Rotations and vibrations of polyatomic molecules

When the potential energy surface $V(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N)$ is known we can compute the energy levels of the molecule. These levels can be an effect of:

- Rotation of a molecule as a whole (end-over-end rotation)
- Small vibrations around equilibrium configuration of the nuclei
- Internal rotation - free or hindered
- Tunneling
- Large amplitude vibrations (van der Waals vibrations)

Transitions between these levels are observed in spectroscopy:

- Infrared/Raman – vibrations
- Terahertz (submillimeter) – rotations, large amplitude vibrations
- Microwave – rotations, tunneling

These transitions occur between the eigenvalues of the Hamiltonian for the nuclear motion:

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \frac{1}{m_i} \Delta \vec{R}_i + V(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N)$$

where $m_i$ is the mass of the $i$-th nucleus.

The Born-Oppenheimer approximation is assumed here.
Rotations and vibrations of polyatomic molecules, continued

For polyatomic molecules rotations and vibrations cannot be separated. The separation is possible only approximately (often with good accuracy) for the so-called rigid molecules such as:

- water
- carbon dioxide
- methane
- ethylene
- benzene

Rotation is then described as a rotation of a rigid body (a rotating top of the right kind).

Vibrations are described as small amplitude oscillations around the (rotating) equilibrium positions of the nuclei.

The total energy is a sum of the rotation energy and the vibration energy.

For nonrigid molecules (floppy molecules), such as:

- dimethylacetylene
- propane
- ammonia
- ethanol
- water dimer

such an approximation does not work and each case must be treated separately.

Theory of nuclear motion in floppy molecules is still in development and will not be presented in these lectures since:

There are no commercial programs offering a possibility of computing rovibrational spectra of nonrigid molecules.
Rotations of polyatomic molecules

Classically, the rotation of a rigid body is described by the vector of angular velocity \( \vec{\omega} \) such that the velocity \( \vec{v}_i \) of \( i \)-th particle (atomic nucleus) is given by:

\[
\vec{v}_i = \vec{\omega} \times \vec{R}_i
\]

The angular momentum of the rigid body is then given by

\[
\vec{L} = \sum_{i=1}^{N} \vec{R}_i \times (m_i \vec{v}_i) = \sum_{i=1}^{N} m_i \vec{R}_i \times (\vec{\omega} \times \vec{R}_i) = \mathbf{I} \vec{\omega},
\]

where \( \mathbf{I} \) is the matrix (tensor) of the moment of inertia:

\[
\mathbf{I} = \begin{bmatrix}
\sum_i m_i (Y_i^2 + Z_i^2) & -\sum_i m_i X_i Y_i & -\sum_i m_i X_i Z_i \\
-\sum_i m_i Y_i X_i & \sum_i m_i (X_i^2 + Z_i^2) & -\sum_i m_i Y_i Z_i \\
-\sum_i m_i Z_i X_i & -\sum_i m_i Z_i Y_i & \sum_i m_i (X_i^2 + Y_i^2)
\end{bmatrix}
\]

The matrix \( \mathbf{I} \) is symmetric, e.g., \( \mathbf{I}_{xy} = \mathbf{I}_{yx} \). In the coordinate system fixed to the rotating molecule the matrix \( \mathbf{I} \) does not depend on time.
Rotations of polyatomic molecules, continued

As each symmetric matrix the matrix $\mathbf{I}$ can be diagonalized. In the new coordinate frame (also fixed to the molecule) this matrix has the form:

$$
\mathbf{I} = \begin{bmatrix}
I_A & 0 & 0 \\
0 & I_B & 0 \\
0 & 0 & I_C
\end{bmatrix}
$$

where $I_A$, $I_B$, and $I_C$ are the so-called principal moments of inertia of the molecule. The normalized eigenvectors vectors $\vec{A}$, $\vec{B}$, and $\vec{C}$, corresponding to the eigenvalues $I_A$, $I_B$, and $I_C$ determines the so-called principal exes of the top (a molecule). If the molecule has a symmetry then $\vec{A}$, $\vec{B}$, i $\vec{C}$ sа coincide with the symmetry axes of the molecule. The principal moments of inertia are given by the formulas:

$$
I_A = \sum_i m_i (B_i^2 + C_i^2) \quad I_B = \sum_i m_i (A_i^2 + C_i^2) \quad I_C = \sum_i m_i (A_i^2 + B_i^2)
$$

where $A_i$, $B_i$ and $C_i$ are the coordinates of the $i$-th nucleus in the coordinate frame determined by the principal axes $\vec{A}$, $\vec{B}$, and $\vec{C}$, for instance $B_i^2 + C_i^2$ is the distance of the $i$-th nucleus form the $\vec{A}$ axis.
Rotations of polyatomic molecules, continued

In the coordinate frame $\vec{A}$, $\vec{B}$, and $\vec{C}$ the matrix $\vec{II}$ is diagonal so the angular momentum vector $\vec{L} = \vec{II}\vec{\omega}$ has the following coordinates in this frame:

$$L_A = I_A \omega_A, \quad L_B = I_B \omega_B, \quad L_C = I_C \omega_C,$$

One can easily show that the kinetic energy of rotations is given by

$$E_{rot} = \frac{1}{2} \sum_{i=1}^{N} m_i \vec{v}_i \cdot \vec{v}_i = \frac{1}{2} \sum_{i=1}^{N} m_i \vec{v}_i \cdot (\vec{\omega} \times \vec{R}_i) = \frac{1}{2} \sum_{i=1}^{N} m_i \vec{\omega} \cdot (\vec{R}_i \times \vec{v}_i) = \frac{1}{2} \vec{\omega} \cdot \vec{L}$$

In the frame of principal axes $\vec{\omega} \cdot \vec{L} = \omega_A L_A + \omega_B L_B + \omega_C L_C$, hence

$$E_{rot} = \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2$$

or

$$E_{rot} = \frac{1}{2I_A} L_A^2 + \frac{1}{2I_B} L_B^2 + \frac{1}{2I_C} L_C^2$$

To quantize and obtain the quantum mechanical Hamiltonian we add hats:

$$\hat{H}_{rot} = \frac{1}{2I_A} \hat{L}_A^2 + \frac{1}{2I_B} \hat{L}_B^2 + \frac{1}{2I_C} \hat{L}_C^2$$
Rotations of polyatomic molecules, continued

Eigenvalues and eigenfunctions of $\hat{H}_{\text{rot}}$ depend significantly on the relative values of the principal moments of inertia. We distinguish four kinds of tops:

- spherical tops, $I_A = I_B = I_C$ (methane, hexafluoride of uranium)
- prolate symmetric tops, $I_A < I_B = I_C$ (ammonia, $\text{CH}_3\text{Cl}$)
- oblate symmetric tops, $I_A = I_B < I_C$ (benzene, $\text{SO}_3$, $\text{CHCl}_3$)
- asymmetric tops, $I_A \neq I_B \neq I_C$ (water, ethylene, naphthalene)

For the oblate symmetric top $I_A = I_B$ so we can write:

$$\hat{H}_{\text{rot}} = \frac{1}{2I_A} \hat{L}_A^2 + \frac{1}{2I_B} \hat{L}_B^2 + \frac{1}{2I_C} \hat{L}_C^2 = \frac{1}{2I_A} \hat{L}_A^2 + \frac{1}{2I_A} \hat{L}_B^2 + \frac{1}{2I_A} \hat{L}_C^2 + \frac{1}{2I_C} \hat{L}_C^2 - \frac{1}{2I_A} \hat{L}_C^2$$

hence

$$\hat{H}_{\text{rot}} = \frac{1}{2I_A} \hat{L}_A^2 + \left( \frac{1}{2I_C} - \frac{1}{2I_A} \right) \hat{L}_C^2$$

Since the eigenvalues of $\hat{L}_A^2$ and $\hat{L}_C^2$ are given by $J(J + 1)\hbar^2$ and $K\hbar$, where $-J \leq K \leq J$, the eigenvalues of $\hat{H}_{\text{rot}}$ must be given by (in atomic units)

$$E_{JK} = \frac{1}{2I_A} J(J + 1) + \left( \frac{1}{2I_C} - \frac{1}{2I_A} \right) K^2$$
Rotations of polyatomic molecules, continued

For the prolate symmetric top we obtain a similar formula only the smallest and largest moments of inertia $I_A$ and $I_C$ are interchanged:

$$E_{JK} = \frac{1}{2I_C} J(J + 1) + \left( \frac{1}{2I_A} - \frac{1}{2I_C} \right) K^2$$

For symmetric tops the degeneracy of the level $E_{JK}$ is $2(2J + 1)$, 2 with respect to $K \ K$ and $2J + 1$ with respect to $M$. For the spherical top $I_A=I_B=I_C$ thus:

$$E_J = \frac{1}{2I_A} J(J + 1)$$

The degeneracy in this case is $(2J + 1)^2$.

For the asymmetric top (water, ethylene,) there is no analytical formula for the rotational levels. The degeneracy with respect to $K$ is lifted. $K$ ceases ti be a good quantum number.

Linear molecules in states with $\Lambda \neq 0$, i.e. $\Pi$, $\Delta$, etc. states are also symmetric tops (prolate ones) with $K = \Lambda$ where $\Lambda = 1$ for the $\Pi$, $\Lambda = 2$ for the $\Delta$, states, etc. The rotational energy of this states is given by:

$$E_{J\Lambda} = \frac{1}{2I_C} [J(J + 1) - \Lambda^2] + \frac{1}{2I_A} \Lambda^2$$

where $I_C=\mu R_e^2$ and $\Lambda^2/(2I_A)$ is a constant included in the electronic energy.
Rotational energies pattern for symmetric rotors

Rys. 4.9. Schemat poziomów rotacyjnych bąka symetrycznego

Rys. 4.10. Ruch obrotowy bąka wydłużonego w przypadku a) $|K| = J$ oraz b) $K = 0$
Rotational energies pattern for asymmetric rotors

Rys. 4.11. Poziomy energetyczne bąka asymetrycznego odpowiadające $J = 0, 1$ i $2$, przedstawione jako przypadek pośredni między strukturą energetyczną bąka symetrycznego wydłużonego i spłaszczonego. Momenty bezwładności $I_A$ oraz $I_C$ są tu ustalone, podczas gdy $I_B$ zmienia się w sposób ciągły między $I_A$ i $I_C$ w kierunku wskazanym strzałką i stanowi rzędna wykresu. Energie poziomów bąka symetrycznego dane są wzorem (4.81), gdzie $A > B$ dla bąka wydłużonego i $A < B$ dla bąka spłaszczonego. Liniowa zależność energii od $I_B$ jest tylko przybliżona.
Vibrations of polyatomic molecules

Consider $N$ atomic nuclei. Position of the $i$-th nucleus will be specified by the Cartesian coordinates $x_i$, $y_i$ and $z_i$ of its displacement from the equilibrium position (assumed fixed in space). The Hamiltonian in this coordinates is:

$$
\hat{H}_{\text{vib}} = - \sum_{i=1}^{3N} \frac{1}{2m_i} \frac{\partial^2}{\partial u_i^2} + V(u_1, u_2, \ldots, u_{3N})
$$

where $u_i, i=1,\ldots,3N$ denote collectively all Cartesian coordinates $x_1, y_1, z_1, x_2, y_2, z_2,\ldots$ and masses are defined such that $m_1=m_2=m_3, \ m_4=m_5=m_6,\ldots$

The potential $V(u_1, u_2, \ldots, u_{3N})$ can be expanded in the Taylor series around $u_1=u_2=u_3=\cdots=0$

$$
V(u_1, u_2, \ldots, u_{3N}) = V_0 + \sum_{i=1}^{3N} \left( \frac{\partial V}{\partial u_i} \right) u_i + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} \left( \frac{\partial^2 V}{\partial u_i \partial u_j} \right) u_i u_j + \cdots
$$

The first derivatives vanish at the minimum, the third ones are neglected (harmonic approximations). The constant $V_0$ is included in the electronic energy, hence:

$$
\hat{H}_{\text{vib}} = - \sum_{i=1}^{3N} \frac{1}{2m_i} \frac{\partial^2}{\partial u_i^2} + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} V_{ij} u_i u_j
$$

where $V_{ij}$ is the matrix of second derivatives (the Hessian) at the minimum.
To find eigenvalues of this Hamiltonian it is convenient to introduce the so-called mass scaled coordinates:

$$w_i = \sqrt{m_i} u_i$$

In these coordinates the Hamiltonian has the form:

$$\hat{H}_{\text{vib}} = -\frac{1}{2} \sum_{i=1}^{3N} \frac{\partial^2}{\partial w_i^2} + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} \frac{V_{ij}}{\sqrt{m_i m_j}} w_i w_j$$

The matrix $V_{ij}/\sqrt{m_i m_j}$ is symmetric so it can be diagonalized with a matrix $U_{ij}$ and one can introduce the normal coordinates $q_k$ using this $U_{ij}$ matrix:

$$q_k = \sum_{i=1}^{3N} U_{ik} w_i \quad \text{henceczyli} \quad u_i = \frac{1}{\sqrt{m_i}} \sum_{k=1}^{3N} U_{ik} q_k \quad \text{e.g.,} \quad u_i^{(k)} = \frac{1}{\sqrt{m_i}} U_{ik} q_k$$

In this normal coordinates the Hamiltonian has a very simple form:

$$\hat{H}_{\text{vib}} = \sum_{k=1}^{3N} \left( -\frac{1}{2} \frac{\partial^2}{\partial q_k^2} + \frac{1}{2} \lambda_k q_k^2 \right)$$

where $\lambda_k$ are eigenvalues of the $V_{ij}/\sqrt{m_i m_j}$ matrix. The eigenvalues of $\hat{H}_{\text{vib}}$ are:

$$E_{v_1, v_2, \ldots} = \sum_{k=1}^{3N} \hbar \omega_k \left( v_k + \frac{1}{2} \right) \quad \text{gdzie} \quad \omega_k = \sqrt{\lambda_k}$$
Translations, rotations, and vibrations of a triatomic molecule

Rys. 4.13. Przemieszczenia jąder w trakcie drgań normalnych cząsteczki $H_3^+$
Harmonic vibration spectrum of water

\[ E_{\text{osc}} \text{ [cm}^{-1}\text{]} \]

\begin{align*}
(0, 0, 2) \\
(1, 0, 1) \\
(2, 0, 0) \\
(0, 2, 1) \\
(1, 2, 0) \\
(0, 4, 0) \\
(0, 1, 1) \\
(1, 1, 0) \\
(0, 3, 0) \\
(0, 0, 1) \\
(1, 0, 0) \\
(0, 2, 0) \\
(0, 1, 0) \\
(0, 0, 0)
\end{align*}

\[ \omega_1 = 3652 \text{ cm}^{-1} \quad \omega_2 = 1595 \text{ cm}^{-1} \quad \omega_3 = 3756 \text{ cm}^{-1} \]
Resonance tunneling in the vibration spectrum of ammonia
Fermie resonance of the vibrational excitations 
\( \hbar \omega_1 = 1333 \text{ cm}^{-1} \) and \( 2\hbar \omega_2 = 1338 \text{ cm}^{-1} \) in the \( \text{CO}_2 \) molecule
Coriolis force effects on the normal vibrations of the CO$_2$ molecule