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Vibration-Rotation Spectrum of HCl

A physical chemistry experiment

Spectroscopy, a technique commonly used in many areas of chemical research, permits the determination of molecular parameters to a very high degree of accuracy. The molecular spectroscopy experiment described below is performed in the undergraduate physical chemistry laboratory. Parts of the experiment may be omitted without damaging its value if spectra of adequate resolution are not obtainable. In its complete form, the experiment yields such molecular parameters as the interatomic distance, the vibration frequency and the anharmonicity constant, and also such macroscopic properties as the "rotational" temperature, dissociation energy, the free energy function and the heat capacity.

The Experiment

The sample of gaseous hydrogen chloride is prepared by mixing a few drops of concentrated sulfuric and hydrochloric acids in a ten-cm quartz sample cell. The sulfuric acid dehydrates the constant-boiling hydrochloric acid producing HCl gas. DCl, if desired, is prepared from D₂O.

Two absorption spectra are used: that of the ($v' = 1 \leftarrow v'' = 0$)¹ band between 3.3 and 4.0 microns, and that of the ($v' = 2 \leftarrow v'' = 0$) band between 1.7 and 1.85 microns. Either spectrum, with the rotational lines resolved, is sufficient for the bulk of the experiment. In practice we have used the Beckman IR-5 or Baird AB-2 infrared spectrophotometers at 3.3 μ , and the Cary model 14 at 1.7 μ . The 1.7 μ spectrum has been observed also with a Beckman DK-2 but the resolution obtained is sufficient to give only the 0'-0" line. New IR grating instruments now coming onto the market offer adequate resolution at low cost and promise to be widely available.

Data

The (1'-0") spectrum at 1.7 μ taken with the Baird AB-2 is shown in Figure 1. Normally this is used only to obtain the (0'-0") line; however, the spectrum shown has been interpreted to give an interatomic distance.² Resolution comparable to that of Figure 2 may be obtained with the more modern grating instruments.

EDITOR'S NOTE: This paper and the one that follows are part of a series designed to provide work suitable for training undergraduates in the interpretation of chemical phenomena in terms of molecular energetics. See also THIS JOURNAL, 39, 626 and 630 (1962).

¹ The single prime in such a notation signifies the upper vibrational state, while the double prime signifies the lower vibrational state. This convention is followed throughout this article.

² From private communication with B. W. Ristow, r (obtained) = 1.28 Å, r (literature) = 1.275 Å.

The (2'-0") spectrum taken with the Cary 14 is shown in Figure 2. The general features are the same as those of Figure 1, except that there is much greater resolution: the individual rotational lines are clearly seen and are labeled $R(0)$, $R(1)$, etc. Of each pair of lines, the more intense member is due to H³⁵Cl, the less intense to H³⁷Cl.

The features of the resolved spectrum may be related to the molecular structure. Figure 3 shows potential energy as a function of the interatomic distance r . Vibrational levels are shown as the horizontal lines. The 1.7 μ spectrum results when the molecule in the 0 level absorbs light and goes to the 2nd level.

Details of these levels are shown in Figure 4. In addition to the vibrational energy, the molecule also has rotational energy $F(J)$ given by

$$F(J) = J(J + 1)B_v \quad (1)$$

where J is the rotational quantum number and B_v is the rotational constant equal to $h/8\pi^2 I_v c$ where I is the moment of inertia, μr^2 . Figure 3 shows that r must be

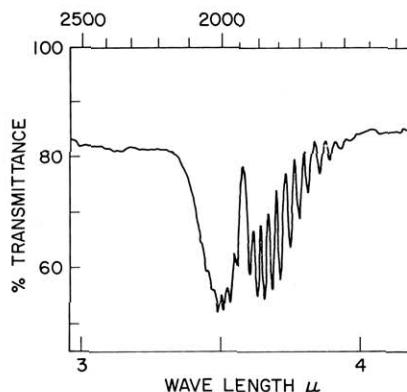


Figure 1. The fundamental (1' \leftarrow 0'') spectrum of HCl under low resolution—per cent transmission versus wavelength in microns.

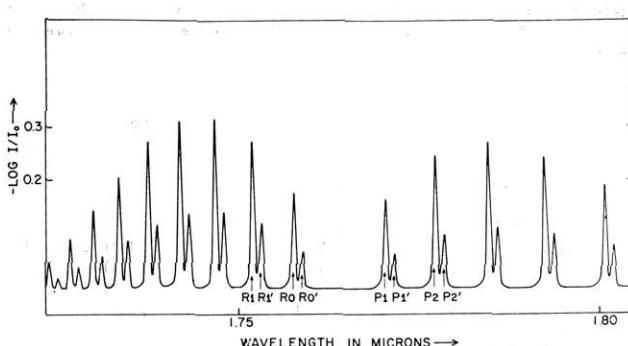


Figure 2. The first overtone (2' \leftarrow 0'') spectrum under high resolution— $-\log I/I_0$ versus wavelength in microns. The lines in the P and R branches are labeled prime ('') for H³⁷Cl and un-prime (') for H³⁵Cl.

larger for the higher vibrational states studied; therefore $B_{v=2}$ must be smaller than $B_{v=1}$. The J value for a transition may change only according to the selection rule:

$$\Delta J = \pm 1 \quad (2)$$

The resulting transitions are shown as vertical arrows and the resulting spectral lines are shown below. The high energy part of the spectrum ($\Delta J = +1$) is called the R branch; the low energy part ($\Delta J = -1$) is called the P branch. Each line is labeled $R(0) \dots$ or $P(1) \dots$, according to the J value of the lower level involved.

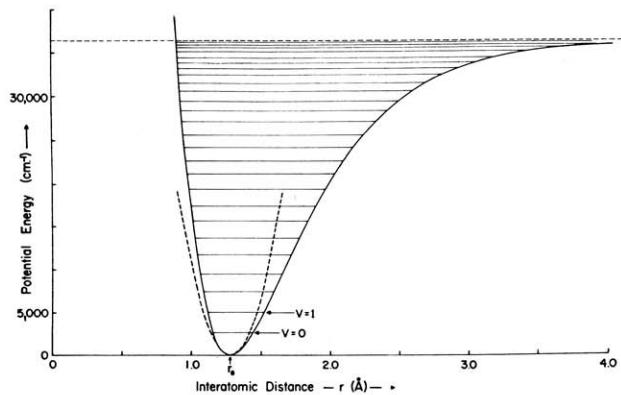


Figure 3. Potential energy curve: the dashed line is the harmonic oscillator (parabola) approximation. The vibrational levels are drawn to scale.

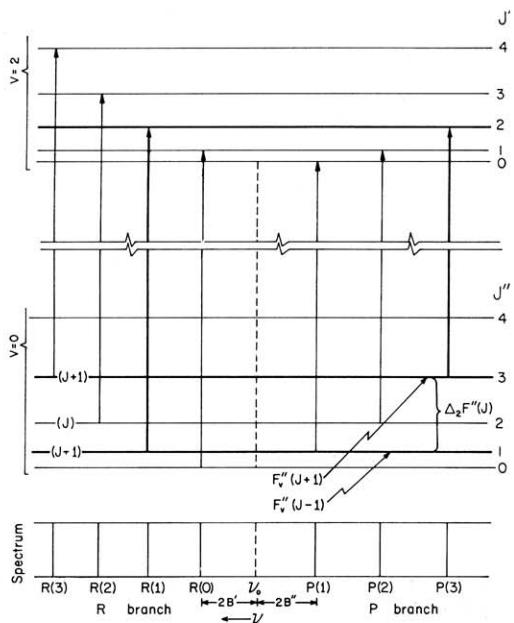


Figure 4. Details of the vibration-rotation transitions showing the origin of the P and R branches. $B_{(v=2)} < B_{(v=0)}$, hence the band is shaded to the red.

Figure 4 shows that because B' (upper level) $> B''$ (lower level) the spacing between spectral lines becomes larger as one goes to lower energy from the R to the P branches. This is called "shading to the red." If the temperature were great enough so that higher rotational levels were populated, it would be observed that the R lines eventually would fall one upon the other; this is called a band "head." In transitions between *different* electronic states we have also $B_v' = B_{v''}$ or $B_v' < B_{v''}$. In the former case the lines are equally spaced; in the latter, the spectrum is "shaded to the violet." The latter case might be expected when an anti-bonding electron is promoted to a non-bonding state.

Treatment of Data (1-6)

Energies of the Observed Transitions. Energies are usually given in terms of reciprocal wavelengths, or wave numbers ($1/\lambda$), in units of cm^{-1} . From Planck's equation

$$E = h\nu \quad (3)$$

and the relation

$$\lambda\nu = c \quad (4)$$

we have

$$E = hc(1/\lambda) \quad (5)$$

The first step, then, is to take the reciprocals of the observed wavelengths for the P and R series of each isotope. The accuracy of the data justifies five significant figures.

A portion of the data obtained from the high resolution $2'-0''$ spectrum is contained in Table 1. In practice there are usually about 20 usable lines in the $2'-0''$ spectrum. From the low resolution $1' \leftarrow 0''$ band, only the average energy of the ($J' = 0 \leftarrow J'' = 0$) transition is obtained.

Interatomic Distance. The rotational spacing constant B_v is defined as

$$B_v = \frac{h}{8\pi^2 I_v c} \quad (6)$$

where $I_v = \mu r_v^2$; μ = reduced mass $= m_1 m_2 / (m_1 + m_2)$; r_v = interatomic distance in vibrational level v ; h = Planck's constant, and c = speed of light. B_v varies slowly as a function of vibrational level. By using the tabulated data, it is possible to determine

³ The value is c_{vacuum} ; these spectra are measured in cells containing air where $c_{\text{air}} = c_{\text{vacuum}} n^{-1}$. The index of refraction n for air in the region of 1.8 microns is 1.00027 (10). However, this correction is approximately of the same magnitude as the experimental scatter and has been ignored.

Table 1. Some Observed Transitions in the $2'-0''$ Spectrum.

Number	Transition $J'-J''$	$\lambda (\mu)$	H^{35}Cl		H^{37}Cl	
			$\nu (\text{cm}^{-1})$	$\lambda (\mu)$	$\nu (\text{cm}^{-1})$	$\lambda (\mu)$
<i>R</i> series						
3	4-3	1.7420 \pm 0.001	5740.5 \pm 3.4	1.7430 \pm 0.001	5737.2 \pm 3.4	
2	3-2	1.7470	5724.1	1.7480	5720.8	
1	2-1	1.7520	5707.8	1.7533	5703.3	
0	1-0	1.7578	5688.9	1.7590	5685.0	
<i>P</i> series						
1	0-1	1.7703	5648.8	1.7715	5644.9	
2	1-2	1.7772	5626.8	1.7785	5622.7	
3	2-3	1.7847	5603.2	1.7859	5599.4	

$B_{v=0}$ and $B_{v=2}$, and to extrapolate to obtain $B_{v=(-\frac{1}{2})}$ (or B_e),⁴ the value at the minimum of the potential energy curve of Figure 3.

The J th rotational level term⁵ is related to B_v by the equation

$$E_J/hc = F(J) = J(J+1)B_v \quad (7)$$

Figure 4 shows that for P and R components that terminate in the same J level in the upper vibrational state,

$$\begin{aligned} R(J-1) - P(J+1) &= F''(J+1) - F''(J-1) = \\ &(J+1)(J+2)B_{v=0} - (J-1)(J)B_{v=0} \end{aligned} \quad (8)$$

or

$$\Delta_2 F''(J) = R(J-1) - P(J+1) = 4B_{v=0}(J + \frac{1}{2}) \quad (9)$$

Similarly, for P and R components starting from the same J level in the lower vibrational state,

$$\Delta_2 F' = R(J) - P(J) = 4B_{v=2}(J + \frac{1}{2}) \quad (10)$$

Table 2 gives sample values calculated for $J = 0$ to $J = 3$ of $H^{35}\text{Cl}$. The values for $B_{v=0}$ and $B_{v=2}$ are obtained by summing and taking the average of the values of $\Delta_2 F/4 (J + \frac{1}{2})$. In practice values for the transitions up to $J \cong 10$ for each series are obtained and used.

For an anharmonic oscillator, one in which the vibrational level spacings may be assumed to decrease linearly with v , B also is assumed to vary linearly according to the equation

$$B_v = B_e - \alpha(v + \frac{1}{2}) \quad (11)$$

By plotting B versus $(v + \frac{1}{2})$ for $B_{v=2}$ and $B_{v=0}$ and graphically extrapolating to $v = -\frac{1}{2}$, the value B_e , the constant at the minimum of the potential energy curve of Figure 3, may be obtained. Using this, the value for the interatomic distance, r_e , may be determined. If desired, the value for α may be determined from the slope of the line. This series of calculations may be done for either isotope.

Vibration and Rotation Frequencies. It is possible to determine very precisely the energy of the (missing) $0'-0''$ transition, and thus the vibration frequencies for both isotopes. In Figure 2, the missing line is *not* equidistant between the $R(0)$ and $P(1)$ lines. The energy between the missing line and the $R(0)$ line for each isotope corresponds to the transition from $v'' = 0, J'' = 0$ to $v' = 2, J' = 1$ and has the energy

$$F(J) = B_{v=2}(J)(J+1) = 2B_{v=2} \quad (12)$$

Similarly, the energy from the $0'-0''$ line to the $P(1)$ line is

⁴ The subscript e indicates an extrapolated value.

⁵ The word *term* is used to signify energy expressed in reciprocal centimeters (cm^{-1}) instead of ergs or other units.

$$F(J) = 2B_{v=0} \quad (13)$$

Interpolation using the two B values permits the determination of the energy of the ($2' \leftarrow 0''$) transition, and thus the calculation of the vibrational frequency for the molecule in the $v = 2$ level. The corresponding transition on the low resolution ($1'-0''$) spectrum is determined merely by inspection.

Using the two values of the ($2', 0' \leftarrow 0'', 0''$) transition for $H^{35}\text{Cl}$ and $H^{37}\text{Cl}$, the experimental isotopic shift may be compared with that predicted from theory.

Since

$$\nu = (\frac{1}{2}\pi) \sqrt{k/\mu} \quad (14)$$

therefore

$$\frac{\nu(0-0, H^{35}\text{Cl})}{\nu(0-0, H^{37}\text{Cl})} = \left(\frac{\mu H^{37}\text{Cl}}{\mu H^{35}\text{Cl}}\right)^{1/2} \quad (15)$$

where the reduced masses must be calculated using extremely precise isotopic masses. If only low resolution instruments are available, the isotopic shift of DCl may be studied.

The frequency of rotation of the HCl molecule varies with the rotational level and to a smaller degree with the vibrational level. The frequency is given by the expression:

$$\nu_{\text{rot}}(J) = 2cB_v \sqrt{J(J+1)} \text{ (sec}^{-1}\text{)}$$

Anharmonicity. In the simplest approximation (harmonic oscillator) the potential energy of the molecule is assumed to vary as the square of the interatomic distance and the vibrational energy levels are equally spaced. In fact, as shown in Figure 3, the actual curve shows a systematic deviation from the parabola (dashed curve). The energy $G(v)$ of the vibrational levels with respect to the minimum of the curve is given by the power series

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 - \omega_e y_e(v + \frac{1}{2})^3 - \dots \quad (16)$$

where $\omega_e x_e$ and $\omega_e y_e$ are called the anharmonicity constants.

Since the missing lines of the ($2' \leftarrow 0''$) and the ($1' \leftarrow 0''$) spectra correspond to $G(v = 2)$ and $G(v = 1)$, $\omega_e x_e$ may be evaluated.

Taking

$$[G(v = 1) - G(v = 0)]$$

and

$$[G(v = 2) - G(v = 1)] [= \Delta G]$$

gives the spacing between levels.

$$\Delta G = \omega_e - 2\omega_e x_e(v + 1) \quad (17)$$

The difference $\Delta G(2-1) - \Delta G(1-0) = \Delta_2 G$ gives the anharmonicity

$$\Delta_2 G = -2\omega_e x_e \quad (18)$$

Table 2. Determination of the Rotational Constant B ($H^{35}\text{Cl}$).

J	$R(J) \text{ (cm}^{-1}\text{)}$	$P(J) \text{ (cm}^{-1}\text{)}$	$\Delta_2 F''(J)^a$	$B_{v=0}$	$\Delta_2 F'(J)^b$	$B_{v=2}$
0	5688.9 ± 3.4					
1	5707.8	5648.8 ± 3.4	62.1	10.350	59.0	9.832
2	5724.1	5626.8	104.6	10.460	97.3	9.731
3	5740.5	5603.2	145.3	10.379	137.3	9.807
			Average	10.396		9.790

^a $\Delta_2 F''(J) = R(J-1) - P(J+1)$ (Equation 9)).

^b $\Delta_2 F'(J) = R(J) - P(J)$ (Equation 10)).

Dissociation Energy. Using the first anharmonicity constant, the dissociation energy of the molecule may be estimated crudely by means of the linear Birge-Sponer extrapolation (2-4, 6). Equation (17) indicates that the spacing between levels decreases with v and eventually reaches zero. Figure 3 shows that the dissociation energy D_0° is the sum of the ΔG values up to $\Delta G = 0$. This summation may be made graphically and is the area under a plot of ΔG ($= \Delta\nu$) versus v . Figure 5 shows such a plot made using the two observed frequencies and the linear extrapolation. The dissociation energy is

$$D_0^\circ = \omega_e^2 / 4\omega_e x_e - 1/2\omega_e = \text{area} - 1/2\omega_e \quad (19)$$

Usually the second and higher anharmonicity terms $\omega_e y_e \dots$ become important for large v and the curve drops more rapidly as shown by the dotted line. Thus linear extrapolation tends to an upper limit for D_0° (6)

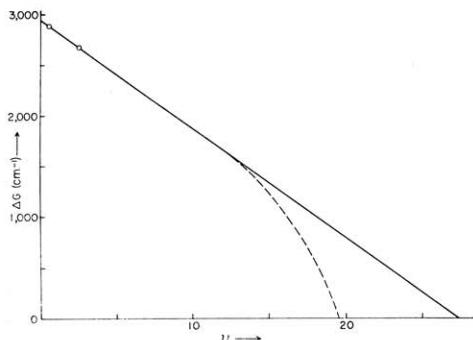


Figure 5. Linear Birge-Sponer extrapolation for HCl. The actual extrapolation (dashed line) is obtained if second and higher anharmonicity terms are used.

Rotational Temperature. Temperature may be defined as the parameter T in the Boltzmann equation

$$n_i = n_0 \frac{g_i}{g_0} e^{-\epsilon_i/kT} \quad (20)$$

where the g 's are statistical weights. For rotation, this becomes

$$n_i = n_0 (2J + 1) e^{-J(J+1)Bhc/kT} \quad (21)$$

where k is the Boltzmann constant and all the other parameters are known except T . Since, by Beer's law, $\log I/I_0$ is related to the number of molecules, the following expression may be derived.

$$\log \frac{(-\log I/I_0)}{(J' + J'' + 1)} = A - \frac{J''(J'' + 1)B''hc}{2.303 kT} \quad (22)$$

where A is a constant; the term in the left hand denominator takes into account that the absorption coefficient for the lines varies slightly with J . (The energy of the lower vibrational levels is used on the right hand side because this is an absorption spectrum.) The temperature then is inversely proportional to the slope of a plot of the left hand side versus $J''(J'' + 1)$. This means of measuring temperature is one of those used for high temperature arcs, jet engines, the sun and stars.

Isotopic Ratio. If the transition probability for any given line in the $H^{35}Cl$ spectrum is the same as for that in $H^{37}Cl$, the $^{35}Cl : ^{37}Cl$ isotope ratio may be determined. Whether this assumption is valid should be tested by comparing the ratio of the logarithms of the intensities with accepted mass spectrographic data.

Results and Discussion

The calculated results are $B_{v=2,0,-1/2}$; α in eq. (11) and r_e for one or both of the isotopic molecules, as well as the isotope shift and average values of $\omega(v = 1,2)$, $\omega_e x_e$, D_0° and T . Literature values for all of the molecular parameters are available (6-8, 11-15).

Table 3. Results ($H^{35}Cl$).

	Experimental ^a	Literature
$\omega_e x_e$	50.60	52.05 ^b
B_e	10.550	10.590 ^b
α_e	0.302	0.3019 ^b
r_e	1.285 Å	1.2746 Å ^b
D_0°	5.2854 ev ^d	4.430 ev ^b
$- \frac{G^\circ - H_0^\circ}{T}$ (298°K)	37.769 cal/deg	37.720 ^c
S° (298°K)	44.685 cal/deg	44.645 cal/deg ^c
C° (298°K)	6.938 cal/deg	6.964 cal/deg ^c

^a From a student report.

^b Herzberg—appendix—Table 23, Ref. (6).

^c JANAF Thermochemical Table, Ref. (7).

^d Linear Birge-Sponer extrapolation.

The basic uncertainty in the wavelength data obtained with the Cary is $\pm 0.001\mu$ or $\pm 0.05\%$. When the differences in wave numbers are taken to obtain the $\Delta_2 F$, an average uncertainty of $\pm 2\%$ results. Since approximately ten sets of differences are averaged to obtain the interatomic distance, this expected uncertainty is reduced to approximately $\pm 1\%$. (Greater deviations from the literature value probably are due to remediable systematic error.) For the other quantities, greater uncertainties result from the way the differences are taken and from the higher uncertainty of the (1'-0") data. In the calculation of T , it was assumed that B is constant with J . In fact, due to centrifugal stretching of the molecule, B decreases with increasing J . This introduces a slight systematic error.

Since about 20 lines are observed for each isotopic molecule, 20 data points are available. With these, the interatomic distance, the frequencies of rotation and vibration as well as the change of interatomic distance with change in vibrational level are calculated. The depth D_0° of the potential energy curve also is estimated. Thus, this one experiment gives a fairly complete and detailed description of the molecule.

Thermodynamic Properties (8). Using the molecular description, the macroscopic thermodynamic properties may be predicted extremely accurately by means of statistical thermodynamics. The dissociation energy is simply D_0° . The free energy function (9) is given by

$$-\frac{G^\circ - H_0^\circ}{T} = R(\frac{3}{2}\ln M + \frac{5}{2}\ln T) - 7.283 \text{ cal/deg} + R(-\ln y - \ln \sigma) - R \ln(1 - e^{-u})$$

The entropy S is

$$S^\circ = R(\frac{3}{2}\ln M + \frac{5}{2}\ln T) - 2.315 \text{ cal/deg} +$$

$$R(1 - \ln y - \ln \sigma) + \left[R \frac{u}{e^u - 1} - \ln(1 - e^{-u}) \right]$$

The specific heat C° is

$$C^\circ = \frac{7}{2}R + R \frac{u^2 e^u}{(e^u - 1)^2}$$

where M = molecular weight, σ = symmetry number (1), $y = hcB/kT$, $u = h\omega c/kT = 1.438\omega/T$.

Related Experiments. The molecule HBr also is suitable for this experiment, but the (1-0) band cannot be obtained using a quartz cell. Studies of the electronic spectra of iodine including the graphical Birge-Sponer extrapolation, and of atoms, also have been described (16, 17).

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