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Theory of Molecular Vibrations. The Origin of Infrared and Raman Spectra

1.1 ELECTRONIC, VIBRATIONAL, ROTATIONAL AND TRANSLATIONAL ENERGY

In classical mechanics, a molecule can be seen as a collection of M nuclei and N electrons. Therefore, the system of $M + N$ particles has $3(N + M)$ degrees of freedom to describe its motions. First, one can fix in space the location of the heavy nuclei (fixed nuclei approximation). The symmetry of this spatial distribution of nuclei can be associated with a ‘molecular point group’, which is a symmetry group corresponding to a fixed point [the center of mass (CM)]. The $3N$ degrees of freedom describe the motion of the electrons around the frozen frame, and the corresponding energy of motion is the electronic energy E_e . We can regroup the nuclei and electrons into $3M$ effective atoms, and fix the origin of the system of coordinates in the CM of the molecule. The motion of this point in space is described by three degrees of freedom, and gives the translational energy of the molecule that is directly related to thermal energy. According to the equipartition principle, the energy is $3/2kT$, where k is the Boltzmann constant. For 1 mol of molecules, we multiply by Avogadro’s number, N_A , and k is simply replaced by $N_A k = R$, the gas constant,

and the thermal energy per mole is $3/2RT$. For the fixed molecule at the CM there are $3M - 3$ degrees of freedom. The fixed molecule can rotate, and to describe the rotation of a nonlinear molecule we need three degrees of freedom (two for a linear molecule). Therefore, we can eliminate six of the $3M$ coordinates and we are left with $3M - 6$ (or $3M - 5$) vibrational degrees of freedom to describe the motions of the nuclei (effective atoms), and the total energy of the molecule has been partitioned into electronic, vibrational, rotational and translational (thermal) [1–3]:

$$E_{\text{molecular}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}}$$

1.1.1 Electronic Structure of Molecules

The origin of electronic, vibrational and rotational spectroscopy is in the quantization of these energies, and we shall briefly refresh the quantum mechanical treatment of molecules [4,5]. In spectroscopy, the word molecule refers to a stable system of nuclei and electrons. When the total number of electrons differs from that of the positive charges, the system is said to be a molecular ion. When the number of electrons is odd, the system is called a free radical (a free radical is defined as a system with a nonzero spin). Nuclei and electrons have well-defined mass, charge and spin. Since molecules are made of nuclei and electrons, molecules have well defined mechanical (mass), electrical (charge) and magnetic (spin) properties. In particular, the ratio of the mass of the proton to the mass of the electron is 1836. Therefore, the mass of the nuclei is at least 1836 times larger than the mass of the electrons. This fact allows for the separate treatment of the motion of the electrons (electronic spectrum) from that of the nuclei (vibrational spectrum) [6].

The total molecular Hamiltonian, \hat{H}_{MOL} , describes a molecule isolated in space, that is, no external field is acting upon the molecule. The external potential V_{ext} equals zero. Further, the total molecular Hamiltonian is written solely in terms of the spatial coordinates, i.e. the spin variables are not included in the Hamiltonian. In the spinless molecular Hamiltonian, two terms can be distinguished:

$$\hat{H}_{\text{MOL}} = T + V \quad (1.1)$$

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Where T is the kinetic energy operator of all M nuclei and N electrons of the system:

$$T = -\frac{\hbar^2}{2m} \sum_{i=1}^N \Delta_i - \frac{\hbar^2}{2} \sum_{\alpha=1}^M \frac{1}{M_\alpha} \Delta_\alpha = T_e + T_n \quad (1.2)$$

where

$$\nabla \cdot \nabla = \nabla^2 = \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The subscript i represents the number of electrons, α is the number of nuclei, M_α is the mass of the nucleus α , T_e is the electronic kinetic energy operator and T_n is the nuclear kinetic energy operator. The terms of the potential energy operator V_T can be classified, as in the case of atoms, into two parts: electrostatic interactions and interactions between momenta:

$$V_T = -\sum_i^N \sum_\alpha^M \frac{z_\alpha e^2}{R_{i\alpha}} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{r_{ij}} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{z_\alpha z_\beta e^2}{R_{\alpha\beta}} + V' \quad (1.3)$$

where r_{ij} is the distance between two electrons i and j , $R_{i\alpha}$ is the distance between the electron i and the nucleus α and $R_{\alpha\beta}$ is the distance between two nuclei α and β . The first term is the electron–nuclear attraction, the second term is the electron–electron repulsion and the third term is the nuclear–nuclear repulsion. V' includes the interactions between the spin angular momenta of nuclei and electrons and the orbital angular momenta of electrons:

$$V' = V_{(\text{spin-orbit})} + V_{(\text{spin-spin})} \quad (1.4)$$

In what follows, only the electrostatic interactions will be taken into account; the interaction between momenta may be considered as a perturbation. Hence the potential energy operator (1.3) can be rewritten as

$$V = V_{ee} + V_{en} + V_{nn} \quad (1.5)$$

where V' has been neglected (later on it can be included as a perturbation to the basic electrostatic problem). The electrostatic potential energy

operator (1.5) is a function of the distances between nuclei and electrons only, and a separation of variables can be carried out on the stationary Schrödinger equation. This means that the three degrees of freedom corresponding to the CM of the system can be separated. Therefore, the Schrödinger equation is a differential equation of $3(N + M) - 3$ variables. Such an equation cannot be solved for most of molecular systems. Under these circumstances, a variety of approximate approaches are used. All these approximate methods have, however, a common starting point: the separation of nuclear and electronic motions, which is known as the Born–Oppenheimer or adiabatic approximation [3,4,7]. The foundation for the approach is the assumption of a large energy splitting between the electronic states. Notably, for molecules adsorbed on metal surfaces the use of the approximation may come into question [8].

1.2 SEPARATION OF NUCLEAR AND ELECTRONIC MOTIONS

The eigenfunction $\psi(r, R)$, with r being electron coordinates and R nuclear coordinates, in the stationary Schrödinger equation is approximated by a product:

$$\psi(r, R) = \Phi(r, R)\chi(R). \quad (1.6)$$

The function $\Phi(r, R)$ depends on R only in a parametric fashion and is known as the electronic wavefunction, and satisfies the completeness relation

$$\langle \Phi(r, R) | \Phi(r, R) \rangle = 1 \quad (1.7)$$

where the integration is only over electronic coordinates. The function $\chi(R)$ is known as the *nuclear wavefunction* and satisfies the condition

$$\langle \chi(R) | \chi(R) \rangle = 1. \quad (1.8)$$

Here the integration takes place over nuclear coordinates only. On the basis of the variational principle, it can be shown that the function $\Phi(r, R)$

is determined by

$$H_e \Phi = (T_e + V) \Phi = E_e(R) \Phi \quad (1.9)$$

where V is the electrostatic potential operator (1.5), $E_e(R)$ are the eigenvalues of the electronic equation and are functions of the nuclear coordinates in a parametric form.

The function $\chi(R)$ is the solution of the equation

$$H_n \chi(R) = [T_n + E_e(R)] \chi(R) = E \chi(R) \quad (1.10)$$

Where E is the total energy of the system. Equation (1.10) is known as the *nuclear equation*. Let us assume that the electronic equation has been solved for fixed values of nuclear coordinates R_0 . Each eigenvalue $E_e(R_0)$ depends on the nuclear coordinates as parameters. Let us take the lowest energy eigenvalue $E_e^0(R_0)$ and study its dependence with variations in nuclear coordinates. A plot of the $E_e^0(R_0)$ values against the internuclear distance in a diatomic case gives rise to well-known potential energy curves. For the case of more than two nuclei a potential energy surface (or hyper surface) is obtained. It is usually the analytical form of this dependence that is included in Equation (1.10) as a potential energy operator $E_e(R)$. For M nuclei there exist $3M$ nuclear coordinates. Assuming that the center of mass is entirely determined by the nuclei, the total number of nuclear coordinates is reduced to $3M - 3$. Of these $3M - 3$ nuclear coordinates, only three are needed to describe the rotation of a nonlinear system in a frame of reference mounted on the molecule with its origin at the center of mass. The other $3M - 6$ nuclear coordinates of a nonlinear molecule describe the vibrational motion of the nuclei within the molecule. For a linear molecule, these numbers are 2 for rotational coordinates and $3M - 5$ for vibrational coordinates. It can be seen that the nuclear Equation (1.10) may be subjected to a 'second' Born–Oppenheimer approximation that will allow one to separate a vibrational equation with eigenvalues E_v and a rotational equation with eigenvalues E_R . In a first approximation, then, the quantized energy of a fixed molecule can be represented as the sum of three parts: the electronic, the vibrational and the rotational energies:

$$E_{\text{TOTAL}} = E_e + E_v + E_R. \quad (1.11)$$

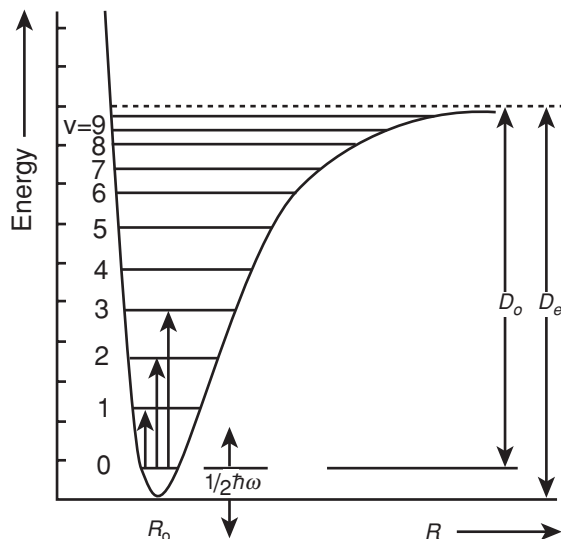


Figure 1.1 Potential energy curve of a diatomic molecule in the ground electronic state with vibrational energy levels. R is the internuclear distance. The electronic energy difference D_e is greater than D_0 , the dissociation energy or heat of dissociation

1.2.1 Example. The Potential Energy Function of Diatomic Molecules

A diatomic molecule can exist in the ground electronic state and also in a series of excited electronic states. Each electronic state is determined by an electronic wavefunction $\psi_e(r, R)$ and an electronic energy $E_e(R)$. The exact form or analytical expression of the function $E_e(R)$ for each electronic state of the molecule can be obtained by solving the electronic Equation (1.1) for different values of the internuclear distance R . A typical potential function and vibrational energy levels in the ground state of a diatomic molecule are shown in Figure 1.1. In molecular spectroscopy and statistical thermodynamics, it is common to set the origin equal to the energy minimum of the ground electronic state, i.e. $E_e^{(0)}(R_e) = 0$. This convention has been applied in Figure 1.1.

Once the potential energy curve has been found, the main characteristics of the electronic state are defined by:

1. The electronic energy value at the minimum of the potential energy curve; $E_e^{(0)}$.
2. The equilibrium internuclear distance, R_e , which is the internuclear distance at the minimum of the potential energy curve.

3. The potential energy of dissociation, D_e , which is the difference between the dissociation limit $E_e^{(\infty)}$ and the minimal value of the electronic energy $E_e^{(0)}$: $D_e = E_e^{(\infty)} - E_e^{(0)}$.
4. The second derivative of the electronic energy with respect to the internuclear distance; this quantity is known as *force constant* or *potential constant*:

$$k_e = \left[\frac{d^2 E_e^{(R)}}{dR^2} \right]_e$$

Different electronic states are characterized by different values for E_e , R_e , D_e , k_e and ω_e (the harmonic vibrational frequency). Typical values for diatomic molecules are given in Table 1.1.

1.3 VIBRATIONS IN POLYATOMIC MOLECULES

The same semiclassical treatment for the vibrational motion of the nuclei on the potential energy surface provided by the electronic energy function can be extended to polyatomic molecules [1,3,7,9,10]. For a system of N

Table 1.1 Observed spectroscopic constants and calculated potential constant for a selection of diatomic molecules

Molecule	$R_e/\text{\AA}$	$k_e/\text{mdyn \AA}^{-1}$	ω_e/cm^{-1}	D_0/eV
H ₂	0.741	5.755	4402.7	4.48
C ₂	1.242	12.160	1854.7	6.24
N ₂	1.097	22.940	2358.1	9.76
O ₂	1.207	11.768	1580.4	5.12
F ₂	1.417	4.451	891.9	1.60
Cl ₂	1.987	3.227	559.7	2.48
Br ₂	2.281	2.461	323.3	1.97
I ₂	2.665	1.720	214.5	1.54
LiH	1.595	1.026	1405.7	2.43
BH	1.232	3.048	2366.9	3.46
CH	1.120	4.478	2859.1	3.45
NH	1.047	5.41	3125.5	3.21
OH	0.970	7.793	3735.2	4.39
FH	0.917	9.651	4137.3	5.86
ClH	1.274	5.163	2991.0	4.43
BrH	1.406	4.166	2650.0	3.76
IH	1.609	3.140	2308.6	3.05
BO	1.205	13.658	1885.4	4.60
CO	1.128	19.019	2169.8	11.10
NO	1.150	15.948	1904.0	6.50

nuclei with nonlinear geometry there are $3N - 6$ vibrational degrees of freedom and for a linear equilibrium geometry there are $3N - 5$ vibrational degrees of freedom. Working within the model of the harmonic oscillator [3,7], the potential energy can be written as

$$V = \frac{1}{2} \sum_{i,j=1}^{3N-6} k_{ij} q_i q_j \quad (1.12)$$

where

$$k_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_{q_i=q_j=0} q_i q_j \quad (1.13)$$

or, in matrix form,

$$2V = \{q\} U_q \|q\|. \quad (1.14)$$

In the same way the kinetic energy is given by

$$2T = \{\dot{q}\} T_q \|\dot{q}\| \quad (1.15)$$

where the ‘dot’ notation represents differentiation with respect to time.

Replacing Equation (1.14) and (1.15) in the Lagrange equation:

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0 \quad (L = T_q - U_q)$$

a system of $n = 3N - 6$ linear differential equations is obtained:

$$\sum_{j=1}^n (t_{ij} \ddot{q}_j + k_{ij} q_j) = 0. \quad (1.16)$$

Considering a solution of the form

$$q_j = l_j \cos(\omega t + \delta) = l_j \cos(\sqrt{\lambda} t + \delta) \quad (1.17)$$

Equation (1.16) transforms to

$$\sum_{j=1}^n (k_{ij} - \lambda t_{ij}) l_j = 0 \quad (1.18)$$

or, in matrix form,

$$(U_q - \lambda T_q)L = 0. \quad (1.19)$$

The problem then reduces to finding the eigenvalues and eigenvectors of the secular equation

$$\det |U_q - \lambda T_q| = 0. \quad (1.20)$$

The molecular vibrational problem of polyatomic molecules is reduced to solving the secular Equation (1.20). This equation, however, is not convenient for practical computations. Thus, multiplying by T_q^{-1} from the left, $\det |T_q^{-1}U_q - \lambda I| = 0$, where I is the unit matrix. It has been assumed that the coordinates q form an independent set of coordinates, otherwise, T_q^{-1} would not exist. The last equation in matrix form is written as

$$T_q^{-1}U_q L = L\Lambda \quad (1.21)$$

and introducing Wilson's notation [4], $T_q^{-1} = G$ and $U_q = F$, Equation (1.21) finally gives

$$GFL = L\Lambda. \quad (1.22)$$

Equation (1.22) is usually known as the G -Wilson method for molecular vibration. G is thus the inverse of the kinetic energy matrix. Practical problems are related to the finding of G - and F -matrix elements.

In quantum mechanics, the harmonic approximation for a nonlinear molecule gives a discrete spectrum of energy values:

$$E_0 = \sum_{i=1}^{3N-6} \hbar\omega_i \left(v_i + \frac{1}{2} \right) \quad v_i = 0, 1, 2, \dots \quad (1.23)$$

where v_i is the vibrational quantum number and ω_i is the harmonic vibrational frequency. Potential energy surfaces for polyatomic molecules

can be obtained using *ab initio* Hartree–Fock (HF) and density functional theory (DFT) methods that are now common analytical tools for infrared and Raman spectral computations. Thereby the $3N - 6$ or $3N - 5$ normal modes of the harmonic approximation can be found. The symmetry of the potential function will allow for the reduction in size of the matrix (1.22) to a group of smaller matrices, one for each irreducible representation of the molecular point group. The methods of group theory will permit the calculation of the number of normal modes in each of the symmetry species and the extraction of their infrared or Raman activity.

The vibrational problem, or finding the infrared and Raman frequencies and intensities, is currently solved directly using quantum chemistry, and we will illustrate this computational approach using Gaussian 98. The detailed example at the end of this chapter was chosen to illustrate the applications to surface-enhanced vibrational problems.

1.4 EQUILIBRIUM PROPERTIES. DIPOLE MOMENT AND POLARIZABILITY

The interpretation of the observed infrared and Raman spectra using the basic models of the rigid rotator and harmonic oscillator are explained in Herzberg's book (Chapter III, p. 66) [2]. This approximation is the basis for the widespread application of vibrational spectroscopy as a tool for the detection, identification and characterization of molecules.

Two molecular properties that are defined by the charge distribution at the equilibrium geometry of the electronic state will change with variations in the internuclear distance (or any of the vibrational degrees of freedom in a polyatomic molecule): the dipole moment μ and the molecular polarizability α . The dipole moment is a vector, $\mu = \mu_x + \mu_y + \mu_z$, and for each of the components we can write a series expansion about the equilibrium geometry:

$$\mu = \mu_0 + \left(\frac{\partial\mu}{\partial q}\right)_0 q + \frac{1}{2} \left(\frac{\partial^2\mu}{\partial q^2}\right)_0 q^2 + \dots \quad (1.24)$$

where μ_0 represents the equilibrium value of the dipole moment. The displacement q has the form $q(t) = q_0 \cos(\omega_0 t)$. It will be seen that the infrared spectrum of fundamental vibrational frequencies is determined by the first partial derivative $(\partial\mu/\partial q)_0$ in the series [11,12]. Since there are three components for each vibration, each vibrational frequency has

up to three chances to be seen in the infrared spectrum. In other words, for a vibrational transition to be allowed in the infrared spectrum, it is necessary that at least one of these three components be different from zero. Notably the first term, the permanent dipole moment, μ_0 , will play no role in the probability of seeing a fundamental vibration in the infrared spectrum. The polarizability is a tensor, a response function that represents the volume and shape of the molecular electronic cloud [13]:

$$\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}. \quad (1.25)$$

For spectroscopic applications, the tensor is considered to be symmetric, reducing the total number of unknowns for each tensor to six. As was seen for the dipole moment, each of the components of the polarizability tensor can be written as a series expansion about the equilibrium geometry:

$$\alpha = \alpha_0 + \left(\frac{\partial\alpha}{\partial q}\right)_0 q + \frac{1}{2} \left(\frac{\partial^2\alpha}{\partial q^2}\right)_0 q^2 + \dots \quad (1.26)$$

where α_0 is the equilibrium value of the polarizability tensor element, and q represents the deviation from equilibrium. The first derivative, $\alpha' = (\partial\alpha/\partial q)_0$, is responsible for determining the observation of vibrational fundamentals in the Raman spectrum [13]. Since polarizability is a response function of the molecule to an external electric field, the polarizability and polarizability derivatives are tensors of the second rank, i.e. for a symmetric tensor each vibration has six chances to be observed in the Raman spectrum. In other words, for a vibrational transition to be allowed in the Raman spectrum, it is necessary that at least one of the six components of the derivative tensor be different from zero. The polarizability derivative tensor (the Raman tensor) is shown in Equation (1.27), where the first partial derivative is represented by α'_{ij} . The α' tensor has certain important properties: it is symmetric and its trace is invariant.

$$\alpha' = \begin{pmatrix} \alpha'_{xx} & \alpha'_{xy} & \alpha'_{xz} \\ \alpha'_{yx} & \alpha'_{yy} & \alpha'_{yz} \\ \alpha'_{zx} & \alpha'_{zy} & \alpha'_{zz} \end{pmatrix}. \quad (1.27)$$

1.5 FUNDAMENTAL VIBRATIONAL TRANSITIONS IN THE INFRARED AND RAMAN REGIONS

The description of the energy states and equilibrium properties of the molecule given above has prepared us for the final step in explaining infrared and Raman spectra: the interaction of the molecule with electromagnetic radiation [13]. The interaction of the electric vector of the electromagnetic radiation with the molecule will give rise to infrared absorption and inelastic scattering (Raman) spectra [14]. The simplest description of the electric field of light is that of plane harmonic waves, which can be written as

$$E(r, t) = E_0 \exp[i(kr - \omega t)] \quad (1.28)$$

where the vector E is perpendicular to k , the propagation direction. The direction of E in space determines its polarization and, thereby, for a wave traveling along z , the light polarization can be either E_x or E_y (light polarization is discussed in Chapter 2). We have a quantum object, the molecule, interacting with the radiation field, a plane wave, as described in classical electromagnetic theory. Thereby, the description of the process is semi-classical, and the interaction is known as the semi-classical theory of quantum transitions. The coupling operator between the quantum molecule and the radiation field is given by $H' = -p \cdot E$, where p is the dipole moment and E is the electric field vector. For infrared p is given by Equation (1.24) and for Raman by $p = \alpha E$. The probability for the absorption (or emission) of electromagnetic radiation per unit time is proportional to the square of the transition dipole moment matrix element along the direction of the light polarization: $|\langle \Psi_v | p \cdot E | \Psi_{v'} \rangle|$. For molecules in the gas phase with a random orientation, and where the average of the square of the angular part is one, the discussion can proceed with $|\langle \Psi_v | p | \Psi_{v'} \rangle|$.

The Raman effect can be explained in terms of the induced dipole moment, $p = \alpha E$, and using Equation (1.26) for the polarizability:

$$p = \alpha_0 E + \left(\frac{\partial \alpha}{\partial q} \right)_0 q E + \frac{1}{2} \left(\frac{\partial^2 \alpha}{\partial q^2} \right)_0 q^2 E + \dots \quad (1.29)$$

However, since $E = E_0 \cos(\omega t)$, and neglecting the second derivative,

$$p = \alpha_0 E_0 \cos(\omega t) + \left(\frac{\partial \alpha}{\partial q} \right)_0 q_0 \cos(\omega_0 t) E_0 \cos(\omega t) \quad (1.30)$$

where ω_0 is the natural vibrational frequency of the molecule and ω is the frequency of the radiation field. Using the trigonometric identity $\cos a \cdot \cos b = \frac{1}{2}[\cos(a + b) + \cos(a - b)]$, the induced dipole expression is

$$p = \alpha_0 E_0 \cos(\omega_0 t) + \alpha' q_0 E_0 \cos(\omega_0 - \omega)t + \alpha' q_0 E_0 \cos(\omega_0 + \omega)t. \quad (1.31)$$

The first term will account for the elastic Rayleigh scattering, the second for the Stokes Raman scattering and the third for the anti-Stokes Raman scattering.

For infrared absorption, neglecting the ‘electrical anharmonicity’ (second derivatives) in Equation (1.24), the transition between two vibrational states is $|\langle \Psi_v | \mu' | \Psi_{v'} \rangle|$, with $\mu' = (\partial \mu / \partial q)_0$. Dipole moment derivatives μ' form a three-dimensional vector, i.e. $\mu' = \mu'_x + \mu'_y + \mu'_z$.

The computation of the transition dipole moment matrix element will answer the question of whether a particular vibrational transition would be allowed or forbidden in the infrared or Raman spectrum. The results are known as the selection rules for infrared and Raman spectra. Ultimately, it should be remembered that for molecular systems other than gases (crystals, organized films, adsorbed molecules and others), the final observation of a particular vibrational transition in the infrared or Raman spectrum also depends on the direction of the incident radiation field.

1.6 SYMMETRY OF NORMAL MODES AND VIBRATIONAL STATES

The first task in the study of the vibrational spectrum of a given molecule should be the finding of the symmetry point group to which the equilibrium molecular geometry belongs. Group theory is discussed in specialized undergraduate textbooks, and we will review here only the basic elements relevant to vibrational spectroscopy [12,15,16]. Groups are a set of operations that satisfy the following four conditions: (i) one of the operations is the identity operation; (ii) each operation in the group has an inverse; (iii) the members of the group fulfill the associative law; and (iv) the product of two members of the group is also a member of the group. The symmetry operations that form the point groups transform the molecule into self-coincidence. Rotations are symmetry operations

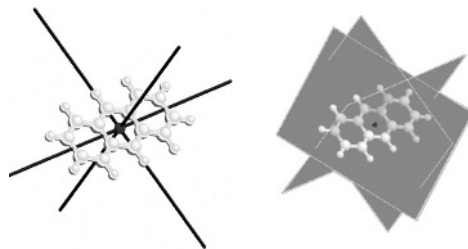


Figure 1.2 Axes of rotation and planes of symmetry in the anthracene molecule

that are called *proper* because they do not change the chirality of the molecule. Rotation–reflection operations are called *improper*, because they are not physically feasible and change the chirality. To carry out the operation of symmetry a *symmetry element* is necessary. This could be a point, a line or a plane. Therefore, symmetry operations are associated with symmetry elements. There are only four symmetry elements, the n -fold axis of rotation C_n , the n -fold rotation-reflection axis S_n , the plane σ and the center of inversion i . Finding them in a molecule allows the assignment of the molecule to one of the 32 point groups. Anthracene is a molecule belonging to the D_{2h} point group where the C_n , σ and i elements of symmetry can be found, and is used here for illustration.

Figure 1.2 (left) illustrates the two axes of rotations, C_2 , found in the molecule. In Figure 1.2 (right), the three planes of symmetry and the center of symmetry are highlighted. Each group has a finite number of symmetry operations and, with them, the group multiplication table can be generated. Since symmetry operations are transformations of coordinates, each of them can be represented by a three-dimensional matrix. For a molecule a reducible matrix representation Γ can be constructed that contains a number of irreducible representations Γ_i . The trace of the matrix in the irreducible representation is called the *character* of the irreducible representation and is denoted with the Greek letter $\chi(R)$, where R represents the symmetry operation [15]. Point group character tables are given in almost all spectroscopy textbooks [16]. Every group contains the identity operation E . The sum of the squares of the characters under E gives the order of the group. The character table for the D_{2h} group of anthracene is given in Table 1.2.

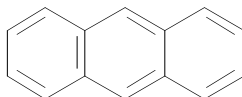


Table 1.2 Character table for the D_{2h} point group of anthracene

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	μ'	A'
A_g	+1	+1	+1	+1	+1	+1	+1	+1		$\alpha'_{xx}, \alpha'_{yy}, \alpha'_{zz}$
B_{1g}	+1	+1	-1	-1	+1	+1	-1	-1		α'_{xy}
B_{2g}	+1	-1	+1	-1	+1	-1	+1	-1		α'_{xz}
B_{3g}	+1	-1	-1	+1	+1	-1	-1	+1		α'_{yz}
A_u	+1	+1	+1	+1	-1	-1	-1	-1		
B_{1u}	+1	+1	-1	-1	-1	-1	+1	+1	μ'_z	
B_{2u}	+1	-1	+1	-1	-1	+1	-1	+1	μ'_y	
B_{3u}	+1	-1	-1	+1	-1	+1	+1	-1	μ'_x	

The sum of the squares under E is equal to 8, the order of the group. A is a one-dimensional representation symmetric with respect to rotation about the principal axis. B is a one-dimensional representation anti-symmetric with respect to rotation about the principal axis. g (*gerade*) is symmetric with respect to the inversion centre and u (*ungerade*) is antisymmetric with respect to the inversion centre. The subscripts 1 (symmetric), 2 and 3 (antisymmetric) are used solely with A and B .

After the point group has been identified, we proceed to the assignment of the fundamental vibrational frequencies (normal modes) to the irreducible representations of the group. For the molecule at hand, anthracene, with 24 atoms, we have $(3 \times 24) - 6 = 66$ normal modes. Since there are three internal cycles in the molecule, the total number of stretching vibrations is $24 - 1 + 3 = 26$, which is also the total number of chemical bonds in the molecule. The 26 stretching modes contain 10 high-frequency C-H stretchings and 16 C-C ring stretching modes. The other 40 modes are deformation of plane angles (angle between three atoms) and dihedral angles (angle between two planes). All of these normal modes expressed in terms of generalized coordinates (Lagrange's formalism) are set up using $3N$ ($N =$ number of atoms) Cartesian displacement coordinates. During the symmetry operation, a number of atoms are shifted while a few remain unshifted (n_R). Accordingly, only unshifted atoms can contribute to the character, and a new character χ_{vib} must be constructed to be added to the given character table. The calculation of this character is different for proper and improper rotations, and eliminating from the outset the pure translations and rotations to leave $3N - 6$ (or $3N - 5$) vibrations, the expressions are (note that reflections are improper rotations):

$$\chi_{\text{vib}}(C_n^k) = (n_R - 2)(1 + 2 \cos \theta) \quad (1.32a)$$

Table 1.3 Contributions of each operation to character

Proper rotation		Improper rotation	
C_n^k	$+1 + 2 \cos \theta$	S_n^k	$-1 + 2 \cos \theta$
$C_1^1 = E$	+3	$S_1^1 = S_1^1 = \sigma$	+1
C_2^1	-1	$S_2^1 = i$	-3
C_3^1, C_3^2	0	S_3^1, S_3^5	-2
C_4^1, C_4^3	+1	S_4^1, S_4^3	-1
C_5^1, C_5^4	$+\tau$	S_5^1, S_5^9	$\tau - 2$
C_5^2, C_5^3	$1 - \tau$	S_5^3, S_5^7	$-1 - \tau$
C_6^1, C_6^5	+2	S_6^1, S_6^5	0
C_7^1, C_7^6	$+1 + 2 \cos \frac{2\pi}{7}$	S_7^1, S_7^{13}	$-1 + \cos \frac{2\pi}{7}$
C_7^2, C_7^5	$+1 + 2 \cos \frac{4\pi}{7}$	S_7^3, S_7^{11}	$-1 + 2 \cos \frac{4\pi}{7}$
C_7^3, C_7^4	$+1 + 2 \cos \frac{6\pi}{7}$	S_7^5, S_7^9	$-1 + 2 \cos \frac{6\pi}{7}$
C_8^1, C_8^7	$1 + \sqrt{2}$	S_8^1, S_8^7	$-1 + \sqrt{2}$
C_8^3, C_8^5	$1 - \sqrt{2}$	S_8^3, S_8^5	$-1 - \sqrt{2}$
C_{10}^1, C_{10}^9	$1 + \tau$	S_{10}^1, S_{10}^9	$-1 + \tau$
C_{10}^3, C_{10}^7	$2 - \tau$	S_{10}^3, S_{10}^7	$-\tau$
C_{12}^1, C_{12}^{11}	$1 + \sqrt{3}$	S_{12}^1, S_{12}^{11}	$-1 + \sqrt{3}$
C_{12}^5, C_{12}^7	$1 - \sqrt{3}$	S_{12}^5, S_{12}^7	$-1 - \sqrt{3}$
C_{14}^1, C_{14}^{13}	$+1 + 2 \cos \frac{\pi}{7}$	S_{14}^1, S_{14}^{13}	$-1 + 2 \cos \frac{\pi}{7}$
C_{14}^3, C_{14}^{11}	$+1 + 2 \cos \frac{3\pi}{7}$	S_{14}^3, S_{14}^{11}	$-1 + 2 \cos \frac{3\pi}{7}$
C_{14}^5, C_{14}^9	$+1 + \cos \frac{5\pi}{7}$	S_{14}^5, S_{14}^9	$-1 + 2 \cos \frac{5\pi}{7}$
C_{16}^1, C_{16}^{15}	$1 + (2 + \sqrt{2})^{\frac{1}{2}}$	S_{16}^1, S_{16}^{15}	$-1 + (2 + \sqrt{2})^{\frac{1}{2}}$
C_{16}^3, C_{16}^{13}	$1 + (2 - \sqrt{2})^{\frac{1}{2}}$	S_{16}^3, S_{16}^{13}	$-1 + (2 - \sqrt{2})^{\frac{1}{2}}$
C_{16}^5, C_{16}^{11}	$1 - (2 - \sqrt{2})^{\frac{1}{2}}$	S_{16}^5, S_{16}^{11}	$-1 - (2 - \sqrt{2})^{\frac{1}{2}}$
C_{16}^7, C_{16}^9	$1 - (2 + \sqrt{2})^{\frac{1}{2}}$	S_{16}^7, S_{16}^9	$-1 - (2 + \sqrt{2})^{\frac{1}{2}}$

for proper rotations and

$$\chi_{\text{vib}}(S_n^k) = (n_R)(-1 + 2 \cos \theta) \quad (1.32b)$$

for improper rotations.

The contributions of each operation to character are tabulated for convenience and they are given in Table 1.3 (J.A. Salthouse and M.J. Ware. Cambridge University Press, 1972).

Table 1.4 Revised character table

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	μ'	α'
A_g	+1	+1	+1	+1	+1	+1	+1	+1		$\alpha'_{xx}, \alpha'_{yy}, \alpha'_{zz}$
B_{1g}	+1	+1	-1	-1	+1	+1	-1	-1		α'_{xy}
B_{2g}	+1	-1	+1	-1	+1	-1	+1	-1		α'_{xz}
B_{3g}	+1	-1	-1	+1	+1	-1	-1	+1		α'_{yz}
A_u	+1	+1	+1	+1	-1	-1	-1	-1		
B_{1u}	+1	+1	-1	-1	-1	-1	+1	+1	μ'_z	
B_{2u}	+1	-1	+1	-1	-1	+1	-1	+1	μ'_y	
B_{3u}	+1	-1	-1	+1	-1	+1	+1	-1	μ'_x	
X_{vib}	66	2	2	-2	0	24	4	0		
n_R	24	0	0	4	0	24	4	0		

We can rewrite the character table adding the character for the normal modes of vibration calculated using Equations (1.32) and Table 1.3, giving Table 1.4.

The number of normal modes a_i of each irreducible representation Γ_i is calculated as follows:

$$a_i = \frac{1}{h} \sum_R g_R \chi_i(R) \chi_{\text{vib}}(R) \quad (1.33)$$

where h is the order of the group and g_R is the number of operations in the R th class. The last two factors in Equation (1.33) are the character of the irreducible representation and the character of the normal modes, respectively.

For instance, for the totally symmetric modes, the number of normal modes is

$$a_{A_g} = \frac{1}{8} (66 \times 1 + 2 \times 1 + 2 \times 1 - 2 \times 1 + 24 \times 1 + 4 \times 1) = 12,$$

and the total representation is found to be

$$\Gamma = 12a_g + 11b_{1g} + 6b_{2g} + 4b_{3g} + 5a_u + 6b_{1u} + 11b_{2u} + 11b_{3u}. \quad (1.34)$$

Lower-case letters are used for species of normal vibrational modes according to IUPAC recommendations. The results obtained for the fixed molecule with an equilibrium geometry belonging to the point group

D_{2h} allows one to know their activity in the Raman and infrared spectra. The caveat is to make sure that the Cartesian coordinates used for the molecular system correspond to the system of coordinates used in the character table provided. Most character tables given in textbooks follow Mullikan's recommendations and notation. Character tables provide the species of symmetry for dipole moment derivatives μ'_i and polarizability derivatives α'_{ij} , in the last two columns of the table. Since anthracene is a centrosymmetric molecule, the mutual exclusion rule applies, and infrared-active modes are not Raman active and vice versa. Therefore, the infrared spectrum is given by

$$\Gamma_{\text{IR}} = 6b_{1u} + 11b_{2u} + 11b_{3u} \quad \text{and} \quad (5a_u)$$

which are silent modes.

The Raman spectrum can contain the following active normal modes:

$$\Gamma_{\text{Raman}} = 12a_g + 11b_{1g} + 6b_{2g} + 4b_{3g}.$$

This concludes our discussion on the vibrational spectrum using symmetry. The number and activity of the fundamental vibrational frequencies of each symmetry species are known. However, we have no information about the intensity with which each normal mode will be observed. The intensity of the infrared and Raman spectra can be computed *ab initio*, and this task will be shown with one more example before the conclusion of the present chapter.

1.7 SELECTION RULES

The conservation of angular momentum and parity impose restrictions on the quantum transitions of a molecule. These restrictions are collectively known as selection rules (reference 4, p. 294). In infrared spectroscopy, using the harmonic approximation, the relevant rules are the electric dipole selection rules. The description of the absorption of light by a molecule requires knowledge of the coupling of the electric dipole to an external electromagnetic field: $H' = -p \cdot E$. The probability for the absorption is therefore proportional to the square of the dipole moment matrix element along the direction E_j of light polarization. The amplitude of the transition is proportional to the scalar product $j \cdot \langle \psi_{v'} | p | \psi_v \rangle$. The selection rules for transitions between vibrational levels $\psi_{v'}$ and ψ_v

are determined by the matrix element $\langle \psi_v | \mathbf{p} | \psi_{v'} \rangle$. Symmetry reduces the electric dipole selection rules to the requirement of equal irreducible representations of the normal mode and one of the coordinates in \mathbf{p} .

The general *selection rule* for an allowed transition between two electronic or vibrational states connected by an operator \mathbf{p} requires that the direct product (triple product) has a totally symmetric component: $\Gamma_{\text{state}} \times \Gamma_{\mathbf{p}} \times \Gamma_{\text{state}'} = \text{totally symmetric}$ (reference 6, p. 129). For an isolated molecule or gas-phase spectrum, the triple product is directly given in the character table as we described in the example in Section 1.6. However, when there is a molecular orientation as in solids, adsorbates and films or low-temperature experiments, the scalar product $\mathbf{j} \cdot \langle \psi_v | \mathbf{p} | \psi_{v'} \rangle$ becomes the most important tool in the spectral interpretation of the observed intensities. Standard point groups can be used for adsorbed molecules and surface complexes, for which we can ignore all but one equilibrium configuration. The reduced representation of the μ' and α'_{ij} operators connecting spectroscopic infrared and Raman transitions are listed in the character table. For example, the electric dipole moment operator μ' transforms as x, y, z whereas the electric polarizability α'_{ij} (second rank tensor) operator transforms as $x^2, y^2, z^2, xy, xz, yz$. For crystals [12], adsorbates or thin solid films, there may exist spatial anisotropy introduced by molecular alignment. Therefore, the observed intensity of the allowed infrared and Raman modes can be modulated by a well-defined spatial orientation (polarization) of the incident electric field. This means that allowed infrared modes of a given symmetry species will be seen with an absorption intensity proportional to the square of the scalar product, $\mathbf{E} \cdot \mu'$, i.e. the square of the cosine of the angle between the polarization of the vector \mathbf{E} and the directional properties of the dynamic dipole μ' ($\partial\mu/\partial Q$). The corollary is that symmetry species of single crystals and adsorbed molecules of known orientation may be distinguished by the use of polarized radiation [12]. For the interaction Hamiltonian, the most notable practical applications are the following:

1. To describe infrared experiments on molecules adsorbed on reflecting metal surfaces one follows the realization that the light at the reflecting surface is highly polarized and, at the appropriate angle of incidence, the p-polarized component of the electromagnetic wave is three orders of magnitude larger than the parallel component. The latter is the basis for the polarization selection rules of specular reflection-absorption infrared spectroscopy (RAIRS). As a result, RAIRS is the most extensively used technique to determine the orientation of nanometric organic films [17,18].

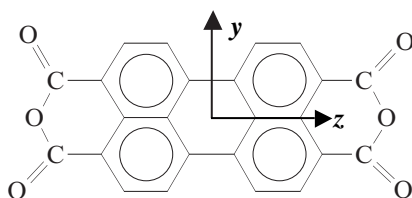
2. To describe Raman experiments on single crystals using plane polarized incident light, one follows the convention of Damen, Porto and Tell (Porto's notation) [19].
3. To describe Raman experiments on molecules adsorbed on metal surfaces using plane polarized radiation, one follows the convention of surface selection rules (propensity rules) [20,21].

Practical applications of the selection rules will be given in the corresponding chapters where we discuss reflection-absorption infrared spectroscopy (RAIRS), surface-enhanced Raman scattering (SERS) and surface-enhanced infrared absorption (SEIRA). However, we finish this chapter with an example of Raman and infrared intensity calculations with special attention to the allowed intensities for an oriented molecule.

1.8 THE EXAMPLE OF *AB INITIO* COMPUTATION OF THE RAMAN AND INFRARED SPECTRA

To illustrate the power of computational chemistry in vibrational spectroscopy, we take as a study case 3,4,9,10-perylenetetracarboxylic acid dianhydride (PTCDA) [22], a planar D_{2h} molecule ($C_{24}H_8O_6$, MW 392.347). There are 108 normal modes and the total irreducible representation calculated using the method described in Section 1.6 is

$$\Gamma = 19a_{1g} + 7b_{1g} + 10b_{2g} + 18b_{3g} + 8a_u + 18b_{1u}(z) + 18b_{2u}(y) + 10b_{3u}(x).$$



The procedures employed use the character table and follow the convention for the selection of the molecular axes for the D_{2h} point group. The conventions for other groups are listed at the end of this section. Therefore, the x -axis is perpendicular to the molecular plane and the z -axis passes through the greatest number of atoms. The latter convention should be strictly followed to maintain correspondence between the species of the total irreducible representation Γ and those given in the character table. This is of paramount importance when studying

molecular orientation on surfaces or solid-state materials. One of the most commonly encountered applications is in RAIRS or reflection Raman scattering from thin films on reflecting surfaces. Correspondingly, the same convention should be followed when interpreting SEIRA or SERS spectra. We will use here the infrared spectra of PTCDA to demonstrate the analytical applications of the quantum chemical computations. The PTCDA molecule was computed using Gaussian 98 [23] at the B3LYP/6-31G(d) level of theory. The initial geometry was minimized within a PM3 calculation, and the corresponding checkpoint file was used as a starting point in the DFT [B3LYP/6-31G(d)] computation. The calculated infrared spectra are compared with the infrared spectrum of the solid PTCDA dispersed in a KBr matrix. The calculated spectra should correspond closely to the infrared spectrum of PTCDA in the gas phase. There can be striking differences between the solid-state and the gas-phase spectra. The quantum chemical calculated frequencies are scaled, and the scaled wavenumbers agree better with the observed spectra. The top spectrum is presented without the scaling factor and the bottom computed frequencies have been scaled using the same factor for the entire spectrum, equal to 0.9614. The rationale and introduction of the numerical scaling factors are discussed in specialized reports [24] and the benefits of scaling can be seen in Figure 1.3.

Notably, the infrared spectrum as shown is composed of $8a_u + 18b_{1u}(z) + 18b_{2u}(y) + 10b_{3u}(x)$. However, the eight a_u are silent and there are 46 active fundamentals to be observed. The $10b_{3u}$ modes are observed in the spectral range below 1000 cm^{-1} ; they are the out-of-plane vibrations that will include twisting or torsion vibrational modes (τ) and wagging modes (ω). The wagging corresponds to changes in dihedral angles, angles between molecular planes. The $18b_{1u}(z) + 18b_{2u}(y)$ infrared-active fundamentals contain bond stretching (ν) modes and deformation or angle bending (δ) modes. In summary, the infrared spectrum shown in Figure 1.3 is the sum of three spectra, $18b_{1u}(z) + 18b_{2u}(y) + 10b_{3u}(x)$, and these spectra could be observed independently for fixed molecular orientation and using the appropriate polarized light. The latter will be demonstrated as an application of polarized infrared spectroscopy in the next chapter. The computed spectra separated by symmetry species are given in Figure 1.4. The same approach applies to computed Raman spectra. Each of the species of symmetry is plotted independently, and therefore the relative intensities are seen with respect to the strongest infrared active mode within the group. For plotting purposes, each calculated wavenumber has been given a full width at half-maximum (FWHM) of 5 cm^{-1} .

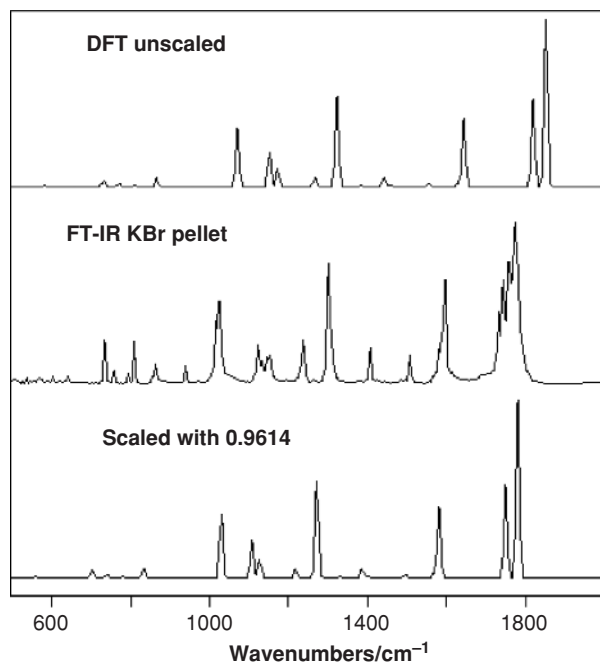


Figure 1.3 DFT [B3LYP/6-31G(d)]-calculated (unscaled and scaled) infrared spectra of PTCDA compared with the infrared spectrum of the solid material dispersed in a KBr matrix

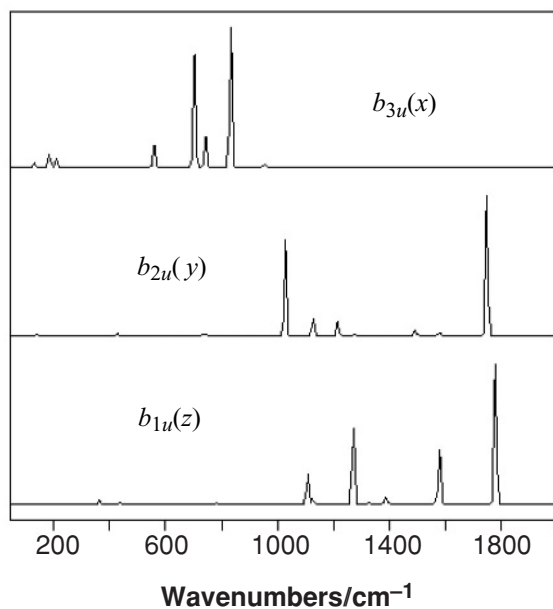


Figure 1.4 DFT-calculated spectra of infrared-active symmetry species in PTCDA

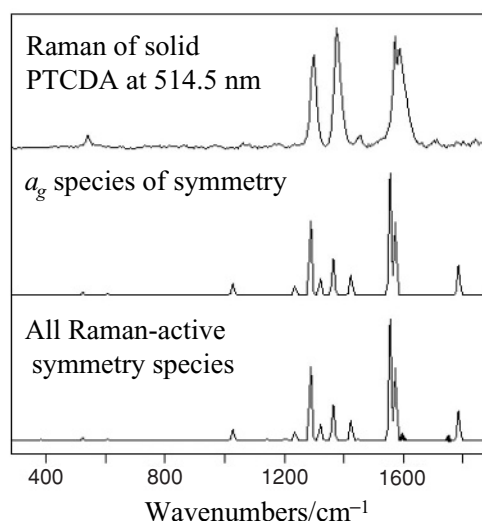


Figure 1.5 Raman spectrum of solid PTCDA recorded with the 514.5 nm laser excitation. DFT-calculated a_{1g} Raman spectrum, and computed spectrum with the sum of all allowed Raman fundamental vibrational modes

It can be speculated that for a perfectly oriented PTCDA molecule, infrared light polarized along x will produce the top spectrum in Figure 1.4. Similarly, infrared light polarized along y would give the middle infrared spectrum and finally the z -polarized infrared light will deliver the spectrum at the bottom. This explains the rapid development of polarization spectroscopy in solid state vibrational spectroscopy and surface vibrational techniques [12,25].

The Raman spectrum was calculated and the Raman-active fundamentals that can be observed are $19a_{1g} + 7b_{1g} + 10b_{2g} + 18b_{3g}$, or 54 bands can be recorded. The spectrum, recorded with 514.5 nm laser radiation, of a solid sample of PTCDA is shown in Figure 1.5 (top spectrum). The calculated spectrum, including all Raman-active species of symmetry, i.e. 54 fundamentals, is plotted at the bottom, for comparison. The agreement here is remarkable, despite the fact the excitation is near resonance (resonance Raman scattering) and the intensities may deviate considerably from those of the normal Raman scattering. The middle spectrum corresponds to the a_g species containing only 19 fundamental vibrational modes. It can be seen that the totally symmetric modes a_g are responsible for the intensity pattern observed in the Raman spectrum of PTCDA, and the other species have minor relative intensity in the Raman spectrum

averaged over all directions of space. The differences can be identified in the 1600–1800 cm^{-1} region, where two Raman bands of weak intensity are seen in the spectrum. However, as in the infrared, spatial molecular orientation and light polarization can produce Raman spectra with quite different intensity patterns [19].

1.8.1 Conventions for Molecular Axes

In the axial groups the z -axis is always chosen as the principal axis of symmetry.

The selection of the x - and y -axes in some groups remains arbitrary. In point groups C_{nv} , D_n and D_{nh} (where n is even), the B species are directly affected by this choice.

For point group C_{2v} , the x -axis is perpendicular to the molecular plane.

For point groups D_{4h} and D_{6h} , the C_2 axes will pass through the greatest number of atoms (or intersect the largest number of bonds).

For point groups C_{nv} with even n , the σ_v plane will pass through the greatest number of atoms (or intersect the largest number of bonds). To define x and y in these groups they may be chosen so that the x -axis lies in one of the σ_v planes.

1.9 VIBRATIONAL INTENSITIES

The probability of the dipole transition is proportional to the square of the magnitude of the transition dipole moment (or ‘dynamic dipole’) [3,7,12]. Working within the ground electronic state, i.e. during the transition there is no change in the molecular electronic states, the vibrational transition moments are defined by [3,7] $|\mu'|^2 = |(\mu)_{v'v''}|^2 = |\langle v' | \mu | v'' \rangle|^2$ for transitions in the infrared spectra and by $|\alpha'|^2 = |(\alpha)_{v'v''}|^2 = |\langle v' | \alpha | v'' \rangle|^2$ for transitions observed in the Raman spectra. Dipole moment and polarizability undergo infinitesimal changes during molecular vibrations. Near the equilibrium geometry, both molecular properties can be expanded as a Taylor series in the normal coordinates. Therefore, we write again here the expansion for the dipole moment and the polarizability:

$$p = \mu \text{ or } \alpha = p_0 + \sum_i^n \left(\frac{\partial p}{\partial Q_i} \right) Q_i + \frac{1}{2} \sum_{i,j}^n \left(\frac{\partial^2 p}{\partial Q_i \partial Q_j} \right) Q_i Q_j + \dots \quad (1.35)$$

Where Q_i is the i th normal coordinate belonging to the set of Q that diagonalizes the potential energy function and is associated with the harmonic frequency ω_i . The expressions (1.35) are used to calculate the transition dipole moments in $|\mu'| = |\langle v' | \mu | v'' \rangle|$ and $|\alpha'| = |\langle v' | \alpha | v'' \rangle|$. Since the functions of the harmonic oscillator are orthonormal, in the harmonic approximation the first term in Equation (1.35) gives zero for μ , and gives rise to the elastic Rayleigh scattering for α . In the harmonic approximation, the third term in both series is neglected and, thereby, the infrared and Raman spectra are completely determined by the first derivatives of the dipole moment and first derivatives of the polarizability. The calculation of the fundamental non-zero transition dipole moment is simply equal to

$$|\mu'| = |\langle v' | \left(\frac{\partial \mu}{\partial Q_i} \right) Q_i | v'' \rangle| = \left(\frac{\partial \mu}{\partial Q_i} \right) \left(\frac{h}{4\pi\omega_i} \right)^{\frac{1}{2}}. \quad (1.36)$$

When all the matrix elements are taken into account in the transition dipole, the final result is

$$|\mu'| = \left(\frac{\partial \mu}{\partial Q_i} \right) \left(\frac{h}{8\pi^2\nu_i} \right)^{\frac{1}{2}} (\nu_i + 1)^{\frac{1}{2}} \quad (1.37)$$

and its squared magnitude is given by

$$|\mu'|^2 = \left(\frac{\partial \mu}{\partial Q_i} \right)^2 \left(\frac{h}{8\pi^2\nu_i} \right) (\nu_i + 1). \quad (1.38)$$

Experimentally, the definition of the absorptivity is usually taken from the equation for the exponential attenuation for irradiance (Lambert's law): $I = I_0 e^{-\kappa z}$, where I_0 is the incident irradiance and I is the irradiance at depth z of the absorber. The frequency-dependent κ (kappa) is the extinction coefficient, sometimes called the absorption coefficient, and is a characteristic property of the material through which the light is passing. Let us consider the irradiance or radiant flux per unit of area of surface I (in W/m^{-2}) of a monochromatic beam of frequency ν traveling along the $+z$ direction with irradiance which is equal to the energy density multiply by its speed: $I_0(z) = c \times \rho(\nu, z)$, c being the speed of light. For the transition in a two-state system, with a density of oscillators in the lower state equal to N_1 , the number of photons absorbed in 1 within a distance dz and unit area is $B_{1,2}(\nu) N_1 \rho(\nu, z) dz$. Each absorption takes

an $h\nu$ amount of energy from the beam, and thereby the change in the irradiance is [7]:

$dI = -h\nu_{1,2}B_{1,2}(\nu)(N_1 - N_2)\rho(\nu, z)dz$. Using the expression for the initial irradiance I_0 , the change is

$$dI = -I_0 \frac{h\nu_{1,2}B_{1,2}(\nu)N_1}{c} dz.$$

Assuming that the attenuation is entirely due to absorption, the absorption coefficient is

$$\kappa(\nu) = \frac{h\nu_{1,2}B_{1,2}(N_1 - N_2)}{c}.$$

Since the Einstein coefficient for the absorption of a vibrating molecule (without rotations) is given in terms of the transition dipole moment [3,7]:

$$B_{\nu'\nu''} = \frac{8\pi^3}{3h^2} [|\langle \nu' | \mu_x | \nu'' \rangle|^2 + |\langle \nu' | \mu_y | \nu'' \rangle|^2 + |\langle \nu' | \mu_z | \nu'' \rangle|^2]$$

or in the SI system of units

$$B_{\nu'\nu''} = \frac{1}{6\epsilon_0\hbar^2} |\langle \nu' | \mu | \nu'' \rangle|^2.$$

With the help of Equation (1.38), an expression is found for the absorption coefficient using $B_{\nu'\nu''}$:

$$\kappa(\nu) = \frac{8\pi^3}{3ch} \nu_{1,2} (N_1 - N_2) |\langle \nu | \mu | \nu \rangle|^2. \quad (1.39)$$

Since the experimental infrared intensity is not a line, but a band with a well-defined FWHM, the corresponding integrated absorption coefficient is given by $A = \int_{\text{Band}} \kappa(\nu) d\nu$. In practice, the quantity A is used for the determination of $(\partial\mu/\partial Q_i)^2$. When the absorbance is proportional to concentration, the Beer extension of the Lambert law (Beer-Lambert law) can be formulated. The absolute infrared intensity of an absorption band is given by the integration over the band, at some standard pathlength

(I) and molecular concentration (c) of the sample [26]:

$$A = \frac{1}{cl} \int_{\text{Band}} \ln \left(\frac{I_0}{I} \right) dv. \quad (1.40)$$

Absorbance, is a term recommended for use with this measurement, in preference to absorbancy, optical density or simply extinction. Equating Equation (1.39) to the integrated absorption, at temperatures where $N_1 - N_2 = N_1$, the final results is

$$A = \frac{\pi N}{3c} \times \left[\left(\frac{\partial \mu_x}{\partial Q_i} \right)^2 + \left(\frac{\partial \mu_y}{\partial Q_i} \right)^2 + \left(\frac{\partial \mu_z}{\partial Q_i} \right)^2 \right] \quad (1.41)$$

It is therefore necessary to specify the units of concentration and length. The most commonly used units in chemistry are mol L⁻¹ and cm. The product concentration (moles cm⁻³) and pathlength (cm), shown as cl in Equation (1.40), has the units of mol cm⁻². The integral has dimensions of cm⁻¹, when the variable for the integration is wavenumber. The units for A are then cm² mol⁻¹/cm⁻¹ or cm mol⁻¹. However, these units produce large numerical values, on the order of 10⁶ for fundamentals. By changing cm to km (multiplying by 10⁻⁵), the intensities can be expressed by numbers in the range from 0 to 10². At present, the absolute integrated intensities A are commonly reported in km mol⁻¹ and these units are also used in quantum chemical computations of infrared intensities. Two alternative units to consider are the ‘dark’ and the ‘intensity unit’, where 1 dark = 10³ cm mol⁻¹ and the ‘intensity unit’ = 10⁷ cm mol⁻¹ [26]. A thorough discussion of the experimental units and conversion factor can be found in a review by Pugh and Rao [27], and for liquid-state band intensities in Ratajczak and Orville-Thomas [28]. Conversion factors are given in Table 1.5.

Table 1.5 Conversion factors to km mol⁻¹ [11]

Intensity unit for A	Concentration units	Conversion factor
cm mol ⁻¹	mol cm ⁻³	10 ⁻⁵
cm/mmol ⁻¹	mol L ⁻¹	10 ⁻²
cm ⁻² atm (273/K)	atm	0.224
cm ⁻² atm, (298/K)	atm	0.245
s ⁻¹ /cm ⁻¹ /atm ⁻¹	atm	7.477 × 10 ⁻¹²

Working within the harmonic approximation, the computation of the magnitude of the dipole moment derivatives can be directly evaluated from the integrated intensities:

$$\left(\frac{\partial\mu}{\partial Q_i}\right)^2 = \frac{3c}{\pi N} \times A \quad (1.42)$$

where the constant depends on the units selected for the calculation. There is, however, an alternative to the integrated absorption coefficient, which has been recommended to be used for work on infrared intensities, namely the integral

$$\Gamma = \frac{1}{cl} \int_{\text{Band}} \ln\left(\frac{I_0}{I}\right) d\ln\nu. \quad (1.43)$$

The relationship between the two integrals is $A = \Gamma \times \nu_i$, where ν_i is the band center. The corresponding dipole moment derivative is related to Γ :

$$\left(\frac{\partial\mu}{\partial Q_i}\right)^2 = \frac{3c\nu_i}{\pi N_0} \times \Gamma. \quad (1.44)$$

In the presence of degeneracy, the right-hand side should be multiplied by the degeneracy factor. An important practical difference is that the units for Γ are $\text{cm}^2\text{mol}^{-1}$, whereas the units of A are cm mol^{-1} . The attractive simplicity of A is in the fact that it is directly proportional to the dipole moment derivative:

$$\left(\frac{\partial\mu}{\partial Q_i}\right)^2 = \frac{3c}{\pi N_0} \times A. \quad (1.45)$$

If A_n is given in km/mol^{-1} , then the absolute value of the dipole moment derivative is given by

$$\left(\frac{\partial\mu}{\partial Q_n}\right)_0 = 0.0320 \times \sqrt{A_n}. \quad (1.46)$$

The HCl band at 2886 cm^{-1} has an integrated absorption $A = 33.2 \text{ km/mol}^{-1}$. For the commonly used units of electric dipole moment, debye, the conversion factor is $1\text{D} = 3.3356 \times 10^{-30} \text{ Cm}$. Correspondingly, the units of the dipole moment derivatives are $1\text{D } \text{\AA}^{-1} = 3.3356 \times 10^{-20} \text{ N}^{\frac{1}{2}} \text{ C g}^{-\frac{1}{2}} = 0.2083 \text{ e}(\text{amu})^{-\frac{1}{2}}$ and $1 \text{ cm}^{\frac{3}{2}} \text{ s}^{-1} = 2.684 \times 10^{-3} \text{ e}(\text{amu})^{-\frac{1}{2}}$.

Table 1.6 Infrared optical cross-sections for fundamental vibration bands of methane and ethane (see Gussoni, in reference 11)

Molecule	Wavenumbers/cm ⁻¹	Γ/cm ² mol ⁻¹	Cross-section/cm ²
CH ₄	3019	2310	3.83 × 10 ⁻²¹
	1306	2554	4.24 × 10 ⁻²¹
CH ₃ CH ₃	2974	4113	6.83 × 10 ⁻²¹
	2915	1640	2.72 × 10 ⁻²¹
	1460	910	1.51 × 10 ⁻²¹

Another measure of intensity is the ‘integrated optical cross-section’ which can be obtained from the A values in km mol⁻¹ by dividing by the factor 6.022×10^{20} , or the most commonly used ‘optical cross-section’, obtained by dividing the Γ values (in cm²mol⁻¹) by 6.022×10^{23} .

Infrared cross-sections for the fundamental bands of methane and ethane are given in Table 1.6.

1.9.1 Raman Intensities

$$p = \alpha E$$

where E = electric field (NC⁻¹ or V m⁻¹) and p = induced electric dipole moment of a molecule, which is a vector pointing from the negative to the positive charge (C m⁻¹) the unit debye (D) is also used: 1 D = 3.336×10^{-30} C m. Using C V = J, α , the polarizability has the units C² m² J⁻¹ or m³. For instance, the average polarizability of CCl₄ is 10.5×10^{-30} m³.

Absolute Raman intensities are reported in terms of the polarizability derivative α' . For instance, the derivative of the polarizability with respect to the normal coordinate for the 2914 cm⁻¹ band of methane has been reported to be [29], $45\alpha^2 = 190 \cdot N_a \cdot 10^{-32} \text{ cm}^4 \cdot \text{g}^{-1}$ (or $190 \text{ \AA}^4 \text{ amu}^{-1}$). The Raman intensities in quantum chemistry computations are commonly reported in $\text{\AA}^4 \text{ amu}^{-1}$, angstroms (10^{-10} meter or also known as tenthmeter) and unified atomic mass units, $1.660531 \cdot 10^{-24}$ g.

1.10 DEFINITION OF CROSS-SECTION

Experimentally, the spontaneous inelastic Raman scattering (RS), the total Stokes scattered light, averaged over all random molecular

orientations, I_{RS} (photons s^{-1}), is proportional to the incoming flux of photons, I_0 (photons $s^{-1} cm^{-2}$): $I_{RS} = \sigma_{RS} I_0$.

The proportionality constant, the Raman cross-section σ_{RS} , has the dimensions of cm^2 and is a function of the frequency of excitation. The Raman cross-section is proportional to the square of the polarizability derivative for the $m \rightarrow n$ vibrational transition, $\alpha' = (\partial\alpha/\partial Q)_0$, and the fourth power of the scattering frequency ω_S : $\sigma_{RS} = C\omega_S^4 |\alpha'_{mm}|^2$. C contains numerical constants.

The efficiencies of the absorption and scattering processes are determined by the function ‘cross-section’, which is the meeting point of experiments with theory. There are three common quantities used by spectroscopists. The spectral differential cross-section is the rate of removal of energy from the light beam into a solid angle $d\Omega$ and frequency interval $d\omega$: $d^2\sigma/d\Omega d\omega$. Integration restricted to include a single intensity peak gives the differential cross-section $d\sigma/d\Omega$.

Integration of the differential cross-section over all directions in space gives the cross-section σ . The units of σ are m^2 , and the cross-section can be interpreted as the target area presented by a molecule (particle) for scattering or absorption. The definition is easily extended to emission processes. Typical values of the cross-section for the spectroscopic processes of interest are illustrated in the Figure 1.6, and specific values for given molecular vibrations can be found in modern books [30] with reference to the original work. For instance, the cross-section σ for absorption in the infrared is ca $10^{-20} cm^2$. Therefore, in Figure 1.6, the value assigned to the y-axis for the infrared cross-section is $-\log(10^{-20}) = 20$. The absolute Raman cross-section for the $666 cm^{-1}$ mode of

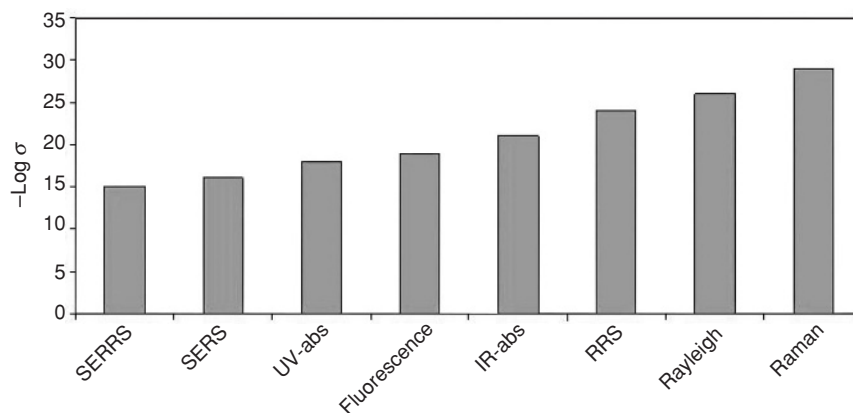


Figure 1.6 A plot of $-\log \sigma$ (cross-section in cm^2 per molecule) for the most common optical processes in linear spectroscopy

Table 1.7 Excitation wavelength λ (nm) and σ_R ($\times 10^{28}$ cm² or $\times 10^{12}$ Å²).

λ	σ_R^a
532.0	0.660 \pm 0.1
435.7	1.660 \pm 0.5
368.9	3.760 \pm 0.3
355.0	4.360 \pm 0.4
319.9	7.560 \pm 0.3
282.4	13.06 \pm 4.0

^aAfter Foster *et al.* [31]. Error represents one standard deviation from the mean.

Table 1.8 Approximate order of magnitude for cross-sections σ (per molecule) for various possible processes in spectroscopy

Process	Cross-section of	σ/cm^2
Absorption	Ultraviolet	10 ⁻¹⁸
Absorption	Infrared	10 ⁻²¹
Emission	Fluorescence	10 ⁻¹⁹
Scattering	Rayleigh scattering	10 ⁻²⁶
Scattering	Raman scattering	10 ⁻²⁹
Scattering	Resonance Raman	10 ⁻²⁴
Scattering	SERRS	10 ⁻¹⁵
Scattering	SERS	10 ⁻¹⁶

chloroform [31] has been determined using several-laser lines. The results are given in Table 1.7.

The approximate cross-sections for the most common spectroscopies are listed in Table 1.8.

The estimated SERS cross-section is taken from the review by Kneipp *et al.* [32]. The SERRS cross-section is the one reported by Nie and Emory [33] for Rhodamine 6G (R6G) excited in resonance at 514.5 nm. Later, Michaels *et al.* [34] reported an average SERRS cross-section for R6G of 2×10^{-14} cm² at 514.5 nm. The SERS/SERRS cross-sections correspond to experimental results with the best observed enhancement factors.

1.11 THE UNITS OF ENERGY AND FORCE CONSTANTS

Force constant: $k_e = 4\pi^2\mu c^2\omega^2$, where ω is the molecular vibration in wavenumbers (cm⁻¹) and $4\pi^2\mu c^2$ is the classical force constant

factor: $4\pi^2\mu c^2 = 5.98180 \times 10^{-9} \text{ N m}^{-1} = 5.98180 \times 10^{-6} \text{ N cm}^{-1} = 5.98180 \times 10^{-6} \text{ dyn } \text{\AA}^{-1}$.

Energy (hartree) (used in Gaussian 98) $= (2\pi)^4 m_e e^4 / h^4 = 27.2115 \text{ eV} = 4.3598138 \times 10^{-18} \text{ J}$.

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