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5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Chemistry 5.76
Spring 1977

Problem Set #4

1. The corners of a cube are numbered 1, 2, 3, 4 clockwise around the top face of the cube, and 5, 6, 7, 8 clockwise around the bottom face, corner 5 lying under corner 1, corner 6 under corner 2, and so on. A face center is denoted by the two numbers of the corners between which a face diagonal can be drawn which passes through that face center (for example, either 13 or 24 would denote the center of the top face).

(a) The structures of several kinds of AB_4 molecules are described as follows with the above numbering system. The A -atom is placed at the center of the cube, and the A — B bond distances are given by the cube dimensions. However, the B -atoms are not necessarily all equivalent, the actual equivalence being determined by the symmetry elements remaining in the AB_4 structures.

(i) $AB_4(1, 2, 3, 4)$

(ii) $AB_4(1, 3, 5, 7)$

(iii) $AB_4(1, 3, 6, 8)$

(iv) $AB_4(1, 5, 16, 18)$

(v) $AB_4(13, 36, 68, 18)$

Give the point-group symbol for each AB_4 structure (for example, C_{3v} , D_{6h} , and so on).

(b) Classify the five molecules of Part (a) as to type of molecular rotator (linear, symmetrical top, and so on).

(c) Which of the five molecules of Part (a) will give a pure-rotational spectrum in the far-infrared or microwave region? Which will give a pure-rotational Raman effect?

2. The harmonic oscillator (mass m) in two dimensions has a potential energy V expressed in polar coordinates r , θ , of the general form $2V = k_1 r^2 \cos^2 \theta + k_2 r^2 \sin^2 \theta$, where k_1 and k_2 are force constants. For the special case $k_1 = k_2 = k$, the oscillator has a single frequency $\nu = (k/m)^{1/2}/2\pi$, and its Schrödinger equation has solutions of the form

$$\psi_{v,\ell} = N_{v,\ell} \exp\left(\frac{-\alpha r^2}{2}\right) \exp(i\ell\theta) P(r)$$

where v , ℓ are quantum numbers ($v = 0, 1, 2, \dots, \infty$; $\pm\ell = 0, 2, 4, \dots, v$ for v even, $\pm\ell = 1, 3, 5, \dots, v$ for v odd); $N_{v,\ell}$ is a normalization constant; $\alpha = 4\pi^2 m \nu / h$; $P(r)$, a polynomial in r only, depends for its form on the values of v and ℓ and is an even function for even v , odd for odd v .

- The energy levels of this two-dimensional oscillator are $E_v = (v + 1)h\nu$. What is the degeneracy of the v -th level?
- Find $N_{v,\ell}$ for $v = 1$, $\ell = +1$, for which $P(r) = \alpha^{1/2}r$.
- Show that any two ψ 's of the same v but different ℓ are orthogonal.
- Find the average value of the angular momentum p_θ for any state v, ℓ .
- Find the average value of r^{-2} for the state $v = 1, \ell = +1$.

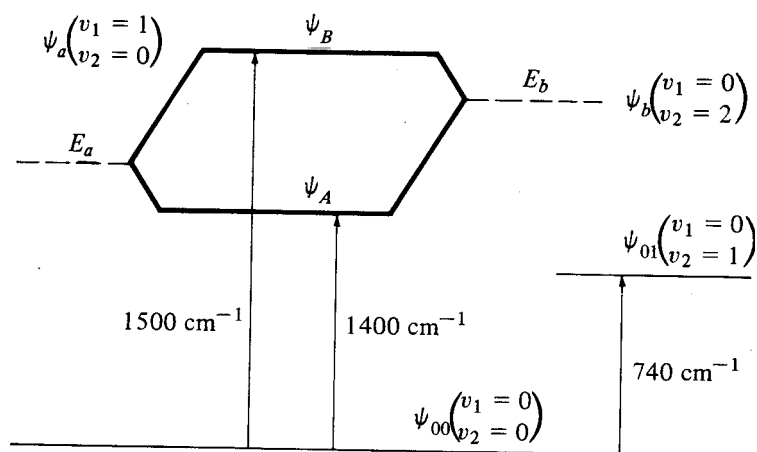
Substitute the results of the above in the equation for the relationship between E and p_θ in the plane rotor and find E for the state $v = 1, \ell = +1$. Explain the difference between this value of E and that given by the equation of Part (a).

- The carbon suboxide molecule C_3O_2 , is believed to be linear and symmetrical.
 - Classify the normal vibrations of C_3O_2 according to the symmetry species of point group $D_{\infty h}$.
 - How many polarized lines should appear in the vibrational Raman spectrum? How many fundamental infrared bands should have P -, Q -, and R -branches?
- Suppose that there are two possible structures for ethylene, planar D_{2h} and nonplanar D_{2d} .
 - Work out the infrared-active and the Raman-active vibrational species for each point group.
 - Work out the distribution of fundamental vibrational frequencies among the different species of the two structures and compare the results. What would you look for spectroscopically to decide between the two structures?
 - What kind of rotational fine structure would you expect in the vibrational infrared bands of the D_{2h} model? What kind for the D_{2d} model?
- Make a complete analysis of the spectrum of BF_3 given below and prove the symmetry of the molecule. (Chemical evidence gives a start.)

$B^{11}F_3$	$B^{10}F_3$	Raman	IR
480.4 cm^{-1}	482.0 cm^{-1}	m	s
691.3	719.5	—	s
888.0	888.0	s	—
1445.9	1497.0	—	vs
1831.0	1928.0	—	w
2903.2	3008.2	—	w

Note that the 888 cm^{-1} band has the same value for both isotopic species. This is a critical point in clinching the symmetry.

6. (a) Let $\psi_a \equiv \psi_{v_1=1}(Q_1)\psi_{v_2=0}(Q_2)$ and $\psi_b \equiv \psi_{v_1=0}\psi_{v_2=2}$ be the normalized harmonic-oscillator wave functions of a polyatomic molecule corresponding to excited vibrational states of unperturbed energies E_a and E_b . If these two states are in Fermi resonance, second-order non-degenerate theory can be applied. Assume that the interaction energies H'_{aa} and H'_{bb} are zero and that H'_{ab} arises from one or more anharmonic terms in the potential function. In a certain molecule, the levels ψ_a and ψ_b are observed to be in Fermi resonance, the transitions to the *perturbed* levels being observed at 1400 and 1500 cm^{-1} , whereas the level $\psi_{v_1=0}\psi_{v_2=1}$ has an energy of 740 cm^{-1} above the zero level (see diagram). Deduce the unperturbed E_a -value from the above data (H'_{ab} is to be evaluated from the data, not by integration).



- (b) The *intensity* of the Raman line for the transition from the ground state $\psi_{0,0}$ to the *unperturbed* state ψ_a in the absence of Fermi resonance is proportional to the square of the matrix element

$$\left\langle \psi_{0,0} \left| \frac{\partial \alpha}{\partial Q_1} Q_1 \right| \psi_a \right\rangle$$

where $\partial \alpha / \partial Q_1$ is a non-zero constant. The corresponding matrix element

$$\left\langle \psi_{0,0} \left| \frac{\partial \alpha}{\partial Q_2} Q_2 \right| \psi_b \right\rangle$$

is zero because $\Delta v_2 = 2$. Find the ratio of the intensities of the two Raman lines for the transitions from state $|\psi_{00}\rangle$ to the *perturbed* states $|\psi_A\rangle$ and $|\psi_B\rangle$.