Chapter 10

Molecular rotations and vibrations

Exercises

10.1 The rates of stimulated and spontaneous emission are given by eqns 6.87 and 6.90:

$$W^{\text{stim}}_{\text{f}\to\text{i}} = B_{\text{fi}}\rho \quad W^{\text{spont}}_{\text{f}\to\text{i}} = A_{\text{fi}}$$

where ρ is the energy density of radiation states and is given by the Planck distribution.

Therefore, the ratio of the rates is (using eqn 6.92b and noting that $B_{\text{fi}} = B_{\text{if}}$):

$$\frac{W^{\text{stim}}_{\text{f}\leftarrow\text{i}}}{W^{\text{spont}}_{\text{f}\leftarrow\text{i}}} = \frac{B_{\text{fi}}\rho}{A_{\text{fi}}} = \frac{1}{\text{e}^{h\nu/kT}-1}$$

where ν is the transition frequency. In terms of the transition wavelength, the ratio is

$$\frac{W^{\text{stim}}_{\text{f}\leftarrow\text{i}}}{W^{\text{spont}}_{\text{f}\leftarrow\text{i}}} = \frac{1}{\text{e}^{hc/\lambda kT}-1}$$

and at 298 K,

(a) for $\lambda = 0.10$ nm: ratio $= 1/(\text{e}^{483\,000} - 1)$

(b) for $\lambda = 10$ nm: ratio $= 1/(\text{e}^{4\,830} - 1)$

(c) for $\lambda = 6000$ nm: ratio $= 1/(\text{e}^{480.5} - 1)$

10.2 Begin with eqn 10.7:

$$\mu(t) = 2\alpha(t)\mathcal{E}_0 \cos \omega t$$

If the polarizability of the molecule α changes between α_{min} and α_{max} at a frequency ω_{int} as a result of its rotation or vibration, we can write

$$\alpha(t) = \alpha + \tfrac{1}{2}\Delta\alpha \cos \omega_{\text{int}}t$$

where α is the mean polarizability and $\Delta\alpha = \alpha_{\text{max}} - \alpha_{\text{min}}$. Since

$$\cos (A + B) = \cos A \cos B - \sin A \sin B$$

$$\cos (A - B) = \cos A \cos B + \sin A \sin B$$

we note that

$$\begin{aligned}\cos (\omega + \omega_{\text{int}})t + \cos (\omega - \omega_{\text{int}})t &= \cos \omega t \cos \omega_{\text{int}}t - \sin \omega t \sin \omega_{\text{int}}t + \cos \omega t \cos \omega_{\text{int}}t + \sin \omega t \sin \omega_{\text{int}}t \\ &= 2 \cos \omega t \cos \omega_{\text{int}}t\end{aligned}$$

and therefore

$$\begin{aligned}\mu(t) &= 2\alpha(t)\mathcal{E}_0 \cos \omega t \\ &= 2\alpha\mathcal{E}_0 \cos \omega t + \Delta\alpha\, \mathcal{E}_0 \cos \omega_{\text{int}}t \cos \omega t \\ &= 2\alpha\mathcal{E}_0 \cos \omega t + \tfrac{1}{2}\Delta\alpha\, \mathcal{E}_0[\cos (\omega + \omega_{\text{int}})t + \cos (\omega - \omega_{\text{int}})t]\end{aligned}$$

which is eqn 10.8.

10.3 The centre of mass is where $m_A R_A = m_B R_B$, where R_A is the distance from atom A of mass m_A to the centre of mass, R_B is the distance from atom B of mass m_B to the centre of mass, and $R_A + R_B = R$. Therefore $m_A R_A = m_B(R - R_A)$ and

$$R_A = m_B R/(m_A + m_B) \text{ and } R_B = R - R_A = m_A R/(m_A + m_B)$$

The moment of inertia is then

$$\begin{aligned}I &= m_A R_A^2 + m_B R_B^2 \\ &= m_A\{m_B/(m_A + m_B)\}^2 R^2 + m_B\{m_A/(m_A + m_B)\}^2 R^2 \\ &= \{m_A\, m_B/(m_A + m_B)\}R^2 = \mu R^2, \quad \mu = m_A\, m_B/(m_A + m_B)\end{aligned}$$

10.4 (a) $^1H_2$:

$$I = \tfrac{1}{2}m(^1\mathrm{H})R^2 = \tfrac{1}{2} \times 1.0078\, m_\mathrm{u} \times (75.09\ \mathrm{pm})^2$$

$$= \underline{4.718 \times 10^{-48}\ \mathrm{kg\ m^2}}\ [1\ m_\mathrm{u} = 1.660\ 56 \times 10^{-27}\ \mathrm{kg, or\ use}\ m = m_\mathrm{e} + m_\mathrm{p}]$$

(b) $^2H_2$:

$$I = \tfrac{1}{2}m(^2\mathrm{H})R^2 = \underline{9.429 \times 10^{-48}\ \mathrm{kg\ m^2}}$$

(c) $^1H^{35}Cl$:

$$I = \left\{\frac{m(^1\mathrm{H})m(^{35}\mathrm{Cl})}{m(^1\mathrm{H}) + m(^{35}\mathrm{Cl})}\right\} R^2 = \underline{2.644 \times 10^{-47}\ \mathrm{kg\ m^2}}$$

Exercise: Find the moments of inertia of H_2O about three perpendicular axes.

10.5 Refer to Fig. 10.1.

$I = 4m_\mathrm{B}R^2$ [only atoms *a, b, c, d* contribute for the axis shown; all axes are equivalent]

Exercise: Repeat the question for an AB_5 trigonal bipyramid with bond lengths R_ax, R_eq.

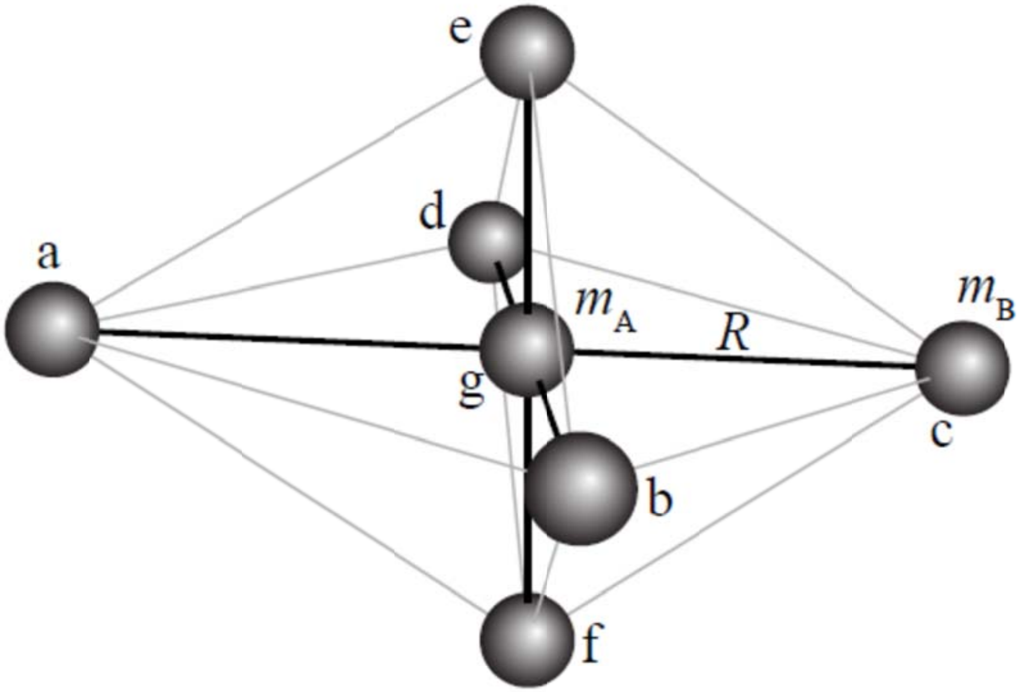


Figure 10.1: An octahedral molecule and the calculation of its moment of inertia.

10.6

$$I' = \sum_i m_i x_i'^2 = \sum_i m_i (x_i + R)^2$$

$$= \sum_i m_i x_i^2 + 2R\sum_i m_i x_i + R^2\sum_i m_i$$

$$= I + 0 + mR^2 = I + mR^2$$

because $\sum_i m_i x_i = 0$ for centre of mass and $\sum_i m_i = m$.

10.7 The NH_3 molecule is a symmetric rotor; its rotational wavenumbers are given by eqn 10.16.

For each value of J, values of both K and M_J extend in steps of 1 from $-J$ to $+J$.

(J, K, M_J)	$\tilde{F} = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$ (cm^{-1})
(0,0,0)	0
(1,±1,±1), (1, ±1,0)	7.321
(1,0,±1), (1,0,0)	1.954
(2,±2,±2), (2,±2,±1), (2,±2,0)	27.330
(2,±1,±2), (2,±1,±1), (2,±1,0)	11.229
(2,0,±2), (2,0,±1), (2,0,0)	5.862
(3,±3,±3), (3,±3,±2), (3,±3,±1), (3,±3,0)	60.027
(3,±2,±3), (3,±2,±2), (3,±2,±1), (3,±2,0)	33.192
(3,±1,±3), (3,±1,±2), (3,±1,±1), (3,±1,0)	17.091
(3,0,±3), (3,0,±2), (3,0,±1), (3,0,0)	11.724

10.8 Polar molecules may show a pure rotational microwave absorption spectrum. Therefore, **(c)**, **(d)**, and **(e)**.

10.9 The line separation is $\Delta E/hc = 2B$. Then, as $\tilde{B} = \hbar/4\pi cI_\perp$, we have (with $I_\perp = \mu R^2$)

$$\tilde{\nu} = \Delta E/hc = \hbar/2\pi cI_\perp = \hbar/2\pi c\mu R^2$$

Therefore,

$$R = \{\hbar/2\pi c\mu\tilde{\nu}\}^{1/2}$$

$$= \underline{162}\text{ pm} \quad [\mu = 0.999\,86\, m_u = 1.6603 \times 10^{-27}\text{ kg}, \Delta E/hc = 12.8\text{ cm}^{-1}]$$

10.10 For $^2H^{127}I$, $\mu = 1.9826\, m_u$. As $\tilde{\nu} \propto 1/\mu$ the line separation will be $0.5043 \times (12.8\text{ cm}^{-1}) = \underline{6.46\text{ cm}^{-1}}$.

Exercise: The bond length of $^1H^2H$ is 74.136 pm. At what wavenumbers would it absorb if its rotational transitions were active?

10.11 Rotational Raman transitions obey the selection rule $\Delta J = \pm 2$ for linear molecules. From the discussion in Section 10.5, with $\tilde{\nu}_0$ the wavenumber of the incident radiation (that is, the Rayleigh line), the wavenumbers of the Stokes and anti-Stokes lines relative to and closest to the Rayleigh line are:

Stokes lines: $\tilde{\nu}_J - \tilde{\nu}_0 = -4\tilde{B}\,(J+3/2) \quad J = 0, 1, 2$

Anti-Stokes lines: $\tilde{\nu}_J - \tilde{\nu}_0 = 4\tilde{B}\,(J-1/2) \quad J = 2, 3, 4$

Since $\tilde{B} = 10.4400\ \text{cm}^{-1}$, the relative wavenumbers are:

Stokes: $J = 0$ $-62.64\ \text{cm}^{-1}$
$J = 1$ $-104.4\ \text{cm}^{-1}$
$J = 2$ $-146.16\ \text{cm}^{-1}$

Anti-Stokes: $J = 0$ $+62.64\ \text{cm}^{-1}$
$J = 1$ $+104.4\ \text{cm}^{-1}$
$J = 2$ $+146.16\ \text{cm}^{-1}$

10.12 The rotational wavenumbers for a linear rotor, including the effects of centrifugal distortion, are given by eqn 10.21:

$$\tilde{F} = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2$$

The rotational wavenumbers for the states involved in the rotational Raman transitions in Exercise 10.11 are

$J = 0$ $\tilde{F} = 0$ $J = 1$ $\tilde{F} = 2\tilde{B} - 4\tilde{D}$

$J = 2$ $\tilde{F} = 6\tilde{B} - 36\tilde{D}$ $J = 3$ $\tilde{F} = 12\tilde{B} - 144\tilde{D}$

$J = 4$ $\tilde{F} = 20\tilde{B} - 400\tilde{D}$

The three Stokes lines closest to the Rayleigh line and their wavenumbers are:

$J = 0 \rightarrow J = 2$ $\tilde{\nu}_J - \tilde{\nu}_0 = -6\tilde{B} + 36\tilde{D} = -62.6256\ \text{cm}^{-1}$

$J = 1 \rightarrow J = 3$ $\tilde{\nu}_J - \tilde{\nu}_0 = -10\tilde{B} + 140\tilde{D} = -104.344\ \text{cm}^{-1}$

$J = 2 \rightarrow J = 4$ $\tilde{\nu}_J - \tilde{\nu}_0 = -14\tilde{B} + 364\tilde{D} = -146.0144\ \text{cm}^{-1}$

The three anti-Stokes lines closest to the Rayleigh line and their wavenumbers are:

$J = 2 \rightarrow J = 0$ $\quad \tilde{\nu}_J - \tilde{\nu}_0 = 6\tilde{B} - 36\tilde{D} = +62.6256\ \mathrm{cm}^{-1}$

$J = 3 \rightarrow J = 1$ $\quad \tilde{\nu}_J - \tilde{\nu}_0 = 10\tilde{B} - 140\tilde{D} = +104.344\ \mathrm{cm}^{-1}$

$J = 4 \rightarrow J = 2$ $\quad \tilde{\nu}_J - \tilde{\nu}_0 = 14\tilde{B} - 364\tilde{D} = +146.0144\ \mathrm{cm}^{-1}$

10.13 The lowest rotational level for a diatomic molecule is $J = 0$ with zero rotational energy (i.e. no zero-point energy). However, for molecular hydrogen, as discussed in Section 10.6, there are two distinct forms: *para*-hydrogen (even J) and *ortho*-hydrogen (odd J). The conversion of *ortho* to *para* is very slow so as a sample of H_2 at room temperature is cooled, the *ortho*-hydrogen settles into its lowest rotational state $J = 1$; even at $T = 0$, it cannot readily convert to *para*-hydrogen $J = 0$. Thus, with the $J = 1$ state having some population, there is an effective zero-point energy.

Exercise: What can be said about zero-point rotational energy for dioxygen?

10.14 The following table lists value of μ/m_u for the species; to obtain absolute values use $m_u = 1.660\,56 \times 10^{-27}$ kg; additional data will be found in Exercises 10.4 and 10.9. [Tables of nuclide masses are given in the *Handbook of the American Institute of Physics*, D.E. Gray (ed.), McGraw-Hill (1972).] Values of k are obtained from $k_f = \mu\omega^2 = 4\pi^2\mu c^2\tilde{\nu}^2$ [$\omega = 2\pi\nu$, $\nu = c\tilde{\nu}$].

	$^1H_2$	$^1H^{19}F$	$^1H^{35}Cl$	$^1H^{81}Br$	$^1H^{127}I$
μ/m_u	0.5039	0.9570	0.9796	0.9954	0.9999
$k_f/(\mathrm{N\ m^{-1}})$	574.9	965.7	516.3	411.5	313.8

10.15 For the effect of replacing ^{1}H by ^{2}H, assume that k_f remains constant, and so form $\tilde{\nu} = (1/2\pi c)(k_f/\mu^*)^{1/2}$, with μ^* the reduced mass of the deuterated species. Draw up the following table:

	$^2H^1H$	$^2H^{19}F$	$^2H^{35}Cl$	$^2H^{81}Br$	$^2H^{127}I$
μ^*/m_u	0.6717	1.8210	1.9044	1.9652	1.9826
$\tilde{\nu}/cm^{-1}$	3811	3000	2145	1885	1639

Exercise: In three dimensions the motion of the centre of mass separates from the internal motion, but rotations and vibrations separate only approximately. Demonstrate these features.

10.16 To show an infrared absorption spectrum, a molecule must have a dipole moment that varies, at least transiently, with atomic displacements (that is, stretching and bending motions). Note that a molecule can be nonpolar but still be infrared active if there is at least one vibrational normal mode that induces, at least temporarily, a dipole moment in the molecule. Homonuclear diatomic molecules are infrared inactive; heteronuclear diatomic molecules are active. Therefore, **(a)**, **(c)**, and **(d)** can show infrared absorption spectra.

10.17 The P-branch line corresponds to a transition from the initial state ($v = 0, J = 2$) to the final state ($v = 1, J = 1$). Since a given vibrational-rotational state (v, J) has an energy (in cm^{-1}) of

$$E/hc = (v + 1/2)\tilde{\nu} + \tilde{B}J(J + 1)$$

the photon wavenumber for the transition is

$E(1,1)/hc - E(0,2)/hc$

$=\{(1 + 1/2) \times 4138.3 + 1(1+1) \times 20.9\}\ \mathrm{cm}^{-1} - \{(0 + 1/2) \times 4183.3 + 2(2+1) \times 20.9\}\ \mathrm{cm}^{-1}$

$= 4054.7\ \mathrm{cm}^{-1}$

10.18 The dipole moment of a homonuclear diatomic molecule does not vary with vibrational motion; the molecule remains nonpolar as the bond length changes. However, the molecular polarizability does vary with distance. Therefore, a homonuclear diatomic molecule is infrared inactive but vibrationally Raman active.

10.19 For a linear molecule, there are $3N - 5$ normal modes where N is the number of atoms in the molecule.-For a non-linear molecule, $3N - 6$. Molecules (a) and (b) are non-linear; (c) and (d) are linear.

(a) $N = 4$; $3N - 6 = \underline{6}$

(b) $N = 12$; $3N - 6 = \underline{30}$

(c) $N = 6$; $3N - 5 = \underline{13}$

(d) $N = 3$; $3N - 5 = \underline{4}$

10.20 The molecule has three normal modes so the ground state has zero quanta in each of the vibrational modes; that is, (0, 0, 0) is the ground state. Within the harmonic approximation, each normal mode makes a contribution of $(v_\mathrm{i} + ½)\hbar\omega_i$ to the vibrational energy where v_i is the vibrational quanta in mode i of frequency ω_i. Therefore, the ground-state energy in wavenumber units is

$$E/hc = (0 + 1/2) \times 1595\ \mathrm{cm}^{-1} + (0 + 1/2) \times 3652\ \mathrm{cm}^{-1} + (0 + 1/2) \times 3756\ \mathrm{cm}^{-1} = \underline{450.1.5\ \mathrm{cm}^{-1}}$$

10.21 The point group for NH_3 is C_{3v}. **(a)** Infrared active normal modes must belong to the same symmetry species as x, y, or z, which are A_1 (z) and E (x, y). Therefore all modes are infrared active. **(b)** Raman active modes must belong to the same symmetry species as one of the components of the electric polarizability (x^2, xy, xz, z^2, etc.) Since z^2 is of A_1 symmetry and (x, y)

of E symmetry, both normal modes are Raman active.

10.22 The ground vibrational state is (0, 0, 0). Letting 1595, 3652 and 3756 be the vibrational wavenumber of modes 1, 2 and 3, respectively, we designate an excited state as (v_1, v_2, v_3). The three-lowest frequency overtones correspond to transitions from (0, 0, 0) to the excited states:

$$(2, 0, 0):\ \text{wavenumber} = 2 \times 1595\ \text{cm}^{-1} = 3190\ \ \text{cm}^{-1}$$

$$(3, 0, 0):\ \text{wavenumber} = 3 \times 1595\ \text{cm}^{-1} = 4785\ \ \text{cm}^{-1}$$

$$(4, 0, 0):\ \text{wavenumber} = 4 \times 1595\ \text{cm}^{-1} = 6380\ \ \text{cm}^{-1}$$

The three-lowest frequency combination bands correspond to transitions from (0, 0, 0) to the excited states:

$$(1, 1, 0):\ \text{wavenumber} = 1595\ \text{cm}^{-1} + 3652\ \text{cm}^{-1} = 5247\ \ \text{cm}^{-1}$$

$$(1, 0, 1):\ \text{wavenumber} = 1595\ \text{cm}^{-1} + 3756\ \text{cm}^{-1} = 5351\ \ \text{cm}^{-1}$$

$$(2, 1, 0):\ \text{wavenumber} = 2 \times 1595\ \text{cm}^{-1} + 3652\ \text{cm}^{-1} = 6842\ \ \text{cm}^{-1}$$

Problems

10.1 (a)

$$I = \int_0^R r^2 \mathrm{d}m(r) = \int_0^R (2\pi\rho r \mathrm{d}r) r^2 \quad [\rho : \text{density}]$$

$$= 2\pi\rho \int_0^R r^3 \mathrm{d}r = \tfrac{1}{2}\pi\rho R^4$$

$$m = \pi R^2 \rho; \text{ therefore } I = \frac{\pi R^4 m}{2\pi R^2} = \underline{\tfrac{1}{2} m R^2}$$

(b) The perpendicular distance of the volume element at (r, θ, ϕ) is $r \sin\theta$; therefore

$$I = \int \rho (r\ \sin\theta)^2 \sin\theta \mathrm{d}\theta \mathrm{d}\phi\, r^2 \mathrm{d}r$$

$$= \rho \int_0^R r^4 \mathrm{d}r \int_0^\pi \sin^3\theta \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi = \rho \left(\frac{R^5}{5}\right)\left(\frac{4}{3}\right)(2\pi)$$

$$m = \tfrac{4}{3}\pi R^3 \rho$$

Therefore,

$$I = \frac{(8\pi/15)m\,R^5}{(4\pi/3)R^3} = \underline{\tfrac{2}{5}mR^2}$$

10.4 $\tilde{F}(J, K, M_J) = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$ [eqn 10.16]

$I_{\parallel} = 4m_{\mathrm{B}}R^2$ [Table 10.1]

$I_{\perp} = 2m_{\mathrm{B}}R^2$ [Table 10.1]

Therefore

$$\tilde{A} = \frac{\hbar}{4\pi c I_{\parallel}} = \frac{\hbar}{16\pi m_{\mathrm{B}} c R^2}, \quad \tilde{B} = \frac{\hbar}{4\pi c I_{\perp}} = \frac{\hbar}{8\pi m_{\mathrm{B}} c R^2}$$

and so $\tilde{A} = \tilde{B}/2$. It follows that

$$\tilde{F}(J, K, M_J) = \tilde{B}J(J+1) - \tfrac{1}{2}\tilde{B}K^2 = \tilde{B}\left\{J(J+1) - \tfrac{1}{2}K^2\right\}$$

Exercise: Establish a similar result for an octahedral AB_6 molecule.

10.7 The wavenumbers of the transitions $J + 1 \leftarrow J$ are given in eqn 10.30. To find a maximum, set the first derivative $\mathrm{d}\tilde{\nu}_J/\mathrm{d}J = 0$:

$$\tilde{\nu}_J = 2\tilde{B}(J+1) - 4\tilde{D}(J+1)^3$$

$$\frac{\mathrm{d}\tilde{\nu}_J}{\mathrm{d}J} = 2\tilde{B} - 12\tilde{D}(J+1)^2 = 0$$

Therefore,

$$\tilde{B} = 6\tilde{D}(J+1)^2$$

$$(J+1)^2 = \tilde{B}/6\tilde{D}$$

$$J = \left(\tilde{B}/6\tilde{D}\right)^{1/2} - 1$$

Using the date in problem 10.5 for HCl, we find

$$J = \ (10.4400/\{6\times 0.0004\})^{1/2} - 1 \ \approx 65$$

10.10

$$\tilde{B}(^1\mathrm{H}^{35}\mathrm{Cl}) = \hbar/4\pi c I(^1\mathrm{H}^{35}\mathrm{Cl}) \qquad [I = 2.644\times 10^{-47}\ \mathrm{kg\ m^2},\ \text{Exercise 10.4}]$$

$$= \underline{10.59\ \mathrm{cm^{-1}}}$$

The relative populations are given by

$$b(J) = (2J+1)\exp\{-hc\tilde{B}J(J+1)/kT\}$$

$$= (2J+1)\exp\{-0.050\,79\,J(J+1)\} \qquad [kT/hc = 208.51\ \mathrm{cm^{-1}}\ \text{at 300 K}]$$

Draw up the following table (b' is discussed below):

J	0	1	2	3	4	5	6	7
$b(J)$	1.000	2.710	3.687	3.805	3.259	2.397	1.540	0.873
$b'(J)$	1.000	1.807	2.212	2.175	1.811	1.307	0.829	0.465

J	8	9	10	11	12	13	14	15
$b(J)$	0.439	0.197	0.079	0.028	0.009	0.003	0.001	10^{-4}
$b'(J)$	0.232	0.103	0.041	0.015	0.005	0.001	10^{-4}	10^{-5}

($\Sigma_j\, b(J) = 20.026$, the rotational partition function at 300 K.) **(a)** If the intensities were determined solely by the populations they would be proportional to $b(J)$, and the most intense transition would be $4 \leftarrow 3$. **(b)** If we take the J-dependence of the transition moment into account we should use

$$b'(J) = \{(J+1)/(2J+1)\}b(J) = (J+1)\exp\{-0.050\,79J(J+1)\},$$

which gives the entries in the table above. The transition of maximum intensity is $3 \leftarrow 2$. Note that we have considered only absorption intensities, not net intensities.

Exercise: Calculate the relative net absorption intensities.

10.13 Only vibrational transitions of DCl are being considered and the lowest four transitions from the $v = 0$ state correspond to the transitions:

$v = 0 \rightarrow v = 1$ $\quad (E_1 - E_0)/hc = 2091\ \text{cm}^{-1} = E_1^{\text{rel}}/hc$

$v = 0 \rightarrow v = 2$ $\quad (E_2 - E_0)/hc = 4128\ \text{cm}^{-1} = E_2^{\text{rel}}/hc$

$v = 0 \rightarrow v = 3$ $\quad (E_3 - E_0)/hc = 6111\ \text{cm}^{-1} = E_3^{\text{rel}}/hc$

$v = 0 \rightarrow v = 4$ $\quad (E_4 - E_0)/hc = 8043\ \text{cm}^{-1} = E_4^{\text{rel}}/hc$

where E_v^{rel}/hc is the energy in wavenumber units of vibrational level v relative to the $v = 0$ level. The vibrational energies are given by eqn 10.53 and, as in Example 10.3, we retain the first two terms. Since we desire energies relative to $v = 0$, we substract the zero-point energy

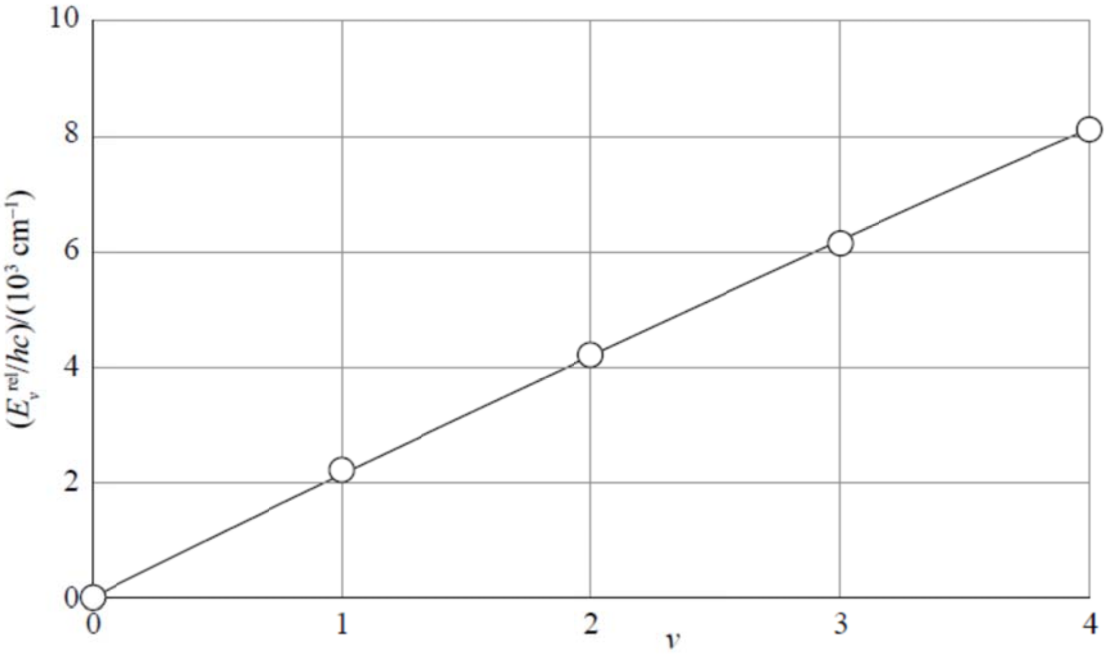
$\frac{1}{2}\hbar\omega - \frac{1}{4}\hbar\omega x_{\text{e}}$. The relative energies are therefore given by

$$E_v^{\text{rel}} = \left(v+\frac{1}{2}\right)\hbar\omega - \left(v+\frac{1}{2}\right)^2 \hbar\omega x_{\text{e}} - \left(\frac{\hbar\omega}{2} - \frac{\hbar\omega x_{\text{e}}}{4}\right)$$

$$= (\hbar\omega - \hbar\omega x_{\text{e}})v - \hbar\omega x_{\text{e}} v^2$$

A plot of E_v^{rel}/hc against v is shown in Fig. 10.4; the best quadratic fit is

$$E_v^{\text{rel}}/hc = 2117.1v - 26.613v^2$$



$$(E_v^{\mathrm{rel}}/hc)/10^3\ \mathrm{cm}^{-1}$$

Figure 10.4: The plot of relative energies against vibrational quantum number for Problem 10.13.

It follows that

$$\hbar\omega - \hbar\omega x_{\mathrm{e}} = (2117.1\ \mathrm{cm}^{-1})hc = 4.206 \times 10^{-20}\ \mathrm{J}$$

$$\hbar\omega x_{\mathrm{e}} = (26.613\ \mathrm{cm}^{-1})hc = 5.287 \times 10^{-22}\ \mathrm{J}$$

and, therefore, $\omega = 4.038 \times 10^{14}\ \mathrm{s}^{-1}$ and $\omega x_{\mathrm{e}} = 5.013 \times 10^{12}\ \mathrm{s}^{-1}$.

10.16

$$\tilde{\nu}^{\mathrm{P}} = \tilde{\nu} - 2(v+1)\tilde{\nu}x_{\mathrm{e}} + \ldots - (\tilde{B}_{v+1} + \tilde{B}_v)J + (\tilde{B}_{v+1} - \tilde{B}_v)J^2 + \ldots \text{ [eqn 10.61]}$$

$$\tilde{\nu}^{\mathrm{Q}} = \tilde{\nu} - 2(v+1)\tilde{\nu}x_{\mathrm{e}} + \ldots + (\tilde{B}_{v+1} - \tilde{B}_v)J + (\tilde{B}_{v+1} - \tilde{B}_v)J^2 + \ldots \text{ [eqn 10.62]}$$

$$\tilde{\nu}^{\mathrm{R}} = \tilde{\nu} - 2(v+1)\tilde{\nu}x_{\mathrm{e}} + \ldots + 2\tilde{B}_{v+1} + (3\tilde{B}_{v+1} - \tilde{B}_v)J + (\tilde{B}_{v+1} - \tilde{B}_v)J^2 + \ldots \text{ [eqn 10.63]}$$

If x_{e} is ignored these equations become

$$\tilde{\nu}^{\mathrm{P}} - \tilde{\nu} = -(\tilde{B}_{v+1} + \tilde{B}_v)J + (\tilde{B}_{v+1} - \tilde{B}_v)J^2 + \ldots$$

$$\tilde{\nu}^{\mathrm{Q}} - \tilde{\nu} = (\tilde{B}_{v+1} - \tilde{B}_v)J + (\tilde{B}_{v+1} - \tilde{B}_v)J^2 + \ldots$$

$$\tilde{\nu}^{\mathrm{R}} - \tilde{\nu} = 2\tilde{B}_{v+1} + (3\tilde{B}_{v+1} - \tilde{B}_v)J + (\tilde{B}_{v+1} - \tilde{B}_v)J^2 + \ldots$$

Then, with $\tilde{B}_0 = 10.4400\ \mathrm{cm}^{-1}$ and $\tilde{B}_1 = 10.1366\ \mathrm{cm}^{-1}$

$$(\tilde{\nu}^{\mathrm{P}} - \tilde{\nu})/\mathrm{cm}^{-1} = -20.5766J - 0.3034J^2$$

$$(\tilde{\nu}^{\mathrm{Q}} - \tilde{\nu})/\mathrm{cm}^{-1} = -0.3034J(J+1)$$

$$(\tilde{\nu}^{\mathrm{R}} - \tilde{\nu})/\mathrm{cm}^{-1} = 20.2732 + 19.9698J - 0.3034J^2$$

The wavenumbers of the branches are plotted in Fig. 10.5.

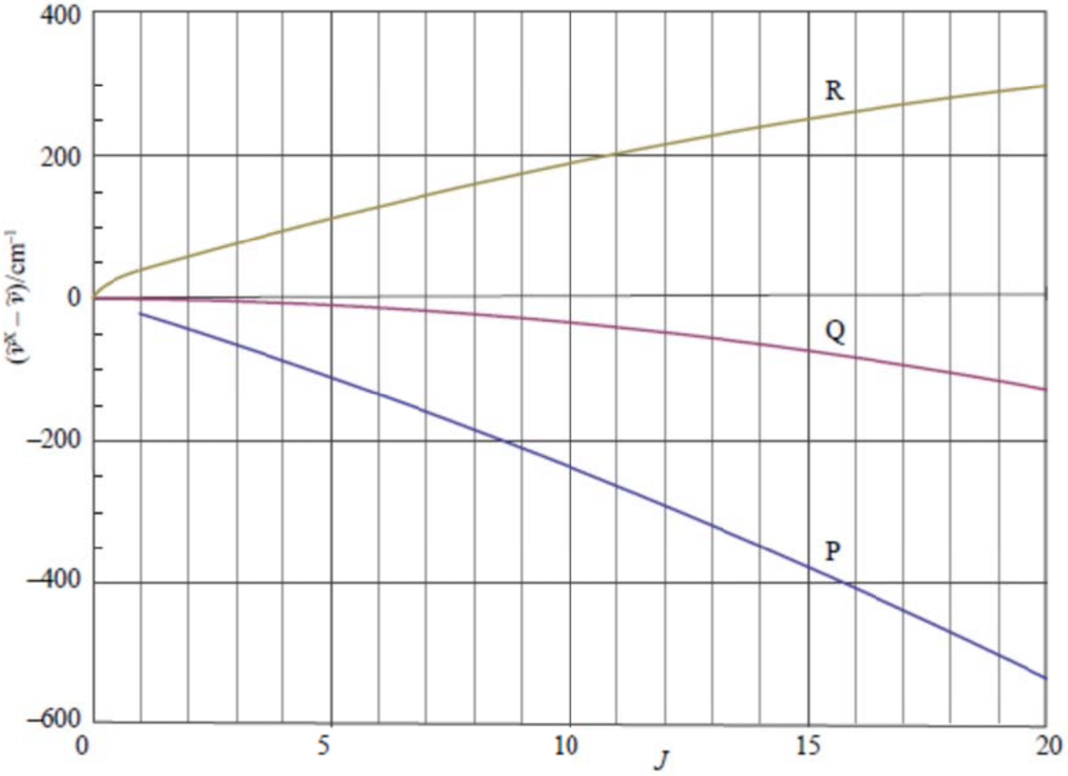


Figure 10.5: The wavenumbers of the P-, Q-, and R-branches calculated in Problem 10.16.

Exercise: Find the location of the lines of the O- and S-branches of the Raman spectrum.

10.19 The energy in wavenumber units of the initial state ($v = 1$, $J = 2$) is [see eqn 10.60 with $\tilde{F} = E/(hc)$]

$$\tilde{F}(v=1, J=2) = (1+\tfrac{1}{2})4401.2\ \text{cm}^{-1} + (2)(2+1)121.3\ \text{cm}^{-1}$$

$$= 7329.6\ \text{cm}^{-1}$$

(a) For the Q-branch Stokes line, $\Delta v = +1$ and $\Delta J = 0$ so the final state of the diatomic molecule is $(v = 2, J = 2)$ with an energy

$$\tilde{F}(v=2, J=2) = (2+\tfrac{1}{2})4401.2\ \text{cm}^{-1} + (2)(2+1)121.3\ \text{cm}^{-1}$$

$$= 11\ 730.8\ \text{cm}^{-1}$$

Therefore, while the diatomic molecule gains an energy given by

$\tilde{F}(v=2, J=2) - \tilde{F}(v=1, J=2)$, the scattered radiation *loses* that energy and therefore has a wavenumber of

$$15\ 873.0 - (11\ 730.8 - 7329.6) = \underline{11\ 471.8\ \text{cm}^{-1}}$$

(b) For the O-branch Stokes line, the final state is $(v = 2, J = 0)$ which has an energy of

$$\tilde{F}(v=2, J=0) = (2+\tfrac{1}{2})4401.2\ \text{cm}^{-1} + (0)(0+1)121.3\ \text{cm}^{-1}$$

$$= 11\ 003.0\ \text{cm}^{-1}$$

Therefore, while the diatomic molecule gains an energy given by

$\tilde{F}(v=2, J=0) - \tilde{F}(v=1, J=2)$, the scattered radiation *loses* that energy and therefore has a wavenumber of

$$15\ 873.0 - (11\ 003.0 - 7329.6) = \underline{12\ 199.6\ \text{cm}^{-1}}$$

(c) For the anti-Stokes line, $\Delta v = -1$ so the final state of the diatomic molecule is ($v = 0$, $J = 2$) with an energy

$$\tilde{F}(v = 0, J = 2) = (0 + \tfrac{1}{2})4401.2\ \text{cm}^{-1} + (2)(2 + 1)121.3\ \text{cm}^{-1}$$

$$= 2928.4\ \text{cm}^{-1}$$

In this case the diatomic molecule loses an energy given by

$\tilde{F}(v = 1, J = 2) - \tilde{F}(v = 0, J = 2)$, and the scattered radiation *gains* that energy; therefore the scattered radiation occurs at a wavenumber of

$$15\,873.0 + (7329.6 - 2928.4) = \underline{20\,274.2\ \text{cm}^{-1}}$$

If anharmonicity effects are included, the spacing between the $v = 1$ and $v = 2$ vibrational levels will decrease (see eqn 10.60) and as a result the scattered Stokes radiation will lose less energy and will thus occur at a <u>higher wavenumber</u> than that computed in part (a).

Exercise: How will the wavenumbers computed in parts (a), (b) and (c) change if the effects of centrifugal distortion are included?

10.22 Consider the system depicted in Fig. 10.6.

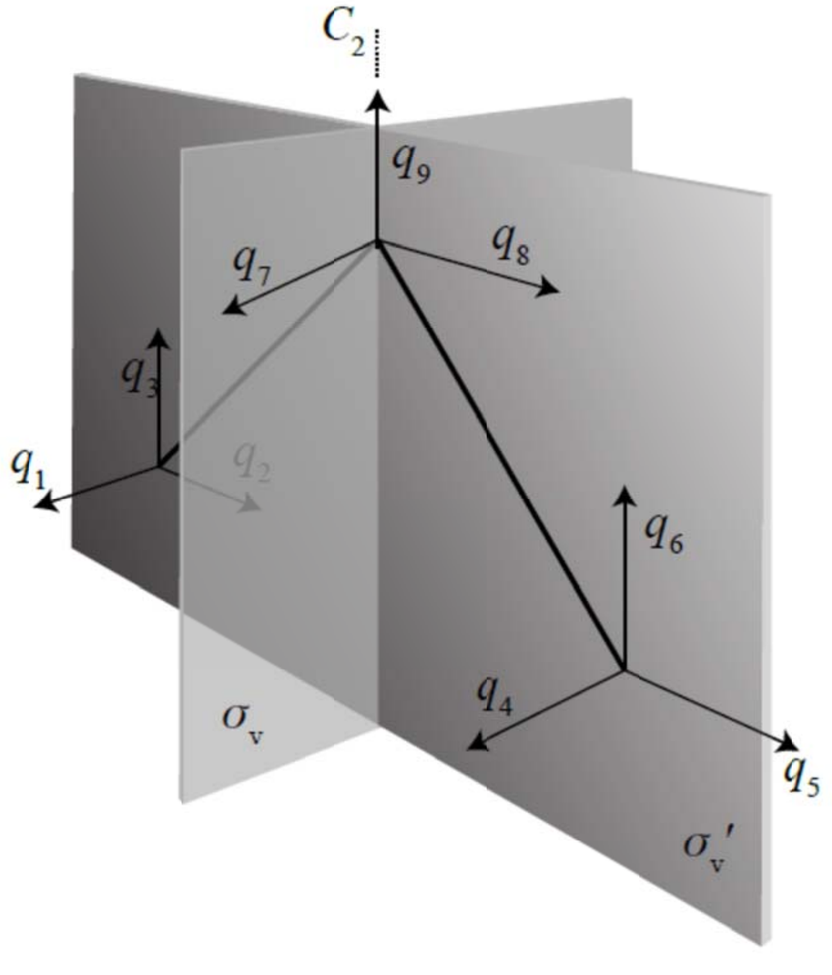


Figure 10.6: The displacement coordinates of a C_{2v} molecule.

Under the operations of the group (C_{2v}) they transform as follows:

	q_1	q_2	q_3	q_4	q_5	q_6	q_7	q_8	q_9	χ

E	q_1	q_2	q_3	q_4	q_5	q_6	q_7	q_8	q_9	9
C_2	$-q_4$	$-q_5$	q_6	$-q_1$	$-q_2$	q_3	$-q_7$	$-q_8$	q_9	-1
σ_v	q_4	$-q_5$	q_6	q_1	$-q_2$	q_3	q_7	$-q_8$	q_9	1
σ'_v	$-q_1$	q_2	q_3	$-q_4$	q_5	q_6	$-q_7$	q_8	q_9	3

[The characters, final column, are given by the net number of displacements left unchanged by the operation.] The representation decomposes as follows [eqn 5.22]:

$$a(\mathrm{A}_1) = \tfrac{1}{4}\{9 - 1 + 1 + 3\} = 3 \quad a(\mathrm{A}_2) = \tfrac{1}{4}\{9 - 1 - 1 - 3\} = 1$$

$$a(\mathrm{B}_1) = \tfrac{1}{4}\{9 + 1 + 1 - 3\} = 2 \quad a(\mathrm{B}_2) = \tfrac{1}{4}\{9 + 1 - 1 + 3\} = 3$$

That is, the basis spans $3\mathrm{A}_1 + \mathrm{A}_2 + 2\mathrm{B}_1 + 3\mathrm{B}_2$. From the C_{2v} character table, translations span $\mathrm{B}_1 + \mathrm{B}_2 + \mathrm{A}_1$ (for x, y, z respectively) and rotations span $\mathrm{B}_2 + \mathrm{B}_1 + \mathrm{A}_2$ (for R_x, R_y, R_z respectively). Consequently the vibrations span $\underline{2\mathrm{A}_1 + \mathrm{B}_2}$.

(a) Infrared-active transitions are those of the same symmetry species as the electric dipole moment, which spans $\mathrm{B}_1 + \mathrm{B}_2 + \mathrm{A}_1$ (for μ_x, μ_y, μ_z respectively). Therefore, all three modes are infrared active (A_1 is z-polarized, B_2 y-polarized).

(b) Raman-active transitions are those of the same symmetry species as the polarizability, which transforms as the quadratic form x^2, xy, etc. These span $2\mathrm{A}_1 + \mathrm{A}_2 + \mathrm{B}_1 + \mathrm{B}_2$ [character table], and so all three modes are Raman active.

Exercise: Establish the symmetry species and activities of the vibrations of H_2O_2.

10.25 The harmonic oscillator wavefunctions are proportional to $H_0 \propto 1$, $H_1 \propto x$ for oscillations in the x-direction and to $H_0 \propto 1$, $H_1 \propto y$ for oscillations in the y-direction. Therefore, the linear combinations $H_0(y)H_1(x) \pm \mathrm{i}H_1(y)H_0(x)$ of the singly-excited degenerate states are proportional to $x \pm \mathrm{i}y \propto \mathrm{e}^{\pm \mathrm{i}\phi}$, which are eigenfunctions of l_z, the angular momentum about the z-axis, with $m_l = \pm 1$.

Exercise: What can be said about the doubly excited bending modes?