6-7\rho_n}\,. \tag{24.4}$$

Attempts have been made to improve the accuracy of (24.3a) and (24.4) by replacing $(n-1)^2$ with $(n-1)(n_\infty - 1)$. The quantity n_∞ is identical with the statistical dielectric constant for nonpolar compounds; for polar substances it may be determined by extrapolating the dielectric constant to $T = \infty$. This procedure assumes that the change of each polarizability component is proportional to the dispersion, whereas, generally, no reason for such an assumption exists.

The difference between statistical and optical polarizabilities arises from the effects of the ultraviolet (electronic polarization) and infrared (atomic polarization) absorptions. The former lowers the statistical polarizability components relative to the optical ones, while the latter raises them. The above assumptions are tenable if the ultraviolet absorptions affected the optical and statistical polarizabilities equally, percentage-wise, and if the absorption regions could be replaced by sharp single bands. However, this usually does not occur. The contribution of the infrared absorptions to the individual statistical polarizability components is independent of the magnitude of these components; they are determined essentially by the ultraviolet transitions, provided the dispersion is assumed to be small.[15] Since there is no theoretical basis for such a functional dependence, expressions (24.3a) and (24.4) should be employed directly. The experimental and calculated data differ, particularly in the case of molecules having small depolarization factors due to the inaccuracy of the ρ_n data. For molecules whose depolarization factors are higher, such as for CO_2 and CS_2, the magnitude of the derivatives seems to fall outside the experimental error.

The situation is simplified considerably for systems having axial symmetry, thus permitting a more rigorous treatment. One obtains:

$$K_e = \frac{2\pi N}{15kT}(a_z - a_x)\left[\frac{\mu^2}{kT} + (\beta_z - \beta_x)\right]$$

$$K_e = \pm\frac{n-1}{5kT}\left(\frac{5\rho_n}{6-7\rho_n}\right)^{1/2}\left[\frac{\mu^2}{kT} + (\beta_z - \beta_x)\right],$$

where the signs + and - apply to $(a_z > a_x)$ and $(a_z < a_x)$, respectively. Here, $\mu_x = \mu_y = 0$, $a_x = a_y$, and $\rho_x = \rho_y$.

Since the dipole and anisotropic parts of K_e depend differently on the temperature, $(\alpha_z - \alpha_x)$ and $(\beta_z - \beta_x)$ may, in principle, be determined from Kerr constants of dipolar molecules. With the aid of additional data on n and n_∞, the optical and statistical polarizability ellipsoids can be evaluated uniquely, while the value for ρ_n can serve as a check. Very few temperature studies on the Kerr effects have been reported. Since the dipole part is greater than the anisotropic part, the sign of the Kerr constant is fixed by the quantity $(\alpha_z - \alpha_x)$. Hence, a knowledge of the Kerr constant removes the ambiguity in the determination of the principal axes from the depolarization factor when ρ_n is less than 2/9 (see Fig. 20).[16] In this manner, the polarizability ellipsoid for HCl, CH_3Cl was found to be prolate, and that for $CHCl_3$ oblate.[17] In the absence of axial symmetry, the polarizability ellipsoid cannot be established unequivocally without specific assumptions.[18]

3. Theoretical Computations of the Polarizability Tensor and its Dependence on Molecular Structure.

The exact calculation of the atomic polarizability tensor has been successful for the most simple cases only (see Chapter 12). The problem is more complicated for molecules and has not yet been accomplished satisfactorily. Unsöld attempted an evaluation of the mean value of the polarizability of H_2^+.[19] He treated the effect of a point charge on the polarizability as a function of its distance from the H atom, by means of perturbation calculation. Although quantitative agreement is not expected for distances of the order of the equilibrium distance, this method demonstrates qualitatively the decrease in polarizability of a negative charge cloud when penetrated by an H nucleus (or by a small cation). This effect should be of particular importance for the polarizability of alkali halides. The treatment could be improved by including exchange effects, which were neglected by Unsöld.

A computation of the polarizability ellipsoid of the H_2 molecule was recently attempted by Mrowka.[20] He considered discrete intermediate states only, without properly orthogonalizing the eigenfunctions. For the hydrogen atom, half of the f-values are in the continuum, and for the hydrogen molecule, which assumes a position between hydrogen and helium, the effect of the continuum is even more pronounced. Therefore, the agreement between the values calculated by Mrowka and the empirical data must be fortuitous. An accurate treatment of H_2^+ and H_2 would be of considerable interest since quantitative, reliable results, although laborious, are feasible with the proper mathematical apparatus.

For the more complex molecules the difficulties are mounting, so that the problem has to be reduced to an evaluation of the molecular polarizability tensor from atomic, ionic, and bond polarizabilities. An attempt was made by Silberstein who proposed the theory of the induced moments. The molecule is assumed to be composed of isotropic polarizable ions and the field affecting the individual ions is regarded as made up of the external field and the homogenous fields of the moments induced in the adjacent molecules (see the article by Debye-Sack). Then, one can derive an anisotropic molecular polarizability which depends on the position of the nuclei. The induced moments differ for the various ions because of their configurations, interatomic distances, and orientation of the molecules with respect to the external field. From these premises, the polarizability ellipsoid of molecules, the refractive indices, and the depolarization of the Rayleigh scattering were calculated using the ionic indices and distances.[21] Cabannes computed the classical limiting case of the Raman effect of a diatomic molecule for such a model.[22] Furthermore, the quantities that determine the intensity and polarization of the Raman effect of such a model may be obtained simply by differentiating the expression given by Debye-Sack (Handbook, VI, Part 2, p. 198).[23]

Since the idealized model of Silberstein is not supposed to yield quantitative, accurate results, molecules have to be investigated that warrant its qualitative application. It is necessary to restrict this model to heteropolar molecules because only these systems may be approximated by separated ions. For other types of molecules--for instance, CCl_4 and homopolar molecules--the penetration of the charge cloud and exchange effects are of major importance. If the ionic polarizabilities of heteropolar molecules are small compared with the ionic volumes, deviations from the assumed homogeneity of the induced dipole fields do not invalidate the results. The general application of the Silberstein model to organize molecules is theoretically unjustifiable on a qualitative basis.

The following factors are usually cited in favor of the theory: 1) It yields small values for the depolarization factor of the Rayleigh scattering, in agreement with experimental results (highest depolarization factor $\rho = 0.12$ for N_2O); theory predicts a maximum value of 0.5. 2) A depolarization factor independent of the chain length is predicted and substantiated by investigations on long-chain hydrocarbons. In addition, the predicted direction of the axis of maximum polarizability agrees with the results obtained from the Kerr effect for simple systems. 3) The mean polarizability is not a function of the interionic distances. The individual principal components could vary considerably, leaving the mean value unchanged. This would explain the observed additivity of the ionic refractive indices.

It should be mentioned that factors 1) and 2) are of such general character that they may be derived from different premises, rather than serve as confirmation of the Silberstein model. Large polarization factors for the Rayleigh scattering are associated with maximum ratios of the principal axes of the polarizability, but they are most improbable. The fact that the depolarization factor is independent of the chain length is due to the rapid decrease in interatomic effects with increasing distance. A similar argument applies to the direction of the axis of maximum polarizability in the few examples that have been studied experimentally.

With regard to the third factor, the very argument gives rise to the complete breakdown of the depolarization calculations for totally symmetric Raman lines.[24] The second-order dependence of the trace on the interatomic distances results in large depolarization factors for totally symmetric Raman lines. This is in sharp contrast to the low values usually observed. Cabannes and Rousset computed the value $\rho_n = 0.8$, for the totally symmetric vibrational line of $CO_3^=$, whereas the value observed was 0.2.

In view of the need for a practical and qualitative theory, it might be of interest to consider a homopolar, rather than heteropolar, molecule having individual bonds with associated anisotropic polarizabilities. The interaction of these bonds then must be treated according to the theory of induced moments. Such an approach appears promising and has been attempted by Otterbein, and Stuart and Volkman.[25]

For a quantum-mechanical model, the laws governing the bond polarizability ellipsoids must be investigated, as well as the changes upon stretching of the bonds. In terms of quantum mechanics, the bonds are groups of electrons which hold the molecule together. A closer study of the motion of the electrons in the two-center problem according to Hund is indicated. The higher levels, which are occupied differently for the various homopolar bonds (σ, π, single, double, etc.), should be examined also. For a simple π-bond, the axis of maximum polarizability is expected to be along the valence-bond direction. For slight perturbations due to adjacent atoms, the rotational symmetry is believed to be preserved.[26]

Without further investigations of this type, a few qualitative statements can be made. For example, Rayleigh lines of molecules like H_2S and NH_3 which are fairly similar to rare gases, and those of alkali halides are expected to possess a small depolarization factor. This has been confirmed experimentally (see Table XVII).[27] Also, it appears reasonable that the intensity of the Raman effect should be a function of the type of chemical bonding. In the case of heteropolar bonds, each electron is associated with an atom (ion) and is predominantly affected by one nucleus; hence, the polarizability will be less sensitive to interatomic distances than for homopolar bonds. Here, the valence electrons are shared between two atoms so that the electrons will be in the field of two nuclei, making the polarizability greatly dependent on changes in the interatomic distances. Molecules that differ only in their type of bonding are expected to show more intense displaced scattered radiation when they are homopolar than when heteropolar,[28] a fact substantiated by experiment.[29] Recently, an attempt was made to utilize the intensity of the Raman effect as a direct measure of the bonding character of the molecule.[30] However, there are additional factors that can affect the intensity since it varies with the type of vibration, even in the case of polarizabilities that have the same dependence on atomic displacements. Aside from symmetry and pseudosymmetry, the force field of the molecule and the masses of the vibrating atoms (larger zero-point amplitudes of the light H atoms) play an important role.

REFERENCES AND FOOTNOTES

1. The author is grateful to Dr. E. Teller for valuable assistance in the preparation of this and the following chapter.

2. This determination can be carried out rigorously in specific instances only; see below.

3. The unresolved scattered lines (inclusive of rotational structure) are referred to here as Rayleigh and Raman lines, as in Chapters 16 and 20.

4. Cabannes and Granier, J. Phys. 4, 929 (1928).

5. R. Rao, Indian J. Phys. 2, 61 (1927).

6. S. Partharasathy, Indian J. Phys. 6, 139 (1932).

7. J. Cabannes, La Diffusion Moléculaire de la Lumière.

8. S. Bhagavantam, Indian J. Phys. 6, 319, 557 (1931).

9. The H_2 molecule constitutes a special case, since a higher value is reported for it.

10. Daure, Ann. phys. 12, 375 (1929); Carrelli and Went, Z. Physik 76, 236 (1932).

11. For CCl_4, Daure reports a value of 3.7%, while Carrelli and Went give 6.2%.

12. A different, although incorrect, interpretation was offered by Carrelli and Went.

13. Compare Cabannes, La Diffusion Moléculaire de la Lumière.

14. This was pointed out originally by R. Gans, Ann. Physik 65, 111 (1921); Z. Physik 17, 356 (1923).

15. This assumption is untenable for polar diatomic molecules, because the infrared term contributes to the polarizability along the bond, and because the atomic polarization is completely anisotropic. Stuart computed the statistical anisotropy for HCl and found a value three times as large as that of the optical one (Ergeb. exakt. Naturwiss. 10, 159 (1931)). He used the quantity $(n - n_\infty)$ by neglecting the dispersion of the electronic polarization; the quantity $(n - n_\infty)$ would be slightly smaller if this were taken into account. Equation (24.3a) is no longer applicable to such systems, and a rigorous treatment must be carried out.

16. The statistical polarizability ellipsoid is also determined by means of (24.5); it does not require a knowledge of the temperature dependence of K_e. However, in most instances the experimental data are not sufficiently accurate.

17. H. A. Stuart, Ergeb. exakt. Naturwiss. 10, 159 (1931).

18. See Stuart, loc. cit.

19. A. Unsöld, Z. Physik 43, 653 (1927).

20. B. Mrowka, Z. Physik 76, 300 (1932).

21. Refer to J. Cabannes, La Diffusion Moléculaire de la Lumière, and H. A. Stuart, loc. cit.

22. J. Cabannes, Trans. Farad. Soc. 25, 813 (1929). J. Cabannes and Y. Rocard. J. phys. et radium 10, 52 (1929).

23. Placzek, Z. Physik 70, 84 (1931).

24. Cabannes and Rousset, Compt. rend. 194, 79 (1931); S. Bhagavantam, Indian J. Phys. 6, 557 (1932).

25. Debye-Sack, this handbook, p. 200; Footnote 2.

26. It appears less certain for other types of bonding, particularly for bonding, since the charge cloud is farther removed from the molecular axis, making an oblate polarizability ellipsoid feasible. If there is a unique plane through the molecular axis because of the presence of additional atoms, considerable deviations from rotational symmetry are expected, because the $\pi\sigma$ eigenfunctions in the plane are different from those perpendicular to it.

27. The depolarization factors for the tetrahedral molecules CH_4 and CCl_4 (see Table XVII) are of the same order of magnitude (within 1%). It is improbable that these depolarization factors arise from the vibrational lines, since they could have only 1/10 to 1/100 of this effect. The isotope effect on the depolarization factor of the Rayleigh line is of smaller magnitude (atoms of different masses posses unequal zero-point amplitudes). The distortion caused by the excitation of degenerate vibrational levels exerts a negligible effect and is completely absent in methane. The absence of rotational structure of the Rayleigh line constitutes an unambiguous confirmation of the isotropy of methane. It is interesting to compare this with the intense rotational spectrum of ammonia (Fig. 18); the depolarization factor is the same as for methane, although, according to the measurements of Kerr constants, the reported value of ρ_n of ammonia is rather high (compare Stuart, loc. cit.). These data indicate that the accuracy with which depolarization factors are measured is less than customarily assumed.

28. Placzek, Z. Physik 70, 84 (1931).

29. Braune and Engelbrecht, Z. phys. Chem. (B) 10, 1 (1930), 11, 409 (1931); 19, 303 (1932).

30. L. Hansen-Damaschun, Z. phys. Chem. (B) 22, 97 (1933).

Chapter 25. Phenomena Excluded by the Polarizability Theory.

1. Scattering Near the Region of Resonance.

The polarizability theory is valid provided the interval between incident and absorption frequency is large compared with the splitting of the electronic levels induced by nuclear vibrations. Moreover, it is assumed that the absorption regions associated with each electronic transition can be replaced by their center of gravity.

If the incident frequency is near an absorption band, the first process to occur is the one for which the frequency interval is small in relation to the width of the vibrational structure of the electronic band, but large relative to the width of the rotational structure of the individual electronic vibrational bands. Then the scattered radiation can no longer be expressed in terms of the dependence of the polarizability of the rigid molecule on the nuclear displacements. Since rotations may be neglected initially, the scattering amplitudes of a vibrating, non-rotating molecule are investigated. The rotational structure of the scattered lines may be obtained subsequently--as in the polarizability theory--by forming the matrix elements of the scattering amplitudes, using the rotational eigenfunctions. The amplitudes will depend on the spatial orientation of the molecules.

For the calculation of the scattering amplitudes, the expressions for the spontaneous transition amplitudes of the electronic vibrational transitions are inserted into the general equation for the scattering tensor, (5. 2). The spontaneous transition amplitudes are derived by considering the transition amplitudes for each electronic transition as functions of the nuclear displacements,

$$M_{nv'}{}^{0v} = (M_n{}^0)_0 \int U_{0v}\, U_{nv'}^*\, dq + \sum_j \left(\frac{\partial M_n{}^0}{\partial q_j}\right)_0 \int U_{0v}\, q_j\, U_{nv'}^* + \ldots \tag{25.1}$$

where U_{0v} denotes the vibrational function of the electronic ground state, and U_{nv} that of the excited state. When (25.1) is substituted into Eq. (45. 2), the latter reduces to the expressions of the polarizability theory, as long as the difference between the resonance denominators for the various vibrational transitions belonging to the same electronic state can be neglected. The frequency dependence of the scattering amplitude stems from the fact that the contribution of the individual electronic states to the scattering amplitude is a function of incident frequency.

In addition, the vibrational structure of the excited electronic levels can appreciably alter the relative intensities of the scattered radiation. Outside the region of resonance, these effects including terms of the order of $(q_j)^n$ and higher for a transition $\Delta v_j = n$ compensate each other. If the incident frequency increases to the extent that the resonance denominators for the vibrational intermediate levels differ markedly, this compensation no longer occurs. Then, the intensity distribution, where the intensity decreases rapidly with increasing vibrational quantum numbers, becomes a Franck-Condon intensity distribution of the resonance spectrum. Here, large changes in the vibrational quantum numbers also give rise to intense lines.[1] Simultaneously, the selection rules based on the power-series expansion of the normal coordinates (they are referred to as approximate rules in Chapter 18), rather than on general symmetry properties, lose their validity. Consequently, fundamentals of degenerate vibrations can give rise to isotropic scattering, thereby lowering the depolarization factor of the corresponding lines.

As was mentioned in Chapter 14, the scattering tensor outside the scope of the polarizability theory may contain an antisymmetric part, provided the symmetry condition is fulfilled. (This is not the case for diatomic molecules.) This condition leads to the appearance of magnetic dipole scattering which causes an increase in the depolarization factor, deviations from the relations given by (15.3), and new lines if the corresponding transition is forbidden for isotropic and quadrupole scatterings. The latter is demonstrated by the A_2 fundamental of the C_{4v} symmetry group. The scattering tensor remains symmetric in the approximations for which the polarizability theory is no longer applicable. It becomes symmetric again when the deviation in (25.1) is restricted to the constant term, which, in the immediate neighborhood of the resonance, is responsible for the major part of the scattered radiation. The effects described here are of secondary importance because of the reasons cited.

The formulae in Chapter 21 apply to the rotational structure of the quadrupole part. If the vibrational scattering tensor possesses an antisymmetric term, its dependence on the orientation of the molecule must be examined in the same manner as in the case of the symmetric part discussed in Chapter 21. Since an antisymmetric tensor transforms like an axial vector, and since there is no difference between polar and axial vectors under spatial rotations, the relative intensities of the rotational lines are identical with those of infrared bands and may be described by the Hönl-London formulae.[2]

The frequency dependence of the scattering amplitude in this region is rather complex. The direction cannot be given unambiguously, because the numerators of the individual terms in the sum of Eq. (5.2) possess different signs. If the resonance frequencies are higher than the incident frequencies, as is true in most experiments, it is possible that initially the scattering amplitude decreases with increasing incident frequency.[3] This possibility does not arise when the scattered radiation is coherent, and when, in the case that the incident frequency is much different from the resonance frequency, the electronic states are approximated by a center of gravity. For coherent scattering, the denominators in Eq. (5.2) must be positive when the axes of the polarizability are fixed by symmetry.

The frequency dependence of the Rayleigh scattering has not been studied experimentally; however, some indications can be obtained from atmospheric-extinction measurements.[4] Daure[5] and Sirkar[6] examined the frequency dependence of the displaced and undisplaced scattered radiation for a set of organic liquids. Direct measurements of the frequency dependence of vibration lines for organic molecules--mostly for liquids--have been reported by Ornstein and Rekveld,[7] Sirkar,[8] Werth,[9] and Ellenberger.[10]

Table XVIII presents data obtained by these authors for two Stokes lines of CCl_4. The intensities are referred to the Hg 5461-A exciting line. Sirkar, who used the Hg 4358-A line, achieved a reduction by relating his 4358 values to the average of those by Ornstein-Rekveld and Werth. Ellenberger's results are systematically higher than those of the other authors. It may be seen that for the 312-cm^{-1} line, the ν'^4 law is well observed in the visible region, while for the 459-cm^{-1} line, deviations are already apparent in the visible range. The question whether these are real or due to experimental error will not be discussed here, although the author believes the latter to be more likely. In the ultraviolet region there is a considerable increase in I/ν'^4 for both lines, indicating that the scattering amplitude is a function of frequency.

Analogous data are available for other substances.[11] The polarizability theory is not applicable to these studies; they can be interpreted in terms of the frequency dependence of the contributions of the electronic state, but the effect of the vibrational structure of the electronic states is not well understood.

Little experimental evidence for the frequency dependence of the depolarization factor is available; none has been observed in the visible range.

Table XVIII

Frequency Dependence of the Scattering Intensity of the CCl_4 Vibrational Lines 312 cm^{-1} and 459 cm^{-1}.

312 cm^{-1}			I				I/ν'^4			
Hg	ν'^4	O.-R.	W.	E.	S.	O.-R.	W.	E.	S.	Average[12]
5461	1	1	1	1	-	1	1	1	-	1
4358	2.44	2.47	2.48	3.41	(2.47)	1.01	1.01	1.40	(1.01)	1.01
4047	3.27	3.33	3.26	5.26	3.65	1.02	1.00	1.00	1.14	1.05
3132	9.01				15.1				1.68	1.68
3022	10.40				22.4				2.15	2.15
459 cm^{-1}										
5461	1	1	1	1	-	1	1	1	-	1
4358	2.43	2.14	2.15	3.50	(2.14)	0.87	0.88	1.48	0.87	0.87
4047	3.26	2.94	3.01	5.56	3.21	0.90	0.92	1.71	0.98	0.93
3132	9.00				13.8				1.53	1.53
3022	10.28				20.6				2.00	2.00

Krishnan and Sarkar, studying benzene vapor in the ultraviolet, noted a slight increase in the depolarization factor of the total radiation.[13] Theoretically, such studies are just as illuminating as those of intensities. Manneback pointed out that, as a result of the selection rule for diatomic molecules (in the Σ-ground state), the $\Sigma \rightarrow \Sigma$ transitions contribute to the parallel component of the molecule-fixed scattering tensor, while only the $\Sigma \rightarrow \Pi$ transitions contribute to the perpendicular component.[14] The depolarization factor ρ_n approaches 1/2 for a Σ intermediate state and 2/9 for a Π intermediate state if the incident frequency coincides with a region where the contribution of a single electronic state to the scattering amplitude predominates but where the rotational structure of the vibration levels does not affect it.

Intensity ratios of Stokes to anti-Stokes lines have been reported for the visible region only. Daure[15] measured chloro compounds; Ornstein and Rekveld[16] and Sirkar[17] studied CCl_4. The data by Sirkar agree well with expression (15.2) which is derived from the polarizability theory and from the ν'^4 law (see Chapter 8), whereas those by Ornstein and Rekveld deviate considerably.

Rotation Resonance. If the incident frequency is so close to the resonance region as to be comparable to the rotational frequency, further changes take place in the scattering spectrum. The vibrations and rotations can no longer be treated separately. The symmetry properties of the total eigenfunction determining the selection rules will give rise to additional vibrational bands. In the case of diatomic molecules, magnetic dipole scattering will appear and the intensity distribution in the rotational spectrum will be altered basically: from the distribution discussed in Chapter 21 and from the one formulated by Hönl-London, broadening of the sharp resonance develops gradually. The total rotational structure is reduced to a few lines and to a doublet in the case of diatomic molecules. Segré attempted to calculate the beginning of this transition for a diatomic molecule.[18, 19] Rasetti reported an experimental study of such a transition.[20] The depolarization factor indicates a strong dispersion in the transition region for the line $\Delta J = 0, \pm 1$, remaining independent of the incident frequency for $\Delta J = \pm 2$. In the latter instance only quadrupole scattering can occur, giving a value for ρ of 3/4 (see Table I).

For the sharp resonance case, the depolarization factor is a function of the J value of the initial, intermediate, and final states, as discussed in Chapter 7. The resonance spectrum of the iodine vapor shows a doublet $\Delta J = 0, +2$ and $\Delta J = 0, -2$.[21] The components $\Delta J = \pm 2$ have depolarization factors $\rho = 3/4$; for the components $\Delta J = 0$, the intermediate level $J + 1$ has (doublet $\Delta J = 0, +2$):

$$\rho = 1/2 \, \frac{J(6J + 7)}{4J^2 + 8J + 5} \; ; \qquad (25.2a)$$

and the intermediate level $J - 1$ (doublet $\Delta J = 0, -2$):

$$\rho = 1/2 \, \frac{(J + 1)(6J - 1)}{4J^2 + 1} \; . \qquad (25.2b)$$

Both expressions converge to $\rho = 3/4$ for high J values; in that case, the polarization of the two doublet components is practically identical. This has been confirmed by polarization measurements of Wood, who found $\rho = 0.71$ for both components.[22] However, the reversal constant differs significantly. For $\Delta J = 0$, $P = 6$, and for terms analogous to (25.2) and high values of J, P converges to $P = 1/6$. Hence, for circularly-polarized incident light, the component $\Delta J = 2$ shows reversal of polarization, while component $\Delta J = 0$ does not. The effect of nuclear spin of iodine on these processes will not be treated here.[23]

2. Degenerate Electronic Ground State.

The general relations have already been presented in Chapter 14. As an example, we choose a diatomic molecule in a $^1\Pi$ ground state. Analogous to Eqs. (18.11) and (21.8), the selection rules are

$$\Delta\Lambda = \lambda' + \mu', \tag{25.3}$$

where Λ denotes the angular momentum about the bond axis and is equal to ± 1 for a Π state. The coherent scattering of rigid molecules ($\Delta\Lambda = 0$), is described by the axially-symmetric polarizability tensor $\lambda' + \mu' = 0$. The incoherent scattering of the undisplaced radiation is associated with the transitions $\Lambda = +1 \rightleftarrows \Lambda = -1$, corresponding to the tensor $\lambda' + \mu' = 2(\lambda' + \mu' = -2)$.

For nonrigid nuclei, the intensity of the scattering line is determined by the dependence of the two tensors on the nuclear positions. It is necessary to set up the matrix elements of the two tensors from the nuclear eigenfunctions. Since the tensor $\lambda' + \mu' = 0$ possesses also an antisymmetric part (the component $c^a_{1',-1'}$), magnetic dipole scattering may appear.

The intensity of the rotational structure of the Rayleigh and vibrational lines can be evaluated by replacing K and K', in Eq. (21.11) and in Table XV, by Λ and Λ' (the electronic angular momenta about the figure axis), respectively. This results in a rotational structure containing all branches ($\Delta J = 0, \pm 1, \pm 2$). Transitions $\Delta\Lambda = 0$, $\Delta J = 0$ give rise to isotropic scattering, and transitions $\Delta\Lambda = 0$, $\Delta J = 0, \pm 1$, to magnetic dipole scattering whose intensity distribution is represented by the Hönl-London expression. These spectra exhibit P and R branches as well as magnetic dipole scattering, in contrast to those of diatomic molecules having nondegenerate electronic ground states.

The Λ-doubling affects the scattering spectrum also. Each rotational state splits into two substates, one even and one odd state (see Krönig, Chapters 18 and 20). The energetically-higher state, for consecutive values of J, is alternatively even and odd.[24] Only even (or odd) states combine in the scattering spectrum since the symmetry character alternates with J, causing a splitting of the rotational lines by an amount equal to twice the Λ-doubling for transitions involving $\Delta J = \pm 1$. There is no splitting for $\Delta J = 0, \pm 2$.[25]

The ground state $^2\Pi$ of NO can be treated analogously. Two types of Hund's interactions, a and b, may be distinguished (see Krönig, Chapter 14). Type a involves the coupling of spin Σ with the molecular bond. The spin combines with the orbital angular momentum Λ to form the total angular momentum Ω about the molecular axis. The $^2\Pi$ state splits into states $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ and the selection rule $\Delta\Omega = \lambda' + \mu'$ applies; moreover, $\Delta\Lambda = \lambda' + \mu'$ because of the small spin-orbital interaction.

Therefore, the following transitions are possible: $\Omega : \pm 1/2 \rightarrow \pm 1/2$; $\pm 3/2 \rightarrow \pm 3/2$; $\pm 1/2 \rightarrow \mp 3/2$. The first four transitions correspond to the undisplaced scattered radiation, the latter two represent radiation displaced by the doublet splitting. The rotational structure is identical with that of the $^1\Pi$ state,[26] except that here the transitions $\Delta\Omega = 0$ and $\Delta\Omega = \pm 2$ are accompanied by separate lines. For the $^1\Pi$ state, lines corresponding to the transitions $\Delta\Lambda = 0$ and $\Delta\Lambda = \pm 2$ overlap. For $\Delta\Omega = 0$ (undisplaced scattered radiation, i.e., vibrational line), one obtains $\Delta J = 0, \pm 1, \pm 2$, and because of the low Ω value, weak $\Delta J = \pm 1$ branches. As in the preceding example, isotropic scattering occurs when $\Delta J = 0$, and magnetic dipole scattering when $\Delta J = 0, \pm 1$. When $\Delta\Omega = 2$ (doublet splitting, or doublet splitting plus scattered displaced radiation corresponding to the vibrational frequency), quadrupole scattering arises, whose intensity is expressed by Eq. (21.11) upon replacing K by Ω. The intensities of all branches are of the same order of magnitude. The band corresponding to $\Delta\Omega = 2$ has a depolarization, $\rho_n = 6/7$.

Type b involves the interaction of spin with the angular momentum of the molecular rotation K, giving the total angular momentum J.[27] The energy depends on K only. There are two term systems, which differ by 2BJ (see Krönig, Chapter 17) but which do not combine because $\Delta\Sigma = 0$. As Λ is a quantum number, the above selection rule holds and the spectrum is analogous to that of the $^1\Pi$ state.

The rules discussed in types a and b no longer apply to transitions in cases between these two because of the selection rule $\Delta\Lambda = \lambda' + \mu'$. The restrictions imposed on the combinations of the Λ-doubling remain valid. The intensity distribution of the rotational lines in this intermediate region can be evaluated with the aid of a perturbation calculation.

The NO molecule, which presently constitutes the only example of a stable diatomic molecule having a degenerate electronic ground state, displays a term system closely resembling type a. Rasetti was able to identify, in the scattering spectrum, the Q-branch of the two transitions $\Delta\Omega = \pm 2$ ($^2\Pi_{1/2} \rightleftarrows {}^2\Pi_{3/2}$) and was able to partially resolve the rotational structure of the line $\Delta\Omega = 0$.[28]

REFERENCES AND FOOTNOTES

1. For a diatomic molecule, it might be of interest to investigate the transitions of the two limiting cases for different potential energy curves of Franck's type. The work by van Vleck (Proc. Nat. Acad. Am. 15, 754 (1929)) might serve as a good starting point.

2. H. Hönl and F. London, Z. Physik 33, 803 (1925); R. Rademacher and F. Reiche, Z. Physik 41, 453 (1927).

3. This possibility has been overlooked in an earlier paper by Placzek (Z. Physik 58, 585 (1929)). Therefore, the statements involving the direction of the frequency dependence of the scattering amplitudes are not generally valid.

4. J. Cabannes, La Diffusion Moléculaire de la Lumière.

5. P. Daure, Ann. phys. 12, 375 (1929).

6. S. C. Sirkar, Indian J. Phys. 5, 159, 593, 663 (1930).

7. L. S. Ornstein, J. Rekveld, Z. Physik 61, 719 (1930); J. Rekveld, Z. Physik 68, 543 (1931); Diss. Utrecht 1931.

8. S. C. Sirkar, Indian J. Phys. 6, 133 (1931).

9. M. Werth, Phys. Rev. 39, 299 (1932).

10. G. Ellenberger, Ann. Physik 14, 221 (1932).

11. It should be noted that the data are not always presented in a manner that permits a direct comparison with theory. For instance, Werth observed benzene spectra in the region between 4358 A and 3650 A and concluded that the scattered intensity is proportional to ν^4 (ν refers to the frequency of the incident light) with an accuracy of 1%. However, the fact that the expression for the intensity of the scattered light involves ν'^4 (ν' refers to the frequency of the emitted light) would mean that there is a deviation of about 10% from the theoretical ν'^4 limiting law. Rekveld, while studying methyl alcohol, noticed that the 2838-cm^{-1} Raman line obeys the ν'^4 law rather than the ν^4 law, the difference being beyond experimental error.

12. The values of Ellenberger have not been incorporated. They deviate systematically from those of the other authors.

13. K. S. Krishnan and A. Sarkar, Indian J. Phys. 6, 193 (1931).

14. Loc. cit.

15. P. Daure, loc. cit.

16. L. S. Ornstein and J. Rekveld, Z. Physik 57, 539 (1929).

17. S. C. Sirkar, Indian J. Phys. 6, 259 (1931).

18. E. Segré, Rend. Lincei 12, 226 (1930).

19. Here it is assumed that the difference between incident and resonance frequencies is large compared with the rotational frequency and that the molecule is rigid, i.e., a single vibrational frequency is being considered. These two assumptions can be fulfilled simultaneously only under very specific conditions. It hardly seems justifiable to apply the results of this calculation to the example discussed by Segré (O_2--rotational spectrum, excited by the 2537-A Hg line).

20. F. Rasetti, Proc. Nat. Acad. Am. 15, 411 (1929); Pringsheim, Hdb. Physik, 21, 632.

21. A more detailed discription may be gained from the article by Hanle in the present Handbuch.

22. R. W. Wood, Physik. Z. 12, 1204 (1911).

23. The problem will be treated in a forthcoming publication by the author.

24. The remaining electronic terms and their influence on the ground state determine whether for J even the even or odd energy state is energetically the higher one.

25. The effect of J on the Λ-doubling results in a doubling of the line $\Delta J = 2$; however, this can ordinarily be neglected.

26. K, K' in Eq. (21.11) is here replaced by Ω, Ω'.

27. This quantity is not to be confused with the one described by K in (21.11).

28. F. Rasetti, Z. Physik 66, 646 (1930).

Conclusion

Originally, it was planned to include another chapter on the scattering properties of aggregated systems such as gases, liquids, and solids. To avoid an undue delay in the publication, however, the author decided to omit this chapter.

A detailed, excellent account of the classical theory of the scattering of gases and liquids has been presented by Cabannes.[1] The scattering by crystals and the important new investigations of the fine structure of Rayleigh lines arising from liquids and crystals have not been summarized. Although the most interesting problems in the theory of scattered radiation concern this aspect, the material discussed in the preceding article represents a self-contained treatment. It constitutes the basis for the study of scattering phenomena of coherent systems. The author hopes to have the opportunity of incorporating the third part into the next edition of this Handbook.[2]

REFERENCES AND FOOTNOTES

1. J. Cabannes, La Diffusion Moléculaire de la Lumière.
2. Additions in the proof: Several papers on new material of spectra discussed in Chapter 19-21 appeared after completion of the above article.

Additions to References:

Chapter 19: Cabannes and Rousset, Ann. phys. 19, 229 (1933). Depolarization measurements.

Chapter 20: Adel and Dennison, Phys. Rev. 43, 716; 44, 99 (1933). CO_2 levels. Horiuti, Z. Physik 84, 380 (1933). Structure of CCl_4 vibrational spectra. Wright and Randall, Phys. Rev. 44, 391 (1933). Determination from infrared rotational spectrum of doublet splitting of the NH_3 ground state.

Chapter 21: Bhagavantam, Indian J. Phys. 7, 549 (1933). Intensity measurements of the H_2 spectrum.