

Chapter 3

Structure and spectra of diatomic molecules

3.1 Hierarchies of time and energy scales in molecules

Different types of motion in a molecule happen on very different time scales. Just as in classical mechanics this property leads to an approximate separability of the motions. Consequently, stationary states of molecules are well approximated by products of electronic $\phi_e(\vec{q}_i)$, vibrational $\phi_v^{(e)}(\vec{Q}_\alpha)$, rotational $\phi_r^{(ev)}(\theta, \varphi, \chi)$ and nuclear spin $\phi_{ns}^{(evr)}(m_\sigma)$ wave functions

$$\Psi = \phi_e(\vec{q}_i)\phi_v^{(e)}(\vec{Q}_\alpha)\phi_r^{(ev)}(\theta, \varphi, \chi)\phi_{ns}^{(evr)}(m_\sigma), \quad (3.1)$$

and sums of electronic E_e , vibrational E_v , rotational E_r , and hyperfine E_{ns} energies

$$E = E_e + E_v + E_r + E_{ns}. \quad (3.2)$$

In Equation (3.1), \vec{q}_i stands for the coordinates of the electrons including spin, \vec{Q}_α represents the internal coordinates of the nuclear framework, (θ, φ, χ) are the Euler angles specifying the orientation of the molecule in space, and m_σ describes the spin state of the nuclei.

The very different time scales of motion leading to Equations (3.1) and (3.2) also result in very different energy intervals between the quantum states resulting from this type of motion (see Table 3.1). Spectroscopies studying electronic transitions therefore mostly rely on visible or ultraviolet radiation, vibrational transitions are best studied using mid-infrared radiation and rotational transitions with microwave radiation.

Motion	Typical period	Typical energy interval
Electronic	0.1–1 fs	$> 5000 \text{ cm}^{-1}$
Vibrational	10–100 fs	$300\text{--}3000 \text{ cm}^{-1}$
Rotational	0.1–10 ps	$1\text{--}100 \text{ cm}^{-1}$

Table 3.1: Typical period and energy interval for electronic, vibrational and rotational motion.

3.2 The Born-Oppenheimer Approximation

The Born-Oppenheimer (BO) approximation is the most important concept in the formal description of molecular quantum mechanics. It consists in separating the electronic and nuclear degrees of freedom of a molecule, thereby simplifying a very complex problem into two simpler tasks. The Hamilton operator of a molecule containing k nuclei and N electrons has the form

$$\hat{H}(\hat{\vec{Q}}_\alpha, \hat{\vec{P}}_\alpha, \hat{\vec{q}}_i, \hat{\vec{p}}_i) = \hat{T}_{\text{nucl}} + \hat{T}_{\text{e}} + V(\vec{Q}_\alpha, \vec{q}_i) \quad \alpha = 1, \dots, k; \quad i = 1, \dots, N, \quad (3.3)$$

with

$$\begin{aligned} \hat{T}_{\text{nucl}} &= \sum_{\alpha=1}^k -\frac{\hbar^2}{2M_\alpha} \Delta_\alpha, \\ \hat{T}_{\text{e}} &= \sum_{i=1}^N -\frac{\hbar^2}{2m_{\text{e}}} \Delta_i. \\ \hat{V}(\vec{Q}_\alpha, \vec{q}_i) &= \sum_{\alpha=1}^k \sum_{\beta>\alpha}^k \frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0 |\vec{Q}_\alpha - \vec{Q}_\beta|} + \sum_{i=1}^N \sum_{j>i}^N \frac{e^2}{4\pi\epsilon_0 |\vec{q}_j - \vec{q}_i|} - \sum_{\alpha=1}^k \sum_{i=1}^N \frac{Z_\alpha e^2}{4\pi\epsilon_0 |\vec{Q}_\alpha - \vec{q}_i|}, \end{aligned} \quad (3.4)$$

and the Schrödinger equation

$$\hat{H} \Psi_n(\vec{Q}_\alpha, \vec{q}_i) = E_n \Psi_n(\vec{Q}_\alpha, \vec{q}_i) \quad (3.5)$$

involves $3k + 3N$ coordinates. In Equation (3.5) n is a set of quantum numbers describing the eigenstates. The BO approximation consists in reducing the dimensionality of the problem. In a first step, one solves an equation of $3N$ variables representing the electronic motion and in a second step, the $3k$ -variable equation for the nuclear motion. The separation of the overall rotation of the molecule and the center-of-mass translational motion (see section 3.3) further reduces the dimensionality of the nuclear equations of motion by 6 for nonlinear molecules and by 5 for linear molecules.

The BO approximation begins by writing the total molecular wave function $\Psi_n(\vec{Q}_\alpha, \vec{q}_i)$ as a product

$$\Psi_n(\vec{Q}_\alpha, \vec{q}_i) = \phi_m^{(n)}(\vec{Q}_\alpha) \phi_n(\vec{q}_i, \vec{Q}_\alpha) \quad (3.6)$$

of a nuclear wavefunction $\phi_m^{(n)}(\vec{Q}_\alpha)$ and an electronic wavefunction $\phi_n(\vec{q}_i, \vec{Q}_\alpha)$. The approximation uses the fact that the nuclei have too little time to move during one period of the electronic motion. The index n is used to distinguish different electronic states of the molecule and m to label different states of nuclear motion (*e.g.* vibrational, rotational). In the following we describe the two steps of the BO approximation.

3.2.1 Solution of the electronic Schrödinger equation

The nuclei are kept fixed at a given molecular geometry described by \vec{R}_α . As a result the kinetic energy vanishes $\hat{T}_{\text{nuc}} = 0$ and the first term of Equation (3.4) becomes constant. A purely electronic Schrödinger equation is then solved in which the nuclear coordinates are treated as parameters, *not* as variables (*i.e.* derivatives vanish, potential energy functions are constants):

$$\hat{H}^{\text{BO}} = \hat{T}_e + \hat{V}(\vec{q}_i, \vec{R}_\alpha). \quad (3.7)$$

Inserting Equations (3.6) and (3.7) in Equation (3.5) we obtain:

$$\left[\hat{T}_e + \hat{V}(\vec{q}_i, \vec{R}_\alpha) \right] \phi_m^{(n)}(\vec{Q}_\alpha) \phi_n(\vec{q}_i, \vec{R}_\alpha) = U_n \phi_m^{(n)}(\vec{Q}_\alpha) \phi_n(\vec{q}_i, \vec{R}_\alpha). \quad (3.8)$$

Because \hat{T}_e and \hat{V} act only on the electronic coordinates, both sides of Equation (3.8) can be divided by $\phi_m^{(n)}(\vec{R}_\alpha)$:

$$\left[\hat{T}_e + \hat{V}(\vec{q}_i, \vec{R}_\alpha) \right] \phi_n(\vec{q}_i, \vec{R}_\alpha) = U_n \phi_n(\vec{q}_i, \vec{R}_\alpha). \quad (3.9)$$

The eigenfunctions and eigenvalues of Equation (3.9) are sets of electronic wavefunctions $\phi_n(\vec{q}_i, \vec{R}_\alpha)$ and energies $U_n(\vec{R}_\alpha)$, where $n = 1, 2, \dots$ is the label for the electronic states introduced above.

In diatomic molecules, $U_n(\vec{R}_\alpha)$ are one-dimensional potential energy curves that belong to different electronic states of the molecule. In polyatomic molecules, $U_n(\vec{R}_\alpha)$ must be evaluated for a large number of possible configurations \vec{R}_α , which leads to the so-called BO potential hypersurfaces. The dimensionality of a BO hypersurface is $3k - 5$ for linear molecules and $3k - 6$ for nonlinear molecules and equals the number of internal degrees of freedom. $U_n(\vec{R}_\alpha)$ does not depend on the mass of the nuclei and is therefore isotope independent.

3.2.2 Solution of the nuclear Schrödinger equation in a given electronic state

The Schrödinger equation describing the nuclear motion on the n -th potential hypersurface is solved. Inserting Equation (3.9) with the solution $\phi_m^{(n)}(\vec{Q}_\alpha)$ and $\phi_n(\vec{q}_i, \vec{Q}_\alpha)$ in Equation (3.3) leads to an equation describing the nuclear motion

$$\begin{aligned}\hat{H}_{\text{nuc}}\phi_n(\vec{q}_i, \vec{Q}_\alpha)\phi_m^{(n)}(\vec{Q}_\alpha) &= -\sum_{\alpha=1}^k \frac{\hbar^2}{2M_\alpha} \phi_n(\vec{q}_i, \vec{Q}_\alpha) \Delta_\alpha \phi_m^{(n)}(\vec{Q}_\alpha) + U_n(\vec{Q}_\alpha) \phi_n(\vec{q}_i, \vec{Q}_\alpha) \phi_m^{(n)}(\vec{Q}_\alpha) \\ &= E_m^{(n)} \phi_n(\vec{q}_i, \vec{Q}_\alpha) \phi_m^{(n)}(\vec{Q}_\alpha).\end{aligned}\quad (3.10)$$

To obtain this result, we have used the relation

$$\frac{\partial^2}{\partial \vec{Q}_\alpha^2} (\phi_n \phi_m^{(n)}) = \frac{\partial^2 \phi_n}{\partial \vec{Q}_\alpha^2} \phi_m^{(n)} + 2 \frac{\partial \phi_n}{\partial \vec{Q}_\alpha} \frac{\partial \phi_m^{(n)}}{\partial \vec{Q}_\alpha} + \phi_n \frac{\partial^2 \phi_m^{(n)}}{\partial \vec{Q}_\alpha^2}, \quad (3.11)$$

and have neglected the first and second terms. This is a good approximation when the variation of the electronic wave function with nuclear coordinates is smooth, as is the case in low lying, well separated electronic states.

Dividing both sides of Equation (3.10) by $\phi_n(\vec{q}_i, \vec{Q}_\alpha)$ enables one to eliminate the electron coordinates \vec{q}_i and to obtain the equation describing the nuclear motion:

$$\hat{H}_{\text{nuc}}\phi_m^{(n)}(\vec{Q}_\alpha) = \left[-\sum_{\alpha=1}^k \frac{\hbar^2}{2M_\alpha} \Delta_\alpha + U_n(\vec{Q}_\alpha) \right] \phi_m^{(n)}(\vec{Q}_\alpha) = E_m^{(n)} \phi_m^{(n)}(\vec{Q}_\alpha). \quad (3.12)$$

This equation has the usual form for a Schrödinger equation and consists of a kinetic energy term (first term in the square brackets) and a potential energy term $U_n(\vec{Q}_\alpha)$. The equation can be solved numerically and $E_m^{(n)}$ represents the total (rovibronic) energy and $\phi_m^{(n)}$ the nuclear wavefunction.

3.3 Separation of the center-of-mass motion

In atoms and molecules in free space the potential energy of their nuclei and electrons $V(q_i)$ only depends on the distance r_{ij} between the nuclei and electrons and therefore the motion of the center of mass is exactly separable from the internal motion:

$$\hat{H} = \hat{H}_{\text{cm}}(\hat{P}_{\text{cm}}, \hat{Q}_{\text{cm}}) + \hat{H}_{\text{int}}(\hat{p}^{\text{int}}, \hat{q}^{\text{int}}), \quad (3.13)$$

where \hat{p}^{int} and \hat{q}^{int} describe the internal motion and $\hat{P}_{\text{cm}}, \hat{Q}_{\text{cm}}$ the center-of-mass motion.

Equation (3.13) fulfills the condition for exact separability:

$$E_n = E_{\text{cm}} + E_{\text{int},n} \quad (3.14)$$

$$\hat{H}_{\text{cm}} = -\frac{\hbar^2}{2M} \left[\frac{\partial^2}{\partial X_{\text{cm}}^2} + \frac{\partial^2}{\partial Y_{\text{cm}}^2} + \frac{\partial^2}{\partial Z_{\text{cm}}^2} \right] + V(X_{\text{cm}}, Y_{\text{cm}}, Z_{\text{cm}}) \quad (3.15)$$

with $M = \sum_{i=1}^k m_i$. The overall translational motion of the atom or molecule can be treated as that of a free particle of mass M in a three dimensional box (see lecture Physical Chemistry III).

In spectroscopy, one studies the transitions between the energy levels associated with the *internal* motion of atoms and molecules and concentrates on a problem of reduced dimensionality $3k - 3$:

$$\hat{H}_{\text{int}}(\hat{p}^{\text{int}}, \hat{q}^{\text{int}}) \phi_n^{\text{int}}(q_i^{\text{int}}) = E_n \phi_n^{\text{int}}(q_i^{\text{int}}). \quad (3.16)$$

Up to now, this introductory sections are valid for any kind of molecules. In the rest of this chapter, we will discuss the case of diatomic molecules only. The case of polyatomic molecules will be discussed in Chapter 5.

3.4 Structure and energetics of diatomic molecules

3.4.1 Nuclear motion and vibrational states

Within the Born-Oppenheimer approximation, the nuclear motion of a diatomic molecule in electronic state n is described by

$$\hat{H}_{\text{nucl}} = \frac{\hat{P}_1^2}{2M_1} + \frac{\hat{P}_2^2}{2M_2} + U_n(|\vec{Q}_2 - \vec{Q}_1|) = \frac{1}{2M} \hat{P}_{\text{cm}}^2 + \frac{1}{2\mu} \hat{P}_{\text{int}}^2 + U_n(|\vec{Q}_2 - \vec{Q}_1|) \quad (3.17)$$

with $M = M_1 + M_2$ and $\mu = \frac{M_1 M_2}{M_1 + M_2}$.

The internal motion of the molecule can be described by that of a fictive particle of mass μ and position $\vec{Q} = \vec{Q}_2 - \vec{Q}_1$, where $|\vec{Q}| = Q$ represents the internuclear separation.

$$\hat{H}_{\text{nucl}} \phi_m^{(n)}(Q) = -\frac{\hbar^2}{2\mu} \Delta_Q \phi_m^{(n)}(Q) + U_n(Q) \phi_m^{(n)}(Q) = E_m^{(n)} \phi_m^{(n)}(Q). \quad (3.18)$$

Expressing Δ_Q in polar coordinates (see lecture Physical Chemistry III, and Figure 3.1), one obtains

$$\Delta_Q = \frac{\partial^2}{\partial Q^2} + \frac{2}{Q} \frac{\partial}{\partial Q} - \frac{1}{\hbar^2 Q^2} \hat{L}^2 \quad (3.19)$$

with

$$\hat{L}^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \varphi^2} \right), \quad (3.20)$$

where \hat{L} is the rotational angular momentum operator. Inserting Equations (3.19) and (3.20) in Equation (3.18) leads to

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial Q^2} + \frac{2}{Q} \frac{\partial}{\partial Q} \right) + \frac{1}{2\mu Q^2} \hat{L}^2 + U_n(Q) - E_m^{(n)} \right] \phi_m^{(n)}(Q) = 0. \quad (3.21)$$

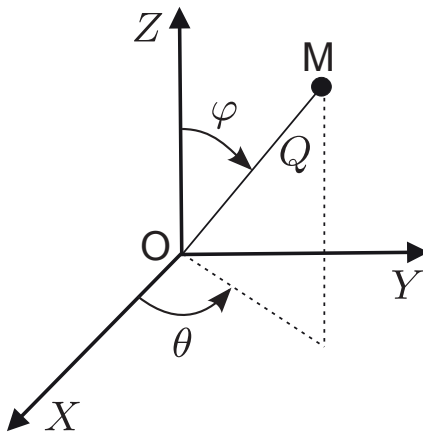


Figure 3.1: Polar coordinates

Since only \hat{L}^2 acts on θ and φ , the equation is separable:

$$\phi_m^{(n)}(Q, \theta, \varphi) = F(Q) Y_{LM}(\theta, \varphi) = \frac{1}{Q} G(Q) Y_{LM}(\theta, \varphi). \quad (3.22)$$

In Equation (3.22), $Y_{LM}(\theta, \varphi)$ are the spherical harmonics that are the eigenfunctions of the angular momentum \hat{L}^2 and \hat{L}_z (see lecture Physical Chemistry III, angular momentum):

$$\hat{L}^2 Y_{LM}(\theta, \varphi) = \hbar^2 L(L+1) Y_{LM}(\theta, \varphi). \quad (3.23)$$

$$\hat{L}_z Y_{LM}(\theta, \varphi) = \hbar M Y_{LM}(\theta, \varphi). \quad (3.24)$$

The reason for writing $F(Q)$ as $\frac{1}{Q}G(Q)$ in Equation (3.22) is to simplify the algebra in later steps of the derivation, just as using the reduced radial wave function $\frac{1}{r}R_{n,\ell}(r)$ in the treatment of the hydrogen atom.

Equation (3.21) can thus be rewritten as:

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial Q^2} G(Q) + \frac{\hbar^2}{2\mu Q^2} L(L+1) G(Q) + \left(U_n(Q) - E_m^{(n)} \right) G(Q) = 0. \quad (3.25)$$

This one-dimensional differential equation can be solved numerically to obtain the vibration-rotation energy levels of any electronic state of a diatomic molecule. To illustrate the meaning of the different terms in Equation (3.25) we make further approximations.

We first restrict our consideration to the region of $U_n(Q)$ close to the minimum $Q_{\min} = R_e$

and write $Q = R_e + \rho$ ($\rho \ll R_e$). We then expand $U_n(Q)$ and $\frac{1}{Q^2}$ into a Taylor series around R_e .

$$U_n(Q) = U_n(R_e) + \left(\frac{\partial U_n(Q)}{\partial Q} \right)_{R_e} \rho + \frac{1}{2} \left(\frac{\partial^2 U_n(Q)}{\partial Q^2} \right)_{R_e} \rho^2 + \dots, \quad (3.26)$$

$$\frac{1}{Q^2} = \frac{1}{R_e^2} - \frac{2}{R_e^3} \rho + \dots. \quad (3.27)$$

The second term on the right-hand side of Equation (3.26) is zero because $U_n(Q)$ reaches a minimum at R_e . Keeping only the first term of Equation (3.27) and the first two nonzero terms of Equation (3.26) (harmonic oscillator approximation and rigid rotor approximation, respectively), inserting into Equation (3.25) and writing $G(Q)$ as $G_\rho(\rho)$ one gets:

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \rho^2} G_\rho(\rho) + \underbrace{\frac{\hbar^2}{2\mu R_e^2} L(L+1)}_{hcB_e J(J+1) = E_{\text{rot}}(J)} G_\rho(\rho) + U_n(R_e) G_\rho(\rho) + \frac{1}{2} k \rho^2 G_\rho(\rho) = E_m^{(n)} G_\rho(\rho) \quad (3.28)$$

with $k = \left(\frac{\partial^2 U(Q)}{\partial Q^2} \right)_{R_e}$. This equation can be rewritten as

$$\underbrace{\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \rho^2} + \frac{1}{2} k \rho^2 \right]}_{\hat{H} \text{ for harmonic osc.}} G_\rho(\rho) = \left[E_m^{(n)} - U_n(R_e) - E_{\text{rot}}(J) \right] G_\rho(\rho). \quad (3.29)$$

The operator in square brackets on the left-hand side of Equation (3.29) can easily be recognized as the Hamilton operator of a harmonic oscillator and we can also write

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \rho^2} + \frac{1}{2} k \rho^2 \right] G_\rho(\rho) = h\nu_{\text{osc}} \left(v + \frac{1}{2} \right) G_\rho(\rho). \quad (3.30)$$

Comparing the right-hand sides of Equation (3.29) and Equation (3.30), one can see that the total energy $E_m^{(n)}$ is a sum of an electronic, a vibrational and a rotational energy:

$$E_m^{(n)} = \underbrace{U_n(R_e)}_{\text{el. energy}} + \underbrace{E_{\text{vib}}(v)}_{\text{vibr. energy}} + \underbrace{E_{\text{rot}}(J)}_{\text{rot. energy}} = U_n(R_e) + h\nu_{\text{osc}} \left(v + \frac{1}{2} \right) + hcB_e J(J+1). \quad (3.31)$$

Taking the orders of magnitude of the different components of the total energy $E_m^{(n)}$, one can draw a diagram as shown in Figure 3.2.

One obtains a better approximation of the exact solution of Equation (3.25) by

- keeping the higher terms in Equation (3.26). The potential becomes anharmonic and therefore

$$\frac{E_{\text{vib}}(v)}{hc} = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \omega_e y_e \left(v + \frac{1}{2} \right)^3 + \dots. \quad (3.32)$$

Here, the constants ω_e , $\omega_e x_e$ and $\omega_e y_e$ are wavenumbers usually given in cm^{-1} .

- keeping higher terms in Equation (3.27). One then can account for the lengthening of the average internuclear distance caused by the anharmonic vibrational motion

$$B_v = B_e - \alpha_e(v + \frac{1}{2}) + \dots, \quad (3.33)$$

- taking into account centrifugal distortion (which corresponds to an elongation of the bond as the rotational motion gets faster, *i. e.* at increasing J values)

$$E_{\text{rot}}^{(v)}(J) = B_v J(J+1) - D_v J^2(J+1)^2 + \dots. \quad (3.34)$$

and thus, the rotational energy depends on the quantum number v .

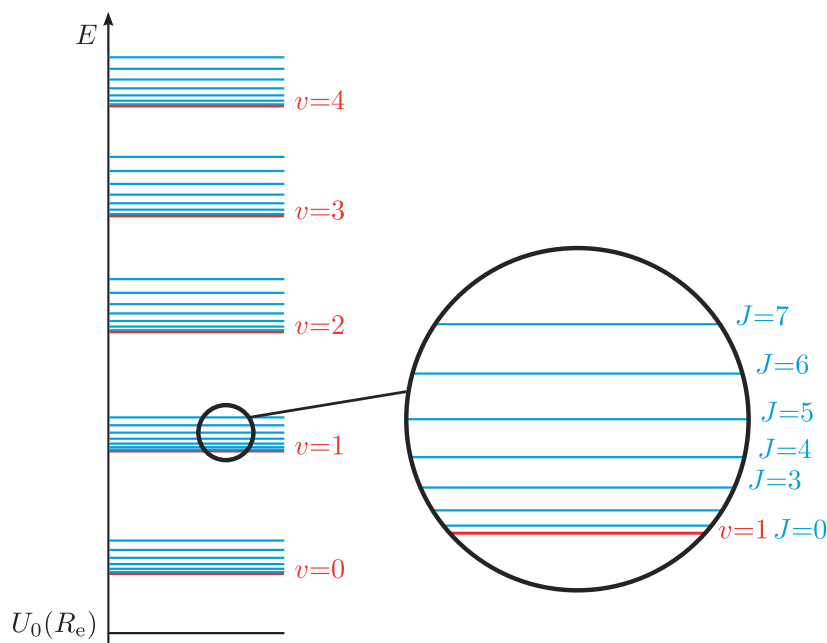


Figure 3.2: Schematic of the rovibronic energy levels of a diatomic molecule.

The constants ω_e , $\omega_e x_e$, $\omega_e y_e$, B_e , α_e , etc. are tabulated for many electronic states of many diatomic molecules (see Huber and Herzberg, 1979, in the literature list) and can be used to calculate the rovibronic energies of a diatomic molecule. Nowadays efficient ways (and good programs) are available to solve Equation (3.25) numerically.

The harmonic oscillator (with its potential $V(Q) = \frac{1}{2}kQ^2$) represents a good approximation to the vibrational motion of a molecule only in the vicinity of R_e . The solution is (see Lecture Physical Chemistry III)

$$\frac{E_{\text{vib}}^{(\text{harm.})}(v)}{hc} = \omega_e \left(v + \frac{1}{2} \right) \quad (3.35)$$

$$\Psi_v(Q) = \frac{1}{\sqrt{\sqrt{\pi} v! 2^v}} H_v(Q) e^{-\frac{1}{2}Q^2}, \quad (3.36)$$

where $H_v(Q)$ represent the Hermite polynomials (see Chapter 1, Section 1.8.1).

The potential energy function of a molecule for Q significantly larger than R_e is no longer well described by a harmonic potential because the molecule eventually dissociates. A better approximation is the anharmonic Morse oscillator with potential

$$V_{\text{Morse}}(Q) = D_e \left(1 - e^{-\beta(Q-R_e)}\right)^2 \quad (3.37)$$

with $V_{\text{Morse}}(Q = R_e) = 0$ and $V_{\text{Morse}}(Q \rightarrow \infty) = D_e$.

The Morse potential and its vibrational levels are displayed in Figure 3.3 where they are compared to those of a harmonic potential. Because of the anharmonicity, the wavefunction $\Psi_v(Q) = \langle Q|v\rangle$ is asymmetrically distributed around R_e with $\langle v|Q|v\rangle \geq R_e$. The vibrational eigenfunctions of the Morse potential are displayed in Figure 3.4.

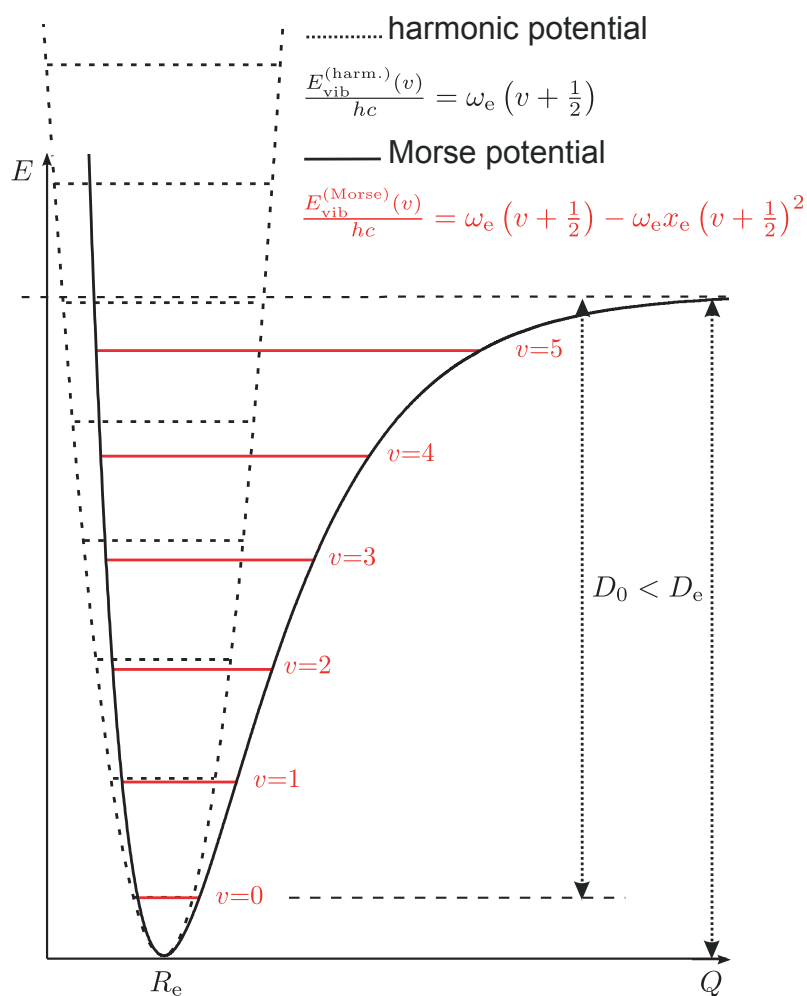


Figure 3.3: Comparison of the Morse potential and its vibrational eigenstates with those of a harmonic potential.

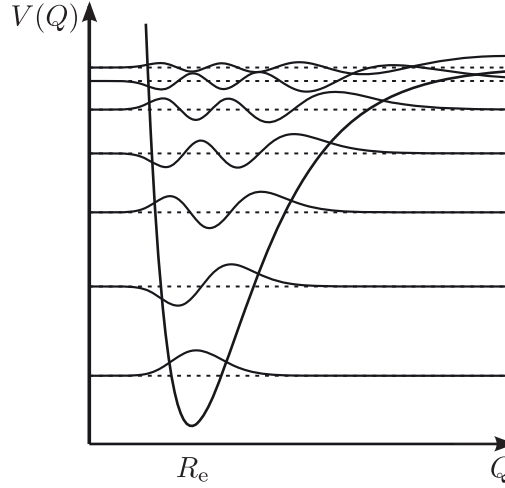


Figure 3.4: Vibrational eigenstates of the Morse potential

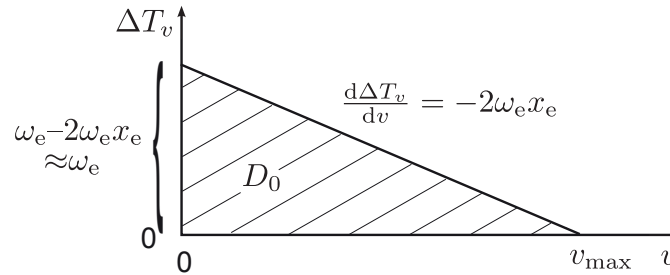
Also the energy spacing between neighboring levels decreases with increasing v :

$$T_v = \frac{E_{\text{vib}}^{(\text{Morse})}(v)}{hc} = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2, \quad (3.38)$$

$$\Delta T_v = T_{v+1} - T_v = \omega_e - 2(v+1)\omega_e x_e. \quad (3.39)$$

Since v is a quantum number, ΔT_v takes discrete values. In the limit of a continuous approach, ΔT_v is a linear function of v as depicted in Figure 3.5. For $v = v_{\text{max}}$, $\Delta T_{v_{\text{max}}} = 0$, the vibrational energy spectrum becomes continuous, *i. e.*, the molecule has dissociated:

$$v_{\text{max}} = \frac{\omega_e - 2\omega_e x_e}{2\omega_e x_e}. \quad (3.40)$$

Figure 3.5: ΔT_v as a function of v

Because $E_{\text{vib}}^{(\text{Morse})}(v_{\text{max}}) = D_e$ (see Figure 3.3), inserting Equation (3.40) into Equation (3.38), one gets

$$D_e = \frac{\omega_e^2 - (\omega_e x_e)^2}{4\omega_e x_e}. \quad (3.41)$$

Usually, $\omega_e x_e \ll \omega_e$ and one uses the following approximation:

$$D_e \simeq \frac{\omega_e^2}{4\omega_e x_e}. \quad (3.42)$$

Example: H_2 (Data from Huber & Herzberg, 1979)

$$\omega_e = 4401.2 \text{ cm}^{-1}$$

$$\omega_e x_e = 121.3 \text{ cm}^{-1}$$

$$D_0 = 4.476 \text{ eV} = 36118.3 \text{ cm}^{-1}$$

$$D_e \cong D_0 + \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e = 38289 \text{ cm}^{-1}$$

$$\text{From Equation (3.42): } D_e = \frac{4401.2^2}{4 \cdot 121.3} \text{ cm}^{-1} = 39923 \text{ cm}^{-1}$$

$$\text{From Equation (3.40): } v_{\max} \cong \frac{2 \cdot D_e}{\omega_e} \cong 18$$

3.4.2 Molecular orbitals and electronic configurations

Labels for electronic states

The ground electronic state is labeled by the letter X for diatomic molecules and \tilde{X} for polyatomic molecules. Electronically excited states are designated in order of increasing energy by the letters A, B, C, ... (\tilde{A} , \tilde{B} , \tilde{C} , ... for polyatomic molecules) if they have the same total electron spin quantum number S as the ground electronic state, or by the letters a, b, c ... (\tilde{a} , \tilde{b} , \tilde{c} , ... for polyatomic molecules) if they have a different spin multiplicity.

The different electronic states of a molecule can have Born-Oppenheimer potential energy surfaces of very different shapes and which reflect different binding mechanisms. Figure 3.6, which displays only a small subset of the adiabatic potential energy functions of molecular hydrogen illustrates this diversity and the complexity of the electronic structure of this seemingly simple molecule. In selected regions of internuclear distances, the states can be classified as

- valence states, *i. e.*, states in which the valence electrons occupy molecular orbitals with significant amplitudes at the positions of more than one atom. Valence states can be entirely repulsive if the valence electrons occupy predominantly antibonding molecular orbitals, or attractive if they occupy predominantly bonding orbitals, in which case rigid molecular structures usually result.
- Rydberg states, *i. e.*, states in which one of the valence electrons has been excited to a diffuse orbital around a positively charged molecular ion core, resembling an excited orbital of the hydrogen atom. In such a state, the excited electron, called the Rydberg electron, is bound to the molecular ion core by the attractive Coulomb potential and can be labeled by a principal quantum number n . At sufficiently high values of n , the

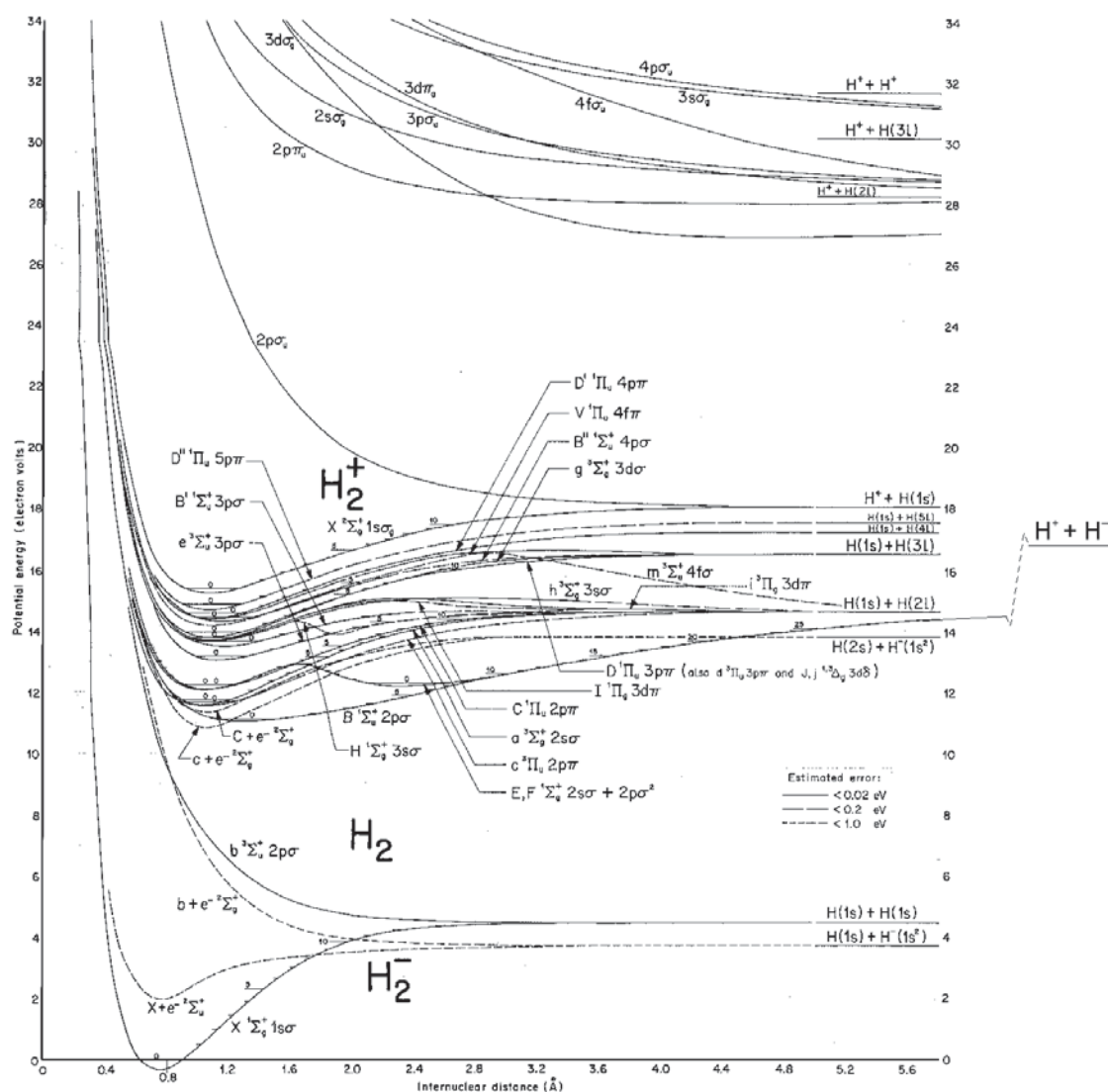


Figure 3.6: Potential energy functions of selected electronic states of H₂, H₂⁺ and H₂⁻ (adapted from T. E. Sharp, *Atomic Data*, **2**, 119-169 (1971)).

Rydberg electron is located, on average, at large distances from the ion core and only interacts weakly with it. The Born-Oppenheimer potential energy functions (or hypersurface in the case of polyatomic molecules) of Rydberg states thus closely resemble that of the electronic state of the molecular ion core to which the Rydberg electron is attached. Rydberg states form infinite series of states with almost identical potential energy functions (or hypersurfaces), and can also be labeled by the orbital angular momentum quantum number ℓ of the Rydberg electron. Rydberg states of H₂ can easily be identified in Figure 3.6 as the states with potential energy functions parallel to that of the X ²Σ_g⁺ ground state of H₂⁺.

- ion-pair states, *i. e.*, states in which the molecule can be described as composed of two atoms A^+ and B^- (or two groups of atoms) of opposite charge that are held together by a Coulomb potential. The potential energy of these states is proportional to $-1/R$ (R is the distance between the atoms of opposite charge) and dissociate at large distances into a cation (A^+) and an anion (B^-). At short internuclear distances, the potential energy function falls rapidly and starts overlapping with valence states with which they interact strongly, giving rise to charge transfer processes and electronic states with multiple potential wells. Ion-pair states are not only encountered in molecules such as NaCl, but also in homonuclear diatomic molecules, an example being the potential function in Figure 3.6 which coincides with the outer well of the potential functions of the E,F $^1\Sigma_g^+$ and B $^1\Sigma_u^+$ states.
- states in which the atoms (or group of atoms) are held together by weak van der Waals interactions which give rise to shallow potential wells at large internuclear distances. The ground electronic states of the rare gas dimers are prototypes of such states.

Molecular orbitals

The symmetry labels of molecular orbitals and electronic states of diatomic molecules are determined using the same procedure as for atoms: Molecular orbitals are designated by lower-case Greek letters (σ^+ , π , δ , ... for heteronuclear diatomic molecules and σ_g^+ , σ_u , π_g , π_u , ... for homonuclear diatomic molecules). Electronic states are designated by capital Greek letters (Σ^+ , Σ^- , Π , Δ , ... for heteronuclear diatomic molecules and Σ_g^+ , Σ_g^- , Σ_u^+ , Σ_u^- , Π_g , Π_u , ... for homonuclear diatomic molecules). As in atoms, the symmetry labels also contain information on the electronic angular momentum. In the absence of spin-orbit coupling, the orbital angular momentum is a conserved quantity in a spherically symmetric potential. L and ℓ are therefore good quantum numbers in atoms (see Section 2.1). In diatomic molecules, the symmetry of the potential is reduced to cylindrical symmetry, so that only the projection of the total orbital angular momentum onto the internuclear axis is conserved as long as spin-orbit coupling can be neglected. The symmetry labels σ , π , δ , ... correspond to orbitals with values of 0, 1, 2, ... of the orbital angular momentum projection quantum number λ on the internuclear axis. Similarly, Σ , Π , Δ , ... are used to label electronic states with total orbital angular momentum projection quantum number $\Lambda = 0, 1, 2, \dots$ on the internuclear axis, respectively. Orbitals of σ^- symmetry do not exist because no σ molecular orbital can

be formed that has a nodal plane containing the internuclear axis, but electronic states of Σ^- result from configurations in which at least two orbitals of symmetry π , or δ , or ϕ , ... are singly occupied.

How the quantum number λ arises in a linear molecule can also be understood by writing the Schrödinger equation for a single electron in an axially symmetric potential in cylindrical coordinates:

$$\frac{\partial^2 \Psi}{\partial z^2} + \frac{\partial^2 \Psi}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial \Psi}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2 \Psi}{\partial \varphi^2} + \frac{8\pi^2 m}{h} (E - V(z, \rho)) \Psi = 0, \quad (3.43)$$

where z is the coordinate of the electron along the symmetry axis, ρ its distance from the axis and φ the azimuthal angle.

Inserting the ansatz

$$\Psi(z, \rho, \varphi) = \chi(z, \rho) f(\varphi) \quad (3.44)$$

in Equation (3.43) and multiplying the equation with ρ^2 / Ψ gives

$$\frac{\rho^2}{\chi} \frac{\partial^2 \chi}{\partial z^2} + \frac{\rho^2}{\chi} \frac{\partial^2 \chi}{\partial \rho^2} + \frac{\rho}{\chi} \frac{\partial \chi}{\partial \rho} + \frac{8\pi^2 m \rho^2}{h} (E - V(z, \rho)) = -\frac{1}{f} \frac{\partial^2 f}{\partial \varphi^2}. \quad (3.45)$$

Equating both sides to a constant λ^2 , one obtains the differential equation in φ

$$\frac{\partial^2 f(\varphi)}{\partial \varphi^2} + \lambda^2 f(\varphi) = 0, \quad (3.46)$$

which has the solutions

$$f_{\pm}(\varphi) = e^{\pm i\lambda\varphi}. \quad (3.47)$$

Because $f(\varphi) = f(\varphi + 2\pi)$, λ must be an integer number. The general solution of Equation (3.43) is therefore

$$\Psi_{\pm}(z, \rho, \varphi) = \chi(z, \rho) e^{\pm i\lambda\varphi}. \quad (3.48)$$

Since the Ψ_{\pm} are energetically degenerate (the $\pm\lambda$ solutions have identical eigenvalues), an arbitrary linear combination is also a solution. The Ψ_{\pm} have a well-defined value of λ , but their linear combination does not. The labels σ , π , δ , ... give the absolute value of λ .

In the qualitative representation of molecular orbitals, it is helpful to discuss two extreme situations: the united-atom limit and the separated-atom limit. In the united-atom limit, the atoms that form the molecule are considered to have coalesced into a single atom. The united atom limit of $^{16}\text{O}_2$ and H_2 are ^{32}S and ^2He , respectively. The molecular structure is determined by progressively separating the atomic components of the molecule towards the equilibrium internuclear separation. In the limit of the separated atoms, the atoms forming

the molecule are considered at an infinite internuclear separation. Molecular states are formed by progressively approaching the atoms towards the equilibrium internuclear separation. The expected form and energetic order of the molecular orbitals can be predicted by linking the two limiting cases in a correlation diagram by making sure that curves of the same symmetry do not cross. Figure 3.7 shows how the two 1s atomic orbitals of the two separated H atoms correlate through the σ_u^+ and σ_g^+ molecular orbitals with the 1s and 2p_z orbitals of the united atom. By convention the z axis is chosen to be the internuclear axis. Figures 3.8 and 3.9 display the correlation diagrams connecting the energy levels of the separated atoms with those of the united atoms in the case of homonuclear and heteronuclear diatomic molecules, respectively. Different molecules with their specific internuclear separation occupy different positions along the horizontal axis of these figures.

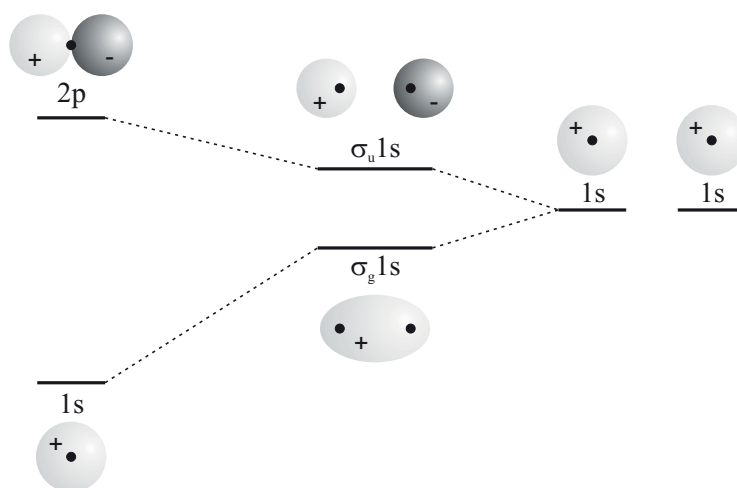


Figure 3.7: Correlation diagram from the two 1s atomic orbitals of two identical separated atoms to the 1s and 2p_z orbitals of the corresponding united atom through the σ_u^+ and σ_g^+ molecular orbitals

The determination of molecular orbitals often relies on the LCAO (linear combination of atomic orbitals) method. Molecular orbitals Φ_j are formed from symmetry-adapted linear combinations of atomic orbitals ϕ_i following

$$\Phi_j = \sum_i c_{ji} \phi_i. \quad (3.49)$$

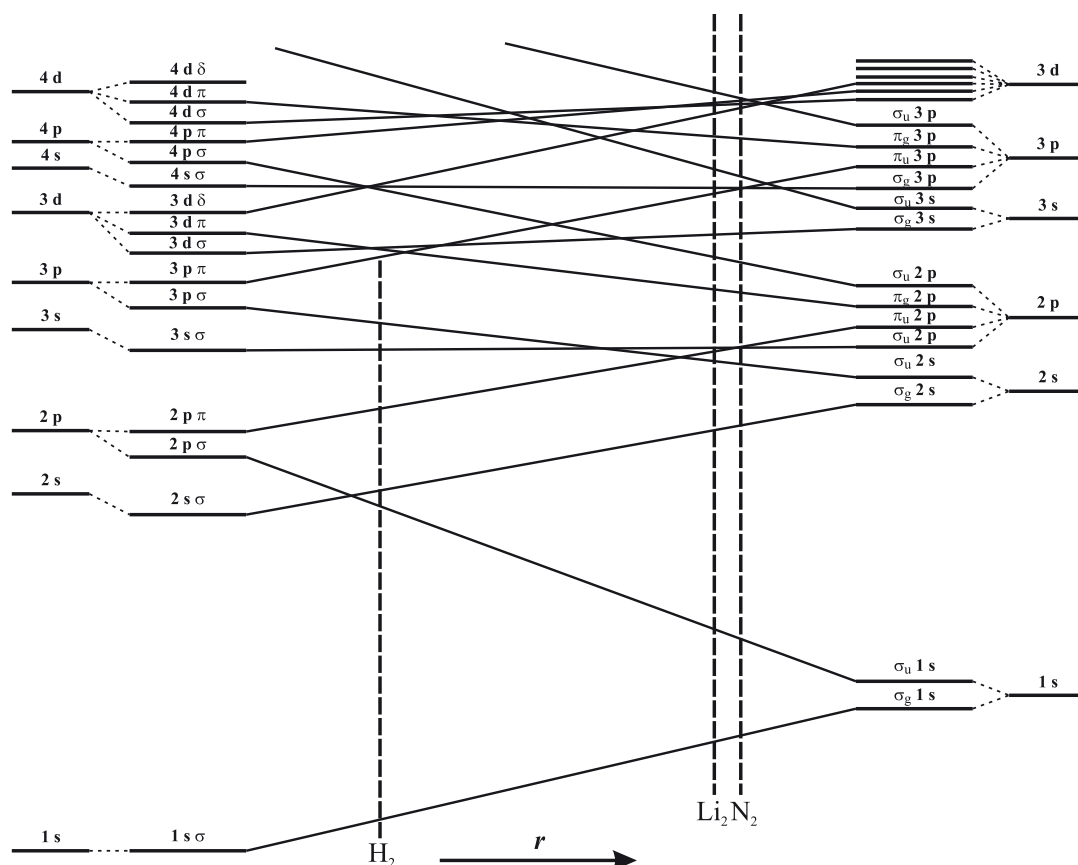


Figure 3.8: Correlation diagram illustrating the evolution of molecular orbitals between the separated atoms limit (right) and the united atoms limit (left) for homonuclear diatomic molecules (Adapted from G. Herzberg, *Molecular Spectra and Molecular Structure, Volume I*, (1989), see reading list).

Several conditions must be fulfilled to form molecular orbitals that are distinct from the original atomic orbitals:

- The atomic orbitals that are combined must lie close in energy.
- The atomic orbitals must overlap at the equilibrium internuclear separation.
- The atomic orbitals must be symmetry compatible.

Figure 3.10a shows the structure of molecular orbitals of homonuclear diatomic molecules consisting of atoms of the second row of the periodic system. For Li_2^+ , Li_2 , Li_2^- , B_2^+ , B_2 , B_2^- , C_2^+ , C_2 , C_2^- , N_2^+ and N_2 , the energetic ordering of the orbitals is

$$1\sigma_g(1s) < 1\sigma_u^*(1s) < 2\sigma_g(2s) < 2\sigma_u^*(2s) < 1\pi_u(2p) < 3\sigma_g(2p) < 1\pi_g^*(2p) < 3\sigma_u^*(2p). \quad (3.50)$$

In the case of O_2^+ , O_2 , O_2^- , F_2^+ , F_2 , F_2^- and Ne_2^+ , it is

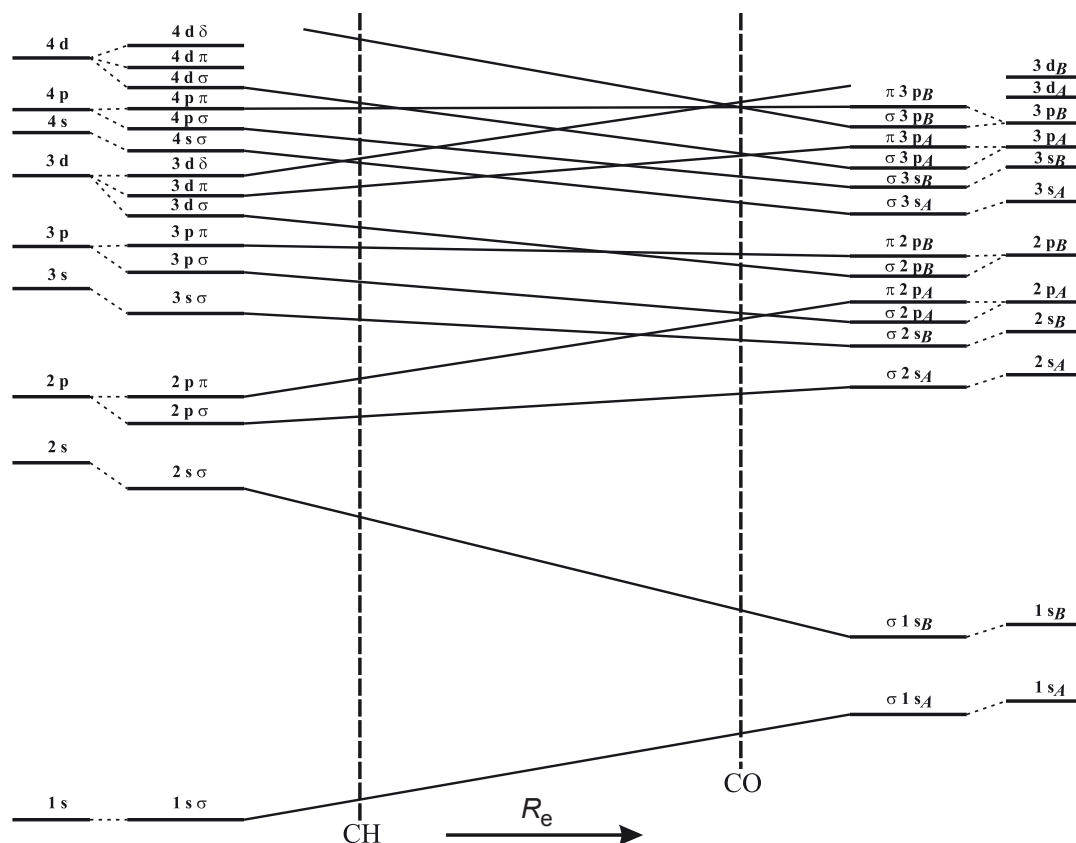


Figure 3.9: Correlation diagram between separated atoms (right) and united atoms (left) for heteronuclear diatomic molecules (Adapted from G. Herzberg, *Molecular Spectra and Molecular Structure, Volume I*, (1989), see reading list).

$$1\sigma_g(1s) < 1\sigma_u^*(1s) < 2\sigma_g(2s) < 2\sigma_u^*(2s) < 3\sigma_g(2p) < 1\pi_u(2p) < 1\pi_g^*(2p) < 3\sigma_u^*(2p). \quad (3.51)$$

These two cases are depicted schematically in Figure 3.10b and c, respectively.

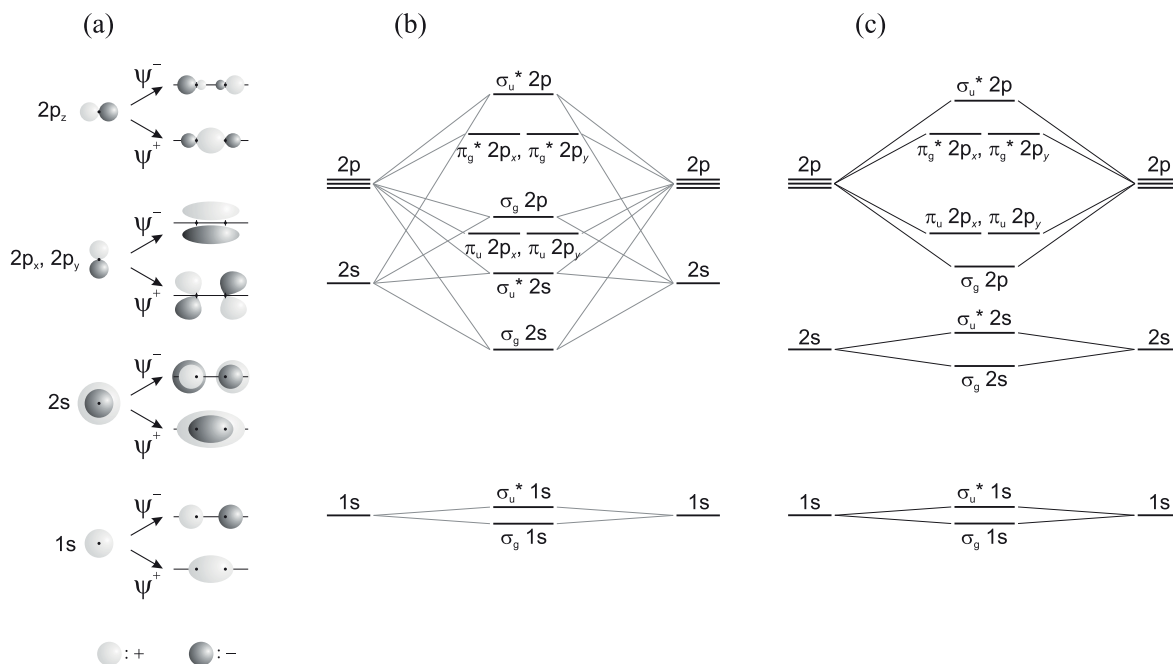


Figure 3.10: (a) Schematic representation of molecular orbitals in homonuclear diatomic molecules made from 1s, 2s and 2p atomic orbitals. Molecular orbital energy diagram for homonuclear diatomic molecules formed from the lighter (b) and the heavier (c) atoms from the second row of the periodic system of elements.

Electronic configurations

Electronic configurations are obtained by filling the spatial orbitals according to the Pauli principle with no more than two electrons. The ground-state configuration of N₂, *e. g.*, is

$$(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(1\pi_u)^4(3\sigma_g)^2 \quad (3.52)$$

and the first two excited configurations are

$$(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(1\pi_u)^4(3\sigma_g)^1(1\pi_g^*)^1 \quad (3.53)$$

and

$$(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(1\pi_u)^3(3\sigma_g)^2(1\pi_g^*)^1. \quad (3.54)$$

The ground-state configuration of O₂ is

$$(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g^*)^2. \quad (3.55)$$

If two electrons are located in the same spatial orbital, they must have opposite spins. As in the case of atoms, an electronic configuration leads in general to several electronic terms and several electronic states.

Electronic wave functions and electronic terms

As explained in Subsection 2.1.2, N -electron wave functions $\Psi(q_1, q_2, \dots, q_N)$ of molecules must obey the generalized Pauli principle. Consequently, they must be antisymmetric under the pairwise permutation of electrons, which is automatically fulfilled by Slater determinants of the general form given by Equation (2.19). The spatial part of the one-electron functions ϕ_i corresponds to a molecular orbital of the form (3.49). To determine the possible electronic terms, only shells and subshells with partially filled orbitals need be considered, because full shells and subshells are of symmetry $^1\Sigma_g^+$ or $^1\Sigma^+$, for homonuclear and heteronuclear diatomic molecules, respectively.

In the following, we will illustrate how electronic states can be derived from an electronic configuration using the configurations (3.52)-(3.55) as examples:

1. Since all orbitals of the configuration (3.52) are fully occupied, the electronic state Σ_g^+ results. Moreover, because all electrons are paired, a unique singlet term of symmetry $^1\Sigma_g^+$ is obtained. Consequently, the ground electronic state of N_2 is designated as $X\ ^1\Sigma_g^+$.
2. The $(3\sigma_g)^1(1\pi_g^*)^1$ part of configuration (3.53) leads to a Π_g term. The corresponding spin multiplicities are derived below in Subsection 3.4.3.
3. Because $(1\pi_u)^3$ can be considered as a $(1\pi_u)^1$ electron hole, the $(1\pi_u)^3(1\pi_g^*)^1$ part of the configuration (3.54) can be treated as the configuration $1(\pi_u)^1(1\pi_g^*)^1$, which leads to the terms Σ_u^+ , Σ_u^- and Δ_u (see Table 3.2). Their energetic order and multiplicities are derived in the next subsection.

Config.	Terms	Config.	Terms
σ^2	$^1\Sigma^+$	$\pi^2\sigma^1\delta^1$	$^1\Sigma^+, ^1\Sigma^-, ^1\Delta(2), ^1\Gamma, ^3\Sigma^+, ^3\Sigma^-, ^3\Delta(3), ^3\Gamma, ^5\Delta$
π^2	$^1\Sigma^+, ^3\Sigma^-, ^1\Delta$	$\pi^2\pi^1\pi^1$	$^1\Sigma^+(3), ^1\Sigma^-(3), ^1\Delta(4), ^1\Gamma, ^3\Sigma^+(4), ^3\Sigma^-(4), ^3\Delta(5), ^3\Gamma, ^5\Sigma^+, ^5\Sigma^-, ^5\Delta$
π^3	$^2\Pi_i$	$\pi^2\pi^2$	$^1\Sigma^+(3), ^1\Sigma^-, ^1\Delta(2), ^1\Gamma, ^3\Sigma^+(2), ^3\Sigma^-(2), ^3\Delta(2), ^5\Sigma^+$
π^4	$^1\Sigma^+$	$\pi^3\sigma^1$	$^1\Pi, ^3\Pi_i$
δ^2	$^1\Sigma^+, ^3\Sigma^-, ^1\Gamma$	$\pi^3\pi^1$	$^1\Sigma^+, ^1\Sigma^-, ^1\Delta, ^3\Sigma^+, ^3\Sigma^-, ^3\Delta$
δ^3	$^2\Delta_i$	$\pi^3\delta^1 (\pi^3\delta^3)$	$^1\Pi, ^1\Phi, ^3\Pi, ^3\Phi$
δ^4	$^1\Sigma^+$	$\pi^3\sigma^1\sigma^1$	$^2\Pi(2), ^4\Pi$
$\pi^2\sigma^1$	$^2\Sigma^+, ^2\Sigma^-, ^2\Delta, ^4\Sigma^-$	$\pi^3\pi^2$	$^2\Pi_i, ^2\Pi(2), ^2\Phi_i, ^4\Pi_i$
$\pi^2\pi^1$	$^2\Pi, ^2\Pi_i(2), ^2\Phi, ^4\Pi$	$\pi^3\pi^3$	$^1\Sigma^+, ^1\Sigma^-, ^1\Delta, ^3\Sigma^+, ^3\Sigma^-, ^3\Delta_i$
$\pi^2\delta^1$	$^2\Sigma^+, ^2\Sigma^-, ^2\Delta, ^2\Delta_i, ^2\Gamma, ^4\Delta$	$\pi^3\pi^2\sigma^1$	$^1\Pi(3), ^1\Phi, ^3\Pi_i(2), ^3\Pi(2), ^3\Phi_i, ^5\Pi_i$
$\pi^2\sigma^1\sigma^1$	$^1\Sigma^+, ^1\Sigma^-, ^1\Delta, ^3\Sigma^+, ^3\Sigma^-(2), ^3\Delta, ^5\Sigma^-$	$\pi^3\pi^3\sigma^1$	$^2\Sigma^+(2), ^2\Sigma^-(2), ^2\Delta, ^2\Delta_i, ^4\Sigma^+, ^4\Sigma^-, ^4\Delta_i$
$\pi^2\sigma^1\pi^1$	$^1\Pi(3), ^1\Phi, ^3\Pi(2), ^3\Pi_i(2), ^3\Phi, ^5\Pi$		

Table 3.2: Terms belonging to the most frequent electronic configurations of diatomic molecules. The index “i” designates inverted term multiplets. The “g” and “u” labels relevant for homonuclear diatomic molecules can be determined from the number N of electrons in MO orbitals of u symmetry. When N is even, the terms are g, otherwise they are u.

3.4.3 Spin multiplicity

As explained in Subsection 2.1.3, polyelectron wave functions can be written as a product of a spatial part ($\Psi^R(q_i)$) and a spin part ($\Psi^S(m_i)$).

$$\Psi(q_1, m_1, q_2, m_2, \dots) = \Psi^R(q_1, q_2, \dots) \times \Psi^S(m_1, m_2, \dots). \quad (3.56)$$

For simplicity, we consider here only two-electron wave functions. The extension to more complicated situations is straightforward. Because a two-electron wave function must be antisymmetric under permutation of the coordinates of the electrons, it must have either a symmetric spatial part ($\Psi_{(s)}^R(q_i)$) and an antisymmetric spin part ($\Psi_{(a)}^S(m_i)$) or vice versa ($\Psi_{(a)}^R(q_i)$ and $\Psi_{(s)}^S(m_i)$).

In the determination of the multiplicity of an electronic term, three cases have to be distinguished:

- The two electrons are located in different molecular-orbital shells, as in the configuration (3.53) $((3\sigma_g)^1(1\pi_g^*)^1)$. Both the symmetric and the antisymmetric spatial parts are nonzero. Consequently, both singlet and triplet states are allowed, and configuration (3.53) leads to the two terms $^1\Pi_g$ and $^3\Pi_g$.
- The two electrons are located in the same molecular-orbital shell and in the same spatial orbital ($\phi_1 = \phi_2$), so that $\Psi_{(a)}^R(q_1, q_2) = 0$. The triplet state thus does not exist. This situation arises in the $(1\pi_g)^2$ configuration of O_2 , when both electrons are located in either the $\lambda = 1$ or the $\lambda = -1$ orbital. In this case, Λ is equal to ± 2 and the corresponding term is $^1\Delta_g$.
- The two electrons are located in the same molecular-orbital shell but in different orbitals. This situation also arises in the $(1\pi_g)^2$ configuration of O_2 , when each of the two $\lambda = \pm 1$ orbitals is occupied by one electron ($\Lambda = 0$). The spatial part may be either symmetric ($\Psi_{(s)}^R(q_1, q_2) = (\pi_+(q_1)\pi_-(q_2) + \pi_+(q_2)\pi_-(q_1))/\sqrt{2}$), which results in a $^1\Sigma_g$ term, or antisymmetric ($\Psi_{(a)}^R(q_1, q_2) = (\pi_+(q_1)\pi_-(q_2) - \pi_+(q_2)\pi_-(q_1))/\sqrt{2}$), which corresponds to a $^3\Sigma_g$ term. To determine whether these $^1\Sigma_g$ and $^3\Sigma_g$ terms are Σ_g^- or Σ_g^+ , one has to determine their symmetry with respect to the operation σ_v (see Chapter 4), which represents the reflection through an arbitrary plane containing the internuclear axis. Using the ansatz (3.48) for the π_+ and π_- functions, we obtain

$$\begin{aligned}\Psi_{(a)}^R(q_1, q_2) &= \frac{1}{\sqrt{2}} [\chi(z_1, \rho_1)e^{i\varphi_1}\chi(z_2, \rho_2)e^{-i\varphi_2} - \chi(z_2, \rho_2)e^{i\varphi_2}\chi(z_1, \rho_1)e^{-i\varphi_1}] \\ &= \frac{1}{\sqrt{2}}\chi(z_1, \rho_1)\chi(z_2, \rho_2) (e^{i(\varphi_1-\varphi_2)} - e^{-i(\varphi_1-\varphi_2)}) \\ &= \sqrt{2}i\chi(z_1, \rho_1)\chi(z_2, \rho_2) \sin(\varphi_1 - \varphi_2).\end{aligned}\tag{3.57}$$

for the $^3\Sigma$ term, and

$$\Psi_{(s)}^R(q_1, q_2) = \sqrt{2}\chi(z_1, \rho_1)\chi(z_2, \rho_2) \cos(\varphi_1 - \varphi_2)\tag{3.58}$$

for the $^1\Sigma$ term.

A σ_v reflection inverts the sign of $(\varphi_1 - \varphi_2)$. Because of the relations $\sin(-x) = -\sin(x)$ and $\cos(-x) = \cos(x)$, $\Psi_{(s)}^R(q_1, q_2)$ corresponds to the $^1\Sigma_g^+$ term and $\Psi_{(a)}^R(q_1, q_2)$ to the $^3\Sigma_g^-$ term.

Consequently, the $(1\pi_g)^2$ configuration of O_2 possesses the three terms $^3\Sigma_g^-$, $^1\Sigma_g^+$ and $^1\Delta_g$. The energetically favorable exchange interaction in the triplet term causes the $^3\Sigma_g^-$ state to be the ground state of O_2 .

This procedure can be applied to arbitrary configurations. Table 3.2 summarizes the terms resulting from the most common electronic configurations of diatomic molecules.

The classification of terms presented in this subsection relies on the assumption that electrostatic (including exchange) interactions are dominant and the effects of spin-orbit coupling can be disregarded. This assumption is justified as long as the $^{2S+1}\Lambda$ terms are separated in energy by an amount larger than the spin-orbit interaction. This tends to be the case in molecules made of light atoms, for which spin-orbit interactions are genuinely weak, and at short internuclear distances, where the atomic orbitals significantly overlap, the electronic motion is strongly coupled to the internuclear axis, and the exchange interaction is substantial. Consideration of the spin-orbit interaction makes it necessary to extend the classification of electronic terms.

3.5 Spectroscopy of diatomic molecules

3.5.1 Selection rules

This section describes elementary aspects of the spectra of diatomic molecules, with emphasis on selection rules and the overall structure of vibrational and electronic transitions.

Vibrational Transitions

The intensity of an electric dipole transition between an initial state i and a final state f is

$$I_{fi} \propto |\langle \Psi_f | \hat{V} | \Psi_i \rangle|^2. \quad (3.59)$$

Using the BO approximation, one can write the wave functions of the two states as products of electronic and vibrational wave functions, *e.g.* $\Psi_i = \phi_{e,i} \phi_{v,i}$. In the case of a vibrational transition, the electronic state remains the same, *i.e.* $\phi_{e,f} = \phi_{e,i}$ and the intensity of the

transition becomes:

$$I_{fi} \propto |\langle \phi_{v,f} | \mu(Q) | \phi_{v,i} \rangle|^2, \quad (3.60)$$

where $\mu(Q)$ is the dipole moment function that, in a diatomic molecule, depends on the internuclear separation Q and has the following properties:

- $\mu(Q) = 0$: homonuclear diatomic molecules (H_2 , N_2 , O_2 , ...)
- $\mu(Q) \neq 0$: heteronuclear diatomic molecules (HCl , CO , ...)

In the limits $Q \rightarrow 0$ (united atoms) and $Q \rightarrow \infty$ (separated atoms), $\mu(Q) = 0$ and the function $\mu(Q)$ goes over a maximum at intermediate internuclear separations.

In a region around R_e , the dipole moment function can be expanded as a Taylor series:

$$\mu(Q) = \mu(R_e) + \left(\frac{\partial \mu}{\partial Q} \right)_{R_e} (Q - R_e) + \frac{1}{2!} \left(\frac{\partial^2 \mu}{\partial Q^2} \right)_{R_e} (Q - R_e)^2 + \dots \quad (3.61)$$

The transition moment for a vibrational transition is:

$$\begin{aligned} \langle v' | \mu(Q) | v'' \rangle &= \underbrace{\mu(R_e) \langle v' | v'' \rangle}_{(1)} + \left(\frac{\partial \mu}{\partial Q} \right)_{R_e} \left(\underbrace{\langle v' | Q | v'' \rangle}_{(2)} - \underbrace{R_e \langle v' | v'' \rangle}_{(3)} \right) \\ &+ \frac{1}{2!} \left(\frac{\partial^2 \mu}{\partial Q^2} \right)_{R_e} \left(\underbrace{\langle v' | (Q - R_e)^2 | v'' \rangle}_{(4)} \right) + \dots \end{aligned} \quad (3.62)$$

Terms (1) and (3) of Equation (3.62) vanish because of the orthogonality of the vibrational wavefunctions.

In the harmonic oscillator the selection rules are:

$$\begin{aligned} \langle v' | Q | v'' \rangle &= \begin{cases} \neq 0 & \text{for } v' = v'' \pm 1 \\ 0 & \text{otherwise} \end{cases} \Rightarrow \Delta v = \pm 1 \\ \langle v' | Q^2 | v'' \rangle &= \begin{cases} \neq 0 & \text{for } v' = v'' \pm 2, v'' \\ 0 & \text{otherwise} \end{cases} \Rightarrow \Delta v = \pm 2 \text{ (first overtone)} \end{aligned} \quad (3.63)$$

Because, in general,

$$\left(\frac{\partial \mu}{\partial Q} \right)_{R_e} \gg \left(\frac{\partial^2 \mu}{\partial Q^2} \right)_{R_e} \gg \dots \quad (3.64)$$

$\Delta v = \pm 1$ transitions are stronger than $\Delta v = \pm 2$ transitions, which are themselves stronger than $\Delta v = \pm 3$ transitions, etc.

Comment: The first term in Equation (3.62) implies $v' = v''$ and represents a selection rule

for a pure rotational transition, namely that $\mu(R_e)$ must be nonzero. It follows that only molecules with a permanent dipole moment have a pure rotational spectrum.

The angular momentum selection rules for vibrational transitions are

$$\Delta J = \pm 1 \quad (3.65)$$

for electronic states of $\Sigma (\Lambda = 0)$ symmetry, and

$$\Delta J = 0, \pm 1 \quad (3.66)$$

for electronic $\Lambda \neq 0$ symmetry, *i. e.* Π, Δ, \dots states.

Figure 3.11 shows the infrared spectrum of the first vibrational transition of the CO molecule. It consists of two series of lines, the so-called P-branch in the lower half of the spectrum and the R-branch in the upper half. Lines of the P-branch correspond to $\Delta J = J' - J'' = -1$ and are labelled $P(J'')$, whereas lines of the R-branch correspond to $\Delta J = J' - J'' = +1$ and are labelled $R(J'')$.

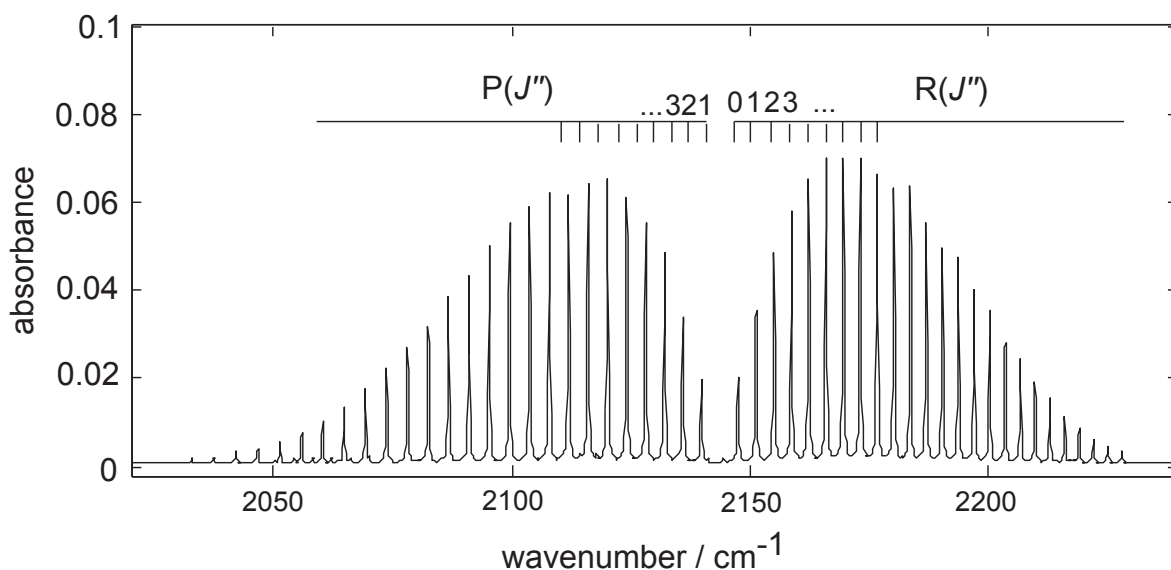


Figure 3.11: Fourier-transform infrared spectrum of the $v = 1 \leftarrow 0$ transition of CO, recorded at a resolution of 0.25 cm^{-1} , a pressure of 10 Pa and a path length of 1 m. The sample is at room temperature. (M. Quack *et al.*, unpublished)

Electronic transitions

We first consider pure electronic transitions, ignoring the motion of the nuclei and, in the next subsection, we include the vibrational structure of electronic transitions.

The intensity of a purely electronic transition between an initial and a final electronic state described by the wave functions $\phi_{e,i}$ and $\phi_{e,f}$, respectively, is given by

$$I_{fi} \propto |\langle \phi_{e,f} | \hat{V} | \phi_{e,i} \rangle|^2. \quad (3.67)$$

A symmetry analysis of this equation for a diatomic molecule shows that the transition moment has two components that are respectively parallel or perpendicular to the molecular axis.

For a transition moment lying **parallel** to the internuclear axis, the selection rules are

$$\Delta\Lambda = 0 \quad (3.68)$$

$$u \leftrightarrow g \text{ for homonuclear diatomic molecules.} \quad (3.69)$$

For a transition moment lying **perpendicular** to the internuclear axis, the selection rules are

$$\Delta\Lambda = \pm 1 \quad (3.70)$$

$$u \leftrightarrow g \text{ for homonuclear diatomic molecules.} \quad (3.71)$$

Examples: In homonuclear diatomic molecules, $\Sigma_g^+ \leftrightarrow \Sigma_u^+$, $\Pi_g \leftrightarrow \Pi_u, \dots$ transitions are allowed parallel transitions, and $\Sigma_g^+ \leftrightarrow \Pi_u$, $\Sigma_u^+ \leftrightarrow \Pi_g$, $\Pi_g \leftrightarrow \Delta_u$, $\Pi_u \leftrightarrow \Delta_g, \dots$ are allowed perpendicular transitions.

3.5.2 Vibronic structure of electronic transitions and the Franck-Condon principle

The vibrational motion of a molecule will now be considered in describing a transition between two electronic states. The intensity of the transition is given by

$$\begin{aligned} I_{fi} &\propto |\langle \phi_{e,f} \phi_{v,f} | \hat{V} | \phi_{e,i} \phi_{v,i} \rangle|^2 \\ &\propto |\langle \phi_{e,f} \phi_{v,f} | \mu | \phi_{e,i} \phi_{v,i} \rangle|^2 \end{aligned} \quad (3.72)$$

Neglecting the dependence of μ on the internuclear separation Q and introducing the quantum numbers α'' and v'' to describe the initial electronic and vibrational states (and α' , v' for the final states), the intensity of the transition can be expressed as

$$I_{\alpha',v',\alpha'',v''} \propto |\langle \phi_{\alpha'} | \mu | \phi_{\alpha''} \rangle \langle \phi_{v'} | \phi_{v''} \rangle|^2 \propto |\langle \phi_{v'} | \phi_{v''} \rangle|^2. \quad (3.73)$$

The square of the integral $\langle \phi_{v'} | \phi_{v''} \rangle$, which is called the Franck-Condon factor, thus indicates how the intensity of an electronically allowed transition between the electronic states α'' and α' is partitioned among the various vibrational bands.

Figure 3.12 shows two schematic illustrations of the Franck-Condon principle applied to the absorption spectrum of diatomic molecules in their ground state. In Figure 3.12a, the Born-Oppenheimer potential energy functions of the two electronic states are almost identical. In this case, vibrational wave functions of the same vibrational quantum number ($v' = v''$) are also almost identical in the two electronic states. The orthogonality of the vibrational wave functions implies the selection rule $\Delta v = 0$ and the electronic spectrum consists of a single dominant vibrational band corresponding to the $v' = 0 \leftarrow v'' = 0$ band (labeled 0-0 in the spectrum drawn at the bottom of the figure).

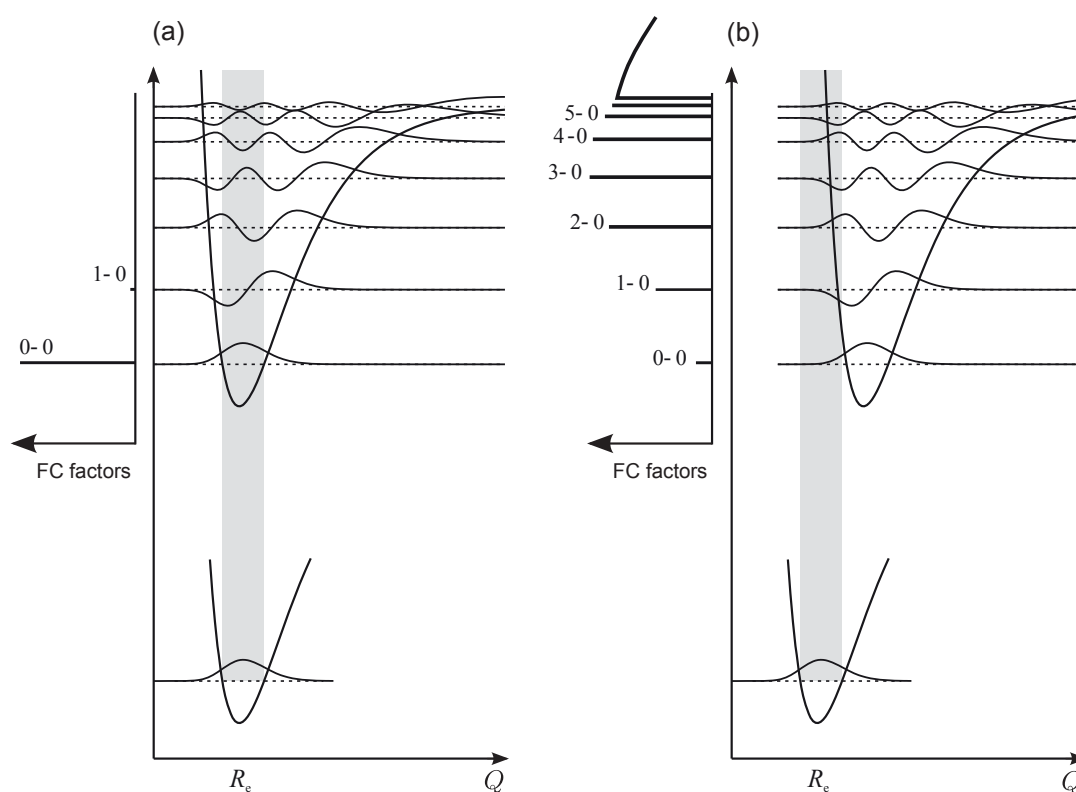


Figure 3.12: Illustration of the Franck-Condon (FC) principle for (a) an electronic transition between two electronic states having almost identical Born-Oppenheimer potential energy functions and (b) an electronic transition between two electronic states with $R_e'' \ll R_e$. The shaded areas in Figure 3.12 represent the regions where the vibrational wave function of the initial state has a significant amplitude. The spectra displayed vertically beside the potential energy diagrams schematically represent the expected appearance of electronic spectra recorded from the $v = 0$ level of the lower electronic state.

In Figure 3.12b, the potential energy functions of the two states differ from each other. The equilibrium internuclear separation R'_e of the upper potential function is larger than that of the lower state. Consequently, transitions originating from the $v'' = 0$ level of the lower electronic state can access several vibrational levels of the upper state. The Franck-Condon factors are therefore nonzero in the energetic region where the repulsive part of the upper potential energy function lies vertically above the region where the ground state vibrational function has a nonzero amplitude. The expected vibrational structure of the corresponding band is represented schematically beside the potential energy diagram and extends beyond the dissociation limit of the upper electronic state where the spectrum becomes continuous. The shaded areas in Figure 3.12 represent the regions where the vibrational wave function of the initial state has a significant amplitude. They help to see which vibrational levels of the final state are accessible from the ground state.

Franck-Condon factors represent an approximation of the relative intensities which relies on the assumption that the electronic transition moment does not vary with internuclear separation, at least not over the range where the relevant vibrational functions have a significant amplitudes. Given that diatomic molecules have zero dipole moments both in the separated-atoms and the united-atoms limits, the dipole moment function must go through at least one maximum at intermediate distances. Neglecting its variation with Q thus represents an approximation, and indeed it is often necessary to include this variation to properly account for the vibrational intensity distribution of an electronic spectrum. The dependence of the electric dipole moment on the nuclear geometry has the largest consequences in the spectra of polyatomic molecules, because it can lead to the observation of electronically forbidden transitions, as will be discussed in Chapter 5.

Figure 3.13 illustrates, with the example of the $C\ 0_u^+ \leftarrow X\ 0_g^+$ electronic band system of Xe_2 , the Franck-Condon principle and some of the limitations in its use that result from the experimental methods chosen to record electronic transitions. Since spin-orbit coupling is large in Xe, the electronic states of Xe_2 are labeled in Hund's case (c), where neither Λ nor Σ , but only their sum $\Omega = \Lambda + \Sigma$ is a good quantum number. The corresponding term symbols are written $\Omega_{g/u}^{+/-}$.

Whereas the ground electronic state of Xe_2 is only weakly bound by van der Waals forces, the A, B, and C electronic states are the lowest members of Rydberg states belonging to series converging on the low-lying electronic states of Xe_2^+ that are more strongly bound and thus have equilibrium internuclear distances shorter than the ground state. This geometry change

results in a long progression of vibrational bands corresponding to excitation of vibrational levels of the C state with $v' = 14-26$ (see Figure 3.13b). The rotational structure of the bands with the lower v' values are strongly degraded to the high wave number side of the spectrum (see Figure 3.13c), which also indicates a shortening of the interatomic distance ($B'_{v'} > B''_{v''}$). Because the rotational constant of the $v' = 20$ level of the C state is significantly larger than that of the ground $v'' = 0$ level, the P-branch of the C $0_u^+ (v' = 20) \leftarrow X 0_g^+ (v'' = 0)$ band displayed in Figure 3.13c possesses a band head at low J'' values ($J'' = 3$). The rotational structure does not show the intensity alternations between lines originating from even- and odd- J'' ground state levels that are characteristic of the spectra of homonuclear diatomic molecules (as it will be shown in the next section in Figure 3.15c). The reason is that the spectrum has been recorded by measuring the ionization signal corresponding to the $^{131}\text{Xe}^{136}\text{Xe}$ isotopomer. One should note that one retains the g/u labels in this case because isotopic substitution does not affect the electronic structure within the Born-Oppenheimer approximation.

A more reliable way to measure intensities of electronic transitions is by recording the absorption signal and will be discussed in the next section.

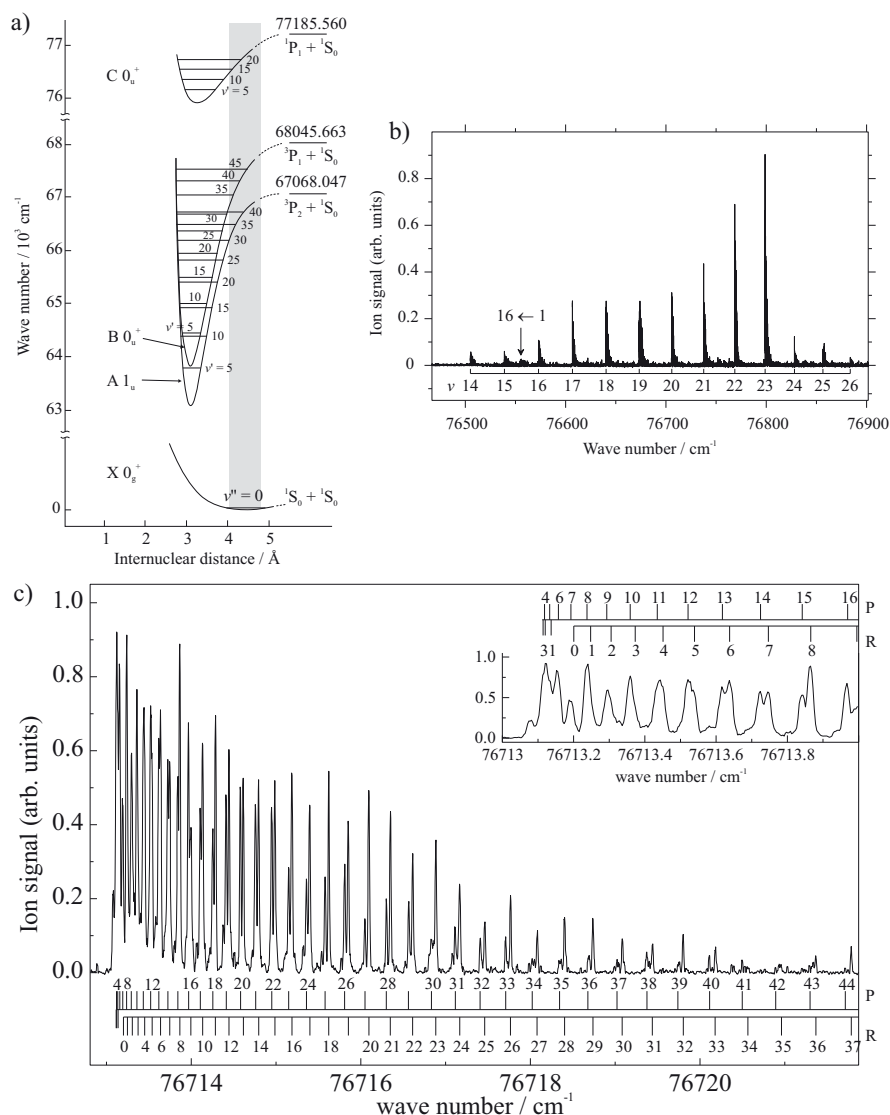


Figure 3.13: (a) Potential energy functions of the $X\ 0_g^+$, $A\ 1_u$, $B\ 0_u^+$, and $C\ 0_u^+$ electronic states of Xe_2 . The Franck-Condon region for excitation from the ground vibrational level of the X state is indicated by the gray area. (b) Spectrum of the $C\ 0_u^+ \leftarrow X\ 0_g^+ (v'' = 0)$ transition recorded with a narrow-band pulsed VUV laser. The transitions are detected by ionizing the levels of the C state with a pulsed UV laser and monitoring the current of $^{131}\text{Xe}^{136}\text{Xe}^+$ ions as a function of the wave number of the VUV laser. The Xe_2 molecules were formed in a supersonic expansion and the population of the rotational levels corresponds to a temperature of 4 K. The vibrational bands are labeled by the vibrational quantum number of the C state. (c) Expanded view of panel (b) showing the rotational structure of the $C\ 0_u^+ (v' = 20) \leftarrow X\ 0_g^+ (v'' = 0)$ band. The numbers along the assignment bars corresponding to the P and R branches designate the rotational quantum number J'' of the ground state (Adapted from U. Hollenstein, Diss ETH Nr. 15237 (2003)).

3.5.3 Rovibronic structure

The description of the rotational structure of electronic transitions requires the parity selection rule ($+$ \leftrightarrow $-$, just like in atoms) and also, in homonuclear diatomic molecules, consideration of the conservation of nuclear spin symmetry, in addition to the selection rules discussed in the previous subsections. The parity of a rovibronic state indicates whether its rovibronic wave function remains invariant under inversion of all space-fixed coordinates, or whether it changes sign. The following sections discuss the parity of rotational states and the spin statistics in diatomic molecules.

The treatment of the rotational structure of diatomic molecules is sometimes reduced to the well-known formula

$$\frac{E_{\text{rot}}^{(v)}(J)}{hc} = B_v J(J+1) - D_v (J(J+1))^2, \quad (3.74)$$

which includes centrifugal distortion effects and also the variation of the rotational and centrifugal distortion constants that results from the anharmonicity of the vibrational motion. Equation (3.74) is adequate to describe the rotational structure of states of $^1\Sigma^+$ symmetry, but it does not account for the details of the rotational energy structure of states of other electronic symmetry, for which the coupling of rotational, orbital and spin angular momenta must be considered. To present a complete treatment would extend beyond the scope of this introductory chapter. We limit ourselves here to qualitative considerations and a presentation of the rotational structures of the simplest situations.

Since diatomic molecules have a vanishing moment of inertia along the internuclear axis, the angular momentum vector \vec{R} describing the rotation of the nuclei lies perpendicular to the internuclear axis. The total angular momentum (without nuclear spins) \vec{J} of a rotating molecule is equal to

$$\vec{J} = \vec{S} + \vec{L} + \vec{R} = \vec{S} + \vec{N}, \quad (3.75)$$

where \vec{N} represents the total angular momentum without electron spins. The quantum number R associated with \vec{R} is only a good quantum number in molecules without electronic angular momentum, *i. e.*, in $^1\Sigma$ states ($\vec{J} = \vec{N} = \vec{R}$), and this is why Equation (3.74) can only be used for such states. In all other cases, the coupling between the spin, orbital and rotational motions must be considered explicitly. The spin-orbit and rotational motions can be described by the effective Hamiltonian

$$\hat{H} = \hat{H}_{\text{el}} + \hat{T}_{\text{nucl}}(Q) + \hat{H}_{\text{rot}} + \hat{H}_{\text{SO}}, \quad (3.76)$$

where the kinetic energy of the nuclei has been divided into rotational motion \hat{H}_{rot} and vibrational motion $\hat{T}_{\text{nuc}}(Q)$.

The relative magnitude of the expectation values of the operators in Equation (3.76) leads to different angular momentum coupling cases, related to the LS and jj coupling cases in atoms, that are called “Hund’s cases” after F. Hund (1896-1997). There are five important cases labeled (a)-(e). Describing them would extend beyond the scope of this lecture and the interested reader is referred to R.N. Zare, *Angular Momentum* (see further reading list).

We will restrict our considerations to singlet states (*i. e.* $\vec{S} = \vec{0}$) and study two examples.

1. The rotational structure of a $^1\Sigma^+$ state is well approximated by Equation (3.74). The parity of the rotational functions is determined in this case by the even/odd nature of the angular momentum quantum number J .
2. In a $^1\Pi$ state, both rotational and electronic angular momenta need to be considered. The rotational energy operator is

$$\hat{H}_{\text{rot}} = \frac{1}{2\mu R^2} \hat{R}^2 = B[\hat{J} - \hat{L}]^2. \quad (3.77)$$

Using the expressions of standard angular momentum algebra

$$\hat{J}_{\pm} = \hat{J}_x \pm i\hat{J}_y, \quad (3.78)$$

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 = \frac{\hat{J}_+\hat{J}_- + \hat{J}_-\hat{J}_+}{2} + \hat{J}_z^2 \quad (3.79)$$

$$\hat{J}_1\hat{J}_2 = \hat{J}_{1x}\hat{J}_{2x} + \hat{J}_{1y}\hat{J}_{2y} + \hat{J}_{1z}\hat{J}_{2z} = \frac{\hat{J}_{1+}\hat{J}_{2-} + \hat{J}_{1-}\hat{J}_{2+}}{2} + \hat{J}_{1z}\hat{J}_{2z}, \quad (3.80)$$

the rotational Hamiltonian can be expressed as

$$\begin{aligned} \hat{H}_{\text{rot}} &= B(\hat{J}^2 + \hat{L}_z^2) - B(\hat{J}_+\hat{L}_- + \hat{J}_-\hat{L}_+ + 2\hat{J}_z\hat{L}_z) \\ &\quad + \frac{B}{2}(\hat{L}_+\hat{L}_- + \hat{L}_-\hat{L}_+). \end{aligned} \quad (3.81)$$

The term in $\hat{J}_+\hat{L}_- + \hat{J}_-\hat{L}_+$ can couple the $^1\Pi$ state to neighboring $^1\Sigma^+$, $^1\Sigma^-$, and $^1\Delta$ states. In the absence of such perturbations, the rotational levels of a $^1\Pi$ state are given by

$$\frac{E(^1\Pi, J, \pm)}{hc} = B[J(J+1) - 1], \quad (3.82)$$

and each rotational level is doubly degenerate and has one component of positive and one of negative parity. Because $|\Lambda| = 1$, the lowest rotational level has $J = 1$. Perturbations caused by the term in the second line of Equation (3.81) may cause a J -dependent splitting of the two components of each rotational level, an effect known as Λ doubling.

The rotational structure of singlet electronic states of diatomic molecules is represented in Figure 3.14.

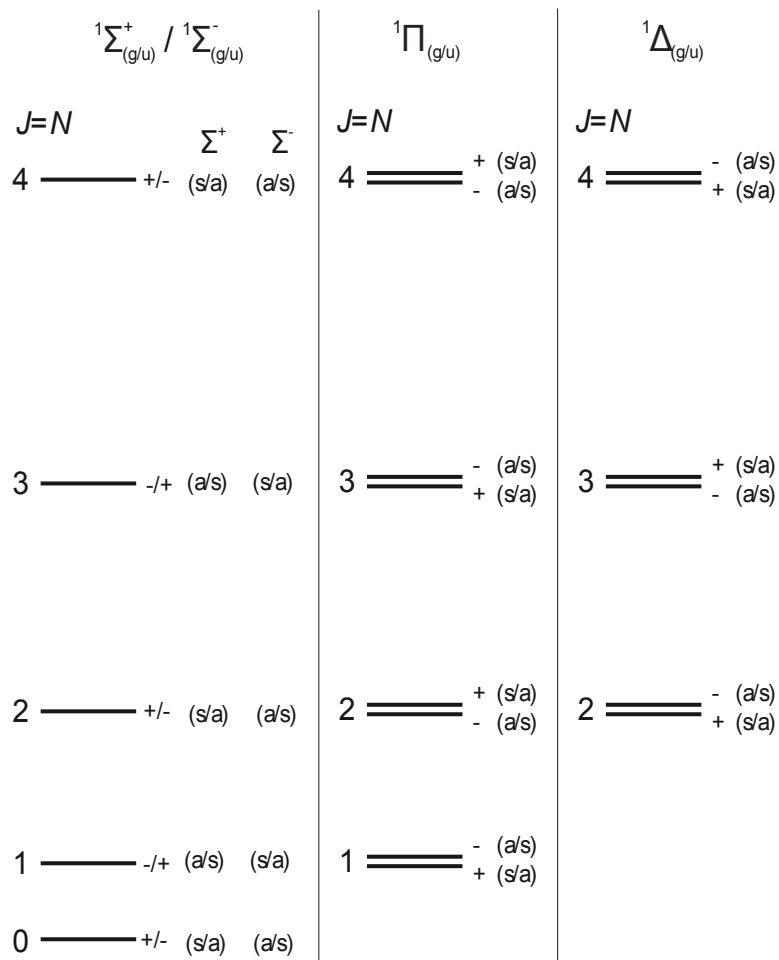


Figure 3.14: Rotational energy level structures of ${}^1\Sigma^+$, ${}^1\Sigma^-$, ${}^1\Pi$ and ${}^1\Delta$ states. The \pm labels next to the rotational levels indicate the parity of the rotational levels. The a/s label is only appropriate for homonuclear diatomic molecules and designates the symmetry of the rovibronic wave functions with respect to permutation of the coordinates of the identical nuclei. The g/u labels only apply to homonuclear diatomic molecules and describe the symmetry of the electronic function with respect to inversion through the center of symmetry.

Combined with the generalized Pauli principle, the conservation of nuclear-spin symmetry leads to a further selection rule for homonuclear diatomic molecules

$$s \leftrightarrow s, \quad a \leftrightarrow a, \quad (s \leftrightarrow a \text{ forbidden}), \quad (3.83)$$

where the "s" and "a" labels indicate whether the rovibronic wave function is symmetric or antisymmetric with respect to permutation of the coordinates of the identical nuclei,

respectively. If the nuclei are bosons (fermions), rovibronic wave functions of "a" symmetry combine with nuclear-spin functions of "a" symmetry ("s" symmetry), whereas rovibronic wave functions of "s" symmetry combine with nuclear wave functions of "s" symmetry ("a" symmetry). For a given value of the nuclear spin quantum number I of the identical nuclei, the numbers N_s and N_a of symmetric and antisymmetric nuclear spin wave functions, respectively, are given by

$$N_s = \frac{(2I+1)^2 + (2I+1)}{2} \quad \text{and} \quad N_a = \frac{(2I+1)^2 - (2I+1)}{2}, \quad (3.84)$$

and are referred to as nuclear-spin statistical factors. The parity (\pm) and permutation (a/s) symmetry of the rovibrational levels of the most common electronic states are indicated in the energy level diagrams presented in Figure 3.14.

In the $X \ ^1\Sigma_g^+$ ground state of H_2 , rotational levels of even $J = N$ values have s symmetry. H is a fermion, with $I = 1/2$, so that $N_s = 3$ and $N_a = 1$. Because the total wave function must be of "a" symmetry with respect to permutation of the coordinates of fermions, states of rovibronic "s" ("a") symmetry only exist if their nuclear-spin symmetry is "a" ("s"). Consequently, transitions from odd- J rotational levels of the ground state of H_2 , which have "a" symmetry, are three-times more intense than those from even- J rotational levels, which have "s" symmetry. The conservation of nuclear-spin symmetry means that rovibronic states of "a" and "s" symmetry are not connected by transitions induced by electromagnetic radiation and can therefore be considered as belonging to two distinct forms of homonuclear diatomic molecules, called para and ortho forms. One should, however, note that the product form of Equation (3.1) is an approximation, and that hyperfine interactions can couple the nuclear-spin motion to other motions.

The rotational states (with parity and nuclear permutation symmetry) that are involved in $^1\Sigma_u^+ \leftarrow ^1\Sigma_g^+$ (parallel) and $^1\Pi_u \leftarrow ^1\Sigma_g^+$ (perpendicular) transitions are drawn schematically in the upper parts of Figures 3.15a and b, respectively. The allowed transitions are marked by arrows and grouped in P, Q and R branches. Figures 3.15c and d present schematic spectra corresponding to the two types of transitions. The alternation of intensities of the lines results from the fact that the spectra have been calculated for a homonuclear diatomic molecule made of atoms with a nuclear spin $I = 1$.

Only $\Delta J = \pm 1$ transitions are allowed in a parallel transition, and the rotational structure of the vibronic transition consists of two branches, one with $\Delta J = 1$ (so-called R branch) and one with $\Delta J = -1$ (so-called P branch; see Figures 3.15a and c). In a perpendicular

transition, $\Delta J = 0$ transitions are also observable which leads to a third branch (so-called Q branch; see Figures 3.15b and d)).

In the case of transitions between singlet states, the rotational structure of a band corresponding to a transition from an initial vibrational level v'' to a final vibrational level v' can be approximately described by Equation (3.74)

$$\begin{aligned} \Delta E(v', J' \leftarrow v'' J'') &= E_{\text{vib}}(v') - E_{\text{vib}}(v'') + B' J'(J' + 1) - D'(J'(J' + 1))^2 \\ &\quad - [B'' J''(J'' + 1) - D''(J''(J'' + 1))^2], \end{aligned} \quad (3.85)$$

where $J' = J''$ for the Q branch, $J' = J'' + 1$ for the R branch, $J' = J'' - 1$ for the P branch. In the case of transitions between doublet or triplet states, the rotational structure is more complicated. The rotational energy level diagrams presented in Figure 3.14 are helpful in predicting the overall rotational branch structure of electronic transitions of diatomic molecules, because they provide the parity and nuclear permutation symmetry of the rotational levels of the most common types of electronic states.

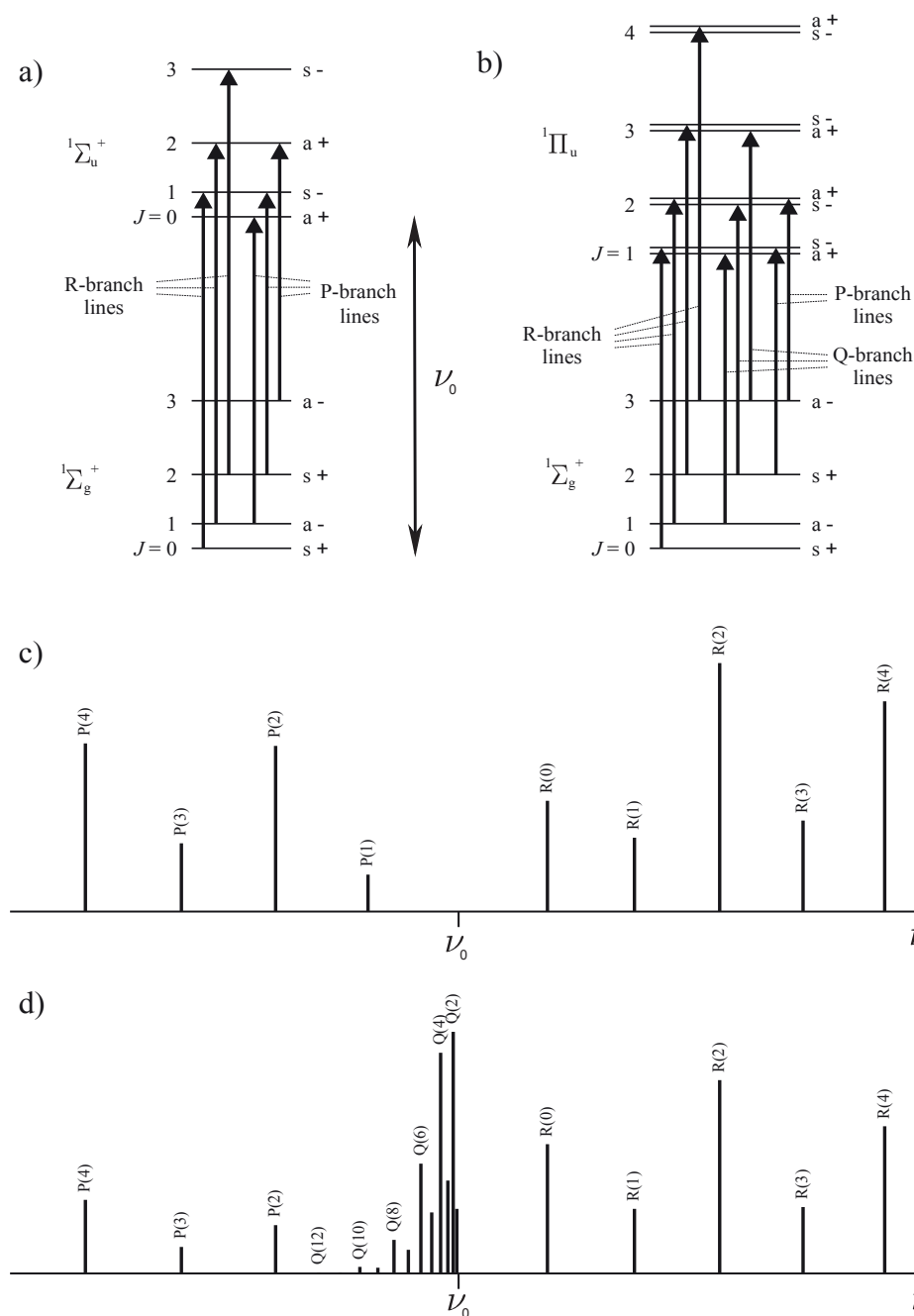


Figure 3.15: (a) Rotational states (with parity and nuclear permutation symmetry) that are involved in a $^1\Sigma_u^+ \leftarrow ^1\Sigma_g^+$ transition. (b) Rotational states (with parity and nuclear permutation symmetry) that are involved in a $^1\Pi_u \leftarrow ^1\Sigma_g^+$ transition. (c) and (d) Schematic structure of the rotational structure of the vibrational bands of a $^1\Sigma_u^+ \leftarrow ^1\Sigma_g^+$ and $^1\Pi_u \leftarrow ^1\Sigma_g^+$ transitions, respectively. The intensity alternation results from the fact that intensities have been calculated for a homonuclear diatomic molecules composed of atoms with a nuclear spin $I = 1$. The frequency ν_0 corresponds to the transition between the lowest rotational levels of the two vibronic states.

Examples of vacuum ultraviolet (VUV) absorption spectra of CO and N₂ are presented in panels a) and b) of Figure 3.16. In these spectra, the normalized transmission signal I/I_0 of the VUV radiation is displayed as a function of the VUV wave number. The CO and N₂ gas samples are cold ($T \approx 12$ K), skimmed supersonic expansions of CO and N₂, which are crossed at right angles by the VUV laser beam to avoid Doppler broadening. Normalization is achieved by dividing the intensity of the VUV radiation transmitted through the sample by the intensity of a reference VUV laser beam.

The rotational structure of the bands represents an essential element of the assignment procedure. Bands recorded from a lower level of $^1\Sigma^+$ symmetry which have P, Q and R branches must have a $^1\Pi$ state as upper level, whereas those which do not have a Q branch are likely to have a $^1\Sigma$ state as upper level. Consequently, the bands centered around 109562 cm^{-1} in the spectrum of N₂ (Figure 3.16b), and the band centered around 109564 cm^{-1} in the spectrum of CO (Figure 3.16a) must have a $^1\Pi$ state as upper level, because they have a Q-branch. However, the absence of a Q branch does not automatically imply that the upper level belongs to a $^1\Sigma$ state, because P and R lines access the components of the rotational doublets with Π^+ electronic character, and Q lines the components with a Π^- electronic character. The absence of the Q branch in a $^1\Pi \leftarrow ^1\Sigma$ transition may therefore occasionally also result from a perturbation of the Π^- state, for instance by a neighboring Σ^- state. Consequently, Σ^+ states can only be unambiguously assigned by the observation of a P(1) transition. Indeed, $J = 0$ rotational levels do not exist in $^1\Pi$ states (see Figure 3.14). The two bands centered around 109449 cm^{-1} and 109481 cm^{-1} in the spectrum of CO and the band centered around 109542 cm^{-1} in the spectrum of N₂ must therefore have a $^1\Sigma$ state as upper level.

The rotational constant of the upper vibronic state provides a further important indication for the assignment, particularly when a spectrum consists of overlapping transitions to Rydberg states belonging to series converging on different ionic states. Because the rotational constants of Rydberg states are almost identical to the rotational constants of the ionic states to which the Rydberg series converge, the determination of the rotational constant of the upper level of an electronic transition can often either enable one to confirm, or rule out possible assignments by comparison with the rotational constants of the vibronic levels of the ion, if these are known. Such comparison, in addition to information on the quantum defects, can be used to assign two bands of the spectrum of CO to transitions to Rydberg states with a $X^+ \ ^2\Sigma^+ (v^+ = 3)$ CO⁺ ion core, and one to a Rydberg state with a $X^+ \ ^2\Sigma^+ (v^+ = 4)$ CO⁺ ion core. Similarly, the band centered around 109564 cm^{-1} in the spectrum of N₂ can be

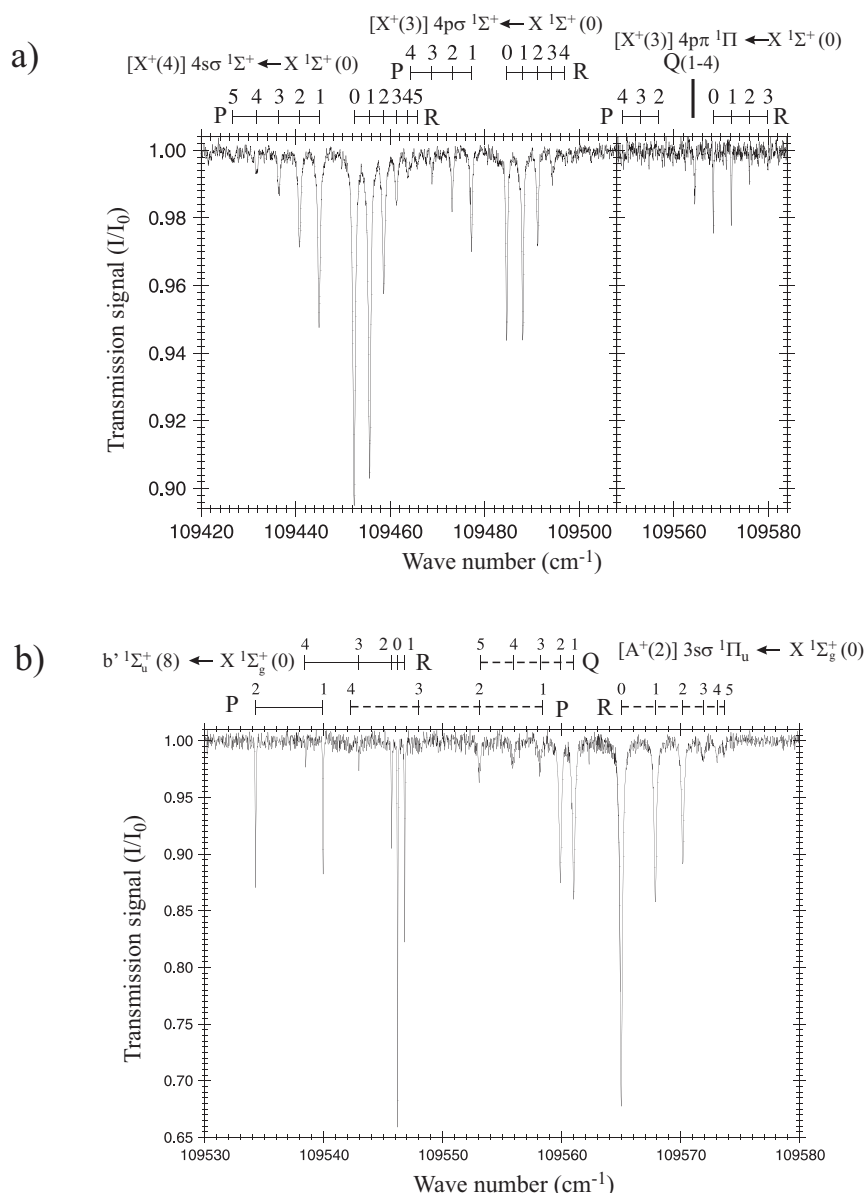


Figure 3.16: (a) VUV absorption spectrum of CO in the region between 109420 cm⁻¹ and 109580 cm⁻¹ displaying transitions from the $^1\Sigma^+$ ($v'' = 0$) ground state to the $4p\pi^+ \Sigma^+$ and $4p\sigma^+ \Sigma^+$ Rydberg states belonging to series converging to the $v^+ = 3$ level of the $X^+ \Sigma^+$ ground electronic state of CO⁺ and to the $3s\sigma^+ \Sigma^+$ Rydberg state belonging to series converging to the $v^+ = 4$ level of the $X^+ \Sigma^+$ ground electronic state of CO⁺. (b) VUV absorption spectrum of N₂ in the region between 109530 cm⁻¹ and 109580 cm⁻¹ displaying transitions from the $^1\Sigma_g^+$ ($v'' = 0$) ground state to the $4s\sigma^+ \Sigma_u^+$ Rydberg state belonging to series converging to the $v^+ = 2$ level of the $A^+ \Sigma_u^+$ first excited electronic state of N₂⁺, and to the $v' = 8$ level of the $b' \Sigma_u^+$ valence state of N₂ (adapted from M. Somavilla, Diss. ETH Nr. 15688 (2004)).

assigned to a transition to a Rydberg state with an $A^+ \ ^2\Pi_u (v^+ = 2) N_2^+$ ion core. The much smaller rotational constant of the upper level of the transition centered around 109542 cm^{-1} in the spectrum of N_2 , which results in an R-branch band head at $J'' = 1$, is incompatible with an assignment of the upper level to a Rydberg state, and must be assigned to the b' valence state.

The bands observed in the VUV absorption spectra of CO and N_2 have different linewidths and, therefore, different predissociation rates. A measurement of the same transitions by resonance-enhanced two-photon ionization spectroscopy would therefore have led to different relative intensities: the bands with broad lines would have appeared less intense in these spectra compared to those with narrow lines than in the case of the absorption spectra displayed in Figure 3.16.

Finally, one could note that the transitions from $J'' = 0$ and 2 levels are more intense compared to the $J'' = 1$ and 3 lines in the spectrum of N_2 than they are in the spectrum of CO. This difference is the manifestation of the nuclear spin statistical factors of 2(1) of rotational levels of even-(odd-) J'' levels of N_2 (see Equation (3.84)).