

## 6 Basics of Optical Spectroscopy

It is possible, with optical methods, to examine the rotational spectra of small molecules, all the Raman rotational spectra, the vibration spectra including the Raman spectra, and the electron spectra of the bonding electrons. Some of the quantum mechanical foundations of optical spectroscopy were already covered in chapter 3, and the optical methods will be the topic of chapter 7. This chapter is concerned with the relation between the structure of a substance to its rotational, and vibration spectra, and electron spectra of the bonding electrons. A few exceptions are made at the beginning of the chapter. Since the rotational spectrum of large molecules are examined using frequency variable microwave technology, this technology will be briefly explained.

### 6.1 Rotational Spectroscopy

#### 6.1.1 Microwave Measurement Method

Absorption measurements of the rotational transitions necessitates the existence of a permanent dipole moment. Molecules that have no permanent dipole moment, but rather an anisotropic polarizability perpendicular to the axis of rotation, can be measured with Raman scattering. Although rotational spectra of small molecules, e.g. HI, can be examined by optical methods in the distant infrared, the frequency of the rotational transitions is shifted to the range of HF spectroscopy in molecules with large moments of inertia. For this reason, rotational spectroscopy is often called microwave spectroscopy.

For the production of microwaves, we could use electron time-of-flight tubes. The reflex klystron is only tunable over a small frequency range. The carcinotron (reverse wave tubes) is tunable over a larger range by variation of the accelerating voltage of the electron beam. The magnetron uses a ring shaped (toroidal) inhomogeneous delay line, which is arranged concentrically as an anode around a central cathode. The radial electrostatic field thus created is perpendicular to an axial static magnetic field, which causes circular electron paths. Microwave generators based on semiconductors are made using Gunn diodes or avalanche diodes. All time-of-flight tubes and diode oscillators together cover a range from 1 to 150 GHz. The individual oscillators and the waveguides are, however, only useful in a certain portion of this range (hollow waveguides are used between 3 and 100 GHz).

The measurement of microwave absorption through the sample is done with a microwave diode. To improve the detection sensitivity, modulation and phase sensitive demodulation is used (e.g. 100 kHz frequency modulation of the microwave generator or modulation in the kHz range of the alternating electric field acting on the sample, producing a Stark effect, see chapter 6.1.5). The gaseous substance to be examined must be at a low pressure (100 to  $10^{-3}$  Pa) to minimize collision broadening of the spectral lines. This happens if the number of collisions per molecule per second is greater than the line width (measured in Hz) of a collision free molecule. To improve the sensitivity, hollow wave guides about 1 meter long are used as absorption cells. A very simplified picture of a microwave spectrometer (without frequency or effect modulation) is shown in Fig. 6.1.

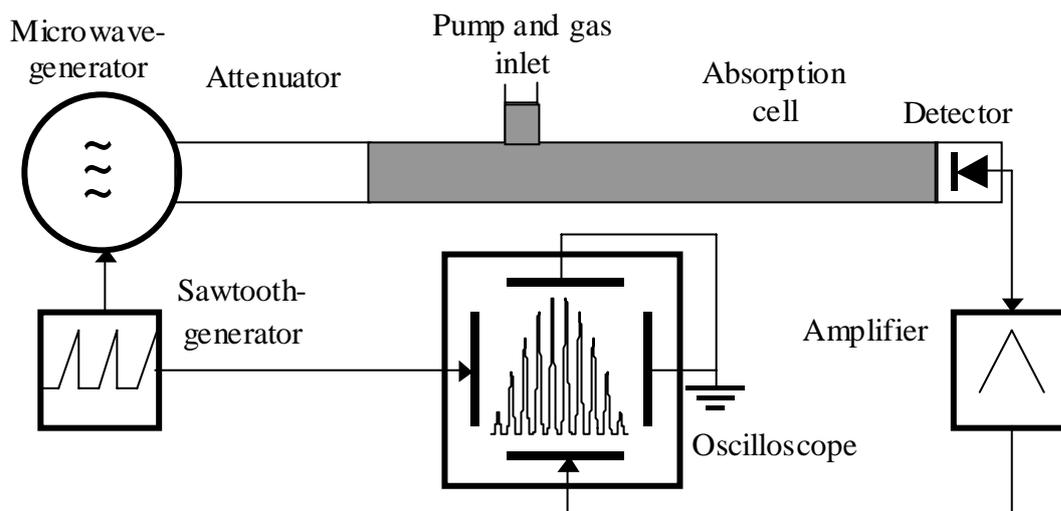


Fig. 6.1 Block diagram of a simple microwave spectrometer.

Frequency modulation of the microwave generator and phase sensitive demodulation of this frequency (with respect to the microwave demodulation) allows a reduction in the bandwidth of the detection channel and therefore an improvement of the signal/noise ratio. An effect modulation is attainable by applying an alternating electric field (50 Hz to 100 kHz, field strength of approx  $100 \text{ V cm}^{-1}$ ). By phase sensitive demodulation with this frequency, the portions of the signal modulated by the Stark effect are captured, see chapter 6.1.5.

### 6.1.2 Energy Levels of the Rigid Rotor

The energy of a body which freely rotates around the axis  $x$ ,  $y$  and  $z$  with the angular frequencies  $\omega_x$ ,  $\omega_y$ ,  $\omega_z$ , the moments of inertia  $I_x$ ,  $I_y$  and  $I_z$  relative to these axes and the angular momentum  $L_{x,y,z} = I_{x,y,z} \omega_{x,y,z}$  is in the classical mechanics

$$E = \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2 = \frac{L_x^2}{2I_x} + \frac{L_y^2}{2I_y} + \frac{L_z^2}{2I_z}. \quad (6.01)$$

In a spherical rotor (tetrahedral or octahedral symmetry of the molecule, e.g. in  $\text{CH}_4$  or  $\text{SF}_6$ ) is  $I_x = I_y = I_z = I$ . In general is  $L_x^2 + L_y^2 + L_z^2 = L^2$ . When we move from the classical to the quantum mechanical description,  $L^2$  is replaced by  $J(J+1)\hbar^2$ , see chapter 3.1.4, and we get

$$E_J = J(J+1) \frac{\hbar^2}{2I} = h B J(J+1). \quad (6.02)$$

Now  $J$  no longer refers to the classical angular momentum but rather the angular momentum quantum number  $J = 0, 1, 2, \dots$ . Equation (6.02) defines the constant of rotation  $B$  as a frequency

$$B = \frac{\hbar}{4\pi I} = \frac{h}{8\pi^2 I}. \quad (6.03)$$

Levels are often labeled with the rotational term  $F_J = E_J/hc$ , which has the units of a wave number, instead of the energy  $E_J$  or the frequency  $E_J/h$ . If we want to use the usual dimensions of  $\text{cm}^{-1}$  for these wave numbers, the numerator in equ. (6.03) has to be multiplied by the speed of light  $c$  in cgs units.

The meaning of the rotational constant  $B$  becomes apparent when we consider two neighboring rotational transitions  $J-1 \rightarrow J$  and  $J \rightarrow J+1$ . If we put this back into equ. (6.02), we end up with the transition energies  $E_J - E_{J-1} = 2hBJ$  and  $E_{J+1} - E_J = 2hB(J+1)$ . If we then construct the difference of these two solutions, we obtain  $2B$  as the frequency difference of neighboring rotational transitions, see Fig. 6.2.

Starting with equ. (6.01), the *symmetric rotor* can also be described. A symmetric rotor has two equal moments of inertia (relative to two axes:  $I_x = I_y = I_B$ ), which are different than the moment of inertia of the distinguished principal axis ( $I_z = I_A$ ). If  $I_A > I_B$ , the rotor is shaped like a pancake (for example  $\text{C}_6\text{H}_6$ ). If  $I_A < I_B$ , it is shaped like a cigar (e.g.  $\text{CH}_3\text{Cl}$ ). The energy values of the Hamiltonian are determined in chapter 3.1.4, see equ. (3.35), by

$$E_{\text{Rot}} = \frac{\hbar^2}{2I_B} [J(J+1) - K^2] + \frac{\hbar^2}{2I_A} K^2, \quad 0 \leq K \leq J. \quad (6.04)$$

$K$  is a magnetic quantum number (directional quantum number), see chapter 3.1.4. If  $K = 0$ , we have a rotational axis which is perpendicular to the symmetry axis of the molecule. If  $K = J$ , the rotational axis is almost parallel with the symmetry axis. The quotients in equ. (6.04) can be replaced by the rotational constants  $A$  and  $B$  multiplied by the Planck constant, analogous to equ. (6.02). When doing this, we must also replace the  $I$  in equ. (6.03) with  $I_B$  and  $I_A$ . The selection rules for the rotational transitions in emission and absorption are  $\Delta J = \pm 1$  and  $\Delta K = 0$ , but in the rotational Raman spectra for the linear rotor it holds that  $\Delta J = 0, \pm 2$ , and finally in the symmetric rotor  $\Delta J = 0, \pm 1, \pm 2$  and  $\Delta K = 0$ .

Equation (6.04) also contains the special case of a linear rotor, which was explained in chapter 3.1.4 using cyclic boundary conditions. In the linear rotor (e.g.  $\text{CO}_2$  and  $\text{HCl}$ ),  $I_A = 0$  and stable axes of rotation are perpendicular to the symmetry axis, from which it follows that  $K = 0$ . With that we have energy eigenvalues for the spherical rotor, see equ. (6.02). Uglier expressions with more quantum numbers are used to describe the asymmetrical rotor and free inner rotations in molecules.

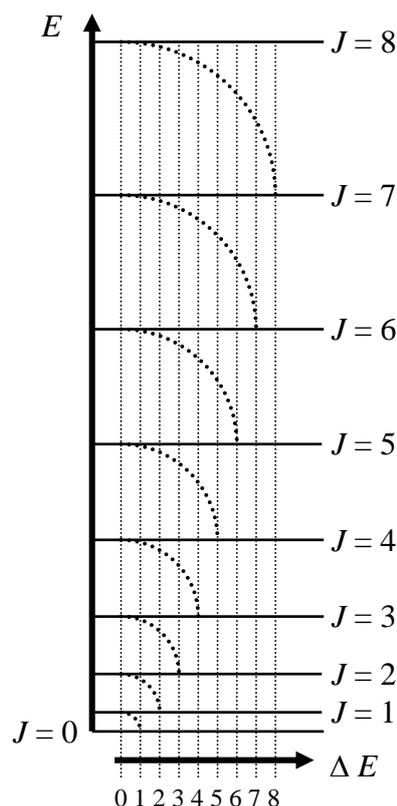


Fig. 6.2 Rotational energy and energy differences

### 6.1.3 Diatomic Rigid Rotor, Specifically HI

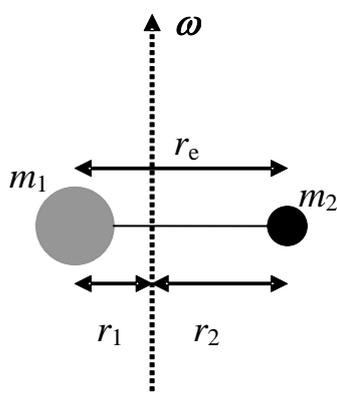


Fig. 6.3 Diatomic rotator

The axis of rotation is perpendicular to the bonding axis and passes through the centre of mass in a heteropolar diatomic molecule with atomic masses  $m_1$  and  $m_2$ . The centre of mass is conserved in a molecular rotation. If  $r = 0$  at the centre of mass, and the nuclear distance  $r_e = r_1 + r_2$ , then from the conservation of the centre of mass we get  $m_1 r_1 = m_2 r_2$ . With  $r_1 = r_e - r_2$  and  $r_2 = m_1 r_e / (m_1 + m_2)$ , we get for the moment of inertia the simple relationship  $I = r_e^2 m_r$  with the reduced mass  $m_r = (m_1 m_2) / (m_1 + m_2)$

$$\begin{aligned}
 I &= m_1 r_1^2 + m_2 r_2^2 = m_1 r_e^2 \left(1 - \frac{m_1}{m_1 + m_2}\right)^2 + m_2 r_e^2 \left(\frac{m_1}{m_1 + m_2}\right)^2 \\
 &= r_e^2 \left(\frac{m_1 m_2^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2}{(m_1 + m_2)^2}\right) = r_e^2 \frac{m_1 m_2}{m_1 + m_2} = r_e^2 m_r.
 \end{aligned}
 \tag{6.05}$$

In HI, the rotational spectrum is composed of equidistant lines separated by 384 GHz for small quantum numbers. (In the transitional range between the far infra-red and microwaves, the observed spectrum has line separations of  $12,8 \text{ cm}^{-1}$ .) From the frequency separation of  $2B = 384 \text{ GHz}$ , we get from equ. (6.03) the moment of inertia

$$I = 4,37 \times 10^{-47} \text{ kg m}^2 = m_r r_e^2. \tag{6.06}$$

Iodine has only one isotope with the mass number 127, the reduced mass is therefore

$$m_r = \frac{127}{127 + 1} \frac{1}{6,02 \times 10^{26}} \text{ kg} = 1,65 \times 10^{-26} \text{ kg}. \tag{6.07}$$

The interatomic distance is determined from

$$r_e^2 = \frac{I}{m_r} = \frac{4,37 \times 10^{-47}}{1,65 \times 10^{-27}} \text{ m}^2 = 2,65 \times 10^{-20} \text{ m}^2 \text{ mit } r_e = 1,63 \text{ \AA}. \tag{6.08}$$

Measurement of the moment of inertia of a molecule allows

- the measurement of distances and valence angles if the isotopic composition is known;
- the determination of the isotopic composition if the interatomic distances are known.

If three different moments of inertia can be determined from the rotational spectra of asymmetric polar molecules, we can determine a maximum of three distances and angles. That allows complete specification of triatomic non-linear molecules. The use of isotopes (e.g. replacement of H with D) increases the number of measurement values.

### 6.1.4 Diatomic Non-Rigid Rotor, Specifically HCl

As consequence of centrifugal distortion, the interatomic distances can grow with increasing rotational frequency, i.e. the constant of rotation  $B$  gets smaller as  $J$  get larger, see equ. (6.03) and equ. (6.05). For an explanation of this effect, let us first consider a harmonic vibration in the rotor. With the force constant  $k$  and the reduced mass  $m_r$ , we have for this vibration that

$$\omega_s = 2\pi\nu_s = \sqrt{\frac{k}{m_r}} \quad \text{and} \quad (6.09)$$

$$r = r_e + f_a \cos \omega_s t. \quad (6.10)$$

Worthy of note is that although the time average of equ. (6.10) is  $r_e$ , the fact that in rotational spectroscopy  $B \propto 1/I \propto 1/r^2$ , we have to average over  $1/r^2$ . The determination of the average value by integrating over  $1/r^2$  leads to a apparent average distance of  $r_e(1 - f_a/r_e)^{3/4}$  where  $f_a < r_e$ . The reduction coefficient is, for example, about 0,74 when  $f_a/r_e = 1/3$ .

Setting the centrifugal force of the rotation equal to the displacement force of the vibration leads us to

$$m_r r \omega_{\text{rot}}^2 = k(r - r_e). \quad (6.11)$$

By using the moment of inertia  $I = m_r r^2$  and the angular momentum  $L = I \omega_{\text{rot}} = m_r r^2 \omega_{\text{rot}}$  we get from equ. (6.11)

$$r - r_e = \frac{m_r r \omega^2}{k} = \frac{I^2 \omega^2}{k m_r r^3} = \frac{L^2}{k m_r r^3}. \quad (6.12)$$

The rotational energy is composed of the rigid part  $L^2/2I$  and the elastic energy  $k(r - r_e)^2/2$ , which leads to a reduction of the total energy due to the increase in the moment of inertia:

$$E_{\text{rot}} = \frac{L^2}{2I} - \frac{k(r - r_e)^2}{2}. \quad (6.13)$$

By setting  $r^3$  equal to  $r_e^3$  in equ. (6.12), putting this into equ. (6.13), and moving from the classical to the quantum mechanical notation [ $L^2 \rightarrow J(J+1)\hbar^2$ ] we get

$$E_{\text{rot}} = \frac{\hbar^2 J(J+1)}{2I} - \frac{\hbar^4 J^2(J+1)^2}{2I^2 r_e^2 k}. \quad (6.14)$$

With term notation analogous to equ. (6.02) we conclude:

$$E_{\text{rot}}/h = B J(J+1) - D J^2(J+1)^2, \quad (6.15)$$

in which  $D$  is the elastic strain constant of the centrifugal distortion. By comparison of equ. (6.15) with equ. (6.14), noting that  $I = m_r r_e^2$ , and considering equ. (6.09) and equ. (6.03) we get

$$D = \frac{\hbar^3}{4\pi I^2 r_e^2 k} = \frac{\hbar^3 m_r}{4\pi I^3 k} = \frac{\hbar^3}{4\pi I^3 \omega_s^2} = \frac{16\pi^2 B^3}{\omega_s^2} = \frac{4B^3}{\nu_s^2}. \quad (6.16)$$

Equ. (6.16) makes two statements:

- Because  $D \propto 1/I^3$ , a large moment of inertia gives a small distortion.
- Because  $D \propto 1/\nu_s^2$ , a large vibrational force constant also gives a small distortion.

**Tab. 6.1.** Some wave numbers calculated using  $E_{\text{rot}}/hc = B J(J+1) - D J^2(J+1)^2$  with  $2B = 20,79 \text{ cm}^{-1}$  and  $D = 0$  (rigid rotor) or for the non-rigid rotor  $D = 0,0005 \text{ cm}^{-1}$  and  $D = 0,00038 \text{ cm}^{-1}$  were compared to experimental values of gaseous HCl.

| Transition                     | Experiment               | Calculations with        |                              |                               |
|--------------------------------|--------------------------|--------------------------|------------------------------|-------------------------------|
|                                |                          | $D = 0 \text{ cm}^{-1}$  | $D = 0,0005 \text{ cm}^{-1}$ | $D = 0,00038 \text{ cm}^{-1}$ |
| $J = 0 \leftrightarrow J = 1$  | $20,79 \text{ cm}^{-1}$  | $20,79 \text{ cm}^{-1}$  | $20,79 \text{ cm}^{-1}$      | $20,79 \text{ cm}^{-1}$       |
| $J = 3 \leftrightarrow J = 4$  | $83,03 \text{ cm}^{-1}$  | $83,16 \text{ cm}^{-1}$  | $83,03 \text{ cm}^{-1}$      | $83,06 \text{ cm}^{-1}$       |
| $J = 6 \leftrightarrow J = 7$  | $145,03 \text{ cm}^{-1}$ | $145,53 \text{ cm}^{-1}$ | $144,84 \text{ cm}^{-1}$     | $145,01 \text{ cm}^{-1}$      |
| $J = 9 \leftrightarrow J = 10$ | $206,38 \text{ cm}^{-1}$ | $207,90 \text{ cm}^{-1}$ | $205,9 \text{ cm}^{-1}$      | $206,38 \text{ cm}^{-1}$      |

Table 6.1 contains the experimentally determined wave numbers for some rotational transitions in HCl gas. Additionally, the values calculated using the rotational constant  $2B = 20,79 \text{ cm}^{-1}$  (experimentally obtained from the transition  $J = 0 \leftrightarrow J = 1$ ) with different elastic strain constants are shown. When  $D = 0,0005 \text{ cm}^{-1}$ , we have much better correlation than with a rigid rotor ( $D = 0$ ). The best correlation is attained with  $D = 0,00038 \text{ cm}^{-1}$ . An elastic strain constant  $D \approx 0,00054 \text{ cm}^{-1}$  is obtained, if we take from the vibrational spectra the vibrational frequency of  $2885,9 \text{ cm}^{-1}$  and use equ. (6.16) with  $2B = 20,79 \text{ cm}^{-1}$ . This demonstrates that equ. (6.16), which was derived for a harmonic oscillation, only approximately describes the real situation.

### 6.1.5 The Stark Effect in Rotational Spectra

The lifting of the degeneration of rotational levels in an external electric field is known as the Stark effect. The original phenomenon, discovered in 1913 by Johannes Stark, was the splitting of the lines of the atomic hydrogen spectrum, when the hydrogen was in glowing canal rays exposed to an external electrostatic field. Since then, the splitting of spectral lines in electric fields is collectively referred to as the Stark effect. It is therefore the electric analogy to the Zeeman effect, which is used to label all the splittings of spectral lines in external magnetic fields. For a linear dependency of the splitting on the strength of the external field, a permanent electric dipole moment in the molecule is necessary. In the quadratic Stark effect, the external field creates a dipole moment in the molecule.

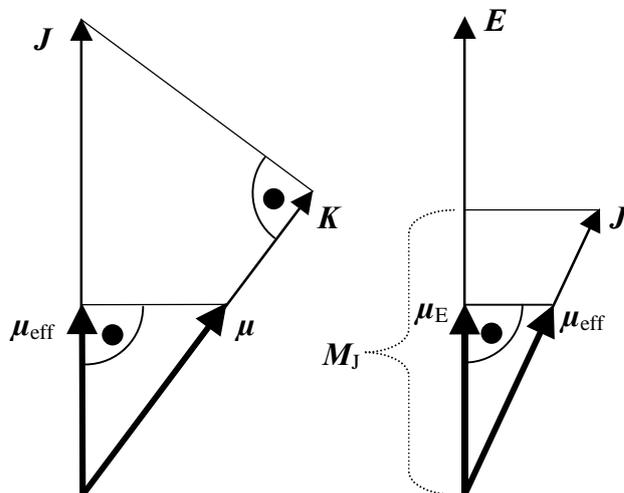
The measurement of the Stark splitting of the rotational lines is often used to determine molecular dipole moments. We will first present the frequency shift of rotational transitions caused by the linear Stark effect.

In a rotationally symmetric molecule, the molecule-specific electric dipole moment  $\mu$  is parallel to the symmetry axis and to the angular momentum  $\mathbf{K}$  with  $|\mathbf{K}| = K \hbar$ , where  $K$  is the rotational quantum number used in chapters 3.1.4 and 6.1.2. We now decompose the dipole moment  $\mu$  into a component  $J$  along the axis of rotation, and a component perpendicular to this axis. The latter is averaged out by quick molecular rotation, so that in the interaction with an external static field  $\mathbf{E}$  only the component  $\mu_{\text{eff}}$  of the dipole moment along the axis of rotation plays a role, in first approximation. The magnitude of the angular momentum along the axis of symmetry is  $|\mathbf{K}| = K \hbar$ , the magnitude of the angular momentum along the axis of rotation is  $|\mathbf{J}| = \sqrt{J(J+1)} \hbar$ .

With that, the equation

$$|\boldsymbol{\mu}_{\text{eff}}| = |\boldsymbol{\mu}| \frac{K}{\sqrt{J(J+1)}} \quad (6.17)$$

follows from the left of Fig. 6.4.



**Fig. 6.4** Angular momentum vectors and the decomposition of the molecular dipole moment into a component that interacts with the electric field. Take note that due to the definition of the angular momentum, the vector  $\mathbf{J}-\mathbf{K}$  is perpendicular to  $\mathbf{K}$ .

By applying a field  $\mathbf{E}$ , the component of  $\mathbf{J}$  aligned with the external field is determined by the magnetic (or directional) quantum number  $M_J = -J, \dots, +J$ . From  $\boldsymbol{\mu}_{\text{eff}}$ , only the component  $\boldsymbol{\mu}_E$  acts, since it points in the same direction as the external field  $\mathbf{E}$ , see the right of Fig. 6.4:

$$|\boldsymbol{\mu}_E| = |\boldsymbol{\mu}_{\text{eff}}| \frac{M_J}{\sqrt{J(J+1)}}. \quad (6.18)$$

In general for the interaction energy, we have  $W = -\boldsymbol{\mu}_{\text{eff}} \mathbf{E} = -|\boldsymbol{\mu}_E| |\mathbf{E}|$  and with equ. (6.17) put into equ. (6.18) we get with  $\mu = |\boldsymbol{\mu}|$  and  $E = |\mathbf{E}|$

$$W_{J,K,M} = -\mu E \frac{KM_J}{J(J+1)}. \quad (6.19)$$

In a waveguide, the static electric field is applied parallel to the electric wave of the high frequency,  $M_J$  and  $K$  do not change, and we consider the transition  $J-1 \leftrightarrow J$ . By constructing  $W(J) - W(J-1)$  with equ. (6.19), we get a linear Stark shift of the rotational spectral lines

$$\Delta \nu_{\text{linear}} = \frac{\mu E}{h} \frac{2KM_J}{J(J^2-1)}. \quad (6.20)$$

By combining  $K$  and  $J$ , we obtain  $2J+1$  values of  $M_J$ , thus  $2J+1$ -fold splitting, from which we can determine the dipole moment  $\mu$  of the molecule, if we know the values  $K$  and  $M_J$ . Our considerations of the rotationally symmetric molecule explain the linear molecule as a special case. In linear molecules,  $K=0$ , and a linear Stark effect does not occur.

Under the influence of an external field, polarization effects occur in molecules. These cause a Stark effect which is proportional to the square of the external electric field strength. In general, a quadratic Stark effect is more often seen especially when there is no permanent dipole moment. For the special case of rotational spectra of linear polar molecules, we will give the quadratic Stark shift for the transitions  $J - 1 \leftrightarrow J$  without derivation:

$$\Delta v_{\text{quadratic}} = \left( \frac{\mu E}{h} \right)^2 \frac{6M_J^2(8J^2 - 3) - 8J^2(J^2 + 1)}{2BJ(J^2 - 1)(4J^2 - 1)(4J^2 - 9)}. \quad (6.21)$$

The  $2J + 1$ -fold  $M_J$ -splitting depends on the squares of the quantities  $\mu$ ,  $E$  and  $M_J$ .

### 6.1.6 The Intensity of the Rotational Lines

In the classical consideration, we have for the occupation number  $N_i$  of state  $i$  for  $N$  total particles the Boltzmann distribution of the form

$$\frac{N_i}{N} = \frac{\exp\left(-\frac{E_i}{kT}\right)}{\sum_i \exp\left(-\frac{E_i}{kT}\right)}. \quad (6.22)$$

In the denominator, we have the so-called state sum, which must be summed over all states  $i$ . Degenerate states (more than one eigenvalue has the same energy) have to be counted multiple times. The molecular angular momentum vector  $\mathbf{J}$  has  $2J + 1$  orientations of different energy in an external electric or magnetic field. For example, when  $J = 1$ , the angular momentum  $|\mathbf{J}| = \hbar\sqrt{2}$  and  $M_J = +\hbar, 0, -\hbar$ , with different energy, see for example equ. (6.19). If no external field is applied, we have  $2J + 1$ -fold degeneracy of the rotational levels, i.e. the corresponding energy values have to be counted  $2J + 1$  times. Because  $E_J = hB J(J + 1)$ , see equ. (6.02), we get as the sum of states for the linear or spherical rotor

$$\sum_i \exp\left(-\frac{E_i}{kT}\right) = \sum_J (2J + 1) \exp\left(-\frac{E_J}{kT}\right) = \frac{kT}{hB}. \quad (6.23)$$

In equ. (6.23) notice that the first summation  $i$  is over  $J$  and  $M_J$ , but the second summation is only over  $J$ . The transition from the middle to the right part of the equation is easy to calculate yourself by putting the product  $hB J(J + 1)$  into  $E_J$ , and replacing the sum by the integral from  $J = 0$  to  $J = \infty$ . With equ. (6.23), we get for the Boltzmann distribution

$$\frac{N_J}{N} = (2J + 1) \frac{hB}{kT} \exp\left(-\frac{E_J}{kT}\right). \quad (6.24)$$

Equation (6.24) is now differentiated with respect to  $J$  and the result is set to zero. From that we get

$$J = \sqrt{\frac{kT}{2hB}} - \frac{1}{2} \quad (6.25)$$

as the quantum number  $J$  with the strongest occupation.

In chapter 2.8, we showed that the intensity of an absorption signal is proportional to the occupation of the starting state. From that we get the maximal intensity of the rotational line with the quantum number given by equation (6.25). This fact can be used to determine the temperature in the absorption cell.

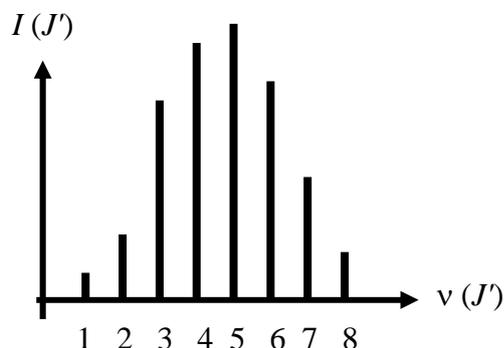


Fig. 6.5 Intensity of the rotational lines

Fig. 6.5 Intensity distribution of rotational lines, which are plotted as functions of the rotational constant  $J'$ , analogous to Fig. 6.1. The transitions are from  $J' - 1$  to  $J'$ .

## 6.2 Vibrations of Molecules

### 6.2.1 Diatomic Molecules

The quantum mechanical treatment of the harmonic oscillator was the subject of chapter 3.1.3. Equation (3.26) describes the eigenvalues  $E_v = (v + 1/2)\hbar\omega$  of the oscillation frequency  $\omega$ , and the selection rule is  $\Delta v = \pm 1$ . It was shown in chapter 3.1.2. that the potential curve for the separation  $r$  of two atoms is not a symmetric function. The simplest anharmonic potential is a Morse (Phillip McCord Morse) function:

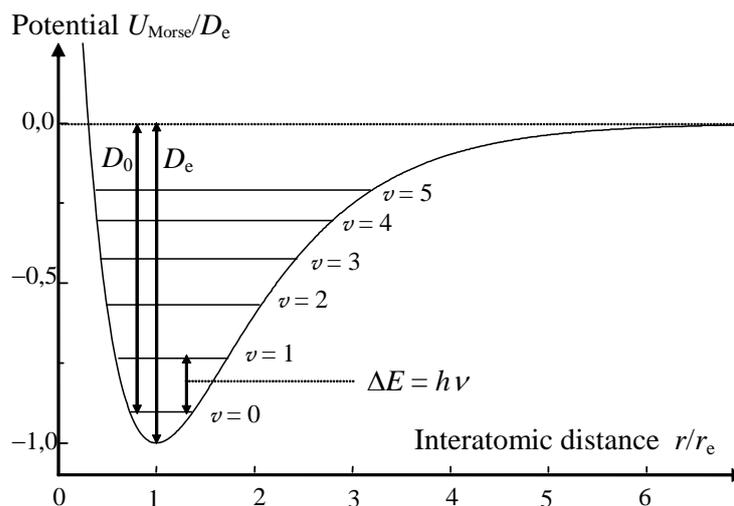


Fig. 6.6 The Morse potential of the anharmonic oscillator.

$$U_{\text{Morse}} = D_e \left(1 - e^{-a(r-r_e)}\right)^2 - D_e. \quad (6.26)$$

The term  $-D_e$  on the right hand side of equ. (6.26) forces the potential energy toward zero as  $r \rightarrow \infty$ . The constant  $a$  in equ. (6.26) is proportional to the vibrational angular frequency:

$$a = \sqrt{\frac{m_r}{2D_e}} \omega. \quad (6.27)$$

The Schrödinger equation is solvable for the Morse potential (not calculated here). The discrete eigenvalues of the anharmonic oscillator are thus, see Fig. (6.6),

$$E_{\text{Morse}}(v) = \left(v + \frac{1}{2}\right)\omega\hbar - \left(v + \frac{1}{2}\right)^2 \frac{(\omega\hbar)^2}{4D_e} - D_e. \quad (6.28)$$

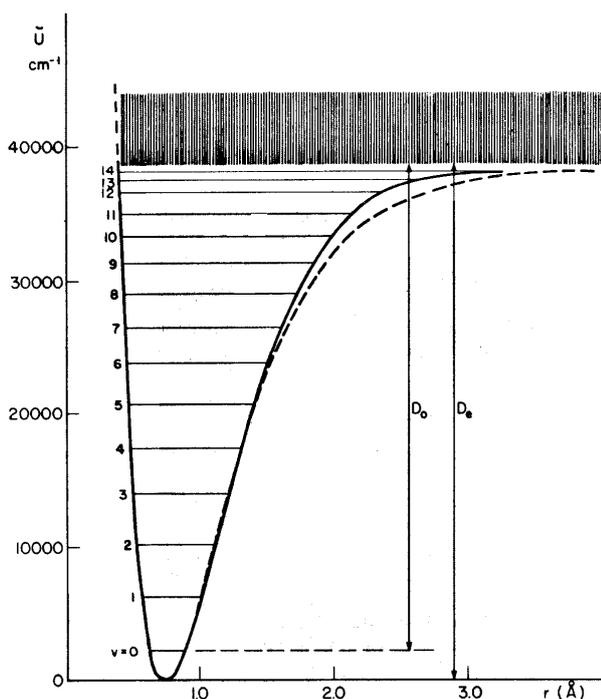
In contrast to the harmonic oscillator, transitions in the anharmonic oscillator in which  $\Delta v = \pm 2, 3, \dots$  are allowed in addition to those in which  $\Delta v = \pm 1$ , although the intensity rapidly decreases with the term of the harmonic. The spectroscopic dissociation constant  $D_e$  is only defined over the potential curve. The chemical dissociation constant  $D_0$  corresponds to the (negative) energy of state  $v = 0$ , which has to be added to dissociate a molecule.

For the hydrogen molecule  $H_2$  the values are:

|                                     |   |
|-------------------------------------|---|
| distance from equilibrium           | $r_e = 0,74 \text{ \AA}$ ,                  |
| chemical dissociation constant      | $D_0 = 4,476 \text{ eV}$ ,                  |
| spectroscopic dissociation constant | $D_e = 4,746 \text{ eV}$ ,                  |
| force constant                      | $k = 520 \text{ N m}$                       |
| vibrational frequency               | $\nu = 1,24684 \times 10^{14} \text{ Hz}$ , |
| wave number                         | $\tilde{\nu} = 4159,2 \text{ cm}^{-1}$ .    |

In optical experiments, the constants of vibration are rarely given in frequencies  $\nu$  and practically never in angular frequencies  $\omega$ . The angular frequency  $\omega = 2\pi\nu$  is only appropriate for theoretical considerations. The wave number  $\tilde{\nu}$ , which is the most frequently used, is defined as:

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{\omega}{2\pi c}. \quad (6.29)$$



Since the wave number is not given in  $m^{-1}$  but rather in  $cm^{-1}$ , the speed of light in equ. (6.29) must be in cgs units. In a vacuum,  $c = c_0 = 2,99792458 \times 10^{10} \text{ cm}^{-1}$ . There is danger of confusion between the wave number  $\tilde{\nu} = 1/\lambda$ , which is the reciprocal of the wave length, and the wave number (wave number vector)  $k = 2\pi/\lambda$ , see chapter 2.1.

In Fig. 6.7, the experimentally observed vibrational levels for  $H_2$  are shown. The solid line potential curve is fit to the levels by using higher terms, and the dotted line is the Morse potential. The Morse potential is only a good approximation up to  $v = 5$ . But for large values of  $v$ , the energy goes wrongly to minus infinite, see equ. (6.28).

**Fig. 6.7** taken from Herzberg: Einführung in die Molekülspektroskopie, page 19.

An arbitrarily good fit can be reached using a potential of the form

$$\frac{E(v)}{\omega\hbar} = \left(v + \frac{1}{2}\right) - x_e \left(v + \frac{1}{2}\right)^2 + y_e \left(v + \frac{1}{2}\right)^3 + \dots \quad (6.30)$$

## 6.2.2 Vibrations in Multi-Atomic Molecules

A general introduction to vibrations in multi-atomic molecules was presented in chapter 3.3.3. Most importantly, normal vibrations and normal coordinates were introduced there.

A different view of these parameters presents itself by sketching the computational technique for normal coordinates and normal vibrations.

Consider the  $3N$  coordinates  $x_i$  of  $N$  atoms, and set the equilibrium position to be at  $x_i = 0$ , see chapter 3.3.3. The Taylor expansion of the potential energy for a displacement of the coordinates  $x_i$  up to the term of second order is

$$U(x_i) \approx U(x_i = 0) + \left( \frac{\partial U}{\partial x_i} \right)_{x_i=0} x_i + \frac{1}{2} \left( \frac{\partial^2 U}{\partial x_i \partial x_j} \right)_{x_i=x_j=0} x_i x_j. \quad (6.31)$$

Without limiting the generality, we can set  $U(x_i = 0) = 0$ . Since the potential minimum is in the equilibrium position  $x_i = 0$ , the first term derivative is zero at this location. From equ. (6.31), the harmonic approximation follows:

$$U(x_i) = \frac{1}{2} \left( \frac{\partial^2 U}{\partial x_i \partial x_j} \right)_{x_i, x_j=0} x_i x_j = \frac{1}{2} U_{i,j} x_i x_j \quad \text{where} \quad U_{i,j} = \left( \frac{\partial^2 U}{\partial x_i \partial x_j} \right)_{x_i, x_j=0}. \quad (6.32)$$

The derivatives are constructed at the point  $x_i, x_j = 0$ , and from the reversibility of the order of the derivatives, it follows that  $U_{ij} = U_{ji}$ . If we also assume for each vibrating particle of mass  $m_i$  a kinetic energy  $T_i = \frac{1}{2} m_i (\partial x_i / \partial t)^2 = \frac{1}{2} m_i \dot{x}_i^2$ , we get as the total energy of all particles

$$E = T + U = \frac{1}{2} \sum_i m_i \dot{x}_i^2 + \frac{1}{2} \sum_{i \neq j} U_{ij} x_i x_j. \quad (6.33)$$

With the substitutions  $x'_i = x_i \sqrt{m_i}$  and  $U'_{ij} = U_{ij} / \sqrt{m_i m_j}$  we conclude from equ. (6.33)

$$2E = \sum_i \dot{x}'_i{}^2 + \sum_{i \neq j} U'_{ij} x'_i x'_j = \dot{\mathbf{x}}' \dot{\mathbf{x}}'^T + \mathbf{x}' \mathbf{U}' \mathbf{x}'^T. \quad (6.34)$$

On the right hand side of equ. (6.34), the summation notation is replaced by matrices, where  $\dot{\mathbf{x}}'$  and  $\mathbf{x}'^T$  as vectors represent row and column matrices. The matrix  $\mathbf{U}'$  undergoes a principal axes transformation by multiplying it with an appropriate unitary matrix  $\mathbf{A}$ , so that for  $\mathbf{A} \mathbf{U}' \mathbf{A}^{-1} = \mathbf{A} \mathbf{U}' \mathbf{A}^T$  we get a matrix with  $3N$  eigenvalues  $\lambda_i$  on the diagonal (and zero for  $i \neq j$ ).

**Rules of Matrix Calculations:**

The following applies to a quadratic matrix  $A$  with the elements  $A_{ik} = (A)_{ik}$ :

The *complex conjugate* is written as  $A^*$ , where  $(A^*)_{ik} = (A)_{ik}^*$ .

The *transpose* of the matrix is  $A^T$  or  $\tilde{A}$ , where  $(\tilde{A})_{ik} = (A)_{ki}$ .

The *adjoint of the matrix or hermitian conjugate* is  $A^\dagger$  or  $A^\ddagger$ , where  $(A^\dagger)_{ik} = (A)_{ki}^*$ .

In a *hermitian or self-adjoint* matrix (physical quantities with real eigenvalues),  $A^\dagger = A$ , and it has an orthogonal basis of eigenvectors.

In a *unitary* matrix,  $A^\dagger = A^{-1}$ , where the *inverse* matrix  $A^{-1}$  is defined by  $E = AA^{-1}$ , and  $E$  is termed the *unit* matrix. In quantum mechanics and for principal axes transformations in general, unitary transformations are used.

The vector  $q$  is introduced so that  $x' = qA$  and  $x'^T = A^T q^T$  hold. With that, the harmonic term on the right hand side of equ. (6.34) is replaced:  $x'U'x'^T \rightarrow qAU'A^T q^T$ . The inner part  $AU'A^T$  is a diagonal matrix with  $\lambda_i$  eigenvalues. Using summation notation, the result is

$$2E = \sum_i \dot{q}_i^2 + \lambda_i q_i^2. \quad (6.35)$$

Normal coordinates are represented by  $q_i$ . The normal frequencies are  $\lambda_i = \omega_i^2$  and  $\omega_i$ . Six values (3 translations and 3 rotations) are zero. If more than one  $\omega_i$  has the same value, we have degeneration.

**6.3 Rotation-Vibration Spectra****6.3.1 Rotation-Vibration Spectra of Diatomic Molecules**

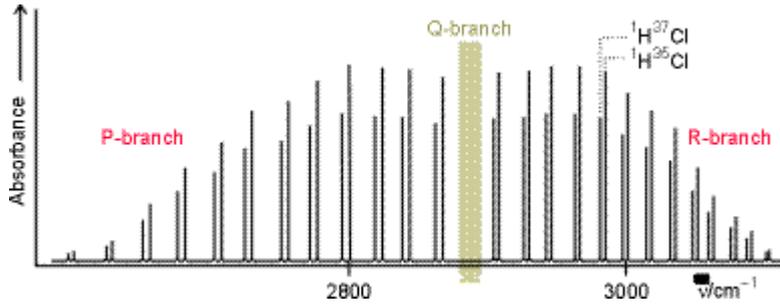
In gases at low pressure (no Doppler broadening), we can observe a rotational structure to the vibrational transitions. By using the rotational constants  $B$ , see equations (6.02), (6.03), and (3.26), the rotation-vibration energy of a diatomic molecule in the harmonic approximation is

$$E(v, J)/h = (v + 1/2)\nu + B J(J + 1). \quad (6.36)$$

With  $''$  we label the ground state and with  $'$  the excited state. Let us now consider the transition  $v' - v'' = \Delta v = 1$  and  $J' - J'' = \Delta J = 0, \pm 1$ . If we make the simplified assumption that the moment of inertia of the molecule remains constant during the transition between the two vibrational states,  $B$  in equ. (6.36) is constant. For arbitrary values of  $v''$  and variable values of  $J''$  we get the equation for the transition frequency discovered by Henry Alexandre Deslandres in 1885.

$$E(v', J')/h - E(v'', J'')/h = \nu + B m, \quad (6.37)$$

In which for the variable values of  $J''$ ,  $m = 0$  when  $\Delta J = 0$ ,  $m$  is a positive whole number when  $\Delta J = +1$ , and a negative whole number when  $\Delta J = -1$ .



**Fig. 6.8** taken from Atkin 6<sup>th</sup> ed. Fig. 16.40 A high-resolution vibration-rotation spectrum of HCl. The lines appear in pairs because both H<sup>35</sup>Cl and H<sup>37</sup>Cl contribute.

Negative values of  $m$  ( $\Delta J = -1$ ) are responsible for the P-branch,  $m = 0$  ( $\Delta J = 0$ ) determine the Q-branch, and positive values of  $m$  ( $\Delta J = +1$ ) create the R-branch. A vibrational transition with a simultaneous rotational transition (Q-branch or  $\Delta J = 0$ ) occur if a rotation around the interatomic axis has a non zero moment of inertia. For diatomic molecules, this is only observed in paramagnetic NO.

From Fig. 6.8 we can already see the discrepancy between the predictions of the Deslandres equation and reality. Equation (6.36) describes a constant line separation  $B$ , but in Fig. 6.8, the line separation gets smaller as the wave number increases (energy, frequency). This is due to the changing average distance in the transition from  $v''$  to  $v'$ , and therefore  $I' \neq I''$  or  $B' \neq B''$ . Taking this into consideration, we conclude

$$\begin{aligned} \Delta E/h &= \nu + (B' + B'')(J'' + 1) + (B' - B'')(J'' + 1)^2 && \text{for } J'' = 0, 1, 2, \dots \text{ R-branch,} \\ \Delta E/h &= \nu + (B' - B'')J' + (B' - B'')J'^2 && \text{for } J'' = 0, 1, 2, \dots \text{ Q-branch,} \\ \Delta E/h &= \nu - (B' + B'')J'' + (B' - B'')J''^2 && \text{for } J'' = 1, 2, 3, \dots \text{ P-branch.} \end{aligned} \quad (6.38)$$

In a diatomic molecule,  $I' > I''$ , i.e.  $B' < B''$ , thus the final term is negative. With that it follows that in the R-branch the second term is positive, but the third term is negative and whose magnitude increases with the square of  $J''$ . From that we get a maximum or an edge, which

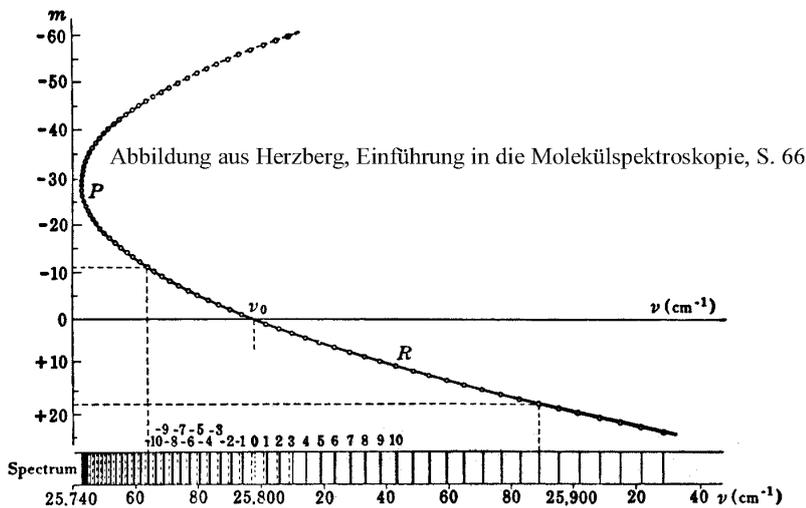


Abb. 42. Fortrat-Diagramm der CN-Bande bei 3883 Å. Zusätzlich zur Fortrat-Parabel wird unten ein schematisches Spektrum in demselben Maßstab gezeigt. Der Bandenursprung ist durch eine gestrichelte Linie markiert. Im Spektrum ist an dieser Stelle keine Linie zu finden.

**Fig. 6.9** Fortrat diagram of a CN band

has a shadow toward **Red**. In the P- and Q-branches, the frequency increases with  $J$  when  $I' > I''$ . In multiatomic molecules, it is possible that  $r'_e < r''_e$ , i.e.  $I' < I''$  or  $B' > B''$ . In this case, the P-branch has an edge which has a shadow toward **Purple** (violet). If the two considered vibrational states also belong to different electron states (additional electron transition), the moments of inertia differ all the more, and it can happen that in a diatomic molecule  $I' < I''$ . It can also happen that  $\Delta J = 0$  is forbidden, in which case the Q-branch does not appear.

### 6.3.2 Classification of Multiatomic Molecules

With the inertial tensor of a molecule transformed onto the principal axes, the following groupings hold:

|                                  |   |
|----------------------------------|---|
| $I_x = I_y = I_z$                | spherical top (spinning) molecules, e.g. CH <sub>4</sub>    |
| $I_x = I_y, I_z = 0$             | linear molecules, e.g. CO <sub>2</sub>                      |
| $I_x = I_y \neq I_z \neq 0$      | symmetric top molecules, e.g. C <sub>6</sub> H <sub>6</sub> |
| $I_x \neq I_y \neq I_z \neq I_x$ | asymmetric top molecules, e.g. ClFClBr                      |

A top is a solid body fixed at one point. In the molecules of the same name, that point is the centre of mass, which remains fixed during a free rotation.

These general groupings of molecules also follows the division of the rotation-vibration spectra. The rotational terms are further split by interactions with vibrations, e.g. by Coriolis interactions. Further selection rules appear which take into consideration whether the dipole moment of the vibrational transition is parallel or perpendicular to the axis of the top. This considerably complicates the classification of the spectra of multi-atomic molecules.

### 6.3.3 Localized Vibrations

Symmetry considerations allow statements to be made about the allocation of certain vibrations to a band found in the IR and/or Raman spectrum. For the determination of the normal coordinates, a consideration as trivial as that done for CO<sub>2</sub> in chapter 3.3.3 is rarely sufficient. Assuming a vibrational model (atomic masses, distances, angles, force constants) followed by normal coordinate analysis (chapter 6.2.2), and the final comparison of the calculated values to the experimentally measured lines is a very lengthy and involved process, which, due to the imprecision of the assumptions and the anharmonic approximation, does not necessarily lead to a correct result. Further complications are introduced into the splittings mentioned above especially by the presence of harmonics and combined vibrations, even if they appear with low intensities. In a few cases, the exchange of atoms or atomic groups (e.g. Cl ↔ Br, D ↔ H) in the ordering of bands can help.

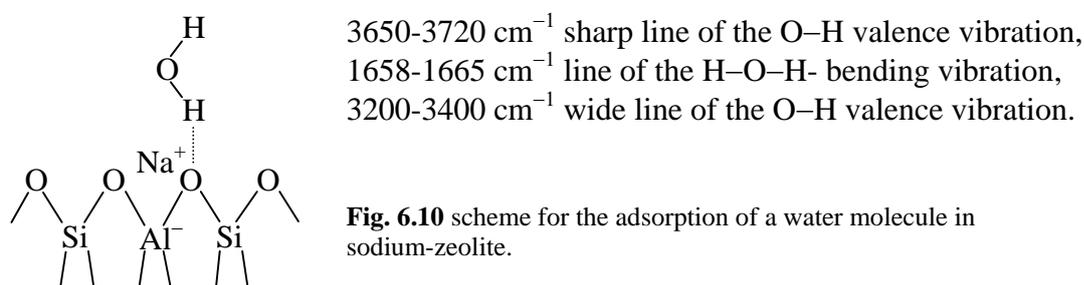
An important simplification which has led to the wide usage of IR-spectroscopy is achieved by using localized vibrations. These appear if a small coupling exists between the vibrations of the atomic groups under consideration and those of the rest of the molecule. The coupling is caused by different frequencies, i.e. force constants or masses. Sufficient frequency differences exist at 10 %, i.e. because  $\omega = \sqrt{k/m_r}$ , a difference in the force constants or the reduced masses of 20 % is necessary. Figure 6.10 shows a grouping of the localized vibrations. Such representations for the bonds in organic chemistry can be used as an aid to the classification of IR-bands in the spectra of substances under study. Take note that the appearance of a band is a necessary but insufficient condition for the presence of the corresponding bond in a substance under study.

### 6.3.4 Influencing the Position of the Characteristic Frequencies

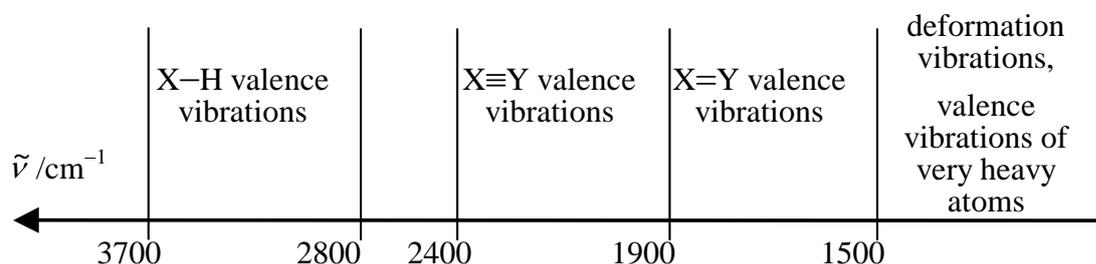
A coupling of the vibration with the rest of the molecule or other molecules causes a shift in the wave number. This can be demonstrated on acetone, in which solvents weaken the C=O bond. The following wave numbers were ascertained for the gas or solvent (in parenthesis):

$$\tilde{\nu}_{\text{C=O}} = \begin{matrix} 1742 \text{ cm}^{-1}, & 1728 \text{ cm}^{-1}, & 1720 \text{ cm}^{-1}, & 1718 \text{ cm}^{-1}, & 1712 \text{ cm}^{-1} \\ \text{(gas state)} & \text{(cyclohexane)} & \text{(dioxane)} & \text{(acetone)} & \text{(bromoform)}. \end{matrix}$$

A further example of the effect of the position of the characteristic frequencies is the shift of the O-H valence vibrations in a water molecule by the creation of a hydrogen bridge bond at an adsorption centre in the microcrystalline porous solid body sodium-zeolite. The following wave numbers for the O-H bonding vibrations is observed:



**Fig. 6.10** scheme for the adsorption of a water molecule in sodium-zeolite.



**Fig. 6.11** Localized vibrations. In the schematic representation below, X stands for the atoms C, O, and N and Y for C, and N, and H stands for the hydrogen atoms.



## 6.4 Absorption Spectroscopy in the Visible and Ultra-Violet Range

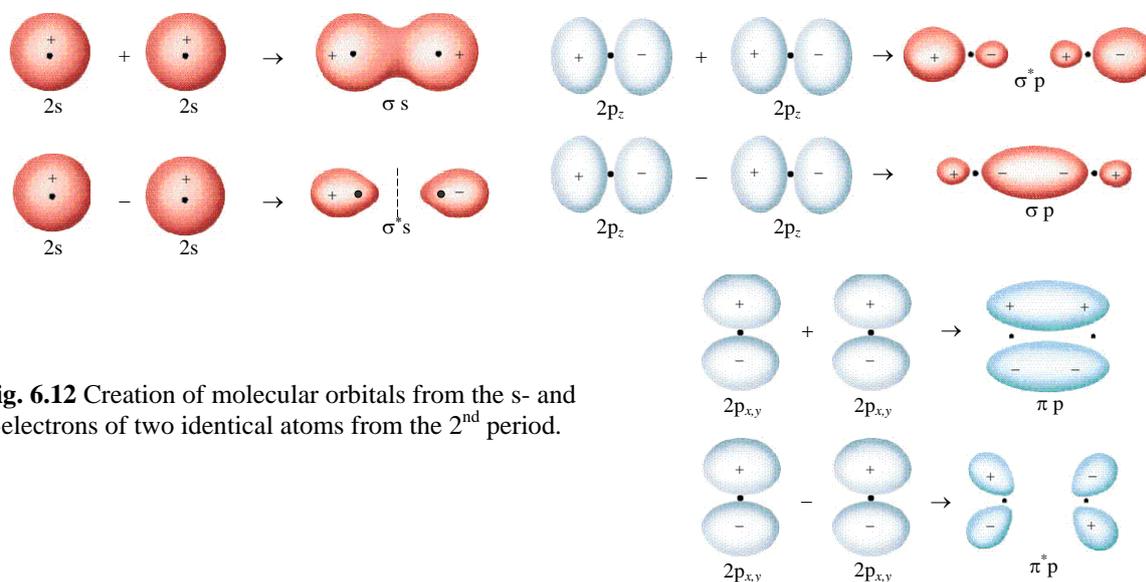
Electron spectroscopy is used for arbitrary electron transitions in which the principal quantum number changes. The transitions between the highest occupied and lowest unoccupied orbital in molecules have energies which range from  $1,5 \times 10^5$  to  $6 \times 10^5 \text{ J mol}^{-1}$ . That corresponds to the ultraviolet and visible range of the electromagnetic spectrum.

The oldest spectroscopic analysis methods lie in the UV/VIS range. Colours appear through the selective absorption of spectral colours, we see the complimentary colour.

The first works of Kirchhoff and Bunsen made the connection between the specific absorption or emission of light in a substance (absorption/emission spectra) and the structural properties of the substance. This is the basis of spectroscopy. Since the beginning of the last century, the connection between the bonding electrons and the UV/VIS spectra has been known.

### 6.4.1 Classification of the Transitions

Figure 6.12 demonstrates the creation of bonding and anti-bonding orbitals from s- and p-electrons, see chapter 3. It is based on the LCAO method for molecules of two identical atoms of the 2<sup>nd</sup> period. The  $\sigma$  orbitals have a rotationally symmetric charge distribution, with respect to the molecular bonding axis (z-direction), in  $\pi$  orbitals there is a nodal plane, which contains the molecular bonding axis. The anti-bonding orbital is denoted with an asterisk.

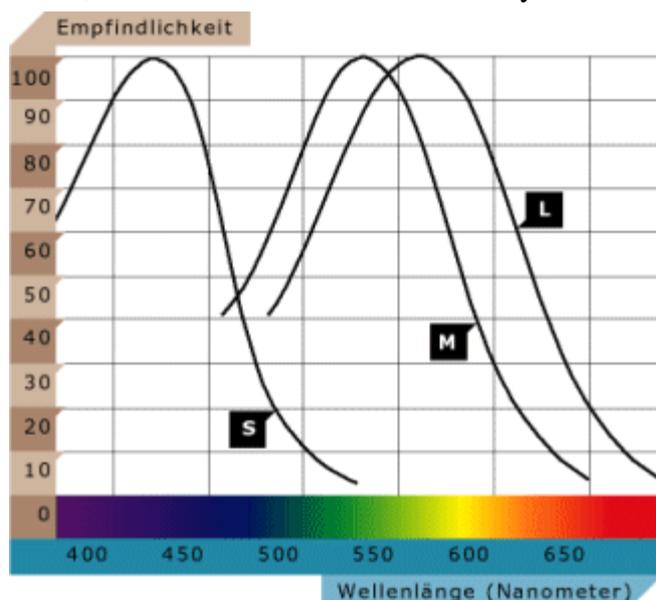


**Fig. 6.12** Creation of molecular orbitals from the s- and p-electrons of two identical atoms from the 2<sup>nd</sup> period.

Beside the bonding and antibonding states in the upper shells, there are in general also nonbonding states. If the d electrons are involved, there are also  $\delta$  bonds. For  $\sigma$ -bonds,  $|\lambda| = 0$ ,  $|\lambda| = 1$  in  $\pi$  bonds, and  $|\lambda| = 2$  in  $\delta$  bonds, see chapter 3.1.2.

The orbital energy normally increases in the sequence  $\sigma$ ,  $\pi$ ,  $n$ ,  $\pi^*$ ,  $\sigma^*$ . The transitions  $\sigma \leftarrow \sigma^*$  and  $n \leftarrow \sigma^*$  are in the UV-range, e.g. for ethane the  $\sigma \leftarrow \sigma^*$  transition in a vacuum is in the UV at 135 nm. (with respect to the wavelengths  $\lambda/\text{nm}$  it holds: infrared <780, red 700, orange 620, yellow 580, green 530, blue 470, violet 420, UV <380, quartz-UV <300, vacuum-UV <150.)

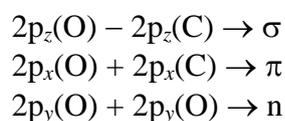
The  $\pi \leftarrow \pi^*$  - and  $n \leftarrow \pi^*$  transitions have lower energies in quartz-UV or for multiply conjugated double bonds in the visible range. 11-*cis*-retinal has six conjugated double bonds and absorbs in solution at 380 nm and in connection with protein even in the visible range. In the eye, the excited double bonds are rotated by photoabsorption, and 11-*trans*-retinal is created, which then isomerizes. The decay of the molecule sends a nerve impulse to the brain.



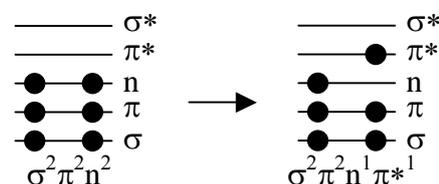
**Fig. 6.13.** The spectral sensitivity of the eye. The sensitivity of the S, M and L cones is proportional to the spectral absorption of the rhodopsins in the cones. Figure from Brockhaus Multimedial 2002.

#### 6.4.2 $n \leftarrow \pi^*$ Transitions, Specifically in Carbonyl Bonding

Unsaturated molecules which contain an oxygen or sulfur, have weak bands, e.g. aldehyde  $R-C=O$ , ketone  $R_2C=O$  at  $\lambda = 270\text{-}300\text{ nm}$ ,  $\epsilon = 1\text{-}2\text{ m}^2/\text{mol}$ . Die Carbonyl-p electrons in the ground state occupy the following orbitals (bonding in the z-direction, principal quantum number = 2, orbital quantum number  $\ell = 1$ , therefore  $2\ell + 1 = 3$  magnetic (directional) quantum numbers  $x$ ,  $y$  and  $z$ ):



Excitation:



In general it holds for the symmetry properties of the orbitals:

- The type of symmetry of the state is equal to the product of the types of symmetry of the individual electrons.
- The type of symmetry of an electron corresponds to the type of symmetry of the orbital of the electron.
- If two electrons are in the same orbital, their product determines the total symmetry type ( $A_{1g}$ ). Only the outer nonclosed orbitals need therefore be considered.

### 6.4.3 Consideration of the Symmetry Properties of the Ketones, Group $C_{2v}$

In the Carbonyl group, with  $z$  as the bonding direction and R,C and O in the  $y$ - $z$  plane, the  $\pi$  and  $\pi^*$  molecular orbitals, which are composed of the  $p_x$  atomic orbitals, lie in the  $x$ - $z$  plane and the  $n$  molecular orbital, constructed with the two  $p_y$  atomic orbitals of the oxygen atom, lie in the  $y$ - $z$  plane.

|  | type of symmetry / class | $E$   | $C_{2(z)}$ | $\sigma_{(yz)}$ | $\sigma_{(xz)}$ |    |
|--|--------------------------|-------|------------|-----------------|-----------------|----|
|  | $\pi$ orbital            | $B_1$ | +1         | -1              | -1              | +1 |
|  | $\pi^*$ orbital          | $B_1$ | +1         | -1              | -1              | +1 |
|  | $n$ orbital              | $B_2$ | +1         | -1              | +1              | -1 |

The ground state of the carbonyl group has the type  $A_1 \times A_1 \times A_1 \equiv A_1$ .

The excited state  $\sigma^2\pi^2n^1\pi^*1$  is of the type  $A_1 \times A_1 \times B_2 \times B_1 \equiv B_2 \times B_1 \equiv A_2$ .

In general, the condition for the existence of a dipole moment of a transition is:

$$\langle \text{ground state} \rangle \times \langle x \text{ or } y \text{ or } z \rangle \times \langle \text{excited state} \rangle \equiv A_{1g}$$

It can be seen from the character table  $C_{2v}$  that  $A_2$  contains no components of translation. The product of the three types is therefore  $\neq A_1$ , and the transition is forbidden. Because of the partial removal of the symmetry by the overlapping of the atomic vibrations, a weak band can still be seen in spite of the prohibition.

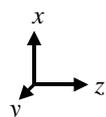
The extinction coefficient  $\epsilon$ , defined in chapter 2 as  $\log(I_0/I)_\lambda = \epsilon c d$

(where  $c$  = concentration,  $d$  = thickness), is for allowed electron transitions greater than 1000  $\text{m}^2/\text{mol}$ , for forbidden transitions below 100  $\text{m}^2/\text{mol}$ , as  $n \rightarrow \pi^*$  below 10, for ketones 1...2.

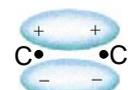
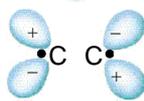
### 6.4.4 $\pi \leftarrow \pi^*$ Transitions, Specifically in Ethylene Bonding

Substances with isolated  $\pi$  electrons absorb at about 170 nm. If two double bonds in a molecule are separated by two or more saturated hydrocarbons, they are called isolated. A stronger interaction between the double bonds gives the following shifts:

|               |        |                 |        |
|---------------|--------|-----------------|--------|
| $>C=C<$       | 174 nm | $-C=C-C=C-$     | 220 nm |
| $-C\equiv C-$ | 170 nm | $-C=C-C=C-C=C-$ | 260 nm |
| $>C=O$        | 166 nm | $-C=C-C=C-C=O$  | 270 nm |



In ethylene bonding (group  $D_{2h}$ ) with  $z$  as bonding direction and all nuclei in the  $y$ - $z$  plane, it holds:

|  | symmetry type/class | $E$ | $C_{2(z)}$ | $C_{2(y)}$ | $C_{2(x)}$ | $i$ | $\sigma_{(xy)}$ | $\sigma_{(xz)}$ | $\sigma_{(yz)}$ |
|--|---------------------|-----|------------|------------|------------|-----|-----------------|-----------------|-----------------|
| <br>$\pi$ orbital   | $B_{3u}$            | +1  | -1         | -1         | +1         | -1  | +1              | +1              | -1              |
| <br>$\pi^*$ orbital | $B_{2g}$            | +1  | -1         | +1         | -1         | +1  | -1              | +1              | -1              |
| $z$ translation  | $B_{1u}$            | +1  | +1         | -1         | -1         | -1  | -1              | +1              | +1              |

It is easy to verify that the following holds:

$$\text{character}(B_{3u}) \times \text{character}(B_{2g}) \times \text{character}(B_{1u}) = \text{character}(A_{1g}) \equiv (1,1,1,1,1,1)$$

From this product we get of the characters of the starting state, the excited state, and for the  $z$ -translation the total symmetric type. We are therefore dealing with an allowed transition. A strong band ( $\varepsilon = 1700 \text{ m}^2/\text{mol}$ ) is observed at 174 nm. Additionally, an excited state with  $\pi^0\pi^{*2}$ , thus  $B_{2g} \times B_{2g}$  can come into being. Since  $A_{g1}$  has no translation, this band is forbidden ( $\varepsilon < 1 \text{ m}^2/\text{mol}$ ,  $\lambda = 200 \text{ nm}$ ).

## 6.5 Franck-Condon Principle

Transitions from one electron state to another happen so quickly that the slow nuclear vibrations of a heavy nucleus cannot follow, i.e. the interatomic distance hardly changes during the transition. In absorption, the transition normally moves an electron from the vibrational ground state into an excited electron state. In the excited electron state, the vibrational states which require no change of the interatomic distance are adopted. From that we get the vibrational structure of the electron spectrum.

James Franck explained this vibrational structure semi-classically. Edward Uhler Condon found the wave mechanical formulation of the Franck-Condon principle. It corresponds to the Born-Oppenheimer approximation formulated by Max Born and Julius Robert Oppenheimer, according to which the states of the electrons are independent of the nuclear states. This fact is also called the adiabatic approximation, since the assumption is made that the electrons follow the nuclei without inertia through their equilibrium states (i.e. adiabatically).

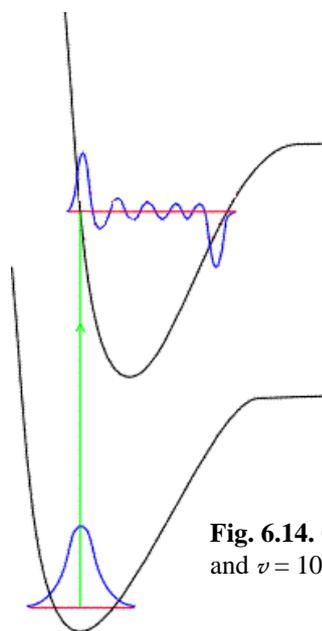
Let us consider the dipole moment of the transition from level 1 to level 2, introduced in chapter 2, equ. (2.56):

$$M_{21} = q \int \psi_2^* \hat{r} \psi_1 d\tau, \quad (6.39)$$

Both states are described by the product of two wave functions each, which characterize the vibrational and electron states (neglecting the rotation). With that,  $\psi_1 = \psi_{1v}\psi_{1e}$  and

$\psi_2 = \psi_{2v}\psi_{2e}$ . Additionally, the operator  $\mathbf{r} = \mathbf{r}_v + \mathbf{r}_e$  is separated into a sum of two operators, which operate on either the wavefunctions of the vibrations or the electrons. From that we get the dipole moment of the transition

$$\begin{aligned} M_{21} &= q \int \psi_2^*(v, e) \hat{\mathbf{r}}(v, e) \psi_1(v, e) d\tau(v, e) \\ &= q \int \psi_2^*(v) \psi_2^*(e) [\hat{\mathbf{r}}(v) + \hat{\mathbf{r}}(e)] \psi_1(v) \psi_1(e) d\tau(v) d\tau(e) \\ &= q \int \psi_2^*(v) \psi_1(v) d\tau(v) \int \psi_2^*(e) \hat{\mathbf{r}}(e) \psi_1(e) d\tau(e) \\ &\quad + q \int \psi_2^*(v) \hat{\mathbf{r}}(v) \psi_1(v) d\tau(v) \int \psi_2^*(e) \psi_1(e) d\tau(e). \end{aligned} \quad (6.40)$$



**Fig. 6.14.** Overlap of the wave functions for  $v = 0$  in the lower and  $v = 10$  in the upper electron level (taken from Atkins 6<sup>th</sup> ed.)

Because of the orthogonality of the electron wavefunctions,  $\int \psi_2^*(e) \psi_1(e) d\tau(e)$  is zero, and the sum on the right in equ. (6.40) disappears. The same is not true for the sum on the left, since the vibrational wavefunctions belong to two different sets of functions. The factor  $q \int \psi_2^*(e) \hat{\mathbf{r}}(e) \psi_1(e) d\tau(e)$  describes the dipole moment of the electron transition and goes quadratically into the intensity of the spectral line, see equ. (2.93) of chapter 2. The square of  $\int \psi_2^*(v) \psi_1(v) d\tau(v)$  describes the relative excitement of the corresponding vibrational band. It increases with increasing overlap of the wavefunctions of the vibration in the excited electron state with the vibrational ground state ( $v = 0$ ) of the lower electron state. This fact is demonstrated in Fig. 6.14.

## 6.6 Literature

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