Electronic Spectroscopy of diatomic molecules

IV.2.1 Molecular orbitals

IV.2.1.1. Homonuclear diatomic molecules

The molecular orbital (MO) approach to the electronic structure of diatomic molecules is not unique but it lends itself to a fairly qualitative description, which we require here.

It consists in considering the two nuclei, without their electrons, a distance apart equal to the equilibrium internuclear distance and constructing MOs around them – just as we construct atomic orbitals (AOs) around a single bare nucleus. Electrons are then fed into the MOs in pairs (with the electron spin quantum number $m_s=\pm1/2$), just as for atoms, along the *Aufbau* principle, to give the ground configuration of the molecule.

The basis of constructing the MOs is the linear combination of atomic orbitals (LCAO) method. This accounts for the fact that, in the region close to a nucleus, the MO wave function resembles an AO wave function for the atom of which the nucleus is a part. It is reasonable, then, to express a MO wave function ψ as a linear combination of AO wave functions χ_i on both nuclei:

$$\Sigma \qquad\qquad\qquad\qquad (IV.1)$$

where c_i is the coefficient of the wave function χ_i. However, not all linear combinations are effective in the sense of producing an MO which is appreciably different from the AOs from which it is formed. For effective linear combinations:

Condition 1: The energies of the AOs must be comparable.

Condition 2: The AOs should overlap as much as possible.

Condition 3: The AOs must have the same symmetry properties with respect to

certain symmetry elements of the molecule.

For a homonuclear diatomic molecule with nuclei 1 and 2, the LCAO gives the MO wave function

$$(IV.2)$$

For example for the N_2 molecule, the nitrogen 1s AOs satisfy Condition 1, since their energies are identical, but not Condition 2 because the 1s AOs are close to the nuclei, resulting in little overlap. In contrast, the 2s AOs satisfy both conditions and since they are spherically symmetrical, Condition 3 as well. Examples of AOs which satisfy Conditions 1 and 2 but not Condition 3 are the 2s and $2p_x$ orbitals shown in Figure IV.1. The 2s AO is symmetric to reflection across a plane containing internuclear z-axis and perpendicular to figure, but $2p_x$ AO is

not.

Important properties of the MO are the energy E and value of c_1 and c_2 in Equation IV.2. They are obtained from the Schrödinger equation

$$(IV.3)$$

Multiplying both sides by ψ *, the complex conjugate of ψ and integrating over all space gives

$$\frac{\int \psi^* H \psi \, d\tau}{\int \psi^* \psi \, d\tau} \qquad (IV.4)$$

E can be calculated only if ψ is known, so what is done is to make an intelligent guess at the MO wave function, say ψ_n, and calculate the corresponding value of the energy E_n from Equation (IV.4). A second guess at ψ, say ψ_m, gives a

corresponding energy $\overline{E}_m$. The variation principle states that if $\overline{E}_m \square \ \overline{E}_n$ then ψ_m is closer than ψ_n to the true MO gs wave function. In this way the true ground state wave function can be approached as closely as we choose but this is usually done

by varying parameters in the chosen wave function until they have their optimum values.

Combining Equations (IV.2) and (IV.4) and assuming that χ_1 and χ_2 are not complex gives

$$\rule{5cm}{0.4pt} \tag{IV.5}$$

If the AO wave functions are normalized

$$1 \tag{IV.6}$$

and, as H is a hermitian operator,

$$\tag{IV.7}$$

The quantity

$$\tag{IV.8}$$

is called the overlap integral as it is a measure of the degree to which χ_1 and χ_2 overlap each other.

In addition, integrals such as $\int \chi_1 H \chi_2 \, dt$ are abbreviated to H_{11}. All this reduces

Equation (IV.5) to:

$$\rule{4cm}{0.4pt} \tag{IV.9}$$

Using the variation principle to optimize c_1 and c_2 we obtain $\dfrac{\partial E}{\partial c_1}$ and $\dfrac{\partial E}{\partial c_2}$ from

Equation (IV.9) and put them equal to zero, giving:

$$0$$
$$\tag{IV.10}$$
$$0$$

Where we have replaced E by $\bar{E}$ since, although it is probably not the true energy, it is the nearest approach to it with the wave function of Equation (IV.2). Equations (IV.10) are the *secular equations* and the two values of E which satisfy them are obtained by solution of the secular determinant:

$$0 \tag{IV.11}$$

H_{12} is the resonance integral, usually symbolized by $\square$. In a homonuclear diatomic molecule $H_{11} = H_{22} = \square$, which is known as the Coulomb integral, and the secular determinant becomes:

$$0 \tag{IV.12}$$

giving

$$0 \tag{IV.13}$$

from which we obtain two values of E,

$$\underline{\hspace{3cm}} \tag{IV.14}$$

If we are interested only in very approximate MO wave functions and energies we can assume that $S = 0$ (a typical value is about 0.2) and that the hamiltonian H is the same as in the atom giving the atom, giving $\square = E_A$, the AO energy. These assumptions result in

$$\cong \tag{IV.15}$$

At this level of approximation the two MOs are symmetrically displaced from E_A with a separation of $2\square$. Since $\square$ is a negative quantity the orbital with energy $(E_A + \square\square)$ lies lowest, as shown in Figure IV.2.

With the approximation S=0, the secular equations become

$$0$$
$$0 \tag{IV.16}$$

Putting $E = E_+$ or E_- we get $c_1/c_2 = 1$ or -1, resp., and therefore the corresponding wave functions ψ_+ and ψ_- are given by:

$$\psi_+ = N_+(\phi_1 + \phi_2) \qquad \psi_- = N_-(\phi_1 - \phi_2)$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (IV.17)$$

N_+ and N_- are normalization constants obtained from the conditions:

$$\int \psi_+^2 \, d\tau = \int \psi_-^2 \, d\tau = 1 \qquad\qquad\qquad (IV.18)$$

Neglecting $\int \phi_1 \phi_2 \, d\tau$, the overlap integral, gives $N_+ = N_- = 2^{-1/2}$ and

$$\psi \quad 2 \, _- \qquad\qquad\qquad\qquad\qquad\qquad\qquad (IV.19)$$

In this way every linear combination of two identical AOs gives two MOs, one higher and the other lower in energy than the AOs. Figure IV.3 illustrates the MOs from 1s, 2s and 2p AOs showing the approximate forms of the MO wave functions. The designation $\sigma_g 1s$, $\sigma_u 1s$, ..., includes the AO from which the MO was derived, 1s in these examples, and also a symmetry species label, here σ_g or σ_u for the MO from the $D_{\infty h}$ point group. However, use of symmetry species labels may be more or less avoided by using the fact that only σ-type and π-type MOs are usually encountered, and these can easily be distinguished by the σ orbitals being cylindrically symmetrical about the internuclear axis whereas the π orbitals are not: this can be confirmed from the examples of orbitals in Figure IV.3.

The 'g' or 'u' subscripts imply symmetry or antisymmetry, respectively, with respect to inversion through the centre of the molecule but are often dropped in favour of the asterisk as in, say, σ^*2s or σ^*2p. The asterisk implies antibonding character due to the nodal plane, perpendicular to the internuclear axis, of such orbitals: those without an asterisk are bonding orbitals.

The MOs from 1s, 2s and 2p AOs are arranged in order of increasing energy in Figure IV.4, which is applicable to all first-row diatomic molecules except O_2 and F_2. Because of the symmetrical arrangement, illustrated in Figure IV.2, of the two

MOs with respect to the AOs, and because the resonance integral for the MO formed from the $2p_z$ AOs is larger than for those formed from $2p_x$ and $2p_y$ MOs, the expected order of MO energies is:

$$1 \quad {}_*1 \quad 2 \quad {}_*2 \quad 2 \quad 2 \quad {}_*2 \quad {}_*2$$

(IV.20)

In fact, this order is maintained only for O_2 and F_2. For all the other first-row diatomic molecules $\square_g$ 2s and $\square_g$ 2p interact (because they are of the same symmetry) and push each other apart such that $\square_g$ 2p is now above $\square_u$ 2p giving the order

$$1 \quad {}_*1 \quad 2 \quad {}_*2 \quad 2 \quad 2 \quad {}_*2 \quad {}_*2$$

(IV.21)

This is the order shown in Figure IV.4.

The electronic structure of any first-row diatomic molecule can be obtained by feeding the available electrons into the MOs in order of increasing energy and taking account of the fact that $\square$ orbitals are doubly degenerate and can accommodate four electrons each. For example, the ground configuration of the 14-electron nitrogen molecule is

$$1 \quad {}_*1 \quad 2 \quad {}_*2 \quad 2 \quad 2$$

(IV.22)

There is a general rule that the bonding character of an electron in a bonding orbital is approximately cancelled by the antibonding character of an electron in an antibonding orbital. In nitrogen, therefore, the bonding of the two electrons in $\square_g$ 1s is cancelled by the antibonding of two electrons in $\square{}^*_u$ 1s and similarly with $\square_g$ 2s and $\square{}^*_u$ 2s. So there remain six electrons in the bonding orbitals $\square_u$ 2p and $\square_g$ 2p and, since

bond order $=$ half the net number of bonding electrons,

the bond order is three, consistent with the triple bond of N_2.

The ground configuration of O_2

$$1 \quad *1 \quad 2 \quad *2 \quad 2 \quad 2 \quad *2 \qquad (IV.23)$$
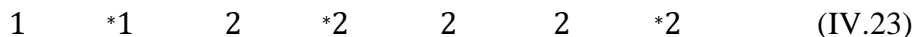
is consistent with a double bond. Just as for the ground configuration of atoms the first of Hund's rules applies and, if several states arise from the gs configuration, the l owe s t (ground) state has the highest multiplicity. In O_2, the two electrons in the unfilled □□$_g$ 2p orbital may have their spins parallel, giving $S =1$ (multiplicity of 3), or $S =0$ (multiplicity of 1).

Therefore, the ground state of O_2 is a triplet state and the molecule is paramagnetic. Singlet states with the same configuration as in Equation (IV.23) with antiparallel spins of the electrons in the □*$_g$ 2p orbital are higher in energy and from the low-lying excited states.

Fluorine has the ground configuration

$$1 \quad *1 \quad 2 \quad *2 \quad 2 \quad 2 \quad *2$$
$$(IV.24)$$
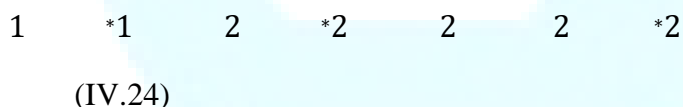
consistent with a single bond.

Just as for atoms, excited configurations of molecules are likely to give rise to more than one state. For example the excited configuration

$$1 \quad *1 \quad 2 \quad *2 \quad 2 \quad 2$$

(IV.25) of the short-lived molecule C_2 results in a triplet and a singlet state because the two electrons in partially filled orbitals may have parallel or antiparallel spins.

IV.2.1.2 Heteronuclear diatomic molecules

Some heteronuclear diatomic molecules, such as nitric oxide (NO), carbon monoxide (CO) and the short-lived CN molecule, contain atoms which are sufficiently similar that the MOs resemble quite closely those of homonuclear diatomics. In NO, the 15 electrons can be fed into MOs, in the order relevant to

O_2 and F_2, to give the ground configuration

$$1 \quad {}_*1 \quad 2 \quad {}_*2 \quad 2 \quad 2 \quad {}_*2$$

(IV.26)

(for heteronuclear diatomics, the 'g' and 'u' subscripts given in Figure IV.4 must be dropped as there is no centre of inversion, but the asterisk still retains its significance.) The net number of bonding electrons is five giving a bond order of 2. This configuration gives rise to a doublet state, because of the unpaired electron in the □*2p orbital, and paramagnetic properties.

Even molecules such as the short-lived SO and PO molecules can be treated, at the present level of approximation, rather like homonuclear diatomics. The reason being that the outer shell MOs can be constructed from 2s and 2p AOs on the oxygen atom and 3s and 3p AOs on the sulphur or phosphorus atom and appear similar to those shown in Figure IV.3. These linear combinations, such as 2p on oxygen and 3p on sulphur, obey all the conditions given on page 1 – notably Condition 1, which states that the energies of the AOs should be comparable.

There is, in principle, no reason why linear combinations should not be made between AOs which have the correct symmetry but very different energies, such as the 1s orbital on the oxygen atom and the 1s orbital on the phosphorus atom. The result would be that the resonance integral □ (Figure IV.2) would be extremely small so that the MOs would be virtually unchanged from the AOs and the linear combination would be ineffective.

In a molecule such as hydrogen chloride (HCl) the MOs bear no resemblance to those shown in Figure IV.3 but the rules for making effective linear combinations

still hold good. The electron configuration of the chlorine atom is $KL3s^2 3p^5$ and it is only the 3p electrons (ionization energy 12.967 eV), which are comparable in energy with the hydrogen 1s electron (ionization energy 13.598 eV). Of the 3p orbitals it is only $3p_z$ which has the correct symmetry for a linear combination to be formed with the hydrogen 1s orbital, as Figure IV.5(a) shows. The MO wave function is of the form in Equation (IV.2) but $c_1 = c_2$ is no longer ± 1. Because of the higher electronegativity of Cl compared with H there is considerable electron concentration near Cl, which go into the resulting $\Box$ bonding orbital. The two electrons in this orbital form the single bond. The $3p_x$ and $3p_y$ AOs of Cl cannot overlap with the 1s AO of H and the electrons in them remain as lone pairs in orbitals which are very little changed in the molecule, as shown in Figure IV.5(b). In fact, we can easily see that the overlap between 2s and $2p_x$ cancels out. We start appreciating how we can use symmetry arguments to say something about our molecule without actually solving the problem. Consider, for example a 2s orbital on the C atom and a $2p_x$ orbital on the O atom (Figure IV.1). If we turn the molecule around by 180 degrees about its axis, the molecule looks the same to us, the Hamiltonian has remained the same and the 2s orbital has remained the same too. The $2p_x$ orbital, on the other hand has changed sign. So the integrals $H_{12} = \langle 2s|H|2p_x \rangle$ and $S = \langle 2s|2p_x \rangle$ also must change sign.

IV.2.2   Classification of electronic states

Here we only consider the non-rotating molecule, so we are concerned only with orbital and spin angular momenta of the electrons. As in polyelectronic atoms the orbital and spin motions of each electron create magnetic moments which behave like small bar magnets. The way in which the magnets interact with each other represents the coupling between the electron motions.

For all diatomic molecules, the best approximation for the SO coupling

is the Russell–Saunders approximation (§ IV.1.2.3). The orbital angular

momenta of all electrons are coupled to give $\vec{L}$ and all the electron spin

momenta to give $\vec{S}$. However, if there is no highly charged nucleus in the

molecule, the spin–orbit coupling between $\vec{L}$ and $\vec{S}$ is sufficiently weak that, instead of being coupled to each other, they couple instead to the electrostatic field produced by the two nuclear charges. This situation is shown in Figure IV.6(a) and is referred to as Hund's case (a).

$\vec{L}$ is so strongly coupled to the electrostatic field and the consequent frequency of

precession about the internuclear axis is so high that the magnitude of $\vec{L}$ is not defined: in other words L is not a good quantum number. Only the component □ℏ of the orbital angular momentum along the internuclear axis is defined, where the quantum number □ can take the values

$$\Lambda \quad 0,1,2,3, \ldots$$

(IV.26)

All electronic states with □ > 0 are doubly degenerate. Classically, this degeneracy can be thought of as being due to the electrons orbiting clockwise or anticlockwise around the internuclear axis, the energy being the same in both cases. If □ = 0 there is no orbiting motion and no degeneracy.

The value of □, like that of L in atoms, is indicated by the main part of the symbol for an electronic state which is designated □□□□□□□□□□□□□ … corresponding to □□0, 1, 2, 3, 4, ... The letters □□□□□□□□□□□□□□.. are the Greek

equivalents of S, P, D, F , G, ... used for atoms. ₋

The coupling of S to internuclear axis is caused not by the electrostatic field, which has no effect on it, but by the magnetic field along the axis due to the orbital motion

of the electrons. Figure IV.6(a) shows that the component of S along the internuclear axis is $\Sigma\hbar$. The quantum number S is analogous to M_S in an atom and can take the values

$$\Sigma \quad , \quad 1, \dots ,$$

(IV.27)

S remains a good quantum number and, for states with $\Lambda > 0$, there are (2S+1) components corresponding to the number of values that S can take.

The multiplicity of (2S+1) and is indicated, as in atoms, by a pre-superscript as, for example, in $^3\Pi$.

The component of the total (orbital plus electron spin) angular momentum along the internuclear axis is $\Omega\hbar$, shown in Figure 7.16(a), where the quantum number Ω is given by:

$$\Omega \quad |\Lambda \quad \Sigma|$$

(IV.28)

Since $\Lambda = 1$ and $\Sigma =1,0,-1$ the three components of $^3\Pi$ have $\Omega=2, 1, 0$ and are symbolized by $^3\Pi$, $^3\Pi$, $^3\Pi$

Spin–orbit interaction splits the components so that the energy level after interaction is shifted by:

$$\Delta \quad \Lambda\Sigma$$

(IV.29)

where A is the spin–orbit coupling constant. The splitting produces what is called a normal multiplet if the component with the lowest Ω has the lowest energy (i.e. A positive) and an inverted multiplet if the component with the lowest Ω has the highest energy (i.e. A negative).

For Σ states there is no orbital angular momentum and therefore no resulting magnetic field to couple $\vec{S}$ to the internuclear axis. The result is that a Σ state has only one component, whatever the multiplicity.

Hund's case (a), shown in Figure IV.6(a), is the most common case but, like all assumed coupling of angular momenta, it is an approximation. However, when there is at least one highly charged nucleus in the molecule, S-O coupling may be sufficiently large that $\vec{L}$ and $\vec{S}$ are not uncoupled by the electrostatic field of the nuclei. Instead, as shown in Figure IV.6(b), $\vec{L}$ and $\vec{S}$ couple to give $\vec{J}$, as in an atom, and $\vec{J}$ couples to the internuclear axis along which the component is $\Omega\hbar$. This coupling approximation is known as Hund's case (c), in which Λ is no longer a good quantum number. The main label for a state is now the value of Ω. This approximation is by no means as useful as Hund's case (a) and, even when it is used, states are often labeled with the value that Λ would have if it were a good quantum number.

For atoms, electronic states may be classified and selection rules specified entirely by use of the quantum numbers L, S and J. In diatomic molecules the quantum numbers Λ, Σ, Ω and S are not quite sufficient. We must also use one (for heteronuclear) or two (for homonuclear) symmetry properties of the electronic wave function ψ_e.

The first is the 'g' or 'u' symmetry property, which indicates that ψ_e is symmetric or antisymmetric respectively to inversion through the centre of the molecule. Since the molecule must have a centre of inversion for this property to apply, states are labeled 'g' or 'u' for homonuclear diatomics only. The property is indicated by a post-subscript .

The second symmetry property applies to all diatomics and concerns the symmetry of ψ_e with respect to reflection across any (σ_v) plane containing the internuclear axis. If ψ_e symmetric to (i.e. unchanged by) this reflection the state is labeled " + " , while if antisymmetric to this reflection it is labeled "-".

This symbolism is normally used only for Σ states.

IV.2.3 Electronic selection rules

Electronic transitions are mostly of the electric dipole type (electric quadrupole or magnetic dipole also occur but are orders of magnitude weaker in intensity). The selection rules for electric dipole transitions are:

$$\cdot\ \Delta\Lambda \quad 0,\ 1 \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(IV.30)}$$

For example, □□□□, □□□□, □□□□ transitions are allowed but not □□□□ or

□□□□

$$\cdot\ \Delta \quad 0 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(IV.31)}$$

As in atoms, this selection rule breaks down as the nuclear charge increases. For example, triplet–singlet transitions are strictly forbidden in H_2 but not in CO (although they are weak).

$$\cdot\ \Delta\Sigma \quad 0; \qquad\qquad\qquad \Delta\Omega \qquad\qquad \text{(IV.32)}$$
$$0,\qquad 1$$

for transitions between multiplet components

$$\cdot + \leftrightarrow\ ;+\leftrightarrow+;\ -\ \leftrightarrow- \qquad\qquad\qquad\qquad \text{(IV.33)}$$

This is relevant only for □□□□□ transitions.

• g↔u; g↮g; u↮u (IV.34)

For Hund's case (c) coupling (Figure IV.6b) the selection rules are slightly different. Those in Equations (IV.31) and (IV.34) still apply but, because □ and □ are not good quantum numbers that in Equation (IV.30) and Equation (IV.32) do not. In the case of Equation (IV.33) the +/- signs refer to the symmetry of ψ_e to reflection in a plane containing the internuclear axis only when □□□□

IV.2.4 . Vibrational coarse structure

IV.2.4.1 Potential energy curves in excited electronic states

Potential energy curves derive from the Born-Oppenheimer approximation and represent the potential due to electrons in which nuclear motion occurs. Figure IV.7

shows a typical curve with a potential energy minimum at r_e, the equilibrium internuclear distance. Dissociation occurs at higher energy and the dissociation energy is D_e, relative to the minimum in the curve, or D_0, relative to the zero-point level (v_0= level). The vibrational term values, $G(v)$, for an anharmonic oscillator are given by

$$-) \qquad\qquad \_ \quad \cdots \qquad\qquad\qquad \text{(IV.35)}$$

Where ω_e is the harmonic constant and $\omega_e x_e$ is the anharmonic constant. This expression can be further expanded but the additional terms are very small and contribute little to the total energy.

For each excited electronic state of a diatomic molecule there is a potential energy curve and, for most states, the curve appears qualitatively similar to that in Figure IV.7.

As an example of such excited state potential energy curves, Figure IV.8 shows curves for several excited states and also for the ground state of the short-lived C_2 molecule. The ground electron configuration is

$$1 \qquad *1 \qquad 2 \qquad *2 \qquad 2 \qquad\qquad \text{(IV.36)}$$

giving the $X^1\Sigma^+_g$ ground state. The low-lying excited electronic states in Figure

IV.8 arise from configurations in which an electron is promoted from the π_u 2p or σ_u 2s orbital to the σ_g 2p orbital. The information contained in Figure IV.8 has been obtained using various experimental techniques to observe absorption or emission spectra. The combination of techniques for observing the spectra, including a high-temperature furnace, flames, arcs, discharges and, for a shortlived molecule, flash photolysis is typical.

In addition to these laboratory-based experiments it is interesting to note that some of the bands of C_2 are important in astrophysics. The so-called Swan bands have

been observed in the emission spectra of comets and also in the absorption spectra of stellar atmospheres, including that of the sun, in which the interior of the star acts as the continuum source.

When C_2 dissociates it gives two carbon atoms which may be in their ground or excited states. We saw, earlier that the ground configuration $1s^2 2s^2 2p^2$ of the C atom gives rise to three terms: ^3P, the ground term, and ^1D and ^1S, which are successively higher excited terms. Figure IV.8 shows that six states of C_2, including the ground state, dissociate to give two ^3P carbon atoms. Other states give dissociation products involving one or both carbon atoms with ^1D or ^1S terms. Just as in the ground electronic state a molecule may vibrate and rotate in excited electronic states. The total term value T for a molecule is

(IV.37)

with the electronic term value T_e, corresponding to an electronic transition between equilibrium configurations and, G(v) and F(J) are the vibrational and rotational term values, resp. .

The vibrational term values for any electronic state, ground or excited, are given by Equation (IV.35), where the constants vary from one electronic state to another. Figure IV.8 shows that the equilibrium internuclear distance r_e is also different for each electronic state.

IV.2.5.2 Progressions and sequences

Figure IV.9 shows sets of vibrational energy levels associated with two electronic states between which we shall assume an electronic transition is allowed. The vibrational levels of the upper and lower states are labeled by the quantum number v' and v''; respectively. We discuss absorption as well as emission processes and it will be assumed, unless otherwise stated, that the lower state is the ground state.

In electronic spectra there is no restriction on the values that □v can take but, as we shall later, the Franck–Condon principle imposes limitations on the intensities of the transitions. Vibrational transitions accompanying an electronic transition are referred to as <u>vibronic</u> transitions. These vibronic transitions, with their accompanying rotational (i.e., <u>rovibronic</u> transitions), give rise to bands in the spectrum, and the set of bands associated with a single electronic transition is called an electronic band system. Vibronic transitions may be divided conveniently into progressions and sequences. A progression, as Figure IV.9 shows, involves a series of vibronic transitions with a common lower or upper level.

Quite apart from the necessity for Franck–Condon intensities (see below) of vibronic transitions to be appreciable, it is essential for the initial state of a transition to be sufficiently highly populated for a transition to be observed.

Under equilibrium conditions the population $N_{v''}$ of any v'' level is related to that of v''=0 via:

$$\underline{\quad} \qquad\qquad 0 \underline{\quad} \qquad\qquad\qquad (IV.38)$$

which follows from the Boltzmann equation.

Because of the relatively high population of the v''= 0, the v''=0 progression is likely to dominate the absorption spectrum.

In emission the relative populations of the v' levels depend on the method of excitation. In a low-pressure discharge, in which there are not many collisions to provide a channel for vibrational deactivation, the populations may be somewhat random. However, higher pressure may result in most of the molecules being in the v'=0 level and its associated progression is prominent. Nowadays, the method of choice for excitation is monochromatic (often laser) light, which can selectively populated specific vibronic levels.

The progression with v''=1 may also be observed in absorption but only in molecules with a vibrational frequency low enough for the v''=1 level to be

populated at kT. This is the case for example with iodine for which $\omega_0=213$ cm^{-1} (while kT= 203 cm^{-1} at T=293 K). As a result the $B^3\Pi_{0u}\leftarrow X\,^1\Sigma_g$ visible transition shows in absorption at RT, not only the v"=0 progressions but also the v=1 and 2 ones (see figure IV.10).

Fluorescence= transitions that are spin-allowed. Their lifetimes are in the nanosecond time domain.

Phosphorescence= spin-forbidden transitions, that however occur due to spinorbit coupling which relaxes the spin selection rule. These transitions have long lifetimes in the 100s of ns to the msec time domain.

Consequently, there is a tendency to distinguish the two processes according to their lifetimes. One has to be careful, in cases of strong spin–orbit coupling, as the lifetime of a transition between states of differing multiplicity may be relatively short, leading to an erroneous description as fluorescence.

If emission is from only one vibrational level of the upper electronic state it is referred to as single vibronic level fluorescence (or phosphorescence).

A group of transitions with the same value of Δv is referred to as a sequence. Because of the population requirements long sequences are observed mostly in emission.

Progressions and sequences are not mutually exclusive (see fig. IV.9). Each member of a sequence is also a member of two progressions. However, the distinction is useful because of the nature of typical patterns of bands found in a band system.

Progression members are generally widely spaced with approximate separations of ω_e' in absorption and ω_e'' in emission. In contrast, sequence members are more closely spaced with approximate separations of $\omega_e'-\omega_e''$.

The general symbolism for indicating a vibronic transition between an upper and lower level with vibrational quantum numbers v' and v", respectively, is v'-v",

consistent with the general spectroscopic convention. Thus the pure electronic transition (i.e. not involving vibrations) is labeled 0–0.

IV.2.5.3 The Franck–Condon principle

In 1925, before the development of the Schrödinger equation, Franck put forward classical arguments to explain the various types of intensity distributions found in vibronic transitions. These were based on the Born-Oppenheimer approximation, i.e., electronic motion is much more rapid than nuclear motion, so during an electronic transition, the nuclei have very nearly the same position and velocity before and after the transition.

Possible consequences of this are illustrated in Figure IV.11a, which shows potential curves for the lower state, which is the ground state if we are considering an absorption process, and the upper state. The curves have been drawn so that r_e' $> r_e$". In absorption, from point A of the ground state in Figure IV.11(a) (zero-point energy can be neglected in considering Franck's semiclassical arguments) the transition will be to point B of the upper state. The requirement that the nuclei have the same position before and after the transition means that the transition is between points which lie on a vertical line in the figure: this means that r remains constant and such a transition is often referred to as a *vertical* transition. The second requirement, that the nuclei have the same velocity before and after the transition, means that a transition from A, where the nuclei are stationary, must go to B, as this is the classical turning point of a vibration, where the nuclei are also stationary. A transition from A to C is highly improbable because, although the nuclei are stationary at A and C, there is a large change of r. An A to D transition is also unlikely because, although r is unchanged, the nuclei are in motion at the point D. Figure IV.11b illustrates the case where r_e' $\approx r_e$". Here the most probable transition is from A to B with no vibrational energy in the upper state. The transition from A

to C maintains the value of r but the nuclear velocities are increased due to their having kinetic energy equivalent to the distance BC.

In 1928, Condon treated the intensities of vibronic transitions quantum mechanically. The intensity of a vibronic transition is proportional to the square of the transition moment $\vec{R}_{ev}$, which is given by Equation II.13:

$$\vec{R}_{ev} = \int \psi'_{ev} \, \vec{\mu} \, \psi''_{ev} \, d\tau_{ev} \qquad\qquad (IV.39)$$

where $\vec{\mu}$ is the electric dipole moment operator and the ψ's are the vibronic wave functions of the upper and lower states, respectively. The integration is over electronic and vibrational coordinates. Within the Born–Oppenheimer approximation, they can be factorized in an electronic and a vibrational part, and eq. IV.39 becomes:

$$\vec{R}_{ev} = \int\int \psi'^*_e \psi'_v \, \vec{\mu} \, \psi''_e \psi''_v \, d\tau_e d\tau_v = \vec{R}_e \int \psi'_{v}{}^* \psi''_{v} \, dr \qquad (IV.40)$$

With

$$\vec{R}_e = \int \psi'^*_e \, \vec{\mu} \, \psi''_e \, d\tau_e \qquad\qquad (IV.41)$$

is the electronic transition moment.

As a consequence of the BO approximation, the electronic part is independent of the nuclear coordinates and we take it outside the integral in Equation (IV.40), regarding it as a constant. The quantity $\int \psi'_{v}{}^* \psi''_{v} \, dr$ is called the <u>vibrational overlap function</u>.

Its square is known as the <u>Franck–Condon factor</u> to which the intensity of the vibronic transition is proportional. In carrying out the integration the requirement that r remain constant during the transition is necessarily taken into account. The

classical turning point of a vibration, where nuclear velocities are zero, is replaced in quantum mechanics by a maximum, or minimum, in ψ_v near to this turning point. Figure IV.11 illustrates a particular case where the maximum of the v'=4 wave function near the classical turning point is vertically above that of the v"=0 wave function. Maximum overlap is indicated by the vertical line but appreciable contributions extend to values of r within the dashed lines. Clearly, overlap integrals for v' close to four are also appreciable and give an intensity distribution in the v"=0 progression with a maximum at v'=4.

The Franck-Condon intensity distribution for a progression starting from v=0 (either in absorption or emission) is strongly dependent on the relative equilibrium distances of the two potential curves. This is illustrated in figure IV.13. In the left panel, $r'_e \approx r"_e$ and the progression starts with the 0-0 transition as the most intense, since the v"=0 and v'=0 wave functions have maximum overlap. 4–0 transition is the most probable. In the middle panel $r'_e < r"_e$ and the maximum overlap is between v"=0 and v'=2, so the progression has a maximum intensity at the 0-2 transition, although the other levels show appreciable overlap too. Finally, for the right panel, $r'_e << r"_e$ and the maximum overlap is close to the dissociation limit of the upper curve and the progression of discrete bands terminates and the absorption continues into the dissociation continuum giving rise to a continuous band.

IV.2.5.3 Dissociation energies

Experimentally the dissociation energy D_0 can only be measured relative to the v=0 level (Figure IV.14):

$$D_0 \square \square \square G_{v\square 1/2}$$
$$_v$$

$$(IV.42)$$

If a sufficient number of vibrational term values are known in any electronic state, D_0 can be obtained by plotting $\Delta G_{v+1/2}$ as a function of v+1/2 (Figure IV.15), where

$$\Delta G_{v+1/2} = G(v+1) - G(v) \qquad\qquad (IV.43)$$

If all anharmonic constants except $\omega_e x_e$ are neglected in equ. IV.42, $\Delta G_{v+1/2}$ is a linear function of v and D_0 is the area under the dashed curve in figure IV.15. in most cases, only a few ΔG values are known and a linear extrapolation to $\Delta G=0$ has to be made, which called the Birge–Sponer extrapolation. This

only gives an approximate value of the dissociation energy, and since most plots deviate from linearity, this delivers an overestimate of D_0 (Fig. IV.14). Whether this can at all be done depends very much on the relative dispositions of the various potential curves in a particular molecule and whether electronic transitions between them are allowed. How many ground state vibrational term values can be obtained from an emission spectrum is determined by the FC principle. To obtain an accurate value of D_0 for the ground electronic state is virtually impossible by vibrational (i.e. IR) spectroscopy because of the problems of a rapidly decreasing population with increasing v. In fact, most determinations are made from electronic emission spectra from one, or more, excited electronic states to the ground state.

Obtaining D_o' for an excited electronic state depends on observing progressions either in absorption, usually from the ground state, or in emission from higher excited states. Again, the length of a progression limits the accuracy of the dissociation energy.

If the values of r_e in the combining states are very different the dissociation limit of a progression may be observed directly as an onset of diffuseness. However, the onset is not always very sharp (see e.g., the spectrum of I_2 in Figure IV.10).

Figure IV.14 shows that

$\tilde{\nu}_{\lim it} = D_{0'} + \tilde{\nu}_0 + D''_0 + \Delta\tilde{\nu}_{atomic}$ (IV.35)

Hence, D'$_0$ can be obtained from $\tilde{\nu}_{\lim it}$ if $\tilde{\nu}_0$ the wavenumber of the 0–0 band, is known.

Figure IV.10 shows that extrapolation may be required to obtain $\tilde{\nu}_0$, limiting the accuracy of D'$_0$.

Equation (IV.35) also shows that D"$_0$ may be obtained from $\tilde{\nu}_{\lim it}$ since $\Delta\tilde{\nu}_{atomic}$ is the wave number difference between two atomic states, the ground state ^{2}P$_{3/2}$ and the first excited state ^{2}P$_{1/2}$ of the iodine atom, known accurately from the atomic spectrum. Thus the accuracy of D"$_0$ is limited only by that of $\tilde{\nu}_{\lim it}$.

D'$_e$ and D"$_e$, the dissociation energies relative to the minima in the potential curves, are obtained from obtained D$_0$' and D$_0$"

$D_e = D + G(0)$ (IV.36)

where G(0)is the zero-point term value.

IV.2.5.6 Repulsive states and continuous spectra

The ground configuration of the He$_2$ molecule is, according to Figure IV.16, $(\sigma_g 1s)^2 (\sigma*_u 1s)^2$ and is expected to be unstable because of the cancelling of the bonding character of a $(\sigma_g 1s)$orbital by the antibonding character of a $(\sigma*_u 1s)$ orbital. The potential energy curve for the resulting X $^1\Sigma^+$ state shows no minimum

but the potential energy decreases smoothly as r increases, as shown in Figure IV.16(a). Such a state is known as a repulsive state since the atoms repel each other. In this type of state, either there are no discrete vibrational levels or there may be a few in a very shallow minimum. All, or most, of the vibrational states form a continuum of levels.

Promotion of an electron in He_2 from the $(\sigma^*_u 1)s$ to a bonding orbital produces some bound states of the molecule of which several have been characterized in emission spectroscopy (e.g. the A-X transition in fig. IV.16a or the a-b transition in fig. IV.16b).
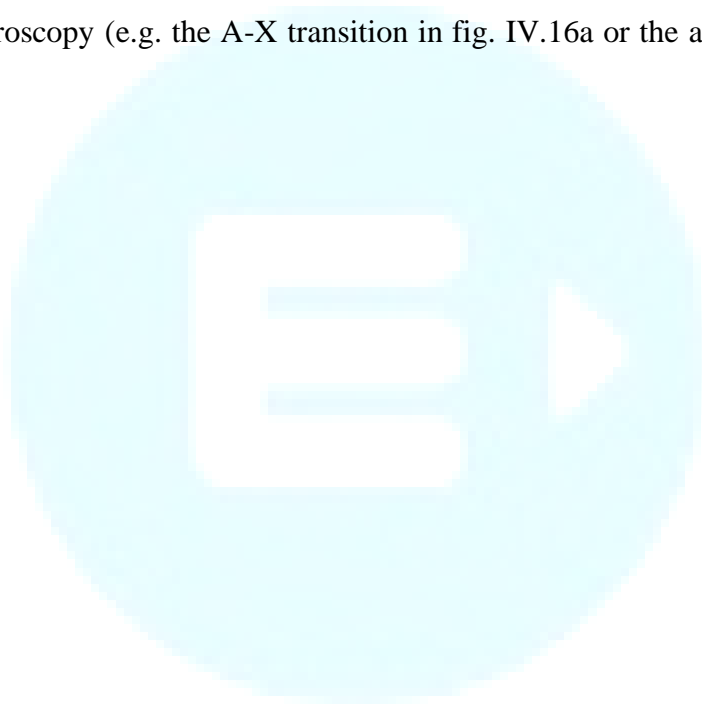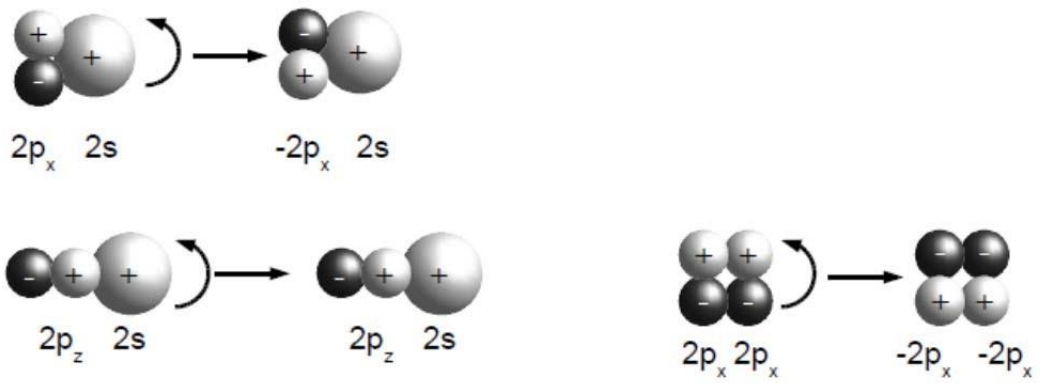
Figure IV.1: Overlap of s and p atomic orbitals.
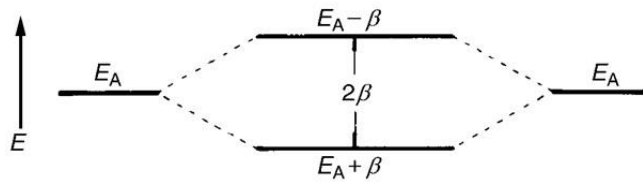
Figure IV.2 Formation of two molecular orbitals from two identical AOs. E_A is the binding energy of the AO.
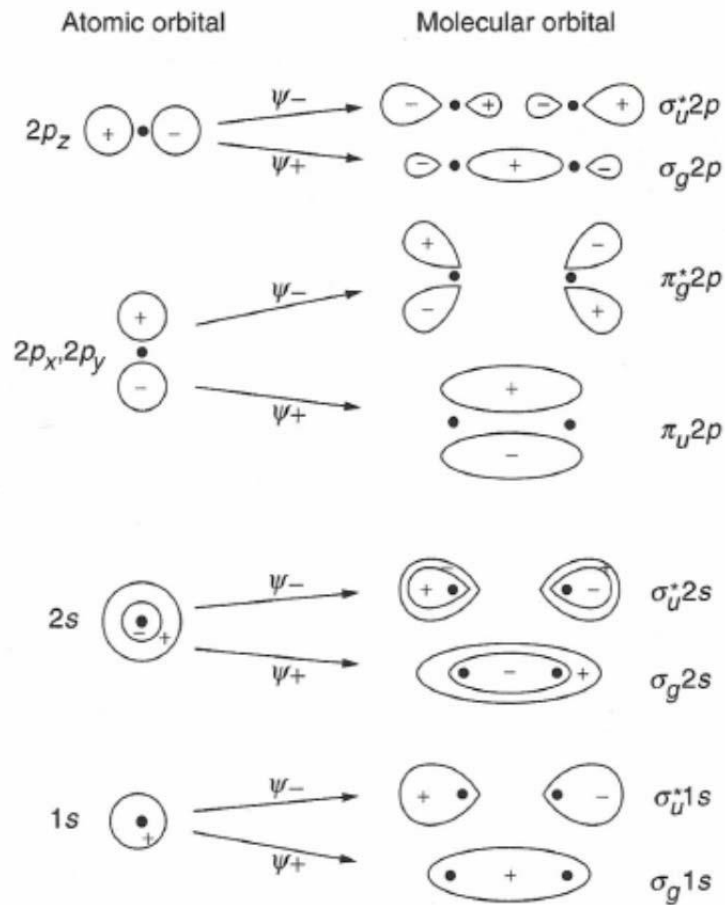
Figure IV.3 Formation of molecular orbitals from 1s, 2s, and 2p atomic orbitals
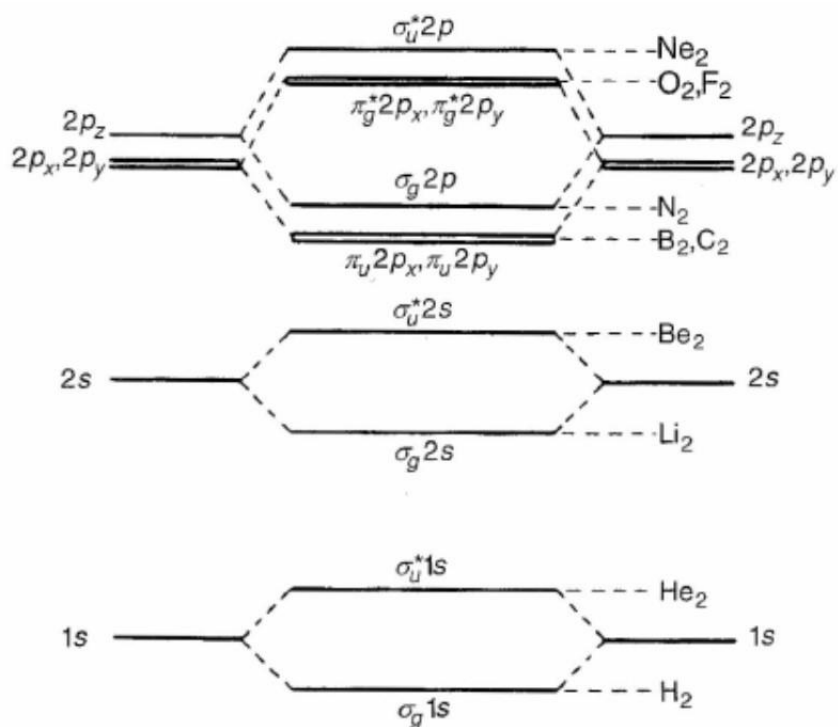
Figure IV.4: Molecular orbital energy level diagram for first-row homonuclear diatomic molecules. The 2px, 2py, 2pz atomic orbitals are degenerate in an atom and have been separated for convenience. (In O_2 and F_2, the order of σ_g 2p and σ_u 2p is reversed.)
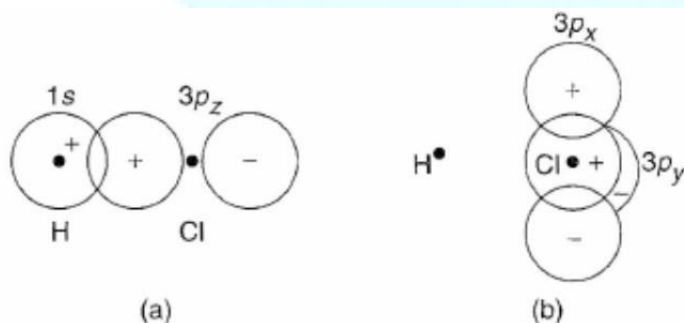
Figure IV.5: In HCl (a) the single-bond molecular orbital is formed by a linear combination of 1s on H and 3pz on Cl, and (b) electrons in the 3px and 3py atomic orbitals on Cl remain as lone pairs.
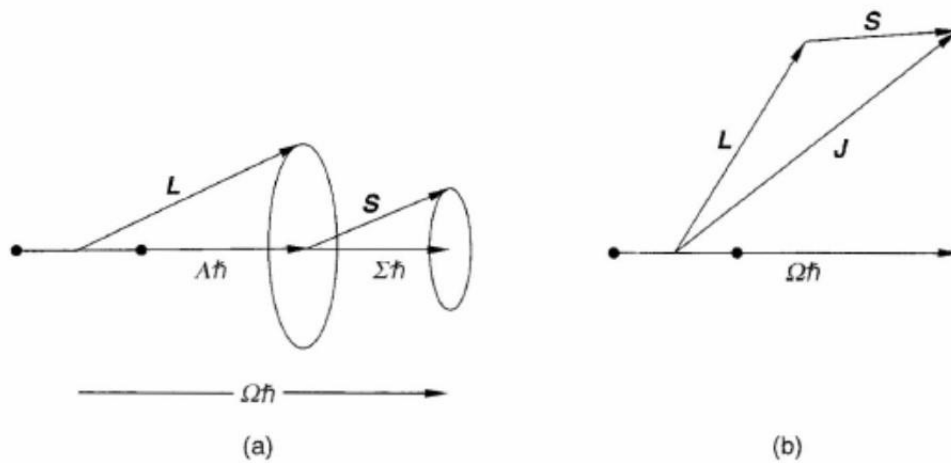
Figure IV.6: (a) Hund's case (a) and (b) Hund's case (c) coupling of orbital and electron spin angular momenta in a diatomic molecule
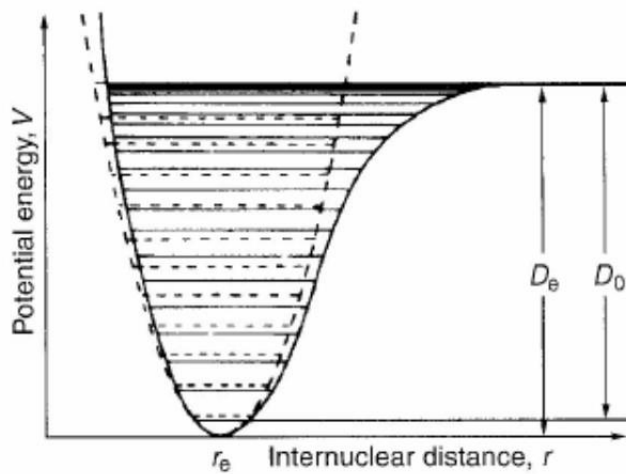
Figure IV.7: Potential energy curves. Dashed line: harmonic potential, full line: anharmonic potential, where D_e is the energy of dissociation measured from the minimum of the curve and D_0 is the energy of dissociation from the v=0 level,
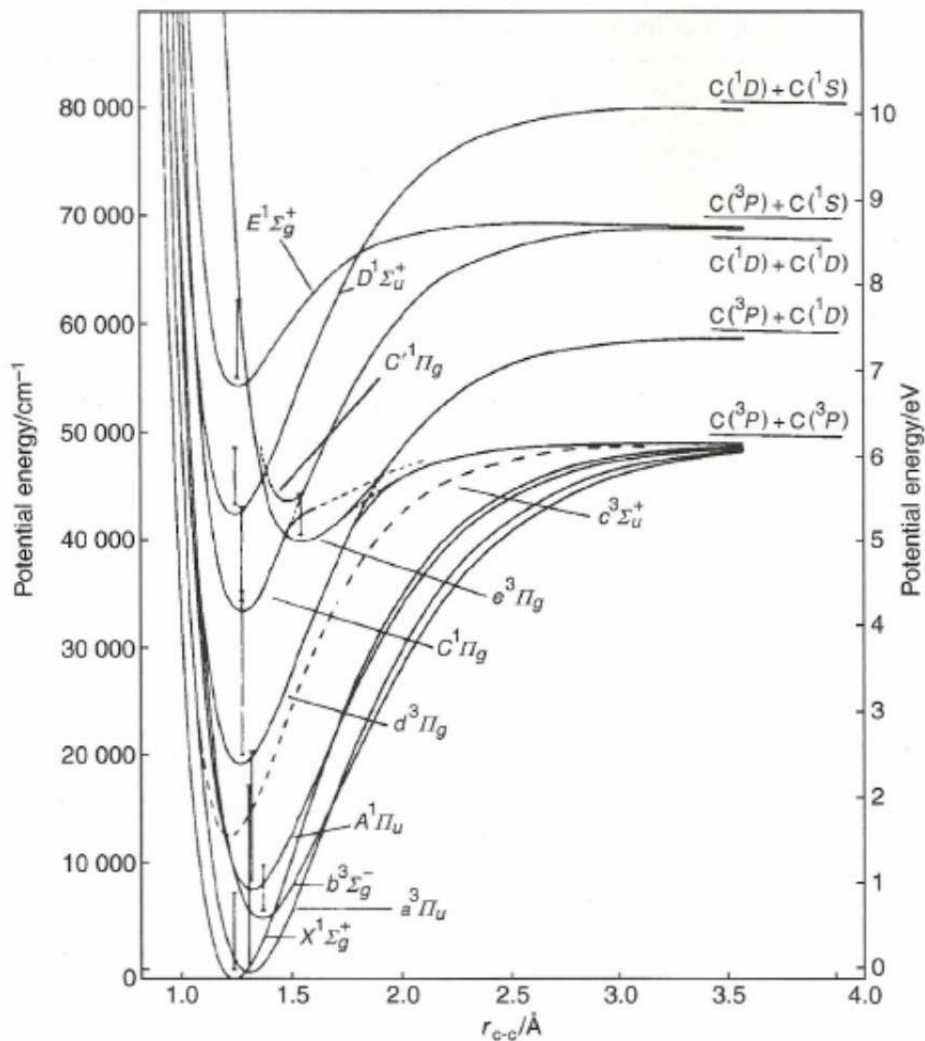
Figure IV.8: Potential energy curves for the ground and several excited states of C2. The ground state is indicated by X, while the excited state of similar multiplicity are indicated by capital letters, those of a multiplicity different to that of the gs are indicated by small letters.
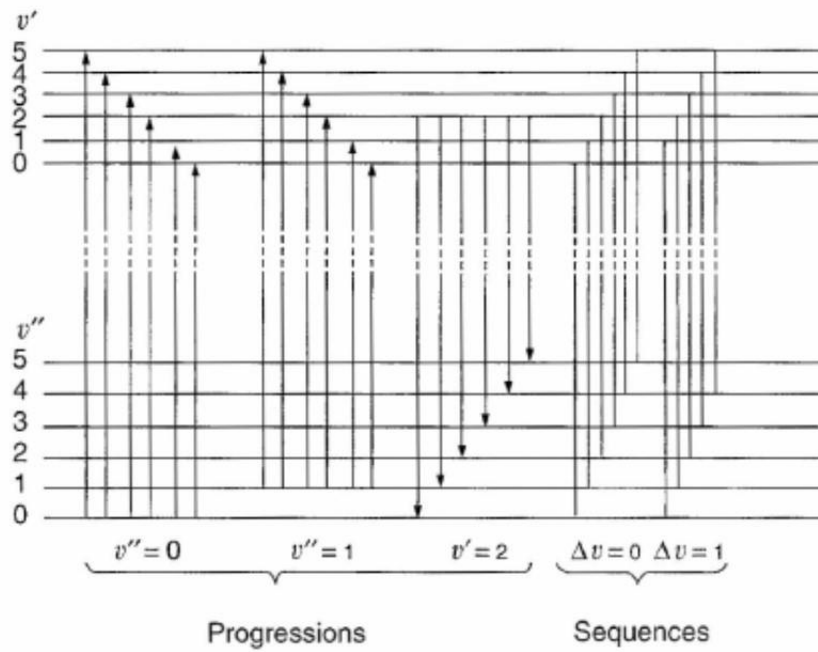
Figure IV.9: Vibrational progressions and sequences in the electronic spectrum of a diatomic molecule.
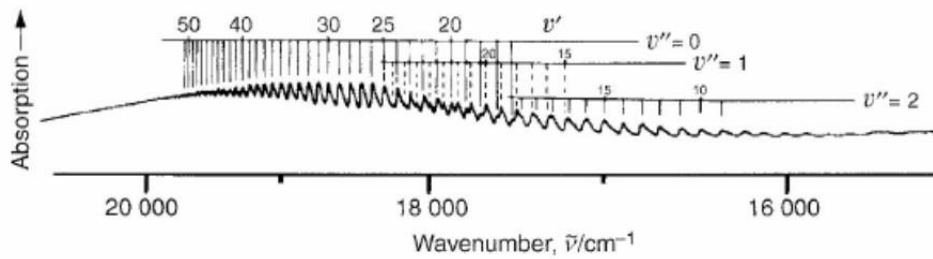
Figure IV.10: Progressions with v"=0, 1 and 2 in the $B3\Pi_{0u}\leftarrow X_1\Sigma_g$ system of gaseous I_2 at room temperature. The v"= 1 and 2 levels are populated as a result of the Boltzmann equilibrium in the room temperature vapour.
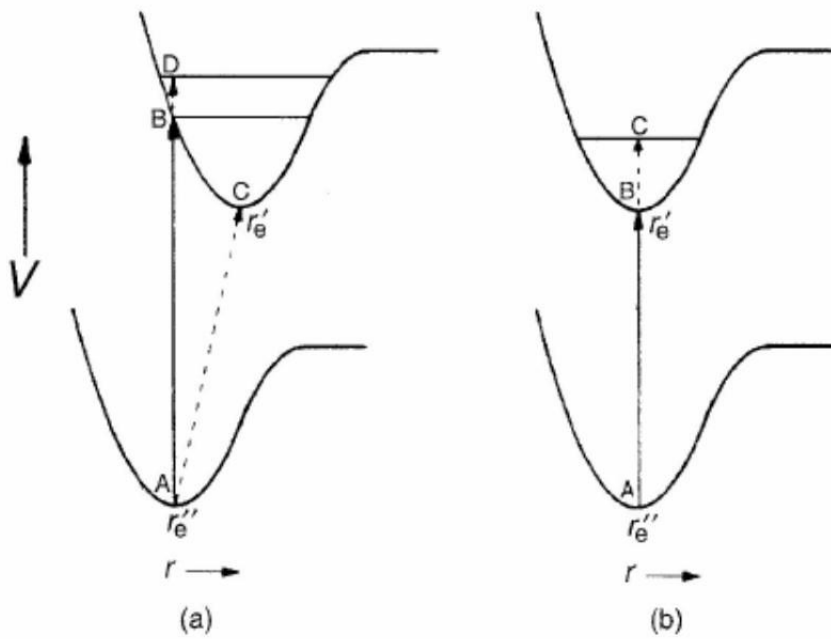
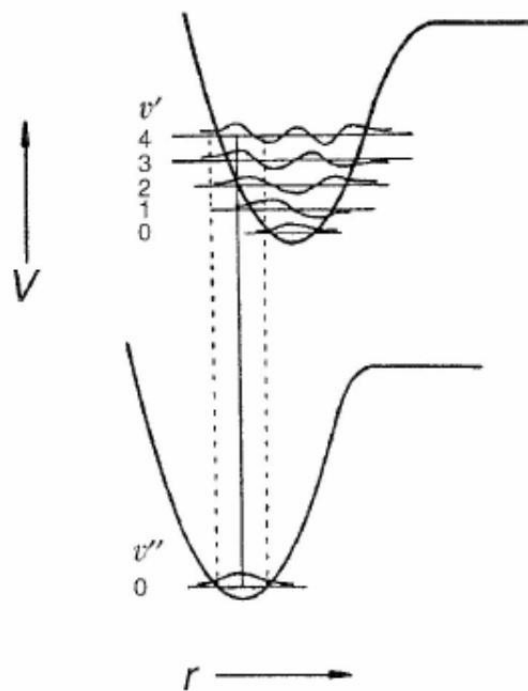Figure IV.11: Illustration of the Franck principle for (a) $r'_e > r''_e$; (b) $r'_e > r''_e$. The vibronic AB transition is the most probable in both cases.

Figure IV.12: Franck–Condon principle applied to a case in which r'$_e$> r"$_e$ and the 4–0 transition is the most probable.
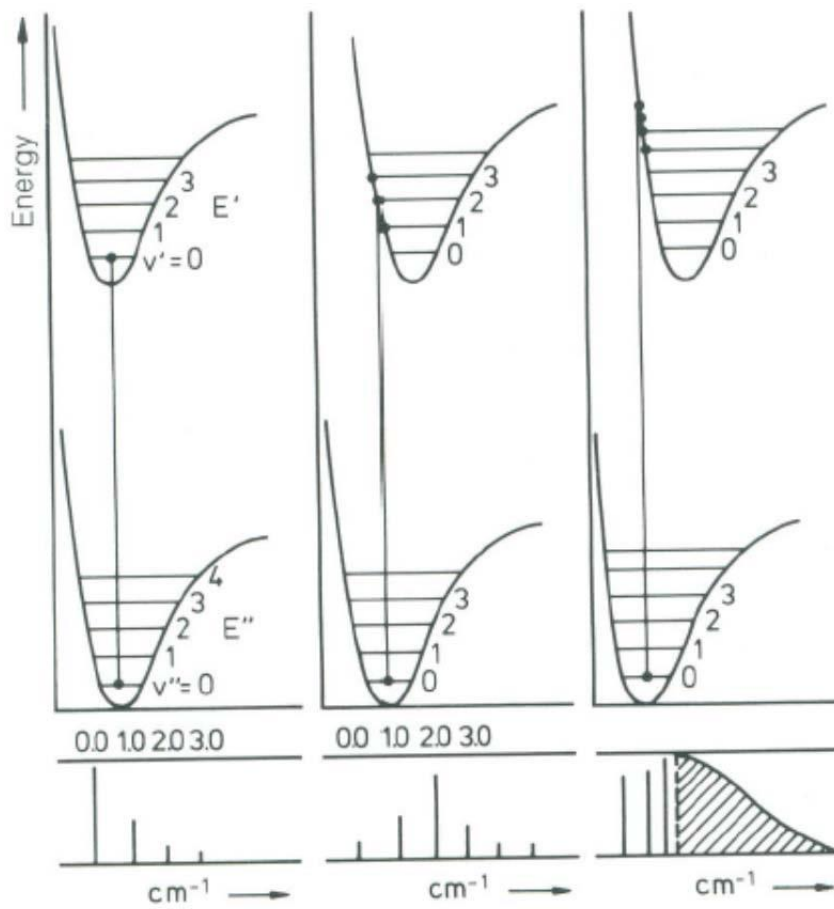
Figure IV.13: general shape of Franck–Condon progression starting from v"=0 (i.e. absorption) for different configurations of the ground and excited states.
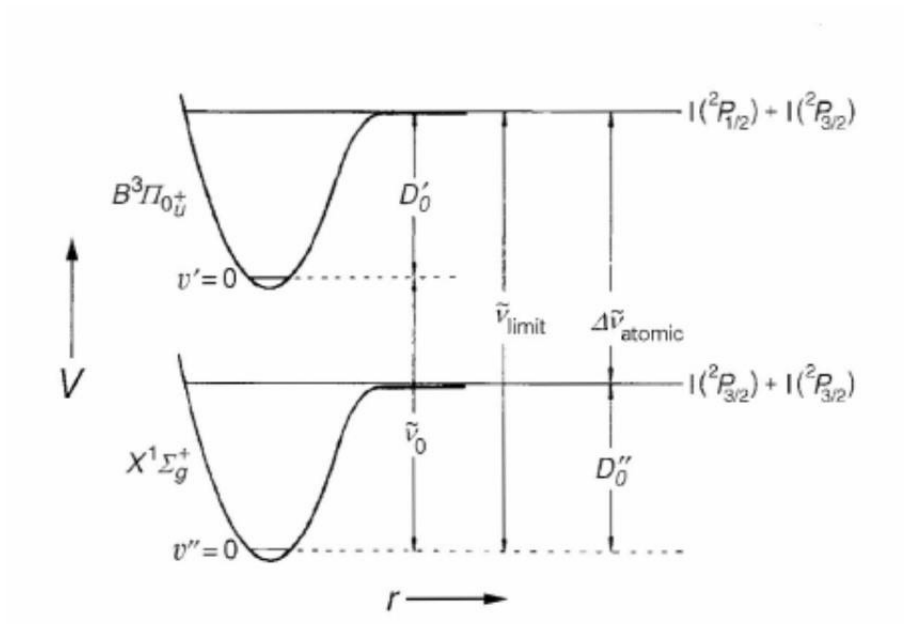
Figure IV.14: Dissociation energies D'$_0$ and D"$_0$ may be obtained from $\tilde{\nu}_{limit}$, the onset of a continuum in a progression of a diatomic molecule (I$_2$ in the present case).

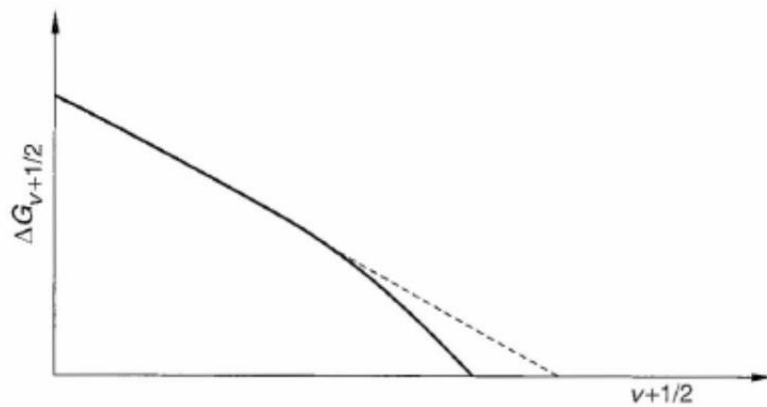

Figure IV.15: Birge-Sponer extrapolation (dashed line) for determining the dissociation energy relative to the v=0 level. Typically, the measured curve is the solid one.
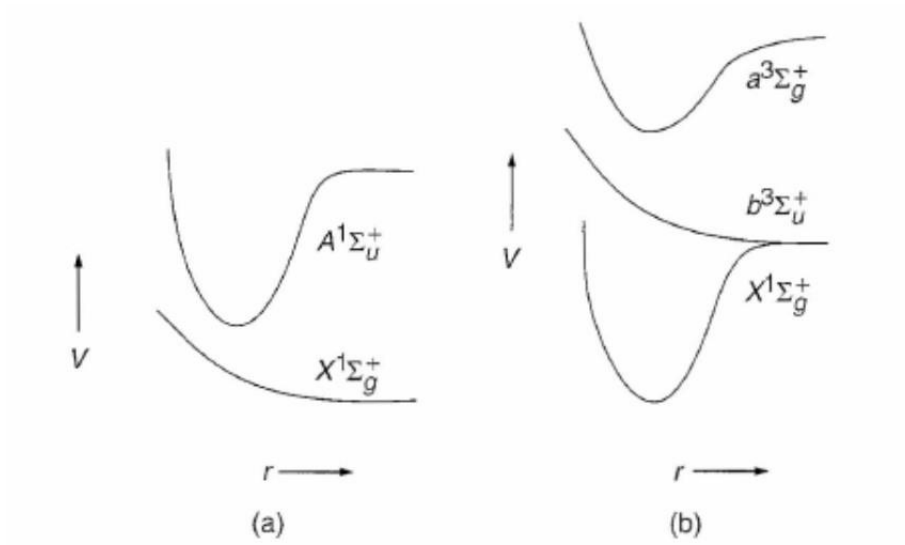
Figure IV.16: (a) The repulsive ground state and a bound excited state of He2. (b) Two bound states and one repulsive state of H2.