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5.80 Small-Molecule Spectroscopy and Dynamics
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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Chemistry 5.76
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Problem Set #4

1. Steinfeld, page 227, # 2.

For the following molecules, give the point group symbol, dipole moment (zero or nonzero), and type of rotator (linear, symmetric top, and so on):

- (a) dichloromethane (CH_2Cl_2);
- (b) planar nitrogen tetroxide (N_2O_4), N's and O's equivalent;
- (c) nitrogen tetroxide with the plane of one NO_2 at right angles to the other, N's and O's equivalent;
- (d) ethane (C_2H_6) "opposed form," that is, with σ_h ;
- (e) ethane, "staggered form";
- (f) SF_4 , nonplanar, all F's equivalent;
- (g) SF_4 , nonplanar, two pairs of equivalent F's.

2. Steinfeld, page 257, # 2.

The linear centrosymmetric four-atomic molecule (example: acetylene) was treated in Section 3.

- (a) Construct the \mathbf{U} matrix of transformations between internal and symmetry coordinates for this system, from the definitions given by equations (8.14a)–(8.14e).
- (b) Using the transformation given by (8.15), derive the \mathcal{G} matrix elements from the Wilson, Decius, and Cross \mathbf{G} matrix elements given in section 3.
- (c) Rederive the \mathcal{G} matrix elements independently using the "effectiveness vector" approach defined by equation (8.12).

3. Steinfeld, page 258, # 4.

The cyclobutane molecule, $(\text{CH}_2)_4$, has the carbon atoms in a four-membered ring. Point groups to which the cyclobutane molecule might belong include $D_{4h}(C_4^z, C_2^x, \sigma_h^{xy}, \sigma_v^{xz}, 2\sigma_d, i)$, $D_{2d}(S_4^z, C_2^x, 2\sigma_d)$, and $C_{4v}(C_4^z, \sigma_v^{xz}, 2\sigma_d)$. More than enough symmetry elements are given in the parentheses to specify each point group.

- (a) List the sets of equivalent nuclei for cyclobutane structures of D_{4h} , D_{2d} , and C_{4v} symmetry and give the characteristic symmetry elements for each set.

- (b) How many totally symmetric vibrations are present in each structure?
 (c) Give the type of rotator for each structure (linear, symmetric top, asymmetric top, spherical top).
 (d) Which structures (if any) have infrared active totally symmetric vibrations?

4. Steinfeld, page 258, # 6.

Make a complete analysis of the spectrum of BF_3 given in the following table and prove the symmetry of the molecule. (Chemical evidence gives a start.)

B^{11}F_3 (cm^{-1})	B^{10}F_3 (cm^{-1})	Raman ^a	Infrared ^a
480.4	482.0	m	s
691.3	719.5	—	s
888.0	888.0	s	—
1,445.9	1,497.0	—	vs
1,831.0	1,928.0	—	w
2,903.2	3,008.2	—	w

a. vs = very strong; s = strong; m = medium; w = weak.

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

5. Steinfeld, pages 259-260, # 8.

The positions of the atoms in the molecule N_4S_4 have been determined by x-ray diffraction. In terms of a set of Cartesian coordinates x, y, z placed within the molecule, these are

$$\begin{array}{ll}
 \text{N}_1: & x = b, y = 0, z = 0; & \text{N}_2: & 0, b, 0; \\
 \text{N}_3: & -b, 0, 0; & \text{N}_4: & 0, -b, 0; \\
 \text{S}_1: & a, -a, a; & \text{S}_2: & -a, a, a; \\
 \text{S}_3: & a, a, -a; & \text{S}_4: & -a, -a, -a.
 \end{array}$$

Here the numbers a and b are unrelated parameters of the order of a few angstroms in size.

- (a) To what point group does the molecule belong?
 (b) What is the distribution of vibrational degrees of freedom among the vibrational symmetry species (that is, irreducible representations)?
 (c) How many different vibrational frequencies does the molecule have?
 (d) How many frequencies should appear in the Raman spectrum as polarized Raman lines and how many as depolarized Raman lines?
 (e) How many frequencies should appear in the infrared absorption spectrum as fundamentals ($\Delta\nu = +1$) and how many of these should coincide with Raman lines?

- (f) Assume the parameter $a = 3 \text{ \AA} = 1.5b$. Compute the moments of inertia in atomic mass units times angstroms squared. What kind of rotator is the molecule (linear rotator, spherical top, oblate or prolate symmetric top, oblate or prolate asymmetric top)?
- (g) The symmetry number of a molecule is defined as the number of indistinguishable configurations that can be obtained by rotating the rigid molecule. Two configurations are rendered "indistinguishable" when the numbering of otherwise identical nuclei is removed. What are the symmetry numbers of molecules belonging to the following groups:

$$C_{2v}, D_{2d}, D_{6h}, T_d, O_h ?$$

6. $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ is a linear molecule. The bond lengths are

$$r_{\text{CO}} = 1.16 \text{ \AA}$$

$$r_{\text{CS}} = 1.56 \text{ \AA}$$

and the observed fundamental vibrational frequencies are

$$\nu_1 = 858.9 \text{ cm}^{-1} \text{ stretch}$$

$$\nu_2 = 520.4 \text{ cm}^{-1} \text{ bend}$$

$$\nu_3 = 2062.2 \text{ cm}^{-1} \text{ stretch.}$$

- (a) Obtain k_{CS} , k_{CS} , and $k_{\Theta} [r_{\text{CO}}r_{\text{CS}}]^{-1}$ in dynes/cm.
- (b) What are the amplitudes for the C–O and C–S stretches in ν_1 ?
- (c) What are the vibrational frequencies for $^{18}\text{O}^{12}\text{C}^{32}\text{S}$?

7. Steinfeld, page 290, # 1.

The SO_2 molecule has two equal S—O distances of 1.43 \AA and a bond angle of 120° in the ground electronic state. Describe qualitatively the vibronic structure expected for absorption of ultraviolet radiation by SO_2 vapor at room temperature, if, in the upper electronic state, the S—O distances are both 1.43 \AA and the bond angle is 110° .