

VI. VIBRATIONS OF POLYATOMIC MOLECULES (INFRARED AND RAMAN SPECTROSCOPY)

In 1800, Sir William Herschel found that if he placed a thermometer beyond the red region of the spectrum of the sun, the spectrum was obtained by dispersing the rays of the sun using a prism, the thermometer warmed up more than when it was placed in the visible region. With this observation, Herschel discovered **infrared radiation**. Study of the absorption of molecules in the infrared (i.r. or IR) region started at the beginning of the XXth century.

Up until the 1940s, IR spectroscopy was used in just a few physics labs, principally to investigate the structure of molecules. Using spectrometers was a complex task requiring a lot of effort and time; for example, infrared spectra were recorded point by point. At the same time, spectrometers were extremely sensitive to even small fluctuations, for example that of the temperature of the measuring room. During WWII the need to use infrared radiation arose, which led to quick development of infrared detectors. The spectrometers built with the new sources and detectors were much less cumbersome, the simplicity and

speed of the measurements made IR spectrometers one of the most important analytical tools in the hands of chemists.

The infrared region of the electromagnetic (EM) spectrum

| Region | $\lambda / \mu\text{m}$ | $\tilde{\nu} / \text{cm}^{-1}$ | Molecular process |
|-----------|-------------------------|--------------------------------|--------------------------------------|
| far i.r. | 25 – 400 | 25 – 400 | large-amplitude, “floppy” vibrations |
| mid i.r. | 2,5 – 25 | 400 – 4000 | fundamental vibrations |
| near i.r. | 0,8 – 2,5 | 4000 – 12500 | overtone vibrations |

NB: The distinctions ‘near’ and ‘far’ are defined with respect to the visible region.

Hallmarks of vibrational spectroscopy

- 1) Observed transitions reveal the **potential energy surface** $V(\mathbf{R})$ (PES, see the Born-Oppenheimer (BO) separation of the motions of the electrons and the nuclei), where \mathbf{R} denotes the set of nuclear coordinates.
- 2) Quadratic, as well as cubic and quartic, force constants supply information about the PES and reflect certain chemical properties, such as bond strengths and dissociation energy.
- 3) Geometrical structures can be obtained by analyzing the rotational contours, “rotational fine structure”, of the vibrational bands

| Branch | P | Q | R | O | S |
|------------|-----|-----|-----|-----|-----|
| ΔJ | -1 | 0 | +1 | -2 | 2 |

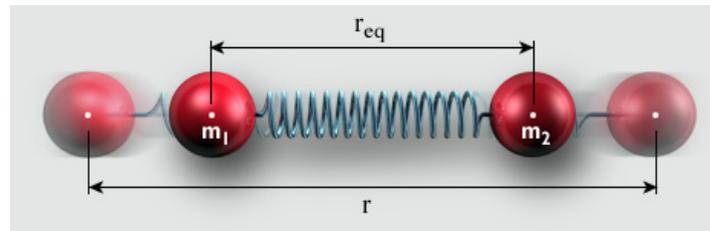
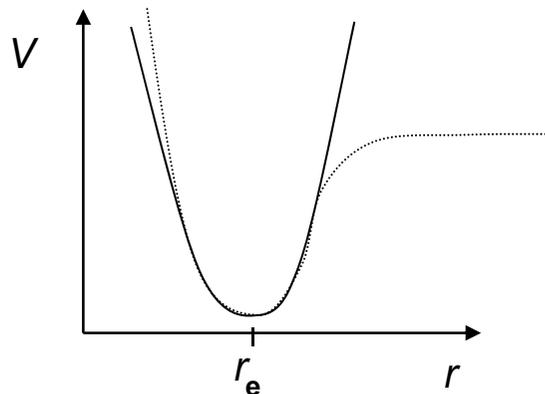
- 4) Local mode transitions are indicative of chemical groups within the molecule → useful for identification purposes.

- ◆ When the bond force constant (“spring constant”) of a moiety is quite different from that of other bonds in the molecule, a characteristic **group frequency** is observed.

Example: C=O stretch in ketones ($1710 - 1720 \text{ cm}^{-1}$).

- ◆ Even if the bond force constants in a molecule are all similar in magnitude, a characteristic group frequency arises if one group involves a large difference in masses.

Example: C–H, C–Cl, C–Br stretches in organic molecules.



Water on the Sun: molecules are everywhere

(T. Oka, *Science* **277**, 328, 1997)

The surface temperature of our own star, the sun is ≈ 5800 K. At this elevated temperature polyatomic molecule, like water, “should” dissociate to its elementary parts ($\text{H}_2\text{O} \rightarrow \text{OH} + \text{H} \rightarrow \text{O} + 2\text{H}$). Despite this expectation scientists observed in the infrared region of the emission spectrum of the sun spectroscopic lines characteristic of the spectrum of water.

How to prove the existence of water: emission laboratory IR spectrum of *hot* water showed high similarity with the observed sun spectrum (Bernath *et al.*, *Science* **268**, 1155, 1995). (Proving the existence of water lines in the emission spectrum of the sun was made difficult by the existence of water vapor in the earth’s atmosphere but this is “cold” water characterized by a very different spectrum.)

Water does not exist everywhere on the sun, only in the cooler surface regions called sunspots, whose temperature is only $T \approx 3200$ K. Note that on several other stars, including high luminosity red giants and a few dwarf stars, whose temperature is below 4000 K, it became possible to identify several molecules, mostly diatomic ones. Chemical modeling

studies show that under about $T < 1000$ K on stellar bodies after H_2 the molecules most abundant molecules are H_2O , CH_4 , and NH_3 . Note that high-resolution spectroscopic experiments have such high accuracy that several molecules could be identified even just by the detection of one spectral line (transition).

The final proof of the existence of water on our own star, the sun, arrived from highly accurate first-principles (*ab initio*) quantum chemical computations (Tennyson *et al.*, *Science* **277**, 346, 1997).

Classical mechanics of molecular vibrations

Basic reference text: E. Bright Wilson, Jr., J. C. Decius, és Paul C. Cross, *Molecular Vibrations, The Theory of Infrared and Raman Vibrational Spectra*, Dover: New York, 1980.

Let's investigate an N -atomic molecule. Affix a coordinate system to the molecule: (a) shift the origin to the center of mass (COM), and (b) direct the molecular axes along the principal axes of rotation (a , b , and c).

Kinetic energy

Define the **Cartesian displacement coordinates** as follows, where subscript 0 refers to the chosen reference (equilibrium) configuration:

$$x_\alpha = a_\alpha - a_{\alpha,0}, \quad y_\alpha = b_\alpha - b_{\alpha,0}, \quad z_\alpha = c_\alpha - c_{\alpha,0} .$$

The form of the kinetic energy is

$$T = \frac{1}{2} \sum_{\alpha=1}^N m_\alpha \left[\left(\frac{d x_\alpha}{d t} \right)^2 + \left(\frac{d y_\alpha}{d t} \right)^2 + \left(\frac{d z_\alpha}{d t} \right)^2 \right] .$$

Define **mass-weighted Cartesian coordinates**:

$$\begin{aligned} q_1 &:= \sqrt{m_1} x_1 & q_4 &:= \sqrt{m_2} x_2 & \dots & q_{3N-2} &:= \sqrt{m_N} x_N \\ q_2 &:= \sqrt{m_1} y_1 & q_5 &:= \dots & & q_{3N-1} &:= \sqrt{m_N} y_N \\ q_3 &:= \sqrt{m_1} z_1 & & & & q_{3N} &:= \sqrt{m_N} z_N \end{aligned}$$

Now the form of the kinetic energy becomes simpler,

$$T = \frac{1}{2} \sum_{i=1}^{3N} \left(\frac{dq_i}{dt} \right)^2 = \frac{1}{2} \sum_{i=1}^{3N} \dot{q}_i^2 = \frac{1}{2} \begin{pmatrix} \dot{q}_1 & \dot{q}_2 & \dots & \dot{q}_{3N} \end{pmatrix} \begin{pmatrix} \dot{q}_1 \\ \dot{q}_2 \\ \vdots \\ \dot{q}_{3N} \end{pmatrix} = \frac{1}{2} \dot{\mathbf{q}}^T \dot{\mathbf{q}}$$

Potential energy

If the molecule is a strongly-bound chemical system, then the nuclei are vibrating in a deep potential well. The lowest vibrational states can be investigated by expanding $V(\mathbf{x})$ about the reference (equilibrium) position:

$$V(\mathbf{x}) = V_0 + \sum_{i=1}^{3N} \left(\frac{\partial V}{\partial x_i} \right)_0 x_i + \frac{1}{2} \sum_{ij} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0 x_i x_j + \frac{1}{6} \sum_{ijk} \left(\frac{\partial^3 V}{\partial x_i \partial x_j \partial x_k} \right)_0 x_i x_j x_k + \dots,$$

where we have re-indexed the Cartesian coordinates:

$$(x_1 \ y_1 \ z_1 \ x_2 \ y_2 \ \dots \ x_N \ y_N \ z_N) \mapsto (x_1 \ x_2 \ x_3 \ x_4 \ \dots \ x_{3N-1} \ x_{3N}).$$

At equilibrium all forces are zero by definition:

$$f_i = -\left(\frac{\partial V}{\partial x_i}\right)_0 = 0 \Rightarrow \text{linear terms vanish.}$$

In the multidimensional **harmonic oscillator** approximation we neglect the cubic and higher-order terms (springs, assumed to exist between the atoms, obey **Hooke's law**):

$$V(\mathbf{x}) = V_0 + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} H_{ij} x_i x_j = V_0 + \frac{1}{2} \mathbf{x}^T \mathbf{H} \mathbf{x}, \text{ or}$$

$$V(\mathbf{x}) = V_0 + \frac{1}{2} \begin{pmatrix} x_1 & x_2 & \dots & x_{3N} \end{pmatrix} \begin{bmatrix} H_{1,1} & H_{1,2} & \dots & H_{1,3N} \\ H_{2,1} & H_{2,2} & \dots & \\ \vdots & \vdots & & \\ H_{3N,1} & H_{3N,2} & & H_{3N,3N} \end{bmatrix} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_{3N} \end{pmatrix},$$

where $H_{ij} := \left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right)_0$ is the Cartesian **force constant matrix**.

⌈One must note that the H_{ij} force constant matrix must be obtained by solving the electronic Schrödinger equation and differentiating the resulting PES. H_{ij} can be determined numerically via ab initio electronic structure computations very efficiently and accurately.⌋

Convert $V(\mathbf{x})$ to mass-weighted Cartesian coordinates:

$$V(\mathbf{q}) = V_0 + \frac{1}{2} \mathbf{q}^T \mathbf{W} \mathbf{q}, \text{ where } W_{ij} = \frac{H_{ij}}{\sqrt{m_i m_j}} .$$

Now we are in the position to state the problem of vibrations of molecules very clearly: we wish to solve [Newton's equations of motion](#) for a molecule with

$$T = \frac{1}{2} \dot{\mathbf{q}}^T \dot{\mathbf{q}} \quad \text{and} \quad V(\mathbf{q}) = V_0 + \frac{1}{2} \mathbf{q}^T \mathbf{W} \mathbf{q}$$

Naturally, during the solution of the vibrational problem we could use the $\mathbf{F} = -\nabla V = m\mathbf{a}$ equation.

Let us apply, however, a more general formulation of Newton's equations, the so-called **Lagrange-formulation** and **Lagrange's equations**.

The **Lagrangian** of the system:

$$L(\mathbf{q}, \dot{\mathbf{q}}; t) = T - V ,$$

Lagrange's equations with generalized coordinates \mathbf{q}_i , $i = 1, \dots, 3N$:

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right) - \frac{\partial L}{\partial q_i} = 0$$

Since \mathbf{q}_i appear only in V , while their time derivatives appear only in T , we can write

$$\left(\frac{\partial L}{\partial \dot{q}_i} \right) = \left(\frac{\partial T}{\partial \dot{q}_i} \right) = \dot{q}_i$$

and

$$\left(\frac{\partial L}{\partial q_i} \right) = - \left(\frac{\partial V}{\partial q_i} \right) = - \sum_{j=1}^{3N} W_{ij} q_j$$

Therefore, for harmonic motion the Lagrange equation has the following simple form:

$$\left(\frac{d^2 q_i}{dt^2} \right) + \sum_{j=1}^{3N} W_{ij} q_j = 0 \quad (i = 1, 2, \dots, 3N).$$

This is a set of coupled differential equations which can be written in matrix form in a particularly elegant form:

$$\ddot{\mathbf{q}} + \mathbf{W}\mathbf{q} = \mathbf{0}.$$

To solve these coupled equations, we seek a **unitary transformation** ($\mathbf{U}^T \mathbf{U} = \mathbf{U} \mathbf{U}^T = \mathbf{I}$) to a new set of coordinates which will be uncoupled:

$$Q_k = \sum_{i=1}^{3N} U_{ik} q_i, \text{ or } \mathbf{Q} = \mathbf{U}^T \mathbf{q} \text{ and } \mathbf{q} = \mathbf{U} \mathbf{Q}.$$

Consequently, $\ddot{\mathbf{q}} = \mathbf{U} \ddot{\mathbf{Q}}$.

Then, the Lagrange equations $\ddot{\mathbf{q}} + \mathbf{W}\mathbf{q} = \mathbf{0}$ of the harmonic oscillator problem becomes:

$$\mathbf{U}\ddot{\mathbf{Q}} + \mathbf{W}\mathbf{U}\mathbf{Q} = \mathbf{0} \Rightarrow \ddot{\mathbf{Q}} + (\mathbf{U}^T \mathbf{W}\mathbf{U})\mathbf{Q} = \mathbf{0} .$$

If the \mathbf{U} unitary matrix is chosen such that

$$\mathbf{U}^T \mathbf{W}\mathbf{U} = \mathbf{\Lambda} = \begin{bmatrix} \lambda_1 & 0 & 0 & 0 \\ 0 & \lambda_2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & \lambda_{3N} \end{bmatrix} ,$$

then

$$\ddot{\mathbf{Q}} + \mathbf{\Lambda}\mathbf{Q} = \mathbf{0} \Rightarrow \left(\frac{d^2 Q_k}{dt^2} \right) + \lambda_k Q_k = 0 , k = 1, 2, \dots, 3N .$$

These are uncoupled equations!

The Q_k s are the **normal coordinates** of vibration representing the **normal modes** of the molecule. A normal mode of vibration is one in which all the nuclei undergo harmonic motions, have the same frequency of oscillation, and move in phase (pass through the extremes of their motion simultaneously) but generally with different amplitudes.

The vibrational frequency associated with normal mode k is

$$\nu_k = \frac{\omega_k}{2\pi} = \frac{\sqrt{\lambda_k}}{2\pi},$$

while the general form of the normal coordinate is

$$Q_k = c_k \sin(\omega_k t + \varphi_k), \quad k = 1, 2, 3, \dots, 3N - 6.$$

The reason we have omitted the last six Q_k 's is that the three coordinates corresponding to translations and the 3(2) coordinates corresponding to rotations are NOT harmonic motions, whence $\lambda_k = 0$. For a linear molecule there is one less rotational coordinate, and thus $3N - 5$ normal coordinates of vibration. In summary, the number of normal modes for a nonlinear(linear) molecule is $3N - 6(5)$.

Numbering of normal vibrations

There is a well-established convention to number normal modes of molecules, established in R. S. Mulliken, *J. Chem. Phys.* **23**, 1997 (1955). The essence of the convention:

- Start with the completely symmetric wavenumbers, sort them from high to low, and this gives the numbering. Do the same with all the other wavenumbers belonging to the other irreducible representation of the molecule.
- Non-degenerate normal modes should be numbered before the degenerate ones. Normal modes with the same wavenumber receive the same number.
- A notable exception: the bending frequencies of linear triatomic molecules are always called ν_2 .

Numbering of normal vibrations of ethylene (D_{2h})

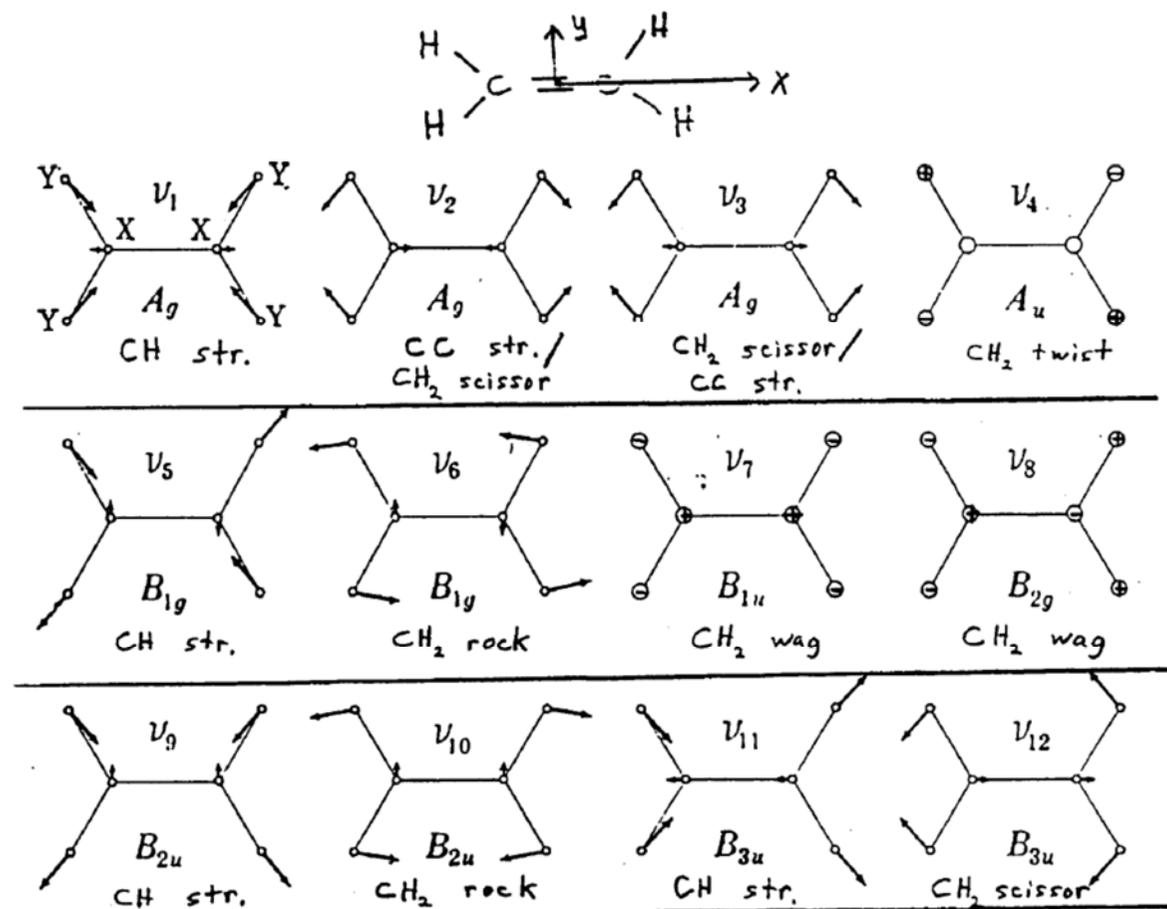


FIG. 44. Normal vibrations of an X_2Y_4 molecule of point group V_h .—It is assumed that the mass of X is larger than that of Y as in C_2H_4 or C_2D_4 .

Quantum mechanical treatment of molecular vibrations

The vibrational Schrödinger-equation for an N -atomic molecule:

$$\left[-\frac{\hbar^2}{2} \sum_{i=1}^{3N} \frac{1}{m_i} \left(\frac{\partial^2}{\partial x_i^2} \right) + V(x_1, \dots, x_{3N}) \right] \Psi(\mathbf{x}) = E \Psi(\mathbf{x})$$

In complete analogy with the classical treatment, assume the molecule is in a deep potential well and expand $V(\mathbf{x})$ about the equilibrium position:

$$V(\mathbf{x}) = V_0 + \sum_{i=1}^{3N} \left(\frac{\partial V}{\partial x_i} \right)_0 x_i + \frac{1}{2} \sum_{ij}^{3N} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0 x_i x_j + \dots$$

In the harmonic approximation

$$V(\mathbf{x}) = V_0 + \frac{1}{2} \sum_{ij}^{3N} H_{ij} x_i x_j,$$

where $H_{ij} := \partial^2 V / \partial x_i \partial x_j$ is the Cartesian force constant matrix.

Similarly to classical mechanics, using a unitary unitary transformation we can change our coordinate system from Cartesian (\mathbf{x}) to mass-weighted Cartesian (\mathbf{q}) to normal (\mathbf{Q}) coordinates. Then

$$\textit{kinetic energy operator: } \hat{T} = -\frac{\hbar^2}{2} \sum_{k=1}^{3N} \frac{\partial^2}{\partial Q_k^2}$$

$$\textit{potential energy operator: } \hat{V} = \frac{1}{2} \mathbf{Q}^T (\mathbf{U}^T \mathbf{W} \mathbf{U}) \mathbf{Q} = \frac{1}{2} \mathbf{Q}^T \mathbf{\Lambda} \mathbf{Q} = \frac{1}{2} \sum_{k=1}^{3N} \lambda_k Q_k^2$$

We are left with the following Schrödinger-equation written in normal coordinates:

$$\left[-\frac{\hbar^2}{2} \sum_{k=1}^{3N-6} \left(\frac{\partial^2}{\partial Q_k^2} \right) + \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 \right] \Psi(\mathbf{Q}) = E \Psi(\mathbf{Q})$$

Note the following:

(a) The sums have now been restricted to the internal, vibrational normal modes only, translations and rotations are thus separated from the problem.

(b) The Hamiltonian is a sum of uncoupled harmonic-oscillator Hamiltonians:

$$\hat{H} = \sum_{k=1}^{3N-6} \hat{H}_k, \text{ where } \hat{H}_k = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_k^2} + \frac{1}{2} \lambda_k Q_k^2 .$$

(c) The vibrational wavefunction is a product of one-dimensional harmonic oscillator wavefunctions:

$$\Psi_{\mathbf{v}} = \prod_{k=1}^{3N-6} \psi_{k, v_k}(Q_k)$$

Solution of the one-dimensional harmonic oscillator problem

The Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right) u(x) = Eu(x)$$

It is well known from classical mechanics that $\frac{1}{2}k \equiv 2\pi^2 m\nu^2$. To simplify the notation, introduce:

$$\alpha := 2\pi m\nu / \hbar \quad \text{and} \quad \beta := 2mE / \hbar^2.$$

Then

$$\left\{ \frac{d^2}{dx^2} + [\beta - \alpha^2 x^2] \right\} u(x) = 0.$$

Let $\eta := \sqrt{\alpha} x$, from which (using the chain rule)

$$\frac{du}{dx} = \frac{du}{d\eta} \frac{d\eta}{dx} = \sqrt{\alpha} \frac{du}{d\eta} \quad \text{and} \quad \frac{d^2u}{dx^2} = \sqrt{\alpha} \frac{d(du/d\eta)}{d\eta} \frac{d\eta}{dx} = \alpha \frac{d^2u}{d\eta^2},$$

and thus

$$\left[\frac{d^2}{d\eta^2} + \left(\frac{\beta}{\alpha} - \eta^2 \right) \right] u(\eta) = 0.$$

The solutions $u(\eta)$ must be continuous and must be finite (to allow normalization). Study the asymptotic form (*i.e.*, $|\eta| \rightarrow \infty$) of the solution. Then $\beta / \alpha \ll \eta^2$, and thus

$$u''(\eta) = \eta^2 u(\eta),$$

for which the general solution is (as can be checked by substitution)

$$u(\eta) = A \exp(\eta^2 / 2) + B \exp(-\eta^2 / 2).$$

Since $u(\eta)$ must remain finite for all values of η , $A = 0$, and the asymptotic solution we searched for is

$$u(\eta) = B \exp(-\eta^2 / 2).$$

Try a solution of the following form, different from the asymptotic solution by an unknown polynomial $H(\eta)$:

$$u(\eta) = H(\eta) \exp(-\eta^2 / 2).$$

The $H(\eta)$ polynomial must vary with η so that $|\eta| \rightarrow \infty$, $\exp(-\eta^2 / 2)$ dominates, *i.e.*, $u(\eta) \rightarrow 0$ as $\eta \rightarrow \infty$.

Thus, our task is to find an equation for $H(\eta)$:

$$u' = H' \exp(-\eta^2 / 2) - \eta H \exp(-\eta^2 / 2)$$

$$u'' = H'' e^{-\eta^2/2} - \eta H' e^{-\eta^2/2} - \left[\eta \left(H' e^{-\eta^2/2} - \eta H e^{-\eta^2/2} \right) \right] - H e^{-\eta^2/2}$$

$$u'' = e^{-\eta^2/2} \left(-H + \eta^2 H - 2\eta H' + H'' \right)$$

Substitute the framed equations into the original differential equation,

$$\left[-H + \eta^2 H - 2\eta H' + H'' + \frac{\beta}{\alpha} H - \eta^2 H \right] \exp(-\eta^2 / 2) = 0$$

and then we arrive at the much studied Hermite differential equation (HDE):

$$H'' - 2\eta H' + (\beta/\alpha - 1)H = 0$$

Well-behaved solutions of the HDE exist only for $\beta/\alpha - 1 = 2n$, where $n = 0, 1, 2, \dots$ (others diverge). Thus, a family of solutions denoted by $H_n(\eta)$ are obtained:

$$u_n(\eta) = N_n H_n(\eta) e^{-\eta^2/2},$$

$$N_n = \left(\frac{\sqrt{\alpha}}{\sqrt{\pi} 2^n n!} \right) \text{ is the normalization factor,}$$

$H_n(\eta)$ are the so-called Hermite polynomials.

Useful recursion relations for the Hermite polynomials:

$$H_{n+1}(\eta) = 2\eta H_n(\eta) - 2nH_{n-1}(\eta)$$

The first few Hermite polynomials:

$$H_0 = 1$$

$$H_1 = 2\eta$$

$$H_2 = 4\eta^2 - 2$$

$$H_3 = 8\eta^3 - 12\eta$$

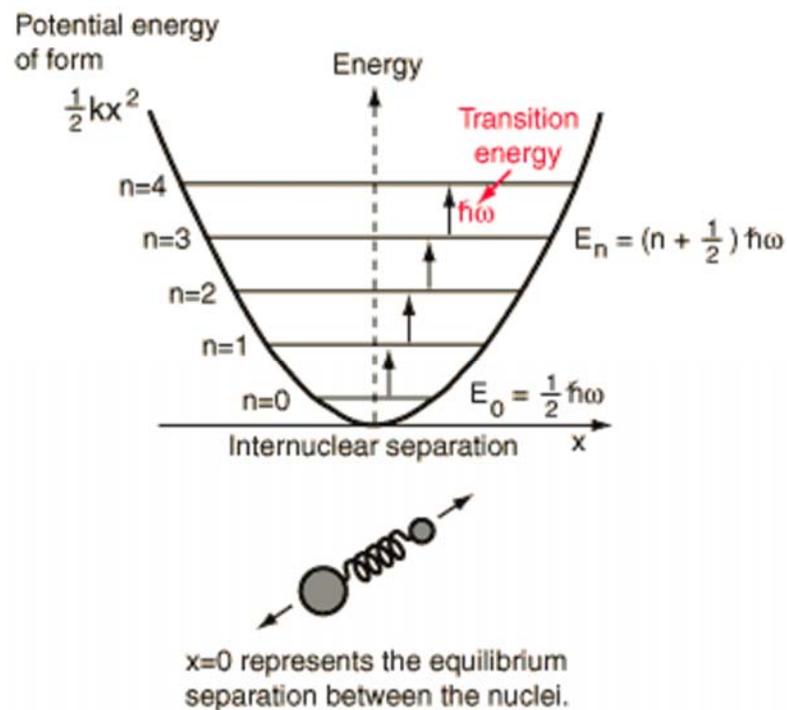
$$H_4 = 12 - 48\eta^2 + 16\eta^4$$

$$H_5 = 120\eta - 160\eta^3 + 32\eta^5$$

The harmonic oscillator energy levels E_n can be obtained from the constraint $\beta/\alpha - 1 = 2n$:

$$\frac{\beta}{\alpha} = \frac{2mE}{\hbar^2} \cdot \frac{\hbar}{2\pi m\nu} = \frac{2E}{h\nu},$$

$$E_n = h\nu \left(n + \frac{1}{2}\right), \text{ where } n = 0, 1, 2, 3, 4, \dots$$



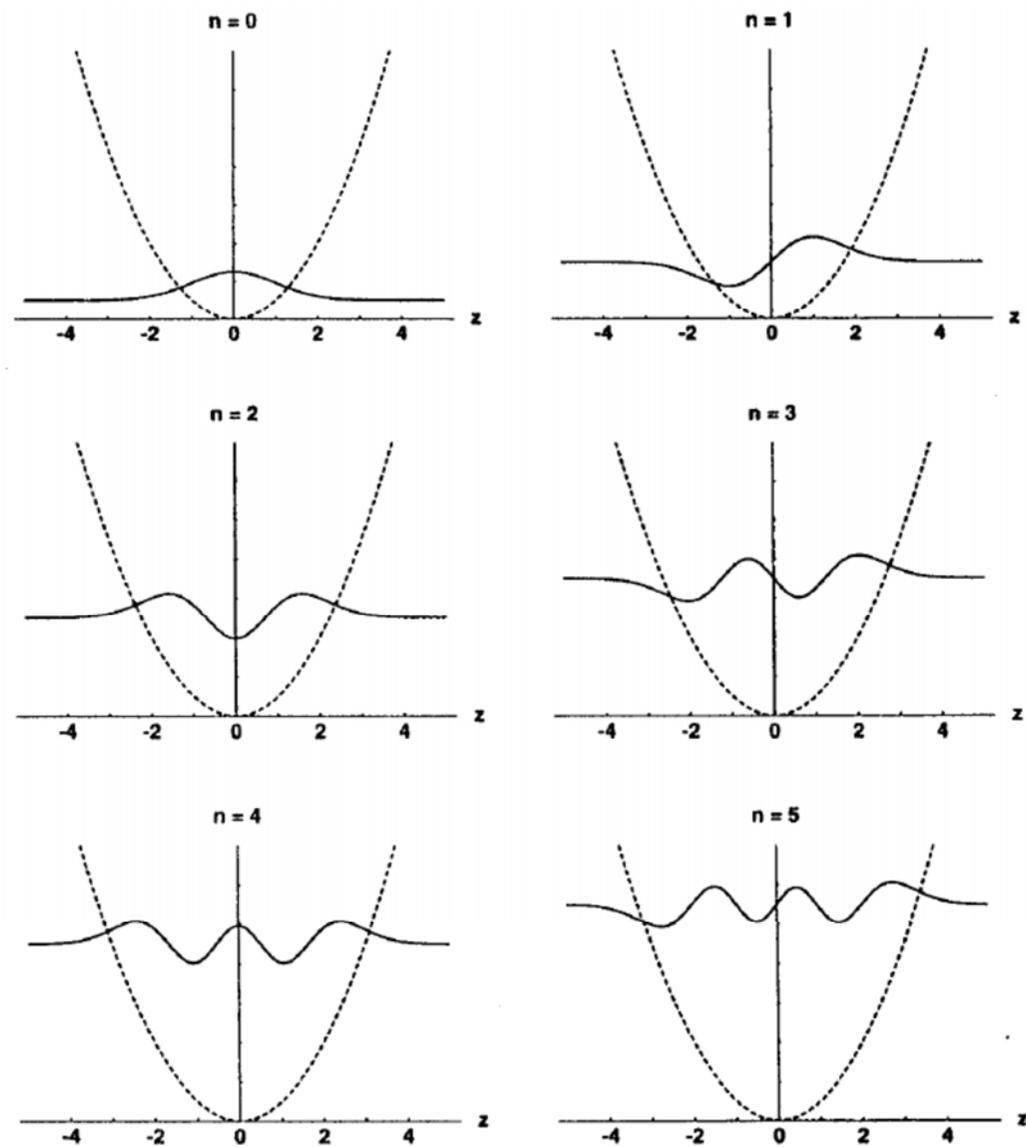


Figure 6.6-1. Dimensionless HO eigenfunctions $\psi_n(z)$.

Summary of results from QM treatment of polyatomic vibrations

- (1) For molecules vibrating in deep potential wells, near equilibrium the total vibrational wavefunction is a product of one-dimensional, harmonic oscillator wavefunctions for the (classical) normal coordinates. The individual harmonic oscillator wavefunctions are products of orthogonal (Hermite) polynomials and Gaussian functions.
- (2) The total vibrational energy is the sum of the quantized vibrational energies for each normal mode which appears in the classical treatment.
- (3) Fundamental vibrational frequencies are obtained by diagonalizing the mass-weighted Cartesian quadratic force constant matrix ($H_{ij} := \partial^2 V / \partial q_i \partial q_j$).
- (4) Vibrations of a polyatomic molecule cannot stop even at $T = 0$ K, resulting in what is called zero-point vibrational energy (ZPVE), a particular consequence of the Heisenberg uncertainty principle:

$$E_0 = \frac{1}{2} \sum_{k=1}^{3N-6} \hbar \omega_k.$$

- (5) Energies of excited vibrational levels in one dimension, at least in the harmonic oscillator approximation, follow each other in an equidistant fashion, there is a constant energy separation, as the energy expression of the harmonic oscillator is linear in the vibrational quantum number.
- (6) As $H_0 = 1$, the wavefunction for the ground vibrational state has a Gaussian shape. Excited vibrational states have nodes, all vibrational wavefunctions have infinite spatial extension.
- (7) The gradual migration of probability of excited vibrational wavefunctions towards high displacements is a general feature of a harmonic oscillator. The regions of greatest probability shift towards the turning points of classical motion (which is where, classically, the oscillator is most likely to be found).

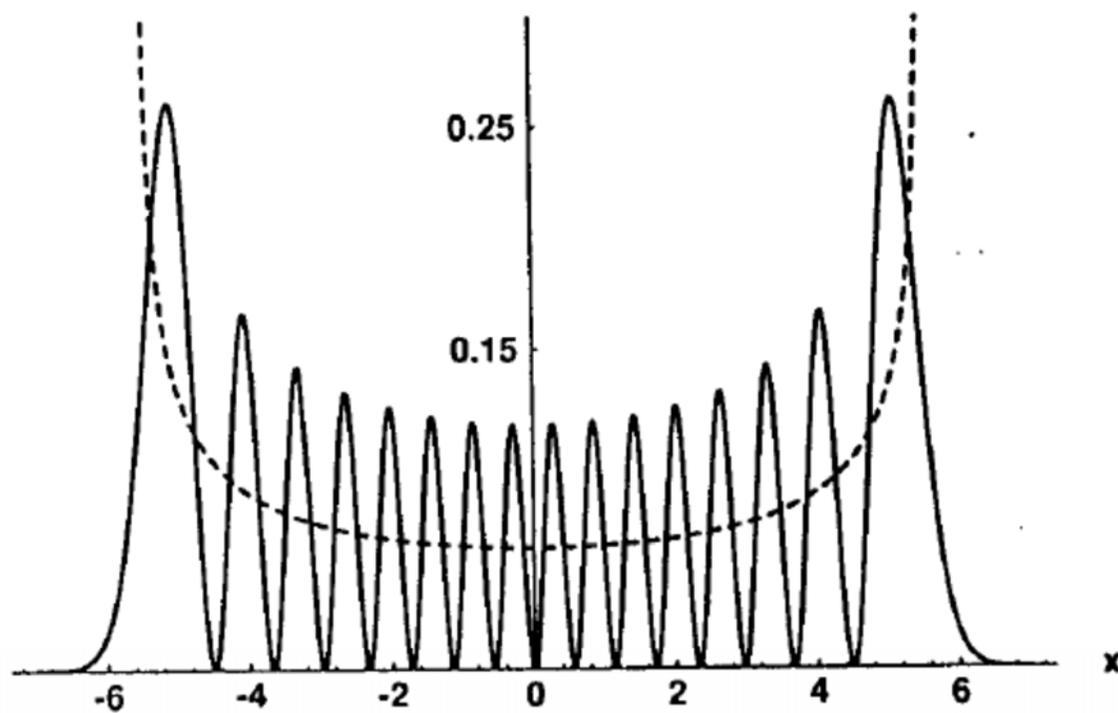


Figure 6.6-3. HO probability distribution for $n = 15$. Dashed curve is the classical distribution.

Symmetry and normal coordinates

Let \hat{R} be a symmetry operator for the point group of the molecule. The potential energy $V(\mathbf{Q})$ of the system MUST be unchanged by the application of the symmetry operator:

$$\hat{R}V(\mathbf{Q}) = V(\mathbf{Q}) = \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 = \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k (\hat{R}Q_k)^2$$

Non-degenerate modes: $\hat{R}Q_k = \pm Q_k$.

Degenerate modes: $\hat{R}Q_k = \sum_m r_{km} Q_m$, where the sum runs over all normal modes with the degenerate eigenvalues λ_k , r_{km} values are the corresponding coefficients.

NB: The normal coordinates form a basis for an irreducible representation of the point group.

Problem: Which are the irreducible representations according to which the normal vibrations of the H₂CO molecule transform?

Answer: Place the molecule in the yz plane. Obtain a reducible representation on the basis of x, y, z coordinates placed on each atom:

| C_{2v} | E | C_2 | $\sigma_v(xz)$ | $\sigma_v(yz)$ | |
|-----------------------|-----|-------|----------------|----------------|----------|
| A_1 | 1 | 1 | 1 | 1 | z |
| A_2 | 1 | 1 | -1 | -1 | R_z |
| B_1 | 1 | -1 | 1 | -1 | x, R_y |
| B_2 | 1 | -1 | -1 | 1 | y, R_x |
| Γ_{red} | 12 | -2 | 2 | 4 | |

Recall the rules to obtain characters of reducible representations:

(1) Only those atoms which are unshifted by a symmetry operation give a contribution to the character.

(2) $\chi(\hat{E}) = 3N$.

(3) $\chi(\hat{C}_n^m) = N_{C_n^m} [1 + 2 \cos(2\pi m / n)]$, for H_2CO , $m = 1$ and $n = 2$, while N the number of unshifted atoms.

(4) $\chi(\hat{\sigma}) = N_\sigma$.

(5) $\chi(\hat{i}) = -3N_i$.

Reduction of the reducible representation is done via the equation

$$a_\ell = \frac{1}{h} \sum_{\hat{R}} \chi^{(\ell)}(\hat{R}) \chi(\hat{R}).$$

For example,

$$a(A_1) = \frac{1}{4} [(1)(12) + (1)(-2) + (1)(2) + (1)(4)] = 4.$$

Similarly, $a(A_2) = 1$, $a(B_1) = 3$, and $a(B_2) = 4$.

Irreducible representations corresponding to translation and rotation:

$$\Gamma_{\text{translation}} = A_1 \oplus B_1 \oplus B_2 \quad \text{and} \quad \Gamma_{\text{rotation}} = A_2 \oplus B_1 \oplus B_2$$

thus,

$$\boxed{\Gamma_{\text{vib}} = 3A_1 \oplus B_1 \oplus 2B_2}.$$

Symmetry of vibrational wavefunctions

$$\Psi_v = \prod_{k=1}^{3N-6} \psi_{k,v_k}(Q_k)$$

$$\psi_{k,v_k}(Q_k) = \frac{1}{\sqrt{2^{v_k} (v_k!)}} \left(\frac{\alpha_k}{\pi} \right)^{1/4} e^{-\frac{\alpha_k Q_k^2}{2}} H_{v_k}(\alpha_k^{1/2} Q_k) \quad \text{and} \quad \alpha_k = \frac{\omega_k}{\hbar}.$$

Thus,

$$\psi_{k,0}(Q_k) = \left(\frac{\alpha_k}{\pi} \right)^{1/4} e^{-\frac{\alpha_k Q_k^2}{2}},$$

$$\psi_{k,1}(Q_k) = \left(\frac{\alpha_k^3}{4\pi} \right)^{1/4} Q_k e^{-\frac{\alpha_k Q_k^2}{2}},$$

$$\psi_{k,2}(Q_k) = \left(\frac{\alpha_k}{4\pi} \right)^{1/4} (2\alpha_k Q_k^2 - 1) e^{-\frac{\alpha_k Q_k^2}{2}}.$$

- (1) Vibrational ground state: $(n_1, n_2, \dots, n_{3N-6}) = (0, 0, \dots, 0)$, always fully symmetric.
- (2) **Fundamentals**: $(n_1, n_2, \dots, n_k, \dots, n_{3N-6}) = (0, 0, \dots, 1, \dots, 0)$, always transform according to $\Gamma[Q_k]$.
- (3) **Vibrational overtones**: $(n_1, n_2, \dots, n_k, \dots, n_{3N-6}) = (0, 0, \dots, L_k, \dots, 0)$, if $L_k = 2$, than the first overtone transforms as $\Gamma[Q_k] \otimes \Gamma[Q_k]$, if $L_k = 3$, than the second overtone transforms as $\Gamma[Q_k] \otimes \Gamma[Q_k] \otimes \Gamma[Q_k]$.
- (4) **Combination vibrations**: $(n_1, n_2, \dots, n_k, \dots, n_{3N-6}) = (0, 0, \dots, L_k, \dots, L_l, \dots, 0)$, if $L_k = 1$ and $L_l = 1$, the combination vibration transforms as $\Gamma[Q_k] \otimes \Gamma[Q_l]$, if $L_k = 2$ and $L_l = 1$, the combination vibration transforms as $\Gamma[Q_k] \otimes \Gamma[Q_k] \otimes \Gamma[Q_l]$.

Example: H_2O $\mathbf{v} = (0, 0, 0) \rightarrow A_1$; $\mathbf{v} = (0, 0, 1) \rightarrow B_2$; $\mathbf{v} = (0, 0, 2) \rightarrow B_2 \otimes B_2 = A_1$ és
 $\mathbf{v} = (0, 2, 1) \rightarrow A_1 \otimes A_1 \otimes B_2 = B_2$.

Selection rules for infrared spectra

Consider the rotational-vibrational transitions for the same electronic state:

$$(\text{rot}'', \text{vib}'', \text{el}) \rightarrow (\text{rot}', \text{vib}', \text{el}).$$

The transition dipole matrix element:

$$\mathbf{R}^{nm} = \int \Psi_n^* \hat{\boldsymbol{\mu}} \Psi_m d\tau \quad \text{and} \quad \hat{\boldsymbol{\mu}} = \sum_i q_i \mathbf{r}_i$$

Upper state $\Psi_n = \psi'_{\text{rot}}(\boldsymbol{\kappa}) \psi'_{\text{vib}}(\mathbf{Q}) \psi_{\text{el}}(\mathbf{r}_e; \mathbf{Q}, \boldsymbol{\kappa})$

Lower state $\Psi_m = \psi''_{\text{rot}}(\boldsymbol{\kappa}) \psi''_{\text{vib}}(\mathbf{Q}) \psi_{\text{el}}(\mathbf{r}_e; \mathbf{Q}, \boldsymbol{\kappa})$

The dipole moment operator is expressed in the space-fixed coordinate system. Switching to a molecule-fixed coordinate system:

$$\hat{\boldsymbol{\mu}} = U(\boldsymbol{\kappa}) \hat{\boldsymbol{\mu}}_{\text{mol}}(\mathbf{r}_{\text{el}}; \mathbf{Q})$$

Elements of the transition dipole matrix are as follows:

$$\mathbf{R}^{nm} = \mathbf{R}_{\text{rot}} \mathbf{r}_{\text{vib}} = \mathbf{R}_{\text{rot}} \int \psi'_{\text{vib}}(\mathbf{Q})^* \boldsymbol{\mu}_{\text{mol}}(\mathbf{Q}) \psi''_{\text{vib}}(\mathbf{Q}) d\tau$$

From the vanishing integral rule, arising from group theory, $R^{nm} = 0$ unless $\Gamma[\psi'_{\text{vib}}] \otimes \Gamma[\mu_{\text{mol}}] \otimes \Gamma[\psi''_{\text{vib}}]$ contains the totally symmetric irrep of the point group. If ψ''_{vib} is the ground vibrational state, then $\Gamma[\psi''_{\text{vib}}]$ is the totally symmetric irrep. Therefore, for a transition to be electric-dipole allowed, $\Gamma[\psi'_{\text{vib}}]$ must contain one of the same irreducible representations as $\Gamma[\mu_{\text{mol}}]$. This is the gross selection rule for vibrational fundamentals.

Example: ethylene (D_{2h})

$\mu_{\text{mol}} = (\mu_x, \mu_y, \mu_z)$ transforms as (B_{3u}, B_{2u}, B_{1u})

$$\Gamma_{\text{vib}} = 3A_g \oplus A_u \oplus 2B_{1g} \oplus B_{1u} \oplus B_{2g} \oplus 2B_{2u} \oplus 2B_{3u}$$

$$(\nu_1, \nu_3) \quad \nu_4 \quad (\nu_5, \nu_6) \quad \nu_7 \quad \nu_8 \quad (\nu_9, \nu_{10}) \quad (\nu_{11}, \nu_{12})$$

Thus, we can conclude that only ν_7 , ν_9 , ν_{10} , ν_{11} , and ν_{12} are IR active.

The specific selection rule in i.r. spectroscopy is that within the harmonic oscillator approximation $\Delta v = \pm 1$, due to the following property of Hermite polynomials:

$$\langle m|x|n \rangle = \sqrt{\frac{n}{2\alpha}} \delta_{m,n-1} + \sqrt{\frac{n+1}{2\alpha}} \delta_{m,n+1}$$

Thus, when the harmonic oscillator approximation is employed for a diatomic molecule, only a single line, the “vibrational fundamental” will appear in the spectrum. For polyatomic molecules the spectrum is still very simple: $\Delta v_k = \pm 1$, $\Delta v_j = 0, j \neq k, k=0, 1, 2, \dots, 3N-6$.

Furthermore, the intensity of an IR absorption depends on the magnitude of the dipole moment derivative along Q_k squared. Fundamental bands, which are not allowed by symmetry have $(\partial\mu/\partial Q_k)_e = 0$.

$$\boldsymbol{\mu}_{\text{mol}}(\mathbf{Q}) = \boldsymbol{\mu}_e + \sum_{k=1}^{3N-6} \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)_e Q_k + \dots$$

$$\mathbf{r}_{\text{vib}} = \int \psi'_{\text{vib}}(\mathbf{Q}) \left[\boldsymbol{\mu}_e + \sum_{k=1}^{3N-6} \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)_e Q_k + \dots \right] \psi''_{\text{vib}}(\mathbf{Q}) d\mathbf{Q}$$

$$\mathbf{r}_{\text{vib}} = \sum_{k=1}^{3N-6} \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)_e \int \psi'_{\text{vib}}(\mathbf{Q}) Q_k \psi''_{\text{vib}}(\mathbf{Q}) d\mathbf{Q}$$

Table 6.3 Typical bond-stretching and angle-bending group vibration wavenumbers ν .

| Bond-stretching | | Bond-stretching | |
|---|------------------------------|-----------------------------------|------------------------------|
| Group | $\tilde{\nu}/\text{cm}^{-1}$ | Group | $\tilde{\nu}/\text{cm}^{-1}$ |
| $\equiv\text{C}-\text{H}$ | 3300 | $-\text{O}-\text{H}$ | 3600‡ |
| $=\text{C}-\text{H}$ except $\text{O}=\text{C}-\text{H}$ | 3020 | $>\text{N}-\text{H}$ | 3350 |
| $>\text{C}-\text{H}$ | 2800 | $\equiv\text{P}=\text{O}$ | 1295 |
| $>\text{C}-\text{H}$ | 2960 | $>\text{S}=\text{O}$ | 1310 |
| $-\text{C}\equiv\text{C}-$ | 2050 | Angle-bending | |
| $>\text{C}=\text{C}<$ | 1650 | $\equiv\text{C}-\text{H}$ | 700 |
| $\equiv\text{C}-\text{C}\equiv$ | 900 | $=\text{C}-\text{H}$ | 1100 |
| $\equiv\text{Si}-\text{Si}\equiv$ | 430 | $-\text{C}-\text{H}$ | 1000 |
| $>\text{C}=\text{O}$ | 1700 | $>\text{C}-\text{H}$ | 1450 |
| $-\text{C}\equiv\text{N}$ | 2100 | $\text{C}\equiv\text{C}-\text{C}$ | 300 |
| $\equiv\text{C}-\text{F}$ | 1100 | | |
| $\equiv\text{C}-\text{Cl}$ | 650 | | |
| $\equiv\text{C}-\text{Br}$ | 560 | | |
| $\equiv\text{C}-\text{I}$ | 500 | | |

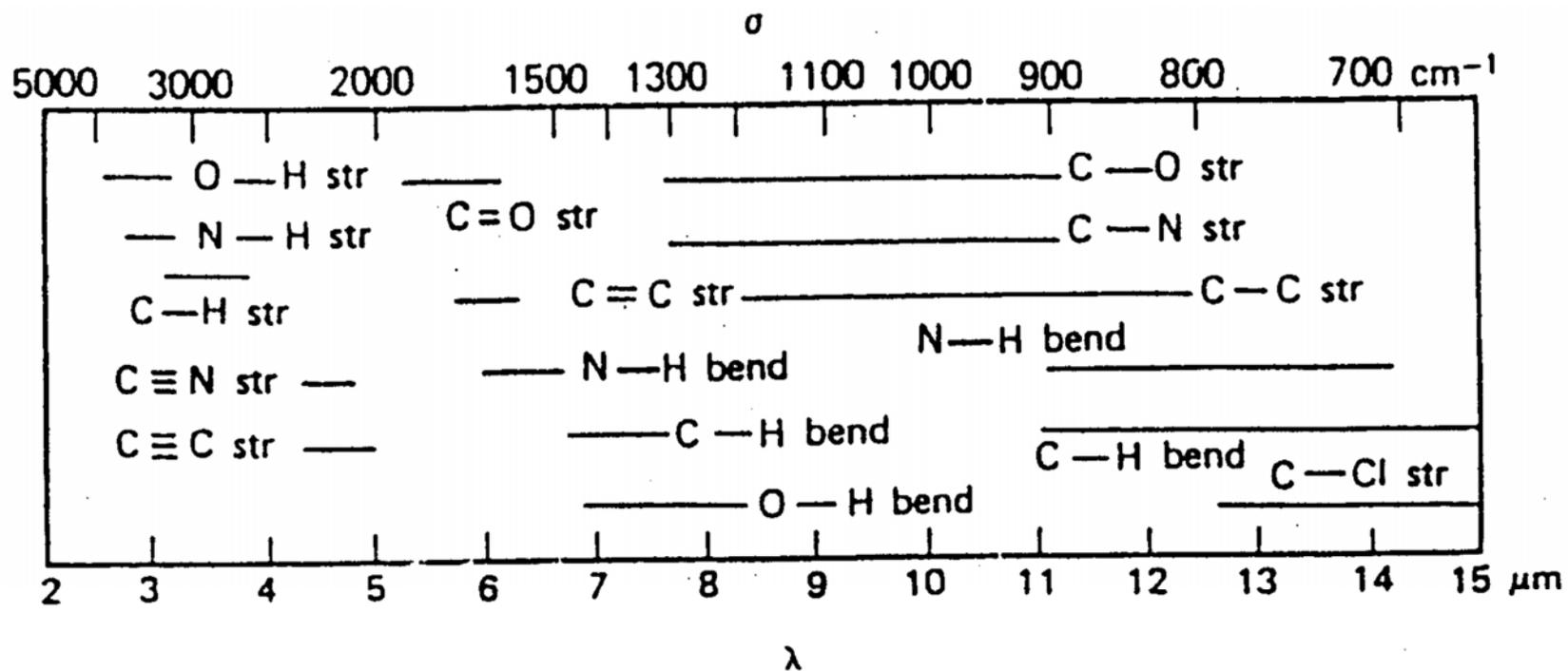
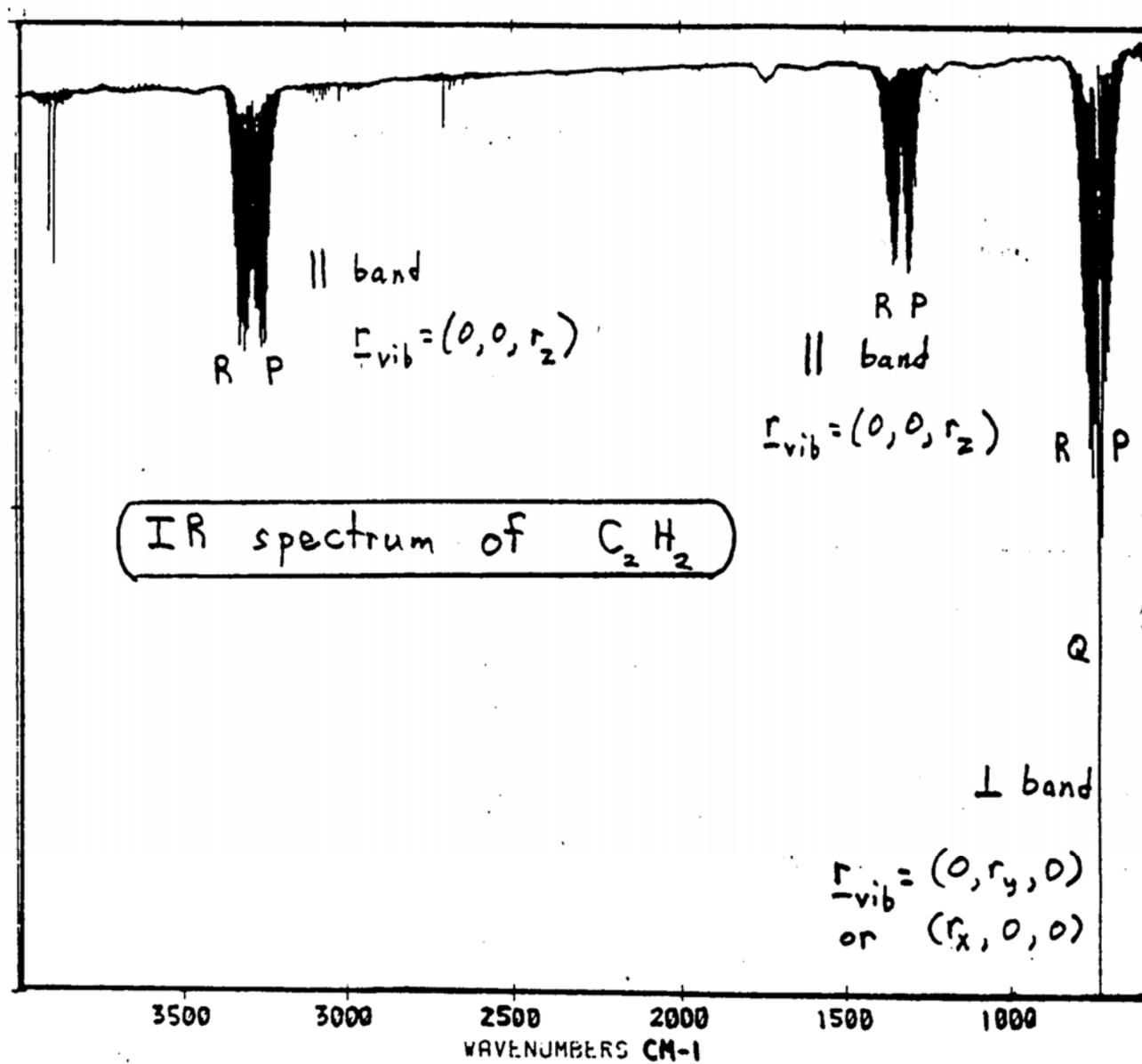
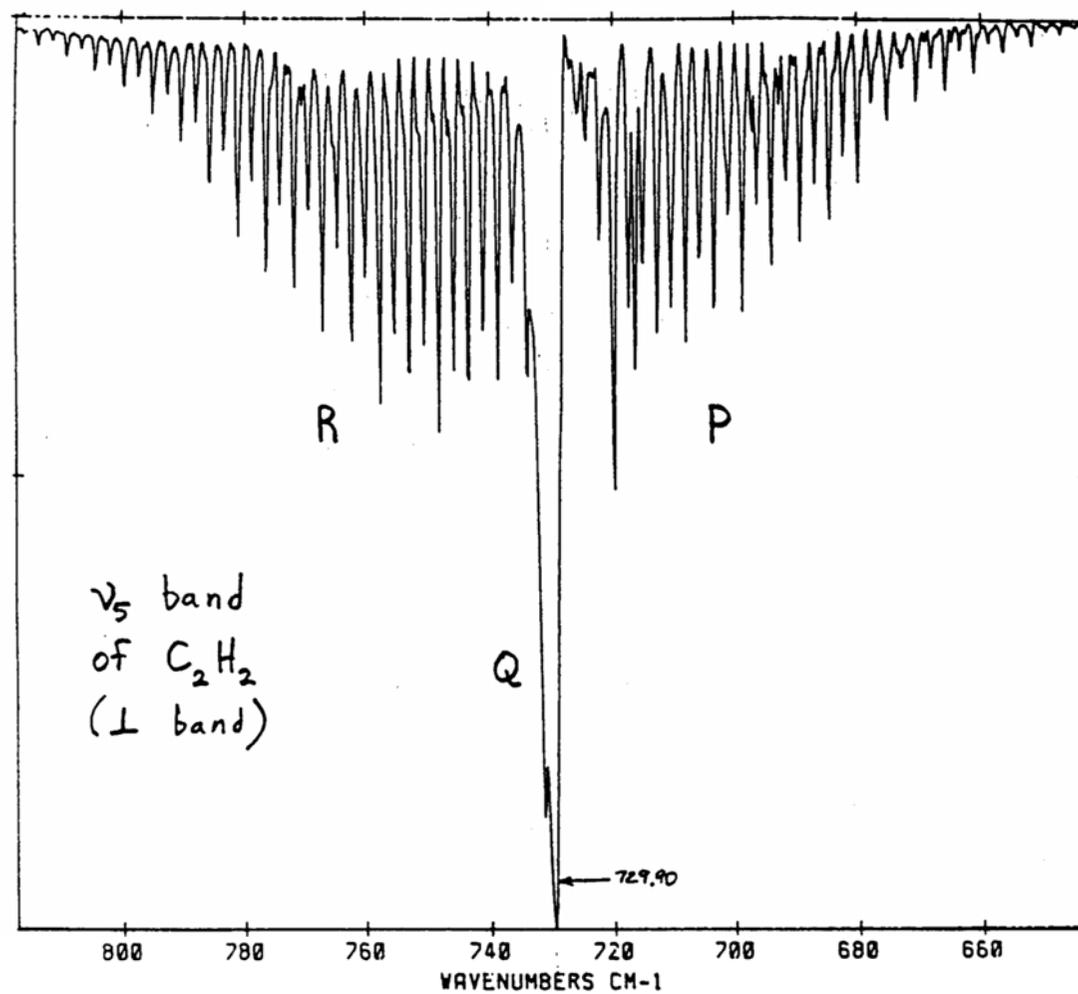


Fig. 6.7 Group frequencies: for IR absorption. The scale is linear in wavelength, not frequency.





Conclusions for band structure of ${}^1\Sigma$ electronic states of linear molecules:

| | | |
|------------------|-----------------------|--------------|
| \parallel band | $\Delta J = \pm 1$ | PR branches |
| \perp band | $\Delta J = 0, \pm 1$ | PQR branches |

Internal coordinates

Changes in interatomic distances or in the angles between chemical bonds, or both, can be used to provide a set of $3N - 6(5)$ **internal coordinates**, *i.e.*, coordinates which are unaffected by translations and rotations of the molecule as a whole. They provide the most physically significant set for use in describing the potential energy of the molecule. Usually they do not depend from the masses of the atoms, thus they are geometrically defined. Note, however, that the kinetic energy is most easily set up in terms of Cartesian displacement coordinates.

Basic types of internal coordinates: (bond) **stretching** (STRE), (valence angle) **bending** (BEND), **out-of-plane bending** (OUT), and **torsion** (TORS).

Let $\mathbf{r}_{ab} = \mathbf{r}_b - \mathbf{r}_a$ a vector pointing from atom a to atom b , $\mathbf{e}_{ab} = \mathbf{r}_{ab} / |\mathbf{r}_{ab}|$ the corresponding unit vector. Then, for example:

$$\text{STRE} \quad r_{ab} = |\mathbf{r}_{ab}| \quad 0 < r_{ab} < \infty$$

$$\text{BEND} \quad \phi_{abc} = \cos^{-1}(\mathbf{e}_{bc} \cdot \mathbf{e}_{ba}) \quad 0 < \phi_{abc} < \pi$$

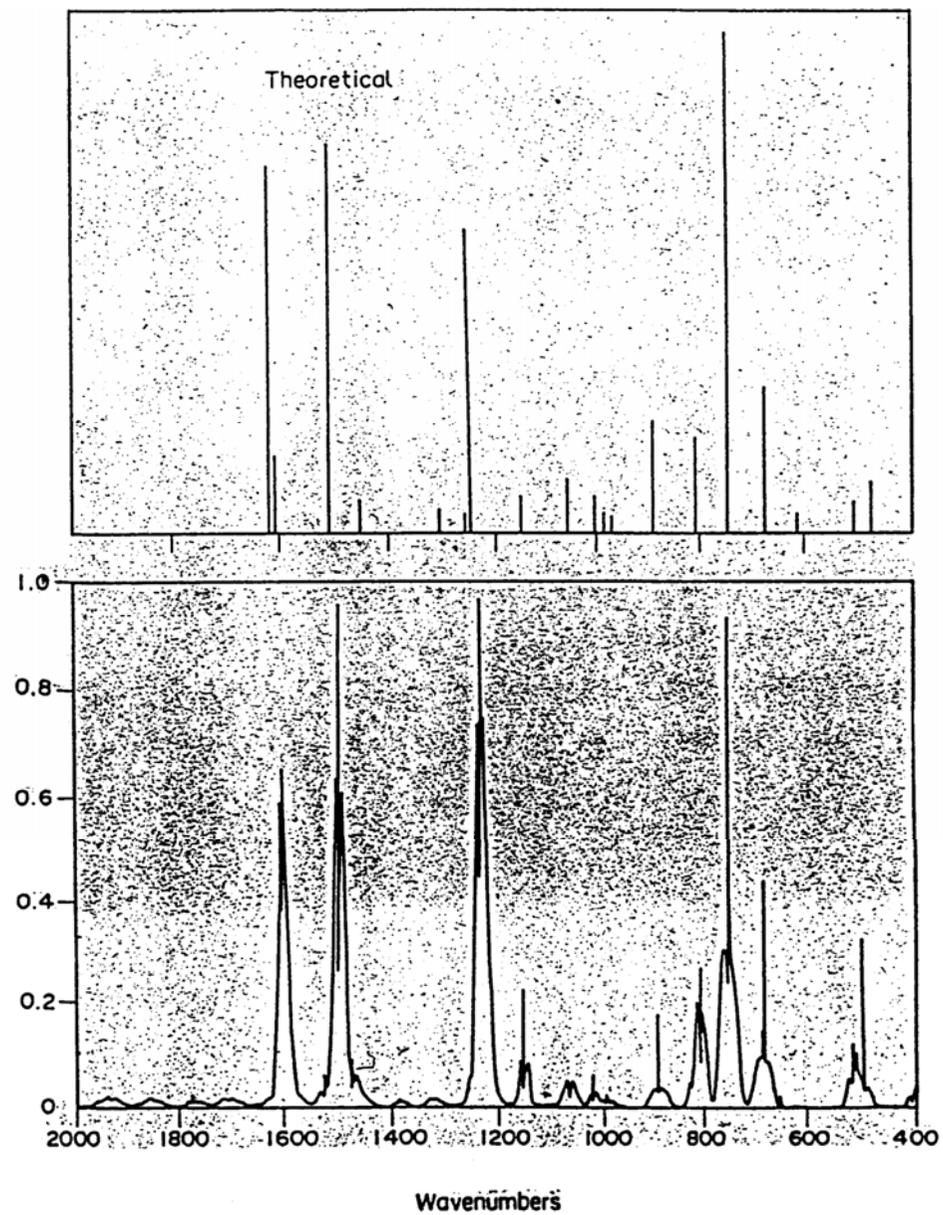
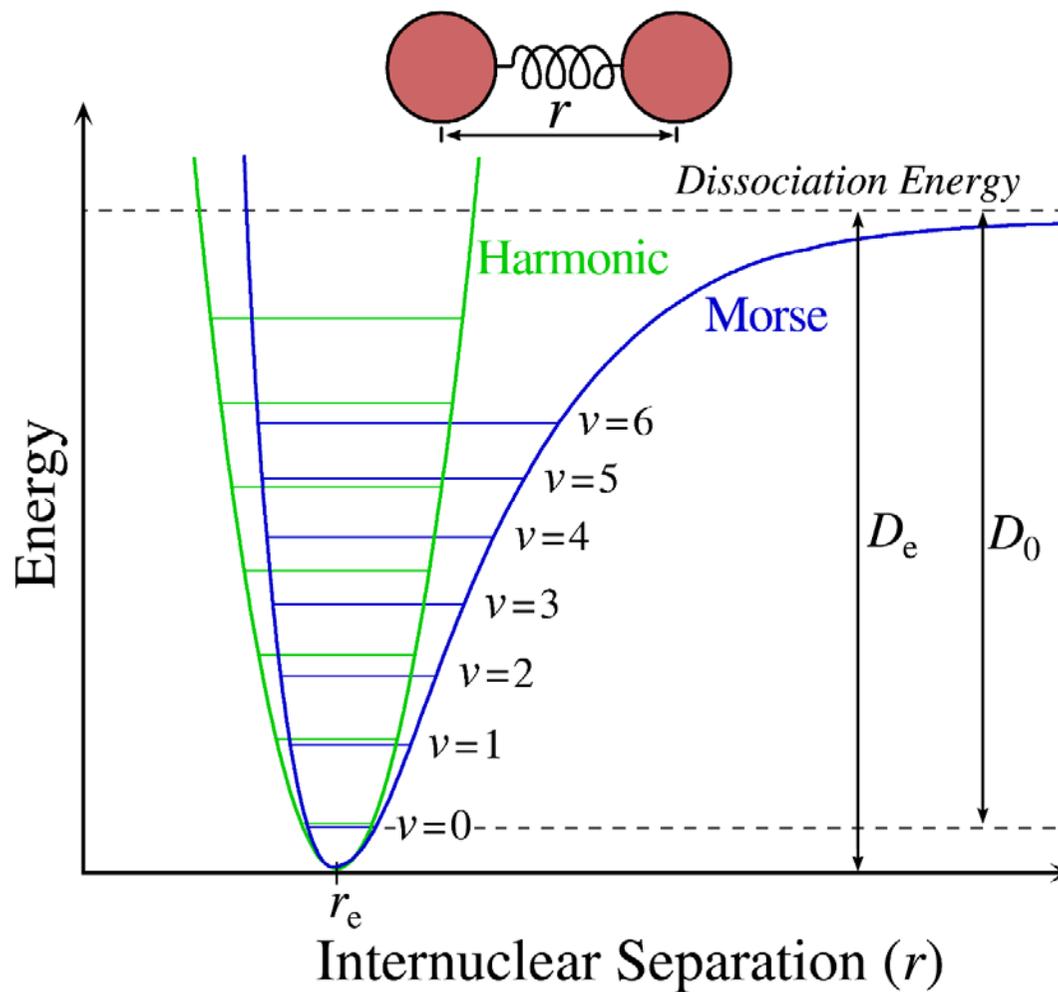


Fig.2. Experimental and theoretical i.r. spectrum of fluorobenzene.

Anharmonicity of molecular vibrations



MOLECULAR MECHANICS (MM)

In the 1960s, while studying vibrational spectra and related potential energy hypersurfaces (PES), different so-called force field models were developed, like the **central force fields**, CFF: the PES is a sum of pair interaction potentials, or the **valence force fields**, VFF: the PES contains terms dependent upon bond lengths and angles.

Spectroscopic VFFs formed an ideal starting point for so-called molecular mechanics models. Essence of MM models: they are not quantum chemical models, molecules are considered as if they were held together by deformable springs between the atoms, only the motions of the nuclei are investigated. Systems of the size of hundreds of thousand of atoms can be investigated on computers.

MM energy function:

$$E_{\text{total}} = E_{\text{stre}} + E_{\text{bend}} + E_{\text{tors}} + E_{\text{nonbonded}}$$

Bond stretching contribution (E_{stre}):

$$E_{\text{stre}} = \sum k_{\text{stre}} (l - l_0)^2$$

$$E_{\text{stre}} = \sum D_e \left[1 - \exp\{-\alpha(l - l_0)\} \right]^2$$

Angle-bending contribution (E_{bend}):

$$E_{\text{bend}} = \sum k_{\Theta} (\Theta - \Theta_0)^2$$

Dihedral angle-bending contribution (E_{tors}):

$$E_{\text{tors}} = \sum V_n (1 + s \cos n\omega)$$

V_n is the rotational barrier, n the rotational periodicity, $s = +1 / -1$ (open/staggered).

Nonbonding interaction contribution ($E_{\text{nonbonded}}$):

$$E_{\text{vdW}} = \sum \varepsilon \left[(r_m / r)^{12} - 2(r_m / r)^6 \right]$$

$$E_{\text{el}} = \sum q_i q_j / D r_{ij}$$

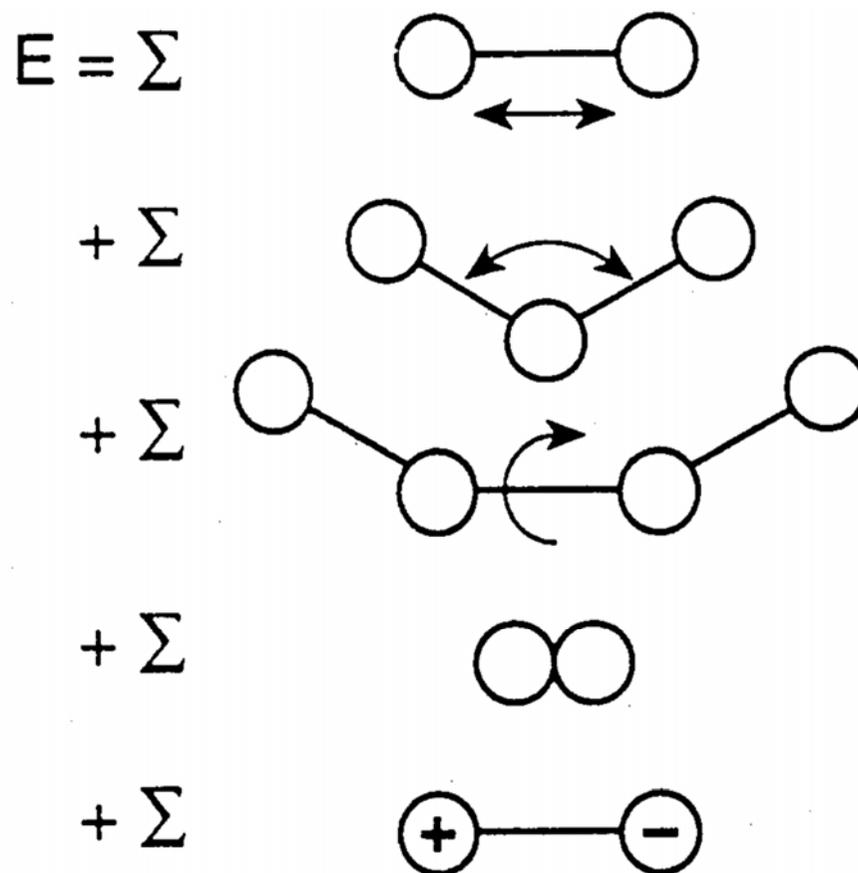


Fig. 3.1 Pictorial representation of the terms included in a molecular mechanics force field.

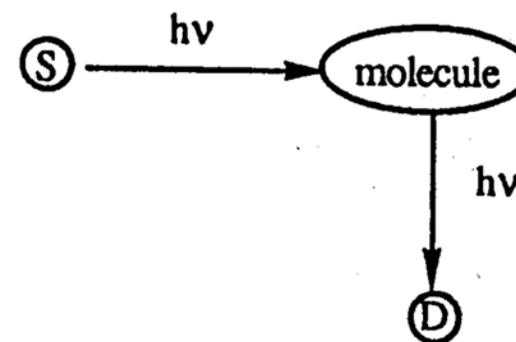
Raman spectroscopy

In 1923, Smekal, an Austrian physicist, predicts that radiation scattered from molecules contains not only photons with the incident frequency but also photons with a changed frequency.

In 1928, Indian physicist Sir Chandrasekhara Venkata Raman (1888-1970) obtains the first positive confirmation from experiments on liquid benzene. The experiments were honored by a Nobel-prize in physics in 1930.

Possible outcomes of radiation-matter interaction:

- (a) stimulated absorption or emission of photons
- (b) elastic scattering ($h\nu_0 = h\nu'$), [Rayleigh scattering](#).
- (c) inelastic scattering ($h\nu_0 \neq h\nu'$), [Raman scattering](#).



The scattering law observed by Lord Rayleigh (John William Strutt Rayleigh, 1842–1919) has no real spectroscopic significance. (Lord Rayleigh received the Nobel-prize in physics in 1904 for the discovery of argon.)

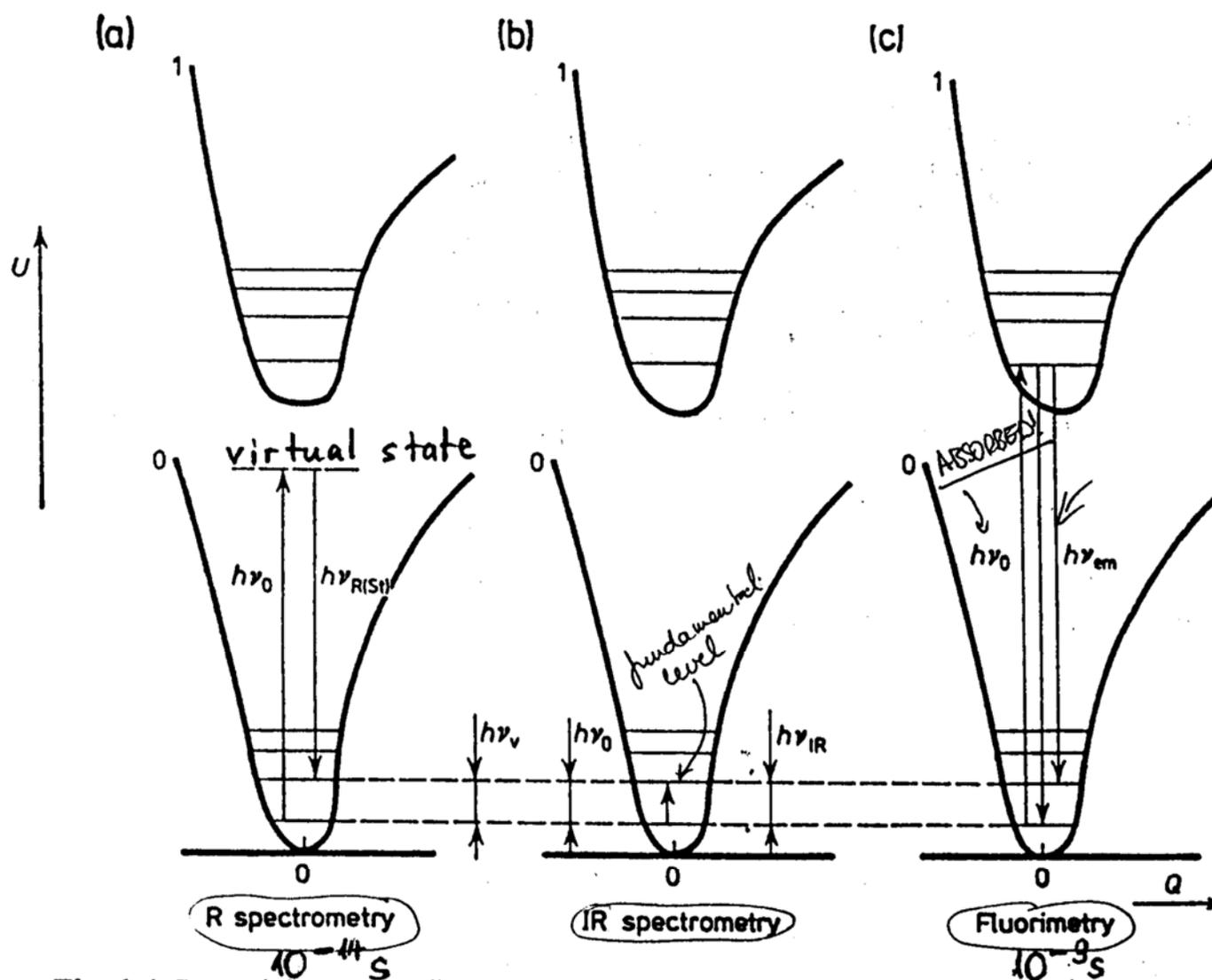


Fig. 1.4 Potential energy (U) curves of the ground (0) and excited (1) states with the energy levels and transitions between them as observed by infrared spectrometry, fluorimetry and Raman spectrometry methods.

Raman scattering is the inelastic scattering of photons from molecules. Scattering of radiation takes place as an “immediate” (within 10^{-14} s) effect of the interaction of the photon and the molecule. Raman scattering is to be distinguished from nonresonant fluorescence, in which the incident photon is absorbed followed, within 10^{-8} s, by the emission of a second photon. Note that Raman scattering can occur even if $h\nu_0$ does not correspond to some energy-level difference in the molecule.

During Raman scattering, the incident radiation is typically in the visible, transfer of energy can be from the radiation to the molecule, resulting in **Stokes lines**, as well from molecules to the radiation, resulting in **anti-Stokes lines**. Anti-Stokes lines are significantly weaker than Stokes-lines because they must originate from excited energy levels, which are less populated than the ground state according to the Boltzmann distribution. Raman scattering is typically only (1/1000)th the intensity of Rayleigh scattering.

Advent of lasers in the 1960s led to a revolution in Raman spectroscopy → sensitive technique. We can talk about rotational and vibrational Raman spectroscopy.

Hallmarks of vibrational Raman spectroscopy

- (1) Raman vibrational spectroscopy is complementary to IR spectroscopy:
 - (a) covalent bonds tend to give strong Raman bands whereas ionic bonds tend to give strong IR bands;
 - (b) homonuclear diatomics are invisible in IR but easily observed in Raman;
 - (c) IR and Raman spectroscopy have different selection rules. **Rule of mutual exclusion**: if a molecule has a center of symmetry (*i*), Raman active vibrations are IR inactive, and vice versa. In highly symmetric molecules some bands may be neither Raman nor IR active.
- (2) Raman spectroscopy is ideal for the study of aqueous solutions, for which IR transmittance is poor → RS is highly useful to study physiological systems.
- (3) Unlike IR spectroscopy, a single Raman instrument can be used over the entire range of the vibrational spectrum.
- (4) Sample preparation is usually simple. Liquids in capillary tubes are common.
- (5) Disadvantage: fluorescence background from organic (or other) molecules can obscure the Raman spectrum.

Classical theory of the Raman effect

Electric field (\mathbf{E}) from radiation induces a dipole moment for a diatomic:

$$\mu_{z,\text{induced}} = \alpha_{zz} E_z$$

In the general 3-dimensional case one has a 3×3 polarizability tensor (with three independent elements, just like for the moment of inertia tensor):

$$\boldsymbol{\mu}_{\text{ind}} = \boldsymbol{\alpha} \mathbf{E} \quad \text{or} \quad \begin{pmatrix} \mu_{x,\text{ind}} \\ \mu_{y,\text{ind}} \\ \mu_{z,\text{ind}} \end{pmatrix} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

Typical values of polarizabilities (\AA^3):

| | α_{xx} | α_{yy} | α_{zz} |
|-----------------|---------------|---------------|---------------|
| CO | 1.62 | 1.62 | 2.60 |
| CO ₂ | 1.93 | 1.93 | 4.03 |
| CH ₄ | 2.62 | 2.62 | 2.62 |
| benzene | 11.1 | 11.1 | 7.4 |

The magnitude of a typical induced dipole is very small (about 10^{-5} D).

Electric field oscillation in time:

$$E = E_0 \sin(2\pi\nu_0 t) \Rightarrow \mu_{\text{ind}} = \alpha E_0 \sin(2\pi\nu_0 t).$$

However, the bond distance R oscillates in time as well:

$$R = R_e + A \sin(2\pi\nu_e t).$$

Accordingly, α is modulated in time:

$$\alpha = \alpha_e + \left(\frac{\partial \alpha}{\partial R} \right)_e (R - R_e) + \dots$$

$$\alpha = \alpha_e + \left(\frac{\partial \alpha}{\partial R} \right)_e A \sin(2\pi\nu_e t) + \dots$$

$$\mu_{\text{ind}} = \alpha_e E_0 \sin(2\pi\nu_0 t) + \left(\frac{\partial \alpha}{\partial R} \right)_e A E_0 \sin(2\pi\nu_0 t) \sin(2\pi\nu_e t) + \dots$$

Employing the trigonometric identity $2\sin A \sin B = \cos(A - B) - \cos(A + B)$, the final result for the induced dipole:

$$\begin{aligned} \mu_{\text{ind}} = & \alpha_e E_0 \sin(2\pi\nu_0 t) + && \text{Rayleigh scattering} \\ & \frac{AE_0}{2} \left(\frac{\partial\alpha}{\partial R} \right)_e \cos[2\pi(\nu_0 - \nu_e)t] + && \text{Stokes lines (Raman)} \\ & \frac{AE_0}{2} \left(\frac{\partial\alpha}{\partial R} \right)_e \cos[2\pi(\nu_0 + \nu_e)t] + && \text{anti-Stokes lines (Raman)} \end{aligned}$$

Summary:

Vibrations of molecules cause a modulation in polarizability leading to emission of radiation from the induced dipole at shifted frequencies $\nu_0 - \nu_e$ and $\nu_0 + \nu_e$, where ν_0 is the incident frequency of radiation and ν_e is the frequency of vibration. However, these Raman-scattered peaks only appear if $(\partial\alpha/\partial Q_k)_e \neq 0$, *i.e.*, the polarizability must change in first order along the vibration for Raman scattering to occur.

Quantum mechanical results for Raman scattering – selection rules

Unlike the spectroscopic techniques discussed thus far, Raman spectroscopy is fundamentally a two-photon process. The interaction between radiation and matter appears in the second-order terms in perturbation theory rather than the first-order terms. Thus, the theory of Raman scattering is more involved than that for the one-photon processes governed by

$$\mathbf{R}^{nm} = \int \psi_n^* \hat{\mathbf{u}} \psi_m d\tau.$$

Raman selection rules are obtained by computing

$$\mathbf{A}^{(r''v'' \rightarrow r'v')} = \int \Psi_{r'v'}^* \boldsymbol{\alpha} \Psi_{r''v''} d\tau_r d\tau_v,$$

where r and v denote rotational and vibrational states and coordinates, respectively. $\boldsymbol{\alpha} = \boldsymbol{\alpha}(\mathbf{Q}, \boldsymbol{\kappa})$ is the 3×3 polarizability tensor, which depends on the normal coordinates \mathbf{Q} of the molecule and the rotational coordinates $\boldsymbol{\kappa}$, which specify the orientation of the molecule-fixed axis system in space.

Vibrational selection rules

From the vanishing integral rule arising from group theory, the Raman “intensity” will be zero, unless

$$\Gamma[\psi_{v'}] \otimes \Gamma[\alpha_{\text{mol}}] \otimes \Gamma[\psi_{v''}]$$

contains the totally symmetric irrep of the point group. If $\psi_{v''}$ is the ground vibrational state, then $\Gamma[\psi_{v''}]$ is the totally symmetric irrep. Thus, for a transition to be Raman allowed, $\Gamma[\psi_{v'}]$ must contain one of the same irreps as $\Gamma[\alpha_{\text{mol}}]$. Just as the components of μ_{mol} transform as (x, y, z) , the elements of α_{mol} transform as $(x^2, y^2, z^2, xy, xz, yz)$. Hence, the Raman-allowed bands can be determined from a character table which lists the irreps of this products of coordinates.

$$\mathbf{A}_{\text{vib}} = \int \psi_{v'}^* \left[\alpha_e + \sum_k \left(\frac{\partial \alpha}{\partial Q_k} \right)_e Q_k + \dots \right] \psi_{v''} d\mathbf{Q} \Rightarrow$$

$$\mathbf{A}_{\text{vib}} = \alpha_e \int \psi_{v'}^*(\mathbf{Q}) \psi_{v''}(\mathbf{Q}) d\mathbf{Q} + \sum_k \left(\frac{\partial \alpha}{\partial Q_k} \right)_e \int \psi_{v'}^* Q_k \psi_{v''} d\mathbf{Q} + \dots$$

The first term on the rhs of the last equation is zero, while the second term is familiar from the study of IR selection rules.

Conclusion: within the harmonic approximation, only the fundamental bands are Raman-allowed. More explicitly: $\Delta v_k = \pm 1$, and $\Delta v_j = 0$, if $j \neq k$. The “intensity” of a Raman absorption depends on the magnitude of the polarizability derivative along Q_k squared. Fundamental bands which are not allowed by symmetry have $(\partial\alpha/\partial Q_k)_e = 0$.

Rotational selection rules

$$\Delta J = 0, \pm 1, \text{ or } \pm 2.$$

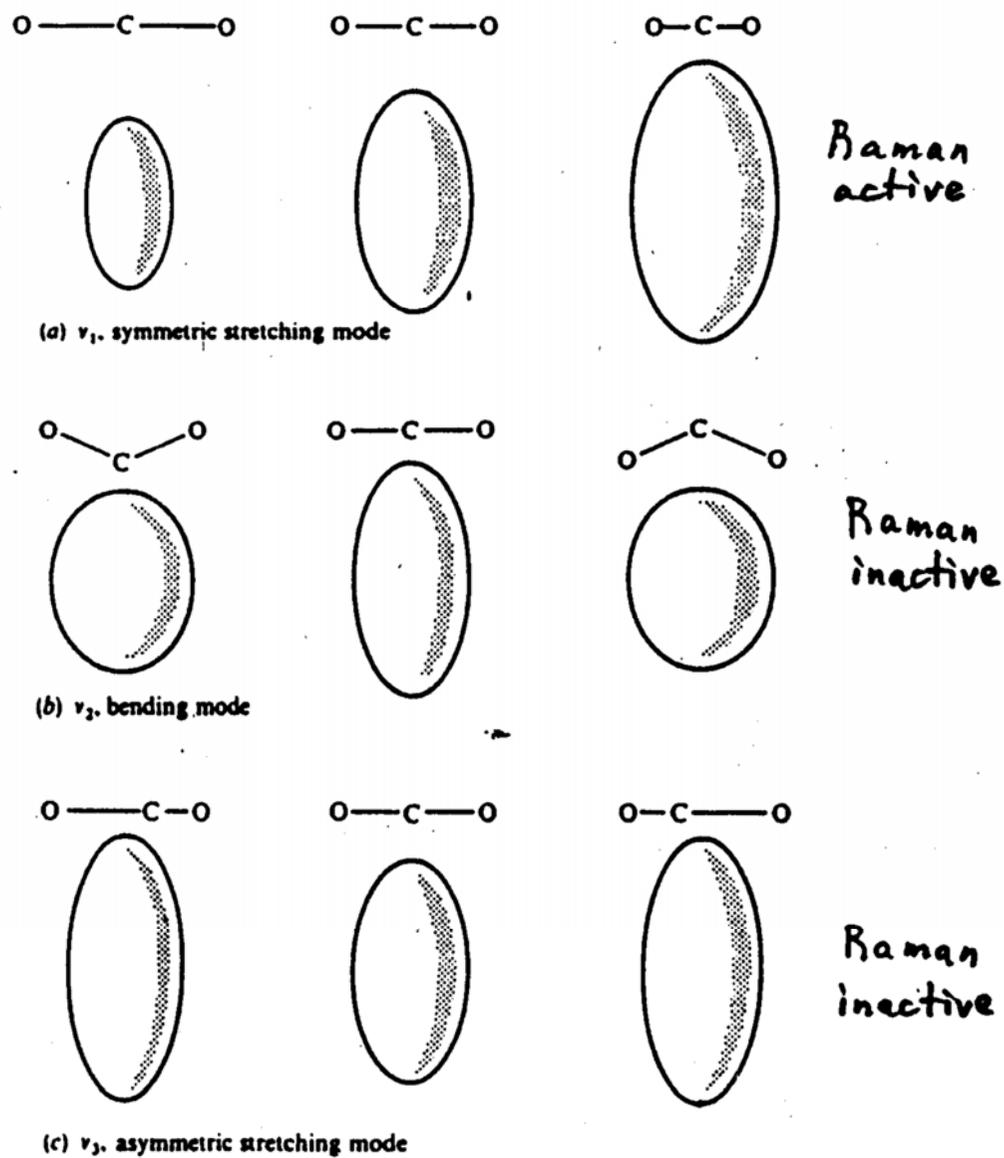
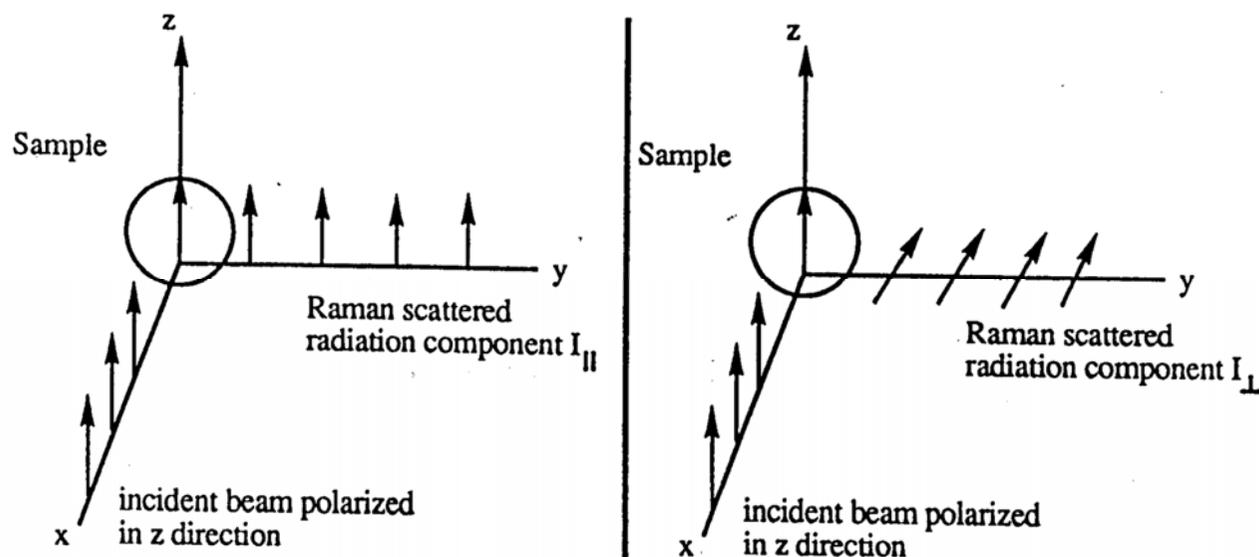


Figure 4.7 The shape of the polarizability ellipsoid of the carbon dioxide molecule during its vibrations.

Depolarization in Raman scattering



$$\rho := \frac{I_{\perp}}{I_{\parallel}} \text{ depolarization ratio}$$

The ρ depolarization ratio can be measured through use of a polarizer in the path of the scattered radiation before it reaches the detector. The value of ρ is indicative of the symmetry of the vibration which is excited.

Theoretical expression for the depolarization ratio:

$$\rho = \frac{3(\gamma')^2}{45(\bar{\alpha}')^2 + 4(\gamma')^2} ,$$

where the primes denote derivatives with respect to Q_k of the following quantities

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \text{ mean polarizability}$$

$$\gamma^2 = \frac{1}{2} \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2) \right], \quad \text{anisotropy of polarizability.}$$

Upon a thorough investigation of the related equations, for totally symmetric vibrations $\rho < 0.75$, while for all other vibrations $\rho = 0.75$.

Depolarization ratios:

| | | ρ | | | | ρ | |
|------------------|---------|--------|---------------------------|-----------------|---------|--------|---------------------------|
| H ₂ O | ν_1 | 0,03 | (<i>a</i> ₁) | NH ₃ | ν_1 | 0,027 | (<i>a</i> ₁) |
| | ν_2 | 0,74 | (<i>a</i> ₁) | | ν_2 | 0,650 | (<i>a</i> ₁) |
| | ν_3 | 0,75 | (<i>b</i> ₂) | | ν_3 | 0,750 | (<i>e</i>) |
| | | | | | ν_4 | 0,750 | (<i>e</i>) |

ν_1 : symmetric O–H stretch

ν_1 : symm. N–H stretch

A specialized situation called [resonance Raman scattering](#) arises, leading to resonance Raman spectroscopy, when the laser frequency is tuned close to resonance with one of the molecular eigenstates, when the transition probability becomes anomalously large. The ordinary Raman selection rules are not applicable in this case.