Universität Leipzig
Fakultät für Physik und Geowissenschaften

Optical spectroscopy
of colour centres and molecules
(Franck-Condon principle)

An experiment of the advanced laboratory

prepared by
Dr. Volker Riede

Contents

Chapter 1

Task

1. By means of absorption bands of a holmium oxide filter determine the wavelength accuracy of the spectrometer Lambda 40. Investigate the influence of slit width and scanning speed on the spectrum.

2. Record and interpret the transmission spectra of glass and quartz glass cuvettes filled with both air and water. Furthermore, record and discuss the transmission spectrum of an interference filter in dependence of the angle of incidence. In addition, determine the visible spectral range of the eye. Moreover, transmission curves of colour filters may be measured.

3. Measure the transmission spectrum of iodine vapour. Determine the convergence energy, the energy of dissociation of the ground and excited state, and the energy of the electronic transition.

4. Generate F-centres in a KBr crystal by means of UV irradiation and measure their transmission spectrum. Determine the concentration of F-centres from the integral absorption in dependence on time after irradiation. In these spectra, identify the excitation energy and the linewidth.

5. In a NaCl crystal, F-centres were generated by irradiation with x-rays. Record the transmission spectrum of these centres and determine excitation energy, linewidth and the concentration of F-centres.

6. Calculate the excitation energy of F-centres in KBr and NaCl using both a classical and quantum mechanical model and compare these values with the experimental ones. Discuss the results of both models. Using the quantum mechanical model, determine the lattice constant from the experimental excitation energy.

Chapter 2

Introduction

It may seem remarkable to investigate colour centres, a typical solid-state phenomenon, and molecular spectra together in one laboratory experiment. However, in both cases one is concerned with electronic transitions that interact with vibrations of atoms. colour centre (F-centre) is an anion vacancy in an alkali metal halide crystal (e.g. NaCl, KBr) that is occupied by one electron. This electron can be excited from the ground state to an excited state by light irradiation. In doing so, it interacts with the surrounding atoms and their motion. Similarly, the electronic transitions in a molecule are coupled with its vibrational and rotational degrees of freedom. The energy scales of the electronic, vibrational and rotational degrees of freedom differ by orders of magnitude.

The common physical problem of colour centres and molecular spectra is hence the interaction of electronic transitions with the vibrations of atoms. The rotation of a molecule is not considered in this experiment due to its small energy scale that requires a very high resolution. Also, rotation does of course not occur in the solid. Let it be pointed out, that in the laboratory experiment *Rotation-vibration spectra of molecules* the interaction of rotation and vibration in a HCl molecule is studied.

Another commonality of the two phenomena is the validity of the Franck-Condon principle. This principle, discussed in more detail below, states that the transition of an electron from one state to another occurs much faster than a vibrational transition. Essentially, this means that position and velocity hardly change during an electronic transition.

This instruction is organized as follows: In section 3, the theoretical basics necessary for understanding I_2 spectra and colour centres are discussed. Section 4 contains information on the experiment, especially on the spectrometer and the procedure of recording spectra. Necessary tables and a bibliography follow.

Chapter 3

Theory

3.1   I$_2$ spectra

3.1.1   Electronic transitions

In the following section, possible energy transitions in a diatomic homonuclear molecule will be discussed. In doing so, three possible physical processes need to be considered. Similar to an atom, there exist electronic transitions in a molecule, e.g. the excitation of a valence electron from the ground state to an excited state. This can be achieved, for example, by light irradiation whose energy can range from the visible to the ultra-violet depending on the particular molecule or transition, i.e. energies of of only a few electron volts (eV). Contrary to atomic spectra, these spectra are superimposed by vibrational and rotational transitions in the molecule. Vibrational and rotational transitions have energy scales of 1/10 eV and 1 meV, respectively.

The calculation of the electronic states is done, like for an atom, by solving the Schrödinger equation which yields the energy eigenvalues and eigenfunctions. But for a diatomic molecule a strong axial symmetry caused by the Coulomb interaction between the two atoms needs to be considered, additionally. In contrast to a single atom, the symmetry of the system is reduced which generally leads to a lifting of degeneracy of energy states. In other words, there are less symmetry operations in a molecule under which the Hamiltonian is invariant.

For a detailed treatment of the above mentioned problems the reader be referred to lecture scripts and corresponding literature, e.g. [1, 2, 3]. In the following, some remarks on the classification and symbolic notation of electronic states of molecules with more than one valence electron will be made. Same as for atoms, the electronic states of molecules are labelled by quantum numbers. The principal quantum number n denoting the electron shell is usually omitted in the symbolic notation. In a many-electron system the properties of the entire electron hull are in good approximation composed of the individual contributions of the single atoms. Thereby, the inner filled shells will not be considered since their resulting angular momentum is equal to zero. Along the connection between the two nuclei, the components λ_i of the outer electron's angular momentum add up to the total angular momentum $|\vec{\Lambda}|$, i.e.,

$$|\vec{\Lambda}| = \sum_{i=1}^{N} \lambda_i$$

where N is the number of electrons. For $|\Lambda|$ the quantisation rule

$$|\vec{\Lambda}| = \Lambda\hbar,$$

with $\Lambda = 0$, 1, 2,... follows from quantum theory.

The corresponding states are denoted as Σ, Π, Δ and Φ. Thus, $\Lambda = 2$ represents a Δ-state. The notation is analogous to S, P, D and F for atoms with several valence electrons. the selection rules for electronic transitions also follow from quantum theoretical calculations and state that

$$\Delta\Lambda = 0 \text{ and } \pm 1\,.$$

Also the intrinsic angular momentum of the electron, the spin, adds up to a total spin momentum $\vec{S}$ whose component along the connecting line of the nuclei is denoted as $\vec{\Sigma}$. It holds that

$$|\vec{\Sigma}| = \Sigma\hbar,$$

with Σ = S, S-1, ..., -S, (2S+1 values) and S the total spin.

The interaction between the total angular momentum Λ and the total spin causes a splitting of molecular states. Every Λ splits into $2S + 1$ values. This is called the multiplicity $M = 2S + 1$. For a total spin of $S = 3/2$ one has a fourfold splitting.

For the characterisation of an electronic state in a molecule, as opposed to an atom, two more pieces of information are necessary that capture the symmetry properties and lead to different states. Under inversion, the wave function can be either symmetric or antisymmetric. The state then either remains unchanged (even, e) or is phase shifted by a factor of π (odd, change of sign, u). The second symmetry property concerns the mirror plane along the long axis between the two atoms. If the wave function is symmetric with respect to mirroring it is denoted by $+$; for the other case with $-$. This differentiation is required in particular for S-states, since there is no degeneracy with respect to the sign of the angular momentum component along the axis of the molecule.

Thus, the electronic state of a molecule can be described as follows:

$$^{\mathrm{M}}\Lambda^{\pm}_{(\mathrm{g,u})}. \tag{3.1}$$

For example, $^3\Lambda^+_\mathrm{g}$ corresponds to $\Lambda = 1$ and $M = 3$. From $M = 3$ it follows that $S = 1$ and hence Σ = -1, 0, 1. The notation g and $+$ was discussed in the text.

Let it be noted as a supplemental remark that some textbooks put an X in front of (3.1) for the characterisation of the ground state and letters A, B, C, ... for the excited states with increasing energy, e.g. X $^1\Lambda^+_\mathrm{g}$ for the ground state and B $^3\Pi^{\pm}_\mathrm{u}$ for the excited state of the iodine molecule.

3.1.2 Oscillatory motion of a diatomic molecule

In the following, some statements about the oscillatory motion of diatomic molecules and their interaction with electronic transitions will be made. In first approximation the oscillation of such a molecule can be described by the harmonic oscillator. In the equilibrium position both atoms with masses m_1 and m_2 are a distance r_0 apart (Fig. 3.1).
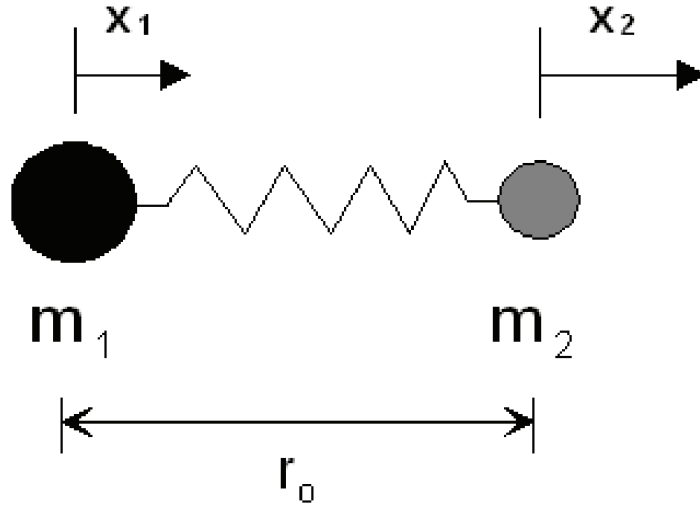
Figure 3.1: Oscillator model.

The restoring force in the harmonic approximation is proportional to the difference in the two displacements of the atoms:

$$m_1\ddot{x}_1 = -k(x_1 - x_2)$$
$$m_2\ddot{x}_2 = -k(x_2 - x_1).$$

With $x = x_1$ - x_2 and $\mu = m_1 m_2/(m_1 + m_2)$ it follows that

$$\ddot{x} = \frac{k}{\mu}x\,. \tag{3.2}$$

This is just the equation of motion of the harmonic oscillator with force constant k and resonance wavenumber

$$\bar{v}_s = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}.$$

The solution of the equation of motion (3.2) yields

$$x = x_0 \sin(2\pi c\bar{v}_s t). \tag{3.3}$$

Thus, in this classical picture the oscillation of the diatomic molecule is described.

For the quantum mechanical treatment the knowledge of U is required. From

$$F = -kx = \frac{\mathrm{d}U}{\mathrm{d}x} \tag{3.4}$$

and equation (3.3) it follows that

$$U = 2(\pi c\bar{v}_s)^2 \mu x^2. \tag{3.5}$$

The Schrödinger equation is then

$$\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} + \frac{8\pi^2\mu}{h}\left(E - 2(\pi c\bar{v}_s)^2\mu x^2\right)\Psi = 0, \tag{3.6}$$
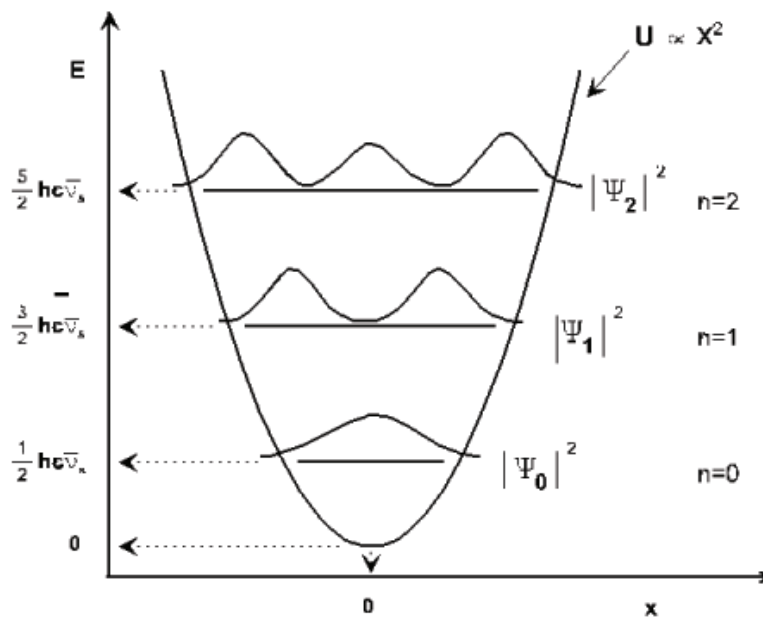
6

Figure 3.2: The harmonic oscillator and its energy levels with vibrational quantum number n.

with total energy E, wave function Ψ and Planck's constant h.

Regarding the solution of eq. (3.6) it must be referred to the lecture or textbooks. For the energy one obtains

$$E(n) = hc\bar{v}_s(n + \frac{1}{2}), \qquad n = 0,1,2,\ldots .$$

So, there exist discrete energy levels for which (if $n = 0$) $E = (1/2)hc\bar{v}_s$ is the zero-point energy. According to quantum mechanical calculations only those transitions are allowed for which $\Delta n = \pm 1$. The wave functions for the individual energy levels are given by

$$\Psi_n \propto H_n x \exp(-\frac{x^2}{2}),$$

with Hermite polynomials of order n, H_n. The graphical representation of the results is shown in Fig. 3.2. The product $|\Psi|^2$ represents the probability to find the mass of the oscillator at position x.

The ansatz in eq. (3.4) is merely an approximation of an oscillating diatomic molecule and there are in fact several reasons to look for a generalisation. First, experiments showed that the spacing of energy levels is not a constant $hc\bar{v}_s$ but instead decreases with increasing n. Second, for sufficiently large displacements the molecule must dissociate into two single atoms since the bonding forces become to small at large nuclear distances. And third, the repulsion of the nuclei for distances smaller than r_0 have to be taken into account. The so-called Morse potential of the anharmonic oscillator represents such a generalisation (cf. Fig. 3.3). It is given by

$$U = E_D(1 - e^{-ax})^2. \tag{3.7}$$

For large x it holds that $U = E_{\mathrm{D}}$ and E_{D} is the energy of dissociation of the molecule. For small x the harmonic approximation must be valid and equation (3.7) can be expanded accordingly:

$$U = E_{\mathrm{D}} \left(1 - (1 - ax)\right)^2 = E_{\mathrm{D}} a^2 x^2. \qquad (3.8)$$

Equations (3.8) and (3.5) must be equal from which follows that

$$a = 2\pi \bar{v}_s c \sqrt{\frac{\mu}{2E_{\mathrm{D}}}} = \omega_s \sqrt{\frac{\mu}{E_{\mathrm{D}}}}.$$

The constant a is characteristic of the molecule. The solution of the Schrödinger equation with eq. (3.7) as potential energy yields the following energy eigenvalues:

$$E(n) = hc\bar{v}_s \left[(n + \frac{1}{2}) - y_e(n + \frac{1}{2})^2 + ... \right]. \qquad (3.9)$$

Higher terms are omitted because eq. (3.9) explains experimental results sufficiently well. y_e is the anharmonicity constant. Figure 3.3 illustrates the anharmonic Morse potential and the probability density $|\Psi|^2$.
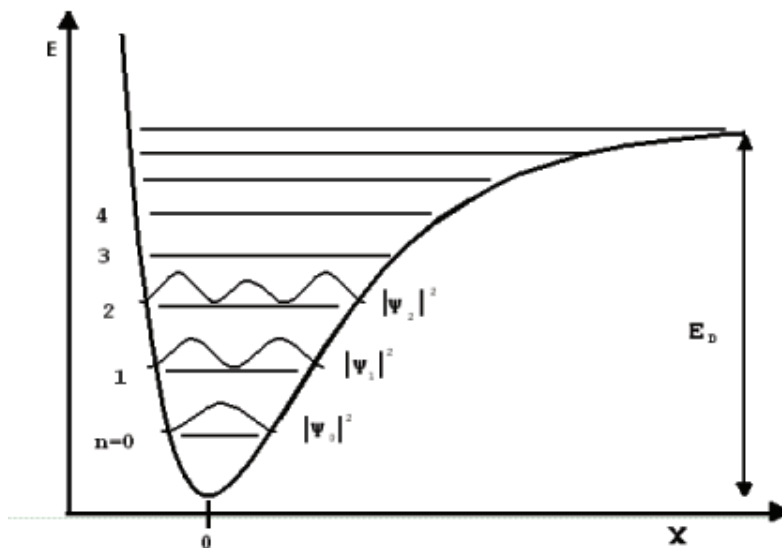

Figure 3.3: Anharmonic oscillator with vibrational energy levels n and probability density $|\Psi_n|^2$.

3.1.3 Electronic and vibrational transitions

Next, one can ask how the transitions look like during which both the electronic and the vibrational state change.

For this, one has first to consider that the equilibrium distance, at position $x = 0$ in Fig. 3.3, actually depends on the current electronic state, i.e., the binding of the two atoms will in general change after an electronic excitation. Figure 3.4 shows three possible arrangements of the potential curves of the electronic ground and excited states. In

Fig. 3.4(a) the binding does not change in the excited state, in Fig. 3.4(b) it is stronger, and in Fig. 3.4(c) - and that is the most probable case - the binding is weaker. Now, the question is which transitions are possible.
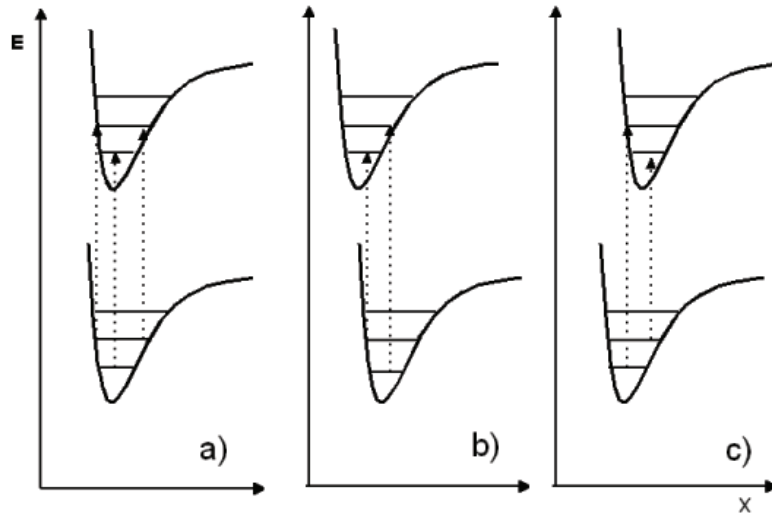

Figure 3.4: Potential curves in dependence on the electronic state. The equilibrium position in the excited state can be either unchanged (a), reduced (b), or larger (c).

Transitions between two potential curves are no longer limited by strict selections rules but are instead determined by the Franck-Condon principle and the probability $|\Psi|^2$. The Franck-Condon principle states that due to the large difference between the electron and nuclear masses an electronic transition happens much faster than a change in nuclear position and momentum. Regarding the position of the nuclei this means that a transition must occur vertically, with $x = $ const., as shown in Fig. 3.4. A constant momentum, or velocity, means that the transition occurs where the probability amplitude $P = \int \Psi'^* \Psi d\boldsymbol{r}$ is maximal. In the classical picture this would coincide with the turning points of the mass. They are at the intersection of an energy level with the potential curve. However, this is not generally in agreement with quantum mechanical results. Thus, one has the situation as shown in Fig. 3.5.

The vibrational states in the electronic ground state are denoted by n'', those in the excited state by n'. The most probable transition in Fig. 3.5 happens from $n'' = 0$ to $n' = 3$. The transition from $n'' = 0$ to $n' = 2$ and $n' = 4$ are less probable. The intensity distribution I for these transitions is shown in Fig. 3.6(a). For the transition energy one obtains together with eq. (3.9)

$$\Delta E(n',n'') = E(n') - E(n'')$$

$$= E_{\text{electr}} + hc\bar{v}'_s(n' + \frac{1}{2}) - hc\bar{v}''_s(n'' + \frac{1}{2})$$

$$- hc\bar{v}'_s y'_e(n' + \frac{1}{2})^2 + hc\bar{v}''_s y''_e(n'' + \frac{1}{2})^2,$$

where higher orders are omitted and E_{electr} is defined in Fig. 3.5.
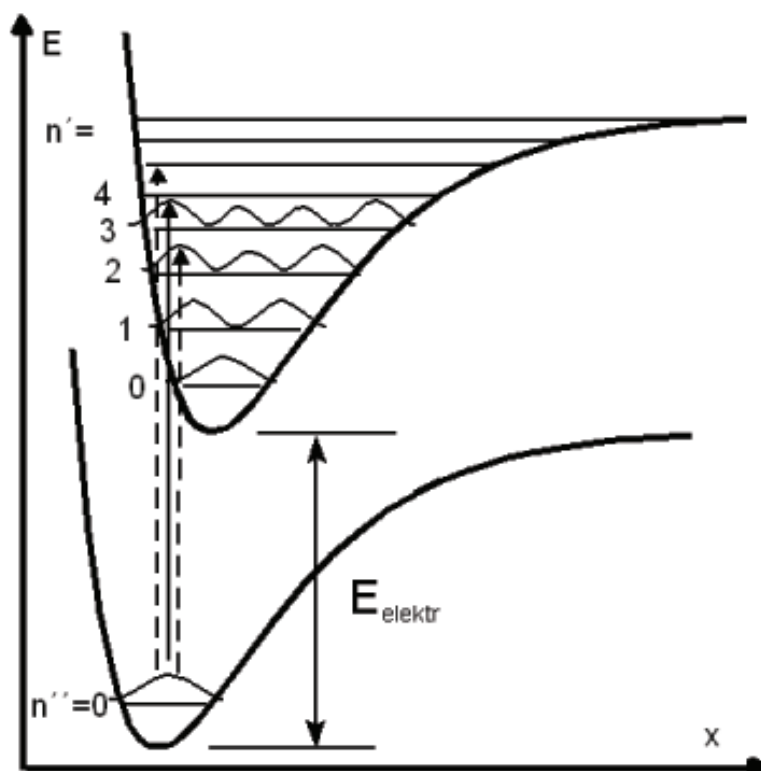
Figure 3.5: Electronic transitions according to the Franck-Condon principle.
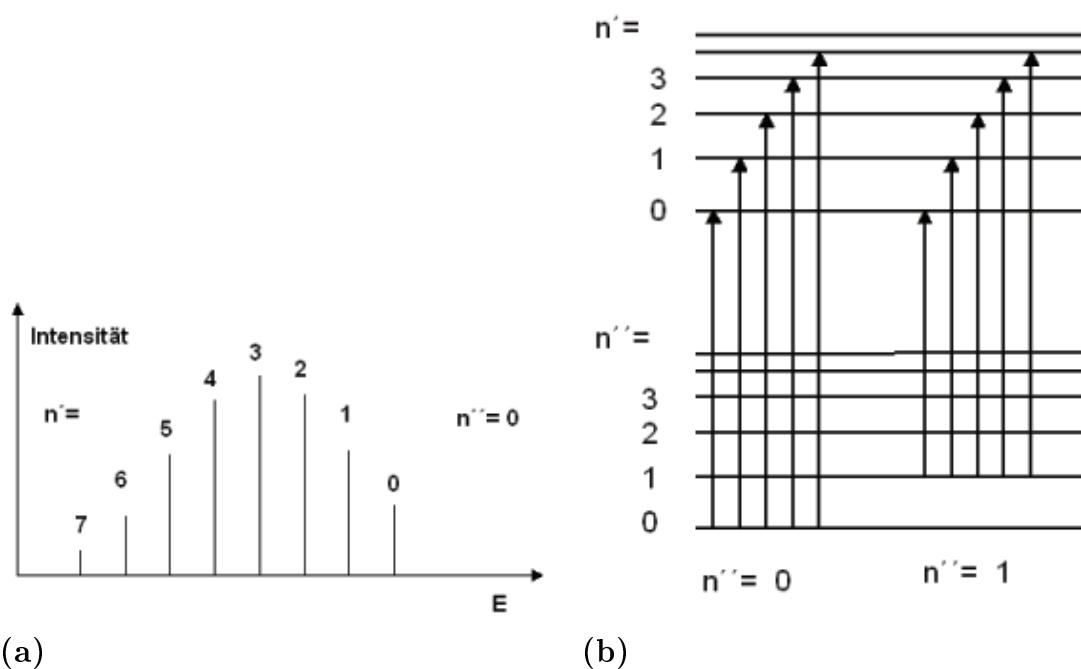

(a)   (b)

Figure 3.6: Intensity distribution of electronic-vibrational transitions (a) and all other ones that are in principle possible (b).

3.1.4 Energy of dissociation

An important parameter for the characterisation of a molecule is the energy of dissociation E_D (see Fig. 3.3). It can be understood as the energy that must be transferred to a
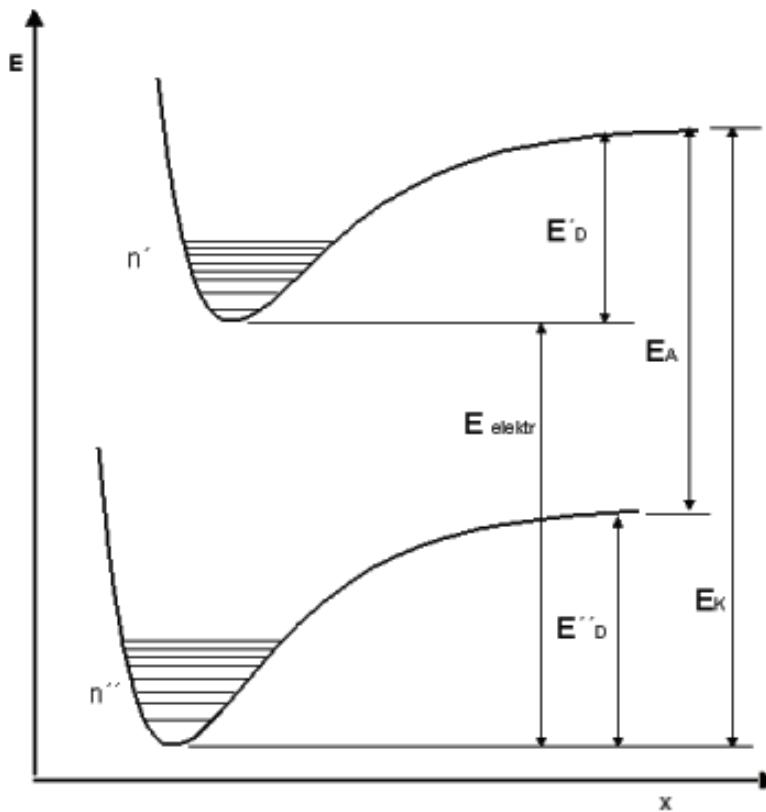
Figure 3.7: Definition of transition energies.

molecule in order to dissemble it into its atoms. One could assume that it was sufficient to transfer an energy of E_D to the system and dissociate the molecule. However, the corresponding transitions with large Δn would be very unlikely according to the selection rules. This fact also agrees with the Franck-Condon principle allowing only vertical transitions. These, in turn, are very unlikely since for higher vibrational states the quantum mechanical probability density is significant only in the vicinity of the potential curve (cf. classical picture: the turning points of the oscillating mass). Hence, a molecule cannot be dissociated in this way. On the other side, the probability amplitude P can be very different, i.e. larger, for a transition involving also an electronic excitation. An illustration of the energetic situation is shown in Fig. 3.7.

The vibrational states of the lower and upper electronic state are denoted as n'' and n', respectively. The energies of dissociation are denoted accordingly, E_D'' and E_D'. Transitions of highest energy converge to the limit E_K. This value cannot be read off the measured spectra. Assuming the transitions have the ground state $n'' = 0$ it follows from eq. (3.10) that

$$\Delta E = E_{\text{electr}} + E_S'(n' + \frac{1}{2}) - E_S' y_e'(n + \frac{1}{2})^2, \tag{3.10}$$

with $E_s' = hc\bar{v}_s$ and negligible zero-point energy.

Plotting the measured transmission minima, corresponding to maxima in absorption, versus n' they converge to an upper limit E_K. At the same time, absolute knowledge of n' is not required for determining E_K. Calculating the energetic difference $\Delta(\Delta E)$ of two

lines at n' and $n' + N$ it follows from eq. (3.10) that

$$
\begin{aligned}
\Delta(\Delta E) &= E_S'(n' + N + \frac{1}{2}) - E_S'(n' + \frac{1}{2}) \\
&\quad - E_S' y_e'(n' + N + \frac{1}{2})^2 + E_S' y_e'(n' + \frac{1}{2})^2 \\
&= E_S' N - E_S' y_e' N(2n' + N + 1).
\end{aligned}
$$

For two neighbouring lines $(N = 1)$ it holds that

$$
D_L = \Delta(\Delta E) = E_S' \left(1 - 2y_e'(n' + 1) \right), \tag{3.11}
$$

i.e., the distance of two lines depends linearly on n'. According to eq. (3.11) the following holds:

1. For $E = E_K$, $\Delta(\Delta E) = 0$ and then with $n' = n_E'$ one obtains from eq. (3.11):

$$
n_E' = \frac{1}{2y_e'} - 1. \tag{3.12}
$$

2. Since D_L depends linearly on n' neighbouring values of D_L have a constant value:

$$
D_L(n') - D_L(n' + 1) = -2E_S' y_e' = \text{const.} \tag{3.13}
$$

E_S' is known from other experiments ($E_S' = 0.0159$ eV for I_2) and one can determine y_e' and n_E' from eqs. (3.13) and (3.12), respectively. According to eq. 3.10 it holds for $n' = n_E'$ that

$$
\Delta E(n' = n_E) = E_K = E_{\text{elektr}} + E_S'(n_E' + \frac{1}{2}) - E_S' y_e'(n_E' + \frac{1}{2})^2.
$$

Since the quantities E_K, n_E', E_S' and y_e' have now been found, one can determine E_{electr}. This quantity corresponds to transition E_{electr} in Fig. 3.7. The energy E_A is assumed to be known from other experiments. It is $E_A = 0.94$ eV for I_2. With it, all quantities in Fig. 3.7 and especially the energy of dissociation are known.

3.2 Colour centres

3.2.1 General remarks on colour centres

In ionic crystals and especially alkaline halides are strongly localized electron systems. They have a wide energy gap between valence and conduction band of about 5 to 12 eV such that visible light with energy from about 1.5 to 3.5 eV is insufficient for lifting an electron from the valence into the conduction band. Consequently, clean ionic crystals are transparent and electrically insulating. Thermal or chemical treatment, as well as irradiation with x-rays or ultra-violet light can lead to the generation of point defects in these alkaline halides, i.e, ion vacancies, interstitials or impurity atoms are incorporated into the crystal lattice. These defects can trap electrons in bound states that are less localized than those in the unperturbed lattice. These bound electronic states lie in the

forbidden energy gap, and for alkaline halides in the visible spectral range. Such crystals then have a characteristic colour, NaCl is red, KBr appears blue, and the defects are called colour centres. There exists a manifold of colour centres with, for historical reasons, various notations. Some of these centres are illustrated in Fig. 3.8 [4]. For further reading refer to the literature in [5, 6].
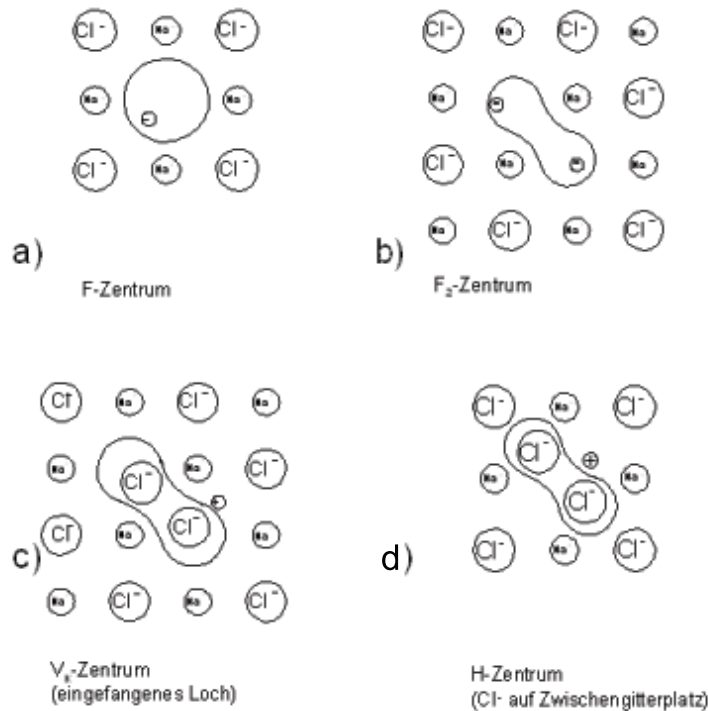

a)
F-Zentrum

b)
F$_2$-Zentrum

c)
V$_k$-Zentrum
(eingefangenes Loch)

d)
H-Zentrum
(Cl- auf Zwischengitterplatz)

Figure 3.8: The defect structure in alkaline halides: (a) Halogen ion vacancy with a trapped electron, F-centre (b) two neighbouring colour centres, (c) self-trapped hole, (d) halogen ion on a interstitial site, Frenkel pair.

F-centres A colour centre (F-centre) is an anion vacancy (halogen vacancy) with a trapped electron (see Fig. 3.8). This centre is most prominent and will be the object of further discussions. To generate F-centres γ, x-ray, electron or ultra-violet irradiation, but also annealing of the crystal in alkali vapour can be used. The underlying process is fairly well understood. The irradiated energy excites an electron of the halogen ion across the band gap that forms an exciton with the hole in the valence band. The electrically neutral halogen atom is no longer tightly confined to its lattice site; it shifts and forms a molecule-like state with the neighbouring halogen ion on which a hole binds. This is the so-called V_K centre. The release of energy during recombination of the exciton is sufficient to generate a Frenkel pair (H-centre) from the V_K centre, i.e., the halogen ion vacancy is now on a interstitial site leaving a vacancy at the former halogen ion site. The result is hence a F-centre and H-centre. The electron binds to the F-centre. The formation of an F-centre via an intermediate V_K-centre is in fact energetically more affordable than a direct shift of the halogen ion to a interstitial site.

For the F-centre, EPR experiments inferred a spin of 1/2 and thus confirmed the idea of a trapped electron at the halogen vacancy. And indeed, optical transmission mea-

surements on F-centres showed a wide absorption band in the visible spectral range that corresponds to the electronic transition from the ground to the first excited state. A schematic illustration of such an absorption band is shown in Fig. 3.9. The frequency width at half maximum (FWHM) is denoted as ΔE_{H}. Material parameters for NaCl and KBr such as lattice constant, index of refraction and reflectivity are given in the tables in the appendix. The quantity E_{m} is called the transition energy and has the following general relation with the wavelength λ_{m}:

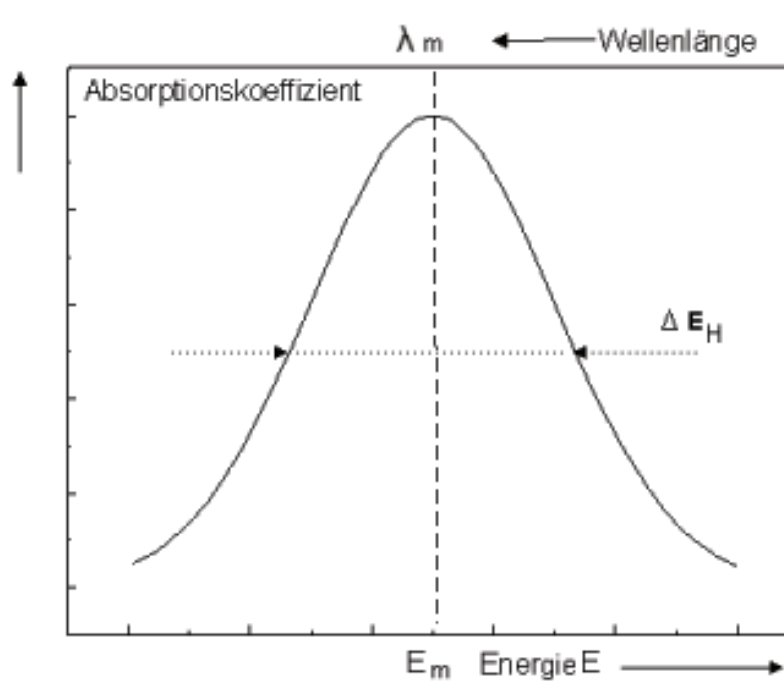$$E = \frac{hc}{\lambda}.$$

Figure 3.9: Schematic absorption line of an F-centre.

3.2.2   Classical description of the F-centre

The classical description of the F-centre, e.g. in NaCl, assumes that due to the Cl$^-$ vacancy the surrounding Na$^+$ ions posses a positive charge. This positive charge e^+ is assigned to a cube with edge length d' and distributed evenly on the surface of a sphere with the same volume. For the radius of the sphere R it follows from Fig. 3.10 that

$$d'^3 = \frac{4\pi}{3}R^3,$$

with

$$d' = d\sqrt{2} = \frac{a\sqrt{2}}{2}.$$

Thus, for R^3 one has:

$$R^3 = \frac{3\sqrt{2}}{16\pi}a^3. \tag{3.14}$$

14

The electron trapped by the F-centre and with charge e^- is now considered inside the homogeneous charge distribution ϱ at a location r. The electron feels the electric field $E = E_r$ that is caused by the homogeneously charged sphere. Due to symmetry, this field only has a radial component. The total positive charge is given by

$$e^+ = \int_V \varrho \mathrm{d}V = \varrho \frac{4\pi}{3} R^3. \tag{3.15}$$

To determine E_r one applies Maxwell's equations

$$div D = \varrho$$

to the sphere with radius r. Then it holds that

$$\int_V \varrho \mathrm{d}V = \int_V div D \mathrm{d}V = \int_f D \mathrm{d}f,$$

$$\varrho \frac{4\pi}{3} r^3 = D_r 4\pi r^2 = \varepsilon \varepsilon_0 E_r 4\pi r^2, \tag{3.16}$$

with $\mathrm{d}f$ the surface element, D_r the radial electric displacement field, $\varepsilon = 1$ the relative permittivity and $\varepsilon_0 = 8.854 \times 10^{-12}$ As/Vm the permittivity of free space. It follows from eq. (3.16) that

$$E_r = \frac{\varrho r}{3\varepsilon\varepsilon_0}.$$

Substituting ϱ according to eq. (3.15) by e^+ yields

$$E_r = \frac{e^+}{4\pi\varepsilon\varepsilon_0} \frac{r}{R^3}.$$

Then the force acting on the electron is

$$F_r = e^- E_r = \frac{e^- e^+}{4\pi\varepsilon\varepsilon_0} \frac{r}{R^3} = -\frac{e^2}{4\pi\varepsilon\varepsilon_0} \frac{r}{R^3}.$$

The equation of motion of the electron with mass m can be derived from Newton's second law:

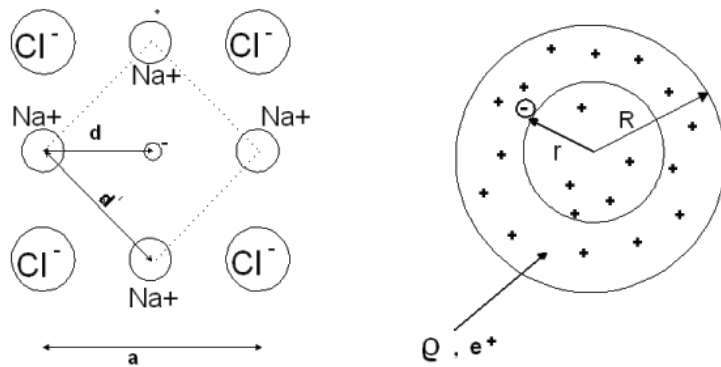$$m\ddot{r} = F_r = -\frac{e^2}{4\pi\varepsilon\varepsilon_0} \frac{r}{R^3}.$$

Figure 3.10: Classical model of the F-centre.

This can be rearranged to an oscillator equation of the form

$$\ddot{r} + \omega r = 0 \tag{3.17}$$

where the harmonic solution has an angular frequency

$$\omega = \frac{e^2}{4\pi\varepsilon\varepsilon_0 m R^3}. \tag{3.18}$$

Taking into account the usual relations between energy E, frequency v, wavenumber $\bar{v}$ and angular frequency ω, i.e.,

$$\bar{v} = \frac{1}{\lambda},$$
$$\omega = 2\pi v = 2\pi c\bar{v},$$
$$E = \hbar\omega = \frac{h}{2\pi}\omega = \hbar v = h\frac{c}{\lambda} = hc\bar{v},$$

where c is the light velocity, one obtains together with eq. (3.18) an excitation energy

$$E = \frac{\hbar e}{(4\pi\varepsilon\varepsilon_0)^{1/2} R^{3/2}}.$$

Replacing R by the lattice constant a according to eq. (3.14) one finally obtains

$$E = \frac{he}{\pi(3\sqrt{2}\varepsilon\varepsilon_0 a^3)^{1/2}}.$$

This excitation energy of the oscillator corresponds to the transition energy E_m that determines the maximum of the absorption line. The classical model of the F-centre is hence a harmonic oscillation of the trapped electron in the electric potential of a homogeneously positively charged sphere.

3.2.3 Quantum mechanical theory of the F-centre

Because the electron is bound rather tightly in the F-centre, one can consider it for the most simple quantum mechanical treatment as being trapped inside a potential box that is shown in Fig. 3.11 in two dimensions. For the three-dimensional case it is assumed that the electron is trapped in a unit cell with lattice constants a, b, c and subjected to a potential

$$V(x,y,z) = \begin{cases} 0 & \text{for } 0 \leq x \leq a,\, 0 \leq y \leq b,\, 0 \leq z \leq c \\ \infty & \text{else} \end{cases}. \tag{3.19}$$

The problem is solved by employing the Schrödinger equation

$$\left[-\frac{\hbar}{2m}\Delta + V(x,y,z) \right]\Psi = E\Psi. \tag{3.20}$$

Making the ansatz that outside the potential box the wave function is $\Psi = \Psi(x,y,z) \equiv 0$, i.e. the electron has zero probability density there, the Schrödinger equation must be
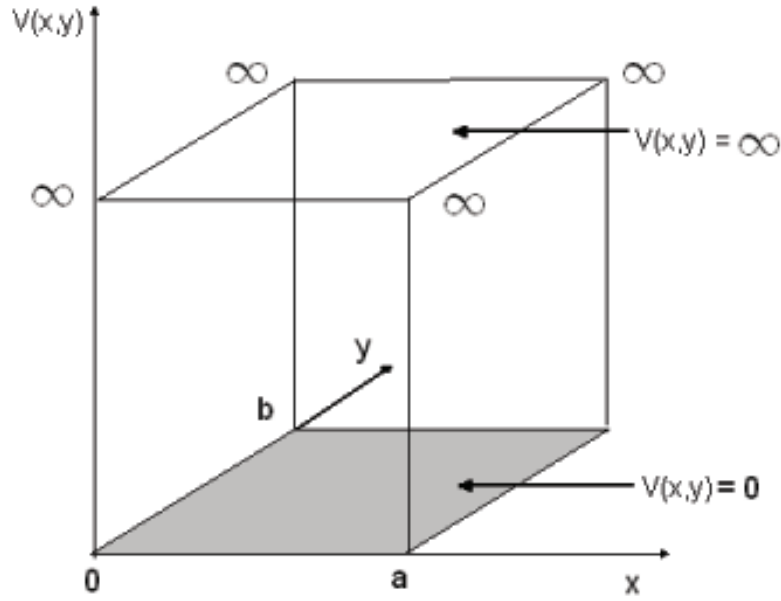
Figure 3.11: Two-dimensional potential box.

solved only within the box, where $V(x,y,z) = 0$. In this way, eq. (3.20) is reduced to a simple wave equation

$$-\frac{\hbar}{2m}\Delta\Psi = E\Psi,$$

or rearranging,

$$\Delta\Psi = -\alpha\Psi, \tag{3.21}$$

with

$$\alpha = \frac{2mE}{\hbar^2}. \tag{3.22}$$

Due to the box potential, eq. (3.19), the energy eigenvalues must be $E > 0$ and equivalently also $\alpha > 0$. The differential equation (3.21) yields the wave function Ψ and the energy eigenvalues E and α, resp., in the following way: Because the Δ operator is of the form

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2},$$

the product wave ansatz is made for Ψ:

$$\Psi = \Psi(x,y,z) = \Psi_1(x)\Psi_2(y)\Psi_3(z). \tag{3.23}$$

With this it follows from eq. (3.21) that

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi_1(x)\Psi_2(y)\Psi_3(z) = -\alpha\Psi_1(x)\Psi_2(y)\Psi_3(z),$$

or when applying the Δ operator,

$$\Psi_1(x)\Psi_2(y)\frac{\partial^2\Psi_3(z)}{\partial z^2} + \Psi_1(x)\Psi_3(z)\frac{\partial^2\Psi_2(y)}{\partial y^2} + \Psi_2(y)\Psi_3(z)\frac{\partial^2\Psi_1(x)}{\partial x^2}$$
$$= -\alpha\Psi_1(x)\Psi_2(y)\Psi_3(z).$$

Dividing both sides with $\Psi_1(x)\Psi_2(y)\Psi_3(z)$ gives

$$\frac{1}{\psi_3(z)}\frac{\partial^2 \psi_3(z)}{\partial z^2} + \frac{1}{\psi_2(y)}\frac{\partial^2 \psi_2(y)}{\partial y^2} + \frac{1}{\psi_1(x)}\frac{\partial^2 \psi_1(x)}{\partial x^2} = -\alpha.$$

Because α is a constant and x, y, z are independent variables, every single term in the above sum must itself be a consatnt. Thus

$$\frac{1}{\psi_1(x)}\frac{\partial^2 \psi_1(x)}{\partial x^2} = -\alpha_1$$
$$\frac{1}{\psi_2(y)}\frac{\partial^2 \psi_2(y)}{\partial y^2} = -\alpha_2 \tag{3.24}$$
$$\frac{1}{\psi_3(z)}\frac{\partial^2 \psi_3(z)}{\partial z^2} = -\alpha_3$$

with $\alpha = \alpha_1 + \alpha_2 + \alpha_3$. In this way, all constants are decoupled and the three differential equations (3.24) can be solved separately. Because they have the same form as eq. (3.17), there exist harmonic solutions and one can again make the following ansatz for the wave function:

$$\Psi_1(x) = A_1 \sin(\beta_1 x)$$
$$\Psi_2(y) = A_2 \sin(\beta_2 y) \tag{3.25}$$
$$\Psi_3(z) = A_3 \sin(\beta_3 z).$$

The coefficients A_1, A_2, A_3 and β_1, β_2, β_3 are constants yet to be determined. Inserting the *ansätze* for the solutions (3.25) into eq. (3.24), one can see that they are indeed a solution of (3.24) if

$$\beta_1^2 = \alpha_1,$$
$$\beta_2^2 = \alpha_2 \text{ and} \tag{3.26}$$
$$\beta_3^2 = \alpha_3.$$

As is common in quantum mechanics, the boundary conditions still have to be satisfied, such that the wave function are continuous. Because they have to be zero outside the potential box, the wave functions (3.25) must disappear at the boundary of the box. Then also $\Psi_1(x) = 0$ for $x = 0$ and $x = a$. The first condition is automatically satisfied by the choice of the solutions (3.25). For $x = a$ this means

$$\Psi_1(a) = A_1 \sin(\beta_1 a) = 0,$$

which holds when $\beta_1 a = n_1 \pi$ or

$$\beta_1 = \frac{n_1 \pi}{a}, n_1 = 1,2,3,... \tag{3.27}$$

Analogously,

$$\beta_2 = \frac{n_2 \pi}{b}, n_2 = 1,2,3,...$$
$$\beta_3 = \frac{n_3 \pi}{c}, n_3 = 1,2,3,... \tag{3.28}$$

With it, the energy eigenvalues are found because from eqs. (3.22) and (3.26) it follows

$$\frac{2mE}{\hbar^2} = \beta_1^2 + \beta_2^2 + \beta_3^2 \tag{3.29}$$

and finally from eqs. (3.27) and (3.28)

$$E = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right) = E_{n_1, n_2, n_3}. \tag{3.30}$$

The coefficients A_1, A_2 and A_3 follow from the normalization of the wave function to 1 via

$$\int\limits_0^a \int\limits_0^b \int\limits_0^c |\Psi(x,y,z)|^2 \mathrm{d}x \mathrm{d}y \mathrm{d}z = 1. \tag{3.31}$$

For the total wave function (3.23) one obtains with (3.25) and (3.27)

$$\Psi = \Psi_{n_1, n_2, n_3} = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_1 \pi x}{a}\right) \sin\left(\frac{n_2 \pi y}{b}\right) \sin\left(\frac{n_3 \pi z}{c}\right).$$

The integers n_1, n_2 and n_3 are quantum numbers that classify the energy states and the spatial probability density of the electron in the unit cell.

For the special case of a cubic unit cell with $a = b = c$ the energy eigenvalues (3.30) are

$$E_{n_1, n_2, n_3} = E_0(n_1^2 + n_2^2 + n_3^2)$$

with

$$E_0 = \frac{\pi^2 \hbar^2}{2ma^2}.$$

In Fig. 3.12 these eigenvalues are illustrated. The degree of degeneracy g states the number of different wave functions belonging to the same energy state. The transition energy E_m of an electron from the 1s-like ground to the 2p-like first excited state is then

$$E_m = E_0 = \frac{3h^2}{8ma^2}.$$

This result is in good agreement with the experimental Mollow-Ivey relation of alkaline halides:

$$E_m \propto 1/a^{1.84}. \tag{3.32}$$

A more refined quantum mechanical theory uses a constant, finite potential inside the unit cell and outside the Coulomb potential of the point charge of the surrounding cations plus another part coming from the interaction of the electron with the polarisation caused by the shift of lattice atoms (polaron coupling). Energy eigenvalues, wave function and parameters of the potential are then calculated in a self-consistent way.

3.2.4   Theory of the line width

The absorption band of a F-centre is rather broad. However, one should expect a sharp line, because according to Fig. 3.12 the electronic transition occurs between two discrete and sharp energy levels. But the electron of the F-centre has a strong interaction with the lattice vibrations of the surrounding ions. such that the total energy E of the F-centre also depends on a configurational coordinate R that corresponds to the distance from the nearest cations to the centre of the F-centre. This dependence is reproduced by the
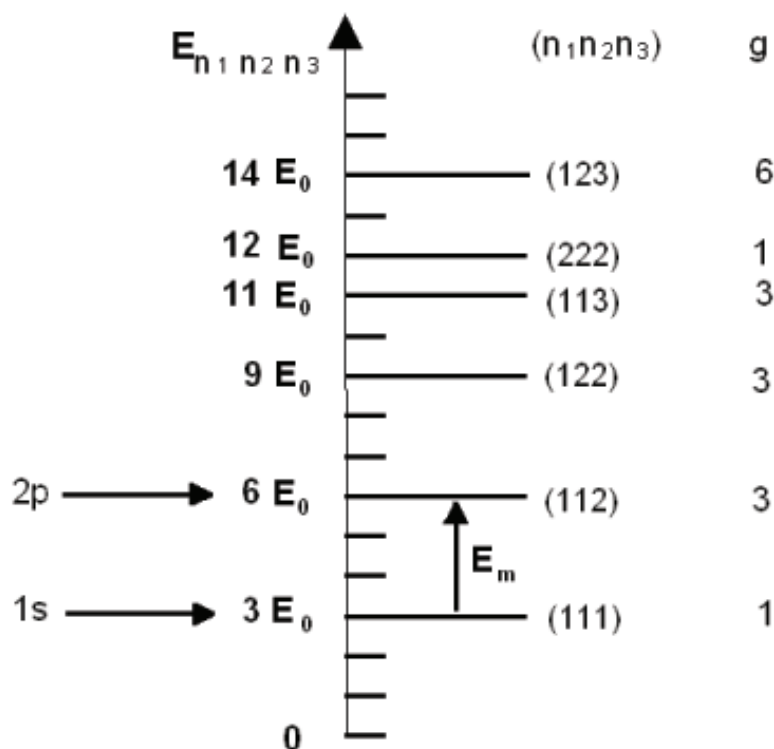
Figure 3.12: Energiy states of the cubic box potential.

parabolas in Fig. 3.13. R_0 is the equilibrium position of the cation if the electron of the F-centre is in a 1s-like ground state, Similarly R_f corresponds to the electron in a 2p-like excited state. Because the excited electron takes up more space, the cations are pushed farther away such that $R_f > R_0$. According to the Franck-Condon principle a electronic transitions is adiabatic, i.e., the transition is fast compared to the motion of the ions and the arrows in Fig. 3.13 are vertical. The transitions are assumed to always start at the vibrational ground state, i.e. the minimum of the vibrational parabola and the state with largest spatial probability. They end in unoccupied states on the parabola. In this way, absorption and emission bands are produced. The farther both parabolas are shifted with respect to each other the broader these bands are. From Fig. 3.13 one sees directly that the frequency v_a of absorption is larger than that of emission v_e. This was validated experimentally. The equidistant energy levels with distance hv_0 in Fig. 3.13 correspond to the interaction of the electron with the localized lattice vibration of frequency v_0, that is caused by the anion vacancy of the F-centre. In this particular case of a discrete phonon energy hv_0 a series of equidistant absorption lines with energy spacing hv_0 is expected. But also lowly energetic phonons of the surrounding lattice can take part in the interaction, because the F-centre represents a perturbation of the lattice periodicity that cancels selection rules. Thereby, the sharp vibrational levels are smeared out such that the above treatment employing parabolas appears justifiable.
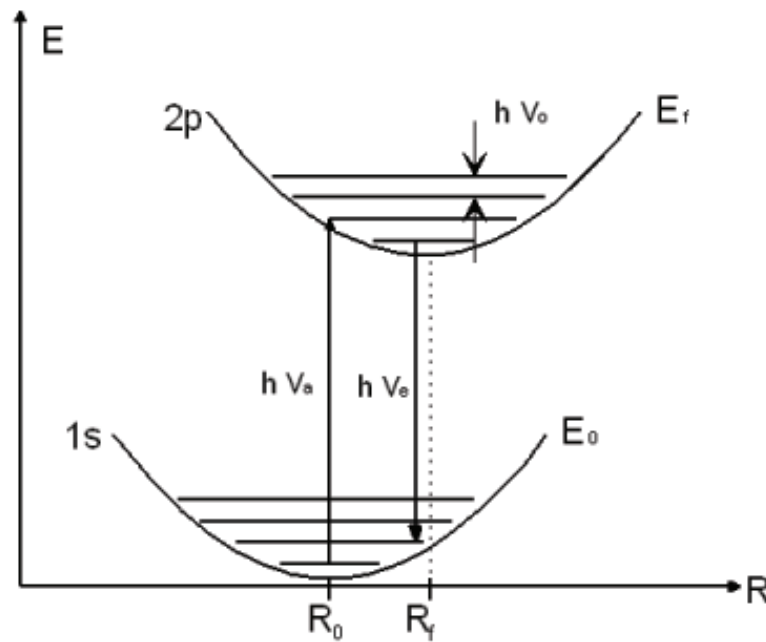
Figure 3.13: The Franck-Condon principle applied to colour centres.

3.2.5 Concentration of F-centres

An analysis of absoprtion spectra of F-centres shows, that their concentration N is proportional to the integral absorption, i.e., the surface below the curve in Fig. 3.9. Under the assumption that the width of the band is not too large und the band itself can be approximated by a Lorentz curve, the absorption band can be described by the classic Drude theory of the dispersion of an oscillator. This gives the integral absorption

$$\int \alpha \mathrm{d}v = \frac{e^2 N}{4c^2 \varepsilon_0 nm} \left(\frac{n^2 + 2}{3} \right)^2 .$$ (3.33)

Here, n is the refractive index and m the electron mass. All quantities on the right side of (3.33) are known and the concentration N can be calculated accordingly.

In order to determine the absorption coefficient α, in most cases the transmission T of plane-parallel crystals in dependence on the wavelength is measured. According to Fig. 3.14 the transmission T is defined as the ratio of transmitted intensity I_t to incident intensity I_0, i.e.,

$$T = \frac{\mathrm{I}_t}{\mathrm{I}_0}.$$

The transmission depends on the absorption coefficient α, refractive index n and the thickness d of the crystal in the following way:

$$t = \frac{(1-R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}},$$ (3.34)

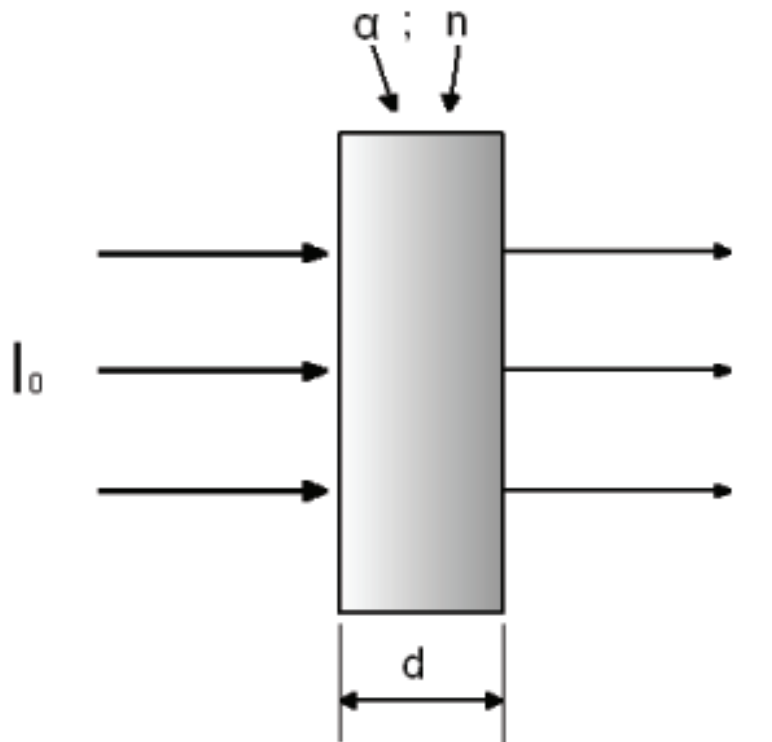where

$$R = \frac{(n-1)^2}{(n+1)^2}$$

Figure 3.14: On the transmission T of a crystal with thickness d.

is the reflectivity at the interface. If $R \ll 1$, and this is the case for NaCl and KBr, the denominator in (3.34) can be replaced by 1 such that the more simple relation

$$I = I_0 e^{-\alpha d} \qquad (3.35)$$

holds (Lambert-Beer law). T can have a wavelength dispersion. Let us denote T and T_0 as the transmission of a crystal with and without colour centres. Measuring T and T_0, one can determine for known thickness d the absorption coefficient α according to (3.35). Integration of α over the wavenumber finally yields the concentration of the F-centres N according to (3.33).

3.2.6 Application of F-centres

The primary application of F-centres is x-ray or γ dosimetry. In Mg doped LiF (LiF:Mg) the recombination of F- and V_K centres is exploited. They are generated under irradiation with x-ray or γ quanta. If the LiF:Mg crystal is subjected to higher temperatures afterwards, the V_K-centres become mobile and recombine with the F-centres. The energy released in the process is emitted as thermoluminescence that is measured by a photomultiplier. The integral luminescence is proportional to the irradiation dose of x- and γ-radiation.

In MgO, F-centres are used for neutron dosimetry: Neutrons in combination with hydrogen generate F^+-centres that trap electrons when heating the crystal to 350°C. and then transform into F-centres. Measuring the concentration of these centres by optical methods, the neutron dose can be detected.

In geology, F-centres in naturally occuring crystals can be used for age determination if they were generated by natural radioactive irradiation. For a temporally constant radioactivity the concentration of the F-centres is a measure of the the age of the crystal. Colour centres can also signal the temperature of natural crystal growth, because certain centres are only generated at certain temperatures. Natural NaCl is usually blue, CaF_2 can be red, green, yellow or blue. Violet SiO_2 is also known as amethyst.

Chapter 4

Experiment

4.1 Arrangement and working principle

All measurements in this experiment are performed with the Lambda 40 double beam spectrometer for the UV/VIS spectral range. The measurable wavelength range is from 190 nm (6.52 eV) to 1100 nm (1.13 eV). The spectral bandwidth can be adjusted to 1 or 2 nm. For the total spectral range two light sources are required: a deuterium lamp ranging from 190 to 326 nm, and a . The scanning speed can be chosen from 7.5 to 2880 nm/min. The beam path is shown in Fig. 4.1.
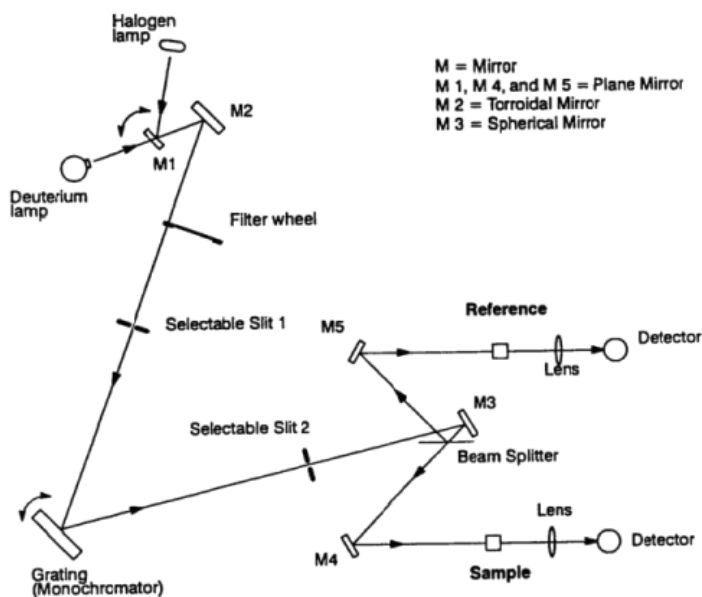

Figure 4.1: Beam path of the Lambda 40 UV/VIS spectrometer.

The light beam coming from the source hits a filter wheel that filters all undesired radiation according to the currently selected wavelength range. Via the entrance slit the beam reaches the monochromator. The monochromator consists of a holografically manufactured, turnable, concave grating as a dispersive element. From there, the beam is reflected through the exit slit and via a tilted mirror to a beam splitter. Here, the light beam is split into a reference and measured beam that are detected by two photo detectors.

The instrument is controlled and the data recorded via a computer interface.

Transmission T is the measured quantity for all samples, i.e., the ratio of transmitted and incoming intensity I_t and I_0, resp. To calibrate the instrument, a measurement without sample but with the respective empty sample holder is performed to set the transmission to 100% (*Autozero*). The subsequent measurement with sample yields the transmission. In principle, it is also possible to measures the reflectivity R with the appropriate optical accessories.

4.2   Data recording

The software *UVWinLab* for data recording and control of the Lambda 40 spectrometer is executed via its respective icon on the desktop. After execution, the following entries are shown in the menu bar:

File
View
Utilities
Application
Data handling
Windows
Help

For those entries that are most important for the measurements, some remarks are made below:

Utilities: Under the *Configuration* entry the measuring methode can be chosen as well as the save folder and the file format (binary, ASCII, JCAMP). JCAMP is a common file format in spectroscopy and ASCII should always be chosen when the data has to be processed with other software, e.g. Origin.

Application: Several measuring modes can be found here: *Scan, Time drive, Goto WL* and others. With *Goto WL* a certain wavelength can be selected. Prior to the measurement, the parameters are to be set up in the *Scan* tab. There exist three settings:

1. **Scan**: Start and end wavelength of the spectrum
   data interval
   save (automatic or not)
   ordinate maximum and minimum

2. **Inst**(rument): lamps
   scanning speed
   slit widths
   type of ordinate (transmission, reflection, absorption)

3. **Sample**: filename
   comments about sample

The measurements are started with *Autozero* and *Start*, resp.

4.3   Experimental advice

(a) The wavelength precision is checked with a holmium oxide filter whose absorption lines are given in Tab. 4.1. The influence if slit width and scanning speed on the absorption line is to be investigated at this point.

(b) Note that for the measurement of the interference filter zeroing has to be performed at every angle. When measuring the visible spectral range a planar mirror put into the measured beam is used to look directly into the monochromator. **For safety reasons, the deuterium lamp must be turned off!**

(c) When measuring the transmission of iodine vapour use glas cuvette no. 8. Consider the proper slit width and measuring interval.

(d) UV irradiation is done for a 8 mm thick, plane-parallel KBr crystal using a deuterium lamp (Attention! UV radiation!). As a standard (T_0) the same non-irradiated sample is used. The duration of irradiation should be above 3 h. The discoloration of the crystal can be observed both in the sample holder and under the ceiling lights. KBr and NaCl are hygroscopic and must not be touched with bare hands. Especially: **Do not breath on or try to clean it!**

(e) The 4 mm thich NaCl crystal is irradiated wiht x-rays in regular intervalls to generate F-centres. In this case a second non-irradiated crystal is used for comparison. The concentration N. of the colour centres in KBr and NaCl are to be given in the commonly used unit cm^{-3}.

4.4   Tables

Table 4.1: Gauge wavenumbers of the holmium oxide filter.

279.3 nm
360.8 nm
536.4 nm

Table 4.2: Refractive index, reflectivity and lattice constants.

	n	R	a [Å]
NaCl	1.544	0.0457	5.63
KCl	1.490	0.0387	6.29
KBr	1.599	0.0477	6.59

Table 4.3: Natural constants.

velocity of light c	$2.9979 \cdot 10^{8}$ m/s
electron mass m_{e}	$9.1094 \cdot 10^{-31}$ kg
elementary charge e	$1.6022 \cdot 10^{-19}$ As
Planck's constant h	$6.6261 \cdot 10^{-34}$ Js
permittivity of free space ε_0	$8.8542 \cdot 10^{-12}$ As/Vm

Bibliography

[1] W. Finkelnburg, *Einführung in die Atomphysik*, Springer Verlag (Berlin 1962).

[2] M. Hollas, *Modern Spectrosocopy*, John Wiley & Sons (Chichester 1992).

[3] M. F. Manfred Böhm, *Höhere Experimentalphysik*, Verlag VCH (Weinheim 1992).

[4] Y.Farge und M. P. Fontana, *Electronic and Vibrational Properties of Point Defects in Ionic Crystals*, Defects in Crystalline Solids **11** (1979).

[5] J. J. Markham, *F-Centres in Alkali Halides*, Solid State Physics Suppl. 8 (1966).

[6] Bergmann-Schaefer, *Lehrbuch der Experimentalphysik*, de Gruyter (Berlin 1992).