The Fundamental Rotational–Vibrational Band of CO and NO

Teaching the Theory of Diatomic Molecules

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Although IR spectroscopy is a well-studied technique in any introductory course on molecular spectroscopy, we find few experiments dealing with the analysis of the fundamental rovibrational band of diatomic molecules (1). We present here, an experiment that explores the effects of angular momentum coupling on molecular spectra.

Few diatomic molecules are chemically stable under ordinary conditions and thus suitable for this study. Among those, we chose carbon monoxide CO and nitric oxide NO because they are easy to obtain and their IR spectra present well-resolved fundamental bands with quite distinct characteristics.

The fundamental band of CO in its ground electronic state $^1\Sigma$ exhibits two branches, P and R, which can be resolved by considering the molecule as a simple vibrating rotor. NO is one of the few stable diatomic molecules with an odd number of electrons and nonzero electronic-internuclear angular momentum Λ. Its ground state $^2\Pi$ is split in two components separated by $124\ cm^{-1}$ due to spin–orbit interaction. Both of them are populated at room temperature ($kT = 208.5\ cm^{-1}$), and the NO IR fundamental band is a superposition of bands corresponding to the two substates $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$. This is also one of the few stable diatomic molecules for which the Q branch, as well as the P and R branches, has been observed in its IR bands.

CO and NO are also very interesting due to their importance in atmospheric chemistry. They are involved in ozone chemistry and are harmful if inhaled. Recently, it has been shown that NO has multiple functions in the human body. It relaxes various vascular and nonvascular tissues, and consequently plays a role in the control of blood pressure by stimulation of vasodilatation (2). NO is a new type of neuronal messenger whose action depends on its free-radical character (3). Therefore, choosing only two diatomic molecules with very interesting chemical and biological properties, we can illustrate angular momentum coupling theory.

Experimental

Collection of CO from Exhaust Gas

The mixture of gas expelled from the exhaust pipe of a polluting automobile contains a considerable amount of CO. A sample was collected in a previously evacuated flask (Fig. 1). It was carefully dried by passing it through a large
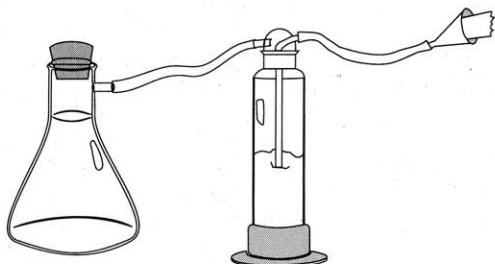
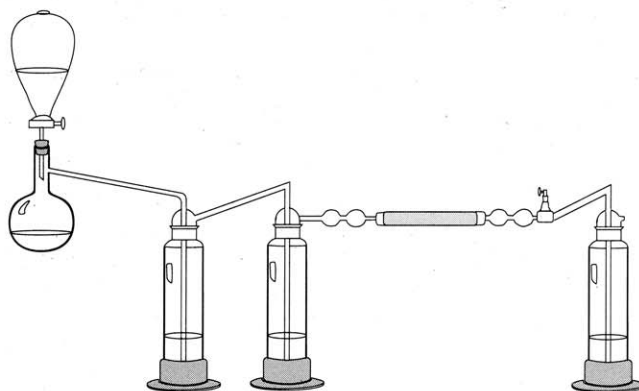Figure 1. Apparatus for collecting CO from an automobile.

Figure 2. Apparatus for NO synthesis.

tube filled with calcium chloride, which also eliminated water and dirt particles. One can also eliminate CO_2 from the mixture by collecting it over water.

Synthesis of NO

Nitric oxide was synthesized by reacting potassium nitrite with sulfuric acid, a classical reaction in introductory inorganic chemistry laboratory (4). To minimize the forma-
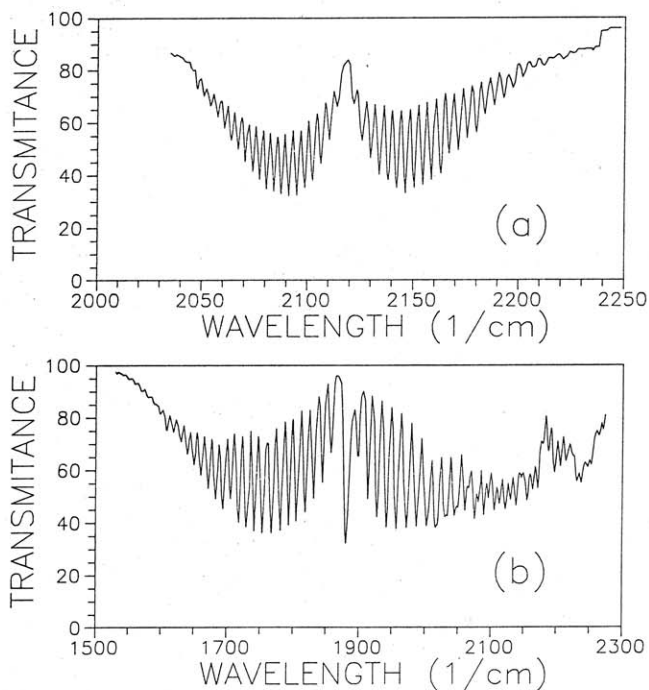
Figure 3. (a) CO (b) NO fundamental band.

tion of N_2O_4, which always contaminates the product, pure nitrogen was pumped through the system before the reaction to eliminate air from the apparatus. The gas was washed with sulfuric acid and potassium hydroxide and dried with calcium chloride. The unused NO was collected over $KMnO_4$ (Fig. 2).

Obtaining IR Spectra

The two spectra were obtained by students using a Perkin–Elmer model 283 IR spectrometer and a gas cell with a NaCl window. The fundamental bands of CO extend from 2051.9 to 2245.9 cm^{-1}; of NO from 1700.0 to 2051.0 cm^{-1} (Fig. 3). With high resolution it is possible to measure the relative wavelengths of the lines within 0.1 cm^{-1}.

To minimize the absolute error in the line frequencies we recalibrated the spectrometer on the maximum of the unresolved Q branch of NO at 1875.52 cm^{-1}, as measured by Gillette and Eyster (5) with correction for a vacuum. The resolution was good enough to observe the superposition of the two spin–orbit states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ in the NO spectra.

Analysis of the Data

The theory of the IR spectra of diatomic molecules is described in detail by several authors (6–9). We give here a brief introduction of the theory needed to derive the equations of the IR line frequencies for $^1\Sigma$ and $^2\Pi$ electronic states.

Evaluating the Energy

CO and NO molecules can be described as three-dimensional rigid rotors and the following approximation to the energy is a good start.

$$E_{vR} = \langle v_R | H | v_R \rangle = \langle v | H_{vib} | v \rangle + \langle R | H_{rot} | R \rangle$$

where H_{vib} and H_{rot} are the vibrational and rotational parts of the Hamiltonian and $|v\rangle$ and $|R\rangle$ are their wavefunctions.

In the Morse potential approach the vibrational energy becomes

$$\langle v | H_{vib} | v \rangle = (v + \tfrac{1}{2})\alpha_e - (v + \tfrac{1}{2})^2 \alpha_e x_e$$

where v is the vibrational quantum number; and α_e and x_e are related to the Morse constants (6). H_{rot} could be expressed as

$$H_{rot} = B_v \mathbf{R}^2 = B_v(\mathbf{N} - \mathbf{L})^2 = B_v((\mathbf{J} - \mathbf{S}) - \mathbf{L})^2 = B_v(\mathbf{J} - (\mathbf{L} + \mathbf{S}))^2$$

where we introduce the set of angular momentum characters used by most authors (7, 8). $\mathbf{R}$ is the nuclear-rotational angular momentum; $\mathbf{L}$ is the electronic-orbital angular momentum; $\mathbf{S}$ is the electronic-spin angular momentum; $\mathbf{N}$ is the total angular momentum excluding electronic spin; and $\mathbf{J}$ is the total angular momentum. B_v is the rotational constant for vibrational state v defined as

$$B_v = \frac{h^2}{8\mu\pi^2 R_v^2}$$

where m is the reduced mass of the molecule and R_v is the bond distance of the molecule in vibrational state v.

Coupling Schemes

Hund's Case A

Instead of diagonalizing H_{rot}, which is a difficult problem, the eigenfunctions of $\mathbf{J}$ can be used as an ansatz and the coupling terms treated as perturbations. Many interactions of various magnitudes occur in the molecule, and there is more than one way in which the three vectors $\mathbf{L}$, $\mathbf{S}$,
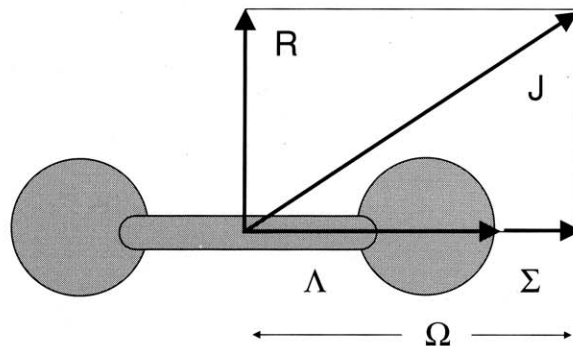

Figure 4. Hund's case A coupling scheme.

and $\mathbf{R}$ can be coupled to form the resultant $\mathbf{J}$. Thus, their eigenfunctions do not describe the system in a unique way.

In the coupling scheme called Hund's case A (Fig. 4), $\mathbf{L}$ and $\mathbf{S}$ precess around the internuclear axis, making the projections Λ and Σ, whereas $\mathbf{R}$ is at right angles to that axis. Λ can always be defined. If we assume that Σ remains quantized even in the rotating molecule, the resulting angular-momentum vector along the internuclear axis $\Omega = \Lambda + \Sigma$ is also a well-defined constant of motion. The total angular momentum $\mathbf{J}$ is the sum $\mathbf{J} = \Omega + \mathbf{R}$, and the quantum number J assume the values

$$|\Omega|, \ |\Omega + 1|, \ ...$$

$\mathbf{J}$ makes also a projection $\mathbf{M}$ on the space-fixed z axis. Consequently, the rotational wavefunctions are the modified spherical harmonics $|\mathbf{J\Omega M}\rangle$ labeled by three quantum numbers: J, Ω, and M. They also have a defined parity under inversion of the spatial coordinates of all particles. Therefore, in case A coupling $|\mathbf{J\Omega M}\rangle$ satisfies the following relations (7).

$$\langle \mathbf{J\Omega M} | \mathbf{J}^2 | \mathbf{J\Omega M} \rangle = J(J + 1)$$

$$\langle \mathbf{J\Omega M} | \Omega | \mathbf{J\Omega M} \rangle = \Omega$$

$$\langle \mathbf{J\Omega M} | \mathbf{L_z} | \mathbf{J\Omega M} \rangle = M$$

$$\mathbf{i} | \mathbf{J\Omega M} \rangle = (-1)^{J-\Omega} | \mathbf{J} - \Omega \mathbf{M} \rangle$$

The rotational energy in first order becomes

$$\langle \mathbf{J\Omega M} | \mathbf{H_{rot}} | \mathbf{J\Omega M} \rangle$$

$$= \langle \mathbf{J\Omega M} | B_v(|\mathbf{J}|^2 - |\Omega|^2) + A\Lambda\cdot\Sigma | \mathbf{J\Omega M} \rangle$$

$$= B_v(J(J+1) - \Omega^2) = A\Lambda\cdot\Sigma$$

where A is the phenomenological molecular spin–orbit coupling constant.

Hund's Case B

Case A occurs in multiplet electronic states where the spin–orbit coupling is strong. It also occurs for sufficiently low rotational frequencies, that is, when B_v and J are small and A is large. However, for high rotational frequencies and very small A, the spin–orbit coupling breaks down, and the molecule is better described in another coupling scheme, known as Hund's case B, with $\mathbf{J}$ defined as

$$\mathbf{J} = ((\Lambda + \mathbf{R}) + \mathbf{S}) = \mathbf{N} + \mathbf{S}$$

The intensities (I_{if}'s) of an IR absorption from initial state $|\mathbf{J_i\Omega_i M_i}\rangle$ to final state $|\mathbf{J_f\Omega_f M_f}\rangle$ are proportional to the square of the transition moment integral

$$\langle \mathbf{J_i\Omega_iM_i}|\,\mu\,|\,\mathbf{J_f\Omega_fM_f}\rangle$$

and to the transition frequency

$$\nu_{if} = E(J_f,\Omega_f) - E(J_i,\Omega_i)$$

where μ is the dipole moment of the molecule.

In the electric-dipole approximation,

$$I_{if} \propto |\langle \mathbf{J_i\Omega_iM_i}|\,\boldsymbol{\epsilon}\cdot\mathbf{r}\,|\mathbf{J_f\Omega_fM_f}\rangle|\,\nu_{if}^2 \qquad (1)$$

where $\boldsymbol{\epsilon}$ is the radiation electric field.

If we write $\boldsymbol{\epsilon}\cdot\mathbf{r}$ as a linear combination of the functions $|1\Omega M\rangle$, then eq 1 will consist of integrals like

$$\langle \mathbf{J_i\Omega_iM_i}|\,1\Omega M\,|\mathbf{J_f\Omega_fM_f}\rangle$$

The IR Spectra

These are easily solved by applying the addition theorem and orthogonality properties of the modified spherical harmonics. Equation 1 vanishes unless

$$\Delta J = J_f - J_i = 1, 0, -1$$

and

$$\Delta\Omega = \Omega_f - \Omega_i = 1, 0, -1$$

Because $\boldsymbol{\epsilon}\cdot\mathbf{r}$ is odd, only levels of opposite parity can be connected in an electric-dipole allowed transition. Consequently, the selection rules are

$$\Delta J = 0 \text{ and } \Delta\Omega = \pm1$$

$$\Delta J = \pm1 \text{ and } \Delta\Omega = 0$$

The IR spectra present branches designated as P, Q, and R according to the value of ΔJ where $\Delta J = 1, 0, -1$. The line frequencies of the fundamental band are

$$\nu_P = \omega_e(1 - 2x_e) + (B_1 - B_0)J(J+1) - 2B_1J - (B_1 - B_0)|\Omega|^2$$

$$\nu_R = \omega_e(1 - 2x_e) + (B_1 - B_0)J(J+1) + 2B_1(J+1) - (B_1 - B_0)|\Omega|^2$$

$$\nu_Q = \omega_e(1 - 2x_e) + (B_1 - B_0)J(J+1) - (B_1 - B_0)|\Omega|^2$$
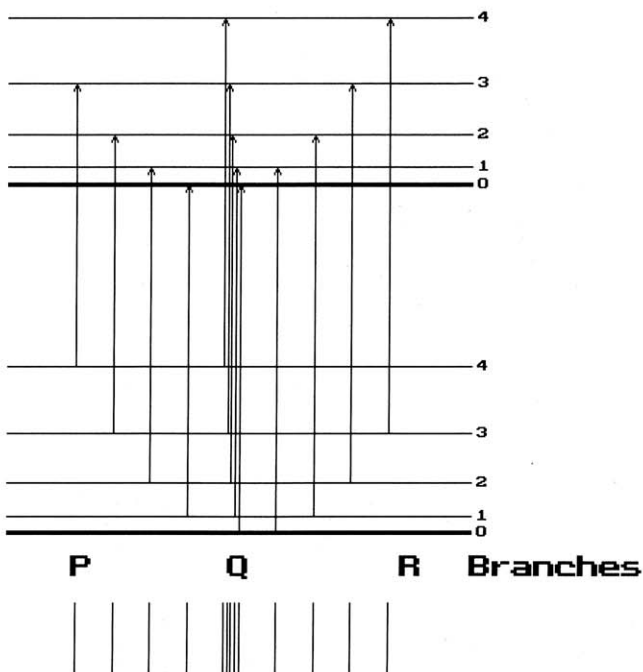$$- B_1 \pm 2B_1\Omega \pm A\Lambda$$

Figure 5. Energy diagram of diatomic molecules.

where the minus sign corresponds to transitions with $\Delta\Omega = +1$, and the plus sign corresponds to transitions with $\Delta\Omega = -1$. Figure 5 shows an energy-level diagram of a diatomic molecule and possible transitions in the fundamental band.

Ground State Bands

The CO molecule in the ground state

$$^1\Sigma(1\sigma^+)^2(2\sigma^+)^2(3\sigma^+)^2(4\sigma^+)^2(1\pi^+)^4(5\sigma^+)^2$$

is the simplest example. There is no spin nor internuclear electronic angular momentum ($S = 0$, $\Lambda = 0$, and $\Omega = 0$). Consequently, the total angular momentum $\mathbf{J}$ is purely rotational, and only P and R branches appear in the IR spectra.

The NO in the ground state is intermediate between Hund's cases A and B.

$$^2\Pi(1\sigma^+)^2(2\sigma^+)^2(3\sigma^+)^2(4\sigma^+)^2(1\pi^+)^4(5\sigma^+)^2(2\pi^+)^1$$

It is better described as case A for low J and case B for high J (9).

Nevertheless, the ratio between the two constants A and $B\nu$ is 73.3, large enough to consider it a case A molecule even at high J values. The IR spectra is a superposition of the bands due to the following two spin–orbit states.

	$^2\Pi_{1/2}$	$^2\Pi_{3/2}$
Λ	1	1
Σ	$-1/2$	$1/2$
Ω	$1/2$	$3/2$

Calculating Molecular Constants

Because $B_1 - B_0$ is very small, the Q branch is narrow and cannot be resolved. Only relations between line frequencies of P and R branches are necessary to calculate the rotational constants for CO and NO.

$$\nu_R(J) - \nu_P(J) = 2B_1(2J+1) \qquad (2)$$

$$\nu_R(J) - \nu_P(J+2) = 2B_0(2J+3) \qquad (3)$$

The values of J for various cases are given below.

CO	$J = 0, 1, 2, \ldots$
NO $^2\Pi_{1/2}$	$J = 1/2, 3/2, 5/2, \ldots$
NO $^2\Pi_{3/2}$	$J = 3/2, 5/2, 7/2, \ldots$

With the line frequencies and assignments listed in Table 1 the experimental values of eqs 2 and 3 are fitted by the least-squares method and plotted in Figure 6. The best values of the rotational constants B_0 and B_1 are given below.

	B_0 cm^{-1}	B_1 cm^{-1}
CO	1.9190	1.9101
NO $^2\Pi_{1/2}$	1.7365	1.7202
NO $^2\Pi_{3/2}$	1.6800	1.6724

Finally, the molecular constants B_e, α_e, and R_e were calculated according to

$$B_v = B_e - \alpha_e(v + \tfrac{1}{2})$$

$$B_e = \frac{h^2}{8\mu\pi^2 R_e^2} \qquad (4)$$

with $v = 0$ and $v = 1$. For NO we used the values of B_0 and B_1 calculated as the average of those determined for the

Table 1. Typical Student Values for CO and NO Line Frequencies and Corresponding Assignments

	CO $^1\Sigma$			NO $^2\Pi_{1/2}$		NO $^2\Pi_{3/2}$	
J	$v_R (J)$	$v_P (J)$	J	$v_R (J)$	$v_P(J)$	$v_R (J)$	$v_P (J)$
0	2129.4	–	1/2	1881.3	–	–	–
1	2133.2	2121.7	3/2	1884.5	1871.3	1884.5	–
2	2137.2	2117.5	5/2	1888.0	1867.6	1888.0	1867.6
3	2140.9	2113.4	7/2	1891.0	1864.1	1891.0	1864.1
4	2144.7	2109.4	9/2	1894.3	1860.6	1894.3	1860.6
5	2148.4	2105.4	11/2	1897.2	1856.8	1897.2	1856.8
6	2152.2	2101.3	13/2	1900.5	1853.1	1900.5	1853.1
7	2155.9	2097.1	15/2	1903.7	1849.1	1903.7	1849.1
8	2159.5	2093.3	17/2	1907.2	1845.5	1907.2	1845.5
9	2163.1	2088.9	19/2	1910.2	1841.6	1910.2	1842.1
10	2166.2	2084.6	21/2	1913.2	1837.6	1913.2	1839.0
11	2169.5	2080.2	23/2	1915.9	1833.7	1915.9	1834.9
12	2172.8	2076.1	25/2	1918.9	1829.7	1918.9	1831.2
13	2176.3	2071.7	27/2	1921.9	1825.9	1921.9	1827.4
14	2179.4	2067.5	29/2	1924.7	1822.4	1924.7	1824.2
15	2182.8	2063.4	31/2	1927.4	1818.4	1927.4	1820.4
16	2185.9	2059.3	33/2	1929.9	1814.0	1929.9	1816.0
17	2189.3	2054.9	35/2	1932.9	1810.0	1932.9	1812.0
			37/2	1935.4		1935.4	1808.0

Table 2. Rotational Constants for CO and NO

	CO		NO	
	experimental	(a)	experimental	(b)
B_e (cm^{-1})	1.928	1.931	1.714	1.7046
α_e (cm^{-1})	0.018	0.01748	0.012	0.0178
R_e(A)	1.129	1.12832	1.148	1.1508
R_0(A)	1.132	1.1307	1.150	1.1538
R_1(A)	1.137	1.1359	1.154	1.1603

[a]From Herzberg (6).
[b]From Gillete and Eyster (5).

ture that fit the maximum of absorption to a maximum of a Boltzmann distribution of rotational states. Because students are greatly interested in air pollution, an introduction to the major reactions involving atmospheric NO and CO, specifically their role in ozone chemistry and acid rain, was also included in their report.

Although the main objective of this experiment is to teach the theory and interpretation of the band spectra of diatomic molecules the two systems chosen here could be further studied in any spectroscopy course. An interesting additional experiment would be the quantitative determination of carbon monoxide in automobile exhaust by FTIR spectroscopy as described by Seasholtz, Pence, and Moe (10).

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two spin–orbit states. Typical students' results, listed in Table 2, are in good agreement with those reported by Herzberg (6) for CO and Gillete and Eyster (5) for NO.

Conclusion

Two 3-h periods were assigned to this experiment. The students were required to

- prepare the samples of CO and NO
- record the spectra
- treat the data in the laboratory
- calculate the constants
- compare them with those reported in the literature

In written reports the students derived the equations for the line frequencies and also estimated the gas tempera-
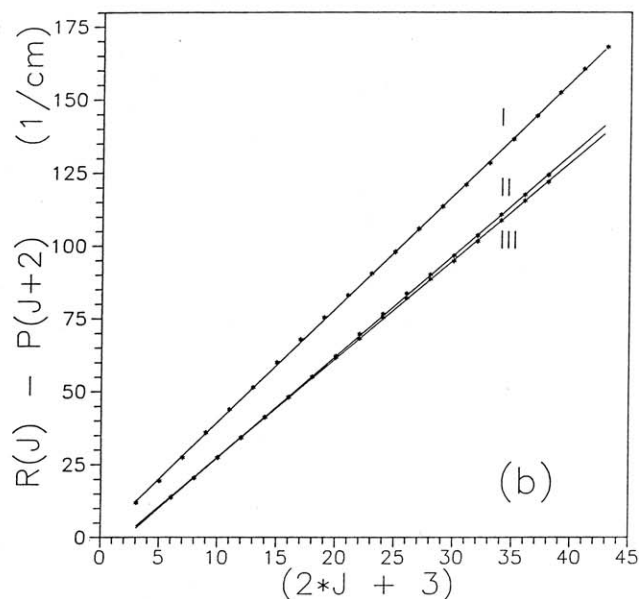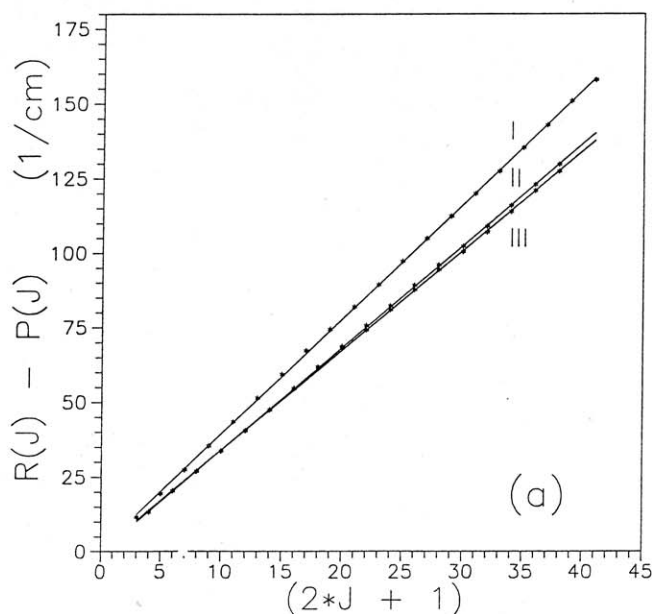

Figure 6A. Plots of eqs 2 (a) and 3 (b). Numerals I, II, and III refer to CO $^1\Sigma$, NO $^2\Pi_{1/2}$, and NO $^2\Pi_{3/2}$.