

Optical Spectroscopy at Colour Centres and Molecules

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1 Introduction

In molecules and in crystals, electronic transitions dominate the spectrum. That is because the energy released by an electron transition is of the order of few eV s. Despite that, other energy transitions exist, namely between the vibrational and rotational states. The interaction between electronic transitions and vibrations allows for further analysis of the spectrum, and creates visible colour centers in some crystals.

The Franck-Condon principle states that the electronic transitions happen much faster than the vibrational changes, the implications of such principle simplify the calculations needed to obtain physical formulas.

In iodine vapour, the diatomic molecule has both electronic and vibrational states. Its spectra will be studied around the visible light range, where some of the characteristic energies are to be estimated.

The colour centers are generated in ionic crystals by high energy radiation, as a consequence of defect creation in the lattice. Classical and quantum mechanical models yield different predictions on the physical properties of this phenomenon, the spectra is to be analysed.

In more details, the following headlines will be discussed:

- Generation of colour centers, energetic position and concentration
- Calculations within the classical and quantum mechanical model
- Morse potential, in-harmonic potential of diatomic molecules
- Energy schemes of molecules, electronic and vibrational states
- Franck-Condon principle of vertical (constant position) transition
- Experimental determination of the characteristic energies

2 Theoretical Background

Here, we discuss the energy scheme of the diatomic molecule **Iodine**, the physical processes creating **color centers** in crystals, as well as deriving key physical quantities concerning both. Starting with I_2

2.1 Iodine Vapour Spectra

Energy states in Iodine, a diatomic homo-nuclear molecule, will be studied. As in a single atom, in Iodine there exists few electron volts electronic transitions from the ground state to an excited state, that is in the visible light to ultra violet range.

Contrary to atomic spectra, in Iodine vibrational and rotational transitions also exist, creating a more complex, superimposed spectra. Vibrational and rotational transitions have energy scales of 1/10 eV and 1 meV, much smaller than electronic transitions. This is a consequence of the strong axial symmetry between the two identical atoms, lifting energy states degeneracy compared to a single atom, creating more spectral lines and details.

2.1.1 Electronic Transitions

Similar to atoms, the electronic states of Iodine are labelled by the appropriate quantum numbers. Since the inner filled shells for each atom don't contribute to the total angular momentum, and are practically shielded, they will not be considered. That is to say; a many-electron system is in good approximation composed of the individual contributions of the single atom's valence electrons.

The total angular momentum in the symmetry line, to be called Λ , is the sum of the components λ_i from the outer electrons. Also the intrinsic spin s_i of the electrons, adds up to a total spin S . The component of the spin along the connecting line is denoted as Σ . It holds that $\Sigma = -S, -S + 1, \dots, S - 1, S$

The multiplicity M is the splitting of the molecular states, in presence of the interaction between Λ and S . Each Λ splits into $M = 2S + 1$ values.

Moreover, to fully capture the symmetry and asymmetry of an Iodine state, two more quantum numbers need to be used. Namely, symmetry (/anti-symmetry) under inversion, denoted by g (/u), and symmetry (/anti-symmetry) with respect to mirroring across the plane along the long axis, it is denoted by $+$ (/−).

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

$$^M \Lambda_{g,u}^{\pm} \quad (1)$$

2.1.2 Vibrational Transitions

Classically, and as a first approximation the oscillation of Iodine molecule is that of a harmonic oscillator. In the equilibrium position both atoms with similar masses m are at some distance apart, and the restoring force is proportional to the deviation from equilibrium as such:

$$m\ddot{x}_1 = -k(x_1 - x_2) \quad (2)$$

$$m\ddot{x}_2 = -k(x_2 - x_1) \quad (3)$$

With $x = x_1 - x_2$ and $\mu = m/2$:

$$\ddot{x} = -\frac{k}{\mu}x \quad (4)$$

This yields the angular frequency $\omega = \sqrt{k/\mu}$.

Quantum mechanically, the Schrödinger equation is to be solved for the harmonic potential $U = kx^2/2$. Giving the following energy states parameterized by the n quantum number.

$$E_n = \hbar\omega(n + 0.5) \quad (5)$$

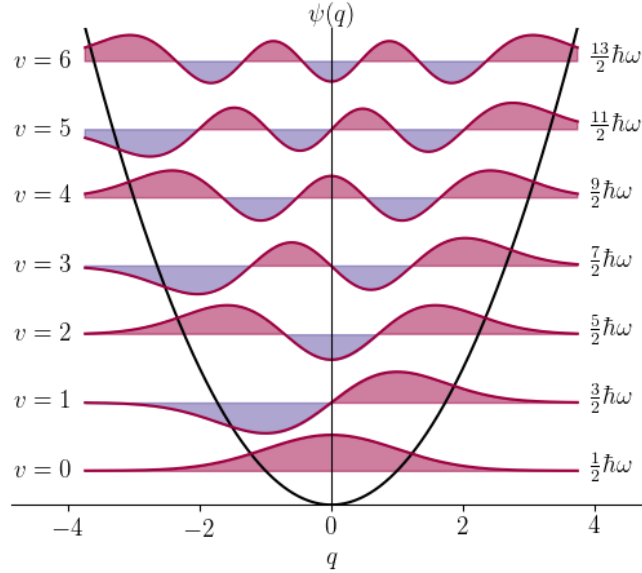


Figure 1: Energy States in Harmonic Potential

This harmonic treatment is merely an approximation, since in reality the strong repulsion of the two nuclei at tiny distances creates the an-harmonic Morse potential. With this, the energy levels spacing is no longer a constant $\hbar\omega$ but decreases with increasing energy, resulting in a dissociation of the two atoms for sufficiently large displacements (dissociation energy E_D).

Morse potential has the following form, with small distance approximation $x \ll 1$:

$$U = E_D(1 - e^{-ax})^2 \approx E_D a^2 x^2 \quad (6)$$

The energy levels of Morse potential are a correction to the harmonic treatment:

$$E_n = \hbar\omega((n + 0.5) - y_e(n + 0.5)^2 + \dots) \quad (7)$$

Where y_e is the anharmonicity constant.

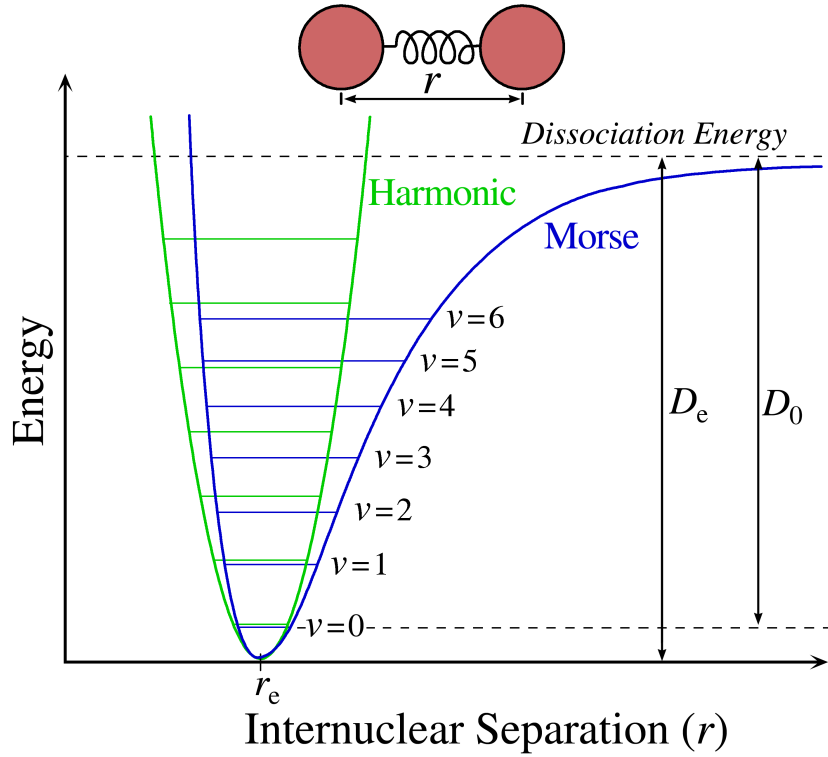


Figure 2: Energy States in Morse Potential

2.1.3 Combined Transitions

Since the vibrational energy separation is much lower than that of the electronic states, it is natural to think of the vibrational states as living inside the electronic ones. Where an electronic state, with some momentum along the axis, determines the equilibrium position of the Morse potential. The equilibrium position, and so the inverse of the binding energy between the two atoms, in the excited state relative to the ground state can be either unchanged, reduced, or enlarged.

Franck-Condon principle governs the combined transitions, which states that an electronic transition happens much faster than a change in nuclear position and momentum. Meaning a transition must occur vertically (at constant position), more likely where the cross probability amplitude is maximal.

Denote the vibrational states in the electronic ground state by n'' , those in the excited state by n' . For the transition energy one obtains:

$$\Delta E_{n'n''} = E_{electron} + \hbar\omega \left((n' + 0.5) - y'_e(n' + 0.5)^2 - (n'' + 0.5) + y''_e(n'' + 0.5)^2 \right) \quad (8)$$

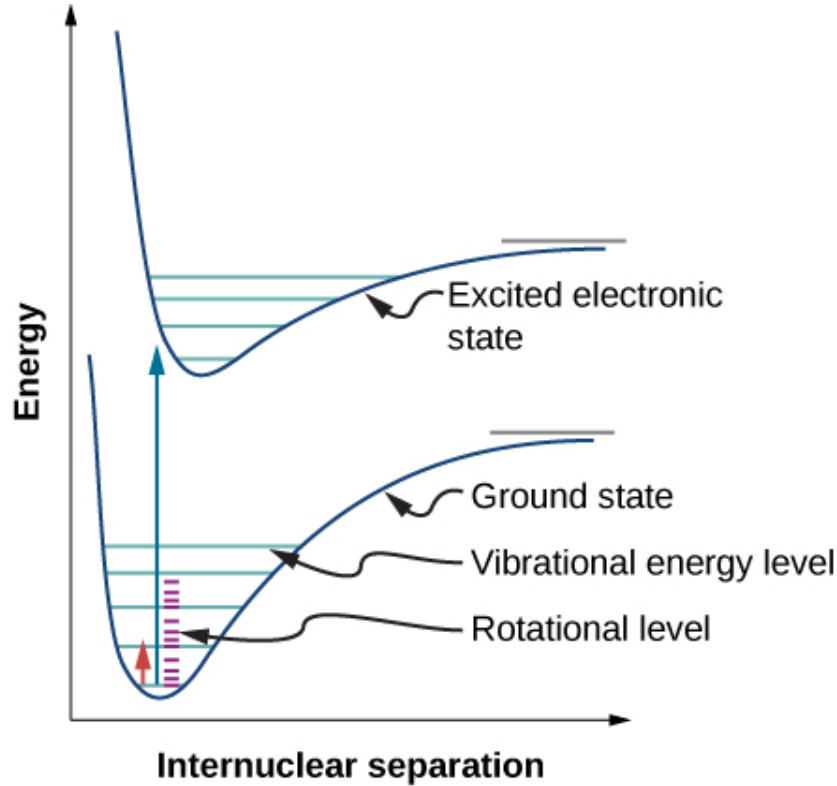


Figure 3: Combined Transitions

2.1.4 Characterisation Parameters

The energy of dissociation is the amount of energy needed to break down the molecule into its separate atoms within one electronic state. Supplying the system with that energy will in fact result in an electronic transition rather than actually dissembling the molecule.

Setting the ground state with zero energy ($n'' = 0$), equation (8) simplifies to a quadratic formula with one variable n' . Plotting the absorption maxima (transmission minima) vs n' should be quadratic converging to the maximum difference in energy between the two states E_K . Calculating the energetic difference between consecutive lines D_L gives insight into the anharmonicity constant.

$$D_L(n') = \hbar\omega(1 - 2y'_e(n' + 1)) \quad (9)$$

$$D_L(n' + 1) - D_L(n') = -2\hbar\omega y'_e \quad (10)$$

One can use the spectra to determine all the mentioned quantities with the knowledge of $E_K - E''_D = E_A = 0.94\text{eV}$.

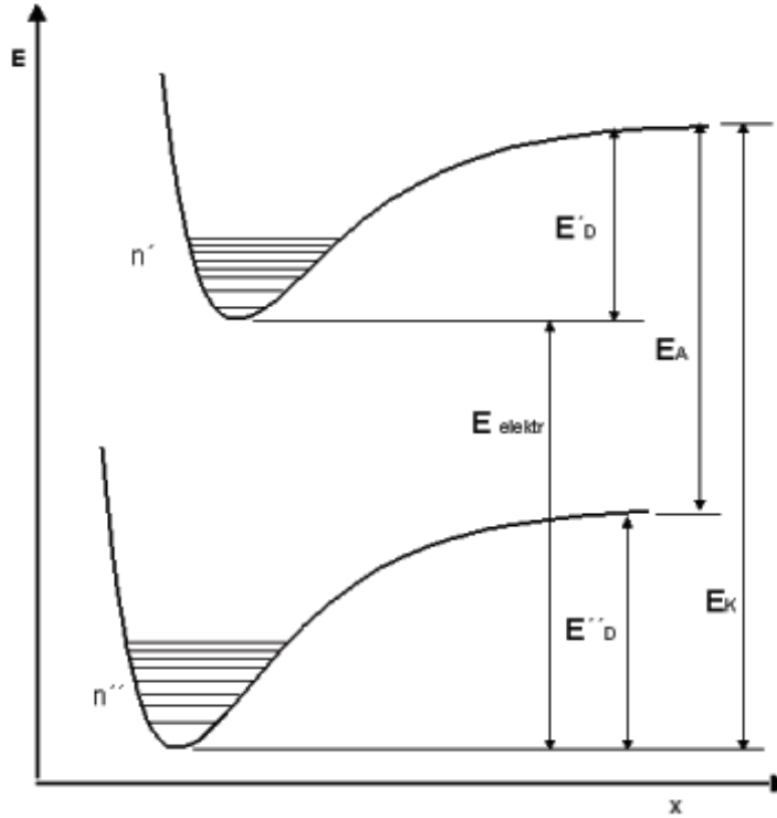


Figure 4: Transition Energies

2.2 Colour Centres

Ionic crystals have a big energy gap (around 10 eV) between valence and conduction bands, meaning electrons don't usually move freely in the lattice but are strongly localized. Visible light doesn't have enough energy to lift the electrons to the conduction band, but more energetic light (UV or x-ray) can generate defects that trap less localized electrons in a bound state still. The resulting bound states live inside the energy gap, creating **color centers**. An F colour centre is an anion vacancy with a trapped electron.

2.2.1 Energy of Colour Centers

One can create a **classical model** to describe the missing negative ion defect, the trapped electron, and the resulting energy of color radiation.

This is achieved by assigning the positive charge from the surrounding positively charged ions homogeneously to a sphere. The radius of that sphere R must be such that the volume of the sphere is equal to the cube volume:

$$R^3 = \frac{3\sqrt{2}}{16\pi}a^3 \quad (11)$$

Where a is the lattice constant. The electric field that is felt by the trapped electron is thus a result of this homogeneous spherically symmetric charge distribution. By Maxwell equation and Gauss theorem, the electric field is given by:

$$E(r) = \frac{e}{4\pi\epsilon\epsilon_0} \frac{r}{R^3} \quad (12)$$

The force felt by the electron is simply $F = -eE(r)$, which is linear in r . With $F = ma$, the electron moves with a harmonic angular frequency ω :

$$\omega^2 = \frac{e^2}{4\pi\epsilon\epsilon_0 m R^3} \quad (13)$$

Since the energy is a function of the angular frequency $E = \hbar\omega$, together with equation (11) we get:

$$E = \frac{he}{\pi(3\sqrt{2}m\epsilon\epsilon_0 a^3)^{1/2}} \propto 1/a^{1.5} \quad (14)$$

Alternatively, a **quantum mechanical model** can be developed using an appropriate potential of the defect.

In a simple treatment, the trapped electron is thought to be free only inside a box with side length equal to the lattice constant a . Finding the energy of the electron means solving the three dimensional Schrodinger equation for zero potential, the resulting energy difference between the ground and first excited state is:

$$E = \frac{3h^2}{8ma^2} \propto 1/a^2 \quad (15)$$

In principle, one can develop a more accurate model by choosing a more realistic potential.

2.2.2 Concentration of F-centres

Although color centers transitions are electronic, the produced line width is rather broad, this is due to the accompanying transition in vibrational states. The defect oscillations (phonons) produce parabola (harmonic) potentials similar to those in the Iodine molecule, such that each electronic state has many vibrational states with various energies. When an electronic transition happens and the equilibrium position for the harmonic potential shifts, the line width overall broadens.

Classical Drude theory of the dispersion of an oscillator gives a relation between the concentration of color centers N and the integral absorption:

$$\int \alpha df = \frac{e^2 N}{4c^2 \epsilon_0 n m} \left(\frac{n^2 + 2}{3} \right)^2 \quad (16)$$

Where the integral is over wavenumber, n is the refractive index, and α is the absorption coefficient given by: $I = I_0 \exp(-\alpha d)$ for non-reflective material.

3 Experimental Setup

3.1 Working Principle of Lambda 365

All measurements in this experiment are performed with the Lambda 365. Lambda 365 is a 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 another to cover the rest of the wavelength range.

The scanning speed can be chosen from 7.5 to 2880 nm/min. The beam path is shown in Fig. 5. 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 holographically 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 . To calibrate the instrument, a measurement without the sample performed to set the transmission as a reference. The subsequent measurement with sample yields the transmission.

In principle, it is also possible to measure the reflectivity R with the appropriate optical accessories.

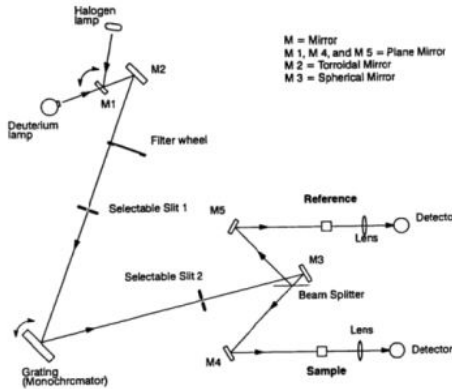


Figure 5: Beam path of the Lambda 40 UV/VIS spectrometer.

3.2 Control Parameters

- **Slit Width:** Ranging from 0.5 to 5 mm, the slit width is positioned before and after the grating [5], where it controls the amount of light passing through.
- **Scanning Speed:** It is the rate of reading that the device performs across the different wavelengths, in units of nm/min. Lambda 365 has scanning speeds that can go from 7.5 to 2880 nm/min.

4 Tasks, Results, and Discussion

4.1 Task 1

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

Starting with a constant slit width of 0.5 mm, many scanning speeds were used to get the holmium oxide filter spectrum:

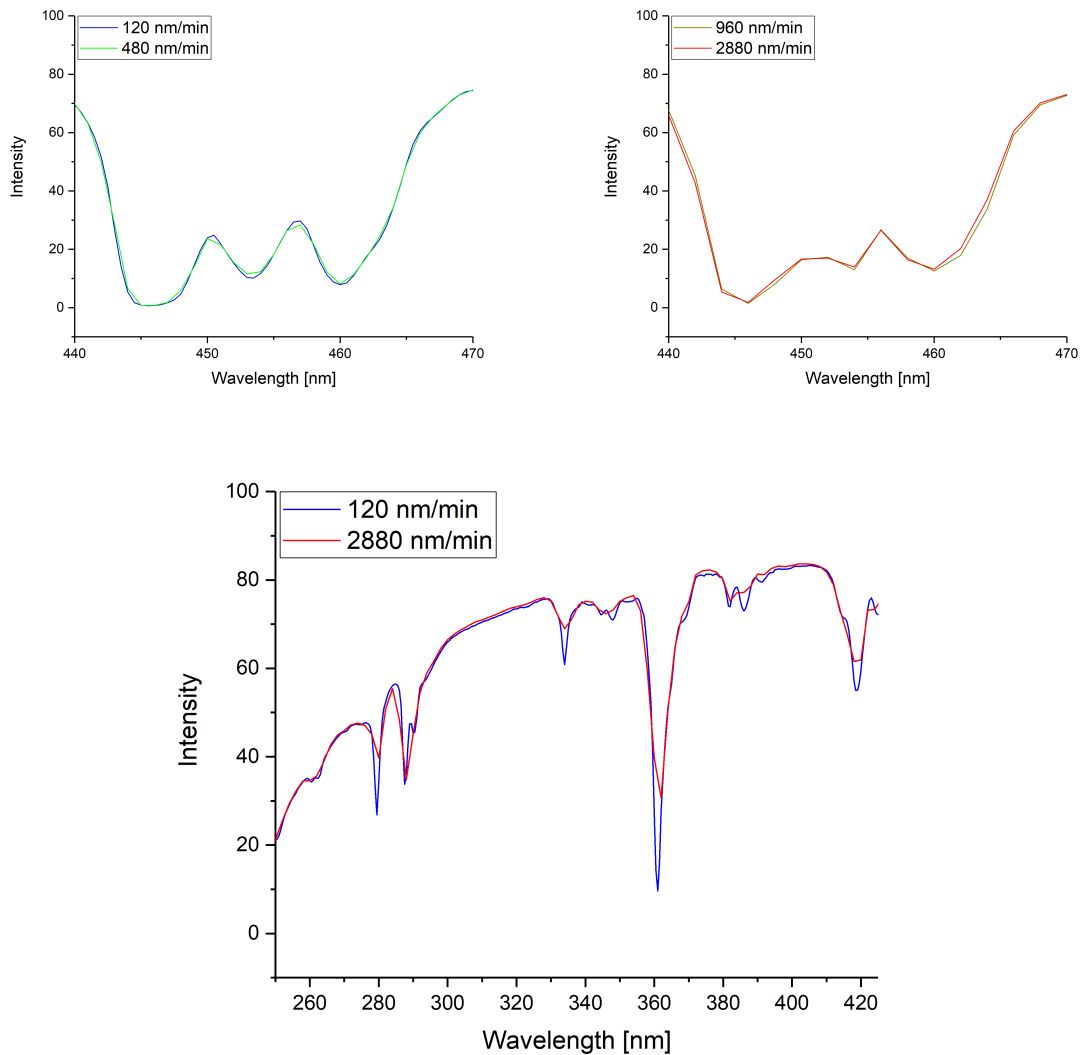


Figure 6: Scan Speeds at 0.5 mm Slit Width

Scanning speeds of 120 and 480 nm/min gave similar accuracy, while speeds of 960 and 2880 nm/min gave noticeably worse results. Generally, with lower scanning speeds the peaks are deeper and clearer. To save time and get suitable resolution, we settle on 480 nm/min scanning speed for all future measurements unless stated otherwise.

Next, at 480 nm/min the slit width was varied:

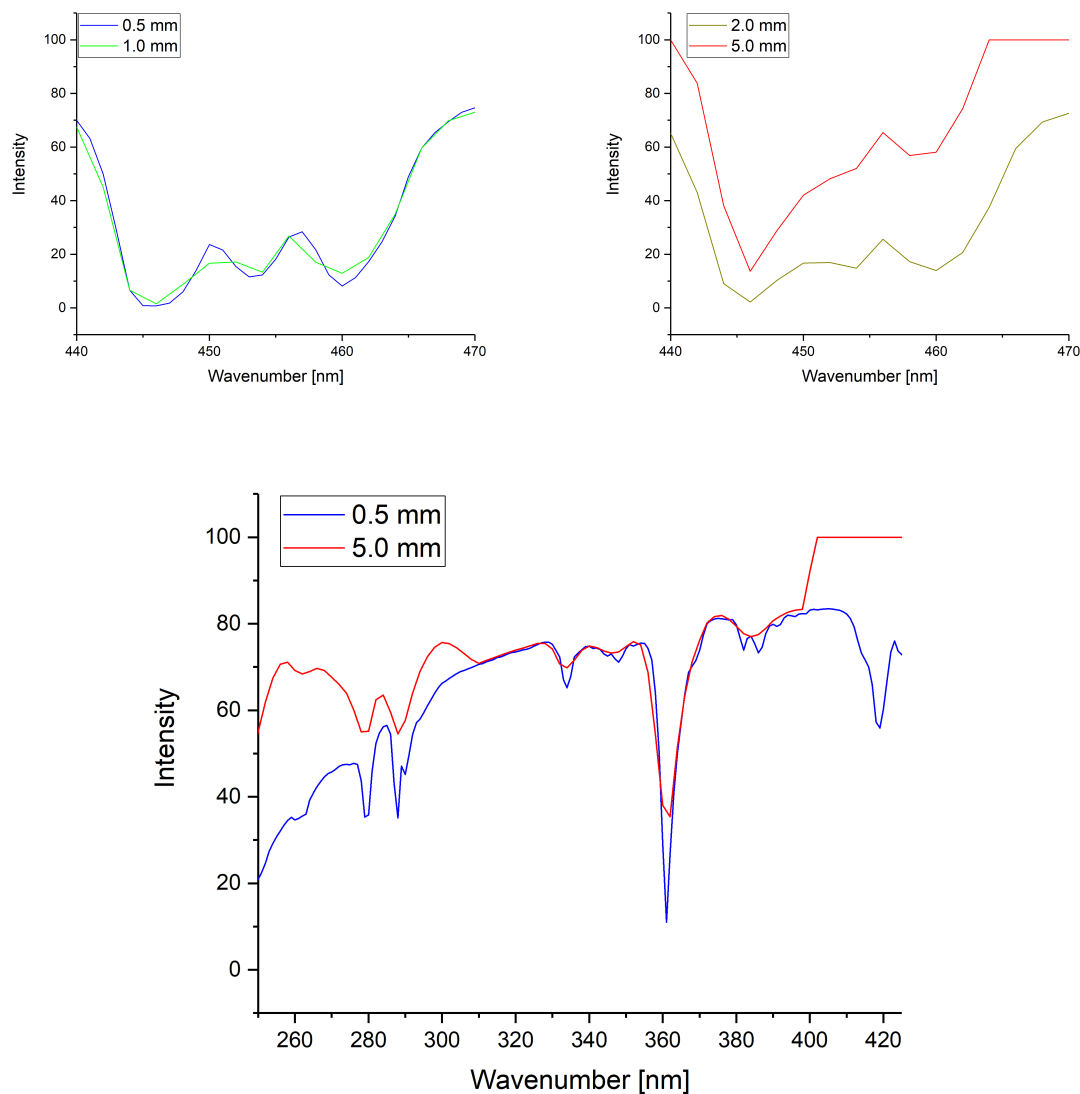


Figure 7: Slit Widths at 480 nm/min Scan Speed

Big slit widths allow for more light to come through and hit the sample, while small produce less spread and therefore more certainty on the light angle and frequency. We found that for slit widths of 2.0 and 5.0 mm the resolution was very low, for 1.0 mm the resolution increased slightly, while it increased considerably for 0.5 mm. We settle on 0.5 mm slit width with a scanning speed of 480 nm/min.

For the chosen measurement parameters, the full spectrum of a holmium oxide filter is measured. With the help of the known absorption bands (279.3, 360.8, 536.4 nm), the wavelength accuracy can be determined.

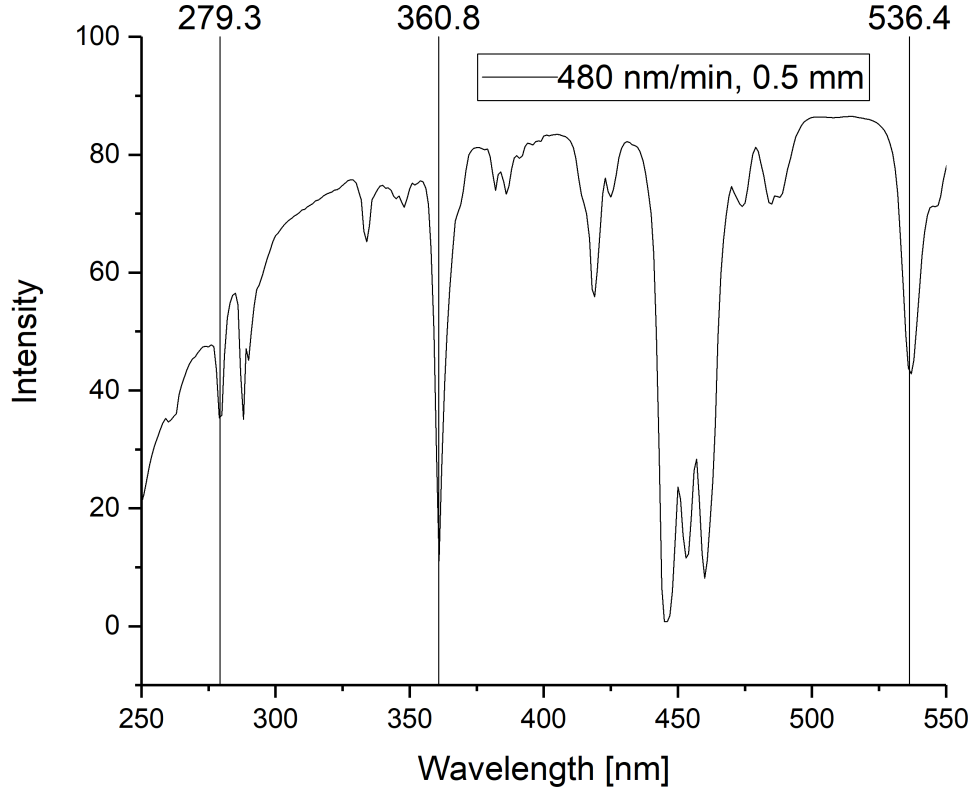


Figure 8: Wavelength Accuracy by Absorption Bands

At optimal values of scanning speed and slit width of 420 nm/min, 0.5 mm slit width, the spectrometer detected absorption bands of a holmium oxide filter with less than 0.5 nm deviation of given values. We continue the experiment with assumed variance of 0.5 nm.

4.2 Task 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. Moreover, transmission curves of colour filters may be measured.

First, the spectra of glass and quartz glass cuvettes filled with air and then water is recorded from 200 to 1100 nm.

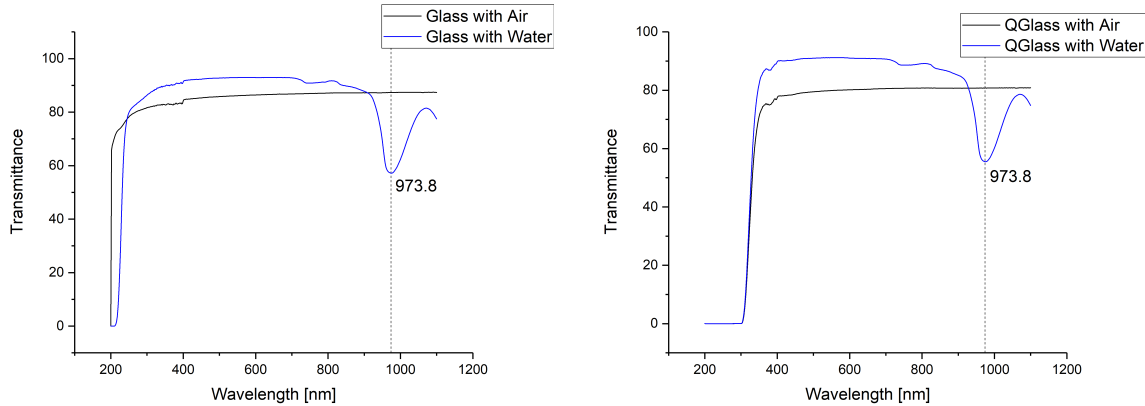


Figure 9: Glass Cuvettes

The blocking range of quartz glass is larger as seen in the spectrum at small wavelengths. We noticed a general increase in transmission when the glasses are filled with water relative to air, with a big dip around 974 nm. The higher transmission with water ($n=1.33$) is expected since water has a closer refractive index to glass ($n=1.52$) and quartz glass ($n=1.46$), the infrared dip must be a water absorption peak. Next, an interference filter transmission spectrum was recorder for different angles:

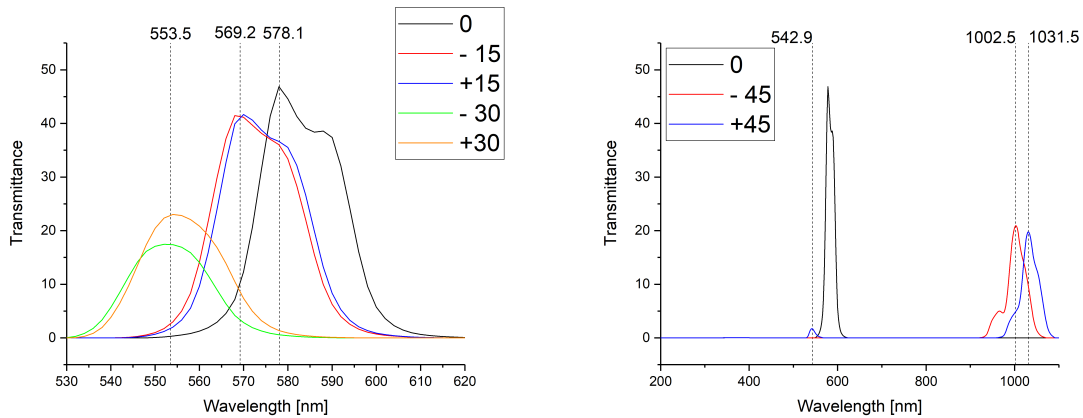


Figure 10: Interference Filter

Interference filters transmit a selected wavelength with high efficiency through reflection or destructive interference of all other wavelengths. When the angle changes, the peak wavelength with constructive interference shifts and the intensity drops. That can be explained by the path length angular dependence of the filter. Finally, transmission curves of various color filters and objects was measured: The

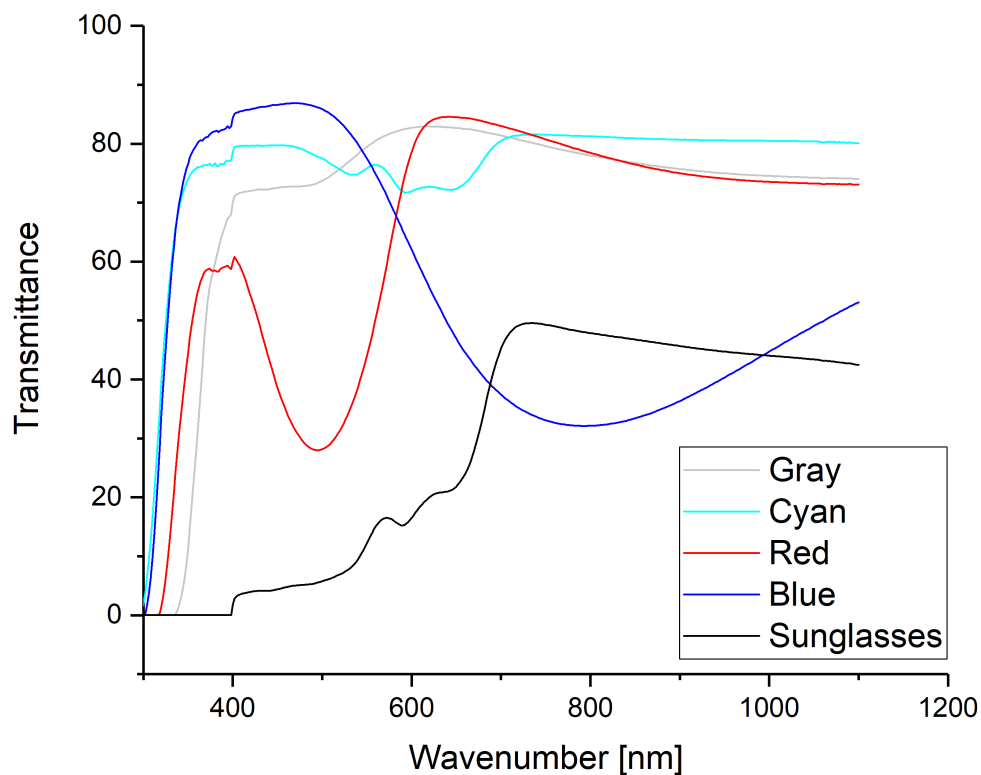


Figure 11: Color Filters and Sunglasses

transmission profile of each object is what defines its color. The blue filter has higher transmission at low wavelengths around 450 nm, the red filter has its peak around 650 nm, whereas sunglasses had a relatively low transmission across all wavelengths.

4.3 Task 3

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

The transmission spectra of Iodine vapour in the range of 500 to 650 nm reveals a strong electronic transition as an absorption peak:

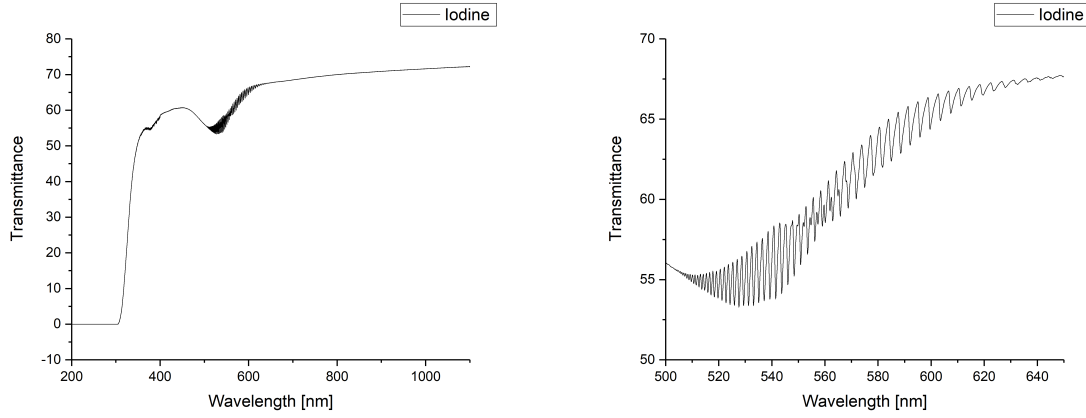


Figure 12: Iodine Vapour Transmission Spectrum

The observed oscillations are a consequence of vibrational states and vibrational transitions combined with the electronic one. Assuming that the transition starts from the vibrational ground state $n'' = 0$ with zero energy, each valley corresponds to a transition with different vibrational quantum number:

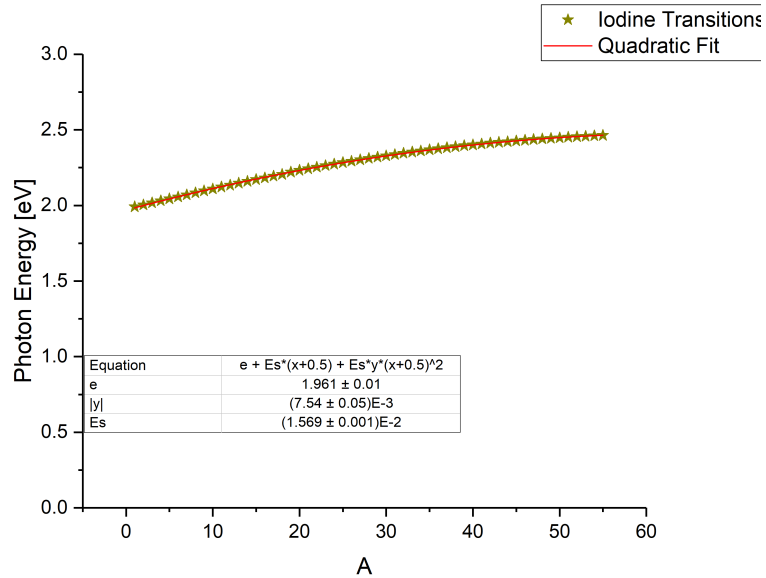


Figure 13: Iodine Vapour Spectral lines

The quadratic fit of the data with the following formula allows us to read off the electronic transition energy $E_{electron}$, the anharmonicity constant y_e , and the Morse potential frequency ω .

$$\Delta E_{n'n''} = E_{electron} + \hbar\omega \left((n' + 0.5) - y'_e(n' + 0.5)^2 \right) \quad (17)$$

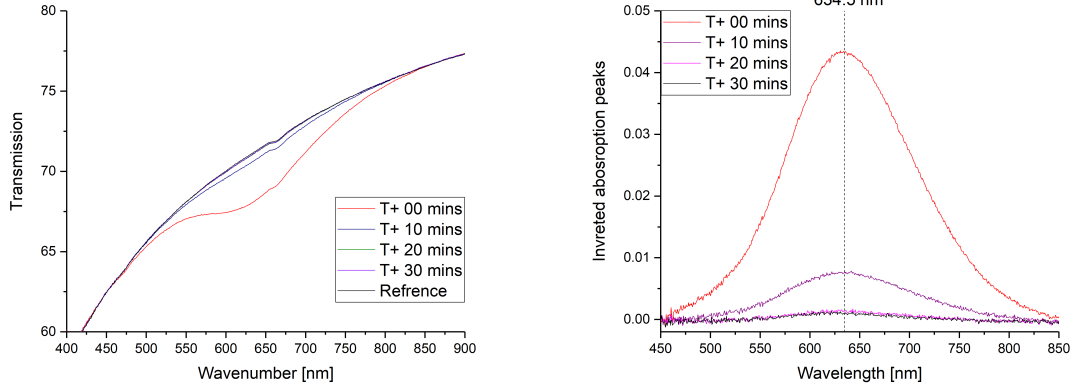
$$E_{electron} = 1.96 \pm 0.01 \text{ eV}, \quad y_e = (7.54 \pm 0.05)10^{-3}$$

From the graph, the convergence energy is the last valley before oscillations end, by converting the corresponding wavelength to energy: $E_k = 2.47 \pm 0.01 \text{ eV}$. The dissociation energies are then: $E''_D = 1.53 \pm 0.01 \text{ eV}$ for the ground state and $E'_D = 0.51 \pm 0.01 \text{ eV}$ for the upper one.

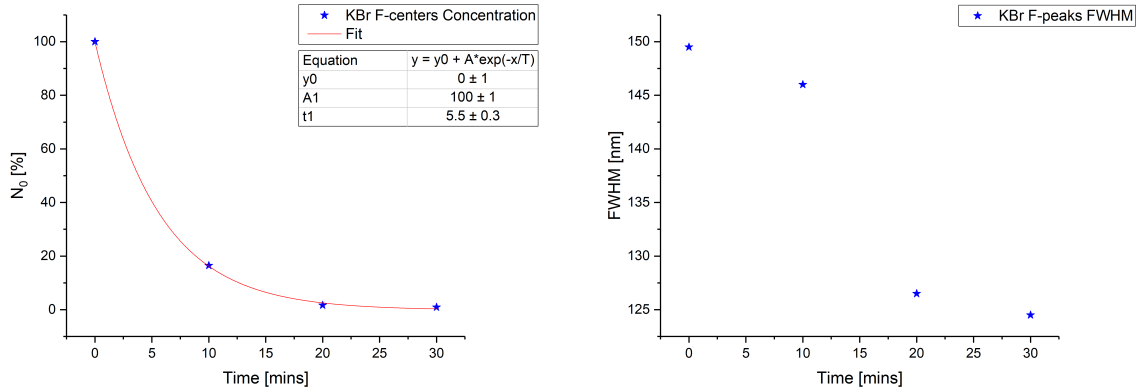
4.4 Task 4

Generate F-centres in a KBr crystal by means of UV irradiation. Determine the concentration of F-centres from the integral absorption in dependence on time after irradiation. Identify the excitation energy and the linewidth.

KBr crystals form F-centers when irradiated by UV, where their concentration decreases with time without UV. These centers effect the transmission profile of the crystal. The transmission spectra of KBr before (reference) and after irradiation:



On the right side, each curve is plotted as the percentage decrease in intensity with respect to the reference in a suitable range of wavelengths. All curves are centered around $634.5 \pm 0.5 \text{ nm}$, so the excitation energy $E = 1.954 \pm 0.002 \text{ eV}$



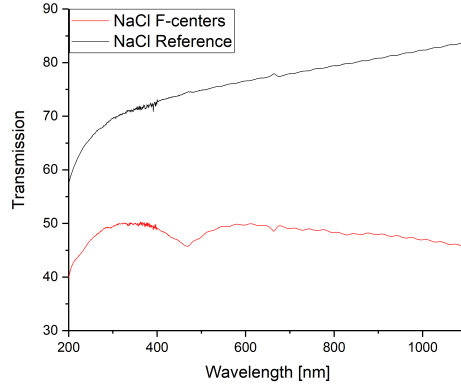
The concentration of F-centers is proportional to the absorption coefficient integral by equation (16). That integral (up to a constant) is exponentially decaying in time as a percentage of the initial concentration at $t = 0 \text{ min}$, to determine the initial N_0 concentration the thickness of the crystal must be known. On the right, the full width at half maximum of the absorption peaks is plotted.

Unfortunately, a 10 minute waiting time between measurements was too long, since the concentration of F-centers dropped to nearly zero only after 4 measurements. Waiting for less time or better isolating the sample would yield more data points and better analysis.

4.5 Task 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.

The transmission spectra of NaCl with and without color centers:



It is difficult to determine exactly where the color centers are in this spectra, since we see a big decrease in transmission across all wavelengths. That said, there is a clear dip around $470 \pm 0.5 \text{ nm}$, so the excitation energy $E = 2.635 \pm 0.003 \text{ eV}$. The line width of that one peak is $80 \pm 1 \text{ nm}$

4.6 Task 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.

The energy of excitation in the classical model E_c and the quantum mechanical model E_q is given by:

$$E_c = \frac{he}{\pi(3\sqrt{2}m\epsilon\epsilon_0a^3)^{1/2}}, E_q = \frac{3h^2}{8ma^2} \propto 1/a^2 \quad (18)$$

Knowing the actual lattice constants a for KBr and NaCl as well as the relative permittivity ϵ , we can use these models to get the value of the energy. For KBr with $\epsilon = 5.65$: classical energy is $E_c \approx 10^{-15} \text{ eV}$, and quantum mechanical energy is $E_q = 2.6 \text{ eV}$. While we experimentally obtained the value: $E = 1.954 \text{ eV}$ For NaCl with $\epsilon = 5.9$: classical energy is $E_c \approx 10^{-15} \text{ eV}$, and quantum mechanical energy is $E_q = 3.6 \text{ eV}$. While we experimentally obtained value: $E = 2.635 \text{ eV}$.

Using the experimentally obtained F-centers energy, we can estimate the lattice constants $a_{KBr} = 5.6 \text{ \AA}$, and $a_{NaCl} = 6.6 \text{ \AA}$. Clearly, the quantum mechanical model is much more accurate. Although a better quantum model can be built with different potential treatment, would be even more accurate.

4.7 References

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