

# Pure Rotational Raman Spectroscopy of Diatomic Molecules

The recent advent of the laser has made the former esoteric field of Raman spectroscopy a common technique in many chemistry laboratories. Low-cost laser Raman spectrometers are now available that give high-quality spectra. The laser instruments also have the advantage over former instruments in that gas-phase spectra are much easier to observe. Rotational Raman spectroscopy provides a convenient method for determining structures of molecules, especially homonuclear diatomic molecules, and also an experimental method for observing the predictions of quantum mechanics, in particular the effects of the Pauli exclusion principle. A major advantage of this method is the simplicity of the theory necessary to interpret spectra.

It is the purpose of this article to outline the experimental procedures and theory necessary to observe and interpret rotational Raman spectra of diatomic molecules. As examples, the spectra of oxygen and nitrogen will be discussed. Sufficient details are presented so that a laboratory experiment could be done to determine bond distances and interpret spectra of diatomic molecules.

## Theory

A molecule in the gas phase is executing both vibrational and rotational motions. In order to discuss rotational Raman spectroscopy, it is necessary to know the energy levels of both of these motions, since they are not completely independent of each other.

To a very good approximation the vibrational energy levels of a diatomic molecule are independent of the rotational energy levels and are given by

$$E(v) = hc\omega_e(v + 1/2) - hc\omega_e x_e(v + 1/2)^2 \quad (1)$$

where  $v$  is the vibrational quantum number ( $v = 0, 1, 2, \dots$ ),  $\omega_e$  is the wave number ( $\text{cm}^{-1}$ ) of the harmonic vibrational frequency  $\nu_e$  ( $\omega_e = \nu_e/c$ ),  $x_e$  is the anharmonicity constant, and  $h$  and  $c$  have their usual meanings.  $\nu_e$  is vibrational frequency the molecule would possess if the amplitude of vibration was infinitesimal. Wave numbers for the different vibrational states are given by

$$\omega_v = (\omega_e - \omega_e x_e) - 2\omega_e x_e v \quad (2)$$

A common approximation to eqns. (1) and (2) is to assume that  $x_e = 0$  (harmonic-oscillator approximation). In this case the wave numbers of all vibrational states are equal and the energy levels are equally spaced.

The rotational energy levels of a diatomic molecule depend on the vibrational state of the molecule and to a very good approximation are given by

$$E(J) = hcB_v J(J + 1) - hcD_v J_2(J + 1)^2 \quad (3)$$

where  $J$  is the rotational quantum number<sup>1</sup> ( $J = 0, 1, 2, \dots$ ),  $B_v$  is the rotational constant for vibrational state  $v$ , and  $D_v$  is the corresponding centrifugal distortion constant. Both constants have units of  $\text{cm}^{-1}$ .

The rotational constant is defined as

$$B_v = \frac{h}{8\pi^2 c} \left\langle \frac{1}{I_v} \right\rangle_{av} \quad (4)$$

where  $\langle 1/I_v \rangle_{av}$  is the average value of the reciprocal of the moment of inertia in vibrational state  $v$ . For a diatomic molecule

$$\left\langle \frac{1}{I_v} \right\rangle_{av} = \frac{1}{\mu} \left\langle \frac{1}{r_v^2} \right\rangle_{av} \quad (5)$$

where  $\mu$  is the reduced mass,  $m_1 m_2 / (m_1 + m_2)$ , and  $\langle 1/r_v^2 \rangle_{av}$  is the mean value of  $1/r^2$  in vibrational state  $v$ . If we define

$$B_e = \frac{h}{8\pi^2 c \mu r_e^2} \quad (6)$$

where  $r_e$  is the equilibrium bond distance, then

$$B_v = B_e - \alpha_e(v + 1/2) \quad (7)$$

where  $\alpha_e$  is a small constant compared to  $B_e$ .

It can be shown (1) that the centrifugal distortion constant  $D_v$  is related to  $B_v$  and  $\omega_v$  by

$$D_v = \frac{4B_v^3}{\omega_v^2} \quad (8)$$

Equation (8) shows that  $D_v \ll B_v$ , and therefore the second term in eqn. (3) becomes important only for large values of  $J$ . In many cases an excellent approximation is to assume that  $D_v$  in eqn. (3) is equal to zero. This is the rigid-rotor approximation.

In Raman scattering an incident photon of frequency  $\nu_0$  interacts with a molecule and is scattered. In rotational Raman scattering the molecule may absorb part of the energy of this photon and be promoted to a higher rotational energy level. The scattered photon would have a frequency  $\nu = \nu_0 - \Delta E/h$ , where  $\Delta E$  is the difference in energy between the rotational levels involved. A transition of this type ( $\nu < \nu_0$ ) is recorded in the spectrum as a Stokes line. Molecules are also capable of losing energy to the incident photon ( $\nu > \nu_0$ ) and the resulting line is called an anti-Stokes line.

The selection rules for transitions involving a lower state  $J''$  and an upper state  $J'$  are found by evaluating the transition moment for rotational Raman scattering (1, 2)

$$[\mathbf{P}]^{J'J''} = \int \psi_{J'} \mathbf{P} \psi_{J''} d\tau \quad (9)$$

where  $\mathbf{P}$  involves the polarizability tensor.<sup>2</sup> Evaluation of the scattering moment gives the selection rule  $\Delta J = J' - J'' = \pm 2$ . Transitions of the type  $J \rightarrow J + 2$  are Stokes lines, while  $J \rightarrow J - 2$  transitions are anti-Stokes lines.

Application of the selection rule  $\Delta J = \pm 2$  to eqn. (3) and setting  $J'' = J$  results in the following expression for the wave number shifts of the Raman lines from the wave number of the laser line

<sup>1</sup> In the case where there is a coupling between electronic and rotational angular momenta, it is the convention to designate the rotational quantum number as  $K$ . This is the case for  $\text{O}_2$  which has a  $\Sigma_g^-$  ground electronic state. For further discussion of electronic coupling the reader is referred to reference (1).

<sup>2</sup> Evaluation of the transition moment is quite difficult and will not be given here. A somewhat simplified evaluation is given in reference (1), but the reader is referred to reference (2) for a general evaluation.

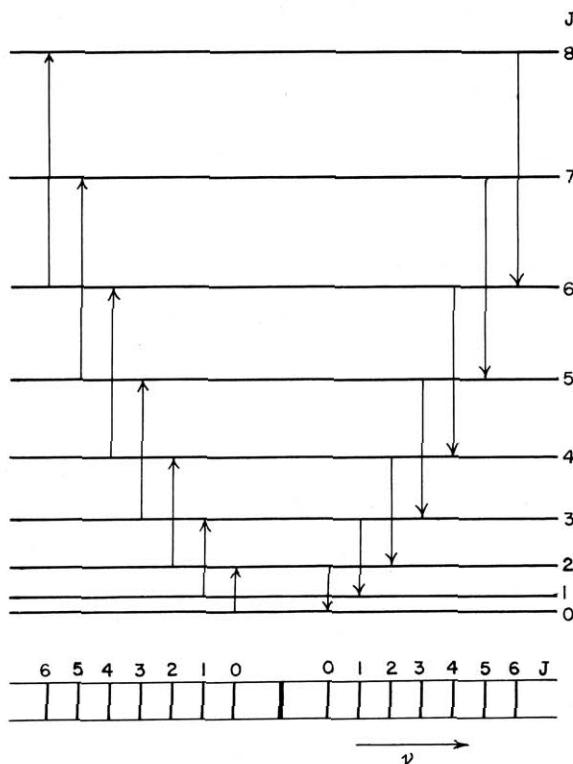


Figure 1. Energy-level diagram and schematic spectrum for a rotational Raman spectrum. The transitions and spectrum at the left are the Stokes lines and those on the right are the anti-Stokes lines. The numbers added to the Raman lines are the  $J$  values of the lower state. The dark line in the center is the undisplaced laser line.

$$|\Delta\omega(J)| = (4B_v - 6D_v)(J + 3/2) - 8D_v(J + 3/2)^3 \quad (10)$$

where  $J = 0, 1, 2, \dots$  for Stokes lines and  $J = 2, 3, \dots$  for anti-Stokes lines. Since  $B_v \gg D_v$  the rotational Raman spectrum for a given vibrational state consists of two series of lines (Stokes and anti-Stokes) centered about the laser wave number. These lines are approximately spaced at  $4B_v$ . Figure 1 illustrates the transitions involved and the schematic spectrum.

Rotational Raman spectra will occur, of course, for molecules in all of the vibrational states, i.e., sets of Raman lines will occur for molecules occupying the  $v = 0, v = 1, \dots$  vibrational states. Since the rotational constant depends on the vibrational state, the different sets of rotational lines occur at different wave numbers, with the relative intensities being given by the Boltzmann factor  $\exp[-E(v)/kT]$ . If the vibrational energy is approximately equal to  $kT$ , then these so-called "hot transitions" will be evident in the Raman spectrum. However, for low molecular weight diatomic molecules like  $O_2$  and  $N_2$ ,  $E(v) \gg kT$  and no "hot transitions" are observed.

A derivation of the line intensities is also quite involved and will not be given here. However, it can be shown (1) that the intensities of the lines in eqn. (10) are given by

$$I(J) \cong g_n S_J \exp[-E(J)/kT] \quad (11)$$

where  $k$  is Boltzmann's constant,  $T$  is the absolute temperature,  $g_n$  is a nuclear degeneracy factor (see next section), and  $S_J = (J + 1)(J + 2)/(2J + 3)$  for Stokes lines and  $S_J = (J - 1)J/(2J - 1)$  for anti-Stokes lines. For heteronuclear diatomic molecules and unsymmetrical linear molecules ( $C_{\infty v}$ ),  $g_n$  is equal to unity. In order to determine  $g_n$  for homonuclear diatomic molecules, the complete wave function must be examined.

The total wave function of a homonuclear diatomic molecule may be written as  $\psi_{\text{total}} = \psi_e \psi_v \psi_r \psi_n$ , where the

subscripts  $e, v, r$ , and  $n$  refer to electronic, vibrational, rotational, and nuclear, respectively. We are interested in the properties of the total wave function when the coordinates  $(x, y, z)$  of the nuclei are replaced by their negatives  $(-x, -y, -z)$ , i.e., the effect of nuclear interchange on  $\psi_{\text{total}}$ . The properties of  $\psi_{\text{total}}$  on nuclear interchange will be determined by considering the effects of interchange on  $\psi_e, \psi_v, \psi_r$ , and  $\psi_n$ .

Interchanging the nuclear coordinates does affect the electronic spatial coordinates, since they are defined with respect to the molecule-fixed  $xyz$  axes which are rigidly attached to the nuclei. It can be shown (3) that the wave functions for molecules with  $\Sigma_g^+$ ,  $\Sigma_u^-$ ,  $\rho_g^+$ ,  $\rho_u^-$ , ... electronic states are symmetric to interchange of the nuclear coordinates, while the wave functions for molecules with  $\Sigma_g^-$ ,  $\Sigma_u^+$ ,  $\rho_g^-$ ,  $\rho_u^+$ , ... electronic states are antisymmetric to nuclear interchange. Since most diatomic molecules have  $\Sigma_g^+$  ground electronic states, the interchange operation does not affect  $\psi_e$ . If  $\hat{i}$  denotes the nuclear interchange operator, we can write

$$\hat{i}\psi_e(\Sigma_g^+) \rightarrow \psi_e(\Sigma_g^+) \quad (12)$$

The notable exception to this rule is oxygen which has a  $\Sigma_g^-$  ground electronic state, and the wave function is therefore antisymmetric to nuclear interchange.

The vibrational wave function of a diatomic molecule depends only on the bond distance  $r$  and is not affected by the interchange operation

$$\hat{i}\psi_v \rightarrow \psi_v \quad (13)$$

The rotational wave functions are known to have the properties (1)

$$\begin{aligned} \hat{i}\psi_r(J \text{ even}) &\rightarrow \psi_r(J \text{ even}) \\ \hat{i}\psi_r(J \text{ odd}) &\rightarrow -\psi_r(J \text{ odd}) \end{aligned} \quad (14)$$

Nuclear interchange does not change the rotational wave function when  $J$  is even, but changes the sign when  $J$  is odd.

The effect of nuclear interchange on the nuclear wave function is probably best illustrated by considering a homonuclear diatomic molecule with nuclear spin of  $1/2$ . In this case the spin eigenfunctions are either  $\alpha$  or  $\beta$ , and the complete nuclear wave functions are the well-known expressions

$$\begin{aligned} \psi_{n_1} &= \alpha(1)\alpha(2) \\ \psi_{n_2} &= \beta(1)\beta(2) \\ \psi_{n_3} &= (2)^{-1/2}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \\ \psi_{n_4} &= (2)^{-1/2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \end{aligned} \quad (15)$$

where 1 and 2 refer to nuclei 1 and 2. Application of the interchange operator to eqns. (15) gives

$$\hat{i} \begin{bmatrix} \psi_{n_1} \\ \psi_{n_2} \\ \psi_{n_3} \\ \psi_{n_4} \end{bmatrix} \rightarrow \begin{bmatrix} \psi_{n_1} \\ \psi_{n_2} \\ \psi_{n_3} \\ -\psi_{n_4} \end{bmatrix} \quad (16)$$

We see that for a nuclear spin of  $1/2$  there are three symmetrical nuclear wave functions and one antisymmetrical function. The number of different symmetric and antisymmetric nuclear wave functions that can be constructed for other nuclear spins depends on the nuclear spin (see the table).

Before selecting the rotational and nuclear wave functions for constructing  $\psi_{\text{total}}$ , it is first necessary to consider the Pauli exclusion principle (4). This principle states that if the coordinates of any two particles with integral spin quantum numbers are interchanged,  $\psi_{\text{total}}$  must re-

main unchanged, i.e., symmetric to interchange. Particles of this type are said to follow Bose-Einstein statistics and are called Bosons. On the other hand, if the coordinates of any two particles with half-integral spin quantum numbers are interchanged,  $\psi_{\text{total}}$  must change sign, i.e., antisymmetric to interchange. Particles with half-integral spins are said to follow Fermi-Dirac statistics and are called Fermions. The Pauli exclusion principle therefore requires

$$\begin{aligned} \hat{i}\psi_{\text{total}} &\rightarrow \psi_{\text{total}} \quad (\text{nuclear spin} = 0, 1, 2, \dots) \\ \hat{i}\psi_{\text{total}} &\rightarrow -\psi_{\text{total}} \quad (\text{nuclear spin} = 1/2, 3/2, \dots) \end{aligned} \quad (17)$$

For a homonuclear diatomic molecule with nuclear spin of 1/2, the total wave function must be antisymmetric to interchange of the nuclei. For a  $\Sigma_g^+$  electronic state the total wave function can be constructed in four ways

$$\begin{aligned} \psi_{\text{total}} &= \psi_e \psi_v \psi_r (J \text{ odd}) & (18) \\ &= \begin{bmatrix} \psi_{n_1} \\ \psi_{n_2} \\ \psi_{n_3} \end{bmatrix} \\ \psi_{\text{total}} &= \psi_e \psi_v \psi_r (J \text{ even}) \quad \psi_{n_4} \end{aligned}$$

For Fermions even  $J$  levels combine with antisymmetric nuclear spin functions and odd  $J$  levels combine with symmetric nuclear spin functions. For Bosons the combinations between  $\psi_r$  and  $\psi_n$  are reversed. As a consequence of nuclear spin, some levels have higher degeneracy due to the larger number of nuclear spin functions that are possible. This so-called statistical weight ( $g_n$  in eqn. (11)) enhances the intensities of rotational lines originating from nuclear states that are degenerate. For a nuclear spin of 1/2 the rotational lines originating from odd  $J$  levels will have intensities three times as great as those originating from even  $J$  levels; i.e.,  $g_n$  in eqn. (11) is equal to three for odd  $J$  and unity for even  $J$ . The statistical weights of the  $J$  states for different nuclear spins are shown in the table.

## Experimental

A common procedure for observing the Raman effect is to pass a laser through a sample of gas and observe the scattered radiation at 90° to the incident laser beam. Gas cells are usually small (a few milliliters) and constructed of glass, including the windows. Cells are filled with gas using standard vacuum techniques that are discussed in detail in physical chemistry laboratory texts (5). In order to maximize the intensity of the Raman spectrum, the laser is passed through the sample several times by using reflecting optics. The optical arrangement is quite specialized, however, and depends on the Raman instrument.

The rotational Raman spectra of N<sub>2</sub> and O<sub>2</sub> gases,

which are shown in Figures 2 and 3, were recorded with a Jarrell-Ash model 25-400 laser Raman spectrometer equipped with a Spectra Physics model 164 argon-ion laser, photon-counting electronics, and standard gas optics. The instrumental conditions are given in the figure captions. With this equipment it was very easy to obtain high-quality spectra. A single pass of the laser through air (without a gas cell) was sufficient to give a good spectrum of air. Gas spectra could also be observed using standard liquid cells filled with gas.

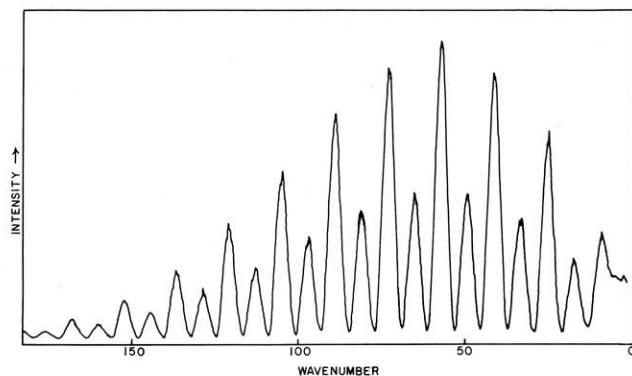


Figure 2. Rotational Raman spectrum of nitrogen. Pressure was 760 torr and the instrumental conditions were:  $5 \times 10^3$  cps,  $3 \text{ cm}^{-1}$  spectral slit-width,  $5 \text{ cm}^{-1}/\text{min}$  scan rate, 2 s time constant, and 400 mW of 4880 angstrom laser power.

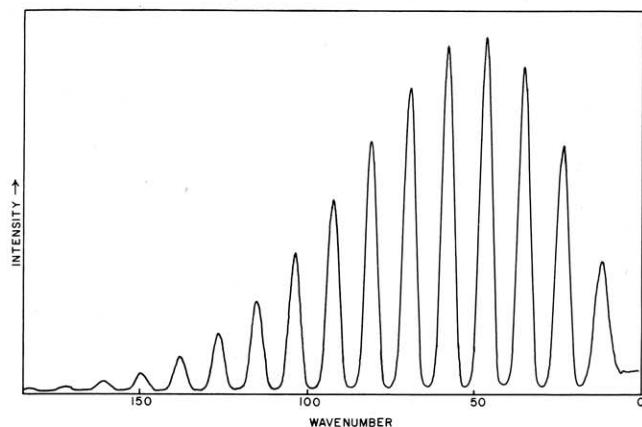


Figure 3. Rotational Raman spectrum of oxygen. Pressure was 760 torr and the instrumental conditions were:  $1 \times 10^4$  cps,  $3 \text{ cm}^{-1}$  spectral slit-width,  $20 \text{ cm}^{-1}/\text{min}$  scan rate, 2 s time constant, and 300 mW of 4880 angstrom laser power.

Molecular Data and Statistical Weights of the  $J$  Levels for some Linear Molecules<sup>a</sup>

Molecule	Molecular data					Nuclear spin	Statistical weight ( $g_n$ )	
	$B_e$ (cm <sup>-1</sup> )	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$\alpha_e$ (cm <sup>-1</sup> )	$r_{e^*}$ (Å)			
<sup>1</sup> H <sub>2</sub>	60.80	4395	117	2.99	0.742	$1/2$	1	3
<sup>2</sup> H <sub>2</sub>	30.43	3118	64.1	1.05	0.742	1	6	3
<sup>14</sup> N <sub>2</sub>	2.010	2360	14.46	0.0187	1.094	1	6	3
<sup>16</sup> O <sub>2</sub>	1.446	1580	12.07	0.0158	1.207	0	0	1
<sup>19</sup> F <sub>2</sub>	0.86	892	...	...	1.435	$1/2$	1	3
<sup>35</sup> Cl <sub>2</sub>	0.2438	565	4.0	0.0017	1.988	$3/2$	6	10
<sup>12</sup> C <sup>16</sup> O	1.931	2170	13.46	0.0175	1.128	...	1	1
<sup>1</sup> H <sup>35</sup> Cl	10.59	2990	52.05	0.302	1.275	...	1	1
<sup>12</sup> C <sup>16</sup> O <sub>2</sub> <sup>b</sup>	0.3906 ( $B_0 = 0.3895$ )				1.162 ( $r_0 = 1.163$ ) 1.202 (CC)	0	1	0
<sup>12</sup> C <sub>2</sub> <sup>1</sup> H <sub>2</sub> <sup>b</sup>	1.1838 ( $B_0 = 1.1769$ )				( $r_0 = 1.207$ ) 1.059 (CH) ( $r_0 = 1.059$ )	$1/2$	1	3

<sup>a</sup> Reference (1).

<sup>b</sup> Reference (6).

Anyone wanting to observe rotational Raman spectra should refer to the instruction manual for their instrument. One should avoid scanning at the laser frequency (zero frequency shift), since this may result in damage to the photomultiplier tube. Since the intensity of a spectrum is proportional to concentration, path length, and laser power, it is advisable to maximize these parameters. If possible one should use gas pressures of about 1 atm, reflecting optics, and high laser power (about 500 mW).

## Discussion

The Stokes lines in the rotational Raman spectrum of  $N_2$  are shown in Figure 2. The spectrum contains a series of lines spaced by about  $8.0 \text{ cm}^{-1}$ . The nuclear spin of  $N^{14}$  is unity and the statistical weights (see the table) are six for even  $J$  levels and three for odd  $J$  levels. The alternation in intensities of strong-weak-strong in the ratio of one to two is evident, with transitions originating from even  $J$  levels being more intense. The most intense line in the spectrum is the transition  $J = 6 \rightarrow J = 8$ , and lines originating from  $J$  levels greater than 20 are observed.

The Stokes lines in the rotational Raman spectrum of  $O_2$  are shown in Figure 3. The lines, which are spaced by about  $11.5 \text{ cm}^{-1}$ , increase in intensity, reach a maximum, and decrease in a uniform manner, with no intensity alternation. A spectrum of this type is indicative of a nuclear spin of zero. In this case either the even  $J$  levels or the odd  $J$  levels are completely missing (no wave function that obeys the Pauli exclusion principle can be constructed for either the even or odd  $J$  levels).

It is possible to determine whether the even or odd rotational levels are missing from measurements of the line spacing and the separation between the first lines in the Stokes and anti-Stokes spectra. If the odd levels are missing the first lines in the Stokes and anti-Stokes spectra will occur at  $6B_0$  from the exciting line with a separation of  $12B_0$ . The spacing between the lines in either branch is  $8B_0$  and the ratio is  $12B_0:8B_0 = 3:2$ . If the even  $J$  levels are missing the spacing between the first lines in the Stokes and anti-Stokes spectra would be  $20B_0$ . Since the line spacing is  $8B_0$  the ratio is  $20B_0:8B_0 = 5:2$ .

If one measures the spacing between the first lines in the Stokes and anti-Stokes spectra and divides this by the line spacing of  $11.5 \text{ cm}^{-1}$ , the ratio is found to be 5:2. We therefore conclude that in the oxygen spectrum only the odd  $J$  levels exist. Furthermore, this requires that the electronic wave function be antisymmetric to nuclear interchange, which is consistent with the known electronic state of  ${}^3\Sigma_g^-$ .

Since the observed rotational Raman spectra of both oxygen and nitrogen originate from molecules in the ground vibrational states, the wave numbers of the Stokes lines (the lines that are usually observed) are given by eqn. (10), where  $B_v = B_0$  and  $D_v = D_0$ . From eqns. (2), (7), and (8), together with the data in the table,  $D_0$  is calculated to be  $4.8 \times 10^{-6}$  for oxygen and  $5.8 \times 10^{-6}$  for nitrogen. Consequently, the last term in eqn. (10) has no appreciable ( $0.1 \text{ cm}^{-1}$  or less) contribution to  $|\Delta\omega(J)|$  for  $J < 12$  for both oxygen and nitrogen.

If only the Stokes lines for  $J < 12$  are considered, an excellent equation for the wave numbers of the Raman lines is obtained from eqn. (10) by setting  $D_v = 0$

$$|\Delta\omega(J)| = 4B_0(J + 3/2) \quad (19)$$

Therefore, a plot of the observed wave numbers of the Raman lines versus  $J$  gives a straight line with a slope of  $4B_0$  and an intercept of  $6B_0$ . Figure 4 shows plots of  $|\Delta\omega(J)|$  versus  $J$  for nitrogen and oxygen.

The precision with which individual lines can be measured varies, of course, with the Raman instrument and the spectroscopist. With the instrument used in this work, line positions could be measured to about  $0.1 \text{ cm}^{-1}$  and

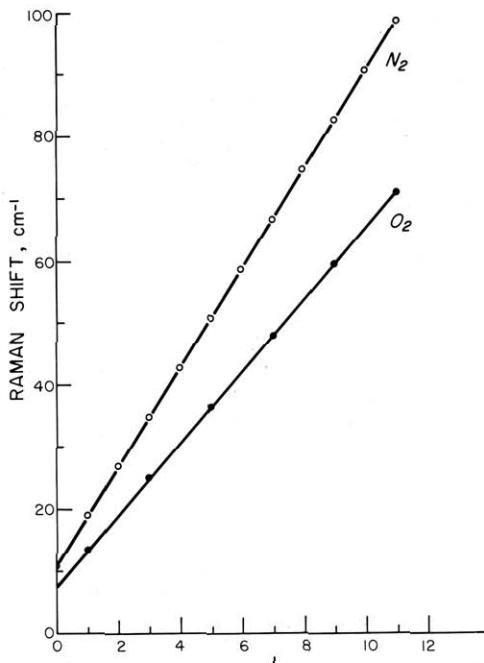


Figure 4. Plot of the wave numbers of the rotational lines of nitrogen and oxygen versus the rotational quantum number  $J$ . The wave numbers were determined from a spectrum with a scale of  $1 \text{ cm}/\text{cm}^{-1}$ . The gas pressure was 760 torr and the instrumental conditions were:  $2 \times 10^3 \text{ cps}$ ,  $1 \text{ cm}^{-1}$  spectral slitwidth,  $5 \text{ cm}^{-1}/\text{min}$  scan rate, 2 s time constant, and 1 W of 5145 angstrom laser power.

least-squares fits to the lines in Figure 4 resulted in standard deviations less than  $0.1 \text{ cm}^{-1}$ . However, since the linearity of the wave number scale on a spectrometer is usually more reliable than the absolute wave number, the value of  $B_0$  should be determined from the slope of the  $|\Delta\omega(J)|$  versus  $J$  plot, since the slope depends only on the linearity of the wave number scale. From the slopes of these lines the rotational constants were determined to be  $1.986 \text{ cm}^{-1}$  for nitrogen and  $1.432 \text{ cm}^{-1}$  for oxygen. The rotational constants calculated from the data in the table are  $2.000 \text{ cm}^{-1}$  and  $1.438 \text{ cm}^{-1}$ , respectively.

From eqns. (4) and (5) the average bond distance in the ground vibrational state is given as

$$r_0 = \left[ \frac{h}{8\pi^2 c \mu B_0} \right]^{1/2} \quad (20)$$

If we define  $M = M_1 M_2 / (M_1 + M_2)$ , the reduced mass in atomic mass units (amu), eqn. (20) yields

$$r_0(\text{\AA}) = 4.106 [MB_0(\text{cm}^{-1})]^{-1/2} \quad (21)$$

From the rotational constants given above, eqn. (21) gives bond distances of  $1.101 \text{ \AA}$  for nitrogen and  $1.213 \text{ \AA}$  for oxygen. The bond distances determined from the data in the table are  $1.097 \text{ \AA}$  and  $1.211 \text{ \AA}$ , respectively. The errors are therefore  $0.004 \text{ \AA}$  (0.35%) for nitrogen and  $0.002 \text{ \AA}$  (0.16%) for oxygen.

If a high-quality Raman spectrometer is available, it may be possible to determine  $D_0$  values for nitrogen and oxygen if wave numbers can be obtained for the lines greater than  $150 \text{ cm}^{-1}$ . However, the uncertainties in the line wave numbers may be large due to the low intensities, and, consequently, the  $D_0$  values may have large errors. In order to minimize these uncertainties it is necessary to use high gas pressures, good gas-phase optics and cells, and high laser power.

Equation (10) shows that if the line wave numbers are fit to a cubic equation in  $(J + 3/2)$ , the coefficient of the  $(J + 3/2)^3$  term is  $-8D_0$ . However, unless accurate line

wave numbers are available the fit will be poor. It is best therefore to rely on the line spacings, since these depend on the linearity of the wave number scale. Since  $D_0 \ll B_0$ , eqn. (10) gives

$$\frac{|\Delta\omega(J)| - |\Delta\omega(0)|}{J} = 4B_0 - 8D_0 \frac{(J + 3/2)^3}{J} \quad (22)$$

If the line wave numbers relative to  $|\Delta\omega(0)|$  are divided by  $J$  and plotted versus  $(J + 3/2)^3/J$ , a straight line results with an intercept of  $4B_0$  and a slope of  $-8D_0$ . A least-squares fit of the lines of nitrogen in this way gave  $B_0 = 1.998 \text{ cm}^{-1}$  and  $D_0 = 14.8 \times 10^{-6} \text{ cm}^{-1}$ . The value of  $B_0$  is in error by 0.1%, but  $D_0$  is in error by about 175%. From eqn. (21) the bond distance is calculated to be  $1.098 \text{ \AA}$ , which is in error by only  $0.001 \text{ \AA}$ .

For oxygen the first line is  $|\Delta\omega(1)|$  and eqn. (10) gives

$$\frac{|\Delta\omega(J)| - |\Delta\omega(1)|}{J - 1} = 4B_0 - 8D_0 \frac{(J + 3/2)^3}{J - 1} \quad (23)$$

A least-squares fit of  $(|\Delta\omega(J)| - |\Delta\omega(1)|)/(J - 1)$  versus  $(J + 3/2)^3/(J - 1)$  for oxygen yielded  $B_0 = 1.434 \text{ cm}^{-1}$  and  $D_0 = 4.3 \times 10^{-6} \text{ cm}^{-1}$ . The error in  $B_0$  is 0.3% and that in  $D_0$  is 10%. This value of  $B_0$  results in a bond distance of  $1.212 \text{ \AA}$ , which is in error by  $0.001 \text{ \AA}$ .

While diatomic molecules have been emphasized in this paper, the extension to the rotational Raman spectra of

linear polyatomic molecules is easily accomplished. If all vibrational modes are in their ground states, then the spectrum has the same appearance as that of a diatomic molecule. If we use the rigid-rotor approximation the spectra can be interpreted using eqns. (3), (4), (11), and (19), except that the moment of inertia  $I = \sum m_i r_i^2$ , where  $r_i$  is the distance of mass  $m_i$  from the center of mass of the molecule, and the statistical weights ( $g_n$  in eqn. (11)) will be different (6). The line wave numbers could be fit to eqn. (19) to determine  $B_0$ , which yields the moment of inertia using eqn. (4). For molecules with one type of bond (e.g.,  $\text{CO}_2$ ), the moment of inertia can be used to determine the bond distance. On the other hand, if more than one type of bond is present (e.g.,  $\text{C}_2\text{H}_2$ ), isotopic spectra (e.g.,  $\text{C}_2\text{D}_2$ ) are needed before the bond distances can be evaluated. A more detailed discussion of linear molecules is given in reference (6).

#### Literature Cited

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