

V. ROTATIONAL (MICROWAVE) SPECTROSCOPY

In 1934 Cleeton and Williams observed absorptions at microwave frequencies by NH_3 , and thus MW spectroscopy began. World War II proved to be a boon to the development of technology for microwave spectroscopy due to the military need for **radar** (RADAR, radio detection and ranging) capabilities. The microwave spectrum of H_2O was discovered when the US Navy found that unusually high attenuation of radar signals occurred at certain frequencies due to atmospheric water vapor.

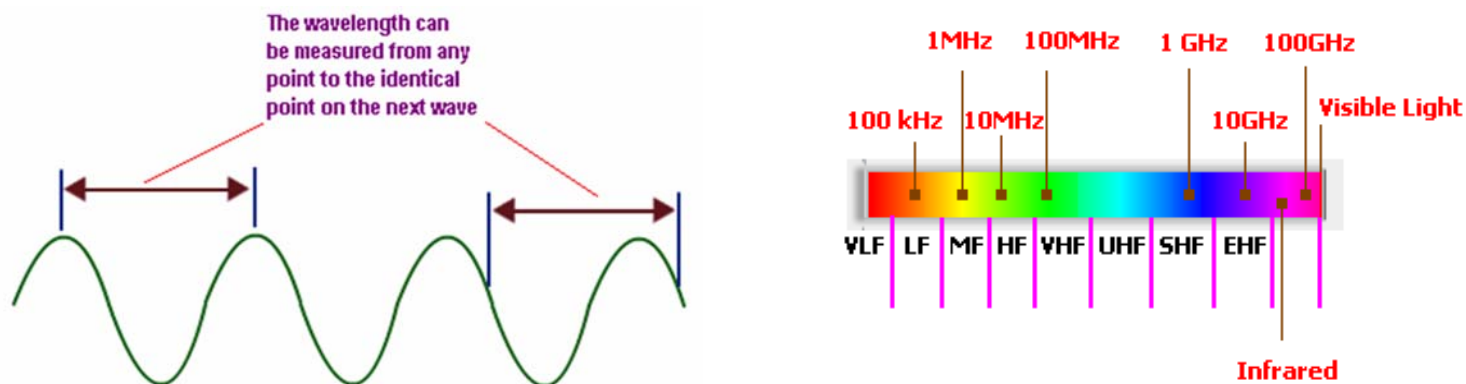
Microwave (MW) region of the electromagnetic (EM) spectrum (MW oven: 2.45 GHz):

wavelength: $\lambda \in (0.1, 100) \text{ cm}$

wavenumber: $\tilde{\nu} \in (0.01, 10) \text{ cm}^{-1}$

frequency: $\nu \in (0.3, 300) \text{ GHz}$

Terahertz (THz) region: principally above 1 THz, up to 3-4 THz



In these regions of the EM spectrum pure rotational transitions dominate.

Nevertheless, there are alternate causes of absorption in the microwave region:

- Tunneling splitting of the inversion (vibrational) mode of NH_3 (at 24 GHz = 0.80 cm^{-1})
- Nuclear hyperfine splitting of the ^2S state of the H atom (0.0475 cm^{-1}), leading to MW emission from outer space
- Splitting of degenerate electronic states due to the interaction of electronic orbital angular momentum and molecular rotation: A -doubling of the $^2\Pi_{1/2}$ state of the OH radical for $J = 1/2$ (0.0556 cm^{-1})

Hallmarks of rotational spectroscopy

A) *High-precision data*

Wavenumbers and frequencies of some measured rotational transitions of CO

$\tilde{\nu}$ (cm ⁻¹)	J''	J'	ν (GHz)	$\Delta \nu_{J''+1}^{J''}$ (GHz)
3.845 033 19	0	1	115.271 195	115.271 195
7.689 919 07	1	2	230.537 974	115.266 779
11.534 509 6	2	3	345.795 900	115.257 926

B) *Determination of geometrical structures*

High precision rotational constants (A_0, B_0, C_0)
for parent molecule and isotopologues



moments
of inertia



accurate bond lengths
and bond angles

[Useful reading: Nemes László: A molekulageometria meghatározása forgási spektroszkópiával (Kémia Újabb Eredményei, 51. kötet, 1981)]

C) *Determination of permanent dipole moments*

In the **Stark effect**, discovered by Hughes and Wilson in 1947, an external electric field is applied in the absorption cell. This effect increases sensitivity and also causes splitting of rotational energy levels in accordance with the magnitude of the dipole moment.

D) *Radiofrequency astronomy*

Detection and identification of molecules in interstellar space from emission and absorption spectroscopy. Background energy densities characteristic of a black body at 2.7 K. Background radiation in the universe is supposedly left over from the Big Bang. Uniqueness of high precision transition frequencies is complicated by the Doppler effect. Many rotational lines from interstellar space remain to be characterized. A challenging question: are there molecules characteristic of life on Earth (*e.g.*, amino acids and sugars) in space?

Lot more than 100 unique neutral molecules, as well as several cations and a few anions, have been observed via their microwave and millimeterwave (emission) spectra. Some of these chemical species are as follows ($\mu \neq 0$ is a requirement, so the most important molecule leading the gas-phase chemistry of cold places, H_3^+ , has only been identified recently, its properties could be investigated only in the laboratory):

diatomics: OH, CO, CN, CS, SiO, SiS, NO, NS, CH, CH^+

triatomics: H_2O , HCN, HNC, OCS, H_2S , N_2H^+ , SO_2 , HNO, C_2H , etc.

10-atoms: $\text{NH}_2\text{-CH}_2\text{-COOH(?)}$

13-atoms: $\text{N}\equiv\text{C-C}\equiv\text{C-C}\equiv\text{C-C}\equiv\text{C-C}\equiv\text{C-C}\equiv\text{C-H}$

Classical mechanics of rigid rotation

Principal reference: H. Goldstein *et al.*, *Classical Mechanics*, 3rd ed., 2001

Assume that we have a rigid body which is freely rotating in space, *i.e.*, its motion is unconstrained and no torque is applied to it. Such is the model for the rotations of polyatomic molecules, and the model is called **rigid rotor**. We have the following equations of motion:

$$\mathbf{L} = \mathbf{I} \boldsymbol{\omega} = \text{const.} \quad (\text{conservation of angular momentum})$$

$$T = \frac{1}{2} \boldsymbol{\omega}^T \mathbf{I} \boldsymbol{\omega} = \frac{1}{2} \mathbf{L}^T \mathbf{I}^{-1} \mathbf{L} = \text{const.} \quad (\text{conservation of energy})$$

where

\mathbf{L} is the rotational angular momentum (a constant vector in the lab-fixed frame)

$\boldsymbol{\omega}$ is the angular velocity of rotation, directed along the instantaneous axis of rotation (a time-dependent vector in the lab-fixed frame)

\mathbf{I} is the inertia tensor (a 3×3 time-dependent matrix in the lab-fixed frame)

T is the kinetic energy of the rotation (a constant since energy is conserved and there is no potential energy involved)

Analogies between translation and rotation

Translational motion along the x axis

coordinate: x

velocity: $v_x = \frac{d x}{d t}$

acceleration: $a_x = \frac{d v_x}{d t} = \frac{d^2 x}{d t^2}$

mass: m

equation of motion: $F_x = m \frac{d^2 x}{d t^2}$

(linear) momentum: $p_x = m v_x$

kinetic energy: $T = \frac{1}{2} m v_x^2$

Rotational motion around rotational axis z

angle (angular distortion): ϕ

angular velocity of rotation: $\omega_z = \frac{d \phi}{d t}$

angular acceleration: $\alpha_z = \frac{d \omega_z}{d t} = \frac{d^2 \phi}{d t^2}$

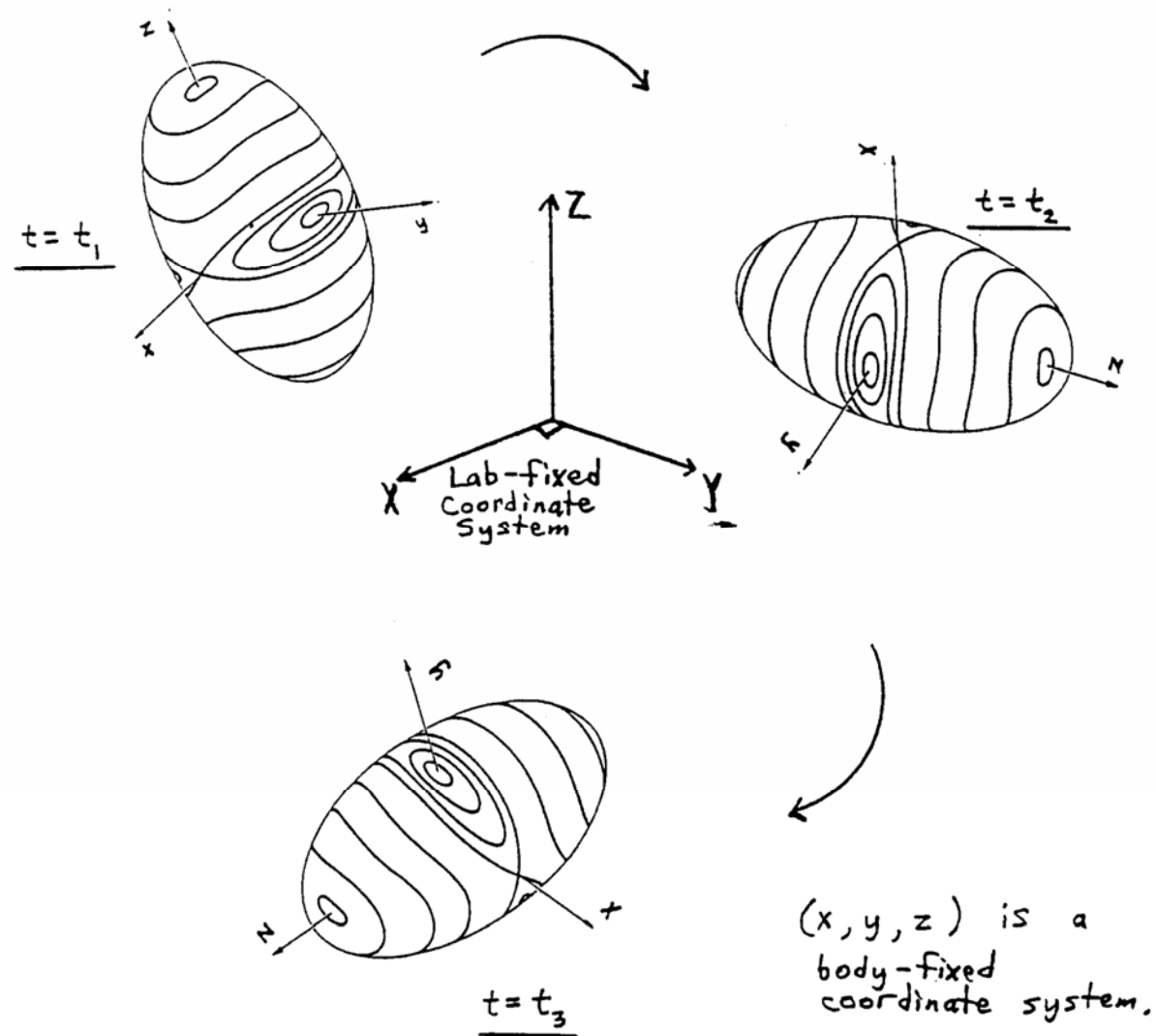
moment of inertia: $I = \sum_i m_i \ell_i^2$

equation of motion: $M_z = I \frac{d^2 \phi}{d t^2}$

angular momentum: $L_z = I \omega_z$

kinetic energy: $T = \frac{1}{2} I \omega_z^2$

Lab-fixed and molecule-fixed axis systems



In each instant in time one can find a unitary matrix $\mathbf{U}(t)$ which relates the body-fixed (x, y, z) coordinate system to the lab-fixed (X, Y, Z) system. The equations of motion in the body-fixed frame are

$$\mathbf{L}'(t) = \mathbf{I}'\boldsymbol{\omega}'(t) \quad \text{and} \quad T = \frac{1}{2}\boldsymbol{\omega}'(t)^T \mathbf{I}'\boldsymbol{\omega}'(t) = \text{constant} ,$$

where $\mathbf{L}'(t) = \mathbf{U}(t)\mathbf{L}$ (\mathbf{L} constant), $\boldsymbol{\omega}'(t) = \mathbf{U}(t)\boldsymbol{\omega}(t)$, and $\mathbf{I}' = \mathbf{U}(t)\mathbf{I}(t)\mathbf{U}(t)^T$.

The convenience of choosing the body-fixed frame is that \mathbf{I}' is a constant with respect to time.

Equations for the moment of inertia tensor

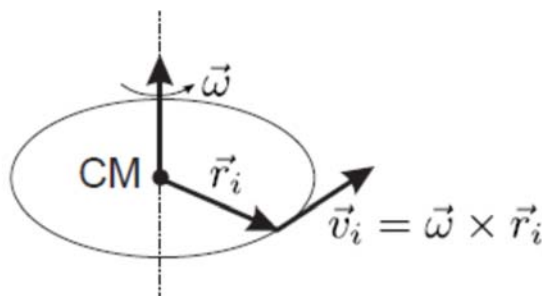


Figure 5.1: Angular velocity $\vec{\omega}$.

For a freely rotating object, the origin of the body-fixed frame is the center of mass (abbreviated as CM or sometimes COM). For a rigid body consisting of N particles with masses m_k , elements of the moments of inertia are as follows (coming from the definition of the angular momentum as $\mathbf{J} = \sum_{k=1}^N m_k (\mathbf{r}_k \times \mathbf{v}_k) = \sum_{k=1}^N m_k [\mathbf{r}_k \times (\boldsymbol{\omega} \times \mathbf{r}_k)]$):

moments of inertia:

$$I'_{11} = I'_{xx} = \sum_{k=1}^N m_k (y_k^2 + z_k^2)$$

$$I'_{22} = I'_{yy} = \sum_{k=1}^N m_k (x_k^2 + z_k^2)$$

$$I'_{33} = I'_{zz} = \sum_{k=1}^N m_k (x_k^2 + y_k^2)$$

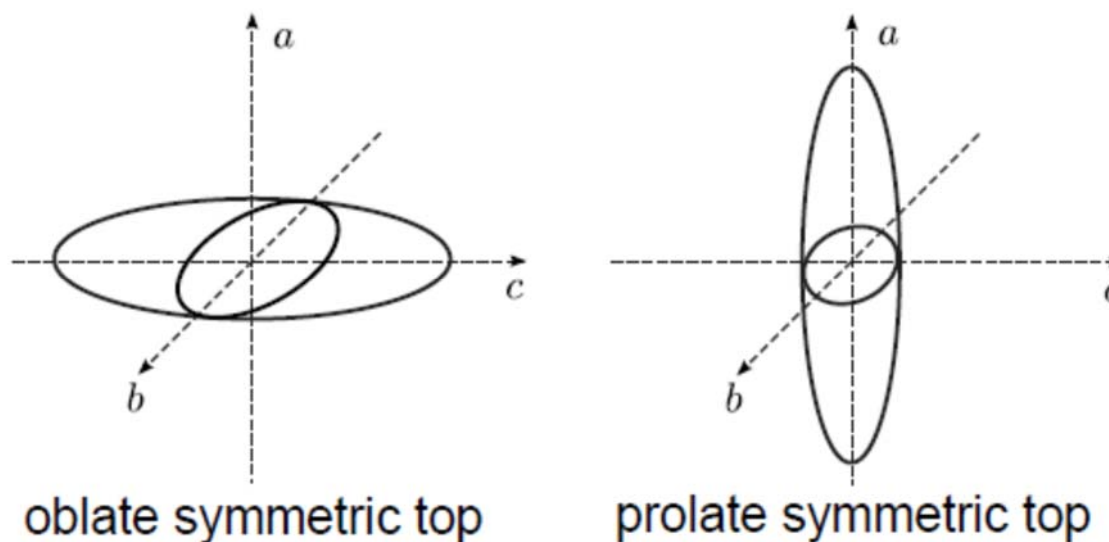
products of inertia:

$$I'_{23} = I'_{32} = I'_{yz} = -\sum_{k=1}^N m_k y_k z_k$$

$$I'_{21} = I'_{12} = I'_{xy} = -\sum_{k=1}^N m_k x_k y_k$$

$$I'_{31} = I'_{13} = I'_{xz} = -\sum_{k=1}^N m_k x_k z_k$$

To visualize the inertia tensor we can do the following. For every possible axis α through the COM compute the moment of inertia $I'_\alpha = \sum_{k=1}^N m_k r_k^2$ (r_k is the perpendicular distance from the particle of mass m_k to the axis α). Lay off on each side of the center of mass a distance numerically equal to $1/\sqrt{I'_\alpha}$. The resulting surface in three dimensions is the **ellipsoid of inertia**.



By choosing the body-fixed frame (embedding) appropriately, we can make \mathbf{I}' diagonal:

$$\mathbf{I}' = \begin{pmatrix} I'_{xx} & I'_{xy} & I'_{xz} \\ I'_{yx} & I'_{yy} & I'_{yz} \\ I'_{zx} & I'_{zy} & I'_{zz} \end{pmatrix} \Rightarrow \begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix}$$

In this case, the kinetic energy expression grossly simplifies,

$$T = \frac{1}{2} \boldsymbol{\omega}'(t)^T \mathbf{I}' \boldsymbol{\omega}'(t) = \frac{1}{2} (I'_{xx} \omega'_x{}^2 + I'_{yy} \omega'_y{}^2 + I'_{zz} \omega'_z{}^2) + \\ + (I'_{xy} \omega'_x \omega'_y + I'_{xz} \omega'_x \omega'_z + I'_{yz} \omega'_y \omega'_z)$$

becomes

$$T = \frac{1}{2} I_a \omega'_a{}^2 + \frac{1}{2} I_b \omega'_b{}^2 + \frac{1}{2} I_c \omega'_c{}^2.$$

The axes which diagonalize the inertia tensor in this manner are called the **principal axes of rotation**. The resulting I_a , I_b , and I_c values are the **principal moments of inertia**.

Algorithm to determine the principal axes and principal moments

(1) Attach an arbitrary coordinate system to the (rigid) body and compute the coordinates of the center of mass:

$$\mathbf{R}_{\text{COM}} = \frac{1}{M} \sum_{k=1}^N m_k \mathbf{r}_k$$

(2) Translate the coordinate system to places the COM at the origin. Recompute all coordinates of the particles in this reference frame.

(3) Compute the inertia tensor \mathbf{I}' in this body-fixed, COM reference frame.

(4) Find the eigenvalues and eigenvectors of \mathbf{I}' :

$$\mathbf{I}' \mathbf{v}_\alpha = I_\alpha \mathbf{v}_\alpha, \quad \alpha = a, b, c$$

The \mathbf{v}_α are the principal axes and the I_α are the principal moments.

Facts which aid the rapid determination of the principal axes:

- (1) The principal axes are mutually orthogonal. (The inertia tensor is symmetric.)
- (2) Any plane of symmetry contains two principal axes and is perpendicular to a third principal axis.
- (3) Any axis of rotation is a principal axis. If it is a C_n axis for $n > 2$, the plane perpendicular to the axis is a **principal plane** corresponding to degenerate moments of inertia.

Examples:

1. H_2O placed in the yz plane

σ_{yz} symmetry plane $\Rightarrow x$ must be a principal axis (based on (2))

σ_{xz} symmetry plane $\Rightarrow y$ is than also a principal axis (based on (2))

(x,y) principal axes $\Rightarrow z$ is a principal axis (based on (1))

2. Ammonia

$C_n(z) \Rightarrow z$ is a principal axis (based on (3))

$n = 3 \Rightarrow (x,y)$ principal plane. Then any two orthogonal vectors of the (x,y) plane can be chosen as principal axes. Axes x and y is one of the possible choices.

Spectroscopic rotational constants and principal moments of inertia

It is a generally accepted convention that the principal moments of inertia corresponding to (a,b,c) must satisfy the following relationship:

$$I_c \geq I_b \geq I_a$$

The **rotational constants**, which will be used to help to interpret rotational spectra, are defined according to the same convention as:

$$\begin{aligned} \tilde{A} &= \frac{1}{hc} \left(\frac{\hbar^2}{2I_a} \right) \\ \tilde{B} &= \frac{1}{hc} \left(\frac{\hbar^2}{2I_b} \right) \\ \tilde{C} &= \frac{1}{hc} \left(\frac{\hbar^2}{2I_c} \right) \end{aligned} \quad \tilde{A} \geq \tilde{B} \geq \tilde{C}$$

Example: Rotational constants of H₂O (C_{2v} , placed in the yz plane)

$$O_1: \mathbf{r}_1 = \{0, 0, 0\} \text{ (natural choice)}$$

$$H_2: \mathbf{r}_2 = \{0, r \sin(\alpha/2), r \cos(\alpha/2)\} \text{ (} r = r_{OH} \text{ and } \alpha = \angle HOH \text{)}$$

$$H_3: \mathbf{r}_3 = \{0, -r \sin(\alpha/2), r \cos(\alpha/2)\}$$

Step 1: Based on $\mathbf{R}_{\text{tkp}} = \frac{1}{M} \sum_{k=1}^N m_k \mathbf{r}_k$ determine the COM:

$$M, \text{ the total mass: } M = m_O + 2 m_H$$

$$\mathbf{R}_{\text{COM}} = \frac{1}{m_O + 2m_H} (0, 0, 2m_H r \cos(\alpha/2))$$

Step 2: Introduce the new coordinates:

$$O_1: \mathbf{r}_1 = r \{0, 0, -2(m_H / M) \cos(\alpha / 2)\}$$

$$H_2: \mathbf{r}_2 = r \{0, \sin(\alpha/2), (m_O/M) \cos(\alpha/2)\}$$

$$H_3: \mathbf{r}_3 = r \{0, -\sin(\alpha/2), (m_O/M) \cos(\alpha/2)\}$$

Step (3): Determination of the elements of the inertia tensor:

$$\begin{aligned}
 I'_{yy} &= \sum_i m_i (x_i^2 + z_i^2) = \sum_i m_i z_i^2 = \\
 &= r^2 \cos^2(\alpha/2) \frac{4m_{\text{H}}^2 m_{\text{O}}}{M^2} + 2r^2 \cos^2(\alpha/2) m_{\text{H}} \frac{m_{\text{O}}^2}{M^2} = \\
 &= \frac{r^2 \cos^2(\alpha/2)}{M^2} (4m_{\text{H}}^2 m_{\text{O}} + 2m_{\text{H}} m_{\text{O}}^2) = 2 \frac{m_{\text{H}} m_{\text{O}}}{M} r^2 \cos^2(\alpha/2)
 \end{aligned}$$

$$I'_{zz} = \sum_i m_i (x_i^2 + y_i^2) = \sum_i m_i y_i^2 = 2m_{\text{H}} r^2 \sin^2(\alpha/2)$$

$I'_{xx} = \sum_i m_i (y_i^2 + z_i^2) \Leftrightarrow I'_{xx} = I'_{yy} + I'_{zz}$, which holds, as can be easily shown, for all planar molecules.

$$I'_{xy} = -\sum_i m_i x_i y_i = 0 \text{ and } I'_{xz} = -\sum_i m_i x_i z_i = 0,$$

$$I'_{yz} = -\sum_i m_i y_i z_i = 0 +$$

$$r \sin(\alpha/2)(m_O / M) \cos(\alpha/2) - r \sin(\alpha/2)(m_O / M) \cos(\alpha/2) = 0$$

Step (4): Note that the moment of inertia tensor is already diagonal, so the eigenvalues are just the diagonal elements and the eigenvectors are simply the vectors (1, 0, 0), (0, 1, 0) and (0, 0, 1). Therefore, the principal axes are (x, y, z), as deduced above using the rules (1)-(3) concerning principal axes.

Recommendation: It is highly advisable to use Facts (1)-(3) concerning principal axes in setting up the initial coordinate system. If there is any point-group symmetry operation characterizing the molecule, an appropriate choice of the initial axis system simplifies the task of diagonalizing the inertia tensor.

We have the following data for the water molecule [$1 \text{ u} = m(^{12}\text{C})/12$]:

$$m_{\text{O}} = 15.99491 \text{ u}, m_{\text{H}} = 1.007825 \text{ u},$$

$r_e(\text{O}-\text{H}) = 0.9572 \text{ \AA}$, $\angle_e\text{HOH} = 104.52^\circ$ (not exactly the correct equilibrium structure of H_2^{16}O , but close)

Based on the relation just obtained:

$$I'_{yy} = 0.61446 \text{ u \AA}^2 = 1.0203 \times 10^{-47} \text{ kg m}^2$$

$$I'_{zz} = 1.15492 \text{ u \AA}^2 = 1.9178 \times 10^{-47} \text{ kg m}^2$$

$$I'_{xx} = I'_{yy} + I'_{zz} = 1.76938 \text{ u \AA}^2 = 2.9382 \times 10^{-47} \text{ kg m}^2$$

Note the association $y \Leftrightarrow \text{a}$, $z \Leftrightarrow \text{b}$, $x \Leftrightarrow \text{c}$.

The associated equilibrium rotational constants ($1 \text{ cm}^{-1} = 2.997925 \times 10^4 \text{ MHz}$ and $1 \text{ MHz} = 3.33564 \times 10^{-5} \text{ cm}^{-1}$):

$$\tilde{A}_e = 822\,476 \text{ MHz} = 27.4348 \text{ cm}^{-1}$$

$$\tilde{B}_e = 437\,588 \text{ MHz} = 14.5964 \text{ cm}^{-1}$$

$$\tilde{C}_e = 285\,625 \text{ MHz} = 9.5274 \text{ cm}^{-1}$$

The equilibrium rotational constants \tilde{A}_e , \tilde{B}_e , and \tilde{C}_e are to be distinguished from the (measurable) rotational constants \tilde{A}_0 , \tilde{B}_0 , and \tilde{C}_0 , which include zero-point vibrational effects and thus are slightly different from their equilibrium counterparts (quantum chemistry provides outstanding estimates for the small but significant differences).

Molecular Rotational Types

(A) Linear molecules

$$I_c = I_b > I_a = 0$$

There exists only one unique rotational constant, which is labelled B and is equal to C .

(B) Spherical tops

$$I_c = I_b = I_a = I \Leftrightarrow A = B = C$$

There exists only one unique rotational constant, which is labelled as B .
Examples: CH_4 , SF_6 , basketball.

(C) [Symmetric tops](#)

Case (1): Prolate symmetric top

$$I_c = I_b > I_a \neq 0 \Leftrightarrow A > B = C$$

There exists two unique rotational constants, A and B , where $A > B$. Examples: CH_3I , CH_3Cl , allene, American football.

Case (2): Oblate symmetric top

$$I_c > I_b = I_a \neq 0 \Leftrightarrow A = B > C$$

There exists two unique rotational constants, B and C , where $B > C$. Examples: NH_3 , chloroform (CHCl_3), benzene, frisbee. Planar oblate symmetric tops, if they are truly symmetric (thus possess at least one rotational axis C_n with $n > 2$) do not have a dipole moment and thus have no pure rotational spectra.

(D) [Asymmetric tops](#)

$$I_c > I_b > I_a \neq 0 \Leftrightarrow A > B > C$$

There exist three unique rotational constants, A , B , and C , where $A > B > C$. Most molecules belong to this top type. Examples: H_2O , H_2CO , C_2H_4 . If $I_c \approx I_b > I_a$, the molecule is a prolate near symmetric top (*e.g.*, HNCO), while if $I_c > I_b \approx I_a$, the molecule is an oblate near symmetric top (*e.g.*, furan, $\text{C}_4\text{H}_4\text{O}$).

Group theory and rotational types

The character table for the point group of the molecule indicates whether it is an asymmetric top, a symmetric top, or a spherical top by showing how the (a, b, c) axes, which correspond to some choices of (x, y, z) , transform.

Asymmetric top: a , b , and c are unique and transform as a one-dimensional irreducible representation (*e.g.*, H_2O , H_2CO).

Symmetric top: (a, b) or (b, c) pair transforms as a two-dimensional irreducible representation. The other axis is unique and transforms as a one-dimensional irrep (*e.g.*, C_6H_6 , CH_3Br).

Spherical top: (a, b, c) triplet transforms as a three-dimensional irrep (*e.g.*, CH_4 , SF_6).

Quantum mechanics of rigid rotation

Consider a molecule rotating in isotropic, field-free space with no applied torque. After invoking the Born–Oppenheimer (BO) approximation (without which electronic and nuclear motions would be scrambled in complicated molecular Hamiltonians, and extensive numerical computations would be necessary to extract even the most qualitative features of vibrational and rotational structure) we wish to solve the nuclear Schrödinger equation:

$$\hat{H}_N \Psi_N = E_N \Psi_N,$$

where

$$\hat{H}_N = \hat{T}_{\text{trans}} + \hat{T}_{\text{rot}} + \hat{T}_{\text{vib}} + \hat{T}_{\text{vib-rot}} + V.$$

Vibrational motion is typically much faster than rotational motion. Thus, the vibration-rotation interaction term, $\hat{T}_{\text{vib-rot}}$, can be averaged over the given vibrational state, whence

$$\hat{H}_{\text{rot,v}} = \hat{T}_{\text{rot}} + \left\langle \hat{T}_{\text{vib-rot}} \right\rangle_{\text{v}}$$

is the rotational Hamiltonian for the given vibrational state (for rotational motion $V_{\text{rot}} = 0$).

Consequently,

$$\Psi_N \approx \Psi_{\text{trans}} \Psi_{\text{vib}} \Psi_{\text{rot},v}$$

and the time-independent Schrödinger equation for the rotational motion is

$$\hat{H}_{\text{rot},v} \Psi_{\text{rot},v} = E_{\text{rot},v} \Psi_{\text{rot},v} ,$$

Classically,

$$T_{\text{rot}} = \frac{1}{2} I_a \omega_a^2 + \frac{1}{2} I_b \omega_b^2 + \frac{1}{2} I_c \omega_c^2$$

or

$$T_{\text{rot}} = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} ,$$

where $J_{a,b,c}$ are components of the rotational angular momentum in the body-fixed (molecule-fixed) frame of reference.

Use quantum mechanical operators:

$$\hat{H}_{\text{rot},\nu} = \frac{\hat{J}_a^2}{2I_{a,\nu}} + \frac{\hat{J}_b^2}{2I_{b,\nu}} + \frac{\hat{J}_c^2}{2I_{c,\nu}},$$

where the moments of inertia depend (slightly) on the vibrational state of concern characterized by the quantum number ν . Understanding this dependence, we henceforth drop the subscript ν .

One could, in principle, use operators for the components of the angular momentum about the space-fixed (lab-fixed) axes \hat{J}_X , \hat{J}_Y , és \hat{J}_Z . We know that

$$\hat{J}^2 = \hat{J}_a^2 + \hat{J}_b^2 + \hat{J}_c^2 = \hat{J}_X^2 + \hat{J}_Y^2 + \hat{J}_Z^2.$$

Note the differences in commutation relations:

$$\begin{array}{ll} [\hat{J}_X, \hat{J}_Y] = i\hbar\hat{J}_Z & [\hat{J}_a, \hat{J}_b] = -i\hbar\hat{J}_c \\ [\hat{J}_Y, \hat{J}_Z] = i\hbar\hat{J}_X & [\hat{J}_b, \hat{J}_c] = -i\hbar\hat{J}_a \\ [\hat{J}_Z, \hat{J}_X] = i\hbar\hat{J}_Y & [\hat{J}_c, \hat{J}_a] = -i\hbar\hat{J}_b \end{array}$$

Solutions to the rotational Schrödinger equation

$$\hat{H}_{\text{rot}} = \frac{\hat{J}_a^2}{2I_a} + \frac{\hat{J}_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$

Regardless of the values of I_a , I_b , and I_c ,

$$[\hat{H}_{\text{rot}}, \hat{J}^2] = 0 \quad \text{and} \quad [\hat{H}_{\text{rot}}, \hat{J}_Z] = 0.$$

Thus, Ψ_{rot} is also an eigenfunction of \hat{J}^2 and \hat{J}_Z .

We know from the theory of angular momenta (see also the outstanding textbook R. N. Zare: *Angular Momentum*, Wiley-Interscience: New York, 1988) that

$$\hat{H}_{\text{rot}} \Psi_{\text{rot}} = E_{\text{rot}} \Psi_{\text{rot}} ,$$

$$\hat{J}_{\text{rot}}^2 \Psi_{\text{rot}} = \hbar^2 J(J+1) \Psi_{\text{rot}} \quad \text{and} \quad J = 0, 1, 2, 3, \dots ,$$

and

$$\hat{J}_Z \Psi_{\text{rot}} = \hbar M \Psi_{\text{rot}} \quad \text{and} \quad M = 0, \pm 1, \pm 2, \dots, \pm J ,$$

where J is the quantum number for total rotational angular momentum, M is the quantum number for the projection of \mathbf{J} on the space-fixed Z axis.

$$\text{Thus, for any rotor } \Psi_{\text{rot}} = \frac{1}{\sqrt{2\pi}} F(\theta, \chi) \exp(iM\phi),$$

where the three rotational coordinates are the three **Eulerian angles** (ϕ, θ, χ) ($0 \leq \phi \leq 2\pi; 0 \leq \theta \leq \pi; 0 \leq \chi \leq 2\pi$), defining the orientation of a rigid body in space. With the help of the Eulerian angles, and some algebra, the angular momentum operator can be expressed both in the space- and body-fixed frames:

$$\hat{J}_a = i\hbar \left(\cos \chi \csc \theta \frac{\partial}{\partial \phi} - \cos \chi \cot \theta \frac{\partial}{\partial \chi} - \sin \chi \frac{\partial}{\partial \theta} \right),$$

$$\hat{J}_b = i\hbar \left(-\sin \chi \csc \theta \frac{\partial}{\partial \phi} + \sin \chi \cot \theta \frac{\partial}{\partial \chi} - \cos \chi \frac{\partial}{\partial \theta} \right),$$

$$\hat{J}_c = -i\hbar \frac{\partial}{\partial \chi},$$

and

$$\hat{J}_X = i\hbar \left(\cos \phi \cot \theta \frac{\partial}{\partial \phi} - \cos \phi \csc \theta \frac{\partial}{\partial \chi} + \sin \phi \frac{\partial}{\partial \theta} \right),$$

$$\hat{J}_Y = i\hbar \left(\sin \phi \cot \theta \frac{\partial}{\partial \phi} - \sin \phi \csc \theta \frac{\partial}{\partial \chi} - \cos \phi \frac{\partial}{\partial \theta} \right),$$

$$\hat{J}_Z = -i\hbar \frac{\partial}{\partial \phi}.$$

It can also be shown that

$$\hat{J}^2 = -\hbar^2 \left(\csc^2 \theta \frac{\partial^2}{\partial \phi^2} + \csc^2 \theta \frac{\partial^2}{\partial \chi^2} - 2 \cot \phi \csc \phi \frac{\partial^2}{\partial \phi \partial \chi} + \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} \right).$$

In what follows let us investigate the different tops separately.

Linear molecules

We learned the following about rigid linear molecules (“pencils”):

$$I_c = I_b > I_a = 0,$$

thus, there is only one rotational constant, the convention is to call it B and its value coincides with C .

The Hamilton operator depend only on the Euler angles (ϕ, θ) but not on χ . Thus,

$$\hat{H}_{\text{rot}} = \frac{\hat{J}^2}{2I_b},$$

$$\hat{J}^2 = -\hbar^2 \left(\frac{1}{\sin^2 \theta} \right) \frac{\partial^2}{\partial \phi^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \theta^2},$$

$$\hat{J}^2 Y_{JM}(\theta, \phi) = \hbar^2 J(J+1) Y_{JM}(\theta, \phi),$$

and

$$\Psi_{\text{rot}} = Y_{JM}(\theta, \phi).$$

We get the following expression for the rotational energy levels of a linear molecule:

$$E_{\text{rot}} = \frac{\hbar^2 J(J+1)}{2I_b},$$

furthermore,

$$J = 0, 1, 2, \dots \quad \text{and} \quad M = 0, \pm 1, \pm 2, \dots, \pm J.$$

All rotational levels depend only on the quantum number J but not on M ; thus, the levels are $(2J + 1)$ -fold degenerate (M can take $2J + 1$ values for each J).

In spectroscopy, it is usual to talk about **term values** (unit: cm^{-1} , the same as that of \tilde{B}):

$$F_{\text{rot}} = \frac{E_{\text{rot}}}{hc} = \tilde{B}J(J+1).$$

Spherical top

We learned the following about rigid spherical tops (“footballs”):

$$I_c = I_b = I_a = I \Leftrightarrow A = B = C ,$$

thus, there is only one rotational constant, usually denoted as B .

The rotational Hamiltonian employed in the Schrödinger equation is thus

$$\hat{H}_{\text{rot}} = \frac{\hat{J}_a^2}{2I} + \frac{\hat{J}_b^2}{2I} + \frac{\hat{J}_c^2}{2I} = \frac{\hat{J}^2}{2I}$$

and the time-independent Schrödinger equation becomes

$$(1/2I)\hat{J}^2\Psi_{\text{rot}} = E\Psi_{\text{rot}} .$$

The eigenfunctions can be written as

$$\Psi_{\text{rot}} = P_J^M [\cos(\theta)] \exp(iM\phi) ,$$

where $P_J^M [\cos(\theta)]$ are **associated Legendre polynomials**.

The corresponding eigenvalues are

$$E_{\text{rot}} = \frac{\hbar^2 J(J+1)}{2I} , \quad J = 0, 1, 2, \dots .$$

While the rotational Hamiltonian does not generally commute with \hat{J}_a ; for spherical tops $[\hat{H}_{\text{rot}}, \hat{J}_a] = 0$. The eigenvalues of \hat{J}_a are $K\hbar$, with $K = 0, \pm 1, \pm 2, \dots, \pm J$. The quantum number K gives the rotational angular-momentum component along a molecule-fixed axis of the spherical top. Naturally, the corresponding eigenfunctions have the form $(1/\sqrt{2\pi})\exp(iK\chi)$. Hence the overall spherical-top eigenfunctions have the form

$$H_{JKM}(\theta) \left(\frac{1}{2\pi} \right) \exp(iM\varphi) \exp(iK\chi) .$$

There are three quantum numbers characterizing this top: J , K , and M . According to the definition of the quantum numbers (in the present case $M = 0, \pm 1, \pm 2, \dots, \pm J$), each rotational level is $(2J + 1)^2$ -fold degenerate.

The rotational term values are

$$F_{\text{rot}} = \frac{E_{\text{rot}}}{hc} = \tilde{B}J(J + 1) .$$

Symmetric top molecules

Case 1: Prolate symmetric top

$$I_c = I_b > I_a \neq 0 \Leftrightarrow A > B = C$$

There are two unique rotational constants, A and B , and according to our convention $A > B$. Examples: CH_3I , CH_3Cl , allene, american football.

$$\hat{H}_{\text{rot}} = \frac{\hat{J}_a^2}{2I_a} + \frac{\hat{J}_b^2 + \hat{J}_c^2}{2I_b} = \frac{\hat{J}_a^2}{2I_a} + \frac{\hat{J}^2 - \hat{J}_a^2}{2I_b} = \frac{\hat{J}^2}{2I_b} + \frac{\hat{J}_a^2}{2} \left(\frac{1}{I_a} - \frac{1}{I_b} \right)$$

The latter form was chosen so that we can take advantage of the following commutation relations during solution of the Schrödinger equation: $[\hat{H}_{\text{rot}}, \hat{J}^2] = 0$ and $[\hat{H}_{\text{rot}}, \hat{J}_a] = 0$.

Based on our knowledge we can write

$$\hat{H}_{\text{rot}} \Psi_{\text{rot}} = E_{\text{rot}} \Psi_{\text{rot}}$$

$$\hat{J}^2 \Psi_{\text{rot}} = \hbar^2 J(J+1) \Psi_{\text{rot}}$$

$$\hat{J}_a \Psi_{\text{rot}} = \hbar K \Psi_{\text{rot}} \quad K = 0, \pm 1, \pm 2, \dots$$

$$\hat{J}_Z \Psi_{\text{rot}} = \hbar M \Psi_{\text{rot}} \quad M = 0, \pm 1, \pm 2, \dots$$

The time-independent Schrödinger equation is

$$\hat{H}_{\text{rot}} \Psi_{\text{rot}} = \left[\frac{\hat{J}^2}{2I_b} + \frac{\hat{J}_a^2}{2} \left(\frac{1}{I_a} - \frac{1}{I_b} \right) \right] \Psi_{\text{rot}} = \Psi_{\text{rot}} \left[\frac{\hbar^2 J(J+1)}{2I_b} + \frac{1}{2} \left(\frac{1}{I_a} - \frac{1}{I_b} \right) \hbar^2 K^2 \right].$$

Thus, we obtain the following equation for the energy levels of a prolate symmetric top:

$$E_{\text{rot}} = \frac{\hbar^2 J(J+1)}{2I_b} + \frac{\hbar^2 K^2}{2} \left(\frac{1}{I_a} - \frac{1}{I_b} \right).$$

The corresponding term value expression is

$$F_{\text{rot}} = \frac{E_{\text{rot}}}{hc} = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2.$$

Case 2: Oblate symmetric top

$$I_c > I_b = I_a \neq 0 \Leftrightarrow A = B > C$$

There are two unique rotational constants, B and C , according to the usual convention $B > C$.

Following a small and trivial modification of the formulas we learned for prolate symmetric tops, we obtain

$$F_{\text{rot}} = \frac{E_{\text{rot}}}{hc} = \tilde{B}J(J+1) + (\tilde{C} - \tilde{B})K^2.$$

Rotational wavefunctions of symmetric tops:

$$\Psi_{\text{rot}} = \Psi_{JKM}(\theta, \varphi, \chi) = \frac{1}{2\pi} G_{JKM}(\theta) e^{iM\varphi} e^{iK\chi}$$

Based on the definition of the Eulerian angles, φ describes the rotation about the space-fixed Z axis (thus, M is associated with the projection of \mathbf{J} on Z), while χ is a rotation about a body-fixed axis (K is associated with the projection of \mathbf{J} on molecule-fixed z , which is identical, in the case of a prolate symmetric top, to a , the at least three-fold principal axis).

Degeneracy of $E_{\text{rot}}(J,K)$:

$K = 0$ $(2J+1)$ -fold degeneracy in M

$K \neq 0$ $2(2J+1)$ -fold degeneracy in M , 2-fold in $|K|$

The degeneracy in M can be lifted if an external electric field is applied on the molecule.

Finally, it is noted parenthetically that the time-independent Schrödinger equation of rigid rotors can be solved analytically for symmetric top molecules, as well as for linear and spherical-top molecules. The analytical solutions for the rotational wavefunctions contain the three-dimensional Wigner rotation matrices, generalization of the one-dimensional orthogonal polynomials and the two-dimensional spherical harmonics.

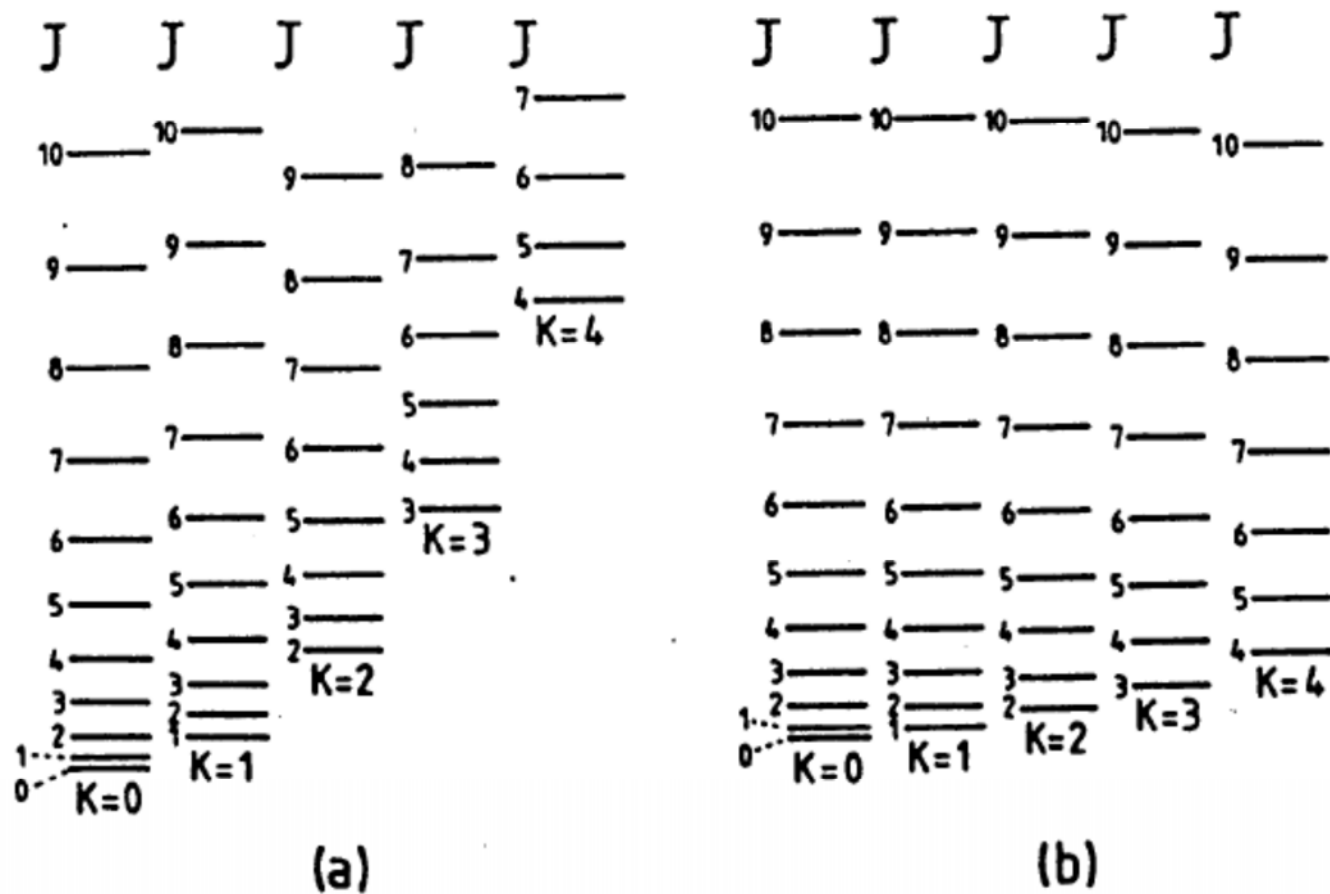


Figure 5.6 Rotational energy levels for (a) a prolate and (b) an oblate symmetric rotor.

Asymmetric top molecules

$$I_c > I_b > I_a \neq 0 \Leftrightarrow A > B > C$$

There are three unique rotational constants, A , B , and C , with $A > B > C$.

$$\hat{H}_{\text{rot}} = \frac{\hat{J}_a^2}{2I_a} + \frac{\hat{J}_b^2}{2I_b} + \frac{\hat{J}_c^2}{2I_c}$$

$$[\hat{H}_{\text{rot}}, \hat{J}^2] = 0 \quad \hat{J}^2 \Psi_{\text{rot}} = \hbar^2 J(J+1) \Psi_{\text{rot}}$$

$$[\hat{H}_{\text{rot}}, \hat{J}_Z] = 0 \quad \hat{J}_Z \Psi_{\text{rot}} = \hbar M \Psi_{\text{rot}}$$

$$[\hat{H}_{\text{rot}}, \hat{J}_a] \neq 0 \quad K \text{ is not a good quantum number}$$

Only the J and M quantum numbers remain good quantum numbers.

The time-independent Schrödinger equation for an asymmetric top cannot be solved in closed form for arbitrary values of J . Analytic solutions can be obtained for low J values, however, and a prescription for obtaining numerical results for arbitrary J is straightforward.

Without further elaboration, the final results, in the two limiting cases, are:

prolate symmetric top limit

$$F(J, K) = \frac{E(J, K)}{hc} \approx \bar{B}J(J+1) + (\tilde{A} - \bar{B})K^2$$

$$\bar{B} = \frac{1}{2}(\tilde{B} + \tilde{C})$$

oblate symmetric top limit

$$F(J, K) = \frac{E(J, K)}{hc} \approx \bar{B}J(J+1) + (\tilde{C} - \bar{B})K^2$$

$$\bar{B} = \frac{1}{2}(\tilde{A} + \tilde{B})$$

Selection rules for polyatomic rotations

Transition dipole matrix elements:

$$R^{nm} = \int \psi_n^* \hat{\mu} \psi_m d\tau$$

where $\hat{\mu} = \sum_i q_i \mathbf{r}_i$ is the dipole moment operator (sum runs over electrons and nuclei).

For pure rotational transitions

$$\psi_m = \psi_{\text{rot},m}(\theta, \varphi, \chi) \psi_{\text{vib}}(\mathbf{Q}; \theta, \varphi, \chi) \psi_{\text{el}}(\mathbf{r}_e; \theta, \varphi, \chi, \mathbf{Q}),$$

$$\psi_n = \psi_{\text{rot},n}(\theta, \varphi, \chi) \psi_{\text{vib}}(\mathbf{Q}; \theta, \varphi, \chi) \psi_{\text{el}}(\mathbf{r}_e; \theta, \varphi, \chi, \mathbf{Q}).$$

Final result:

$$R^{nm} = \int \psi_{\text{rot},n}^* \psi_{\text{vib}}^* \left[\int \psi_{\text{el}}^* \hat{\mu} \psi_{\text{el}} d\tau_{\text{el}} \right] \psi_{\text{vib}} \psi_{\text{rot},m} d\mathbf{Q} d\tau_{\text{rot}}$$

$$R^{nm} = \int \psi_{\text{rot},n}^* \left[\int \psi_{\text{vib}}^*(\mathbf{Q}) \hat{\mu}(\mathbf{Q}) \psi_{\text{vib}}(\mathbf{Q}) d\mathbf{Q} \right] \psi_{\text{rot},m} d\tau_{\text{rot}}$$

The integral in the bracket is the expectation value of the dipole moment. To conclude, the transition dipole integral will be zero unless the molecule possesses a permanent dipole moment μ_0 . Thus, only polar molecule exhibit pure rotational spectra.

Linear molecules

Selection rules:

$$\Delta J = \pm 1, \Delta M = 0, \pm 1, \text{ and } \mu_0 \neq 0.$$

The transition with $\Delta J = +1$ corresponds to absorption, the transition with $\Delta J = -1$ corresponds to emission (here and later on).

Symmetric top

Selection rules:

$$\Delta J = \pm 1, \Delta K = 0, \Delta M = 0, \pm 1 \text{ and } \mu_0 \neq 0.$$

The $\Delta K = 0$ restriction arises from the fact that the molecule has no component of electric dipole moment perpendicular to its symmetry axis \Rightarrow no torque by the field. In other words, quantum number K determines the speed of rotation around the principal axis and this does not have an effect on the permanent dipole.

Spherical top

A special case of the symmetric top; thus, the same selection rules pertain. However, by symmetry $\mu_0 = 0$ holds for spherical tops. Therefore, pure rotational spectra cannot be observed for (rigid) spherical tops. In practice, extremely weak transitions may be observed due to centrifugal distortion effects (deviations from a rigid body).

Asymmetric top

Selection rules:

$$\Delta J = 0, \pm 1, \Delta M = 0, \pm 1, \text{ and } \mu_0 \neq 0.$$

Because K is not a good quantum number, there is no general restriction on K . Consider the dipole moment in the molecule-fixed axis system: $\boldsymbol{\mu} = (\mu_a, \mu_b, \mu_c)$. For molecules of certain symmetry not all the dipole components have a non-zero value. Based on these values, we can talk about *a*-type ($\mu_a \neq 0$), *b*-type ($\mu_b \neq 0$), and *c*-type ($\mu_c \neq 0$) transitions. For example, for the main water isotopologue H_2^{16}O only *b*-type transitions can be observed.

Appearance of rotational spectra

When we substitute the selection rules into the energy expressions governing rotations of rigid rotors, we can obtain the transitions which can be observed. For example, for the $J + 1 \leftarrow J$ transition and based on the energy expression $E_{\text{rot}} = B J(J + 1)$

$$\Delta E = B(J + 1)(J + 2) - BJ(J + 1) = 2B(J + 1)$$

or

$$\tilde{\nu} = 2B(J + 1).$$

If we also take centrifugal distortion into account

$$\tilde{\nu} = 2B(J + 1) - 4D_J(J + 1)^3 .$$

The spectroscopic constant D_J (called quartic centrifugal distortion constant) is about 1-2 orders of magnitude smaller than the rotational constant B ; thus, its contribution is minuscule for small J values. Thus, in the rigid-rotor approximation rotational spectra contain lines separated by $2B$.

Example: rotational spectrum of NH_3

For ammonia $B = 9.977 \text{ cm}^{-1}$; thus, for the $J + 1 \leftarrow J$ transitions:

$J =$	0	1	2	3
$\tilde{\nu} / \text{cm}^{-1}$	19.95	39.91	59.86	79.82

Thus, measured rotational lines are uniformly separated by about 19.95 cm^{-1} .

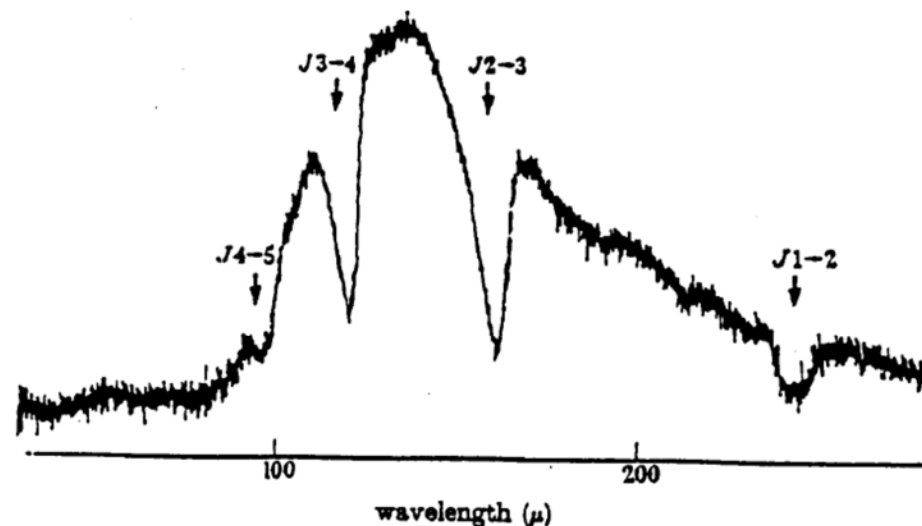


Figure 3.2 Far-infrared absorption spectrum of HCl gas. The vertical coordinate is light intensity transmitted by the gas sample; the horizontal coordinate is wavelength. Reproduced by permission from D. Bloor et al., *Proc. London Ser. A* 260: 510 (1961).

Intensity of rotational lines

We know that the observed absorption is the difference of stimulated absorption and stimulated emission. Intensity of the lines corresponding to the given transitions thus basically depend upon the relative population of the two levels. According to the Boltzmann distribution population of the rotational states decreases exponentially when J increases. However, as we learned from the rotational energy expressions, almost all rotational levels are degenerate and the degree of degeneracy increases as J increases. Due to this degeneracy and the small difference between the rotational energies it is not the level with the smallest J which will have the largest population.

Intensity of absorption lines (assuming thermal equilibrium and the validity of the Boltzmann distribution) is determined by

$$q_J \exp(-E_J / kT) = (2J + 1) \exp(-hcBJ(J + 1) / kT),$$

where J is the quantum number of the lower (absorbing) state.

For typical molecules at room temperature the J_{\max} quantum number with maximum population can reach $J_{\max} \approx 20$.

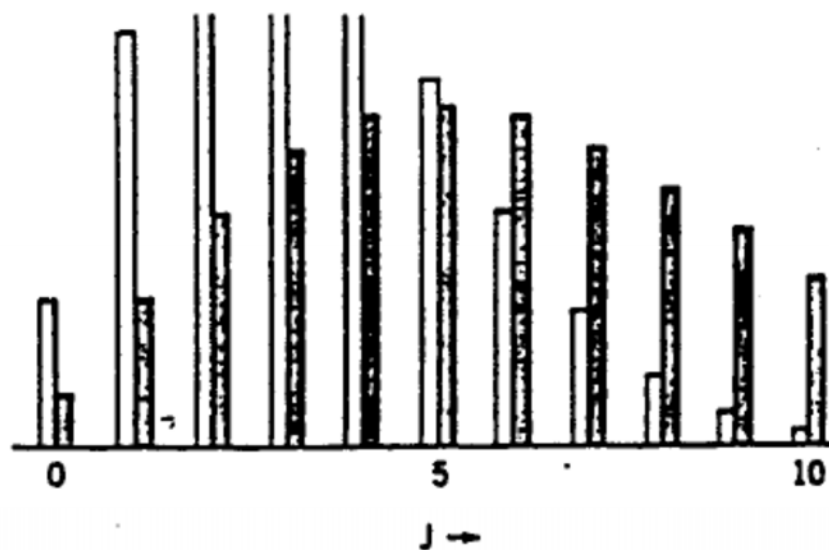


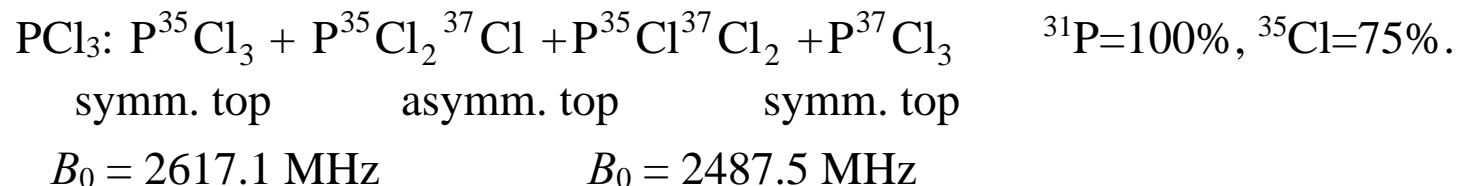
Figure 3.6 Relative rotational state populations, given by $g_J \exp[-hcBJ(J+1)/kT] / \sum g_J \exp[-hcBJ(J+1)/kT]$, versus rotational quantum number J for $B = 10.6 \text{ cm}^{-1}$.

Applications of rotational spectroscopy

A) Structure determination

Assignment of spectral lines to transitions between specific rotational levels $\Rightarrow A_0$, B_0 , C_0 rotational constants \Rightarrow moments of inertia. Not enough data to determine complete structure (*e.g.*, for a symmetric top we get only B_0) \Rightarrow MW spectra of isotopically substituted species are examined. Isotopic substitution will cause a negligible change in the equilibrium geometric parameters (nuclear masses do not appear in the electronic Schrödinger equation, thus the usual Born-Oppenheimer PESs are isotope independent).

Example: structure of PCl_3



Two rotational constants are sufficient to determine the structure:

$$r(\text{P-Cl}) = 2.04 \text{ \AA} \text{ és } \angle \text{Cl-P-Cl} = 100^\circ.$$

The largest source of error in structure determinations based on microwave spectroscopy is related to zero-point vibrations. For example, for the linear OCS molecule if we choose four different pairs of rotational constants available for the different isotopologues, the CO distance will change between 1.155 and 1.165 Å, which is clearly unacceptable.

B) *Determination of dipole moment (Stark effect)*



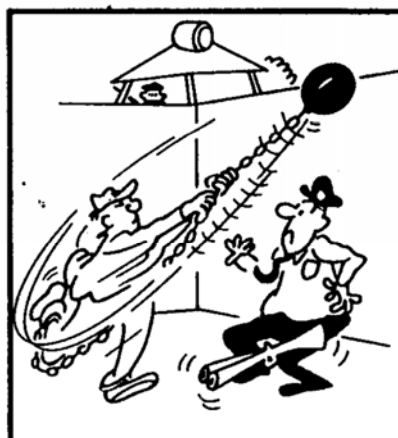
Ground Level



One Quantum



Large J



Transition Moment



Forbidden Transition



Excited State