Advanced Quantum Mechanics & Spectroscopy (CHEM 7520)

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Week 2-3: Rotations of polyatomic molecules

IV. SELECTION RULES IN ROTATIONAL SPECTROSCOPY

1) A transition between two states ψ_n and ψ_m is allowed if the corresponding **transition dipole matrix element** is non-zero:

$$\mathbf{R^{nm}} = \langle \psi_n | \hat{\mu} | \psi_m \rangle = \int \psi_n^* \hat{\mu} \, \psi_m \mathrm{d}\tau \tag{1}$$

The **dipole moment operator** $\hat{\mu}$ is given by

$$\hat{\mu} = \sum_i q_i \mathbf{r}_i \tag{2}$$

where the sum runs over electrons and nuclei. Note that $\mathbf{R^{nm}}$ has three components corresponding to the three components of the dipole moment operator (e.g., x, y, z).

2) Within the Born-Oppenheimer approximation, ψ_m can be written as a product of the rotational, vibrational, and electronic wavefunctions. For pure rotational transitions, we can write:

$$\psi_m = \psi_{rot,m}(\theta, \phi, \chi) \psi_{vib}(\mathbf{Q}; \theta, \phi, \chi) \psi_e(\mathbf{r_e}; \theta, \phi, \chi, \mathbf{Q}) \tag{3}$$
$$\psi_n = \psi_{rot,n}(\theta, \phi, \chi) \psi_{vib}(\mathbf{Q}; \theta, \phi, \chi) \psi_e(\mathbf{r_e}; \theta, \phi, \chi, \mathbf{Q}) \tag{4}$$

where $\mathbf{Q}$ are the vibrational normal coordinates and $\mathbf{r_e}$ are the coordinates of the electrons.

3) We therefore obtain for the transition dipole matrix element:

$$\mathbf{R^{nm}} = \int \int \psi_{rot,n}^* \psi_{vib}^* \left[\int \psi_e^* \hat{\mu} \, \psi_e \, \mathrm{d}\tau_e \right] \psi_{vib} \psi_{rot,m} \, \mathrm{d}\mathbf{Q} \, \mathrm{d}\tau_{rot} \tag{5}$$

The integral over the electronic coordinates (in square brackets) can be written as a vector $\boldsymbol{\mu}(\mathbf{Q})$ that depends on the normal coordinates of vibrations. Furthermore,

integrating over the vibrational wavefunction

$$\mathbf{R^{nm}} = \int \psi^*_{rot,n} \left[\int \psi^*_{vib} \boldsymbol{\mu}(\mathbf{Q}) \psi_{vib} \, d\mathbf{Q} \right] \psi_{rot,m} \, d\tau_{rot} \tag{6}$$

the transition dipole matrix element can be expressed as

$$\mathbf{R^{nm}} = \int \psi^*_{rot,n}(\theta,\phi,\chi) \boldsymbol{\mu}(\theta,\phi,\chi) \psi_{rot,m}(\theta,\phi,\chi) \, d\tau_{rot} \tag{7}$$

where $\boldsymbol{\mu}(\theta,\phi,\chi)$ denotes *vibrationally averaged permanent dipole moment.*

4) We can express $\boldsymbol{\mu}(\theta,\phi,\chi)$ as

$$\boldsymbol{\mu}(\theta,\phi,\chi) = \mu_0 \mathbf{n}(\theta,\phi,\chi) \tag{8}$$

where μ_0 is the *magnitude of the dipole moment of the molecule* and $\mathbf{n}(\theta,\phi,\chi)$ is the unit vector for the *direction of $\boldsymbol{\mu}$* in space as a function of the Euler angles. Combining all of these results and introducing the integration limits we can write:

$$\mathbf{R^{nm}} = \mu_0 \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \int_0^{2\pi} d\chi \, \psi^*_{rot,n}(\theta,\phi,\chi) \mathbf{n}(\theta,\phi,\chi) \psi_{rot,m}(\theta,\phi,\chi) \tag{9}$$

An important result is that $\mathbf{R^{nm}} = 0$ *if the molecule does not have a permanent dipole moment ($\mu_0 = 0$).* In such cases, *no microwave spectrum is observed.* Examples of molecules that don't have microwave spectrum: H_2, O_2, N_2, F_2, CO_2, BF_3, CH_4, benzene. Selection rules for the various rotational types are governed by the integral over (θ,ϕ,χ) in Eq. (9). We will summarize the main results below.

5) **Spherical top molecules:**
Spherical tops can be considered as a special case of symmetric tops and should have the same selection rules. However, due to high symmetry, *their permanent dipole moment must be zero* ($\mu_0 = 0$). Therefore, *pure rotational absorption spectra cannot be observed for (rigid) spherical tops.* In practice, extremely weak transitions may be observed due to vibration-rotation interaction (e.g., centrifugal distortion).

6) **Linear molecules:**
In this case, $\psi_{rot,m}$ and $\mathbf{n}$ do not actually depend on χ. The selection rules for this

rotational type are:

$$\mu_0 \neq 0; \qquad \Delta J = \pm 1; \qquad \Delta M = 0, \pm 1 \tag{10}$$

Mathematically, these rules can be derived by expressing $\psi_{rot,m}$ in terms of the spherical harmonics and evaluating the integral in Eq. (9). Physically, $\Delta J = \pm 1$ represents the absorption (or emission) of a single photon with one $\hbar$ quantum of the angular momentum.

Consider an allowed transition between two states with quantum numbers J and $J + 1$. Using the rotational energy expression for linear molecules, we can write the excitation energy as:

$$\Delta F_{rot} = B(J+1)(J+2) - B(J)(J+1) = 2B(J+1) \tag{11}$$

Thus, the lowest-energy absorption line corresponding to the $J = 0 \rightarrow 1$ transition will appear in the spectrum at energy $2B$. The second line for the $J = 1 \rightarrow 2$ will give rise to a line at energy $4B$. We note that *all absorption lines in the microwave spectrum of a linear molecule are equally-spaced with an energy difference of $2B$*. In practice, this energy difference may deviate from $2B$ due to the vibration-rotation interaction.

7) **Symmetric top molecules:**

Symmetric tops can have a permanent dipole moment, but due to symmetry it must lie along the principal axis that corresponds to the unique principal moment of inertia (*a* for prolate, *c* for oblate). As a result, the vector $\mathbf{n}(\theta, \phi, \chi)$ must be aligned with this symmetry axis and its components in the space-fixed coordinate are:

$$\mathbf{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta) \tag{12}$$

Since the components of $\mathbf{n}$ do not depend on χ, integration over χ in Eq. (9) will give a non-zero result only if $\Delta K = 0$. Thus, for the symmetric-top molecules the following selection rules apply:

$$\mu_0 \neq 0; \qquad \Delta J = \pm 1; \qquad \Delta M = 0, \pm 1; \qquad \Delta K = 0 \tag{13}$$

Although the symmetric-top energy depends on both J and K, the energy spacing between the absorption lines in the symmetric-top microwave spectra will depend only on the rotational constant B, since $\Delta K = 0$ according to the selection rules.

Similar to the case of the linear molecules, we obtain:

$$\Delta F_{rot} = 2B(J+1) \tag{14}$$

Thus, the *symmetric top lines are equally-spaced with an energy difference of* $2B$. As for the linear molecules, the vibration-rotation coupling may affect the spacing between the lines and, in addition, introduce dependence of the allowed transitions on K.

8) **Asymmetric top molecules:**
Because K is not a good quantum number for the asymmetric-top molecules, there is no general restriction on K. In this case, the following selection rules apply:

$$\mu_0 \neq 0; \qquad \Delta J = 0, \pm 1; \qquad \Delta M = 0, \pm 1 \tag{15}$$

We note that the *asymmetric-top transitions with* $\Delta J = 0$ *correspond to lines with non-zero frequency*, which is not the case for the symmetric top. In addition, it is possible that the asymmetric-top levels with quantum number $J-1$ lie above a level with quantum number J, giving rise to microwave absorption lines with $\Delta J = -1$ in the spectrum. Microwave transitions with $\Delta J = -1$, 0, and $+1$ are called P-, Q-, and R-branch lines, respectively. These lines usually do not appear as branches in the spectrum and are usually interspersed together.

The dipole moment of an asymmetric top can be resolved into components along the three principal axes

$$\boldsymbol{\mu}(\theta, \phi, \chi) = \mu_a \mathbf{e_a} + \mu_b \mathbf{e_b} + \mu_c \mathbf{e_c} \tag{16}$$

Transitions due to a non-vanishing dipole-moment component d_a are called a-type transitions. For each type of transitions the following selection rules apply:

a-type:	$\mu_a \neq 0$	$\Delta K_{pr} = 0, \pm 2, \pm 4, \ldots$	$\Delta K_{ob} = \pm 1, \pm 3, \pm 5, \ldots$ (17)
b-type:	$\mu_b \neq 0$	$\Delta K_{pr} = \pm 1, \pm 3, \pm 5, \ldots$	$\Delta K_{ob} = \pm 1, \pm 3, \pm 5, \ldots$ (18)
c-type:	$\mu_c \neq 0$	$\Delta K_{pr} = \pm 1, \pm 3, \pm 5, \ldots$	$\Delta K_{ob} = 0, \pm 2, \pm 4, \ldots$ (19)

In general, an asymmetric top can have non-zero components of $\boldsymbol{\mu}$ along all three axes, and all three types of transitions are possible. However, if there is a C_2 axis, then this is a principal axis, and the dipole moment lies along this axis. In this case, we get only one type of transitions. The patterns of the asymmetric-top absorption lines are complex. In the microwave spectrum, P-, Q-, and R-branch,

a-, *b-*, and *c*-type lines with high and low values of *J* are scattered among each other, with no clear-cut pattern.

9) At room temperature, many rotational levels are well-populated because of the small energy differences between rotational levels. Thus, in contrast to electronic or vibrational absorption spectra, most of the lines in a pure-rotational absorption spectrum do not involve the ground state.

V.   VIBRATION-ROTATION INTERACTION

1) So far we described rotations of molecules using the rigid rotor approximation by assuming that the nuclear Hamiltonian takes the form

$$\hat{H}_N = \hat{T}_{rot} + \left[\hat{T}_{vib} + U\right] = \hat{H}_{rot} + \hat{H}_{vib} \tag{20}$$

where we neglected a contribution from the coupling of the rotational and vibrational kinetic energy ($\hat{T}_{rot-vib} \approx 0$). In reality, molecules vibrate and thus are not completely rigid. *As the vibrational energy of the molecule increases, the average internuclear distance increases.* This increases the effective moments of inertia, and therefore decreases the rotational energy.

2) We can define an **effective rotational constant** $B_{[v]}$ for a given vibrational state

$$B_{[v]} = B_e - \sum_i \alpha_i^B (v_i + \frac{1}{2}) \tag{21}$$

where B_e is the **equilibrium rotational constant** (a rotational constant with moments of inertia calculated at the equilibrium geometry) and the sum is over all vibrational modes of the molecule (including separate terms for each mode of a degenerate vibration). The constant α_i^B is called **rotation-vibration interaction constant**. Its value is positive for most of the molecules. Eq. (21) was obtained using perturbation theory where the rotation-vibration term $\hat{T}_{rot-vib}$ was treated as a perturbation in the Hamiltonian. There are higher-order terms in this expansion [of the type $\gamma_{ij}^B (v_i + \frac{1}{2})(v_j + \frac{1}{2})$], which are usually very small. Similar expressions for the effective rotational constants $A_{[v]}$ and $C_{[v]}$ can be obtained:

$$A_{[v]} = A_e - \sum_i \alpha_i^A (v_i + \frac{1}{2}) \tag{22}$$

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$$C_{[v]} = C_e - \sum_i \alpha_i^C \left(v_i + \frac{1}{2}\right) \tag{23}$$

3) The constants α_i^B can be measured experimentally; however, more common way is to evaluate α_i^B from theoretical computations. By combining the experimentally measured effective rotational constants $B_{[v]}$ with the computed values of α_i^B, empirical values for the equilibrium constants B_e can be obtained. The latter constants can be used to obtain information about the equilibrium structure of the molecule directly from the experiment.

4) Another effect that influences the rotational energies of molecules is called **centrifugal distortion**. Because molecules are not completely rigid, as the rotational quantum number increases, the mean values of bond distances in a polyatomic molecule increase. This again decreases the rotational energy as compared to that of rigid rotor. Taking into account the centrifugal distortion, the energy of an oblate symmetric top can be written as:

$$F = B_{[v]}J(J+1) + (C_{[v]} - B_{[v]})K^2 - D_J J^2(J+1)^2 - D_{JK}J(J+1)K^2 - D_K K^4 \tag{24}$$

Usually, the **centrifugal-distortion constants** D_J, D_{JK}, and D_K are very small ($\sim 10^{-3}$ of the rotational energy), and thus their effect on the energy is very small. For $CF_3C\equiv CH$, $B_0 = 0.095998$ cm^{-1}, while $D_J = 8 \times 10^{-9}$ cm^{-1} and $D_{JK} = 2 \times 10^{-7}$ cm^{-1}. However, for molecules with light atoms (such as hydrogen), it can be significant.