Chemistry 21b – Spectroscopy

Lecture # 5 – Rotation of Polyatomic Molecules

The rotational spectra of molecules can be classified according to their "principal moments of inertia". Assume that the molecule rotates as a rigid body, that is, the relative nuclear positions are fixed. The moment of inertia I of any molecule about any axis through the center-of-mass is then given by

$$I = \sum_i M_i R_i^2 \tag{5.1}$$

where M_i and R_i are the mass and perpendicular distance of atom i from the axis. Recall that the center-of-mass position for a given axis may be found from the equation:

$$R_\alpha(C.M.) = \sum_i M_i R_i / \sum_i M_i \quad .$$

In general, for any rigid three dimensional body, there exists a $3{\times}3$ moment of inertia tensor (that is, matrix). If we use any three axes defined by (xyz), the moment of inertia tensor has diagonal elements defined as $I_{xx} = \sum_i M_i(y_i^2 + z_i^2)$ (using the x-axis, for example), and off-diagonal elements given by $I_{xy} = -\sum_i M_i x_i y_i$, etc. (Note the minus sign in the off-diagonal terms).

Clearly, the moment-of-inertia tensor is Hermetian, and so can be diagonalized to yield three (potentially) distinct eigenvalues. These eigenvalues are called the "principal moments of inertia," and the eigenvectors corresponding to the diagonalized coordinate system are referred to as the "principal axes" of the molecule. Mathematically, the eigenvectors of the matrix in any coordinate system form the *direction cosines* that relate the arbitrary coordinate system to the principal axis coordinate system, that latter of which must rotate with the molecule.

One can always find one axis, called the c-axis, about which the moment of inertia has its *maximum* value, and another axis, labeled the a-axis, about which I has its *minimum* value. It can be shown that the a and c axes must be mutually perpendicular. Thus, according to convention, the principal axes are ordered:

$$I_c \geq I_b \geq I_a. \tag{5.2}$$

Why do we care? If we use these principal axes, then the components of the rotational angular momentum **P** along these axes can be shown to be

$$P_a = I_a \omega_a \quad , \qquad P_b = I_b \omega_b \quad , \qquad P_c = I_c \omega_c \quad , \tag{5.3}$$

and the kinetic energy operator for a rigid-rotor simply becomes

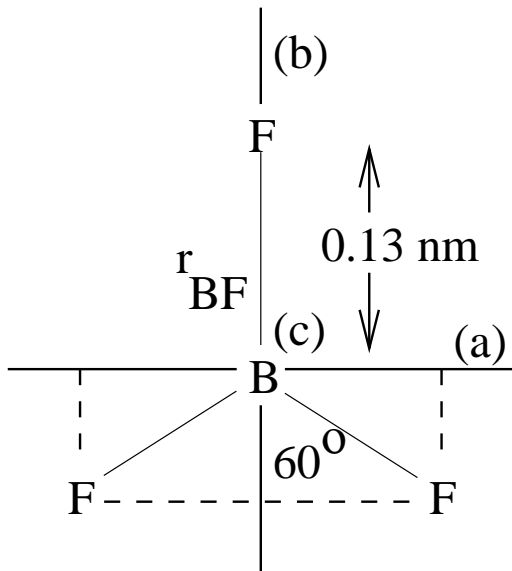$$T_{rot} = \frac{P_a^2}{2I_a} + \frac{P_b^2}{2I_b} + \frac{P_c^2}{2I_c}$$

Figure 5.1: The structure and principal axes of boron trifluoride (BF_3).

In all other coordinate systems things are much more complicated!

As a simple example, let us calculate the moments of inertia for the molecule BF_3. This molecule is planar, with the three F atoms arranged around a central B atom at angles of $120°$ and a B-F distance of 1.30Å. (See Figure 5.1). The center of mass is clearly at the B atom. One principal axis is perpendicular to the plane of the molecule, and since this axis will possess the largest moment of inertia, it is the c-axis. A second axis will pass through one of the B-F bonds, and the third will be mutually perpendicular to the first two.

For the c-axis, we find:

$$I_c = M_B \times 0.0 + 3M_F R_{BF}^2 = 3 \times 19(amu) \times (1.3\text{Å})^2 = 1.6 \times 10^{-38}\text{g cm}^2$$

For the other moments, we obtain:

$$I_a = M_B \times 0.0 + M_F R_{BF}^2 + 2M_F(R_{BF}sin30°)^2 = 3/2\ M_F R_{BF}^2$$

$$I_b = M_B \times 0.0 + M_F \times 0.0 + 2M_F(R_{BF}sin60°)^2 = 3/2\ M_F R_{BF}^2$$

Thus, we find that $I_a = I_b = I_c/2$ for BF_3. This result is a consequence of the (numerous) symmetry properties of the molecule. For any planar molecule the c-axis is always perpendicular to the plane containing the nuclei, and in any coordinate system the moment-of-inertia tensor can be diagonalized simply by diagonalizing a 2×2 matrix. The direction cosines then simply collapse to a single rotation about the c-axis that brings the arbitrary axes into coincidence with the principal a, b-axes. For three-dimensional molecules the calculation of the moments and principal axes is straightforward, but tedious! (Not surprisingly, computer routines now exist which can calculate the moment-of-inertia
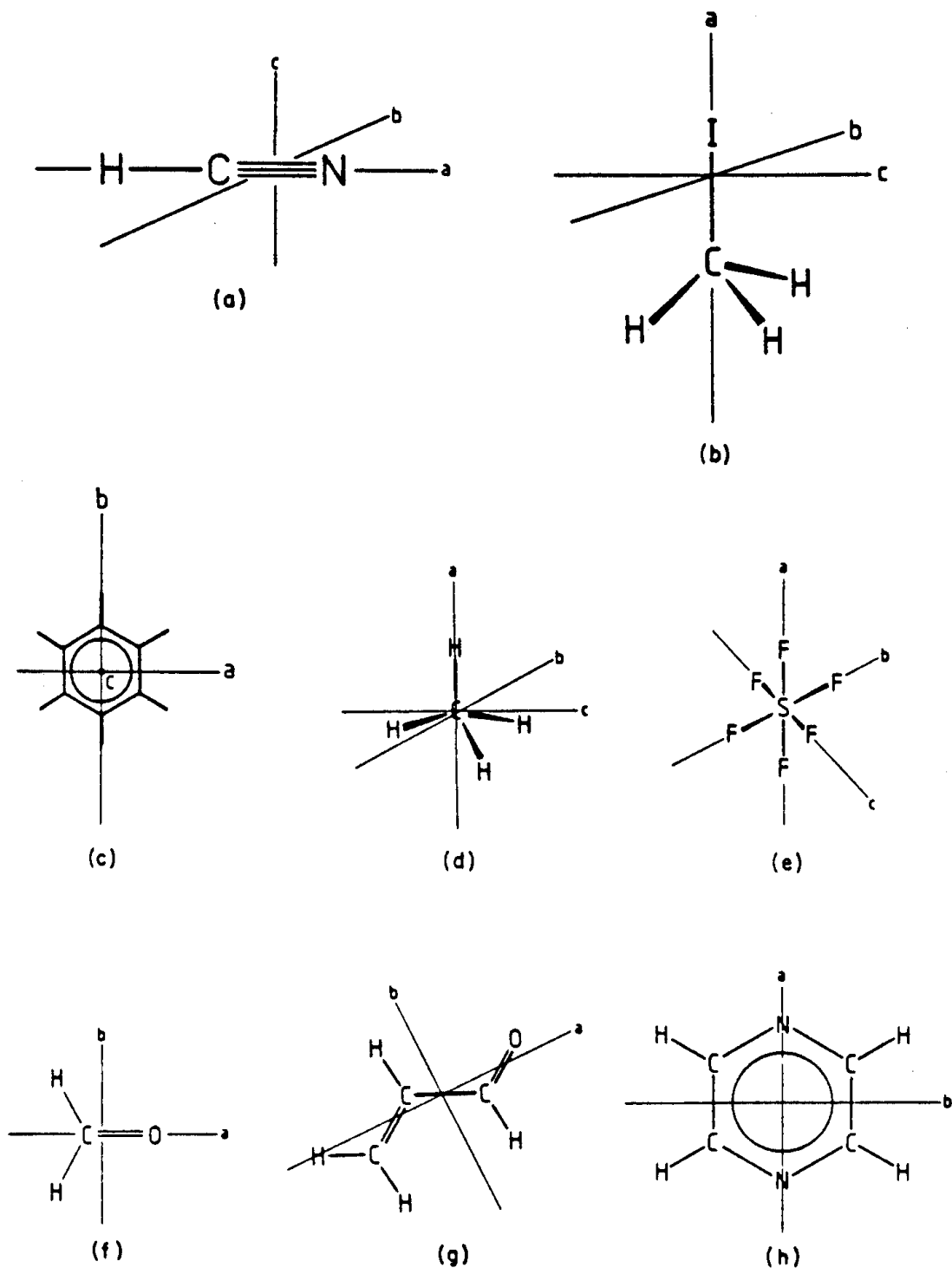
Figure 5.2. Principal inertial axes of (a) HCN, (b) methyl iodide, (c) benzene, (d) methane, (e) sulphur hexafluoride, (f) formaldehyde, (g) s-*trans*-acrolein, and (h) pyrazine.

tensor for any molecule, and diagonalize it to obtain the principal axes and rotational constants).
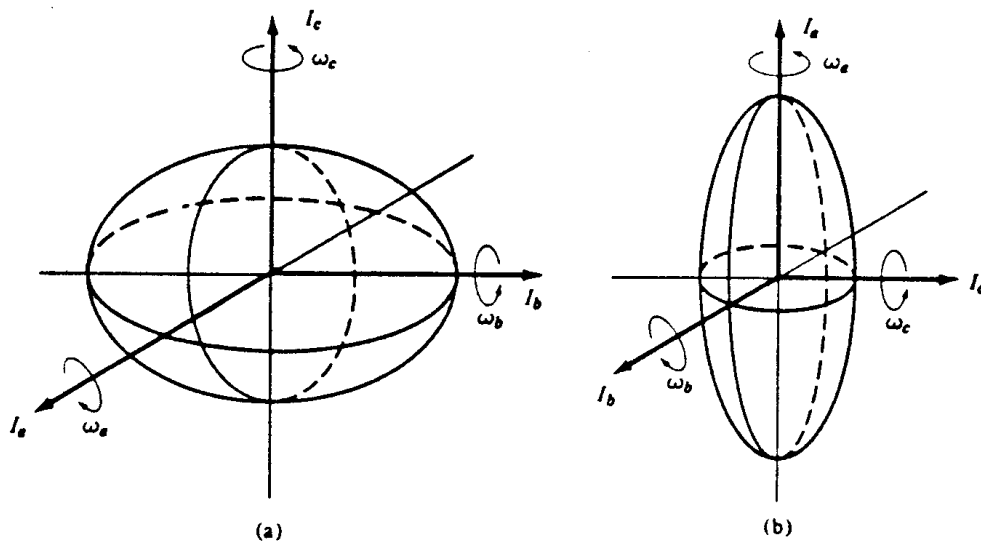
Figure 5.3. Principal axes for (a) an oblate symmetric top and (b) a prolate symmetric top.

Figure 5.2 illustrates the principal inertial axes for a number of molecules of different symmetry types. For a linear molecule such as HCN, one can easily see that

$$I_c = I_b > I_a = 0 \tag{5.3}$$

where the b and c axes may be in any direction perpendicular to the internuclear a-axis. If the nuclei are taken to be point masses on the a-axis, it is clear that I_a must be zero since all R_i in eq. (5.1) are zero. HCN is an example of a linear, symmetric rotor, and like BF_3, is a "symmetric top" molecule.

In general, for a symmetric top, two of the principal moments of inertia are equal and the third is non-zero. If

$$I_c = I_b > I_a \tag{5.4}$$

the molecule is a "prolate" symmetric top. A prolate top is the general shape of a football or a cigar (see Figure 5.3); molecular examples are methyl iodide (Figure 5.2b) and ammonia, NH_3. On the other hand, if

$$I_c > I_b = I_a, \tag{5.5}$$

we have an "oblate" symmetric top. Examples are a hockey puck, a frisbee, or in the case of molecules, benzene (Figure 5.2c).

A symmetric rotor always has a rotation axis C_n with $n > 2$, which coincides with one of the principal axes of inertia, and two of the moments are always equal.

A special type of symmetric top occurs if

$$I_c = I_b = I_a \tag{5.6}$$

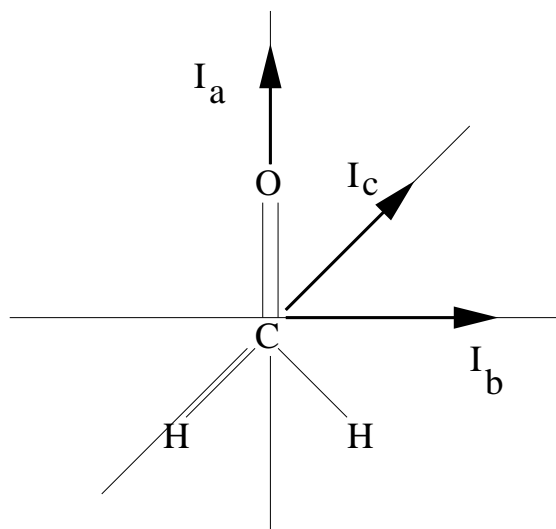$$A = 281.98 \quad B = 38.83 \quad C = 34.00 \quad \text{GHz}$$

Figure 5.4. H_2CO as an example of a near prolate top. The two σ_v planes contain the A and B and A and C axes. The rotational constants lead to a Ray's asymmetry parameter of $\kappa = (2B - A - C)/(A - C) = -0.90$.

as in the case, for example, of CH_4 (methane) and SF_6 (Figure 5.2d and e). These are called "spherical top" molecules.

If the molecule possesses no C_n rotational symmetry axis with $n \geq 3$, all three principal moments of inertia are unequal,

$$I_c \neq I_b \neq I_a, \tag{5.7}$$

and the molecule is an "asymmetric top". Most molecules fall into this category. An example is formaldehyde, H_2CO, shown in Figure 5.2f.

Although only a small fraction of all known molecules are true symmetric or spherical tops, there is more sizable group that falls into the category of "near-prolate" tops with

$$I_c \simeq I_b > I_a \tag{5.8}$$

or "near-oblate" tops with

$$I_c > I_b \simeq I_a. \tag{5.9}$$

Examples of near-prolate tops are C_{2v} molecules such as H_2O and H_2CO, and a molecule such as ethylene, C_2H_4. The convenience of classifying a molecule as a near-symmetric top will become evident soon.

2. A Word About Coordinate Systems and Good Quantum Numbers

Now that we have the moments-of-inertia, converting the **P** in Eq. (5.3) into operators gives us the quantum mechanical formulation for calculating the rotational energy. The abc-axes are tied to the rotating molecule, while laboratory (xyz)-axes are fixed in space.
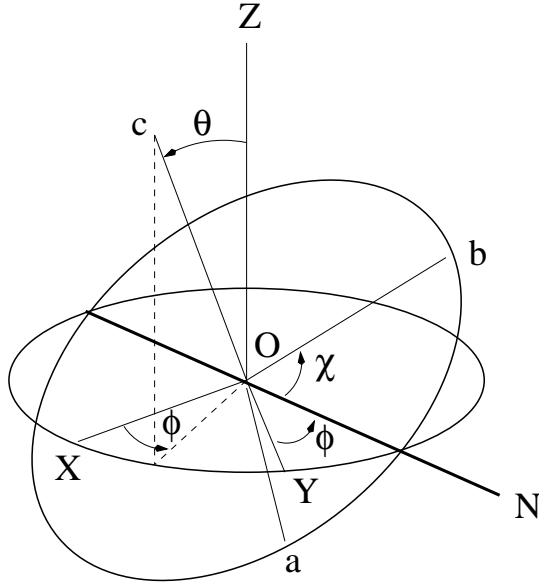
Figure 5.5. The Eulerian angles. ON is the intersection of the xy and ab planes, and is called the *line of nodes*. θ is the angle of rotation about ON; φ that about OZ; χ that about Oc.

Thus, the former are called *body-fixed* coordinates, while the latter are called *space-fixed* coordinates. In order to calculate the differential operators involving the coordinates describing the rotation, it is necessary to define the relationship between these two coordinate systems. This requires three angles, called the *Euler angles*, which we'll denote θ, φ, χ. Figure 5.5 presents a pictorial outline. The first two are analogous to spherical coordinates, while the latter accounts for the freedom of rotation about the c-axis, which, as Figure 5.5 shows does not change θ or φ.

The momentum operators can be defined in either coordinate system. With lots of messy algebra it is possible to demonstrate the following commutation relations:

$$[\hat{P}_x, \hat{P}_y] = \imath\hbar\hat{P}_z \qquad \text{etc.}$$

$$[\hat{P}_a, \hat{P}_b] = -\imath\hbar\hat{P}_c \qquad \text{etc.}$$

With respect to $\hat{P}^2$, however, some commutators are zero, such as:

$$[\hat{P}^2, \hat{P}_z] = 0 \qquad \text{etc.}$$

$$[\hat{P}^2, \hat{P}_c] = 0 \qquad \text{etc.}$$

Thus, for the rigid rotor, the total angular momentum and the space-fixed projection on one-axis of the system should be good quantum numbers. To avoid confusion with the hydrogen atom, these are called J and M_J (instead of L and M_L):

$$\hat{P}^2\psi = J(J+1)\psi \ , \qquad J = 0, 1, 2, ... \tag{5.10a}$$

Figure 5.6. J, K (J_a) definitions for a prolate top.

$$\hat{P}_z \psi = M_J \psi \ , \qquad M_J = 0, \pm 1, \pm 2, ... \tag{5.10b}$$

The rotor eigenfunctions have the form $\psi = F(\theta, \chi)(2\pi)^{-1/2} e^{iM\varphi}$. Interestingly, for the component of $\hat{P}^2$ along a body-fixed axis, it is found that

$$[\hat{H}_{rot}, \hat{P}_c] = i\hbar \left(\frac{1}{2I_a} - \frac{1}{2I_b} \right) (\hat{P}_a \hat{P}_b + \hat{P}_b \hat{P}_a) \ . \tag{5.11}$$

3. Symmetric top molecules

In general, the rotational Hamiltonian can be written as

$$H^{rot} = \frac{1}{2} \left(\frac{J_a^2}{I_a} + \frac{J_b^2}{I_b} + \frac{J_c^2}{I_c} \right) \tag{5.12}$$

where $J^2 = J_a^2 + J_b^2 + J_c^2$. For a prolate top, $I_b = I_c$, so we can write

$$H^{rot} = \frac{1}{2} \left(\frac{J^2}{I_b} - \frac{J_a^2}{I_b} - \frac{J_c^2}{I_b} + \frac{J_a^2}{I_a} + \frac{J_c^2}{I_c} \right) \tag{5.13a}$$

or

$$H^{rot} = \frac{1}{2} \left(\frac{J^2}{I_b} + \frac{J_a^2}{I_a} - \frac{J_a^2}{I_b} \right). \tag{5.13b}$$

We know that $J^2 Y_{JM} = J(J+1) Y_{JM}$. Any one of the components corresponding to angular momentum along one of the principal axes is quantized in units of K, with energy proportional to K^2, and given the commutation relations above we know that K will be a good qauntum number for this system. For example, for a prolate top like CH_3I, J_a represents the angular momentum due to motion about the a-axis, see Figure 5.6. The energies are degenerate w.r.t. K because it does not matter (in isotropic space at least) if the rotation about the symmetry axis is "clockwise" or counterclockwise (as viewed down the symmetry axis).
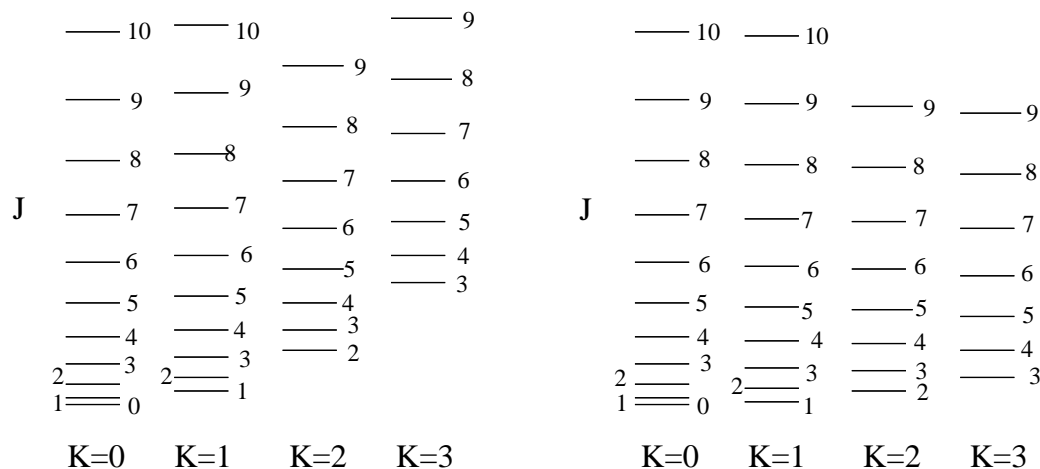
Figure 5.7. Rotational energy levels for (a) a prolate and (b) an oblate symmetric top.

Thus, we find for a prolate top:

$$E^{rot} = \frac{J(J+1)}{2I_b} + \frac{K^2}{2}\left(\frac{1}{I_a} - \frac{1}{I_b}\right) \tag{5.14}$$

$$= BJ(J+1) + (A-B)K^2.$$

For an oblate top, we use similar steps to obtain:

$$E^{rot} = BJ(J+1) + (C-B)K^2. \tag{5.15}$$

The quantum number K can take values $K = 0, 1, 2, ...J$ where all levels for $K > 0$ are doubly degenerate. For a closed shell linear rotor, which is special case of a symmetric top, $K = 0$. Thus, each J level then has the usual $2J+1$ different K states, corresponding to the different possible projections of J on a 'molecule-fixed' axis. Each (J, K) level then has $2J + 1$ different M_J levels, corresponding to the different possible projections of J on a 'space-fixed' axis. Thus, the statistical weight for each J level is $(2J + 1)^2$, rather than the $2J+1$ as is true for a linear (or diatomic) rotor. Figure 5.7 illustrates the energy levels for a prolate and an oblate top. Since $A > B > C$, the energy of a certain J level increases with K for a prolate top, but decreases with K for an oblate top.

The selection rules for symmetric tops are

$$\Delta J = \pm 1, \Delta K = 0, \tag{5.16}$$

in addition to the requirement that the molecule must have a permanent dipole moment. Thus, transitions between the various K-ladders are forbidden. The $\Delta K = 0$ rule also results in a simple expression for the transition frequencies

$$\nu = F(J+1, K) - F(J, K) = 2B(J+1) \tag{5.17}$$

which is the same for a diatomic or linear polyatomic molecule.
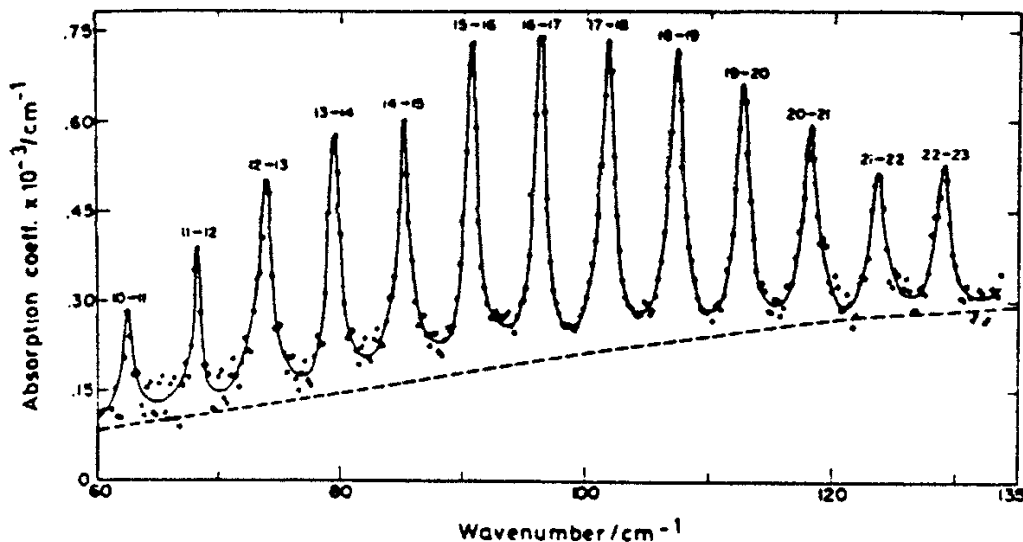
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Figure 5.8. Far-infrared pure rotational spectrum of the silane spherical top.

4. Spherical top molecules.

Using similar arguments as for prolate tops, we find that with $I_a = I_b = I_c$

$$E^{rot} = BJ(J + 1). \qquad (5.19)$$

In the absence of vibration-rotation interactions, all $(2J + 1)^2$ levels are degenerate. The selection rule is again $\Delta J = \pm 1$.

The spherical top molecule of prime astrophysical and atmospheric importance is CH_4. Since the molecule has no permanent dipole moment, one would not expect it to have a millimeter (rotational) spectrum. However, rotation about any of the four axes containing a C-H bond results in a 'centrifugal distortion' in which the other 3 hydrogen atoms are thrown outwards slightly from the axis. This converts the molecule into a symmetric rotor and gives it a small dipole moment, 10^{-6} D, resulting in a very weak rotational spectrum. Part of the far-infrared ($\lambda \approx 10 - 100$ μm) spectrum of SiH_4 is shown in Figure 5.5. It has the same regular spacing as the spectrum of a linear rotor.