Chapter 1

Brief introduction to molecular symmetry

It is possible to understand the electronic structure of diatomic molecules and their interaction with light without the theory of molecular symmetry. But understanding molecular symmetry is essential, e.g., for the treatment of selection rules in polyatomic molecules. In this course, we only present the most basic elements of molecular symmetry, and we do it in a largely non-mathematical way. See Chapter 5 in Molecular Quantum Mechanics (Atkins and Friedman) for more details of the underlying mathematical theory: group theory.

1.1 Symmetry operations and elements

A **symmetry operation** is an operation that leaves an object apparently unchanged. For example, a rotation of a sphere through any angle around its center is a symmetry operation. Every object has at least one symmetry operation: the **identity**, the operation of doing nothing. To each symmetry operation there corresponds a **symmetry element**, the point, line or plane with respect to which the operation is carried out. In order to discuss the symmetry of molecules, we need five symmetry elements.

I or E The **identity** operation, the act of doing nothing. The corresponding symmetry element is the object itself.

C_n An **n-fold rotation**, a rotation by $2\pi/n$ around an *axis of symmetry*.

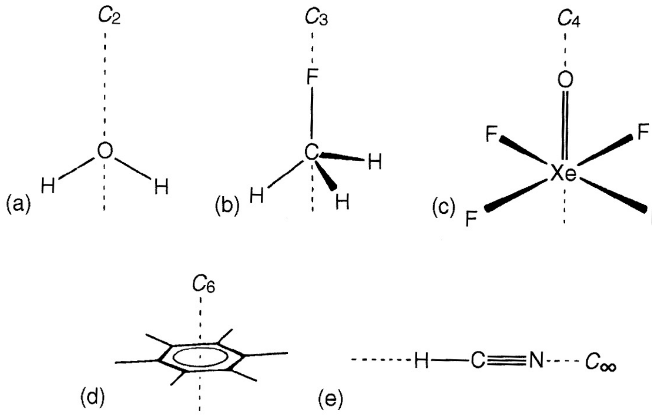


Figure 1.1: Examples of the C_n axes of rotation.

If an object has several axes of rotation, the one with the largest value of n is called the principal axis. In this course, we assume that the rotations are performed clockwise, when viewed from above.

σ A **reflection** in a *mirror plane.* When the mirror plane includes the the principal axis of symmetry, it is called a vertical plane and denoted σ_v. If the principal axis is perpendicular to the mirror plane, the latter symmetry element is called a horizontal plane (σ_h). A dihedral plane (σ_d) is a vertical plane that bisects the angle between two C_2 axes that lie perpendicular to the principal axis.

i An **inversion** through a *centre of symmetry.*

S_n An **improper rotation** through an *axis of improper rotation.* An improper rotation is a composite operation, where an n-fold rotation is followed by a reflection in a plane that is perpendicular to the n-fold axis. Neither operation alone is in general a symmetry operation, but the overall outcome is.

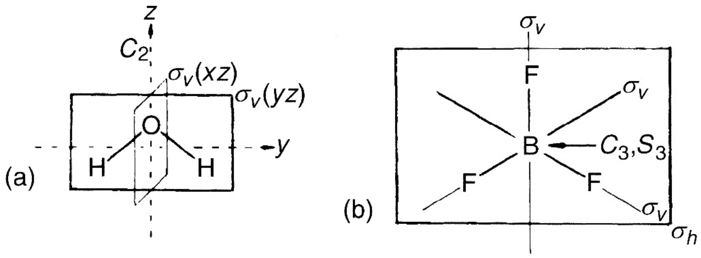


Figure 1.2: Symmetry elements of the (a) H_2O and (b) BF_3 molecules.

1.2 The classification of molecules

To classify a molecule according to its symmetry, we list all of its symmetry operations, and then ascribe a label, the **point group** to the molecule based on the list of those operations. The term 'point' indicates that after performing all the operations of the point group, at least one point of the molecule does not move at all. For the notation we use the Schoenflies system, where the name of the point group is based on a dominant feature of the symmetry of the molecule.

The point groups are:

1. The groups C_1, C_s and C_i. These groups consist of the identity alone (C_1), the identity and reflection (C_s), and the identity and an inversion (C_i).

2. The groups C_n. These groups consist of the identity and an n-fold rotation.

3. The groups C_{nv} In addition to the operations of the groups C_n, these groups also contain n vertical reflections. An important example is the group $C_{\infty v}$, the group to which heteronuclear diatomic molecules belong.

4. The groups C_{nh}. In addition to the operations of the groups C_n, these groups also contain a horizontal reflection (together with whatever operations the presence of the operations implies).

5. The groups D_n. In addition to the operations of the groups C_n, these groups possess n two-fold rotations perpendicular to the n-fold (principal) axis (together with whatever operations the presence of the operations implies).

6. The groups D_{nh}. These groups consist of operations present in D_n, together with a horizontal reflection (and together with whatever operations the presence of the operations implies). An important example is the group $D_{\infty h}$, the group to which homonuclear diatomic molecules belong.

7. The groups D_{nd}. These groups consist of operations present in D_n and n dihedral reflections (together with whatever operations the presence of the operations implies).

8. The groups S_n, with n even. These groups contain the identity and an n-fold improper rotation (together with whatever operations the presence of the operations implies).

9. The cubic (T, T_h, T_d, O, O_h) and icosahedral (I, I_h) groups. These groups contain more than one n-fold rotation with $n \geq 3$.

10. The full rotation group, R_3. The group consists of all rotations through any angle and in any orientation. This is the symmetry group of the sphere and atoms.

1.3 Calculus of symmetry elements

In the list above, we have indicated that the presence of certain symmetry operations implies that some other symmetry operations automatically exist. For example, the point group C_{2h} automatically possess an inversion, because a rotation by 180° followed by a horizontal reflection is equivalent to inversion. This can be written as an equation

$$\sigma_h C_2 = i. \tag{1.1}$$

It is a general feature of symmetry operations that the outcome of a joint symmetry operation is *always* equivalent to a single symmetry operation

$$RS = T, \tag{1.2}$$

where R, S and T all are symmetry operations of the group. The operation S is carried out first, R after that.

We can say that σ_h and C_2 generate the element i; they can be regarded as generating elements. We can generate other elements from the symmetry element C_n by raising it to the power of 1, 2, 3, ..., (n-1). For example, if there is an element C_3, there must be also C_3^2, where

$$C_3^2 = C_3 \times C_3. \tag{1.3}$$

C_3^2 is a rotation clockwise by $2 \times (2\pi/3)$ radians. It also corresponds to a rotation counterclockwise by $(2\pi/3)$, which can labeled with a symbol C_3^{-1}. This is the inverse of the operation C_3. Generally

$$C_n^{n-1} = C_n^{-1}. \tag{1.4}$$

We can also generate the powers of S_n from the element S_n. For example, we obtain for S_4

$$\begin{array}{rcl} S_4^2 & = & C_2 \\ S_4^3 & = & S_4^{-1}, \end{array} \tag{1.5}$$

where S_4^{-1} means a counterclockwise rotation by $2\pi/4$ rad followed by a reflection. The inverse σ^{-1} of the reflection is the reflection itself.

The properties of the symmetry operations in point groups fulfil the same requirements that are necessary for a set of entities to form a group in mathematics. Consequently, the mathematical theory of groups, **group theory**, may be applied to the study of the symmetry of molecules.

1.4 Character tables

Point groups are either non-degenerate or degenerate. A degenerate point group contains a C_n axis with $n > 2$ or an S_4 axis. A molecule belonging to such a point group may have degenerate properties, e.g., electronic wavefunctions or vibrational wavefunctions that have the same energies. A molecule that belongs to a non-degenerate point group cannot have degenerate properties.

We have seen how molecules can be classified into point groups according to the locations of their nuclei in the equilibrium geometry. Molecules can, however, have properties such as the above mentioned wave functions that do not have all the symmetry elements of the point group. Character tables are used to classify the symmetries of these properties. We will inspect the character tables of the C_{2v}, C_{3v} and $C_{\infty v}$ point groups. The first of them is non-degenerate, the second degenerate and the third an example of a point group with an infinite number of symmetry elements.

1.4.1 The C_{2v} character table

For example, the vibrational wavefunction of H_2O may or may not have a certain symmetry element. If it has the element, the application of the corresponding symmetry operation does not affect the wavefunction, which we can write

$$\psi_v \xrightarrow{\sigma_v} (+1)\psi_v \tag{1.6}$$

and say that ψ_v is *symmetric* with respect to σ_v. The only other possibility in a non-degenerate point group is that the wavefunction changes sign in the operation

$$\psi_v \xrightarrow{\sigma_v} (-1)\psi_v, \tag{1.7}$$

in which case ψ_v is *antisymmetric* with respect to σ_v. The numbers +1 and -1 appearing in equations (1.6) and(1.7) are known as the *characters* of ψ_v with respect to σ_v (in this particular case).

Any two of the elements C_2, $\sigma_v(xz)$ and $\sigma_v'(yz)$ can be regarded as *generating elements*. There are four possible combinations of characters with respect to these generating elements: +1 and +1, +1 and -1, -1 and +1, and +1, -1, -1. These are listed in the third and fourth columns of the character table below. We have selected C_2 and $\sigma_v(xz)$ as the generating elements. The characters under I have to be always 1. Just as $\sigma_v'(yz)$ can be generated by C_2 and $\sigma_v(xz)$, the characters under $\sigma_v'(yz)$ are the products of the characters under C_2 and $\sigma_v(xz)$. Each of the four rows of the characters is called an irreducible representation of the group and are labeled for practicality with the **symmetry species** A_1, A_2, B_1 and B_2. The A_1 is said to be totally symmetric because all of its characters are +1. The three other species are non-totally symmetric.

The notation of the symmetry species follows the convention. A indicates the symmetry with respect to C_2, B antisymmetry. The subscripts indicate symmetry (1) and antisymmetry (2) with respect to $\sigma_v(xz)$.

In the sixth column of the character table, the symmetry species are given for the translations (T) of the molecule along the coordinate axes and for the rotations (R) around the axes. In Fig. 1.4 the vectors attached to the nuclei

Table 1.1: The character table of the C_{2v} point group.

C_{2v}	I	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	T_z	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
A_2	1	1	-1	-1	R_z	α_{xy}
B_1	1	-1	1	-1	T_x, R_y	α_{xz}
B_2	1	-1	-1	1	T_y, R_x	α_{yz}

of the H_2O molecule represent these displacements, which have the symmetry species according to how they behave under the operations C_2 and $\sigma_v(xz)$. Figures 1.4(a) and (b) show that

$$\Gamma(T_x) = B_1; \;\; \Gamma(T_y) = B_2; \;\; \Gamma(T_z) = A_1 \tag{1.8}$$

$$\Gamma(R_x) = B_2; \;\; \Gamma(R_y) = B_1; \;\; \Gamma(R_z) = A_2. \tag{1.9}$$

The symbol Γ stands generally for a representation. In this case it is an irreducible representation of the symmetry species. The symmetry species of the translations are needed, when selection rules of electronic transitions are determined for polyatomic molecules. The symmetry species for the components of the symmetric polarizability tensor α, given in the last column of the character table, are needed in Raman spectroscopy.

Let us look at an N-atomic molecule. $3N$ coordinates are needed to specify its location accurately, i.e. three Cartesian coordinates for each atom. Each atom may change its location by varying one of its three coordinates, so the total number of displacements available is $3N$. We say that the molecule has $3N$ degrees of freedom. These can be arranged in a physically sensible way. Three coordinates are needed to specify the location of the centre of mass along the coordinate axes (translational degrees of freedom). Furthermore, three coordinates are needed to specify the orientation of the molecule with respect a coordinate system that is fixed in space. The movement about these coordinates corresponds to the rotational motion of the molecule (rotational degrees of freedom). The remaining $3N - 6$ coordinates represent the movements of the nuclei with respect to each other, that is vibrations (vibrational degrees of freedom). Linear molecules have, however, $3N - 5$ vibrational degrees of freedom, because the moment of inertia about the molecular axis is zero and the corresponding rotational motion has no degree of freedom.

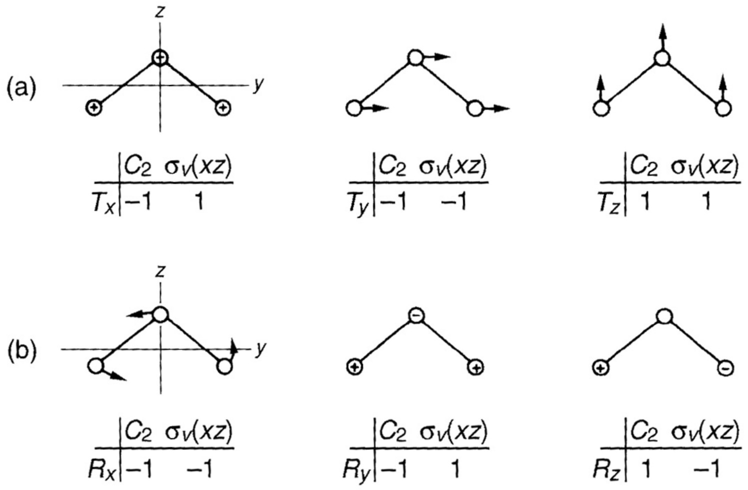


Figure 1.3: The (a) translations and (b) rotations of the H_2O molecule.

The molecule has the same number of normal modes (of vibration) as it has vibrational degrees of freedom. A normal mode means an idealized vibrational motion where all the nuclei move harmonically with the same frequency and phase, but generally with different amplitudes. Every normal mode has its characteristic frequency. Every vibrational motion of a molecule can be represented as a sum of normal modes.

The H_2O molecule has thus three normal modes, which are shown in Fig. 1.5. The arrows fixed to the nuclei indicate the directions and amplitudes of the displacements. The symmetry species of each vibration can be determined using the C_{2v} character table. We obtain the following characters under the operations C_2 and $\sigma_v(xz)$: +1 and +1 for ν_1, +1 and +1 for ν_2, and -1 and -1 for ν_3. Therefore

$$\Gamma(\psi_{\nu(1)}) = A_1; \quad \Gamma(\psi_{\nu(2)}) = A_1; \quad \Gamma(\psi_{\nu(3)}) = B_2. \tag{1.10}$$

The classification of molecular properties into the symmetry species depends on the choice of the axes. The convention for a planar molecule of C_{2v} symmetry is that the z axis is parallel to the C_2 axis and the x axis is perpendicular to the molecule. We follow this convention. If we interchanged x and y axes, then $\Gamma(\psi_{v(3)})$ would be B_1, not B_2. It is important to mark the axes chosen on the picture.

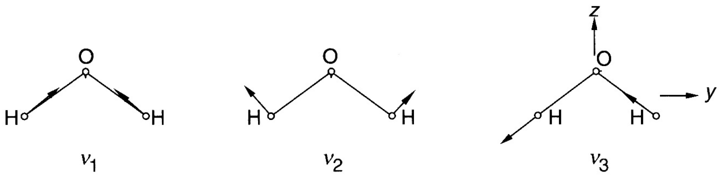


Figure 1.4: The normal modes of the H_2O molecule.

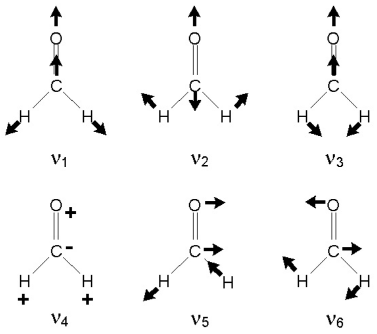


Figure 1.5: The normal modes of formaldehyde.

Example 1.1. Formaldehyde is a planar molecule and it has six normal modes that can be roughly illustrated as in the figure below. Determine the symmetry species of the normal modes in the proper point group using the axes drawn on the picture.

Solution. Formaldehyde belongs to the C_{2v} point group. Using the C_{2v} character table, the characters of the vibrations can be classified as shown on the following page.

It follows from these that symmetry species $\Gamma(\psi_v)$ of the vibrations are:

$$\begin{aligned}
\Gamma(\psi_{v(i)}) &= A_1 \\
\Gamma(\psi_{v(ii)}) &= B_2 \\
\Gamma(\psi_{v(iii)}) &= A_1 \\
\Gamma(\psi_{v(iv)}) &= B_2 \\
\Gamma(\psi_{v(v)}) &= A_1 \\
\Gamma(\psi_{v(vi)}) &= A_2
\end{aligned}$$

The classification can be done using any two of the symmetry elements C_2,

Table 1.2: The characters of the normal modes of formaldehyde.

Vibration	I	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
(i)	1	1	1	1
(ii)	1	-1	-1	1
(iii)	1	1	1	1
(iv)	1	-1	-1	1
(v)	1	1	1	1
(vi)	1	-1	1	-1

$\sigma_v(xz)$ and $\sigma'_v(yz)$, because they generate the third one and the character under E is always 1 in this point group.

These vibrations can be described with terms: (i) symmetric CH stretch, (ii) antisymmetric CH stretch, (iii) CH_2 scissors, (iv) CH_2 rocking, (v) CO stretch and (vi) out-of-plane bending.

Often we have to multiply symmetry species, or as expressed in the language of group theory, form their direct product. For example, if one quantum is excited in both the ν_1 and ν_3 modes, the symmetry species of the wavefunction of this state is

$$\Gamma(\psi_v) = A_1 \times B_2 = B_2. \tag{1.11}$$

In order to form the direct product of two symmetry species we multiply the characters under each symmetry element using the rules

$$(+1) \times (+1) = 1; \quad (+1) \times (+1) = -1; \quad (-1) \times (-1) = 1. \tag{1.12}$$

The result of Eq. (1.11) has been obtained in this way. If two ν_3 quanta are excited in H_2O

$$\Gamma(\psi_v) = B_2 \times B_2 = A_1. \tag{1.13}$$

The results of multiplications in Eqs. (1.11) and (1.13) generally apply to non-degenerate point groups. Thus (a) the product of any symmetry species with a totally symmetric species does not change the symmetry species and (b) the product of any symmetry species with itself gives a totally symmetric species.

It can also be shown that in the C_{2v} point group

$$A_2 \times B_1 = B_2; \quad A_2 \times B_2 = B_1. \tag{1.14}$$

Table 1.3: The C_{3v} character table.

C_{3v}	I	$2C_3$	$3\sigma_v$		
A_1	1	1	1	T_z	$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$
A_2	1	1	-1	R_z	
E	2	-1	0	$(T_x, T_y), (R_x, R_y)$	$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy}), (\alpha_{xz}, \alpha_{yz})$

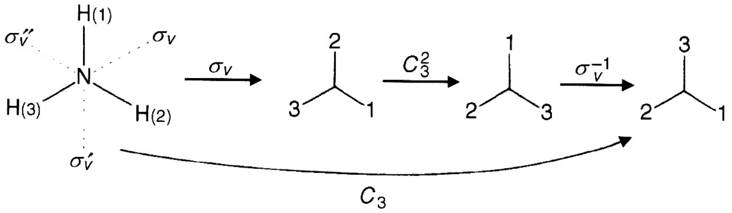


Figure 1.6: In the C_{3v} point group the elements C_3 and C_3^2 belong to the same class.

1.4.2 The C_{3v} character table

The character table of the C_{3v} is given above. There are two obvious differences from the character tables of any non-degenerate point groups. Firstly, the elements of the same class are grouped together, namely C_3 and $C_3^2 \rightarrow 2C_3$, and σ_v, σ_v' and $\sigma_v'' \rightarrow 3\sigma_v$.

Two elements P and Q belong to the same class, if there is a third element so that

$$P = R^{-1} \times Q \times R. \tag{1.15}$$

From Fig. 1.6 we see that in the C_{3v} point group

$$C_3 = \sigma_v^{-1} \times C_3^2 \times \sigma_v \tag{1.16}$$

and therefore C_3 and C_3^2 belong to the same class. The symmetry elements belonging to the same class have the same characters. The number of the symmetry species is equal to the number of the classes. This also applies to non-degenerate point groups, where each element forms its own class.

The other difference in the character table is the appearance of the doubly degenerate symmetry species E. Its characters are not always +1 or -1, in contrast to those in non-degenerate point groups.

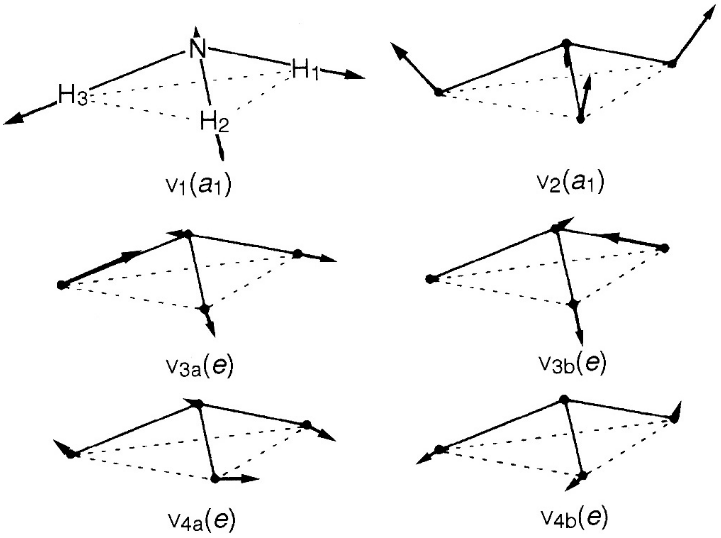


Figure 1.7: The normal modes of the NH_3 molecule.

The characters of the symmetry species A_1 and A_2 have the same meaning as in the non-degenerate point group. The characters of the symmetry species E can be understood from the example of the normal modes of the NH_3 molecule, shown in Fig. 1.7. The vibrations ν_1 and ν_2 are clearly of the species a_1 (A recommendation: small letters are used for the symmetry species of the vibrations and electron orbitals, whereas capital letters are used for the symmetry species of the corresponding wavefunctions.) The vibrations ν_{3a} and ν_{3b} are degenerate; it requires the same amount of energy to excite one quantum in either of them, but they clearly have different wavefunctions. Similarly, ν_{4a} and ν_{4b} are degenerate.

Normal coordinates are such a set of coordinates for a coupled system that the equations of motion only contain one of these coordinates. The symmetry properties of the vibrational wavefunction ψ_v are identical to those of the corresponding normal coordinate. If in the C_{3v} point group the C_3 operation is applied to Q_1, which is the normal coordinate of the ν_1 vibration, it changes to Q'_1, where

$$Q_1 \xrightarrow{C_3} Q'_1 = (+1)Q_1. \tag{1.17}$$

If the symmetry operation is applied to a degenerate normal coordinate, it doesn't simply remain the same or change its sign, but generally changes to a linear combination of two degenerate normal coordinates. Thus when applying a symmetry operation S

$$\begin{aligned} Q_{3a} \xrightarrow{S} Q'_{3a} &= d_{aa}Q_{3a} + d_{ab}Q_{3b} \\ Q_{3b} \xrightarrow{S} Q'_{3b} &= d_{aa}Q_{3a} + d_{ab}Q_{3b}. \end{aligned} \tag{1.18}$$

This can be written with the help of matrices

$$\begin{pmatrix} Q'_{3a} \\ Q'_{3b} \end{pmatrix} = \begin{pmatrix} d_{aa} & d_{ab} \\ d_{ba} & d_{bb} \end{pmatrix} \begin{pmatrix} Q_{3a} \\ Q_{3b} \end{pmatrix} \tag{1.19}$$

The relation $d_{aa} + d_{bb}$ is called the trace of the matrix, and it is the character of the property (in this case of the normal coordinate) with respect to the symmetry operation S.

The character of the symmetry species E with respect to the identity I can be obtained from the relations

$$\begin{aligned} Q_{3a} \xrightarrow{I} Q'_{3a} &= 1 \times Q_{3a} + 0 \times Q_{3b} \\ Q_{3b} \xrightarrow{I} Q'_{3b} &= 0 \times Q_{3a} + 1 \times Q_{3b} \end{aligned} \tag{1.20}$$

or

$$\begin{pmatrix} Q'_{3a} \\ Q'_{3b} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} Q_{3a} \\ Q_{3b} \end{pmatrix} \tag{1.21}$$

The trace of the matrix is 2, which is the character of the symmetry species E under I.

One of the two ν_3 vibrations, ν_{3a}, is symmetric in reflection through that σ_v plane, which bisects the angle between H_1 and H_2, and the other vibration is antisymmetric. We obtain

$$\begin{pmatrix} Q'_{3a} \\ Q'_{3b} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} Q_{3a} \\ Q_{3b} \end{pmatrix} \tag{1.22}$$

Therefore the character of E under σ_v is 0. Because all the mirror planes are equivalent, the character must be the same also under σ'_v and σ''_v.

When the operation is a rotation by the angle ϕ around the C_n axis (in this case $\phi = 2\pi/3$ rad), the transformation of the coordinates becomes

$$\begin{aligned} \begin{pmatrix} Q'_{3a} \\ Q'_{3b} \end{pmatrix} &= \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix} \begin{pmatrix} Q_{3a} \\ Q_{3b} \end{pmatrix} \\ &= \begin{pmatrix} -\frac{1}{2} & \sqrt{\frac{3}{2}} \\ -\sqrt{\frac{3}{2}} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} Q_{3a} \\ Q_{3b} \end{pmatrix} \end{aligned} \tag{1.23}$$

The trace of the matrix is -1, which is also the character of the symmetry species E under C_3.

Apart from $E \times E$, direct products are formed using the same rules as in non-degenerate point groups: the characters of the product are obtained by multiplying the characters of the symmetry species. We get

$$A_1 \times A_2 = A_2; \quad A_2 \times A_2 = A_1; \quad A_1 \times E = E; \quad A_2 \times E = E. \tag{1.24}$$

In the product $E \times E$ we again use the normal modes of the NH_3 molecule as an example. The result depends on whether we need a representation $\Gamma(\psi_v)$, when (a) one quantum of each vibration is excited or (b) when two quanta of the same vibration are excited (= overtone). In the case (a), for example for the combination $\nu_3 + \nu_4$, the product is written $E \times E$ and the result is obtained by squaring the characters with respect to each operation

$$\begin{array}{c|ccc} & I & 2C_3 & 3\sigma_v \\ \hline E \times E & 4 & 1 & 0 \end{array} \tag{1.25}$$

The characters 4, 1 and 0 span a reducible representation in the C_{3v} point group. We have to reduce it to a set of irreducible representations, whose sum of the characters is the same as in the reducible representation. This can be expressed as an equation

$$\chi_C(k) \times \chi_D(k) = \chi_F(k) + \chi_G(k) + \ldots \tag{1.26}$$

where χ is the character of whatever operation k and the multiplication of the degenerate symmetry species C and D gives the result

$$C \times D = F + G + \ldots \tag{1.27}$$

The reduction of the representation $E \times E$ yields a unique set of irreducible representations, which is

$$E \times E = A_1 + A_2 + E. \tag{1.28}$$

We can see from Table 1.3 that the sum of the characters of A_1, A_2 and E under I, C_3 and σ_v gives the irreducible representation of equation (1.25).

In the case (b), when two quanta of the same vibration are excited (e.g., $2\nu_3$), the product is written $(E)^2$, where

$$(E)^2 = A_1 + E. \tag{1.29}$$

Table 1.4: $The C_{\infty v}$ character table.

$C_{\infty v}$	I	$2C_{\infty}^{\phi}$	...	$\infty\sigma_v$		
$A_1 \equiv \Sigma^+$	1	1	...	1	T_z	$\alpha_{xx} + \alpha_{yy}, \alpha_{zz}$
$A_2 \equiv \Sigma^-$	1	1	...	-1	R_z	
$E_1 \equiv \Pi$	2	$2\cos\phi$	...	0	$(T_x, T_y), (R_x, R_y)$	$(\alpha_{xz}, \alpha_{yz})$
$E_2 \equiv \Delta$	2	$2\cos 2\phi$	...	0		$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
$E_3 \equiv \Phi$	2	$2\cos 3\phi$	...	0		
$\vdots$	$\vdots$	$\vdots$	...	$\vdots$		

This is called the symmetric part of $E \times E$; it is symmetric to the particle interchange. The result of Eq. (1.29) is obtained by forming first the product $E \times E$. One part of the product is forbidden. In a degenerate point group it is an A symmetry species, and if possible a non-totally symmetric. In the present case, the symmetry species A_2 is forbidden and it forms the antisymmetric part of the product $E \times E$.

There are tables that give the symmetry species for all degenerate combined vibrations in all degenerate point groups (See Appendix 1 in MQM).

1.4.3 The $C_{\infty v}$ character table

The $C_{\infty v}$ point group has an infinite number of classes, since the rotation around the C_∞ axis can be performed by whatever angle ϕ and each of the elements C_{∞}^{ϕ} belongs to a different class. However, $C_{\infty}^{-\phi}$, a counterclockwise rotation by ϕ belongs to the same class as C_{∞}^{ϕ}. Because the number of classes is infinite, so is also the number of symmetry species. Their labels are A_1, A_2, E_1, E_2, $\ldots E_\infty$, if we follow the convention used in other character tables. Unfortunately, another practice had been taken into use particularly in electron spectroscopy of diatomic molecules before the notations for the symmetry species had been widely accepted. The electronic states were given symbols Σ, Π, Δ, Φ, ...corresponding to the orbital angular momentum quantum number Λ that can have values 0, 1, 2, 3, ...(we will tell more about Λ later). These latter symbols are predominantly used in the $C_{\infty v}$ and $D_{\infty h}$ point groups. Both the systems are shown in the $C_{\infty v}$ character table above.

The multiplication of the symmetry species is performed following the usual rules. Thus, for example

$$\Sigma^+ \times \Sigma^- = \Sigma^-; \quad \Sigma^- \times \Pi = \Pi; \quad \Sigma^+ \times \Delta = \Delta. \tag{1.30}$$

The reducible representation of the product $\Pi \times \Pi$ is

$$\begin{array}{c|ccc} & I & 2C_\infty^\phi & \infty\sigma_v \\ \hline \Pi \times \Pi & 4 & 4\cos^2\phi & 0 \\ & & (= 2 + 2\cos 2\phi) & \end{array} \tag{1.31}$$

which is reduced as follows

$$\Pi \times \Pi = \Sigma^+ + \Sigma^- + \Delta. \tag{1.32}$$

The same rule that was used to obtain $(E)^2$ from $E \times E$ in the C_{3v} point group gives

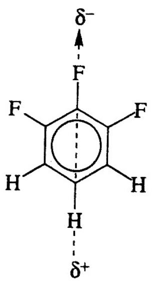
$$(\Pi)^2 = \Sigma^+ + \Delta. \tag{1.33}$$

Example 1.2. List the symmetry elements of the following molecules: (a) 1,2,3-trifluoro benzene, (b) 1,2,4-trifluoro benzene, (c) 1,3,5-trifluoro benzene, (d) 1,2,4,5-tetrafluoro benzene, (e) hexafluoro benzene, (f) 1,4-dibromo-2,5-difluoro benzene.

A molecule has a permanent dipole moment if one or more of the symmetry species of the translations T_x, T_y and T_z is totally symmetric. Apply this principle for each molecule by using a relevant character table and draw the directions of the dipole moments, if it $\neq 0$.

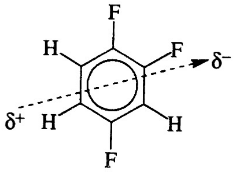
Solution. The picture on the next page
(a) In the C_{2v} point group, $\Gamma(T_z) = A_1$ (see table 1.1). Thus a permanent dipole moment exists and its direction is along the C_2 axis. Because of the large electronegativity of fluorine, the negative end $\delta-$ of the dipole is towards the fluorine atoms and the positive end $\delta+$ towards the hydrogen atoms.
(b) In the C_s point group, $\Gamma(T_x, T_y) = A'$ (totally symmetric). The dipole moment is therefore on the xy plane. Symmetry doesn't determine for it to be in any specific direction in this plane. As compared to 1,2,3-trifluoro benzene, the transfer of a fluorine atom from the place 3 to place 4 deviates the dipole moment towards the place 4.
(c)-(f) These molecules don't have permanent dipole moments, confirmed by the relevant character tables.

(a)



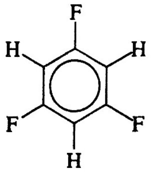
I, C_2, $2\sigma_v$
Point group C_{2v}

(b)



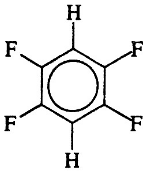
I, σ
Point group C_s

(c)



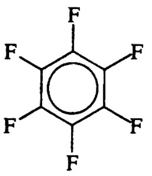
I, C_3, $3C_2$, σ_h, $3\sigma_v$, S_3
Point group D_{3h}

(d)



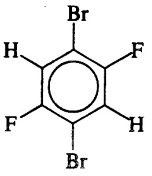
I, $3C_2$, 3σ, i
Point group D_{2h}

(e)



I, C_6, $3C_2'$, $3C_2''$, σ_h, $3\sigma_v$, $3\sigma_d$, i, S_6
Point group D_{6h}

(f)



I, C_2 (perpendicular to the molecular plane), i, σ_h
Point group C_{2h}

Chapter 2

Potential energy curves and vibrations of diatomic molecules

2.1 Harmonic oscillator

The model of two balls connected by a spring is sufficient to describe approximatively the vibration of a diatomic molecule. The stretching and contraction of the bond is represented by the change of the length of the spring. Hooke's law is valid for small deviations:

$$\text{Restoring force} = -\frac{dV(x)}{dx} = -kx, \tag{2.1}$$

where V is potential energy, k is force constant, whose magnitude describe the strength of the bond, and $x(= r - r_e)$ is the deviation from the equilibrium bond length. Integration of this equation gives

$$V(x) = \frac{1}{2}kx^2. \tag{2.2}$$

Figure 4.1 shows $V(r)$ as a function of r. The curve is a parabola.

The Hamiltonian operator of the one-dimensional quantum mechanical harmonic oscillator is:

$$H = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2, \tag{2.3}$$

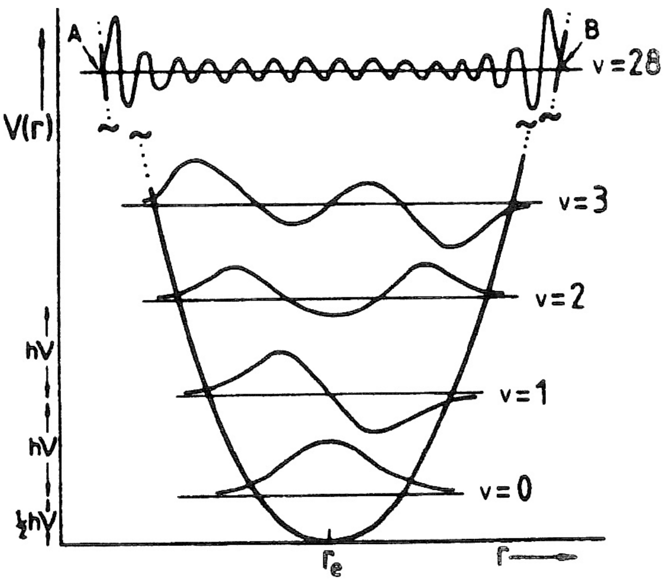


Figure 2.1: The energy levels, wavefunctions and potential energy $V(r)$ of the harmonic oscillator.

where $\mu = m_1 m_2/(m_1+m_1)$ is the reduced mass of the atoms. The Schrödinger equation for the system is

$$\frac{d^2\psi_v}{dx^2} + \left(\frac{2\mu E_v}{\hbar^2} - \frac{\mu k x^2}{\hbar^2}\right)\psi_v = 0. \tag{2.4}$$

It can be shown that

$$E_v = h\nu(v + 1/2), \tag{2.5}$$

where ν is the classical frequency of the oscillator, which can be obtained from

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}. \tag{2.6}$$

As expected, the frequency increases when the bond becomes stronger (when k increases) and decreases when μ becomes larger. The vibrational quantum number v can have values 0, 1, 2, ...

According to Eq. (2.5) the vibrational energy levels are spaced by a constant interval of $h\nu$ and the lowest energy of the oscillator (when $v = 0$) is not zero but $\frac{1}{2}h\nu$. This zero-point energy is the lowest energy that a molecule

Table 2.1: Hermite polynomials.

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

can have even at absolute temperature of 0 K. It is a result of the uncertainty principle.

The crossing points of an energy level with the potential energy curve correspond to the classical turning points of vibration, where the velocities of the nuclei are zero and all energy is in the form of potential energy. In the middle point of each energy level all energy is conversely kinetic energy.

The solutions of Eq. (2.4) are wavefunctions

$$\psi_v = \left(\frac{1}{2^v v! \pi^{1/2}}\right)^{1/2} H_v(y) \exp(-y^2/2), \tag{2.7}$$

where $H_v(y)$ is a Hermite polynomials and

$$y = \left(\frac{4\pi^2 \nu \mu}{h}\right)^{1/2} (r - r_e). \tag{2.8}$$

Some of the Hermite polynomials are given in Table 4.1. Examples of vibrational wavefunctions are presented in Fig. 4.1. We note the following important properties of the wavefunctions:

1. They extend to the region outside of the parabola, which is forbidden in a classical system.
2. When v increases those two points where the probability density ψ^2 reaches its maximum value occur close to the classical turning points. This is illustrated in Fig. 4.1 for the quantum number $v = 28$, with A and B being the classical turning points. In contrast, for $v = 0$ the highest probability density is in the middle of the region.

The force constant k can be regarded as a measure for the strength of the bond. Table 4.2 gives some typical values in the units of aJ Å^{-2}($= 10^2$ N/m). The values describe how k increases with the bond order. Molecules HCl,

Table 2.2: The force constants of some diatomic molecules.

Molecule	k [aJ Å^{-2}]	Molecule	k [aJ Å^{-2}]	Molecule	k [aJ Å^{-2}]
HCl	5.16	F_2	4.45	CO	18.55
HF	9.64	O_2	11.41	N_2	22.41
Cl_2	3.20	NO	15.48		

HF, Cl_2 and F_2 have single bonds and relatively low values of k even though k of HF is exceptionally high. The bond orders of O_2, NO, CO and N_2 are 2, $2\frac{1}{2}$, 3 and 3, respectively, and are reflected in the values of their force constants. The force constant is affected by the delicate balance between the attraction and repulsion forces in the molecule. These forces remain the same in the isotopic substitution.

For vibrational levels, one often uses term values instead of energies. The term values $G(v)$ have the unit of wavenumber (cm^{-1})

$$G(v) = \frac{E_v}{hc} = \omega(v + \frac{1}{2}), \tag{2.9}$$

where ω is the wavenumber of vibration (often called improperly as vibrational frequency).

Exercise 4.1. Calculate the reduced masses of (a) $^1H^{81}Br$ and (b) $^1H^{127}I$. The wavenumbers of the vibrations of these molecules are (a) 2648.98 cm^{-1} and (b) 2308.09 cm^{-1}. Calculate the force constants of the bonds. Predict the vibrational wavenumbers of the deuterium halides. m(^{81}Br)=80.9163 u, m(^{127}I)=126.9045 u, m(^{1}H)=1.0078 u, m(^{2}H)=2.0141 u.

2.2 Anharmonicity

Figure 4.1 shows the potential energy, vibrational wavefunctions and energy levels of the harmonic oscillator. In reality, the vibrations of diatomic molecules follow Hooke's law, Eq. (4.1), relatively well only when the internuclear distance does not deviate largely from the equilibrium distance r_e, i.e. when x is small. We know that the molecule dissociates at large values of r: two neutral atoms are formed and they do not affect each other any

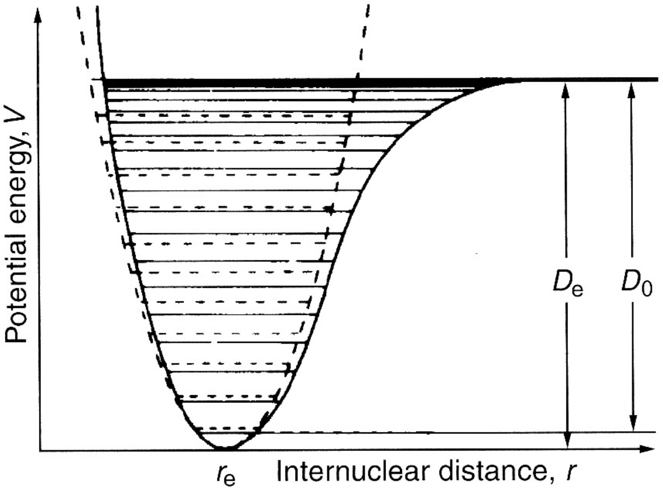


Figure 2.2: The potential energy curve and energy levels of a diatomic molecule when it behaves as an anharmonic oscillator. Dashed curves give the same properties for a harmonic oscillator.

longer. Then the force constant is zero and r can be increased to infinity without influencing the potential energy V. This is illustrated in Fig. 4.2. The potential energy curve levels at a value $V = D_e$, where D_e is the dissociation energy as measured from the potential energy at the equilibrium distance. Thus for $r > r_e$, the potential energy becomes lower than in the case of the harmonic oscillator. At small values of r, the positive charges of the nuclei cause a repulsion that opposes bringing the nuclei closer each other and the potential energy curve is steeper than that of the harmonic oscillator.

Anharmonicity changes the wavefunctions and term values. The term values of the harmonic oscillator in Eq. (4.9) become a power series in $(v + 1/2)$

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \ldots \tag{2.10}$$

where ω_e is the vibrational wavenumber that a classical oscillator would have infinitely close to the equilibrium position. $\omega_e x_e$, $\omega_e y_e$ ... are anharmonicity constants. The terms ω, $\omega_e x_e$, $\omega_e y_e$ ... in the series (2.10) become fast smaller. For example for HCl ω_e=2990.946 cm^{-1}, $\omega_e x_e$=52.8186 cm^{-1}, $\omega_e y_e$=0.2244 cm^{-1} and $\omega_e z_e$=-0.0122 cm^{-1}. The value of $\omega_e x_e$ is always positive, which makes the energy levels to approach each other when v increases. These energy levels are compared with those of the harmonic oscillator in Fig. 4.2. The levels of the anharmonic oscillator converge to the dissociation limit D_e, above which they have a continuous distribution (continuum).

ω_e can no longer be measured directly. The wavenumber differences $\Delta G_{v+1/2}$ for vibrational transitions $(v+1)-v$ are obtained from the equation

$$\begin{aligned} \Delta G_{v+1/2} &= G(v+1) - G(v) \\ &= \omega_e - \omega_e x_e(2v+2) + \omega_e y_e(3v^2 + 6v + \tfrac{13}{4}) + \ldots \end{aligned} \tag{2.11}$$

The wavenumbers of at least two transitions (e.g. $G(1) - G(0) = \omega_0$ and $G(2) - G(1) = \omega_1$) are required to determine ω_e and $\omega_e x_e$.

For the dissociation energy D_e

$$D_e \simeq \frac{\omega_e^2}{4\omega_e x_e}, \tag{2.12}$$

where the approximately sign results from the neglect of the anharmonicity constants other than $\omega_e x_e$.

Example 4.1 Calculate ω_e, $\omega_e x_e$ and dissociation energy D_e for the electronic ground state of the CO molecule from the following differences between the vibrational levels:

$v' - v''$	$1-0$	$2-1$	$3-2$	$4-3$	$5-4$	$6-5$
$G(v+1) - G(v)$[cm^{-1}]	2143.1	2116.1	2088.9	2061.3	2033.5	2005.5

Solution. By neglecting $\omega_e y_e$ and higher terms in Eq. (2.11) we obtain

$$G(v+1) - G(v) = \omega_e - 2\omega_e x_e(v+1).$$

We draw $G(v+1) - G(v)$ as a function of $(v+1)$, which produces a straight line with a slope of $-2\omega_e x_e$ and a crossing point of ω_e with the y-axis.

Fitting a straight line to the points with a computer gives

$$\begin{aligned} \omega_e &= 2171.4 \pm 0.4 \text{ cm}^{-1} \\ \omega_e x_e &= 13.8 \pm 0.1 \text{ cm}^{-1} \end{aligned}$$

The given uncertainties are standard deviations. The dissociation energy

$$D_e \simeq \frac{\omega_e^2}{4\omega_e x_e} \simeq 85400 \text{ cm}^{-1} \simeq 10.6 \text{ eV}.$$

Experimentally, the dissociation energy can only be measured with respect to the zero-point energy D_0. It is obvious from Fig. 4.2 that

$$D_0 = \sum_v \Delta G_{v+1/2}. \tag{2.13}$$

Experimental values for $\Delta G_{v+1/2}$ with large quantum numbers of v cannot generally be determined with infrared and Raman spectroscopy, because the intensities of the transitions with $\Delta v = \pm 2, \pm 3, \ldots$ are weak and the populations of highly excited vibrational states is low. Information about higher vibrational levels can mostly be obtained from transitions between electronic states.

The dissociation energy D_e is the same for the different isotopes of the same molecule because the potential energy curve and, consequently, the force constant do not depend on the neutron number. On the other hand, the vibrational energy levels change, as ω depends on the mass as $\mu^{-1/2}$ (μ is the reduced mass), resulting in the change of D_0 in different isotopes.

Morse suggested in 1929 that

$$V(x) = D_e[1 - \exp(-ax)]^2 \tag{2.14}$$

would be a useful potential energy function for an anharmonic oscillator. In the Morse potential a and D_e are characteristic constants of the electronic state. For this function, $V(x) \rightarrow D_e$, when $x \rightarrow \infty$, as it should. On the other hand, when $r \rightarrow 0$ (i.e. $x \rightarrow -r_e$), $V(x)$ becomes large but not infinite. This deficit in the Morse potential is not very serious, since the region where $r \rightarrow 0$ is not experimentally important. The vibrational term values obtained using the Morse potential only include the terms $(v + 1/2)$ and $(v + 1/2)^2$ in Eq. (4.10). Even though the quantitative use of the potential is limited, its ease of use has made it popular compared to more accurate, but also more complicated functions.

2.3 The potential energy curves of excited states

Each excited electronic state has its own potential energy curve, which in most cases looks similar to the potential energy curve of the ground state.

Figure 2.3 shows the potential energy curves for the ground state and excited electronic states of the short-lived molecule C_2. The ground electron configuration of C_2 is

$$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^0, \tag{2.15}$$

which gives the ground state $X^1\Sigma_g^+$. The lowest electronic states are formed from the electron configurations when an electron from the $\pi_u 2p$- or $\sigma_u^* 2s$-orbital has been promoted to the $\sigma_g 2p$-orbital. The information in Fig. 2.3 has been obtained by observing absorption and emission spectra using different techniques.

When C_2 dissociates the two carbon atoms released can be either in the ground state or in excited states. The ground electron configuration of the C atom, $1s^2 2s^2 2p^2$, gives three terms $^3P, {}^1D$ and ^1S in the order of increasing energy. Figure 2.3 shows that six of the states of C_2 dissociate producing both C atoms with term ^3P. Other states give dissociation products where one or both of the carbon atoms have the term symbols ^1D or ^1S.

Like in the ground state, a molecule can vibrate and rotate in the electronically excited states. The total term value (or total energy)

$$S = T + G(v) + F(J), \tag{2.16}$$

is the sum of the electronic term value T, vibrational term value $G(v)$ and rotational term value $F(J)$. The vibrational term value can be obtained from Eq. (4.10), but the wavenumber ω_e and the anharmonicity constants $\omega_e x_e, \omega_e y_e, \ldots$ are different for different excited states. Figure 2.3 also shows that the equilibrium distances r_e are different.

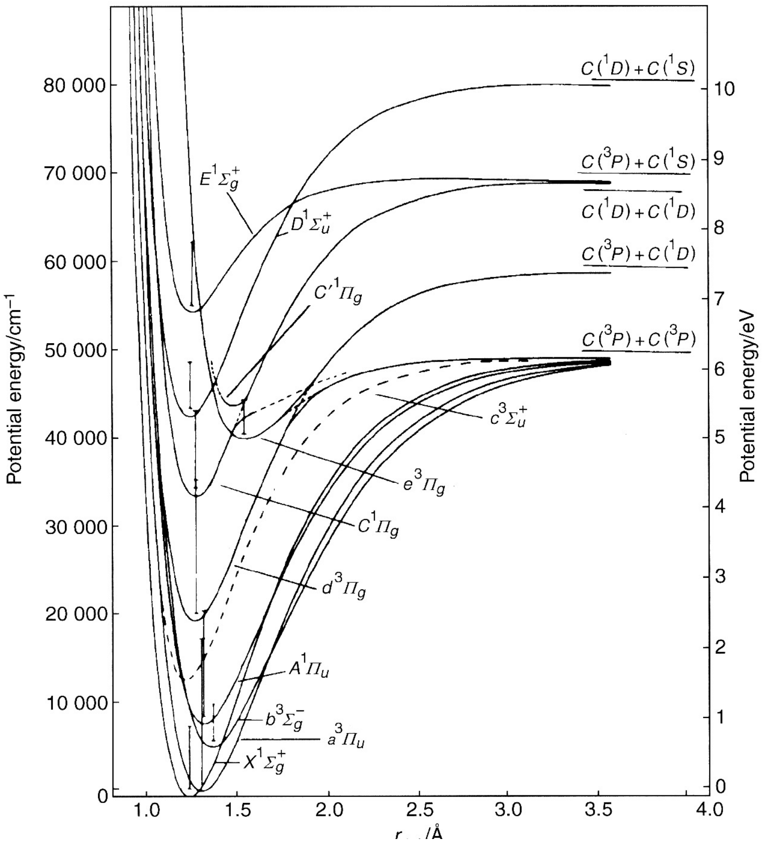


Figure 2.3: The potential energy curves of the C_2 molecule for the ground state and several excited states.

Chapter 3

Electronic transitions in diatomic molecules

3.1 On the coupling of angular momenta

The orbital motion and spin of each electron induce magnetic momenta that behave like small bar magnets. The way in which magnets interact with each other corresponds to coupling of angular momenta. For all diatomic molecules, the coupling mechanism that describes best the electronic states is similar to the LS coupling in atoms. We have already already talked about this in Chapter 2. Figure 5.1(a) shows how the orbital angular momenta of each electrons are coupled together to form the resultant $\mathbf{L}$ whose component along the internuclear axis is $\Lambda\hbar$. Similarly, the spins of individual electrons couple to give $\mathbf{S}$ to give the component $\Sigma\hbar$ along the axis. The quantum number Σ can have values

$$\Sigma = S, S-1, \ldots - S. \tag{3.1}$$

S remains a good quantum number.

We can couple $\Lambda\hbar$ and $\Sigma\hbar$ together to get the component of the total angular momentum along the axis, $\Omega\hbar$. This way of coupling is known as Hund's case (a). The quantum number Ω can be obtained from the equation

$$\Omega = \Lambda + \Sigma. \tag{3.2}$$

For the $^2\Pi$ molecule NO, for instance, for which $\Lambda = \pm 1$ and $\Sigma = \pm\frac{1}{2}$, Ω can take the values $\pm\frac{1}{2}, \pm\frac{3}{2}$. Term symbols are written in this case as $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{\frac{3}{2}}$.

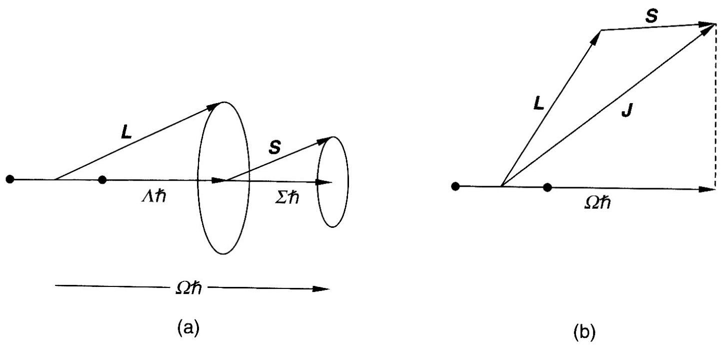


Figure 3.1: (a) Hund's case (a) and (b) Hund's case (c) to couple the total angular momentum and total spin of a diatomic molecule.

Hund's case (a) is the most common, but it is still an approximation, as all couplings of angular momenta. If a molecule has at least one heavy nucleus, the spin-orbit interaction is so strong that the electron spin and angular momenta couple to give the resultant **J**. This angular momentum has a component $\Omega\hbar$ on the internuclear axis, so Ω is a good quantum number, but Λ and Σ are not. This coupling approximation is known as Hund's case (c) and it is presented in Fig. 3.1(b).

3.2 Selection rules in general

The selection rules for the orbital parts of the wavefunctions of two electronic states depend totally on symmetry properties. Electronic transitions are mainly caused by the interaction of the electronic component of electromagnetic radiation with a molecule. The selection rules are therefore for the electric dipole transitions.

The intensity of an electronic transition is proportional to the square of the transition dipole moment $\mathbf{R_e}$, where

$$\mathbf{R_e} = \int \psi_e'^{*} \hat{\mu} \psi_e'' d\tau_e. \tag{3.3}$$

For an allowed transition $|\mathbf{R_e}| \neq 0$. The symmetry requirement is

$$\Gamma(\psi_e') \times \Gamma(\mu) \times \Gamma(\psi_e'') = A \tag{3.4}$$

for a transition between non-degenerate states and

$$\Gamma(\psi_e') \times \Gamma(\mu) \times \Gamma(\psi_e'') \supset A \tag{3.5}$$

for a transition between states, from which at least one is degenerate. The symbol $\supset$ means 'is included'. A is the totally symmetric symmetry species of the point group in question.

The components of the transition dipole moment $\mathbf{R_e}$ along the Cartesian axes are

$$\begin{array}{rcl} R_{e,x} & = & \int \psi_e'^* \mu_x \psi_e'' d\tau_e \\ R_{e,y} & = & \int \psi_e'^* \mu_y \psi_e'' d\tau_e \\ R_{e,z} & = & \int \psi_e'^* \mu_x \psi_e'' d\tau_e . \end{array} \tag{3.6}$$

Since

$$|\mathbf{R_e}|^2 = (R_{e,x})^2 + (R_{e,y})^2 + (R_{e,z})^2, \tag{3.7}$$

an electronic transition is allowed, if any of the terms $R_{e,x}$, $R_{e,y}$ or $R_{e,z}$ is different from zero. Thus, we must have for a transition to be allowed

$$\begin{array}{rrcl} & \Gamma(\psi_e') \times \Gamma(T_x) \times \Gamma(\psi_e'') & = & A \\ \text{and/or} & \Gamma(\psi_e') \times \Gamma(T_y) \times \Gamma(\psi_e'') & = & A \\ \text{and/or} & \Gamma(\psi_e') \times \Gamma(T_z) \times \Gamma(\psi_e'') & = & A \end{array} \tag{3.8}$$

when a transition is between non-degenerate states. T_x, T_y, and T_z are the translations along the respective axes. In case of a degenerate state, '=' is replaced by '$\supset$' in the above equation.

If the product of two symmetry species is totally symmetric, the symmetry species must be the same. Thus Eq. (3.8) can be written

$$\Gamma(\psi_e') \times \Gamma(\psi_e'') = \Gamma(T_x) \text{ and/or } \Gamma(T_y) \text{ and/or } \Gamma(T_z). \tag{3.9}$$

If a degenerate state is involved, '=' is replaced by '$\supset$' in the above equation. This is a general selection rule for an electronic transition between two electronic states.

3.2.1 Selection rules for diatomic molecules

The dipole selection rules for diatomic molecules can be summarized (apart from the spin selection rule, they can be obtained from the above treatment):

1. $\Delta\Lambda = 0, \pm 1$ (5.10)
   For example, $\Sigma - \Sigma$, $\Pi - \Sigma$ and $\Delta - \Pi$ transitions are allowed but $\Delta - \Sigma$ or $\Phi - \Pi$ transitions are not allowed.

2. $\Delta S = 0$ (5.11)
   This selection rule breaks down when the nuclear charge becomes large. For example, triplet-singlet transitions are absolutely forbidden in H_2, but in CO the $a^3\Pi - X^1\Sigma^+$ transition is observed but weak.

3. $\Delta\Sigma = 0; \qquad \Delta\Omega = 0, \pm 1$ (5.12)
   between the components of the same multiplet.

4. $+ \longleftrightarrow -; \qquad + \longleftrightarrow +; \qquad - \longleftrightarrow -$ (5.13)
   This is relevant only for $\Sigma - \Sigma$ transitions so that $\Sigma^+ - \Sigma^+$ and $\Sigma^- - \Sigma^-$ transitions are allowed.

5. $g \longleftrightarrow u; \qquad g \longleftrightarrow g; \qquad u \longleftrightarrow u$ (5.14)
   For example, $\Sigma_g^+ - \Sigma_g^+$ transitions are forbidden, but $\Sigma_u^+ - \Sigma_g^+$ and $\Pi_u - \Sigma_g^+$ are allowed.

In Hund's case (c) (Fig. 3.1b) the selection rules are slightly different. The rules (5.11) and (5.14) still valid, but since Λ and Σ are no longer good quantum numbers, the rules (5.10) and (5.12) do not work. The applicability of the rule (5.13) becomes more limited.

Exercise 5.1. Using Eq. (3.8) or Eq. (3.9) show that a $\Sigma_g^+ \rightarrow \Sigma_u^+$ is allowed in a diatomic homonuclear molecule (like O_2). The relevant character table is given on page 25. Note that the translations are marked as x, y, and z in that table.

3.3 Vibronic transitions

Figure 3.2 displays the vibrational energy levels related to two electronic states. We assume that the electronic transition between the states is allowed. The vibrational levels of the upper (lower) states are denoted with quantum numbers v' (v''). In the electronic spectrum, there are no selection rules that would limit the value of Δv, but the Franck-Condon principle set the limits for the intensities of the transitions.

Vibrational transitions that occur during electronic transitions are called vibronic transitions. These vibronic transitions (with related rotational transitions) give rise to bands in the spectrum. A set of bands belonging to one electronic transitions is called an electronic band system. Vibronic transitions can be divided into progressions and sequences that have been illustrated in

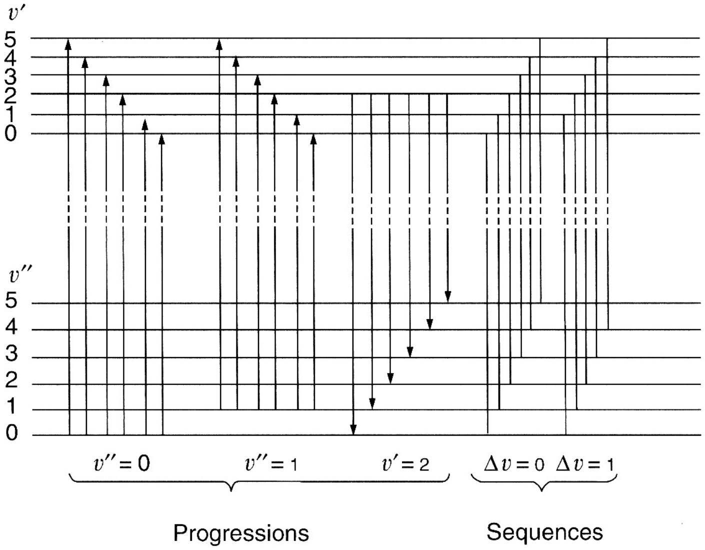


Figure 3.2: Progressions and sequences in the electron spectrum of a diatomic molecule.

Fig. 3.2. A progression includes a series of vibronic transitions that have a common upper or lower vibrational level. A group of vibrations for which Δv is constant forms a sequence.

A symbol to denote a vibronic transition is $v' - v''$ where v' and v'' are the vibrational quantum numbers of the upper and lower states, respectively. This follows the convention in spectroscopy. Thus a purely electronic transition is written $0 - 0$.

3.4 The Franck-Condon principle

In 1925, before the presentation of the Schrödinger equation, Franck studied different intensity distributions of vibronic transitions. His conclusions were based on the fact that the electronic transition takes place much faster than the vibration of the molecule. Therefore in a vibronic transition the nuclei have very accurately the same locations and velocities before and after the transition. The possible consequences are illustrated in Fig. 3.3 that shows the potential energy curves of two electronic states. The curves are plotted so that $r_e' > r_e''$.

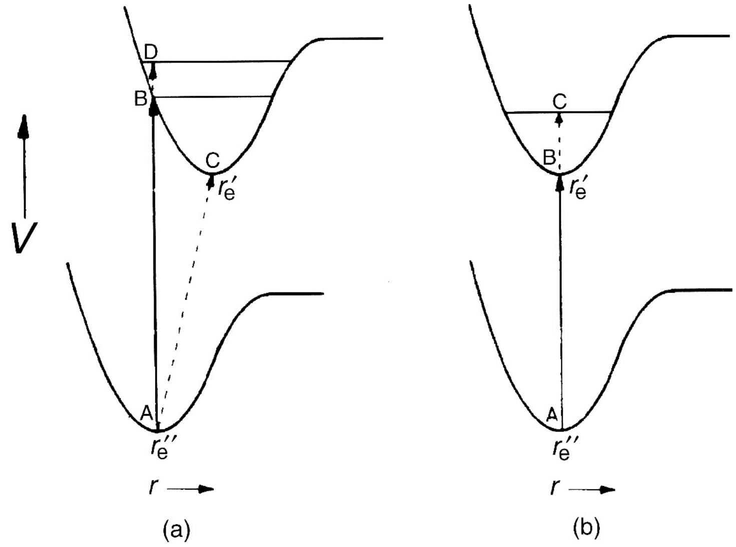


Figure 3.3: The Franck principle when (a) $r_e' > r_e''$ and (b) $r_e' \simeq r_e''$. The vibronic transition B–A is the most probable in each case.

In an absorption process of Fig. 3.3(a) the transition goes from the point A in the lower state to the point B in the upper state. (Zero-point energy can be neglected when considering Franck's semiclassical arguments.) The requirement on the same location before and after the transition means that the transition occurs between the points that are on the same vertical line. Then r remains constant, and we speak of a vertical transition. The requirement on the same velocity means that the transition from point A, where the nuclei do not move, must go to point B, which is a classical turning point and where the nuclei also are motionless. The transition from A to C is very improbable because the change in r is very large. The transition from A to D is also improbable, even though r is the same the nuclei are moving in point D.

In Fig. 3.3(b) $r_e' \simeq r_e''$. Now the most probable transition is from point A to B without any vibrational energy in the upper state. A transition from A to C keeps the same r, but the velocities of the nuclei have increased, because they have kinetic energy corresponding to the distance BC.

Condon treated the intensities of vibronic transitions quantum mechanically in 1928. The intensity is proportional to the square of the transition dipole moment $\mathbf{R}_{ev}$ (see Eq. (3.13))

$$\mathbf{R}_{ev} = \int \psi_{ev}'^{*} \hat{\mu} \psi_{ev}'' d\tau_{ev}, \tag{3.15}$$

where $\hat{\mu}$ is the electric dipole moment operator, and ψ_{ev}' and ψ_{ev}'' are the vibronic wavefunctions of the upper and lower states, respectively. Integration is over the electronic and vibrational coordinates. Assuming that the Born-Oppenheimer approximation is valid, ψ_{ev} can be represented as a product $\psi_e \psi_v$. Then it follows from Eq. (3.15) that

$$\mathbf{R}_{ev} = \int \int \psi_e'^{*} \psi_v' \hat{\mu} \psi_e'' \psi_v'' d\tau_e dr, \tag{3.16}$$

where r is the internuclear distance. We integrate first over the electronic coordinates τ_e

$$\mathbf{R}_{ev} = \int \psi_v' \mathbf{R}_e \psi_v'' dr, \tag{3.17}$$

where $\mathbf{R}_e$ is the electric transition dipole moment:

$$\mathbf{R}_e = \int \psi_e'^{*} \hat{\mu} \psi_e'' d\tau_e. \tag{3.18}$$

The possibility to carry out the integration to give Eq. (3.17) results from the Born-Oppenheimer approximation which assumes that nuclei can be treated as stationary with respect to much faster electrons. This approximation also allows us to take out $\mathbf{R}_e$ from the integral (3.17) and treat it as a constant that does not depend on r. We obtain then

$$\mathbf{R}_{ev} = \mathbf{R}_e \int \psi_v' \psi_v'' dr. \tag{3.19}$$

The integral $\int \psi_v' \psi_v'' dr$ is a measure for the overlap of the two vibrational wavefunctions. Its square is known as the Franck-Condon factor.

In quantum mechanics, the classical turning point of a vibration is replaced by the maximum or minimum of the wavefunction ψ_v close to this turning point. Figure 3.4 presents a case where the the vibrational wavefunction of the upper state $v' = 4$ has a maximum close to the turning point and is directly above the maximum of the wavefunction $v'' = 0$. The largest contribution to the overlap integral of the vibrational wavefunctions is indicated by a solid line, but considerable overlap occurs when r is between

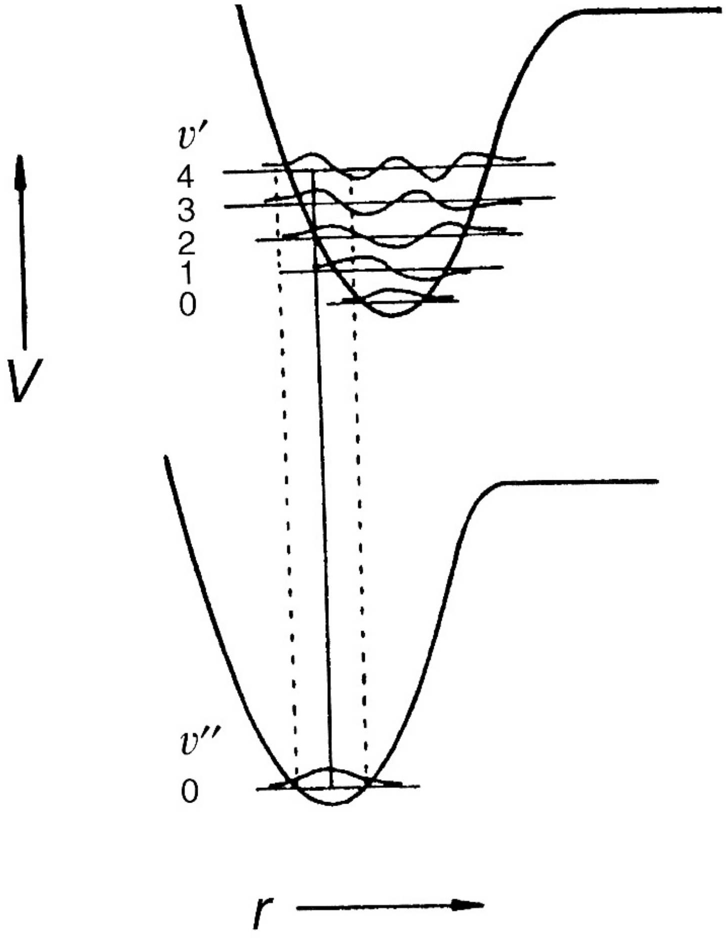


Figure 3.4: The Franck-Condon principle applied to the case $r_e' > r_e''$ when the $4-0$ transition is the most probable.

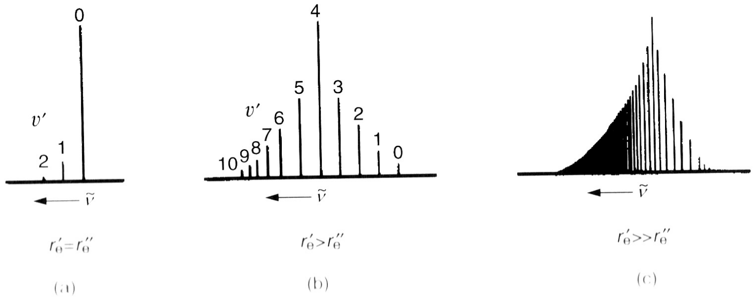


Figure 3.5: Typical intensity distributions for vibronic transitions.

the dashed lines. Clearly, the overlap is considerable also for wavefunctions whose v' is close to four. We get an intensity distribution shown in Fig. 3.5(b).

If $r_e' \gg r_e''$, a large fraction of the intensity may go the vibrational states in the continuum above the the dissociation limit. A progression (from the lower state $v'' = 0$) shown in Fig. 3.5(c) then follows, with an intensity maximum at high values of v' or in the continuum. Figure 3.5(a) shows the intensity maximum to the vibrational state $v' = 0$, when $r_e' \simeq r_e''$. The intensity falls usually down rapidly in such a case.

The case with $r_e' < r_e''$ can happen if an electron makes a transition from an antibonding or non-bonding orbital to a bonding orbital. It is most likely between two excited electronic state. The situation is similar to the one in Fig. 3.4, but the upper potential energy curve is shifted to a smaller value of r, for example, in such a way that the right maximum of the wavefunction $v' = 4$ is above the maximum of $v'' = 0$. A result is the intensity distribution in Fig. 3.5(b). Thus the observation of the intensity maximum at the vibrational quantum number $v' > 0$ indicates a substantial change in the equilibrium distance r_e between the upper and lower states, but it does not tell the sign of the change. This is quantitatively quite not true because the progressions are slightly different for the cases $r_e' > r_e''$ and $r_e' < r_e''$. The analysis of the intensities of the vibronic transitions yields a lot of information about the shapes of the potential energy curves of the electronic states.

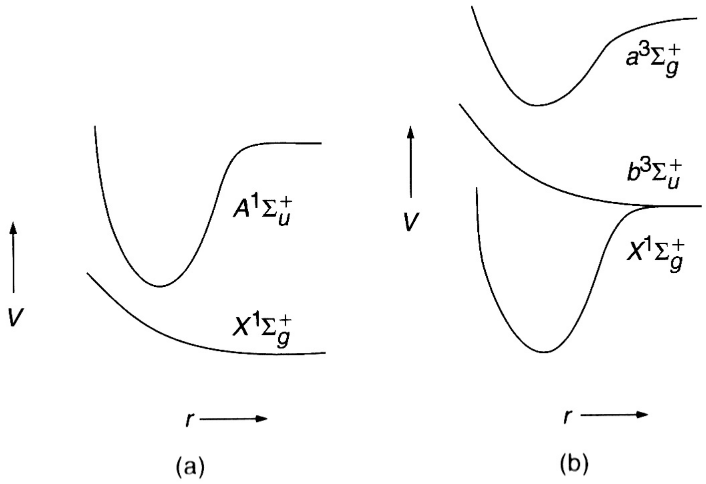


Figure 3.6: The repulsive ground state and the bound excited state of the He_2 molecule.

Repulsive states and continuous spectra

The ground electron configuration $(1\sigma_g 1s)^2(1\sigma_u^* 1s)^2$ of the He_2 molecule is expected to be unstable, because the bonding character of the $\sigma_g 1s$ orbital is cancelled by the antibonding character of the $\sigma_u^* 1s$ orbital. The potential energy curve of the $X^1\Sigma_g^+$ state has no minimum but it decreases gradually as a function of r. This is shown in Fig. 3.6. Such a state is called repulsive, because the atoms repel each other. The state has no discrete vibrational energy levels but the levels form a continuum.

By promoting an electron from the σ_u^* orbital to an binding orbital can give bound states of the He_2 molecule. Several of them have been observed in emission spectroscopy. For example, the configuration $(\sigma_g 1s)^2(\sigma_u^* 1s)^1(\sigma_g 2s)^1$ leads to the bound states $A^1\Sigma_u^+$ and $a^3\Sigma_u^+$. Figure 3.6 shows the shape of the potential energy curve of the $A^1\Sigma_u^+$ state. The transition $A - X$ is allowed and produces a strong continuous intensity in the wavelength region 60–100 nm. This can be used as a source of far ultraviolet radiation, like other diatomic noble-gas molecules.