8

Molecular Vibrations, Infrared, and Raman Activity

In this chapter we review molecular vibrations and present the use of group theory to identify the symmetry and degeneracy of the normal modes. Selection rules for infrared and Raman activity are also discussed and are illustrated for a variety of molecules selected for pedagogic purposes.

8.1 Molecular Vibrations: Background

In this section we briefly indicate how group theory helps to simplify the solution of the dynamical matrix for molecular vibrations to obtain the symmetries and degeneracies of the normal modes and their characteristic displacements more quickly and directly. A molecule having its atoms at their equilibrium sites is in an energy minimum. If the atoms are displaced from their equilibrium positions, a restoring force will be exerted which will tend to bring the atoms back to equilibrium. If the displacement is small, the restoring forces and molecular motion will be harmonic. The harmonic nature of the force implies that the system can be in a quantum mechanical eigenstate, or normal mode of vibration.

Suppose that a molecule contains N atoms (depending on whether a net charge can be assigned to a specific atomic site) and suppose further that the potential function describing the forces, such as bond bending and bond stretching forces, can be expressed in terms of the $3N$ coordinates for the N atoms, as $V(\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N)$. We are particularly interested in $V(\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N)$ about its equilibrium coordinates at $\boldsymbol{R}_1^\circ, \ldots, \boldsymbol{R}_N^\circ$, and we expand V about these equilibrium coordinates, utilizing the fact that a minimum in energy implies the vanishing of the first derivative of the potential. We can then conveniently take our zero of energy at the potential minimum and obtain a Hamiltonian for molecular vibrations in terms of the small displacements from equilibrium:

$$\mathcal{H} = \underbrace{\sum_k \frac{1}{2} m_k \dot{\xi}_k^2}_{\text{kinetic energy}} + \underbrace{\sum_{k,\ell} \frac{1}{2} \frac{\partial^2 V}{\partial \xi_k \partial \xi_\ell} \xi_k \xi_\ell}_{\text{potential energy}} , \tag{8.1}$$

where m_k denotes the mass of the *kth* ion, ξ_k denotes its displacement coordinate, and the potential energy depends on the second derivative of $V(\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N)$. The Hamiltonian in (8.1) gives rise to a $(3N \times 3N)$ secular equation. The roots of this secular equation are the eigenfrequencies ω_K^2 and the eigenvectors denote the normal modes of the system.

The usual procedure for finding the normal modes involves two transformations, the first being used to eliminate the mass term in the kinetic energy:

$$q_k = \sqrt{m_k}\, \xi_k , \tag{8.2}$$

and a second transformation is used to express q_k in terms of the normal mode coordinates Q_K:

$$q_k = \sum_K a_{kK} Q_K , \tag{8.3}$$

where a_{kK} denotes the amplitude of each normal mode Q_K that is contained in q_k.

Thus, by a proper choice of the a_{kK} amplitudes, we can use (8.2) and (8.3) to reduce the potential energy V to a sum of squares of the form $\omega_K^2 Q_K^2/2$. These transformations yield for the potential function in (8.1):

$$V = \frac{1}{2} \sum_{\substack{k,\ell \\ K,L}} \left(\frac{\partial^2 V}{\partial q_k \partial q_\ell} \right) a_{kK} a_{\ell L} Q_K Q_L = \frac{1}{2} \sum_K \omega_K^2 Q_K^2 , \tag{8.4}$$

where the coefficients a_{kK} are chosen to form a unitary matrix satisfying (8.4). Thus we obtain the relations $a_{Kk}^\dagger = a_{Kk}^{-1} = a_{kK}$ if the matrix elements of a_{kK} are real. The a_{kK} coefficients are thus chosen to solve the eigenvalue problem defined in (8.4). To achieve the diagonalization of the $V_{k\ell}$ matrix implied by (8.4) we must solve the secular equation

$$\sum_{k,\ell} a_{Kk}^{-1} \left(\frac{\partial^2 V}{\partial q_k \partial q_\ell} \right) a_{\ell L} = \omega_K^2 \delta_{KL} . \tag{8.5}$$

Solution of the secular equation (8.5) yields the eigenvalues or normal mode frequencies ω_K^2 and the eigenfunctions or normal mode amplitudes a_{kK} for

Table 8.1. Correspondence between important quantities in the electronic problem (see Sect. 7.1) and the molecular vibration problem

quantity	electronic	molecular vibration
matrix element	$H_{k\ell}$	$\frac{\partial^2 V}{\partial q_k \partial q_\ell} = V_{k\ell}$
eigenvalue	E_n	ω_K^2
eigenfunction[a]	$\psi_n(r)$	a_{kK}

For the molecular vibration problem, it is the normal mode amplitude a_{kK} which describes the physical nature of the small amplitude vibrations and is analogous to the wave function $\psi_n(r)$ for the electronic problem. The eigenvalues and eigenfunctions are found by diagonalizing $H_{k\ell}$ (electronic problem) or $V_{k\ell}$ (vibrational problem)

$K = 1, \ldots, 3N$. From the form of the secular equation we can immediately see the correspondence between the electronic problem and the molecular vibration problem shown in Table 8.1.

The transformation defined by (8.2)–(8.5) leads to a simpler form for the Hamiltonian

$$\mathcal{H} = \sum_K P_K^2/2m_K + \omega_K^2 Q_K^2/2\,, \tag{8.6}$$

which is a sum of harmonic oscillators, where Q_K^2 is the normal coordinate.

The Hamiltonian in (8.6) can become quite complicated, but group theory can greatly simplify the required work by finding the normal modes that directly put $\mathcal{H}$ into block diagonal form. As an example, one can compare the analytical solution for the “oscillator formed by three equal masses at the corners of an equilateral triangle”, as developed by Nussbaum [56], with the group theory analysis of this same pedagogic molecule to be developed in Problem 8.1.

8.2 Application of Group Theory to Molecular Vibrations

In an actual solution to a molecular vibration problem, group theory helps us to diagonalize the $V_{k\ell}$ matrix, to classify the normal modes and to find out which modes are coupled when electromagnetic radiation interacts with the molecule, either through electric dipole transitions (infrared activity) or in inelastic light scattering (the Raman effect). We discuss all of these issues in this chapter.

We make use of the symmetry of the molecule by noting that the molecule remains invariant under a symmetry operation of the group of the Schrödinger equation. Therefore, application of a symmetry operation $\hat{P}_R$ to an eigenfunction of a normal mode f_K just produces a linear combination of other normal modes of the same frequency ω_K. That is, f_K forms a basis for a representation for the symmetry operators $\hat{P}_R$ of the molecule

$$\hat{P}_R f_K^{(i,\alpha)} = \sum_{K'} D^{(i)}(R)_{K'K} f_{K'}^{(i,\alpha)} , \tag{8.7}$$

where $D^{(i)}(R)_{K'K}$ denotes the matrix elements of the matrix representation for symmetry operator R, and i denotes the irreducible representation which labels both the matrix and the basis function (normal mode coordinate in this case) and α denotes the partner of the basis function in representation i. Since the basis functions for different irreducible representations do not couple to each other, group theory helps to bring the normal mode matrix $V_{k\ell}$ into block diagonal form, with each eigenvalue and its corresponding normal mode labeled by an appropriate irreducible representation. This is similar in concept to the solution of the electronic eigenvalue problem discussed in Chap. 7, except that for the vibrational problem every atom (or ion) in the molecule has three degrees of freedom, and a vector must be assigned to each atomic site. Thus the molecular vibration problem is analogous to the electronic problem for p-functions, where the p-functions also transform as a vector.

Therefore, to find the normal modes for the vibration problem, we carry out the following steps:

(a) Identify the symmetry operations that define the point group G of the molecule in its equilibrium configuration.

(b) Find the characters for the equivalence representation, $\Gamma_{\text{equivalence}} = \Gamma^{\text{a.s.}}$ (a.s. stands for atom site). These characters represent the number of atoms that are invariant under the symmetry operations of the group. Since $\Gamma^{\text{a.s.}}$ is, in general, a reducible representation of the group G, we must decompose $\Gamma^{\text{a.s.}}$ into its irreducible representations.

(c) We next use the concept that a molecular vibration involves the transformation properties of a vector. In group theoretical terms, this means that the molecular vibrations are found by taking the direct product of $\Gamma^{\text{a.s.}}$ with the irreducible representations for a radial vector [such as (x, y, z)]. The representation for the molecular vibrations $\Gamma_{\text{mol.vib.}}$ are thus found according to the relation

$$\Gamma_{\text{mol.vib.}} = (\Gamma^{\text{a.s.}} \otimes \Gamma_{\text{vec}}) - \Gamma_{\text{trans}} - \Gamma_{\text{rot}} , \tag{8.8}$$

where Γ_{trans} and Γ_{rot} denote the representations for the simple translations and rotations of the molecule about its center of mass. The characters found from (8.8), in general, correspond to a reducible representation of group G. We therefore express $\Gamma_{\text{mol.vib.}}$ in terms of the *irreducible* representations of group G to obtain the normal modes. Each eigen-mode is labeled by one of these irreducible representations, and the degeneracy of each eigen-frequency is the dimensionality of the corresponding irreducible representation. The characters for Γ_{trans} are found by identifying the irreducible representations of the group G corresponding to the basis functions (x, y, z) for the radial vector $\boldsymbol{r}$. The characters for $\Gamma_{\rm rot}$ are found by identifying the irreducible representations corresponding to the basis functions (R_x, R_y, R_z) for the axial vector (e.g., angular momentum which for example corresponds to $\boldsymbol{r} \times \boldsymbol{p}$). Since the radial vector $\boldsymbol{r}$ (x, y, z) and the axial vector $\boldsymbol{r} \times \boldsymbol{p}$ denoted symbolically by (R_x, R_y, R_z) transform differently under the symmetry operations of group G, every standard point group character table (see Appendix A) normally lists the irreducible representations for the six basis functions for (x, y, z) and (R_x, R_y, R_z).

(d) From the characters for the irreducible representations for the molecular vibrations, we find the normal modes, as discussed in the next section. The normal modes for a molecule as defined by (8.8) are constrained to contain only internal degrees of freedom, and *no translations or rotations* of the full molecule. Furthermore, the normal modes must be orthogonal to each other.

(e) We use the techniques for selection rules (see Sect. 6.6 in Chap. 6) to find out whether or not each of the normal modes is infrared active (can be excited by electromagnetic radiation, see Sect. 8.6) or Raman-active (see Sect. 8.7).

It is important to recall that $\Gamma_{\rm vec}(R)$ is obtained by summing the irreducible representations to which the x, y, and z basis functions belong. If (x, y, z) are the partners of a three-dimensional irreducible representation T, then $\Gamma_{\rm vec}(R) = \Gamma^T(R)$. If, instead, x, y, and z belong to the same one-dimensional irreducible representation A, then $\Gamma_{\rm vec}(R) = 3\Gamma^A(R)$. If the x, y, and z basis functions are not given in the character table, $\Gamma_{\rm vec}(R)$ can be found directly from the trace of the matrix representation for each rotation R. All the point group operations are rotations or combination of rotations with inversion. For proper rotations, $\chi_{\rm vec}(R) = 1 + 2\cos\theta$, so that the trace for the rotation matrix can be always be found directly from

$$\begin{pmatrix} \cos(\theta) & \sin(\theta) & 0 \\ -\sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix} . \tag{8.9}$$

Improper rotations consist of a rotation followed by a reflection in a horizontal plane resulting in the character $-1 + 2\cos\theta$ where the $+1$ for the proper rotation goes into -1 for an improper rotation, since z goes into $-z$ upon reflection. Table 8.2 shows characters for $\Gamma_{\rm vec}$ for several selected point group operations. For C_5, we need to consider $\cos 72° = 0.30901\ldots$ and the corresponding character becomes $\chi_{\rm vec}(C_5) = 1.61803\ldots$..

To illustrate the procedure for finding molecular vibrations, we consider in the next sections the molecular vibrations of several different molecules to illustrate the methods discussed above and to provide more practice in using the various point groups. However, before going to specific molecules,

Table 8.2. Characters χ_{vec} for the vector for selected point group operations

E	C_2	C_3	C_4	C_6	i	σ	S_6	S_4	S_3
3	-1	0	1	2	-3	1	0	-1	-2

we present the general procedure used to find the eigenvectors for the normal modes associated with a specific irreducible representation of a group.

8.3 Finding the Vibrational Normal Modes

In searching for the vectors which describe the normal mode displacements, we identify the point group of the molecule, thus providing us with the symmetry operations and the character table. Therefore, to find the normal mode eigenvector associated with an irreducible representation, we apply the projection operator algebra (see Chap. 4) to a chosen elementary motion of the atoms in the molecule (see (4.38))

$$\hat{P}^{(\Gamma_n)} = \frac{\ell_n}{h} \sum_R \chi^{(\Gamma_n)}(R)^* \hat{P}_R\,. \tag{8.10}$$

This operation, however, projects out a function transforming as Γ_n but not a specific partner of Γ_n. While this is not a problem in dealing with 1D irreducible representations, for the case of multidimensional irreducible representations, physical insights are usually needed for finding physically meaningful partners of Γ_n quickly. The projection operators can also be used to check if the normal modes that are found are a combination of partners or not, and to find the other partners orthogonal to the first partner (see Chap. 4). Furthermore, a given set of partners is not unique, but the partners can be transformed among each other to get another orthonormal set. As an example, we can find the eigenfunction (normal mode) for a tetrahedral molecule (e.g., CH_4, point group T_d) belonging, for example, to the totally symmetric A_1 irreducible representation. Since the four H atoms in CH_4 are equivalent (can be brought one into another by any of the symmetry operations of the group), the initial mode displacements of the atoms (denoted by ψ_0) can be chosen so that only one of the H atoms and the C atom are moving in an arbitrary direction, as shown in Fig. 8.1a. The identity operator applied to ψ_0 keeps it unchanged. The operation $(E + C_2)\psi_0$ gives the result shown in Fig. 8.1b, where the chosen axis for C_2 is displayed. By applying the complete set $\hat{P}^{(A_1)}\psi_0$ and summing up all the vectors, we find the A_1 mode, as shown in Fig. 8.1c, where the C atom does not move.

Through this example, we show how physical insight helps to find the eigenvectors. The mode in Fig. 8.1c is the stretching of the C–H bonds (the

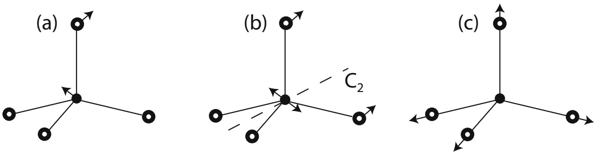


Fig. 8.1. Schematic for obtaining the totally symmetric normal mode of a tetrahedral (T_d point group) molecule. (**a**) The initial chosen arbitrary motion ψ_0 of two nonequivalent atoms; (**b**) the result of applying the operations E and C_2 on ψ_0; and (**c**) the normal mode displacements for the A_1 symmetry mode of CH_4 obtained from the projection operator $\hat{P}^{(A_1)}\psi_0$ after summing up all the vectors

so-called breathing mode) that keeps the tetrahedral symmetry unchanged, as it should, since it belongs to the totally symmetric A_1 irreducible representation. Therefore, this normal mode could be visualized without doing any of the procedures shown in Fig. 8.1a,b. In other cases, the final normal mode vector may not be so obvious, but still the use of physical insights are useful. For example, for finding the normal modes belonging to other irreducible representations of the tetrahedron, it is interesting to start with atomic motions that are not the ones found for the A_1 eigenvector, so that you increase the likelihood of finding displacements that may be orthogonal to the partners belonging to the normal modes that you already have. More about the normal modes of the tetrahedron will be discussed in Sect. 8.8.3.

Finding the normal vibrational modes is not a difficult procedure, but it gets more and more complicated as the number of atoms in the molecule increases. For dealing with a large molecule composed of N atoms, we can calculate

$$Q^{\Gamma_n} = \hat{P}^{(\Gamma_n)} \otimes \zeta \, . \tag{8.11}$$

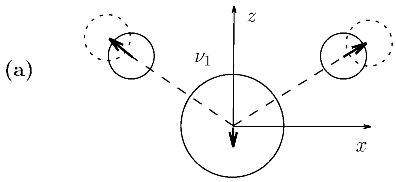
Here ζ is a vector of dimensions $3N$ with the coordinates of an arbitrary initial motion of the atoms, and $\hat{P}^{(\Gamma_n)}$ is a $3N \times 3N$ matrix having all the atomic coordinates for the N atoms in their equilibrium positions, and describing the symmetry operations of the molecule. The Q^{Γ_n} is another $3N$-dimensional vector giving the normal mode belonging to Γ_n, or a combination of normal modes if Γ_n is not a one-dimensional irreducible representation. In this way the partners can be found by using a less arbitrary initial vector ζ.

In the next sections we start to illustrate the procedure for finding molecular vibrations for specific and simple molecules. In doing so, we can better illustrate the physical insights for finding the normal modes, rather than using the formal procedure discussed above. We start by considering the molecular vibrations of an isolated H_2O molecule to illustrate finding the normal modes. Then we introduce additional theoretical issues associated with the observation of combination modes as well as infrared active and Raman active modes before returning to additional examples of molecular vibrations, for which we also include a discussion of their infrared and Raman activity.

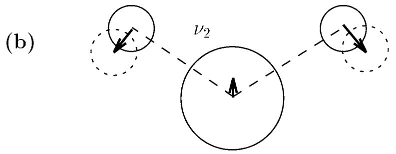
8.4 Molecular Vibrations in H_2O

We start by considering the vibrations of an isolated H_2O molecule. This molecule is chosen because it is a simple molecule, has two different chemical species and involves a point group $C_{2v}(2mm)$ (Table A.5) we have not discussed previously. The four symmetry operations for the H_2O molecule (see Fig. 8.2) include E the identity operation, a 180° rotation C_2 around the z-axis, a reflection plane σ_v in the plane of molecule and a σ_v' reflection perpendicular to the plane of the molecule. The σ_v plane is a vertical reflection plane since the xz plane contains the highest symmetry axis C_2. The reflection plane $\sigma_{v'}$ which goes through C_2 is $\perp$ to the plane of the molecule. In labeling the axes, the plane of the H_2O molecule is denoted by xz, with the x-axis parallel to a line going through the two hydrogens, and the perpendicular y-axis goes through the oxygen atom. The appropriate point group for the H_2O molecule is the group C_{2v} and the character table is given in Table 8.3 and Table A.5.

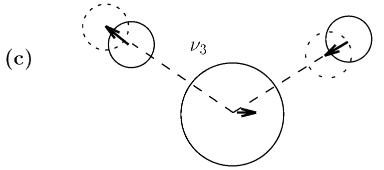
Next we find $\Gamma^{\text{a.s.}}$. For H_2O we have to consider the transformation of three atoms under the symmetry operations of the group. In writing down $\Gamma^{\text{a.s.}}$, we recall that for each site that is invariant under a symmetry operation,



A_1 mode of H_2O



A_1 mode of H_2O



B_1 mode of H_2O

Fig. 8.2. Normal modes for the H_2O molecule with three vibrational degrees of freedom. (**a**) The breathing mode with symmetry A_1, which changes only bond lengths. (**b**) The symmetric stretch mode of H_2O with A_1 symmetry, which changes bond angles. (**c**) The antisymmetric stretch mode with B_1 symmetry

a contribution of $+1$ is made to the character of that operation; otherwise the contribution is zero. Thus, we obtain for the characters for $\chi^{\text{a.s.}}(H_2O)$ for all three atoms in the H_2O molecule as given in Table 8.4.

From the character table for group $C_{2v}(2mm)$ we see that the radial or polar vector transforms as

$$\Gamma_{\text{vec}} = A_1 + B_1 + B_2\,,$$

where z, x, y, respectively, transform as A_1, B_1 and B_2. Likewise the irreducible representations for the rotations $\Gamma_{\text{rot.}}$ are $A_2+B_1+B_2$, corresponding to the rotations R_z, R_y, and R_x, respectively. We then calculate the irreducible representations $\Gamma_{\text{mol.vib.}}$ contained in the molecular vibrations:

$$\begin{aligned}\Gamma_{\text{mol.vib.}} &= \Gamma^{\text{a.s.}} \otimes \Gamma_{\text{vec}} - \Gamma_{\text{translations}} - \Gamma_{\text{rot}}\\ &= (2A_1+B_1) \otimes (A_1+B_1+B_2) - (A_1+B_1+B_2) - (A_2+B_1+B_2)\\ &= [3A_1 + 3B_1 + 2B_2 + A_2] - (A_1 + B_1 + B_2) - (A_2 + B_1 + B_2)\\ \Gamma_{\text{mol.vib.}} &= 2A_1 + B_1\,. \qquad (8.12)\end{aligned}$$

The three modes in $\Gamma_{\text{mol.vib.}}$ are all one-dimensional irreducible representations and therefore have nondegenerate or distinct vibrational frequencies.

We must now find the normal modes corresponding to each eigenfrequency. It is easy to use physical insights in such a simple symmetry. The two normal modes with A_1 symmetry must leave the symmetry undisturbed and this can be accomplished by the stretching of bonds and flexing of bond angles. These modes are the breathing and symmetric stretch modes (see Fig. 8.2). All molecules have a "breathing" mode which leaves the symmetry unchanged. To get the eigenvectors for the breathing mode of the H_2O molecule, assume that one of the hydrogen atoms is displaced in some way. With A_1 symmetry, this implies (under operation C_2) that the other H

Table 8.3. Character Table for Group $C_{2v}(2mm)$

$C_{2v}(2mm)$			E	C_2	σ_v	σ_v'
x^2, y^2, z^2	z	A_1	1	1	1	1
xy	R_z	A_2	1	1	−1	−1
xz	R_y, x	B_1	1	−1	1	−1
yz	R_x, y	B_2	1	−1	−1	1

Table 8.4. Characters for the Atomic Site Transformation for H_2O

	E	C_2	σ_v	σ_v'	
$\Gamma^{\text{a.s.}}(H_2O)$	3	1	3	1	$\Rightarrow 2A_1 + B_1$

atom must be correspondingly displaced (see Fig. 8.2(a)). To prevent translations and rotations of the molecule, O must be displaced as shown in Fig. 8.2(a). (The actual vibration amplitude for each atom is constrained to avoid translation and rotation of the molecule.)

The same arguments can be applied to obtain the A_1 symmetric stretch mode shown in Fig. 8.2(b). Application of the symmetry operations of group $C_{2v}(2mm)$ (Table A.5) confirms that this mode has A_1 symmetry. The H atom motion is taken so that the two A_1 modes are orthogonal. Since the breathing mode and symmetric stretch mode have the same symmetry they can mix (or couple to each other) and for this reason the directions of the H atom motion for each of the modes in Fig. 8.2(a), (b) are not uniquely specified.

To obtain the normal mode for B_1 symmetry, we observe that the character for the C_2 operation is -1, so that the two hydrogen atoms must move in opposite directions relative to the O atom. Likewise, the motion of the O atom must be odd under C_2. These arguments determine the normal B_1 mode shown in Fig. 8.2(c).

As mentioned above, all molecules have a breathing mode which transforms as A_1 and preserves the molecular symmetry. As a practical matter in checking whether or not the calculated normal modes are proper normal modes, it is useful to verify that the normal mode motion does not involve motion of the center of mass or rotation about the center of mass, and that all normal modes are orthogonal to each other.

8.5 Overtones and Combination Modes

In addition to the first-order molecular vibrations discussed above, harmonics (or multiples of the fundamental mode frequency such as 2ω, 3ω, etc.) and combination modes (which refer to the sum and differences of the mode frequencies, such as $\omega_1 \pm \omega_2$) are observed. The observation of these modes usually involves a perturbation to excite these modes, but this perturbation will also perturb their frequencies somewhat. We consider in this section the group theory of harmonics and combination modes in the limit of small perturbations so that the perturbation to the mode frequencies is minimal.

Since the two phonon state is a product of the normal modes, the mode frequency for the lowest overtone mode (or second harmonic) is at $\sim 2\omega_{\Gamma_i}$ and the symmetry of the harmonic is given by the direct product $\Gamma_i \otimes \Gamma_i$ and the irreducible representations combined therein. Similarly, the combination modes are at frequencies $\simeq (\omega_{\Gamma_i} + \omega_{\Gamma_j})$ in the limit of a very weak perturbation and have symmetries given by $\Gamma_i \otimes \Gamma_j$. In Sect. 8.8.3 where we consider the overtones (harmonics) and combination modes of the methane molecule, we can see which modes are activated in the infrared and Raman spectra for a real molecule and we can see the frequency shifts produced by the perturbation exciting these higher order molecular vibrations. Some of these modes for the

Table 8.5. Observed vibrational frequencies for the methane molecule[a]

assignment	symmetry	mode	frequency (cm^{-1})
$\nu_1(A_1)$	A_1	fundamental	2914.2
$\nu_2(E)$	E	fundamental	1526
$\nu_3(T_2)$	T_2	fundamental	3020.3
$\nu_4(T_2)$	T_2	fundamental	1306.2
$2\nu_2$	$A_1 + A_2 + E$	overtone[b]	3067.0
$2\nu_3$	$(A_1 + E) + T_1 + T_2$	overtone[b]	6006
$3\nu_3$	$(A_1 + T_1) + 2T_2$	overtone[c]	9047
$2\nu_4$	$(A_1 + E) + T_1 + T_2$	overtone[b]	2600
$\nu_4 - \nu_3$	$(A_1 + E) + T_1 + T_2$	combination	1720
$\nu_2 + \nu_4$	$T_1 + T_2$	combination	2823

[a] Herzberg, “Infrared and Raman Spectra of Polyatomic Molecules”, “Molecular Spectra and Molecular Structure II”, 1949, “Van Nostrand Reinhold”, “New York” [40]

[b] For overtones, only the symmetric combinations of basis functions are Raman allowed

[c] For $3\nu_3$ the symmetric combinations correspond to the angular momentum states $L = 1$ which transforms as T_2 and $L = 3$ which transforms as $A_1 + T_1 + T_2$

methane molecule CH_4 are given in Table 8.5 and are further discussed in Sect. 8.8.3.

8.6 Infrared Activity

If electromagnetic radiation is incident on a molecule in its ground state, then the radiation will excite those vibrational modes which give rise to a dipole moment. In the ground state, the molecule is in a zero phonon state and therefore has A_1 symmetry. We can use group theory to decide whether or not an electromagnetic transition will occur, i.e., if a given excited mode can be connected by the electromagnetic wave to the ground state A_1 (or more generally to the initial state of a highly excited molecule). The perturbation Hamiltonian for the interaction of the molecule with the electromagnetic (infrared) interaction is

$$\mathcal{H}'_{\text{infrared}} = -\boldsymbol{E} \cdot \boldsymbol{u}\,, \tag{8.13}$$

where $\boldsymbol{E}$ is the incident oscillating electric field and $\boldsymbol{u}$ is the induced dipole moment arising from atomic displacements. In this interaction, $\boldsymbol{u}$ transforms like a vector. To find out whether the incident photon will excite a particular vibrational mode, we must examine the selection rules for the process. This means that we must see whether or not the matrix element for the excitation $(\psi_f|\boldsymbol{u}|\psi_i)$ vanishes, where ψ_f denotes the normal mode which we are trying to excite and $\boldsymbol{u}$ is the vector giving the transformation properties of $\mathcal{H}'_{\text{infrared}}$, while ψ_i denotes the initial state of the molecule, which for most cases is the ground state. The ground state has no vibrations and is represented by the totally symmetric state A_1 of the unperturbed molecule, while $\mathcal{H}'_{\text{infrared}}$ transforms like a vector, since the applied field is external to the molecule.

To determine whether or not a molecule is infrared active, we use the usual methods for finding out whether or not a matrix element vanishes. That is, we ask whether the direct product $\Gamma_{\text{vec}} \otimes \Gamma_i$ contains the representation Γ_f; if $(\Gamma_{\text{vec}} \otimes \Gamma_i)$ does not contain Γ_f, or equivalently if $\Gamma_f \otimes \Gamma_{\text{vec}} \otimes \Gamma_i$ does not contain A_1, then the matrix element $\equiv 0$. Since molecular vibrations are typically excited at infrared frequencies, we say that a molecule is *infrared active* if any molecular vibrations can be excited by the absorption of electromagnetic radiation. The particular modes that are excited are called *infrared-active modes*. Correspondingly, the modes that cannot be optically excited are called *infrared inactive*. Considering infrared excitation from the vibrational ground state (no phonon), we write $\Gamma_{\text{vec}} \otimes A_1 = \Gamma_{\text{vec}}$. The infrared active modes thus transform as the irreducible representations for the basis vector x, y, and z (usually given in the character tables), and the specific basis vector indicates the polarization of the light needed to excite that specific mode.

As applied to the H_2O molecule (see Sect. 8.4) we have the following identification of terms in the electromagnetic matrix element. Suppose that the initial state has A_1 symmetry for the unexcited molecule and that the vector $\boldsymbol{u}$ transforms as

$$\boldsymbol{u} \rightarrow A_1 + B_1 + B_2$$

corresponding to the transformation properties of z, x, y, respectively. The case of the H_2O molecule shows that the components of the vector may transform according to different irreducible representations of the point group for the molecule. Thus, we obtain for the direct product between the vector and the initial state:

$$(A_1 + B_1 + B_2) \otimes (A_1) = A_1 + B_1 + B_2 \tag{8.14}$$

showing the irreducible representations that are infrared active.

Therefore the two A_1 modes and the B_1 mode of water are all infrared-active. Each of the three vibrations corresponds to an oscillating dipole moment. As far as polarization selection rules are concerned, we can excite either of the two A_1 modes with an optical electric field in the z-direction, the twofold axis of the molecule. To excite the B_1 mode, the optical electric field must be along the x-direction, the direction of a line connecting the two hydrogen atoms. An electric field in the y direction (perpendicular to the plane of the molecule) does not excite any vibrational modes. Since all vibrational modes of the water molecule can be excited by an arbitrarily directed $\boldsymbol{E}$ field, all the vibrational modes of the water molecule are infrared-active. It is not always the case that *all* vibrational modes of a molecule are infrared-active. It can also happen that for some molecules only a few of the modes are infrared-active. This situation occurs in molecules having a great deal of symmetry.

To observe infrared activity in the second-order infrared spectra, we require that the combination of two vibrational modes be infrared-active. From a group theoretical standpoint, the symmetry of the combination mode arising from constituent modes of symmetries Γ_i and Γ_j is given by the direct product $\Gamma_i \otimes \Gamma_j$. Since groups containing inversion symmetry have only odd parity infrared-active modes, such symmetry groups have no overtones in the second-order infrared spectrum.

8.7 Raman Effect

In the Raman effect the inelastically scattered light from a system is detected. The *induced* dipole moment is

$$\boldsymbol{u} = \overset{\leftrightarrow}{\alpha} \cdot \boldsymbol{E}_{\mathrm{i}} \cos \omega t \,, \tag{8.15}$$

where $\overset{\leftrightarrow}{\alpha}$ is the Raman polarizability tensor, a second rank symmetric tensor. Because the inelastic scattering of the incident light $\boldsymbol{E}_i$ can excite molecular vibrations, the polarizability tensor has frequency dependent contributions at the molecular vibration frequencies ω_v

$$\overset{\leftrightarrow}{\alpha} = \overset{\leftrightarrow}{\alpha}_0 + \Delta \overset{\leftrightarrow}{\alpha} \cos \omega_v t \,, \tag{8.16}$$

so that

$$\begin{aligned} \boldsymbol{u} &= \left(\overset{\leftrightarrow}{\alpha}_0 + \Delta \overset{\leftrightarrow}{\alpha} \cos \omega_v t \right) \cdot \boldsymbol{E}_{\mathrm{i}} \cos \omega t \\ &= \overset{\leftrightarrow}{\alpha}_0 \cdot \boldsymbol{E}_{\mathrm{i}} \cos \omega t + \frac{\Delta \overset{\leftrightarrow}{\alpha}}{2} \left[\cos(\omega - \omega_v)t + \cos(\omega + \omega_v)t \right] \cdot \boldsymbol{E}_{\mathrm{i}} \,, \end{aligned} \tag{8.17}$$

where the first term in (8.16 and 8.17) is the Rayleigh component at incident frequency ω, the second term is the Stokes component at frequency $(\omega - \omega_v)$, and the third term is the anti-Stokes component at frequency $(\omega + \omega_v)$. In observing the first-order Raman effect,[1] the scattered light is examined for the presence of Stokes components at frequencies $(\omega - \omega_v)$ and of anti-Stokes components at frequencies $(\omega + \omega_v)$. Not all normal modes of the molecule will yield scattered light at $(\omega \pm \omega_v)$, although if the Stokes component is excited, symmetry requires the anti-Stokes component to be present also, though its intensity may be small.

---

[1] The first-order Raman process is the interaction of light with one vibrational mode. The second-, third-, ... *n*th-order Raman effect is related to combination or overtones involving two, three, ... *n*th vibrational modes.

To find whether or not a vibrational mode is Raman active, we ask whether or not the matrix element for the Raman perturbation vanishes. The Raman perturbation is of the $-\boldsymbol{u} \cdot \boldsymbol{E}$ form and using (8.15), $\mathcal{H}'_{\text{Raman}}$ is written as

$$\mathcal{H}'_{\text{Raman}} = -\frac{\Delta \overset{\leftrightarrow}{\alpha}}{2} \boldsymbol{E}_{\text{i}} \boldsymbol{E}_{\text{s}} \cos(\omega \pm \omega_v)t \,. \tag{8.18}$$

The transformation properties of $\mathcal{H}'_{\text{Raman}}$ are those of a second rank symmetric tensor $\Delta\alpha_{ij}$ (where $i, j = x, y, z$). The vectors $\boldsymbol{E}_{\text{i}}$ and $\boldsymbol{E}_{\text{s}}$ for the incident and scattered light are external to the molecular system and it is only the symmetry of the polarizability tensor $\Delta\alpha_{ij}$ that pertains to the molecule. To find out whether a particular normal mode is Raman-active we need only consider the matrix element:

$$(\psi_{\text{f}}|\mathcal{H}'_{\text{Raman}}|\psi_{\text{i}}) \;, \tag{8.19}$$

where ψ_{f} is the final state corresponding to a normal mode we are trying to excite, $\mathcal{H}'_{\text{Raman}}$ is the Raman perturbation which has the transformation properties of a symmetric second rank tensor, and ψ_{i} is the initial state generally taken as the ground state which has the full symmetry of the group of Schrödinger's equation. A vibrational mode is Raman active if the direct product ($\Gamma_{\text{i}} \otimes \Gamma_{\mathcal{H}'_{\text{Raman}}}$, where $\mathcal{H}'_{\text{Raman}}$ transforms as a second rank symmetric tensor) contains the irreducible representation for the final state Γ_{f}. This is the basic selection rule for Raman activity. The group theory associated with tensors is discussed in more detail in Chap. 18.

Since the Raman process is a second-order process, it involves an intermediate state. The process involves an electron–photon interaction to produce an excited state where an electron–phonon scattering event occurs creating (Stokes process) or absorbing (anti-Stokes process) a phonon, and finally the scattered photon is emitted in an electron–photon interaction. In terms of the spectroscopy of molecular systems with inversion symmetry, the Raman effect is especially important because it is a *complementary technique to infrared spectroscopy.* Since the infrared excitation is a first-order process and the dipole operator transforms as a vector, selection rules for a vector interaction couple states with opposite parity. On the other hand, the Raman process, being a symmetric second-order process, is characterized by an interaction $\mathcal{H}'_{\text{Raman}}$ which transforms as a tensor that is even under inversion and therefore couples an initial and final state of similar parity. Thus for molecules with inversion symmetry infrared spectroscopy probes molecular vibrations with odd parity, while Raman spectroscopy probes modes with even parity.

If the molecule does not have inversion symmetry, some vibrational modes are both Raman and infrared active, and others can be neither Raman nor infrared-active. The latter symmetry modes are called silent modes.

The use of *polarized light* plays a major role in the assignment of experimentally observed Raman lines to specific Raman-active modes. In Raman experiments with polarized light, it is customary to use the notation:

$\boldsymbol{k}_{\mathrm{i}}(\boldsymbol{E}_{\mathrm{i}}\boldsymbol{E}_{\mathrm{s}})\boldsymbol{k}_{\mathrm{s}}$ to denote the incident propagation direction $\boldsymbol{k}_{\mathrm{i}}$, the incident and scattered polarization directions $(\boldsymbol{E}_{\mathrm{i}}\boldsymbol{E}_{\mathrm{s}})$ and the scattered propagation direction $\boldsymbol{k}_{\mathrm{s}}$. From (8.18) we see that the Raman tensor $\mathcal{H}'_{\mathrm{Raman}}$ depends on both $\boldsymbol{E}_{\mathrm{i}}$ and $\boldsymbol{E}_{\mathrm{s}}$ and on the change in the polarizability tensor $\Delta \overset{\leftrightarrow}{\alpha}$, where $\boldsymbol{E}_{\mathrm{i}}$ and $\boldsymbol{E}_{\mathrm{s}}$ are, respectively, the incident and the scattered electric fields. It is customary to designate the scattered light as having *diagonal* Raman components $(\boldsymbol{E}_{\mathrm{i}} \parallel \boldsymbol{E}_{\mathrm{s}})$, or *off-diagonal* Raman components $(\boldsymbol{E}_{\mathrm{i}} \perp \boldsymbol{E}_{\mathrm{s}})$.

To find the selection rules for the Raman effect, we observe that the polarizability $\Delta \overset{\leftrightarrow}{\alpha}$ in (8.15) is a *second rank symmetric tensor* (see Chap. 18) and has the same transformation properties as a general quadratic form (e.g., $x^2, y^2, z^2, xy, yz, zx$). The transformation properties of these basis functions are usually found in the table of characters for the point groups, indicating the irreducible representations to which the Raman-active vibrational modes belong. The polarization selection rules for specific modes according to their incident and scattered polarization is also obtained from the basis functions. We note here that the symmetric off-diagonal components correspond to combinations $(xy + yx)/2$ and the corresponding terms for yz and zx. The antisymmetric terms for a second rank tensor correspond to $(xy - yx)/2$ and its partners, which transform as the axial vectors (R_x, R_y, R_z), and are so listed in the character tables. In a second-order Raman spectrum, a combination mode or overtone will be observable if $\Gamma_i \otimes \Gamma_j$ contains irreducible representations that are themselves Raman-active, since the $\mathcal{H}'_{\mathrm{Raman}}$ matrix element in this case will couple a no-phonon ground state to a combination mode excited state (see (8.19)). Since $x^2 + y^2 + z^2$ transforms as the identity transformation and the direct product $\Gamma_i \otimes \Gamma_i$ always contains the identity representation, all second harmonics at $2\omega_i$ are Raman-active modes. Thus, some silent modes that cannot be found in the first-order spectrum can thus be observed in the second-order spectrum.

In the following subsections we discuss molecular vibrations for specific molecules, and in so doing, we will also include comments about the infrared and the Raman activity of these molecules.

8.8 Vibrations for Specific Molecules

In this section we consider molecular vibrations for specific molecules, starting with linear molecules in Sect. 8.8.1 and then going to more complex multiatomic molecules. We also discuss the infrared (Sect. 8.6) and Raman (Sect. 8.7) activity of the normal modes for each of the molecules that are considered.

8.8.1 The Linear Molecules

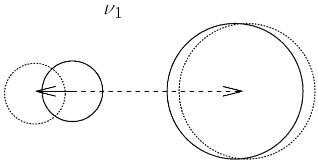
The procedure for dealing with the molecular vibrations of linear molecules such as CO or H_2 is special and is slightly different from what has been described in Sect. 8.2. We now present a method for handling the linear molecules and give some examples. For a linear molecule, the irreducible representations for the rotations just involves the rotations R_x and R_y, assuming the molecular axis to be along $\hat{z}$. Thus for the linear molecule, only two degrees of freedom are removed by Γ_{rot}, since rotations along the axis of the molecule correspond to the identity operation, considering the atoms as homogeneous balls without any internal degrees of freedom. First we consider the heterogeneous CO linear molecule (group $C_{\infty v}$ in Table A.33) followed by the homogeneous H_2 linear molecule (group $D_{\infty h}$ in Table A.34). With these simple molecules, we illustrate both molecular vibrations of linear molecules and the use of the semi-infinite point groups $C_{\infty v}$ and $D_{\infty v}$ in this context.

The appropriate symmetry group for CO is $C_{\infty v}$ (see Sect. 7.4.2). The symmetry operations $2C_\phi$ denote rotations about the $\hat{z}$ axis in clockwise and counter-clockwise senses by an arbitrary angle ϕ. Thus C_ϕ is a class with an ∞ number of symmetry operations. The symmetry plane σ_v is a vertical plane through the molecular axis at an angle ϕ with respect to an arbitrary direction denoted by $\phi = 0$. Since the $2C_\phi$ and σ_v classes are of infinite order, the number of irreducible representations is also infinite.

The first step in finding $\Gamma_{\text{mol.vib.}}$ for a linear molecule is to compute $\Gamma^{\text{a.s.}}$. For the CO molecule shown in Fig. 8.3, the equivalence transformation yields $\Gamma^{\text{a.s.}}$ (see Table 8.6), from which we find the irreducible representations for the molecular vibrations of CO, remembering that Γ_{rot} only contains rotations in the xy plane normal to the rotation axis of the molecule, and therefore Γ_{rot} transform as E_1 while Γ_{vec} transform as $A_1 + E_1$:

$$\Gamma_{\text{mol.vib.}} = \Gamma^{\text{a.s.}} \otimes \Gamma_{\text{vec}} - \Gamma_{\text{trans}} - \Gamma_{\text{rot}}\,,$$

$$\Gamma_{\text{mol.vib.}} = (2A_1) \otimes (A_1 + E_1) - (A_1 + E_1) - E_1 = A_1\,.$$



A_1 **mode of CO**

Fig. 8.3. CO molecule only has an A_1 breathing mode. The lighter mass of the C atom results in a larger displacement to maintain the center of mass

Table 8.6. Characters for the Atomic Site Transformation for the CO molecule

	E	$2C_\phi$	σ_v	
$\Gamma^{\text{a.s.}}$	2	2	2	$\Rightarrow 2A_1$

The A_1 mode is the breathing mode for the CO molecule (see Fig. 8.3). Since the C and the O atoms are distinct, this molecule has a dipole moment along the z direction so that CO is infrared active. From the character table for $C_{\infty v}$ we see that the components of the Raman tensor $(x^2 + y^2)$ and z^2 transform as A_1, so we conclude that CO is also Raman active.

If we now consider the O_2 molecule (see Fig. 8.4), we have a homo-nuclear molecule following the symmetry group $D_{\infty h}$ (see Character Table A.34). Here the displacements are now fully symmetric unlike the situation for the CO molecule where the center of mass of the molecule must be conserved so that the lighter atom has a larger vibrational amplitude. In the case of the O_2 molecule the characters for $\Gamma^{\text{a.s.}}$ are listed in Table 8.7. Thus the irreducible representations for the molecular vibrations of O_2 become:

$$\begin{aligned}\Gamma_{\text{mol.vib.}} &= \Gamma^{\text{a.s.}} \otimes \Gamma_{\text{vec}} - \Gamma_{\text{trans}} - \Gamma_{\text{rot}} \\ \Gamma_{\text{mol.vib.}} &= (A_{1g} + A_{2u}) \otimes (A_{2u} + E_{1u}) - (A_{2u} + E_{1u}) - E_{1g} \qquad (8.20)\\ &= A_{1g} \ ,\end{aligned}$$

where $\Gamma_{\text{rot}} = E_{1g}$ for the rotations R_x, R_y. Because of the inversion symmetry of the O_2 molecule, all the normal modes have either even (gerade) or odd (ungerade) symmetries. Thus for O_2 the breathing mode (see Fig. 8.4) has A_{1g} symmetry and is infrared-inactive. From simple physical considerations the breathing mode for O_2 has no oscillating dipole moment nor can a dipole moment be induced. Hence O_2 does not couple to an electromagnetic field through an electric dipole interaction, in agreement with our group theoretical result, so O_2 is not infrared active. The A_{1g} mode of the O_2 molecule is however Raman active, as is also the CO molecular vibrational mode mentioned above.

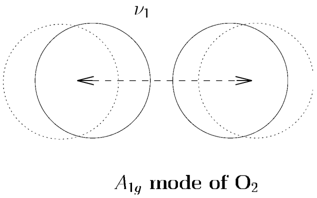


Fig. 8.4. The O_2 molecule only has an A_{1g} breathing mode with symmetric displacements of the atoms in the normal mode vibration

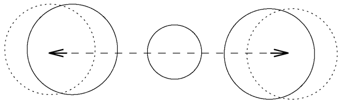
Table 8.7. Characters for the Atomic Site Transformation for the O_2 molecule

	E	$2C_\phi$	C'_2	i	$2iC_\phi$	iC'_2	
$\Gamma^{\text{a.s.}}$	2	2	0	0	0	2	$\Rightarrow A_{1g} + A_{2u}$

Table 8.8. Characters for the Atomic Site Transformation for the CO_2 molecule

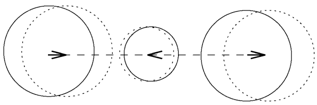
	E	$2C_\phi$	C_2'	i	$2iC_\phi$	iC_2'
$\Gamma^{\text{a.s.}}$	3	3	1	1	1	3

(a) ν_1 **breathing**



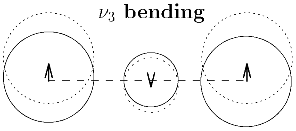
A_{1g} **mode of** CO_2

(b) ν_2 **stretch**



A_{2u} **mode of** CO_2

(c) ν_3 **bending**



E_{1u} **mode of** CO_2

Fig. 8.5. The three vibrational normal modes of CO_2: (**a**) the breathing mode with A_{1g} symmetry, (**b**) the antisymmetric stretch mode with A_{2u} symmetry, and (**c**) the doubly degenerate E_{1u} mode where the mode displacements for the two partners are orthogonal (i.e., $\|$ and $\perp$ to the page)

The CO_2 molecule is chosen for discussion to show the various types of modes that can be expected for linear molecules involving three or more atoms. Below we consider another molecule (C_2H_2) described by the same symmetry group $D_{\infty h}$ but having slightly more complexity.

For the case of CO_2 (see Fig. 8.5), we again have a linear molecule with $D_{\infty h}$ symmetry and now $\Gamma^{\text{a.s.}}$ corresponds to a three-dimensional representation (see Table 8.8), so that $\Gamma^{\text{a.s.}} = 2A_{1g} + A_{2u}$.

$$\begin{aligned}
\Gamma_{\text{mol.vib.}} &= \Gamma^{\text{a.s.}} \otimes \Gamma_{\text{vec}} - \Gamma_{\text{trans}} - \Gamma_{\text{rot}} \\
\Gamma_{\text{mol.vib.}} &= (2A_{1g} + A_{2u}) \otimes (A_{2u} + E_{1u}) - (A_{2u} + E_{1u}) - E_{1g} \qquad (8.21) \\
&= A_{1g} + A_{2u} + E_{1u}\,.
\end{aligned}$$

The normal modes for CO_2 are easily found with the help of the character table, and are shown in Fig. 8.5. The A_{1g} mode is the breathing mode, the

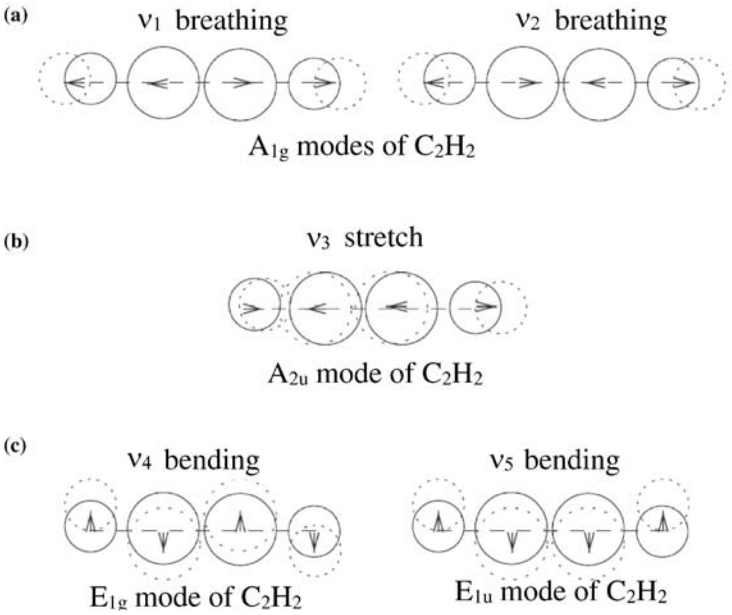


Fig. 8.6. Schematic diagram of the normal modes of the linear C_2H_2 molecule: (**a**) two breathing modes of A_{1g} symmetry, (**b**) an antisymmetric stretch mode of A_{2u} symmetry, and (**c**) and (**d**) two doubly-degenerate bending modes of E_{1g} and E_{1u} symmetries

A_{2u} mode is the antisymmetric stretch mode and the E_{1u} mode is a doubly degenerate bending mode where the displacements of the carbon and the two oxygens are normal to the molecular axis for each partner of the E_{1u} bending mode. Of these modes only the A_{1g} mode is Raman active. In this case, the A_{2u} and E_{1u} modes are infrared-active while the symmetric A_{1g} mode is infrared-inactive as can be seen from the character table for $D_{\infty h}$ (Table A.34).

For the case of the linear C_2H_2 molecule, H–C≡C–H, also following group $D_{\infty h}$ symmetry, we obtain

$$\Gamma^{\text{a.s.}} = 2A_{1g} + 2A_{2u} \tag{8.22}$$

using the result for O_2. Thus $\Gamma_{\text{mol.vib.}}$ for the C_2H_2 molecule becomes

$$\Gamma_{\text{mol.vib.}} = (2A_{1g} + 2A_{2u}) \otimes (A_{2u} + E_{1u}) - (A_{2u} + E_{1u}) - E_{1g}$$

$$\Gamma_{\text{mol.vib.}} = 2A_{1g} + A_{2u} + E_{1u} + E_{1g}\,.$$

The five normal modes for the molecular vibrations of C_2H_2 are shown in Fig. 8.6, again illustrating the breathing, antisymmetric stretch and bending modes corresponding to five different vibrational frequencies. These concepts can of course be generalized to give normal modes for more complex linear molecules. For the C_2H_2 molecule, the two A_{1g} modes correspond to basis functions (z^2 and x^2+y^2) while the E_{1g} modes correspond to the (zx, zy) basis functions. These two different symmetry modes can be distinguished using optical polarization experiments whereby the A_{1g} modes will be observable when the incident and scattered light are polarized parallel to each other, but the E_{1g} mode will be observed when the polarization of the incident beam is along the molecular axis but the scattered beam is perpendicular to the molecular axis.

In Problem 8.3 it is shown that $\Gamma_{\text{mol.vib.}}$ and the normal modes of the C_2H_2 linear molecule can be easily found by considering the C_2H_2 molecule as being composed of two C–H blocks or of the two hydrogen atoms and the two carbon atoms as two other blocks, each with internal degrees of freedom vibrating against each other. Such considerations help in providing intuition about obtaining the internal vibrational modes of complex molecules.

We now illustrate how symmetry is used to assist in the solution of molecular vibration problems for several 3D molecules of pedagogic interest.

8.8.2 Vibrations of the NH_3 Molecule

The NH_3 molecule is one of two molecules selected for illustrating normal mode properties of three-dimensional molecular vibrations. To illustrate some features of degenerate normal modes, let us consider the NH_3 molecule (see Fig. 8.7). The hydrogen atoms in NH_3 are at the corners of an equilateral triangle and the nitrogen atom is either above or below the center of the triangle. If the molecule were planar, it would have D_{3h} symmetry, but because the N atom is not coplanar with the three hydrogen atoms, the appropriate symmetry group is C_{3v} (see Table A.10). We note that $\Gamma^{\text{a.s.}}$ for the three hydrogen atoms at the corners of a triangle transforms as $A_1 + E$ and we further note that $\Gamma^{\text{a.s.}}$ for the nitrogen atom transforms as A_1 under all the symmetry operations of the group. The results are written in Table 8.9 first for all four atoms. We can also consider the three hydrogen atoms separately and build up $\Gamma_{\text{mol.vib.}}$ from the N atom plus the three hydrogen LCAOs as two building blocks (see Problem 8.1).

$$\begin{aligned}
\Gamma_{\text{mol.vib.}} &= \Gamma^{\text{a.s.}} \otimes \Gamma_{\text{vec}} - \Gamma_{\text{trans}} - \Gamma_{\text{rot}} \\
\Gamma_{\text{mol.vib.}} &= (2A_1 + E) \otimes (A_1 + E) - (A_1 + E) - (A_2 + E) \\
&= 2A_1 + 2E\,. \qquad (8.23)
\end{aligned}$$

Table 8.9. Characters for the Atomic Site Transformation for the NH_3 molecule

	E	$2C_3$	$3\sigma_v$	
$\Gamma^{\text{a.s.}}_{\text{total}}$	4	1	2	$\Rightarrow 2A_1 + E$
$\Gamma^{\text{a.s.}}_{\text{H}}$	3	0	1	$\Rightarrow A_1 + E$

- One mode of the NH_3 molecule with A_1 symmetry is the breathing mode, where the nitrogen atom is at rest and the equilateral triangle expands and contracts (see Fig. 8.7(a)).
- For the A_1 out-of-plane breathing mode, the H atoms move in the $+z$ direction while the N atom moves in the $-z$ direction, such that no translation of the center of mass occurs (see Fig. 8.7(b)).
- One of the E modes is a doubly-degenerate in-plane mode. One eigenvector is made from the linear combination of hydrogen atom motions $(H_1 + \omega H_2 + \omega^2 H_3)$ where the motion of each H atom bears a phase relation of $\omega = e^{2\pi i/3}$ relative to the next H atom. The second eigenvector is

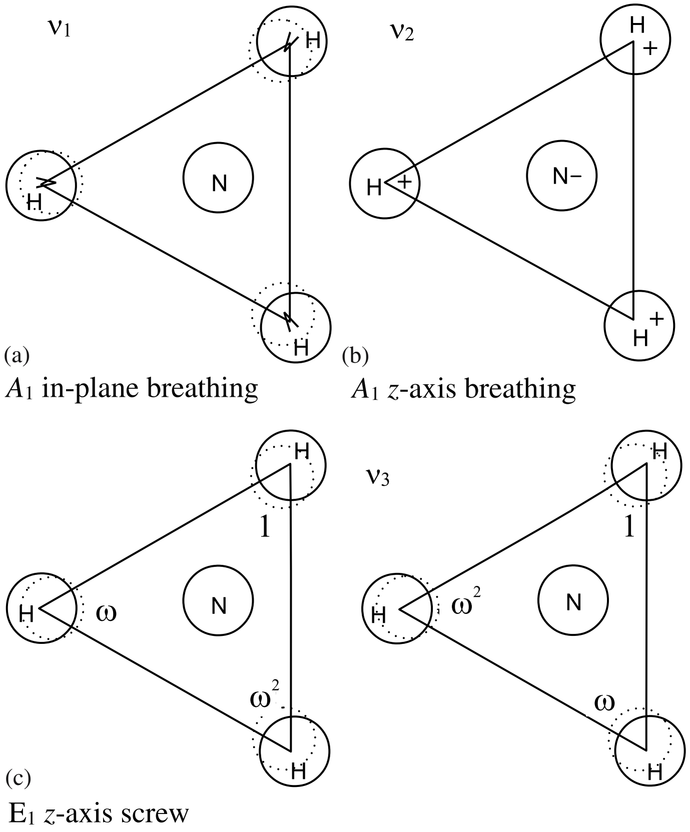


Fig. 8.7. Normal modes for the NH_3 molecule: (**a**) the in-plane breathing mode, (**b**) the out-of-plane (z-axis) breathing mode for which + and − refer to above and below the plane, respectively, and (**c**) the two partners of the in-plane mode of E symmetry which are complex conjugates of each other. The phase factor ω is $\exp(2\pi/3)$. There is also another doubly-degenerate E mode for z-axis (out-of-plane) motion that is not shown

$H_1 + \omega^2 H_2 + \omega H_3$ which is orthogonal to the first. The nitrogen atom moves in the xy plane in such a way as to prevent translation of the center of mass and rotation of the molecule (see Fig. 8.7(c)).
- For the second doubly degenerate E mode, the hydrogen atoms move in the out-of-plane direction with a phase difference between adjacent hydrogen atoms. For one partner, the three hydrogen atoms have phase factors of 1, ω and ω^2 while the second partner has motions with phases for its three hydrogen atoms that are the complex conjugates of the phases of the first partner $\omega = \mathrm{e}^{2\pi i/3}$ for one partner and $\omega^2 = \mathrm{e}^{4\pi i/3}$ for the other partner. The nitrogen atom again moves in such a way as to prevent translations or rotations of the molecule (not shown in Fig. 8.7(c)).

The molecular vibrations for the NH_3 molecule illustrate the concept of phase relations between the motions of various atoms in executing a normal mode. Though it should be emphasized that in the case of degenerate modes, the normal mode (basis function) picture is not unique, and therefore linear combinations of modes of the same symmetry are also possible. Since the normal modes for the NH_3 molecules have A_1 and E symmetries and since $\Gamma_{\text{vec}} = A_1 + E$, all the vibrational modes for NH_3 are infrared-active, with one of the two A_1 modes excited by polarization $\boldsymbol{E} \parallel \hat{z}$, the other being excited by polarization $\boldsymbol{E} \perp \hat{z}$. The same is true for the two E modes. The connection of the normal modes of NH_3 to the normal modes of three atoms at the vertices of a triangle is considered in Problem 8.1. For the case of the NH_3 molecule which has C_{3v} symmetry, the two Raman-active modes with A_1 symmetries have normal mode displacements $x^2 + y^2$ and z^2 and the two modes with E symmetries have normal mode displacements $(x^2 - y^2, xy)$ and (xz, yz), so that all the normal modes for the NH_3 molecule $(2A_1 + 2E)$ are Raman-active. Polarization selection rules imply that the A_1 modes are diagonal (i.e., scattering occurs when the incident and scattered polarizations are parallel $\boldsymbol{E}_{\mathrm{i}} \parallel \boldsymbol{E}_{\mathrm{s}}$), while the E modes are off-diagonal (i.e., scattering occurs when $\boldsymbol{E}_{\mathrm{i}} \perp \boldsymbol{E}_{\mathrm{s}}$).

8.8.3 Vibrations of the CH_4 Molecule

The CH_4 molecule is chosen to illustrate the vibrational modes of a five atom molecule with high symmetry and to give more practice with the T_d point group symmetry (Table A.32) because of the importance of this point group symmetry to semiconductor physics.

The equivalence transformation for the four hydrogen atoms of the CH_4 molecule yields $\Gamma_{4\mathrm{H}}^{\text{a.s.}} = A_1 + T_2$ (see Sect. 7.5.2) while for the carbon atom $\Gamma_{\mathrm{C}}^{\text{a.s.}} = A_1$ since the carbon atom is at the center of the regular tetrahedron. Thus for the whole CH_4 molecule with T_d symmetry we have $\Gamma^{\text{a.s.}} = 2A_1 + T_2$. In T_d symmetry, the radial vector transforms as T_2 while the angular momentum (or axial vector for rotations) transforms as T_1. We thus get the following result for $\Gamma_{\text{mol.vib.}}$ for the CH_4 molecule.

For the symmetry types in the molecular vibrations $\Gamma_{\text{mol.vib.}}$ (see Fig. 8.8):

$$\Gamma_{\text{mol.vib.}} = \Gamma^{\text{a.s.}} \otimes \Gamma_{\text{vec}} - \Gamma_{\text{trans}} - \Gamma_{\text{rot}}$$

$$\begin{aligned}
\Gamma_{\text{mol.vib.}} &= [(2A_1 + T_2) \otimes (T_2)] - \underbrace{T_2}_{\text{translations}} - \overbrace{T_1}^{\text{rot}} \\
&= 2T_2 + (T_1 + T_2 + E + A_1) - T_2 - T_1 \\
&= A_1 + E + 2T_2 \,.
\end{aligned}$$

For many molecules of interest, the normal modes are given in [40]. We give in Fig. 8.8 the normal modes adapted from this reference. For the CH_4 molecule only the modes with T_2 symmetry are infrared active. The modes with A_1, E, and T_2 symmetries are Raman active, where (xy, yz, zx) transforms as T_2 and

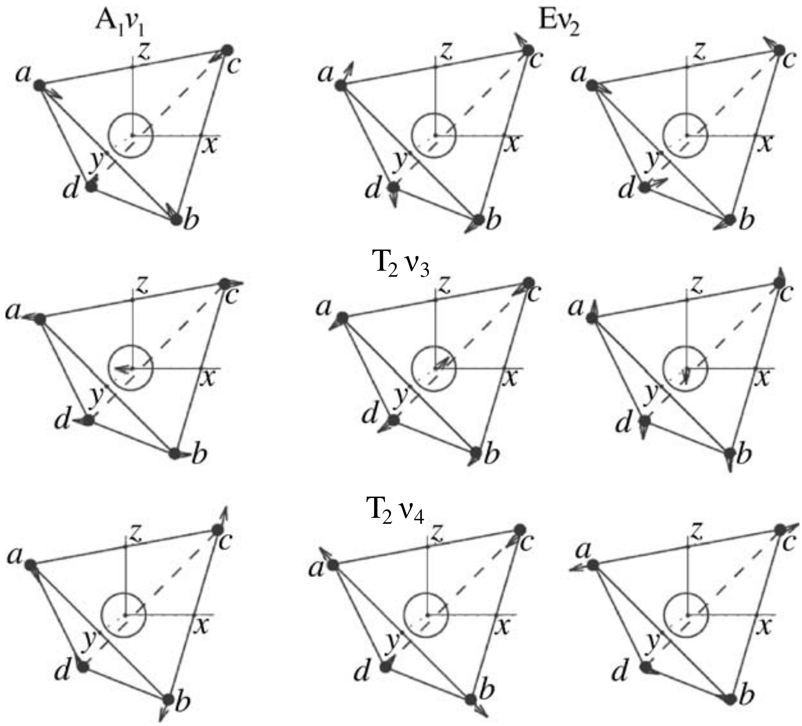


Fig. 8.8. Normal vibrations of a tetrahedral CH_4 molecule [40]. The three twofold axes (*dot-dash lines*) are chosen as the x-, y-, and z-axes. The exact directions of the H atom displacements depend on the nature of the C–H bond strength and the masses of H and C. Although CH_4 and CCl_4 have, of course, the same symmetry modes, the H and Cl atom displacement directions will differ. This issue was also discussed in Sect. 8.4 for the modes of H_2O (see Fig. 8.2)

the basis functions $x^2 - y^2$, and $3z^2 - r^2$ transform as E, while r^2 transforms as A_1 (see Table A.32).

We now give an example of harmonics and combination modes that can be observed in the second-order Raman and infrared spectra in terms of the CH_4 molecule. In Table 8.5 the frequencies of the four fundamental modes in the Raman spectra are given along with some of the overtones and combination modes. The symmetries of the overtones (harmonics) and combination modes are found by taking the direct product $\Gamma_i \otimes \Gamma_j$ between these modes. We see that the mode frequencies can deviate significantly from $\omega_i \pm \omega_j$ and the reason for this is that the perturbation which excites the harmonics and combination modes also perturbs the harmonic oscillator potential for the molecule with some combination mode frequencies being increased and others being decreased. We note that the T_2 modes are observed in the first-order infrared spectrum for CH_4. Some of the direct products of importance in interpreting the second-order spectra are

$$E \otimes E = A_1 + A_2 + E$$

and

$$T_2 \otimes T_2 = A_1 + E + T_1 + T_2 \,.$$

8.9 Rotational Energy Levels

In practice all molecules have rotational levels (labeled by quantum number j). In the approximation that we can discuss the rotational motion as distinct from the vibrational motion, the rotational motion of molecules should be much lower in frequency than the vibrational motion, and of course *very* much lower in frequency than the electronic motion. Typical rotational energies are of the order of $\sim 1\,\text{meV}$ and occur at far-infrared frequencies. The vibrational modes are observed in the mid-IR range, typically in the range 20–200 meV.

In Sect. 8.9.1 we discuss rotational energy levels of a molecule in terms of the rigid rotator as a simple example. Then in Sect. 8.9.2 we state the Wigner–Eckart theorem which gives in succinct form the selection rules for IR and Raman activity for rotational energy levels. Finally in Sect. 8.9.3 we introduce the coupling between the vibrational and rotational levels, giving some examples of rotational energy levels for a few simple molecules.

8.9.1 The Rigid Rotator

To illustrate molecular vibrations, we consider the simple case of the rigid rotator neglecting the effect of the molecular vibrations. The Hamiltonian for

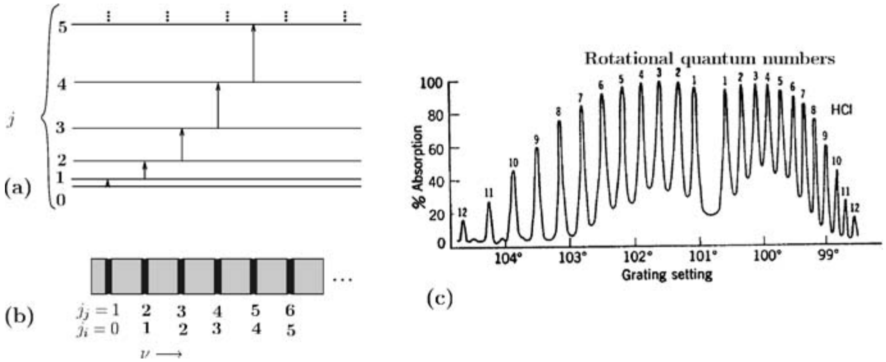


Fig. 8.9. (**a**) Rotational levels of a diatomic molecule. (**b**) Energy separation between sequential rotational levels. (**c**) The rotational absorption spectrum for gaseous HCl

rotational motion is written as

$$\mathcal{H}_{\text{rot}} = \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z}\,, \tag{8.24}$$

where I_x, I_y, I_z are the principal moments of inertia and J_x, J_y, J_z are the angular momentum operators. The coordinates x, y, z are chosen so that the z axis is along the main symmetry axis of the molecule. If we have a diatomic molecule, one principal moment of inertia vanishes $I_z = 0$, while the other two become equal $I_x = I_y$. In this case the Hamiltonian is simply

$$\mathcal{H}_{\text{rot}} = \frac{J^2}{2I}\,, \tag{8.25}$$

and has eigenvalues

$$E_j = \hbar^2 j(j+1)/2I\,.$$

Unlike the vibrational energy levels which are all equally spaced with a level separation $\hbar\omega_v$, the rotational energy levels are unequally spaced:

$$E_{j+1} - E_j = \mathcal{C}[(j+1)(j+2) - j(j+1)] = 2\mathcal{C}(j+1) \tag{8.26}$$

with $\mathcal{C} = \hbar^2/2I$ and the level spacing depends on the quantum number j (see Fig. 8.9(a)). If the molecule contains a permanent electric dipole moment, then it is possible to excite the molecule into higher rotational energy states by electric dipole transitions. The selection rules for transitions between rotational energy levels follow from the Wigner–Eckart theorem (Sect. 8.9.2).

According to this theorem, for light polarized along the principal axis of rotation of the HCl molecule, the selection rule for electric dipole transitions is $\Delta j = 0$ while for light polarized in the plane ⊥ to this axis, the selection rule is $\Delta j = \pm 1$. If there is no vibrational–rotational interaction, $\Delta j = 0$ does not give rise to optical absorption.

Thus, the first rotational transition will require a photon energy $2\mathcal{C}$, the second $4\mathcal{C}$, the third $6\mathcal{C}$, etc. This pattern is indicated in Fig. 8.9(a) for the HCl molecule and in Fig. 8.9(b) we see that $(E_j + 1 - E_j)$ increases proportional to (j_1) with a constant coefficient of $2C$. The actual spectrum for HCl is shown in Fig 8.9(c). It is clear that diatomic molecules like H_2 have a *center of inversion* and hence *no permanent dipole moment.* Thus, molecules of this type do not exhibit any pure rotational infrared spectra. On the other hand, heterogeneous diatomic molecules like CO and HCl can exhibit rotational infrared spectra.

8.9.2 Wigner–Eckart Theorem

The Wigner–Eckart theorem, based on the full rotation group, gives the selection rules for transitions between rotational levels observed for molecules in IR and Raman spectroscopy and their polarization effects.

For proof of the Wigner–Eckart theorem, see Tinkham, p. 131–132 [70]. This theorem deals with the matrix elements of a tensor T^{ω}_{μ} where ω is the rank of the tensor and μ is a component index, to be discussed further below. The theorem is discussed for angular momentum states which correspond (through the group of Schrödinger's equation) to the full rotation group.

The full rotation group has only odd-dimensional representations:

$$\begin{aligned} \text{One-dimensional} \quad & \ell = 0 \ s\text{-states} \\ \text{Three-dimensional} \quad & \ell = 1 \ p\text{-states} \\ \text{Five-dimensional} \quad & \ell = 2 \ d\text{-states}\,. \end{aligned}$$

Thus, a scalar ($\ell = 0$) corresponds to a tensor with $\omega = 0$ and $\mu = 0$. A vector corresponds to a tensor with $\omega = 1$, $\ell = 1$, and $\mu = \pm 1, 0$, which denote the three m_ℓ values for $\ell = 1$. A general second rank tensor can be considered as the direct product

$$\Gamma^{\ell=1} \otimes \Gamma^{\ell=1} = \Gamma^{\ell=0} + \Gamma^{\ell=1} + \Gamma^{\ell=2} \tag{8.27}$$

having dimensions $3 \times 3 = 1 + 3 + 5 = 9$. Thus the second rank tensor will have a part which transforms as $\omega = 0$ and $\mu = 0$, another part which transforms as $\omega = 1$, $\mu = \pm 1, 0$ and a third part which transforms as $\omega = 2$, $\mu = \pm 2, 1, 0$, thereby accounting for all nine components of the second rank tensor. The parts that transform as $\omega = 0$ and $\omega = 2$ constitute the symmetric components and correspond to the Raman tensor. The parts that transform as $\omega = 1$ constitute the antisymmetric components of a second rank tensor and correspond to the angular momentum components.

Because of the form of the Wigner–Eckart Theorem given by

$$\left(N'j'm'\left|T^{\omega}_{\mu}\right|Nj\right) = A^{j\omega j'}_{m\mu}\,\delta_{m',m+\mu}\,(Nj'||T^{\omega}||Nj)\ , \tag{8.28}$$

the selection rules for a tensor operator T^{ω}_{μ} between states having full rotational symmetry can be obtained quickly. Here j' lies in the range

$$|j-\omega| \le j' \le (j+\omega)\,, \tag{8.29}$$

which is related to the properties of the addition of angular momentum vectors. In (8.28), N and N' are principal quantum numbers, j and j' are quantum numbers for the total angular momentum, while m and m' are quantum numbers for the z component of the angular momentum. The coefficients $A^{j\omega j'}_{m\mu}$ are called Wigner coefficients [2] and are tabulated in group theory texts (see for example, Tinkham) [70]. The reduced matrix element $(Nj'||T^{\omega}||Nj)$ in (8.28) is independent of μ, m, and m' and can therefore be found for the simplest case $\mu = m' = m = 0$. This generality makes the Wigner–Eckart theorem so powerful. The selection rules on both j and m are obtained by rewriting the restrictions implied by (8.28) and (8.29), yielding

$$\begin{aligned}|\Delta j| &= |j-j'| \le \omega\\ |\Delta m| &= |m'-m| = \mu \le \omega\,.\end{aligned} \tag{8.30}$$

We now write down some special cases of (8.30).

For electric dipole transitions, we have $\omega = 1$ and the selection rules

$$\begin{aligned}\Delta j &= 0, \pm 1\\ \Delta m &= 0 \quad \text{for} \quad \boldsymbol{E} \parallel \hat{z}\\ \Delta m &= \pm 1 \quad \text{for} \quad \boldsymbol{E} \perp \hat{z}\,,\end{aligned} \tag{8.31}$$

where $\boldsymbol{E} \parallel \hat{z}$ refers to linear polarization along the quantization axis and $\boldsymbol{E} \perp \hat{z}$ refers to circular polarization about the quantization axis.

For Raman transitions (where $\mathcal{H}'_{\text{Raman}}$ transforms as a second rank symmetric tensor), we have either $\omega = 0$ or $\omega = 2$ and the corresponding selection rules

$$\begin{aligned}\omega = 0: &\quad \Delta j = 0\,, \quad \Delta m = 0\,,\\ \omega = 2: &\quad \Delta j = 0, \pm 1, \pm 2\,, \quad \Delta m = 0, \pm 1, \pm 2\,.\end{aligned} \tag{8.32}$$

In specific geometries, not all of these transitions are possible.

In applying the Wigner–Eckart theorem to the *rotational selection rules* for a *linear diatomic molecule*, we know that the dipole moment must be along the molecular z-axis, so that only $\mu = 0$ applies. In this case the *Wigner–Eckart Theorem* gives the selection rules

$$\begin{aligned}\Delta j &= 0, \pm 1\,; \quad \Delta m = 0 \quad \text{for I.R. activity}\\ \Delta j &= 0, \pm 2\,; \quad \Delta m = 0 \quad \text{for Raman activity}\,.\end{aligned} \tag{8.33}$$

8.9.3 Vibrational–Rotational Interaction

Since the nuclei of a molecule are actually in vibrational motion, there is consequently an interaction between the vibrational and rotational motions. These interactions become important when the energy of a rotational energy level becomes comparable to a vibrational energy level. Let us illustrate this coupling in terms of a diatomic molecule, where we write for the Hamiltonian

$$\mathcal{H} = \frac{p^2}{2\mu} + \frac{J^2}{2\mu R^2} + a_2\xi^2 + a_3\xi^3\,, \tag{8.34}$$

in which the first term is the kinetic energy (and μ is the reduced mass of the molecule). The second term denotes the rotational energy of the molecule, while $a_2\xi^2$ is the harmonic restoring force for the vibrational energy, and $a_3\xi^3$ is an anharmonic restoring term arising in the vibrational problem. The distance between the nuclei is now modified by the vibrational displacements from equilibrium

$$\frac{R - R_{\mathrm{eq}}}{R_{\mathrm{eq}}} = \xi \quad \text{where} \quad R = R_{\mathrm{eq}}(1+\xi)\,. \tag{8.35}$$

We therefore write

$$\frac{1}{R^2} = \frac{1}{R_{\mathrm{eq}}^2(1+\xi)^2} = \frac{1}{R_{\mathrm{eq}}^2}\left[1 - 2\xi + 3\xi^2 + \cdots\right] \tag{8.36}$$

so that we can express the Hamiltonian in terms of an unperturbed term $\mathcal{H}_0$ and a perturbation term $\mathcal{H}'$:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'\,, \tag{8.37}$$

where

$$\mathcal{H}_0 = \frac{p^2}{2\mu} + B_{\mathrm{eq}}J^2 + a_2\xi^2 \tag{8.38}$$

and

$$B_{\mathrm{eq}} = \frac{1}{2\mu R_{\mathrm{eq}}^2}\,. \tag{8.39}$$

The first term in (8.38) denotes the kinetic energy and the second term defines the rotational energy when the molecule is in its equilibrium configuration, while the third term denotes the vibrational potential energy for the harmonic restoring forces. Thus $\mathcal{H}_0$ gives the energies for the vibrational and rotational motion in the limit where the vibrational and rotational motions are decoupled. For the $\mathcal{H}_0$ limit the selection rules are the same as if the vibrations and rotations occurred independently. The perturbation Hamiltonian then becomes

$$\mathcal{H}' = a_3\xi^3 - 2B_{\mathrm{eq}}\xi J^2 + 3B_{\mathrm{eq}}\xi^2 J^2\,, \tag{8.40}$$

where the first term is an anharmonic term that gives rise to overtones and combination modes in the vibrational spectrum. The second and third terms in (8.40) are associated with coupling between rotational and vibrational levels and give corrections to the rotational levels. The term in ξJ^2 makes a contribution in second-order perturbation theory, while the term in $\xi^2 J^2$ makes a contribution in first-order perturbation theory which is proportional to

$$\left(n+\frac{1}{2}\right)\hbar\omega_v j(j+1)\,.$$

Thus, the application of perturbation theory results in energy levels for the vibrational–rotational problem:

$$E_{n,j} = \underbrace{\hbar\omega_v\left(n+\frac{1}{2}\right)}_{\text{pure vibrational}} + \underbrace{\mathcal{A}_1 j(j+1)}_{\text{pure rotational}} + \underbrace{\mathcal{A}_2\,\hbar\omega_v\left(n+\frac{1}{2}\right)j(j+1)+\cdots}_{\text{interaction terms}} \qquad (8.41)$$

in which $\mathcal{A}_1$ and $\mathcal{A}_2$ are constants. For the diatomic molecule $\mathcal{A}_1 = (\hbar/2I)$ in accordance with (8.25). From a group theoretical point of view, the interaction terms modify the selection rules and new features in the IR and Raman spectra can be seen. In general, the symmetry of an interacting vibrational and rotational level is given by the direct product $\Gamma_{\text{vib}} \otimes \Gamma_{\text{rot}}$.

In making rotational transitions on absorption between different vibrational levels, we not only can have $\Delta j = 1$ (*the R-branch*) but we also can have $\Delta j = -1$ (*the P-branch*). This is illustrated in the vibrational–rotational spectrum shown in Fig. 8.10 for the HCl molecule. We note here that the spectral lines in the R-branch (upshifted in frequency) are not symmetrically spaced with respect to the down-shifted P-branch. The *Q-branch* ($\Delta j = 0$) occurs very close to the central frequency ν_0, and would in fact be coincident with ν_0 if the moment of inertia would be independent of the vibrational state. Study of the *Q*-branch requires high resolution laser spectroscopy.

If there were no vibrational–rotational interaction, the spacing of all spectral lines (shown in the top portion of Fig. 8.10) would be the same for all vibrational levels n. For the case of diatomic molecules and for the polarization where $\boldsymbol{E}$ is along the molecular axis, then the selection rules $\Delta n = +1$ and $\Delta j = 0$ determine the vibrational–rotational spectrum, while for $\boldsymbol{E}$ perpendicular to the main symmetry axis of the molecule, the selection rules are $\Delta n = 0$ and $\Delta j = +1$.

Rotational Raman Spectra are also observed. Here the transitions with $\Delta j = 2$ are excited for the pure rotational transitions, $\Delta n = 0$ (see Figs. 8.9 and 8.10). This series is called the *S-branch.* When vibrational–rotational Raman spectra are excited, transitions with $\Delta j = 0$ and $\Delta j = -2$ are also possible and these are called the *O-branches.* Because of the anharmonic terms in the Hamiltonian, there are vibrational–rotational spectra which occur between vibrational states separated by $\Delta n = 2, 3, \ldots$, etc. These anharmonic transitions would be expected to have lower intensity.

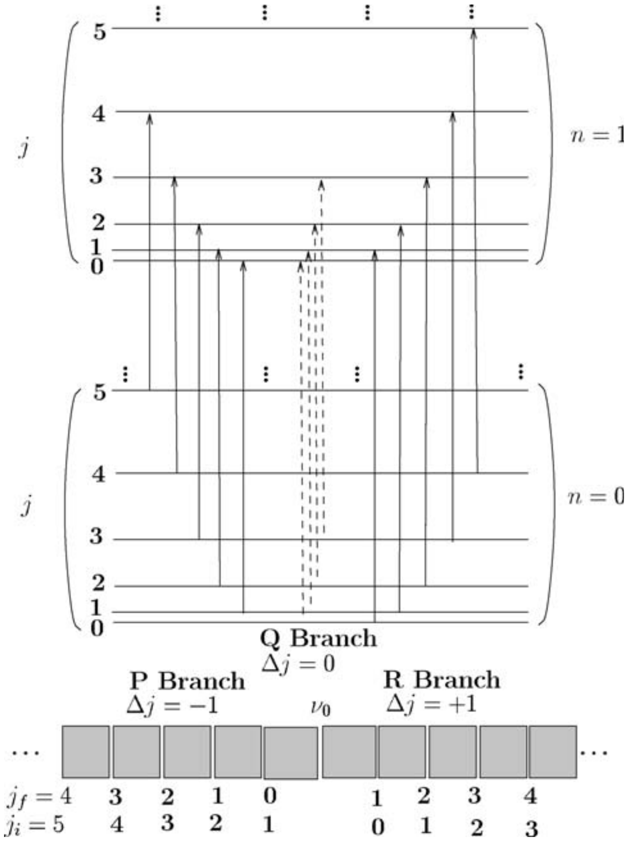


Fig. 8.10. P ($\Delta j = -1$), R ($\Delta j = +1$) and Q ($\Delta j = 0$) branches of the rotational structure of the HCl vibrational–rotational band near 2,885 cm^{-1} shown schematically

The above discussion focused on the vibrational degrees of freedom. There are in addition the electronic levels which generally are separated by much greater energies than are the vibrational and rotational levels. There is however some interaction also between the vibrational and rotational states and the electronic levels. *Interactions between the electronic and rotational levels* give rise to "*Λ-doubling*" of the rotational levels, and *coupling between the electronic and vibrational levels* gives rise to *vibronic levels.*

Selected Problems

8.1. This problem relates to the interrelation of fundamental group theory concepts from small molecular clusters to the molecular vibrations of actual molecules of interest. We illustrate this approach using the normal modes for three equal masses at the corners of an equilibrium triangular (see Sect. 8.1).

(a) Find the normal modes for a triangular cluster containing three hydrogen atoms at the corners of an equilateral triangle. Indicate which modes are IR active and which are Raman active.
(b) Find the normal modes for a hypothetical planar NH_3 molecule where the N atom is at the centroid of the triangle and coplanar with the three hydrogens. Which point group describes this molecule? Which modes are infrared active and which are Raman active?
(c) Relate the results in (a) and (b) to the normal modes, and to the IR and Raman activity for the NH_3 molecule with C_{3v} group symmetry.
(d) Relate the normal modes of the water molecule (Sect. 8.4) to the normal modes of the triangular cluster in (a). Account for the similarities and differences between the two cases.

8.2. Both CO_2 and N_2O are linear molecules, but have different equilibrium arrangements giving rise to different symmetry groups (see Fig. 8.11).

(a) What are the appropriate point groups for CO_2 and N_2O?
(b) What symmetries are involved for the bonding and antibonding electronic orbitals for these molecules?
(c) What are the differences in the symmetries of the normal modes for these two molecules?
(d) Show schematically the atomic displacements for the normal modes of each molecule.
(e) What are the expected differences in their IR spectra? Raman spectra?
(f) What are the expected differences in the rotational spectra of these two molecules?
(g) Which of these rotational modes can be excited by infrared or Raman spectroscopy?

8.3. Consider the linear C_2H_2 molecule (H–C=C–H) as being composed of either two C–H blocks or of another configuration with the two hydrogen atoms vibrating against the two carbon atoms as another block, each with internal degrees of freedom. Such block grouping approaches help in providing intuition about the internal vibrations of complex molecules.

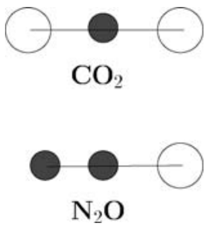


Fig. 8.11. Configurations for the linear molecules CO_2 and N_2O

(a) Show that the same results for $\Gamma_{\text{mol.vib.}}$ are obtained for C_2H_2 by taking the direct product of the $\Gamma_{\text{mol.vib.}}$ for the constituent C–H blocks considered above.
(b) By applying appropriate symmetry operations on the basis functions, show that the bending and stretching modes as given in Fig. 8.6 belong to the E_{1g} and E_{1u} irreducible representations.

8.4. C_2H_4 (ethylene) is a planar molecule which has the configuration shown on Fig. 8.12.

(a) Using the point group and $\Gamma^{\text{a.s.}}$ found in Problem 7.4, find the symmetries of the allowed molecular vibrations for the C_2H_4 molecule.
(b) Sketch the normal mode displacements for each of the allowed molecular vibrations in (a).
(c) Which modes are infrared-active? Which are Raman-active? What are the polarization selection rules?

8.5. This problem is designed to show that group theory becomes increasingly important for treating molecular vibrations for high symmetry molecules

(a) Find the molecular vibrations for the hypothetical molecule XH_{12} where the 12 hydrogen atoms are at the vertices of a regular icosahedron and the atom X is at the center of the icosahedron. Find $\Gamma^{\text{a.s.}}$ for XH_{12} for the icosahedral group I_h.
(b) What are the symmetries for the normal modes? Which are infrared-active? Raman active?
(c) What are the polarization selection rules for observing the infrared modes? for the Raman modes?

8.6. Consider the methane molecule CH_4.

(a) What is the group symmetry and to which irreducible representations do the R_x, R_y, and R_z basis functions belong (see Sect. 7.5.2 and Sect. 8.8.3)?
(b) Describe the symmetries and eigenvectors for the rotational levels.
(c) What are the symmetries for the vibrational–rotational interactions?
(d) Describe the infrared and Raman spectra of methane including rotational, vibrational modes, and the interaction between them. Consider also the combination modes (see Table A.32).
(e) What are the expected polarization effects in these spectra?

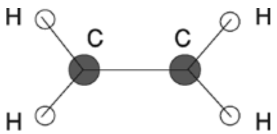


Fig. 8.12. Configurations of the C_2H_4 ethylene molecule