See also: **Chemiluminescence**: Overview; Liquid-Phase. **Fluorescence**: Overview. **Indicators**: Acid–Base.

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INDUCTIVELY COUPLED PLASMA

See **ATOMIC EMISSION SPECTROMETRY: Inductively Coupled Plasma**

INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

See **ATOMIC MASS SPECTROMETRY: Inductively Coupled Plasma**

INFRARED SPECTROSCOPY

Contents

Overview

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Introduction

The infrared (IR) region of the electromagnetic spectrum lies between ~10 and 12 800 cm^{-1}. The energy of IR photons is thus of the same order of magnitude as the energy differences between quantized molecular vibrational states. Transitions between these vibrational modes can be induced by IR radiation if there is a change in the molecular electric dipole moment in the course of the vibrational motion. IR spectroscopy is the study of the interaction of IR radiation with matter as a function of photon frequency. This interaction can take the form of absorption, emission, or reflection. IR spectroscopy is a fundamental analytical technique for obtaining quantitative and qualitative information about a substance in the solid, liquid, or vapor state.

Table 1 The IR region of the spectrum

Region	*λ (cm)*	*$\bar{\nu}$ (cm^{-1})*	*ν (Hz)*
Near-IR	2.5×10^{-4}–7.8×10^{-5}	4000–12 800	1.2×10^{14}–3.8×10^{14}
Mid-IR	5×10^{-3}–2.5×10^{-4}	200–4000	6×10^{12}–1.2×10^{14}
Far-IR	$0.1-5\times10^{-3}$	10–200	3×10^{11}–6×10^{12}

It is convenient to divide the IR region into three parts (**Table 1**): the far-IR (10–200 cm^{-1}); the mid-IR (200–4000 cm^{-1}); and the near-IR (4000–12 800 cm^{-1}). (The regions are not exactly defined: slightly different boundaries for the IR regions are found in the literature. In particular, most Fourier transform infrared (FTIR) spectrometers operating in the mid-IR region have a low-wave-number limit of 400 cm^{-1}.) Each part of the spectrum plays a different role in analysis according to the different character of the transitions involved in each case.

Mid-IR radiation corresponds to fundamental transitions in which one vibrational mode is excited from its lowest energy state to its first excited state. For routine analysis a spectrum is normally taken from 400 to 4000 cm^{-1}. The mid-IR spectrum of a substance is effectively a unique fingerprint that can be used for the purpose of identification by comparison with a reference spectrum. When no reference spectrum is available, an IR spectrum can be used to identify the presence of certain structural units that, irrespective of their molecular environment, give rise to characteristic spectral features in a narrow frequency range.

Near-IR spectroscopy arises from transitions in which a photon excites a normal mode of vibration from the ground state to the second or higher excited vibrational state (overtones, *vide infra*) or transitions in which one photon simultaneously excites two or more vibrational modes (combinations bands, *vide infra*). The use of the near-IR, especially diffuse reflection spectroscopy, in both quantitative and qualitative analysis has increased significantly due to better instrumentation and the development of chemometrics to better handle the effect of seriously overlapping bands.

The far-IR region of the spectrum (<200 cm^{-1}) results from transitions involving low-frequency torsions and internal rotations in liquids and lattice vibrations in solids and is not commonly used for analysis, although recent developments in instrumentation for terahertz spectrometry may change the situation.

The scope and flexibility of IR spectroscopy in the mid-IR region have been greatly increased by the advent of FTIR spectroscopy. The multiplex and throughput advantages of this technique allow spectra to be run faster and with a greater signal-to-noise ratio than dispersive spectroscopy, i.e., measurements made with prism or grating monochromators.

The following brief description of the principal IR techniques – using the near- or mid-IR – illustrates the range of sample handling possible with IR spectroscopy.

'Diffuse reflection' is the term used to describes the reflection of electromagnetic radiation from a sample after the radiation has undergone multiple scattering inside a powdered sample or at the surface of a matte substance. The radiation passes through the 'microstructural' elements of the sample, e.g., the microcrystallites of a powder or the surface fibers of a fabric, and is absorbed in the process before being scattered out of the sample to detector. The use of diffuse reflection spectroscopy in the ultraviolet (UV) region of the spectrum is a long-established technique. However, until FTIR was established, the weakness of the signal prevented the extension of the technique into the mid-IR. Diffuse reflection IR Fourier transform (DRIFT) spectroscopy has become a useful technique for obtaining IR spectra from powdered samples (or any matte material) with little or no sample preparation.

Photoacoustic IR spectroscopy has similar advantages to DRIFT spectroscopy in its ability to handle solids with the minimum of preparation. The principle of this technique is that when a modulated beam of IR radiation is absorbed by a sample, temperature oscillations set up thermal waves. If the sample is sealed in a cell and surrounded by gas, then a microphone can pick up the sound waves in the gas and an IR absorption spectrum generated.

'Specular reflection' is the term used to describe 'mirror-like' reflection, from the surface of a sample (angle of reflection equals angle of incidence). Specular reflected radiation ostensibly carries no information about the IR absorption of a sample and is a source of interference in diffuse reflection experiments when the sample is not completely matte, i.e., has an element of 'shininess' about it. However, if the reflected intensity from a sample is due 'principally' to reflection from the front surface of the sample, then an absorption index spectrum of the sample can be generated from the reflected intensity over the whole spectrum using the Kramers–Krönig transformation. (This complex transformation is an integral part of the software packages driving most modern FTIR spectrometers.)

Aqueous solutions have traditionally posed a problem for IR spectroscopy due to the fact that water is a strong absorber of IR radiation. This difficulty, for aqueous solutions and other strongly absorbing liquid and solid samples, can be overcome by using attenuated total reflection spectroscopy. In this technique, the phenomenon of total internal reflection is used in such a way that it is only the evanescent wave associated with total internal reflection that enters the sample. The evanescent wave penetrates the sample very short distances only, hence the advantage for strongly absorbing species.

FTIR microscopy, in which IR spectra can be obtained from picogram quantities, is an invaluable nondestructive analytical tool in fields such as forensic science and pharmaceutical analysis.

The short data-capture times possible with the FTIR spectrometer means that time-resolved spectroscopy has become an important means of following the course of a chemical reaction in order to obtain information about kinetics, equilibria, and the nature of reaction intermediates.

Matrix isolation IR spectroscopy involves mixing trace amounts of solute into a rare gas matrix at low temperature. The advantage is that the solute molecules are isolated so that reactive species can be analyzed. Also, the absence of rotational structure and lattice modes increases resolution.

For chiral molecules a small difference in the magnitude of absorption of left- and right-circularly polarized IR radiation is observed. This is known as vibrational circular dichroism and, since the effect can be observed from each normal mode, absolute stereochemical information can be obtained from the entire molecule. This is different from the UV analog of this effect, where there may often be only one chromophore present.

The Vibration of Diatomic Molecules

The Classical Diatomic Rigid Vibrator

An understanding of the nature of vibrational motion is best obtained by first studying a simple system. To introduce some of the basic concepts involved it is useful to study the classical diatomic vibrator before going on to consider the quantum theory.

The simplest model for a diatomic molecule consists of two atoms of mass m_1 and m_2 connected by a rigid, massless spring of length r, which has the value r_0 at equilibrium (**Figure 1**). If the z-axis is taken to lie along the internuclear line, then the Cartesian coordinates of the two atoms, referred to the center of mass, may be written as

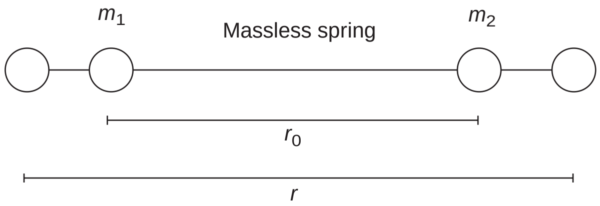


Figure 1 Model for a rigid diatomic vibrator.

$$z_1 = z_1^0 + \Delta z_1 \qquad [1a]$$

$$z_2 = z_2^0 + \Delta z_2 \qquad [1b]$$

where z_1^0 and z_2^0 are the equilibrium coordinates of atoms 1 and 2, respectively, and Δz_1 and Δz_2 are the 'Cartesian displacements coordinates'. An 'internal coordinate' R can be defined as the differences in the bond length from its equilibrium value

$$R = \Delta z_2 - \Delta z_1 = r - r_0 \qquad [2]$$

The potential energy of the molecule $V(R)$, which increases as the bond is stretched or compressed, may be expressed as a power series in the internal coordinate

$$V(R) = V(0) + \left(\frac{\mathrm{d}V(R)}{\mathrm{d}R}\right)_0 R + \frac{1}{2}\left(\frac{\mathrm{d}^2V(R)}{\mathrm{d}R^2}\right)_0 R^2 + \frac{1}{6}\left(\frac{\mathrm{d}^3V(R)}{\mathrm{d}R^3}\right)_0 R^3 + \cdots \qquad [3]$$

The subscripts (zero) indicate that the derivatives are to be taken at the equilibrium bound length. Only changes in the potential energy from the equilibrium value are important, so the energy scale may be chosen such that $V(0)$ is zero. Also, the first derivative of the potential energy $(\mathrm{d}V(R)/\mathrm{d}R)_0$ must be zero by definition at the equilibrium position since this corresponds to the energy minimum. This leaves only the quadratic and higher terms in the potential function

$$V(R) = \frac{1}{2}\left(\frac{\mathrm{d}^2V(R)}{\mathrm{d}R^2}\right)_0 R^2 + \frac{1}{6}\left(\frac{\mathrm{d}^3V(R)}{\mathrm{d}R^3}\right)_0 R^3 + \cdots \qquad [4]$$

The cubic and higher terms are generally small for small departures from the equilibrium position. The effects of including these contributions in the potential energy expression will be considered later. It is, however, a good first approximation to set these higher-order terms to zero to give

$$V(R) = \frac{1}{2}\left(\frac{\mathrm{d}^2V(R)}{\mathrm{d}R^2}\right)_0 R^2 = \frac{1}{2}KR^2 \qquad [5]$$

A system with a potential function given by eqn [5] is said to be 'mechanically harmonic' and K is known as the 'force constant' for the bond where

$$K = \left(\frac{d^2V(R)}{dR^2}\right)_0 \qquad [6]$$

The harmonic approximation corresponds to a restoring force F acting on the atoms that is proportional to the displacement of the bond length from its equilibrium value (Hooke's law)

$$F = -KR \qquad [7]$$

With the center of gravity as the coordinate origin, it is straightforward to show that the problem reduces to that of a single particle oscillating around the center of mass subject to a harmonic restoring force whose displacement is equal to the change in the internuclear distance of the molecule, i.e., the internal coordinate R. The mass μ of this particle is known as the reduced mass of the molecule and is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad [8]$$

Applying Newton's second law gives

$$\frac{\mu}{2}\frac{d^2R}{dt^2} = -KR \qquad [9]$$

This equation describes the simple harmonic oscillator. The solution is

$$R = R^0 \sin(2\pi v t + \delta) \qquad [10]$$

which corresponds to simple harmonic motion with maximum amplitude R^0, phase factor δ, and frequency v given by

$$v = \frac{1}{2\pi}\left(\frac{K}{\mu}\right)^{1/2} \qquad [11]$$

It can be shown that the maximum amplitude of vibration for each atom is inversely proportional to the atomic mass.

The Quantum-Mechanical Harmonic Diatomic Vibrator

The harmonic potential function obtained in eqn [5]

$$V(R) = \tfrac{1}{2}KR^2$$

can be used in Schrödinger's equation to yield the following wave function:

$$\Psi_v(R) = \frac{(\alpha/\pi)^{1/4}}{(2^v v!)^{1/2}} \exp\left(-\frac{\alpha R^2}{2}\right) H_v(\alpha^{1/2}R) \qquad [12]$$

where v is the vibrational quantum number, and

$$\alpha = 2\pi\frac{(\mu K)^{1/2}}{h} = \frac{4\pi^2 \mu v}{h}$$

where $H_v(\alpha^{1/2}R)$ are Hermite polynomials (**Table 2**).

Table 2 The first few Hermite polynomials

v	$H_v(x)$
0	1
1	$2x$
2	$4x^2 - 2$
3	$8x^3 - 12x$
4	$16x^4 - 48x^2 + 12$
5	$32x^5 - 160x^3 + 120x$

The vibrational energy levels are given by

$$E_v = \left(v + \tfrac{1}{2}\right)hv, \quad v = 0, 1, 2, \ldots \qquad [13]$$

where

$$v = \frac{1}{2\pi}\left(\frac{K}{\mu}\right)^{1/2}$$

Note that this expression is exactly the same as eqn [11], the classical vibration frequency.

Vibrational term values $G(v)$ in wave numbers can be defined from eqn [13]:

$$G(v) = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right)\frac{v}{c} = \left(v + \frac{1}{2}\right)\tilde{v} \qquad [14]$$

Inspection of eqn [13] shows that the vibrational zero-point energy E_0 is given by

$$E_0 = \tfrac{1}{2}hv \qquad [15]$$

or

$$G(0) = \tfrac{1}{2}\tilde{v} \qquad [16]$$

Figure 2 shows plots of the harmonic diatomic vibrator wave functions.

For harmonic wave function, the properties of the Hermite polynomials are such that the selection rules for vibrational transitions are

$$\Delta v = \pm 1 \qquad [17]$$

There also exists the gross selection rule that, in order for electromagnetic radiation to be absorbed, the dipole moment of the molecule must change during the vibration, which means that a diatomic molecule must possess a permanent dipole moment in order to absorb IR radiation. (These selections rules will be discussed in detail in the section on the intensity of IR transitions.)

Since all energy levels are equally spaced for a harmonic diatomic vibrator, one line will appear in the IR absorption spectrum with wave number

$$\tilde{v} = \frac{1}{2\pi c}\left(\frac{K}{\mu}\right)^{1/2} \qquad [18]$$

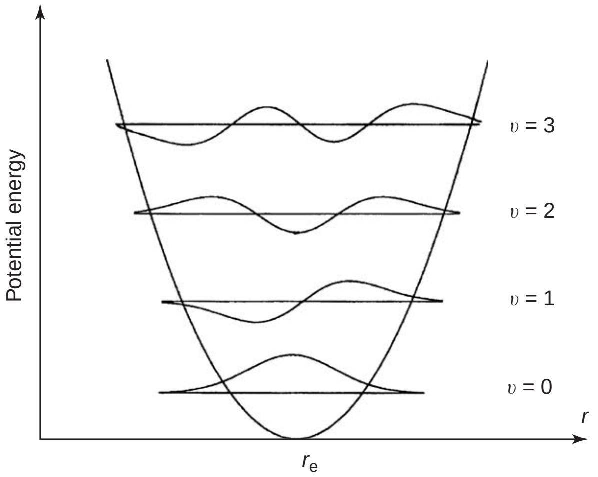


Figure 2 Harmonic diatomic vibrator wave functions.

Table 3 Vibrational frequencies and force constants for selected bonds

Bond	*$\bar{\nu}$ (cm^{-1})*	*K ($\times 10^2$ N m^{-1})^a*
C–H	2960	4.7
=C–H	3020	5.0
≡C–H	3300	5.9
(OC)–H	2800	4.3
C–C	900	2.9
C=C	1650	9.6
C≡C	2050	15
C=O	1700	12
C≡N	2100	17
O–H	3600	7.2
N–H	3350	6.2
C–F	1100	5.3
C–Cl	650	2.2
C–Br	560	1.9
C–I	500	1.6

[a] 1 mdyne Å^{-1} = 100 N m^{-1}.

Equation [18] can be used to provide approximate values for the force constants of bonds (**Table 3**).

Isotopic Substitution

If one of the atoms in the diatomic molecule is replaced by another isotopic species, then to a good approximation the electronic structure is unchanged. Hence, the force constant will be the same for both molecules. The change in the vibrational frequency will therefore be completely due to the change in the reduced mass. If μ' and $\tilde{\nu}'$ are the reduced mass and wave number of the isotopically substituted molecule, then

$$\frac{\tilde{\nu}}{\tilde{\nu}'} = \left(\frac{\mu'}{\mu}\right)^{1/2} \qquad [19]$$

Similar relationships for frequency shifts induced by isotopic substitution in polyatomic molecules are given later.

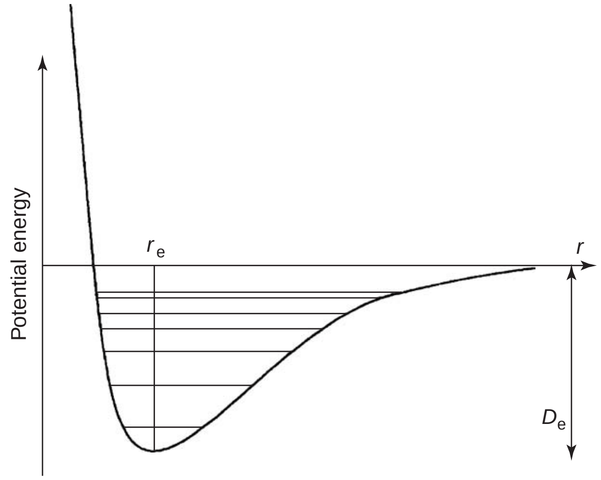


Figure 3 The Morse potential function.

Anharmonic Vibrations of a Diatomic Molecule

The true potential function for a diatomic molecule departs from harmonicity, especially for large amplitude vibrations. It is useful to approximate an anharmonic potential using a Morse function (**Figure 3**)

$$E_{\mathrm{anh}} = D_e\{1 - \exp[-a(r - r_e)]\}^2 \qquad [20]$$

where D_e is the thermodynamic dissociation energy and

$$a = \omega\left(\frac{\mu}{2D_e}\right)^{1/2}, \quad \omega = 2\pi\nu \qquad [21]$$

When this potential energy is used in the Schrödinger equation the vibrational levels become

$$G(\upsilon) = \left(\upsilon + \frac{1}{2}\right)\tilde{\nu}_e - \left(\upsilon + \frac{1}{2}\right)^2 x_e\tilde{\nu}_e, \ldots, \quad x_e = \frac{a^2\hbar}{2\mu\omega} \qquad [22]$$

where $\tilde{\nu}_e$ is the wave number corrected for anharmonicity, and x_e is the anharmonicity constant, a positive number $\sim 10^{-2}$. The negative term in eqn [22] results in the gap between successive vibrational energy levels decreasing as υ increases. The point at which the levels merge into a continuum corresponds to the dissociation of the molecule.

Another effect of anharmonicity is to relax the selection rules to give

$$\Delta\upsilon = \pm 1, \pm 2, \pm 3, \ldots \qquad [23]$$

Along with the fundamental vibrations, 'harmonics' are now observed in the IR spectrum: the second harmonic (or first overtone) ($\upsilon = 2 \leftarrow \upsilon = 0$), third harmonic (or second overtone) ($\upsilon = 3 \leftarrow \upsilon = 0$) and so on occur with decreasing intensity. A knowledge of the wave numbers of the fundamental and first

Table 4 Anharmonicity constants for some diatomic molecules

Bond	$\bar{\nu}_e$ *(cm^{-1})*	$x_e\bar{\nu}_e$ *(cm^{-1})*
H–^{12}C	2861.6	64.3
H–^{19}F	4138.5	90.07
H–^{16}O	3735.2	82.81
H–^{35}Cl	2991.0	52.85
H–Br	2649.7	45.21

overtone vibrations allows the anharmonicity constants to be calculated using eqn [22]. **Table 4** shows values of anharmonicity constants for a selection of diatomic molecules.

Normal Coordinates

Computational and interpretational aspects of vibrational spectroscopy are greatly simplified by the introduction of 'normal coordinates'. First, mass-weighted Cartesian displacement coordinates for an N-atom molecule $q_1, q_2, \ldots, q_{3N}$ are defined according to

$$\begin{aligned} q_1 &= \sqrt{m_1}\Delta x_1, \quad q_2 = \sqrt{m_1}\Delta y_1, \\ q_3 &= \sqrt{m_1}\Delta z_1, \quad q_4 = \sqrt{m_2}\Delta x_2, \ldots \end{aligned} \qquad [24]$$

In these coordinates the kinetic energy T is given by

$$T = \frac{1}{2}\sum_{i=1}^{3N} \dot{q}_i^2 \qquad [25]$$

where the dot indicates a time derivate. The potential energy is given by

$$\begin{aligned} V &= \frac{1}{2}\sum_{i,j=1}^{3N}\left(\frac{\partial V}{\partial q_i \partial q_j}\right)_0 q_i q_j \\ &= \frac{1}{2}\sum_{i,j=1}^{3N} b_{ij} q_i q_j \end{aligned} \qquad [26]$$

where the b_{ij} denote the force constants in the Cartesian displacement coordinate system. (Note that there are cross-terms in the potential function involving two coordinates.)

The total energy is therefore given by

$$E = \frac{1}{2}\sum_{i=1}^{3N} \dot{q}_i^2 + \frac{1}{2}\sum_{ij=1}^{3N} b_{ij} q_i q_j \qquad [27]$$

If the potential energy term did not include any cross-terms, then Newton's equation could be applied

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial T}{\partial \dot{q}_i}\right) + \left(\frac{\partial V}{\partial q_i}\right) = 0, \quad i = 1, 2, \ldots, 3N \qquad [28]$$

In this case the problem would reduce to the solution of $3N$ independent equations. Therefore, in order to enable the use of Newton's equation, the mass-weighted Cartesian coordinates q_i are transformed into a set of new coordinates Q_i which results in no cross-terms in the potential function.

The Q_i are called the 'normal coordinates' of the system, and this transformation from Cartesian displacement to normal coordinates is the essence of the vibrational problem. Using normal coordinates, the kinetic and potential energy become

$$T = \frac{1}{2}\sum_{i=1}^{3N} \dot{Q}_i^2 \qquad [29]$$

$$V = \frac{1}{2}\sum_{i=1}^{3N} \lambda_i Q_i^2 \qquad [30]$$

Using eqns [29] and [30] in eqn [28] instead of the mass-weighted Cartesian coordinates gives

$$\ddot{Q}_i + \lambda_i Q_i = 0, \quad i = 1, 2, \ldots, 3N \qquad [31]$$

These are simply harmonic oscillator equations with solutions

$$Q_i = Q_i^0 \sin(\sqrt{\lambda_i} t + \delta_i) \qquad [32]$$

with frequencies

$$\nu_i = \frac{1}{2\pi}\sqrt{\lambda_i} \qquad [33]$$

Each vibration associated with a normal coordinate is known as a 'normal vibration'. Each atom involved in a normal coordinate vibrates in phase with all the other atoms involved in the same vibration. Each atom passes through its equilibrium position at the same time and reaches each turning point at the same time.

An analysis of the stretching vibrational motion of a symmetrical linear triatomic molecule (**Figure 4**) reveals that in terms of mass-weighted Cartesian coordinates q_1, q_2, and q_3 the normal vibrations (excluding a zero-frequency translational solution) are given by

$$Q_+ = \frac{1}{2^{1/2}} q_1 - \frac{1}{2^{1/2}} q_2 \qquad [34a]$$

$$Q_- = \left[\frac{M}{2(M+2m)}\right]_1^q - \left[\frac{2m}{M+2m}\right]_2^q + \left[\frac{M}{2(M+2m)}\right]_3^q \qquad [34b]$$

with frequencies

$$\nu_+ = \frac{1}{2\pi}\left(\frac{K}{m}\right)^{1/2} \qquad [35a]$$

$$\nu_- = \frac{1}{2\pi}\left[\frac{K(M+2m)}{Mm}\right]^{1/2} \qquad [35b]$$

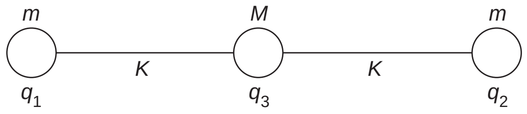


Figure 4 The symmetrical linear diatomic molecule.

The + and − labels have been used to denote that the two normal vibrations are symmetric and antisymmetric stretches, respectively.

The two bonds in this system are known as 'coupled oscillators'. This type of system occurs often in the vibrations of polyatomic molecules in which two oscillators (which can be bonds or groups of bonds) couple to give symmetric and antisymmetric combinations. (In this case, where the system is exactly symmetrical, the symmetric combination will not be observed in the IR spectrum because the dipole moment of the molecule does not change.)

High-Resolution IR Spectra of Linear Molecules

Each vibrational transition of vapor-phase molecules is accompanied by rotational transitions. In the liquid state the effect of molecular collisions is to broaden the rotational lines so that they cannot be resolved. This is why one observes IR bands as opposed to lines in solution spectra. In the vapor phase, however, it is possible to resolve the rotational structure in a vibrational transition.

The Diatomic Vibrating-Rotator

It is normally a good approximation to express the total energy due to the motion of the nuclei E_{nuc} as the sum of the separate energies E_{vib} and E_{rot} (the Born–Oppenheimer approximation)

$$E_{\mathrm{nuc}} = E_{\mathrm{vib}} + E_{\mathrm{rot}} \qquad [36]$$

To a first approximation, wave numbers of the rotational levels are given by

$$\frac{E_J}{hc} = BJ(J+1)\,\mathrm{cm}^{-1}, \quad J = 0, 1, 2, \ldots \qquad [37]$$

when J is the rotational quantum number and B is the rotational constant given by

$$B = \frac{h}{8\pi^2 Ic}\,\mathrm{cm}^{-1} \qquad [38]$$

where I is the moment of inertia of the molecule given by

$$I = \mu r_{\mathrm{e}}^2 \qquad [39]$$

where r_{e} is the equilibrium bond length.

Using eqns [22] and [37] the total vibrational and rotational energy is given by

$$\frac{E_{v,J}}{hc} = BJ(J+1) + \left(v + \frac{1}{2}\right)\tilde{\nu}_{\mathrm{e}} - x_{\mathrm{e}}\left(v + \frac{1}{2}\right)\tilde{\nu}_{\mathrm{e}} \qquad [40]$$

The selection rules for vibration–rotation transitions are the same as for separate transitions:

$$\Delta v = \pm 1, \pm 2, \pm 3, \ldots$$

and

$$\Delta J = \pm 1 \qquad [41]$$

Labeling the initial and final levels by double and single primes, respectively, and making the assumption that the rotational constants for the lower and upper vibrational states are the same, then the transition energies are given by

$$\tilde{\nu}_{J',J''} = \tilde{\nu}_0 + B(J' - J'')(J' + J'' + 1) \qquad [42]$$

when v_0 is the band center (or band origin) given by

$$\tilde{\nu}_0 = \tilde{\nu}_{\mathrm{e}}(1 - 2x_{\mathrm{e}}) \qquad [43a]$$

$$\tilde{\nu}_0 = 2\tilde{\nu}_{\mathrm{e}}(1 - 3x_{\mathrm{e}}) \qquad [43b]$$

$$\tilde{\nu}_0 = 3\tilde{\nu}_{\mathrm{e}}(1 - 4x_{\mathrm{e}}) \qquad [43c]$$

for the fundamental and first and second overtones, respectively. For $\Delta J = +1$,

$$\tilde{\nu}_{J''+1,J''} = \tilde{\nu}_0 + 2B(J'' + 1), \quad J'' = 0, 1, 2, \ldots \qquad [44]$$

For $\Delta J = -1$,

$$\tilde{\nu}_{J''-1,J''} = \tilde{\nu}_0 - 2B(J' + 1), \quad J' = 0, 1, 2, \ldots \qquad [45]$$

So it can be seen that the high-resolution spectrum will consist of two series of lines, one on either side of the band center. The series corresponding to $\Delta J = -1$ is known as the P branch, and the series corresponding to $\Delta J = +1$ is known as the R branch. Note that there is zero intensity at the line center. **Figure 5** shows a schematic diagram of the transitions involved and a stick representation of the line intensities which will be discussed below. **Figure 6** shows the high-resolution IR spectrum of the fundamental vibration of carbon monoxide and the same spectrum of the fundamental vibration of carbon monoxide and the same spectrum at lower resolution where only the envelope of the P and R branches can be seen.

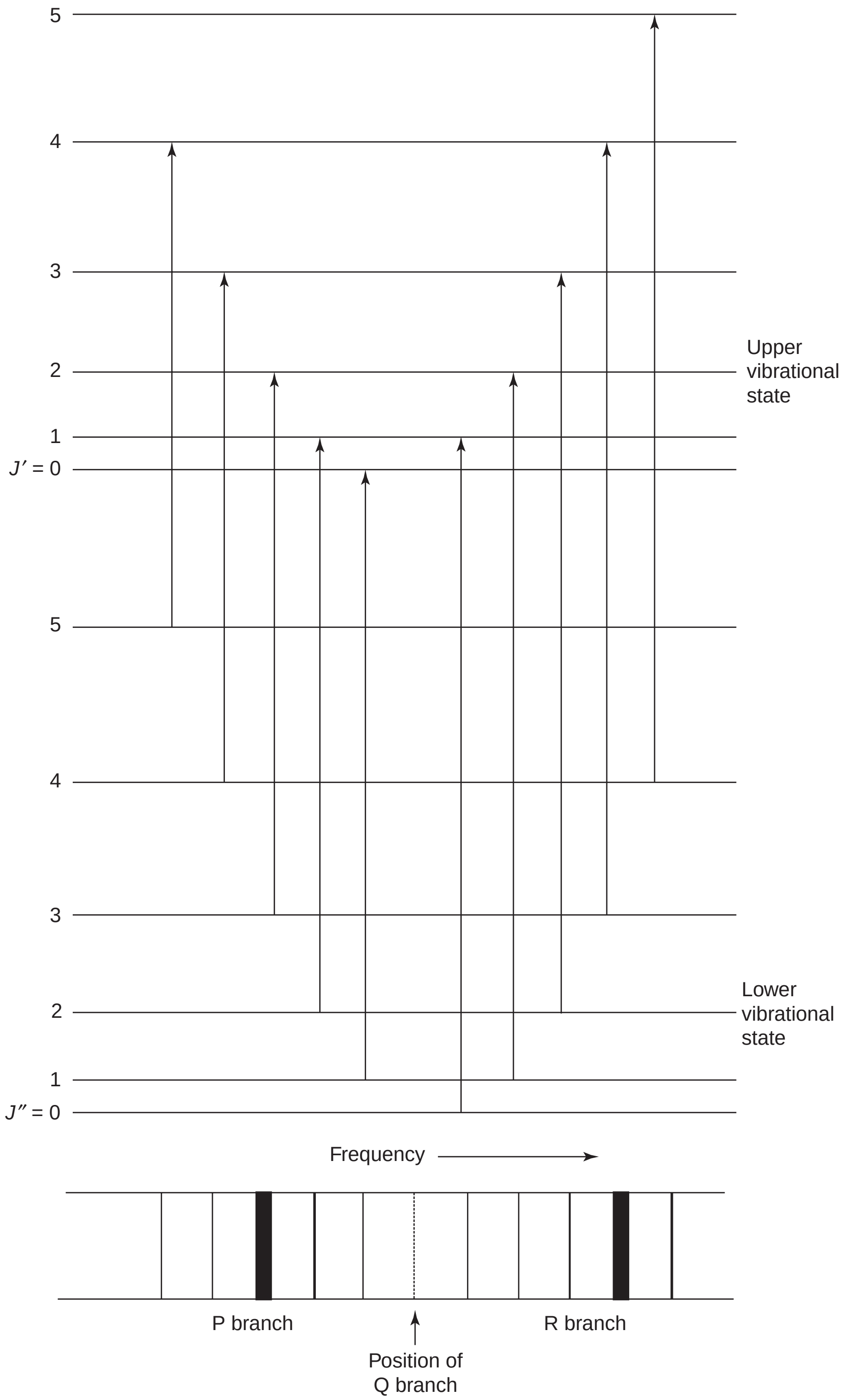


Figure 5 Schematic diagram of P and R branch transitions for a diatomic molecule, where the line thickness compounds to the intensity of the transition.

It has been assumed that the rotational constant B is the same for the upper and lower vibrational states and that the vibrational terms will be unaffected by the rotational state (interaction between rotation and vibration, i.e., a breakdown of the Born–Oppenheimer approximation). When these assumptions are not made, eqn [40] becomes

$$\frac{E_{v,J}}{hc} = B_v J(J+1) + \left(v + \frac{1}{2}\right)\tilde{\nu}_e + x_e\left(v + \frac{1}{2}\right)^2 \nu_e - D_v J^2 (J+1)^2 + \cdots \qquad [46]$$

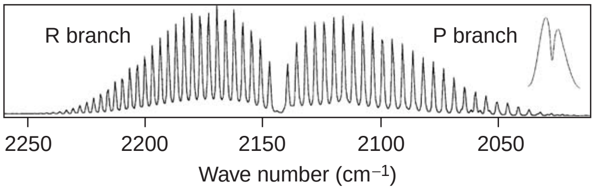


Figure 6 The high-resolution infrared spectrum of carbon monoxide showing P and R branches. (Inset on right is the same band at lower resolution.)

where B_v is the rotational constant associated with the vibrational level with quantum number v and D_v is the centrifugal distortion coefficient associated with the vibrational level v. Centrifugal distortion arises due to the fact that a bond will lengthen hence weaken as the molecule rotates. The resultant vibrational–rotational energy change is therefore

$$\tilde{\nu}_{v'J',v''J''} = \tilde{\nu}_0 + B_{v'}J'(J'+1) - D_{v'}J'^2(J'+1)^2 - B_{v''}J''(J''+1) + D_{v''}J''^2(J''+1)^2 \quad [47]$$

Intensity of Lines in the P and R Branches

The intensity of each rotational line depends on the number of molecules occupying the initial rotational state. Using the Boltzmann distribution formula, at thermal equilibrium the ratio of the number of molecules N_J in rotational state J to the number N_0 in the rotational ground state is given by

$$\frac{N_J}{N_0} = (2J+1)\exp\left[-\frac{BhcJ(J+1)}{kT}\right] \quad [48]$$

where the $(2J+1)$-fold degeneracy of each rotational state has been taken into account. By differentiating eqn [48] with respect to J and setting the derivative to zero it can be shown that the maximum population and hence the maximum intensity line occurs at

$$J_{\max} = \left(\frac{kT}{2Bhc}\right)^{1/2} - \frac{1}{2} \quad [49]$$

This corresponds to a maximum intensity at wave number $\tilde{\nu}_{\max}$ given by

$$\tilde{\nu}_{\max} = \tilde{\nu}_0 \pm 2B\left[\left(\frac{kT}{2Bhc}\right)^{1/2} + \frac{1}{2}\right] \quad [50]$$

where the + and − signs refer to the R and P branches, respectively.

High-Resolution Vibrational Spectra of Linear Polyatomic Molecules

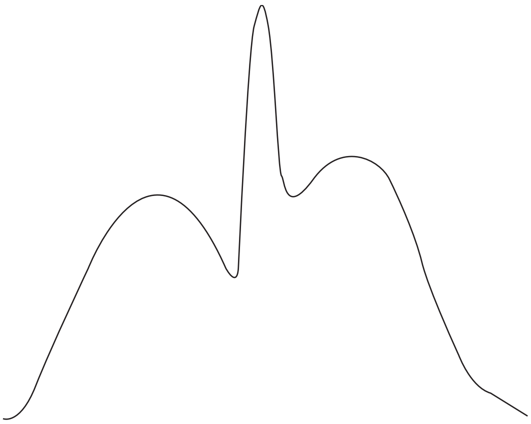


Figure 7 Typical PQR branch envelope for the perpendicular vibration of a linear polyatomic molecule.

The normal vibrations of a linear polyatomic molecule which result in a change in the molecular dipole moment (i.e., are IR allowed) can be classified into two types: parallel vibrations and perpendicular vibrations, for which the directions of the changes in the molecular dipole moment are parallel and perpendicular to the internuclear axis, respectively. The rotational selection rules for parallel vibrations are the same as for the vibration of a diatomic molecule and one observes P and Q branches as before. However, for perpendicular vibrations, rotational transitions are allowed in which the rotational quantum number does not change, i.e.,

$$\Delta J = 0 \quad [51]$$

If rotational constants in both vibrational states are equal then all Q branch transitions occur at the same wavelength, the band origin. For a fundamental vibration of a perpendicular vibration with unequal rotational constants in the two vibrational levels and introducing centrifugal distortion

$$\tilde{\nu}_{v'J',v''J''} = \tilde{\nu}_0 + (B_{v'} - B_{v''})J^2 + (B_{v'} - B_{v''})J + (D_{v'} - D_{v''})J^2 + (D_{v'} - D_{v''})J, \quad J = 0, 1, 2, \ldots \quad [52]$$

A typical band contour for perpendicular bands is shown in **Figure 7**.

Polyatomic Molecules

Internal Coordinates

The set of internal coordinates required to describe the vibrational motion of a general polyatomic molecule consists of the bond stretch r, the bond angle bend ϕ, the out-of-plane (o.o.p.) angle bend γ, and the bond torsion τ (**Figure 8**).

In a polyatomic molecule with $3N$–6 vibrational degrees of freedom ($3N$–5 for a linear molecule) a set

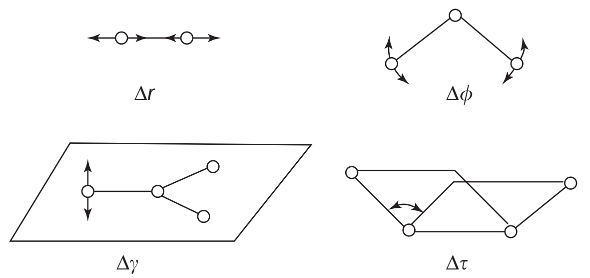


Figure 8 Internal coordinates for polyatomic molecules.

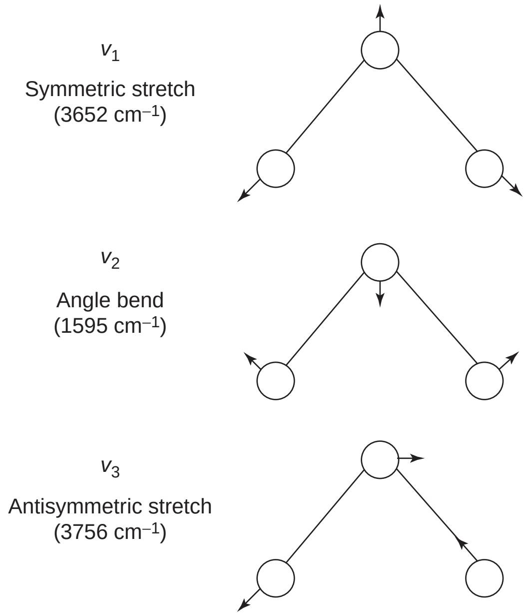


Figure 9 The normal vibrations of H_2O.

of $3N$–6 internal coordinates can be chosen to describe the molecular vibrations.

A normal coordinate for a polyatomic molecule can be expressed as a linear combination of the internal coordinates. The vibrational behavior of the atoms can be represented by attaching arrows to show their direction of motion. The lengths of the arrows are in proportion to the maximum amplitudes of each atom's normal coordinate excursion. The normal vibrations of water (H_2O) are shown in **Figure 9**.

Characteristic or group frequencies With a knowledge of atomic masses, the molecular geometry and force constants, it is possible to calculate the internal coordinate composition of the normal vibrations of any molecule. Without this mathematical help, it is not possible to specify the origin of most of the bands in an IR spectrum which will, in general, contain major contributions from several internal coordinates.

However, it is found that certain structural units in a molecule give rise to bands that appear in the spectra of different molecules within a sufficiently narrow range of frequencies for these bands to be used to identify the presence of the structural unit. These relatively constant bands are known as the characteristic frequencies or group frequencies of a molecule. The vibrations associated with methylene and methyl groups, which give rise to important group frequencies, are shown in **Figures 10** and **11**, respectively.

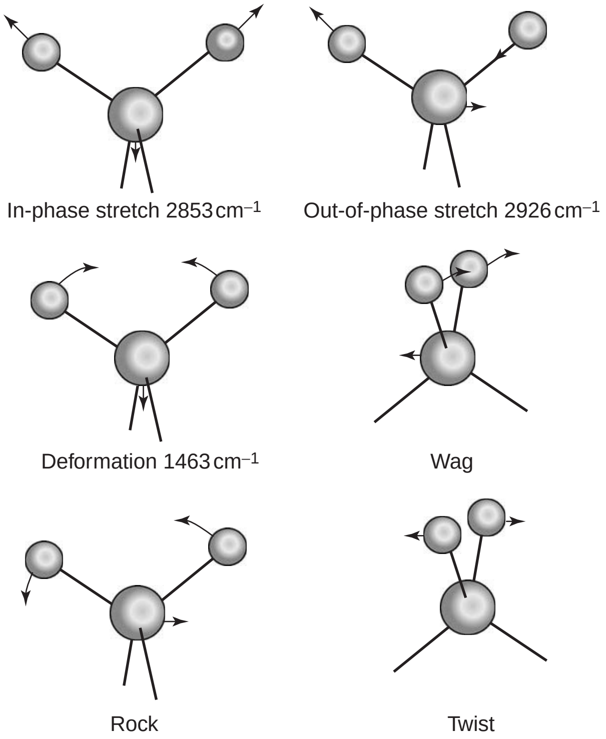


Figure 10 Characteristic vibrations of the methylene group.

Intensity of IR Transitions

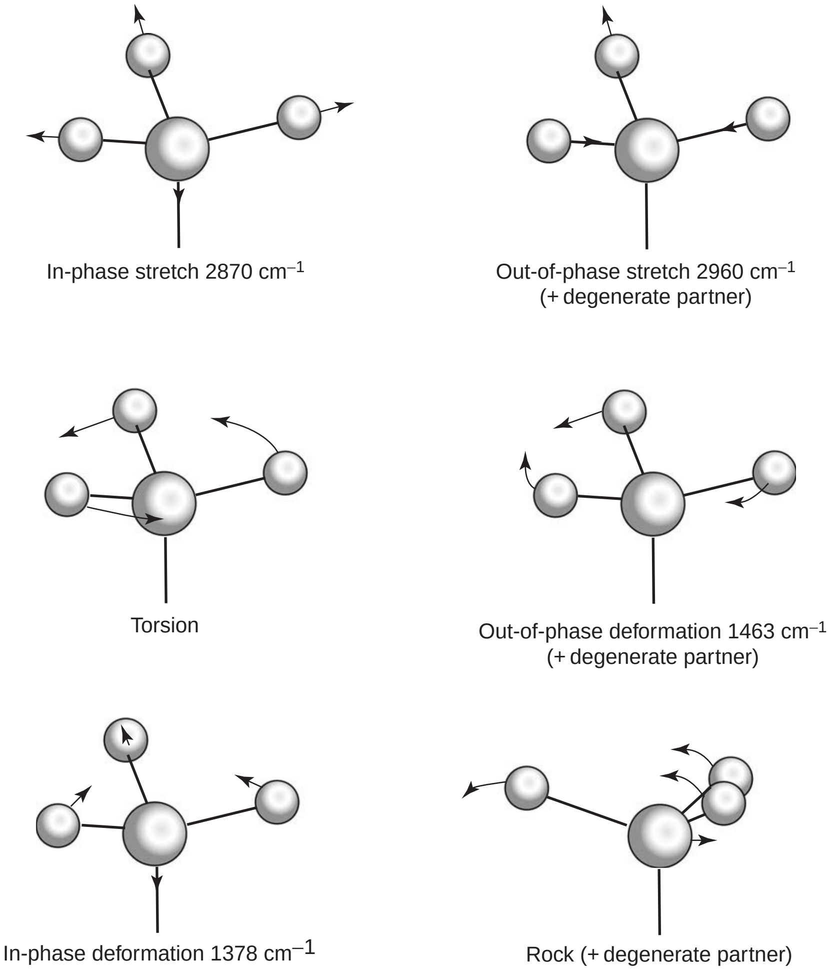
Let I_0 and I be the incident and transmitted intensities, respectively, when infrared radiation passes through a sample of concentration C and cell length l. The transmittance T is defined as

$$T = \frac{I}{I_0} = 10^{-aCl} \qquad [53]$$

where the quantity a, a function of wavelength, is called the absorptivity of the sample. Taking logarithms of the last equation, the absorbance of the sample is defined as

$$A = \log_{10}\left(\frac{I_0}{I}\right) = aCl \qquad [54]$$

Equation [54] is known as the Beer–Lambert law: the absorbance of a sample is proportional to its concentration and the cell pathlength. Since A is a



In-phase stretch 2870 cm^{-1}

Out-of-phase stretch 2960 cm^{-1} (+ degenerate partner)

Torsion

Out-of-phase deformation 1463 cm^{-1} (+ degenerate partner)

In-phase deformation 1378 cm^{-1}

Rock (+ degenerate partner)

Figure 11 Characteristic vibrations of the methyl group.

dimensionless quantity, the units of a are the product of the units for reciprocal concentration and reciprocal pathlength. For example, with concentration in mol m^{-3} and pathlength in meters, the units of a are $\text{m}^2\,\text{mol}^{-1}$. When concentration is expressed as molarity and the pathlength is either in meters of centimeters, the absorptivity a is known as the molar absorptivity and is given the symbol ε.

The Beer–Lambert law is often used in quantitative IR analysis using peakheights in the absorbance spectrum as values for A, frequently after baseline correction. Peakheights, however, are strongly dependent on instrumental resolution and an alternative measure of the absorbance of a band is its integrated intensity, which is the intensity integrated over the whole IR band. The integrated intensity may be expressed using the integrated absorptivity $\mathscr{A}$, the absorptivity integrated over the whole IR band, given by

$$\mathscr{A} = \int_{\text{band}} a(\tilde{\nu})\,\mathrm{d}\tilde{\nu} \qquad [55]$$

where $a(\tilde{\nu})$ has been written to highlight the dependence of the absorptivity on wave number. Due to the integration with respect to the wave number the dimensions of the integrated absorptivity are that of the absorptivity divided by the dimension of length. Using eqn [54], the last equation may be expressed as

$$\mathscr{A} = \frac{1}{Cl}\int_{\text{band}} \log_{10}\left(\frac{I_0}{I}\right)\mathrm{d}\tilde{\nu} \qquad [56]$$

While the peakarea is a better measure of band intensity than peakheight in theory, the effect of absorption by neighboring bands leads to baseline errors that affect the calculation of area more adversely than peakheight. It is probably true to say that most contemporary quantitative determinations are made using peakheight.

The major interaction between the electromagnetic radiation and a molecule is due to the interaction of the electric field of the former, $\mathbf{E}$, with the dipole moment of the latter, $\boldsymbol{\mu}$. (Magnetic interactions are much smaller and generally are not important in vibrational spectroscopy, although they are responsible for IR circular dichroism.) The interaction gives rise to a time-dependent perturbation of the quantum states of a molecule equal to $-\boldsymbol{\mu}\cdot\mathbf{E}$. Using the results of time-dependent perturbation theory (Fermi's Golden Rule) it can be shown that the integrated absorptivity of a transition between initial state $\langle i|$ and final state $\langle f|$ for an isotropic system is given by

$$\mathscr{A} = \frac{N_{\mathrm{A}} 2\pi^2 \tilde{\nu}_{if}}{3\varepsilon_0 hc \ln_{\mathrm{e}} 10} |\langle i|\boldsymbol{\mu}|f\rangle|^2 \qquad [57]$$

where $\langle i|$ and $\langle f|$ are the initial and final states of the transition, $\boldsymbol{\mu}$ is the molecular dipole moment operator, N_{A} is Avogadro's number, $\bar{\nu}_{if}$ is the wave number corresponding to the band center, ε_0 is the permittivity of free space, h is Planck's constant, and c is the speed of light. The quantity

$$\langle i|\boldsymbol{\mu}|f\rangle \left[\equiv \int \boldsymbol{\Psi}_i^0 \boldsymbol{\mu} \boldsymbol{\Psi}_f \,\mathrm{d}\tau\right] \qquad [58]$$

is known as the electric dipole transition moment and its magnitude determines the intensity of a transition.

The appearance of $\ln_{\mathrm{e}} 10$ in eqn [57] is to be consistent with the definition of absorbance using base-10 logs. Often the equation will be seen without divisor, in which case it should be noted that the absorptivity has been defined using the natural log scale.

It should be noted that eqn [57] strictly only applies to dilute gases. In condensed phases refractive index effects become important.

Equation [57] often appears in Gaussian units. The Gaussian version is obtained by replacing ε_0 by $1/4\pi$ to give

$$\mathscr{A} = \frac{N_{\mathrm{A}} 8\pi^3 \tilde{\nu}_{if}}{3hc \ln_{\mathrm{e}} 10} |\langle i|\boldsymbol{\mu}|f\rangle|^2 \qquad [59]$$

The transition electric dipole moment in eqn [57] can be developed by invoking the Born–Oppenheimer approximation to express the total molecular wave function as a product of electronic and vibrational parts. (Rotational wave functions do not have to be included here since eqn [57] refers to an isotropic system. That is, the equation is a result of a rotational average which is equivalent to a summation over all the rotational states involved in the transition.) A general molecular state can now be expressed as the product of vibrational and electronic parts. Assuming that the initial and final electronic states are the ground state $|e_{\mathrm{g}}\rangle$,

$$|i\rangle = |i_{\mathrm{vib}}\rangle|e_{\mathrm{g}}\rangle \qquad [60a]$$

$$|f\rangle = |f_{\mathrm{vib}}\rangle|e_{\mathrm{g}}\rangle \qquad [60b]$$

and the transition moment becomes

$$\begin{aligned}\langle i|\boldsymbol{\mu}|f\rangle &= \langle v_i|\langle e_{\mathrm{g}}|\boldsymbol{\mu}|e_{\mathrm{g}}\rangle|v_f\rangle \\ &= \langle v_i|\boldsymbol{\mu}_{\mathrm{e}}|v_f\rangle\end{aligned} \qquad [61]$$

where $|v_i\rangle$ and $|v_f\rangle$ are the initial and final vibrational states, respectively, and $\boldsymbol{\mu}_{\mathrm{e}}$ is the permanent dipole moment of the molecule. The permanent dipole moment is now treated as a parametric function of the normal coordinates and expressed as a power series

$$\begin{aligned}&\langle v_i|\boldsymbol{\mu}_0 + \sum_{p=1}^{3N-6}\left(\frac{\partial\boldsymbol{\mu}}{\partial Q_p}\right)_0 Q_p \\ &\quad + \frac{1}{2}\sum_{p=1}^{3N-6}\sum_{r=1}^{3N-6}\left(\frac{\partial^2\boldsymbol{\mu}}{\partial Q_p \partial Q_r}\right)_0 Q_p Q_r + \cdots |v_f\rangle\end{aligned} \qquad [62]$$

Ignoring the quadratic terms (assuming the system is electrically harmonic) gives

$$\langle v_i|\boldsymbol{\mu}_{\mathrm{e}}^0|v_f\rangle + \sum_{p=1}^{3N-6}\langle v_i|\left(\frac{\partial\boldsymbol{\mu}_{\mathrm{e}}}{\partial Q_p}\right)_0 Q_p|v_f\rangle \qquad [63]$$

The total vibrational wave function $\langle v|$ is given by the product of the $3N-6$ normal coordinate wave functions

$$\langle v| = \langle v_1|\langle v_2|\langle v_3|\cdots\langle v_{3N-6}| \qquad [64]$$

where v_p is the vibrational quantum number of the pth normal vibration.

The total vibrational energy is given by

$$\begin{aligned}G(v_1, v_2\cdots v_{3N-6}) &= \left(v_1 + \frac{1}{2}\right)\tilde{\nu}_1 + \left(v_2 + \frac{1}{2}\right)\tilde{\nu}_2 \\ &\quad + \cdots + \left(v_{3N-6} + \frac{1}{2}\right)\tilde{\nu}_{3N-6}\end{aligned} \qquad [65]$$

Let the vibrational ground state $\langle 0|$ be represented by

$$\langle 0| = \langle 0_1|\langle 0_2|\langle 0_3|\cdots\langle 0_{3N-6}| \qquad [66]$$

and the state with the pth normal mode in the $v_p = 1$ state be represented by

$$\langle 1_p| = \langle 0_1|\langle 0_2|\langle 0_3|\cdots\langle 1_p|\cdots\langle 0_{3N-6}| \qquad [67]$$

Using the properties of harmonic oscillator wave functions (the Hermite polynomials) that

$$\langle 0|Q_p|1_r\rangle = \left(\frac{h}{8\pi^2 \nu}\right)^{1/2}\delta_{pr} \qquad [68]$$

where δ_{pr} is the Kronecker delta (which is unity if $p = r$ and zero otherwise), and

$$\langle 0|1_p\rangle = 0 \qquad [69]$$

Eqn [63] becomes

$$\left(\frac{h}{8\pi^2 v_p}\right)^{1/2}\left(\frac{\partial \boldsymbol{\mu}}{\partial Q_p}\right)_0 \qquad [70]$$

Substituting in eqn [57],

$$\mathscr{A} = \frac{N_A}{12\varepsilon_0 c^2 \ln_e 10}\left|\left(\frac{\partial \boldsymbol{\mu}}{\partial Q_p}\right)_0\right|^2 \qquad [71]$$

$$\left|\left(\frac{\partial \boldsymbol{\mu}}{\partial Q_p}\right)_0\right| = \left(\frac{12\varepsilon_0 c^2 \ln_e 10}{N_A}\right)^{1/2}\mathscr{A}^{1/2} \qquad [72]$$

Note that the sign of the derivative of the dipole moment cannot be determined directly by measuring the integrated absorbance of an IR band.

Equation [71] shows the origin of the gross selection rule that the dipole moment of a molecule must change in the course of a normal coordinate excursion for the vibration to absorb IR radiation. The transition moment in eqn [57] is only nonzero for the case where only one vibration is excited and for the situation in which the quantum number of the vibration involved changes by ± 1. Hence the selection rule given earlier in eqn [17].

Anharmonic Effects in Spectra of Polyatomic Molecules

Combination and difference bands Besides overtones, anharmonicity also leads to the appearance of combination bands and difference bands in the IR spectrum of a polyatomic molecule. In the harmonic case, only one vibration may be excited at a time (the transition dipole moment integral vanishes when the excited state is given by a product of more than one Hermite polynomial corresponding to different excited vibrations). This restriction is relaxed in the anharmonic case and one photon can simultaneously excite two different fundamentals. A weak band appears at a frequency approximately equal to the sum of the fundamentals involved. (Only approximately because the final state is a new one resulting from the anharmonic perturbation to the potential energy mixing the two excited state vibrational wave functions.)

A difference band is the result of a transition from an excited level of one normal vibration to a higher energy level of another vibration. The frequency of the difference band occurs at exactly the difference in the frequencies of direct transitions to the excited states involved from the vibrational ground state. (‘Exactly’ equal in this case because no new vibrational state is involved.)

Because difference bands originate from thermally populated excited states, they will be more frequently observed at lower frequencies and increase in intensity as the temperature is raised. (Transitions which occur from states other than the ground state are known as hot bands. They are generally weak in mid-IR spectra at room temperature due to vibrational energy gaps which are relatively large compared to kT).

Fermi resonance If an overtone or combination transition occurs with nearly the same frequency as a fundamental transition of the same symmetry, then the anharmonic term in the potential function causes the two vibrations to interact or ‘mix’. This is known as Fermi resonance. The extent of the mixing increase as the frequency difference decreases. The result is that the overtone or combination band acquires intensity through having some of the fundamental vibration mixed into it. Fermi resonance causes the two bands involved to split apart from the positions they would have occupied had no interaction occurred.

Symmetry of molecular vibrations Every normal coordinate of a molecule must transform according to an irreducible representation of the molecular point group. If the molecular geometry is known, then it is a routine matter to use the methods of group theory to deduce how many vibrations occur for each irreducible representation. The procedure is to assign three Cartesian displacement coordinates to each atom and to use the $3N$ coordinates as basis functions for a $3N \times 3N$ matrix representation of the point group. A reducible representation is then obtained by taking the trace of these matrices. This representation is then reduced to a sum of irreducible representations using

$$N_i = \frac{1}{h}\sum_{\hat{R}} \chi_i(\hat{R})\chi_{\text{red}}(\hat{R}) \qquad [73]$$

where N_l is the number of times that symmetry species i occurs, h is the order of the group, $\chi_i(\hat{R})$ is the character associated with symmetry species i and symmetry operation $\hat{R}$, and $\chi_{\text{red}}(\hat{R})$ is the character of the reducible representation associated with symmetry with symmetry operation $\hat{R}$.

One must then remove the irreducible representation which result from the three translational and three rotational degrees of freedom (two for a linear molecule). These can be identified from the character table of the molecular point group: the translational degrees of freedom transform as the functions x, y, and z (denoted T_x, T_y, T_z or x, y, z in the character tables); and the rotational degrees of freedom transform as the components of an axial vector (denoted R_x, R_y, and R_z in the character tables). The method is illustrated below for a bent triatomic molecule which belongs to the C_{2v} point group.

Figure 12A shows the molecule with three Cartesian coordinates associated with each atom. **Figure 12B** shows the effect of C_2 rotation on the coordinates. This transformation can be described in matrix form as

$$C_2 \begin{array}{c}\Delta x_1\\ \Delta y_1\\ \Delta z_1\\ \Delta x_2\\ \Delta y_2\\ \Delta z_2\\ \Delta x_3\\ \Delta y_3\\ \Delta z_3\end{array} = \begin{array}{c}-\Delta x_3\\ -\Delta y_3\\ \Delta z_3\\ -\Delta x_2\\ -\Delta y_2\\ -\Delta z_2\\ -\Delta x_1\\ -\Delta y_1\\ \Delta z_1\end{array} = \begin{array}{ccccccccc} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1\\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0\\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0\end{array} \begin{array}{c}\Delta x_1\\ \Delta y_1\\ \Delta z_1\\ \Delta x_2\\ \Delta y_2\\ \Delta z_2\\ \Delta x_3\\ \Delta y_3\\ \Delta z_3\end{array} \qquad [74]$$

From eqn [74] it can be seen that the trace of the C_2 matrix $\chi(C_2)$ is -1. Using the same procedure for the other symmetry operations, the complete reducible representation formed from the traces of the matrices corresponding to all the symmetry operations of the $C_{2\text{v}}$ group is given by

	$\chi_{\text{red}}(E)$	$\chi_{\text{red}}(C_2)$	$\chi_{\text{red}}(\sigma_v)$	$\chi_{\text{red}}(\sigma_{v'})$
Γ_{red}	9	-1	1	3

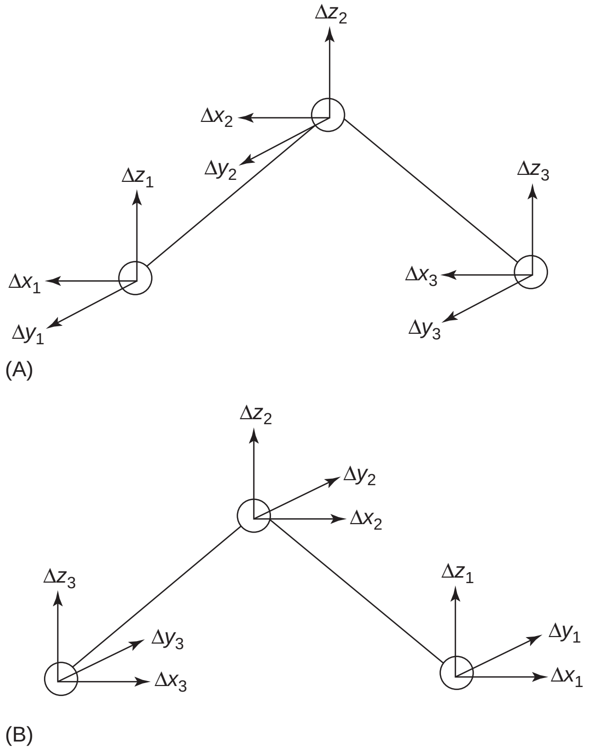


Figure 12 (A) Cartesian displacement coordinates of symmetric triatomic molecules. (B) Cartesian coordinates after C_2 rotation.

This representation can be reduced using eqn [73] and the information in C_{2v} character table. For example, the number of times N_{A_1} (the A_1 irreducible representation) is contained in Γ_{red} is given by

$$N_{A_1} = \tfrac{1}{4}[(1)(9) + (1)(-1) + (1)(1) + (1)(3)] = 3$$

The same procedure can be carried out for each symmetry species of C_{2v} to give

$$\Gamma_{\text{red}} = 3A_1 + A_2 + 2B_1 + 3B_2 \qquad [75]$$

From the C_{2v} character table, the three translations span A_1, B_1, and B_2, and the three rotations span A_2, B_1, and B_2. If these are taken away from eqn [75], this leaves $2A_1$ and B_2. The three normal vibrations of the bent triatomic molecule, therefore, span these irreducible representations. (See **Figure 9**: the antisymmetric stretch is B_2.)

This method may be simplified by noting that only Cartesian coordinates associated with atoms whose positions are unchanged by a symmetry operation may contribute to the trace of a matrix. If a symmetry operation $\hat{R}$ leaves the position of $U_{\hat{R}}$ atoms unchanged, then it can be shown that the character of the transformation matrix for not including transformations and rotations is given by

$$\chi(\hat{R}) = (U_{\hat{R}} - 2)(1 + 2\cos\phi) \qquad [76a]$$

for proper rotations, and

$$\chi(\hat{R}) = U_{\hat{R}}(-1 + 2\cos\phi) \qquad [76b]$$

for improper rotations (reflection, rotation–reflection, inversion) where ϕ is the angle through which the molecule is rotated. (Inversion through the center of symmetry is equivalent to an improper rotation through 180°, a reflection in a plane of symmetry is an improper rotation through 0°, and the identity element is a proper rotation through 0°.)

For the molecule $ClCH_3$, which belongs to the point group C_{3v}, the number of atoms left unchanged by the three symmetry operations I, C_3, and σ_v is

$$U_I = 5, \quad U_{C_3} = 2, \quad U_{\sigma_v} = 3 \qquad [77]$$

Using eqn [77] in eqn [76] gives:

$$\begin{array}{cccc} & \chi(I) & \chi(C_3) & \chi(\sigma_v) \\ \Gamma_{\text{red}} & 9 & 0 & 3 \end{array}$$

This representation can be reduced using eqn [73] to give $3A_1 + 3E$, Thus, $ClCH_3$ ($3N - 6 = 9$) has three totally symmetric vibrations and three doubly degenerate vibrations.

Symmetry Selection Rules

Using eqn [61] for a fundamental vibration Q_p it can be seen that the band intensity is proportional to the following transition dipole moment integral:

$$\langle 0|\mu_\alpha|1_p\rangle, \quad \alpha = x, y, z \qquad [78]$$

Unless the integrand is totally symmetrical the integral will be identically zero. Since the vibrational ground state is always totally symmetric, an IR fundamental will only be allowed when one or more components of the dipole moment operator span the same irreducible representation as the normal vibration. The components of the dipole moment operator μ_x, μ_y, and μ_z span the same irreducible representations as the functions x, y, and z, respectively. Hence a fundamental vibration will only be allowed if it spans the same irreducible representations as x, y, or z (T_x, T_y, or T_z).

It was shown before that a bent triatomic molecule undergoes two A_1 and one B_2 vibrations. Inspection of the C_{2v} character table revels that z spans A_1 and y spans B_2. Therefore, all the vibrations are allowed. This is not to say that all three bands will appear. The magnitude of the transitions dipole moments may be so small that a transition may not be observed.

If a molecule has several possible structures which belong to different molecular point groups then the methods above can be used for structure elucidation, especially in conjunction with the results of the analogous analysis for vibrational Raman bands. For example, if a molecule is known to have the molecular formula AB_4, a group theoretical analysis predicts that a tetrahedral molecule would have two active IR fundamentals, whereas a square planar molecule would have three.

Infrared Spectroscopy of Crystals

In molecular crystals the molecules are held together by van der Waals forces, and since these bonds are very much weaker than chemical bonds, the molecular vibrations are normally very similar to those of the free molecule. However, the crystal environment will generally lower the symmetry of the molecule, with the result that the degeneracy of vibrations may be lifted and vibrations, which were forbidden in the free molecule can become allowed in the crystal so that extra bands can appear. The formal treatment of the symmetry of vibrations in molecular crystals is obtained by considering the local symmetry in the crystal unit cell (site group analysis). A more complete theory, which includes lattice modes, is provided by factor group analysis.

Vibrations due to the crystal lattice occur in the far-IR from ~ 50 to $400\,\text{cm}^{-1}$. It is possible to distinguish between some molecular and lattice vibrations using the fact that molecular vibrations are relatively insensitive to the effects of temperature and pressure while the frequencies of lattice vibrations generally increase with a decrease in temperature and with an increase in pressure.

Infrared Linear Dichroism

For oriented single crystals there will generally be a difference in the absorption between two linearly polarized IR beams that are mutually orthogonal and orthogonal to the direction of propagations. The dichroic ratio is defined as

$$R = \frac{\int_{\text{band}} \varepsilon_\parallel(\tilde{\nu})\,d\tilde{\nu}}{\int_{\text{band}} \varepsilon_\perp(\tilde{\nu})\,d\tilde{\nu}} \qquad [79]$$

where $\varepsilon_\parallel$ and $\varepsilon_\perp$ refer to polarization parallel and perpendicular to the crystal axis, respectively. If the symmetry of the crystal is known, then the dichroic ratio can give information about the symmetry of the vibration.

Calculation of Normal Coordinates

Given the molecular geometry and a set of force constants for a polyatomic molecule, it is a routine matter to calculate the normal coordinates, a procedure known as normal coordinate analysis. Suites of computer programs are readily available that will calculate vibrational frequencies and the internal coordinate composition of each normal vibration. Most of the early calculation of vibration frequencies were made by Wilson's FG-matrix method, which is briefly summarized below. Today, a number of alternative techniques based on semiempirical methods, molecular mechanics, or density functional theory are also available, in convenient commercial software packages.

In the Wilson FG-matrix method, the problem is framed in internal coordinates rather than in

Cartesian displacement coordinates because the force constants involved are more meaningful in relation to the chemical structure of the molecule and are more readily transferred between similar molecules. Also, the theoretical procedure using internal coordinates are such that the translational and rotational motion of a molecule are automatically taken into account.

The F Matrix

In the harmonic approximation the potential energy of a molecule can be expressed as

$$2V = \sum_{ij} F_{ij} R_i R_j = \tilde{\mathbf{R}}\mathbf{F}\mathbf{R} \qquad [80]$$

where R_i are the internal coordinates, **F** is the $3N-6 \times 3N-6$ matrix formed by the force constants, **R** is a column vector formed by the internal coordinates and $\tilde{\mathbf{R}}$ is its transpose. (In order to have the same dimensions for all coordinates, and therefore all the force constants, the angle bending internal coordinates are sometimes scaled with a bond length, e.g., in water the angle bend coordinate $\Delta\alpha$ would become $r\Delta\alpha$ where r is the O–H bond length.)

Collectively, the F_{ij} are known as the force field of the molecule. These force constants are treated as empirical parameters whose values are optimized by obtaining the best fit of calculated to experimental results for vibrational frequencies, Coriolis coupling constants (which govern a type of coupling between rotational and vibrational motion), centrifugal distortion constants, and mean-square amplitudes of vibration. The simplest force field neglects all off-diagonal or interaction force constants. This valence force field (VFF), in general, gives poor results due to the poor number of adjustable parameters (the nonzero force constants).

In the generalized valence force field (GVFF) there is no neglect of the off-diagonal terms. However, for molecules of any appreciable size the number of force constants to be determined becomes too large to evaluate them with accuracy. Hence the simplified general valence force field (SGVFF) is frequently used in which all off diagonal force constants are set to zero except those involving two internal coordinates with common atoms.

The Urey–Bradley force field (UBFF) is also commonly used. This consists of diagonal stretch and bend force constants together with repulsive force constants representing nonbonded atom–atom interaction.

The G Matrix

The kinetic energy part of the vibrational problem is expressed in the **G** matrix whose elements depend on atomic masses and molecular geometry. It can be shown that the vibrational kinetic energy T is given by

$$2T = \tilde{\dot{\mathrm{R}}}\mathrm{G}^{-1}\dot{\mathrm{R}} \qquad [81]$$

where a dot denotes the time derivative.

The elements of the **G** matrix are given in **Figure 13**.

As an example, the **G** matrix for a nonlinear triatomic molecule (**Figure 14**) is given by

$$\mathbf{G} = \begin{bmatrix} \mu_1 + \mu_3 & \mu_3 \cos\phi & -\dfrac{\mu_3 \sin\phi}{r_2} \\ \mu_3 \cos\phi & \mu_2 + \mu_3 & -\dfrac{\mu_3 \sin\phi}{r_1} \\ -\dfrac{\mu_3 \sin\phi}{r_2} & \dfrac{\mu_3 \sin\phi}{r_1} & \dfrac{\mu_1}{r_1^2} + \dfrac{\mu_2}{r_2^2} + \mu_3\left(\dfrac{1}{r_1^2} + \dfrac{1}{r_2^2} - \dfrac{2\cos\phi}{r_1 r_2}\right) \end{bmatrix} \qquad [82]$$

(The exact from of the elements of **G** depends on whether scaled or unscaled coordinates are being used. The above is for unscaled.)

The Secular Equation

The relationship between internal coordinates and normal coordinates is defined as

$$\mathbf{R} = \mathbf{L}\mathbf{Q} \qquad [83]$$

It can be shown that the matrix vibrational secular equation is given by

$$\mathbf{G}\mathbf{F}\mathbf{L} = \mathbf{L}\mathbf{\Lambda} \qquad [84]$$

where A is the diagonal eigenvalue matrix and **L** is the matrix of eigenvectors of the matrix product **GF**. This last equation is solvable when

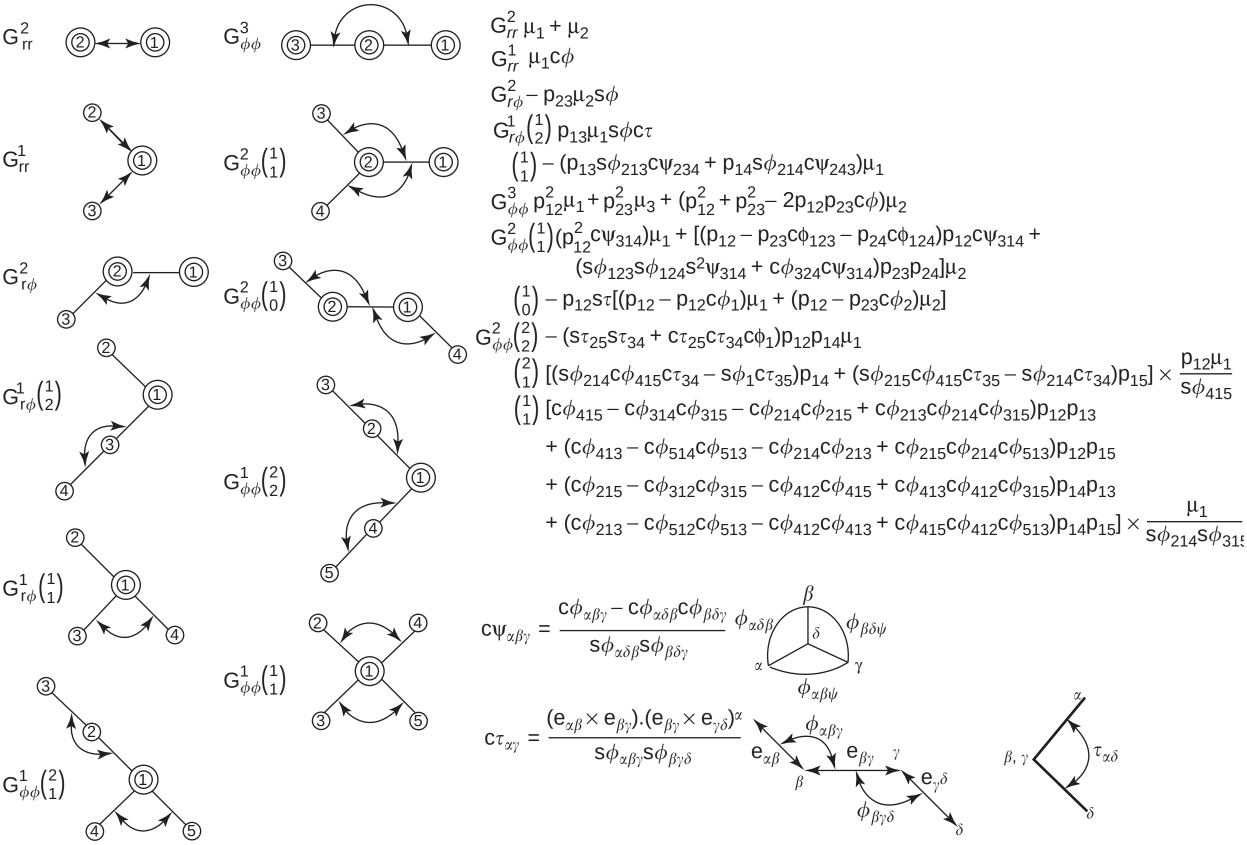
$$|\mathbf{G}\mathbf{F} - \mathbf{E}\lambda| = 0 \qquad [85]$$

where **E** is the unit matrix and λ is a root of the secular polynomial. There will be $3N-6$ nonzero roots, which are equal to the squares of vibrational angular frequencies. So the problem is essentially the diagonalization of **GF**, a process which is easily carried out by computer using numerical methods.

From eqn [83] we have

$$\mathbf{Q} = \mathbf{L}^{-1}\mathbf{R} \qquad [86]$$

so that the elements of $\mathbf{L}^{-1}$ can be used to obtain a picture of the normal vibration in terms of the internal coordinates. However, the reported results of a normal coordinate analysis often include the potential energy distribution (PED) for this information. The PED is the fraction of the potential energy



$$G_{rr}^2\ \mu_1 + \mu_2$$
$$G_{rr}^1\ \mu_1 c\phi$$
$$G_{r\phi}^2 - p_{23}\mu_2 s\phi$$
$$G_{r\phi}^1\binom{1}{2}\ p_{13}\mu_1 s\phi c\tau$$
$$\binom{1}{1} - (p_{13}s\phi_{213}c\psi_{234} + p_{14}s\phi_{214}c\psi_{243})\mu_1$$
$$G_{\phi\phi}^3\ p_{12}^2\mu_1 + p_{23}^2\mu_3 + (p_{12}^2 + p_{23}^2 - 2p_{12}p_{23}c\phi)\mu_2$$
$$G_{\phi\phi}^2\binom{1}{1}(p_{12}^2 c\psi_{314})\mu_1 + [(p_{12} - p_{23}c\phi_{123} - p_{24}c\phi_{124})p_{12}c\psi_{314} + (s\phi_{123}s\phi_{124}s^2\psi_{314} + c\phi_{324}c\psi_{314})p_{23}p_{24}]\mu_2$$
$$\binom{1}{0} - p_{12}s\tau[(p_{12} - p_{12}c\phi_1)\mu_1 + (p_{12} - p_{23}c\phi_2)\mu_2]$$
$$G_{\phi\phi}^2\binom{2}{2} - (s\tau_{25}s\tau_{34} + c\tau_{25}c\tau_{34}c\phi_1)p_{12}p_{14}\mu_1$$
$$\binom{2}{1}\ [(s\phi_{214}c\phi_{415}c\tau_{34} - s\phi_1 c\tau_{35})p_{14} + (s\phi_{215}c\phi_{415}c\tau_{35} - s\phi_{214}c\tau_{34})p_{15}] \times \frac{p_{12}\mu_1}{s\phi_{415}}$$
$$\begin{aligned}\binom{1}{1}\ [&c\phi_{415} - c\phi_{314}c\phi_{315} - c\phi_{214}c\phi_{215} + c\phi_{213}c\phi_{214}c\phi_{315})p_{12}p_{13} \\ &+ (c\phi_{413} - c\phi_{514}c\phi_{513} - c\phi_{214}c\phi_{213} + c\phi_{215}c\phi_{214}c\phi_{513})p_{12}p_{15} \\ &+ (c\phi_{215} - c\phi_{312}c\phi_{315} - c\phi_{412}c\phi_{415} + c\phi_{413}c\phi_{412}c\phi_{315})p_{14}p_{13} \\ &+ (c\phi_{213} - c\phi_{512}c\phi_{513} - c\phi_{412}c\phi_{413} + c\phi_{415}c\phi_{412}c\phi_{513})p_{14}p_{15}] \times \frac{\mu_1}{s\phi_{214}s\phi_{31}}\end{aligned}$$

$$c\psi_{\alpha\beta\gamma} = \frac{c\phi_{\alpha\beta\gamma} - c\phi_{\alpha\delta\beta}c\phi_{\beta\delta\gamma}}{s\phi_{\alpha\delta\beta}s\phi_{\beta\delta\gamma}}$$

$$c\tau_{\alpha\gamma} = \frac{(e_{\alpha\beta} \times e_{\beta\gamma}).(e_{\beta\gamma} \times e_{\gamma\delta})^{\alpha}}{s\phi_{\alpha\beta\gamma}s\phi_{\beta\gamma\delta}}$$

Figure 13 Representation of common elements of the **G** matrix. Key: atoms common to both coordinates are double circles in horizontal line; number of common atoms as superscript; atoms above horizontal belong to first coordinate; those below belong second; $\binom{n}{m}$ – n and m are numbers of (noncommon) atoms above horizontal on left and below horizontal on left, respectively. c, cos; s, sin; $\rho_{\alpha\beta} = 1/r_{\alpha\beta}$; $\mu_\alpha = 1/\text{mass}\,\alpha$.

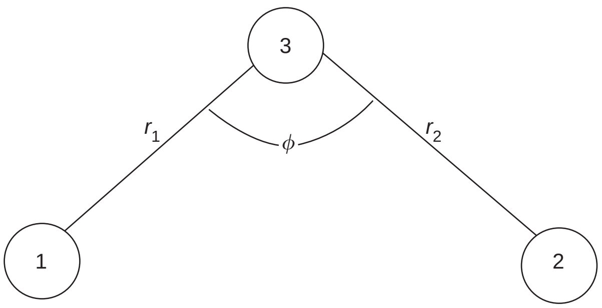


Figure 14 Nonlinear triatomic molecule.

of a normal mode contributed by each force constant F_{ij}. The diagonal elements of this distribution for the major components of a normal vibration are quoted as a percentage. For vibration Q_p and internal coordinate R_i

$$\text{PED}\,(R_i) = \left(\frac{100F_{ii}L_{ip}^2}{\sum_i F_{ii}L_{ip}}\right)\% \qquad [87]$$

The sum of the diagonal elements in the PED can exceed 100% due to the neglect of the off-diagonal contributions.

Use of Symmetry

When a molecule possesses symmetry the vibrational problem may be simplified by transforming the internal coordinates to symmetry coordinates. A vibration of a certain symmetry will be composed solely of symmetry coordinates belonging to the same symmetry species.

The transformation to symmetry coordinates $\mathbf{R}^S$ is given by

$$\mathbf{R}^S = \mathbf{UR} \qquad [88]$$

The symmetry coordinates and hence the coefficients of the (unitary) symmetrization matrix are obtained by applying symmetry projection operators to the internal coordinates. For irreducible representation i

$$R_i^S = N \sum_{\hat{R}} \chi_i(\hat{R})\hat{R} \times R \qquad [89]$$

where N is a normalization factor.

A similarity transformation using **U** is carried out on the **F** and **G** matrices

$$\mathbf{F}^S = \mathbf{UF\tilde{U}} \qquad [90a]$$

$$\mathbf{G}^S = \mathbf{UG\tilde{U}} \qquad [90b]$$

The symmetrization process produces the block-factored matrices $\mathbf{F}^S$ $\mathbf{G}^S$. Hence the product $\mathbf{G}^S\mathbf{F}^S$ will be block-factored and each block may be diagonalized separately.

Isotopic Substitution in Polyatomic Molecules: The Teller–Redlich Product Rule

Observation of the changes in frequency that occur in a vibrational spectrum as a result of isotopic substitution of one or more atoms is an important method for assessing the accuracy of molecular force fields. Isotopic substitution is also important for making band assignments in large molecules: the only vibrations to be shifted will be those involving the isotopically substituted atoms.

For isotopic substitution in which the molecular point group is unchanged, the Teller–Redlich product rule links the two sets of vibrational frequencies. There is one product rule for each symmetry species of the molecule as follows

$$\frac{\Pi \nu}{\Pi \nu'} = \left\{ \left(\frac{M}{M'}\right)^t \left(\frac{I_x}{I'_x}\right)^{r_x} \left(\frac{I_y}{I'_y}\right)^{r_y} \left(\frac{I_z}{I'_z}\right)^{r_z} \Pi \left(\frac{m'}{m}\right)^a \right\}^{1/2} \qquad [91]$$

where a prime is used to distinguish properties of the two molecules and Π denotes a product. The products on the left-hand side include all vibrations in the particular symmetry species to which the equation applies. M is the molecular mass; t is the number of translations belonging to the symmetry species in question (which can be deduced using the methods described in the section on symmetry); I_x, I_y, and I_z are moments of inertia about the three Cartesian axes; r_x, r_y, and r_z are 1 if the respective rotation belongs to the symmetry species concerned and 0 otherwise; m is the mass of an atom which is a member of a set of symmetrically equivalent atoms and a is the number of external (rotational and translational) symmetry coordinates which these atoms give rise to. The product on the right-hand side involves all sets of symmetrically equivalent atoms.

See also: **Chemometrics and Statistics**: Optimization Strategies. **Chiroptical Analysis**. **Fourier Transform Techniques**. **Infrared Spectroscopy**: Sample Presentation; Near-Infrared. **Photoacoustic Spectroscopy**.

Further Reading

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Sample Presentation

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Introduction

Since an infrared spectrum can be recorded from almost any material, infrared spectroscopy is an extremely important analytical technique. Mid-infrared spectroscopy is used extensively in applications involving qualitative analysis, providing either functional group or structural information about a sample or fingerprinting (identifying) a material. There is also widespread use of the technique for quantitative purposes, since the absorbance of a band is proportional to the concentration of the species that gives rise to the absorption band.