Contents

Contents						
1	Introduction					
2	Physical basics					
	2.1	Molecular States	5			
	2.2	Electronic Transitions and Selection Rules	5			
	2.3	Born-Oppenheimer approximation	6			
	$\frac{2.0}{2.4}$	Franck-Condon principle	6			
	2.1	Morse Potential	7			
	2.6	Birge-Sponer plot	8			
3	Seti	up and Procedure	9			
	3.1	Setup	9			
	3.2	Procedure	10			
	0.2		10			
4	Ana	alysis	12			
	4.1	Absorption Spectrum	12			
		4.1.1 Identification of Transitions	12			
		4.1.2 Birch-Sponer Plot	13			
		4.1.3 Determination of the Potential Depth	14			
		4.1.4 Determination of the Dissociation Energy	15			
		4.1.5 Determination of the Excitation Energy	16			
		4.1.6 Approximation of the Morse potential	17			
	4.2	Emission Spectrum	18			
		4.2.1 Calibration of the Monochromator	18			
		4.2.2 Laser Peak	18			
		4.2.2 Emission Spectrum of Iodine	20			
		4.2.9 Emission Spectrum of fourie	20			
5	Discussion					
	5.1	Absorption Spectrum	21			
	5.2	Emission Spectrum	23			
A	App	pendix	24			
Li	st of	Figures	24			
Li	st of	- Tables	<u></u> ۶۲			
L 13						
Bi	Bibliography					

Symbol	Meaning				
a	Molecular constant				
A, B, \ldots	First, second, excited states				
D_e	Potential well depth				
D_0	Energy difference between lowest potential and				
	continuum				
\mathbf{FC}	Franck-Condon factor				
g	Eigenvalue of point reflection operator				
G	Energy term				
k	Wave number				
λ	Wavelength				
Λ	Quantum number of projection of orbital angular				
	momentum				
μ	Reduced mass of iodine				
u	Vibrational quantum number				
Ω	Quantum number of projection of total angular				
	momentum				
ω_e	Molecular constant				
$\omega_e x_e$	Molecular constant				
ψ	Wave function				
П	Term symbol				
r_i	Electronic coordinates				
R_{j}	Nuclear coordinates				
S	Spin quantum number				
Σ	Term symbol				
u	Eigenvalue of point reflection operator				
X	Ground state				
lpha,eta	Parameters of regression				
s_x	Error on the quantity x				

Table 1 contains an overview of all symbols used in this lab report.

Table 1: Symbols used in this lab report. Quantities belonging to the ground state are labelled using a single prime (\prime) ; quantities belonging to the excited state are labelled using two primes $(\prime\prime)$.

1 Introduction

This experiment serves as an introduction to molecular spectroscopy, where important molecular constants, such as the vibrational constants and dissociation energies of a molecular state can be determined. The measurements are carried out on the diatomic iodine molecule I_2 , since its molecules have an extraordinarily defined band structure. With an absorption and an emission measurement involving different experimental setups, not only should important constants of the first excited iodine state be determined, but also the relevant transitions shall be identified.

2 Physical basics

If not indicated in any other way, the theory explained in the following section of this report is based on the instructions [1] and the staatsexamen [2].

2.1 Molecular States

So called molecular term symbols are used to identify a molecular state. Using a specific notation, this allows for a concise and complete description and characterization of all relevant molecular quantum numbers. Molecular term symbols are written in the following form:

$${}^{2S+1}\Lambda^{(+/-)}_{\Omega(g/u)}.$$
(1)

In the above term,

- S indicates the (total) spin quantum number of the molecule. It is often associated with the multiplicity 2S + 1 which gives the amount of magnetic spin quantum numbers.
- Λ is the projection of the orbital angular momentum onto the molecular axis. For the sake of clarity, the absolute values are replaced by Greek letters: Σ stands for the ground state (i. e. $\Lambda = 0$), whereas II stands for the first excited state (i. e. $\Lambda = 1$).
- +/- indicate the sign change of the wave function, if the molecule is mirrored on a plane passing through the intermolecular axis. It the sign changes, one writes and + otherwise.
- Ω describes the projection of the total angular momentum of the molecule onto its molecular axis.
- g/u characterizes the behaviour of the wave function with regard to the point reflection at the center of symmetry: If the sign of the wave function changes, u (ungerade) is written and g (gerade) if it does not.

As the molecular term symbols traditionally don't include the electronic state, the latter are often indicated by adding a letter in front of the whole term: If the molecule is in its electronic ground state, one prepends an X to the term. The excited states are labelled using A, B, \ldots according to their energetic order.

2.2 Electronic Transitions and Selection Rules

There are several selection rules that describe which transitions are allowed for molecules and which are not. Some selection rules are universally valid, whereas other rules are only valid if both the original state and the end state feature a specific angular momentum coupling (so called Hund's coupling cases). In our experiment, the relevant selection rules are

- $\bullet \ g \leftrightarrow u, \, g \nleftrightarrow u, \, u \nleftrightarrow g$
- $\Delta\Omega = 0, +1, -1$
- $\Delta \Lambda = 0, +1, -1$ (Case c)
- $\Delta S = 0$ (Case a)

In this experiment, the transition

$$X^{1}\Sigma_{0,q}^{+} \leftrightarrow B^{3}\Pi_{0,u}^{+} \tag{2}$$

of the iodine molecule I_2 is observed. This transition is only permitted due to the strong spin-orbit interaction of the iodine molecule. In addition, several rotational transitions are possible for this transition, but they differ energetically only so slightly that they can no longer be resolved with the setup used in this experiment.

2.3 Born-Oppenheimer approximation

The Born-Oppenheimer approximation is an assumption to greatly simplify the process of solving the Schrödinger equation: The approximation consists in considering the movements of the electrons and the nucleons separately. This results in the total wave function of the molecule as a product of the individual wave functions:

$$\psi_{\text{Mol}}(r_i, R_j) = \psi_{\text{vib}}(R_j) \cdot \psi_{\text{el}}(r_i, R_j) \tag{3}$$

In the above equation, ψ_{Mol} refers to the wave function of the molecule, whereas ψ_{vib} and ψ_{el} stand for the nuclei's and electron's wave functions, respectively; r_i and R_j refer to the electronic and nuclear coordinates. The Born-Oppenheimer approximation is based on the fact that the nuclei, due to their high mass, move much more slowly than the electrons, meaning that the electron interactions happen on a completely different time scale.

2.4 Franck-Condon principle

An electron transition takes place so quickly that it does not interfere with the slow movement of the nuclei. Thus, an electron transition can be drawn as a vertical line in a potential curve diagram, as shown in fig. 1.

The Franck-Condon principle states that the probability of a transition is given through the overlap of the potential curves of the ground and excited states. This probability can be determined with the Franck-Condon factor:

$$FC(\nu_i, \nu_k) = \left| \int \psi_{\rm vib}(\nu_i) \psi_{\rm vib}(\nu_k) \,\mathrm{d}R \right|^2. \tag{4}$$

 ψ_{vib} denotes the normalized vibration wave functions and ν_i and ν_k the vibration quantum numbers for the ground and excited state.



Figure 1: Visualization of the Franck-Condon principle [4] on two separate energetic states. The electron transition happens at a much shorter time scale than the nuclei's movements, meaning that the nuclear coordinates don't change.

2.5 Morse Potential

In order to determine the eigen energies of the molecular Hamiltonian, the Schrödinger equation has to be solved. As the latter involves the potential energy of the molecule which is quite complex to describe, the potential is often approximated. A polynomial ansatz using a Taylor approximation yields good results close to the equilibrium distance R_e , but approaches infinity when the distance gets too large. The Morse potential is an alternative exponential approach which approximates the potential particularly well for large distances between the nuclei up to the distance R_e . It is given by the following form:

$$V(R) = D_e \cdot \left[1 - e^{-a(R - R_e)}\right]^2.$$
 (5)

In this equation, D_e is the well depth and refers to the energy that has to be supplied in order to break the molecular bond. R describes the distance between both nuclei, R_e is the equilibrium distance, i. e. the distance for which the potential becomes minimal and a is a constant. For distances much smaller than R_e , the approximation does not work well anymore. From the Morse potential, the energy eigenvalues of the vibration states can be calculated exactly to

$$E_{\rm vib}(\nu) = hc\omega_e \left(\nu + \frac{1}{2}\right) - hc\omega_e x_e \left(\nu + \frac{1}{2}\right)^2,\tag{6}$$

where ω_e and $\omega_e x_e$ are vibrational constants and ν is the vibrational quantum number. As the factor hc often occurs in expressions for energy levels, the energy levels are often written as energy terms G = E/hc. This leads to

$$G(\nu) = \omega_e \left(\nu + \frac{1}{2}\right) - \omega_e x_e \left(\nu + \frac{1}{2}\right)^2.$$
(7)

The vibrational constants are given as

$$\omega_e = a \sqrt{\frac{\hbar D_e}{\pi \mu c}},\tag{8a}$$

$$\omega_e x_e = \frac{\hbar a^2}{4\pi\mu c}.$$
(8b)

2.6 Birge-Sponer plot

In the later analysis, a Birge-Sponer plot is used to calculate the molecular constants given in eqs. (8a) and (8b). For this, the energy term difference ΔG of two neighbouring vibration levels ν and $\nu + 1$ is used:

$$\Delta G\left(\nu + \frac{1}{2}\right) = G(\nu + 1) - G(\nu)$$

$$= \omega_e \left(\nu + \frac{3}{2}\right) - \omega_e x_e \left(\nu + \frac{3}{2}\right)^2 - \omega_e \left(\nu + \frac{1}{2}\right) + \omega_e x_e \left(\nu + \frac{1}{2}\right)^2$$

$$= \omega_e - \omega_e x_e \left[1 + 2\left(\nu + \frac{1}{2}\right)\right]$$

$$= \omega_e - \omega_e x_e (2 + 2\nu).$$
(9)

The x-axis intercept of the Birge-Sponer plot corresponds to the vibrational quantum number ν_{diss} , which is the highest state of the potential well. As the potential in a quantum mechanical system allows for a non-zero energy ground state, the energy needed for a molecule in its ground state is actually lower than the total well depth. One can calculate this dissociation energy D_0 by summing up all the energy term differences:

$$D_0 = \sum_{\nu=0}^{\nu_{\text{diss}}} \Delta G\left(\nu + \frac{1}{2}\right). \tag{10}$$

The potential depth is then simply given as the dissociation energy plus the energy G(0) of the ground state:

$$D_e = G(0) + D_0 = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e + \sum_{\nu=0}^{\nu_{\text{diss}}} \Delta G\left(\nu + \frac{1}{2}\right).$$
(11)

3 Setup and Procedure

3.1 Setup

Figure 2 shows the setup of the first part of the experiment. The parts needed to assemble the setup for the second part is also pictured.



Figure 2: Setup of the first part of the experiment. 1: Halogen lamp, 2: Lens, 3: Mirror, 4: Tube containing iodine, 5: Mirror, 6: Lens, 7: Filter (not used), 9: Lamp power supply, 10: Mercury lamp, 11: Helium-Neon laser, 12: Monochromator, 13: Photo-multiplier.



Figure 3: The setup used to measure the absorption spectrum of iodine. Lens 1 has a focal length of 150 mm and lens 2 a focal length of 70 mm. The used spectrometer is a CCD.

Absorption spectrum The experimental setup used to measure the absorption spectrum is shown in fig. 3. The light source is a halogen lamp with a continuous spectrum. The light is parallelized through a lens (focal length: 150 mm) about 15 cm

behind the lamp and directed into the iodine filled tube using a mirror. At the other end of the tube is an aperture with which the intensity of the emitted light can be regulated. The light coming out of the tube is directed through another mirror onto the CCD. To focus the light onto the CCD, another lens (focal length: 70 mm) is mounted about 6.5 cm in front of it. The CCD is connected to a computer on which the measured spectrum can be read with the program "SpectraSuite".



Figure 4: The setup for measuring the emission spectrum. Lens 1 has a focal length of 150 mm and lens 2 a focal length of 70 mm. A mercury lamp which is not shown in this figure was used for calibration during the experiment.

Emission spectrum To measure the emission spectrum, the experimental setup must be slightly modified as shown in fig. 4. As light source, a He-Ne laser is used. Instead of redirecting the light coming out of the tube with a mirror, the two lenses used previously are mounted behind the tube. The lenses focus the light on the input of the monochromator. The width of the input slit of the monochromator and the speed at which the grating within the monochromator rotates can be adjusted with a control element on the monochromator. As the angle of the grating controls the wavelength to be measured, the control unit allows for adjustment of the range and speed at which the wavelength is measured.

A photomultiplier is placed behind the monochromator with which the optical signal can be measured as voltage. The resolution and sensitivity of the photomultiplier signal can be adjusted with a discriminator. The signal of the photomultiplier can be recorded on the computer using the program "JodAnalog". To calibrate the program, a mercury lamp was temporarily used instead of the He-Ne laser.

3.2 Procedure

Absorption spectrum At first, the experimental setup described in the previous section was set up. The lenses and mirrors were adjusted in a way that the light of the halogen lamp was focused as well as possible on the CCD. The program SpectraSuite was used to measure the absorption spectrum. The upper peaks of the

spectrum were initially cut off. To prevent this, the aperture at the end of the tube was reduced until the intensity was low enough so that the measurements were no longer overdriven. Afterwards, test measurements were carried out with different integration times and numbers of scans set for averaging. Depending on the setting, the aperture had to be adjusted to prevent an overdrive. For the measurement used for the analysis, an integration time of 100 ms and a number of scans for averaging of 1000 was selected.

Emission spectrum In order to evaluate the emission spectrum, the spectrum of the mercury lamp had to be measured first in order to perform a wavelength calibration. For this, the monochromator was set to a value of 4050 nm which coincides with one of the peak wavelengths of mercury. Then the lenses were adjusted so that the signal of the photomultiplier became maximum. The spectrum was then recorded in the range from 4000 Å to 6000 Å. On the monochromator the slit opening was set to $34 \,\mu\text{m}$ and a velocity of $2 \,\text{\AA s}^{-1}$. For the photomultiplier the discriminator was set to 0 with a range of 10^6 . After the measurement was complete, the mercury lamp was switched off and the He-Ne laser switched on. The monochromator was set to $6330 \,\text{\AA}$ which should correspond to the wavelength of the laser peak, and the slit opening to $50 \,\mu\text{m}$. The lenses and the discriminator were then adjusted to again maximize the signal. Then, the laser peak was measured in a range of: The settings used to measure the laser peak were a velocity of $2 \,\text{\AA s}^{-1}$ for the monochromator and the discriminator was set to 0.4 with a range of 10^7 . Measurements were taken from $6300 \,\text{\AA}$ to $6370 \,\text{\AA}$.

Then, the monochromator was set to 6500 Å and the signal was maximized again. For the emission measurement used for later analysis, the monochromator was set to a slit width of 370 μ m and the spectrum was measured at a velocity of 1 Å s⁻¹. The discriminator was set to 0.4 with a range of 300. The spectrum was measured from 6400 Å to 8000 Å.

4 Analysis

4.1 Absorption Spectrum



Figure 5: Absorption spectrum of iodine. The expected transition of $\nu'' = 0 \rightarrow \nu' = 25$ is shown in red.

At first, the absorption spectrum has to be evaluated. The spectrum was measured using a CCD spectrometer and is shown alongside the expected transition in fig. 5. In order to be able to create the Birge-Sponer-plot, some transitions have to be identified.

4.1.1 Identification of Transitions

According to the manual [1], the transition of $\nu'' = 0 \rightarrow \nu' = 25$ features a wavelength of $\lambda = 545.8 \,\mathrm{nm}$. Using the Franck-Condon-principle, one can now number the neighbouring transitions which are clearly visible as dips in the spectrum with the quantum number ν' . Because we are only interested in the zeroth transition between the ground state and the excited state $B^3\Pi_{0u}^+$, one has to be careful not to select transitions belonging to other states. In order to do so, only a small window of the spectrum can be used to find the appropriate wavelengths and respective transition energies. Figure 6 shows an excerpt of the whole spectrum where the transitions are numbered using the Franck-Condon-principle.

Because of the additional rotational transitions, the data appears a bit noisy with additional peaks clearly visible. In order not to count the uninteresting transitions, the lines were selected by hand rather than by use of an analytical way. Because of this, we estimated the error on each wavelength $\lambda_{\nu'}$ to be $s_{\lambda} = 0.2 \text{ nm}$. The transitional wave numbers $k_{\nu'} = 1/\lambda_{\nu'}$ can now be calculated. One can estimate the



Figure 6: Closer view of the spectrum shown in fig. 5 with transition ν' values.

error on each wave number using Gaussian error propagation, i.e.

$$s_{k_{\nu'}} = \frac{s_{\lambda_{\nu'}}}{\lambda_{\nu'}^2}.$$
(12)

The wave numbers and the wavelengths can be found in the appendix in table 3.

4.1.2 Birch-Sponer Plot

Using the wave numbers $k_{\nu'}$ determined above, the Birch-Sponer plot can be created: For each of the neighbouring wave numbers ν and ν' , one defines the difference

$$\Delta G\left(\nu' + \frac{1}{2}\right) = G(\nu' + 1) - G(\nu') = k_{\nu'+1} - k_{\nu'}.$$
(13)

The error on these differences propagate according through Gaussian error propagation:

$$s_{\Delta G\left(\nu'+\frac{1}{2}\right)} = \sqrt{s_{k_{\nu'+1}}^2 + s_{k_{\nu'}}} \tag{14}$$

The differences of the wave numbers are now plotted against $\nu' + \frac{1}{2}$ and can be found in the appendix (cf. table 4). The plot is shown in fig. 7. Using the method curve_fit from the Python module scipy.optimize, a linear regression of the form

$$\Delta G\left(\nu' + \frac{1}{2}\right) = \alpha \cdot \left(\nu' + \frac{1}{2}\right) + \beta \tag{15}$$

is performed. In the equation shown above, α and β are parameters to be determined by the fit which yielded $\alpha = (-2.08 \pm 0.11) \text{ cm}^{-1}$ for the slope and $\beta =$



Figure 7: Birch sponer plot with the values shown in table 4.

 $(132 \pm 3) \,\mathrm{cm^{-1}}$ for the axis intercept. The plot is shown alongside the data in fig. 7. The molecular constants of the Morse potential can be calculated through the use of the Birch-Sponer plot: Substituting the eigenenergies (6) of the Morse potential in eq. (13), one finds

$$\Delta G\left(\nu' + \frac{1}{2}\right) = \omega_e - \omega_e x_e(2\nu' + 2) = -2\omega_e x_e\left(\nu' + \frac{1}{2}\right) + (\omega_e - \omega_e x_e).$$
(16)

If one compares the equation above with eq. (15), the molecular constants can be calculated by the regression parameters:

$$\omega_e = \beta - \frac{\alpha}{2} = (133 \pm 3) \,\mathrm{cm}^{-1}$$

$$\omega_e x_e = -\frac{\alpha}{2} = (1.04 \pm 0.06) \,\mathrm{cm}^{-1}$$
(17)

The errors above were calculated by applying Gaussian error propagation on the uncertainties s_{α} , s_{β} given by the covariance matrix returned by the linear regression:

$$s_{\omega_e} = \sqrt{s_\beta^2 + \frac{s_\alpha^2}{4}}$$

$$s_{\omega_e x_e} = \frac{s_\alpha}{2}$$
(18)

4.1.3 Determination of the Potential Depth

Now, the potential depth D'_e of the Morse potential will be determined. In the following, the potential depth is calculated in two different ways.

The first way consists of summing up the differences $\Delta G(\nu' + \frac{1}{2})$ for each transition ν' up to the vibrational quantum number ν_{diss} where the molecule dissociates.

Additionally, the energy G(0) has to be added to the sum. However, one can estimate the sum of the differences by calculating the area under the curve given by eq. (15). Anyhow, ν_{diss} has to be determined beforehand: Its value is given by the *x*-axis intercept of the regression curve (15):

$$\nu_{\rm diss} = -\frac{\beta}{\alpha} = 63 \pm 4 \tag{19}$$

The error on the dissociation vibrational quantum number was calculated from the errors of the fit parameters by use of Gaussian error propagation:

$$s_{\nu_{\rm diss}} = \sqrt{\left(\frac{s_{\beta}}{\alpha}\right)^2 + \left(\frac{\beta}{\alpha^2} \cdot s_{\alpha}\right)^2} \tag{20}$$

The area below the regressional curve which approximates the sum of wave number differences is given by the area of a triangle with base ν_{diss} and height β :

$$D'_{e,1} = \frac{1}{2}\nu_{\text{diss}} \cdot \beta$$

= (4250 ± 290) cm⁻¹ (21)

Again, the error on the potential depth $D'_{e,1}$ is given by Gaussian error propagation:

$$s_{D'_{e,1}} = \frac{1}{2} \sqrt{(s_{\nu_{\text{diss}}} \beta)^2 + (s_{\nu_{\text{diss}}} s_{\beta})^2}.$$
 (22)

The potential depth can also be calculated directly through the Morse potential: If one substitutes a in eq. (8a) using eq. (8b), the resulting equation can in turn be solved for $D'_{e,2}$:

$$D'_{e,2} = \frac{\omega_e^2}{4\omega_e x_e}$$
(23)
= (4300 ± 300) cm⁻¹

The error on $D_{e,2}$ was propagated in the following way:

$$s_{D_{e,2}} = \sqrt{\left(\frac{2\omega_e}{4\omega_e x_e} \cdot s_{\omega_e}\right)^2 + \left(\frac{\omega_e^2}{4(\omega_e x_e)^2} \cdot s_{\omega_e x_e}\right)^2} \tag{24}$$

4.1.4 Determination of the Dissociation Energy

After determining the potential depth D'_e of the excited state $B^3\Pi^+_{0u}$, the dissociation energy E_{diss} can be determined. This quantity refers to the energy needed for a photon to excite the molecule from the vibrational ground state ($\nu' = 0$) of the electronic ground state $X^1\Sigma^+_{0g}$ to the state of dissociation reached at $\nu'' = \nu''_{\text{diss}}$. Because the electronic state must change when the molecule is excited by a photon, this state of dissociation is located within the excited state $B^3\Pi^+_{0u}$.



Figure 8: Crop of the absorption spectrum near the point where no more dips occur in the spectrum. The smallest wavelength λ_{diss} where no absorption is observed anymore is marked by the red line. Its uncertainty is represented by the dotted lines.

The dissociation energy can be determined quite easily by visually analyzing the spectrum (cf. fig. 8): By looking at the spectrum and searching for the lowest wavelength λ_{diss} where no absorption occurs anymore, we find the the corresponding energy to be E_{diss} . In the case of our spectrum, the location of the smallest wavelength isn't exactly clear, meaning that we have to compensate for this by estimating a larger error. This way, the wavelength $\lambda_{\text{diss}} = (502 \pm 2)$ nm was determined. The corresponding energy can be easily calculated as

$$E_{\rm diss} = \frac{1}{\lambda_{\rm diss}} = (19\,920\pm80)\,{\rm cm}^{-1},$$
 (25)

in which the error was calculated by use of Gaussian error propagation as $s_{E_{\rm diss}} = s_{\lambda_{\rm diss}}/\lambda_{\rm diss}^2$.

4.1.5 Determination of the Excitation Energy

With E_{diss} determined, the excitation energy T_e which refers to the energy difference between the minima of the excited molecular state and the ground state can now be calculated. The dissociation energy can be expressed in terms of the excitation energy as

$$E_{\text{diss}} = T_e - G''(0) + D'_e \approx T_e - G'(0) + D'_e = T_e + D'_0.$$
(26)



Figure 9: Morse potential determined by the molecular constants from the absorption spectrum plotted alongside the Morse potential obtained by use of the literature values.

As we have no way of determining G''(0) for the ground state, it was approximated as the vibrational energy of the excited state G'(0). D'_0 can easily be calculated as

$$D'_{0} = D'_{e,2} - G'(0)$$

= $D'_{e,2} - \frac{1}{2}\omega_{e} + \frac{1}{4}\omega_{e}x_{e}$
= $(4200 \pm 300) \,\mathrm{cm}^{-1}.$ (27)

The error was propagated as

$$s_{D'_0} = \sqrt{s_{D'_{e,2}}^2 + \frac{s_{G'(0)}^2}{4} + \left(\frac{s_{\omega_e x_e}}{4}\right)^2}.$$
(28)

Now, by rearranging eq. (26) one arrives at the excitation energy of

$$T_e = E_{\rm diss} - D'_0 = (15\,600 \pm 400)\,{\rm cm}^{-1}$$
 (29)

in which the error was propagated in the usual way.

4.1.6 Approximation of the Morse potential

With the molecular constants ω_e and $\omega_e x_e$ determined earlier, it is now possible to create a plot of the Morse potential given by

$$V(R) = D'_{e,2} \cdot \left[1 - e^{-a(R-R_e)}\right]^2,$$
(30)

where a is a constant given by

$$a = \sqrt{\frac{4\pi c\mu}{\hbar} \cdot \omega_e x_e} = (19.8 \pm 1.1) \,\mathrm{nm}^{-1}.$$
 (31)

In the above equation, c refers to the speed of light, \hbar stands for the reduced Planck constant, μ is the reduced mass of the iodine molecule and $\omega_e x_e$ is the molecular constant determined earlier. As only the latter has an uncertainty, the error of a can be calculated as

$$s_a = \frac{s_{\omega_e x_e}}{2\sqrt{\omega_e x_e}} \cdot \sqrt{\frac{4\pi c\mu}{\hbar}}.$$
(32)

The Morse potential is shown alongside the expected potential in fig. 9.

4.2 Emission Spectrum

In this section, the measured emission spectrum will be analyzed. As each of the measurements needed for the analysis of the spectrum were taken using a software which wasn't able to measure the wavelength correctly, a manual correction was necessary: Instead of using the wavelength given in the files generated by the measurement program, we noted the correct start and end values of the wavelength shown on the display on the monochromator. By generating a linear set of wavelengths with these start and end values as well as the original amount of data points, the faulty wavelength was corrected.

4.2.1 Calibration of the Monochromator

As the wavelength shown on the monochromator and used in further analysis could very well be faulty, a calibration is needed to verify the wavelengths and do optional adjustments. The calibration was carried out using a mercury lamp which features a very distinct and easily recognizable spectrum. After applying the aforementioned correction of the wavelength in order to correct the faulty program, the spectrum could now be plotted. The intensity is shown in fig. 10 alongside the expected lines of the mercury lamp as given in the manual [1]. As one can see, the peaks are not as sharp as we'd hoped, spanning multiple nanometers. The distinct orange double line could not be resolved and looks like a single peak. The position of the peaks, however, do match the spectrum quite well. As we aren't able to make out the exact centers of the peaks in the spectrum, we didn't correct the wavelength any further.

4.2.2 Laser Peak

The laser used in the measurement of the emission spectrum features a wavelength of $\lambda = 633 \text{ nm} = 6330 \text{ Å}$. Figure 11 shows our measurement of the laser spectrum. As one can clearly see, the laser peak is neither really Gaussian shaped nor is it at the right position but rather a bit off-center. Because the laser spectrum is of this rather large width, we weren't able to make out one specific wavelength. For this reason we could not determine the molecular transition of iodine with certainty.



Figure 10: Measured spectrum of the mercury lamp for calibration of the monochromator wavelength. The intensity is given by the photomultiplier voltage U. In addition to the spectrum, the expected lines are also shown.



Figure 11: Measured spectrum of the laser as voltage U of the photomultiplier. Additionally, the expected laser wavelength of $\lambda = 633$ nm is shown.



Figure 12: Measured emission spectrum of iodine with marked peaks. The dashed lines show the estimated uncertainty of the location of each peak.

4.2.3 Emission Spectrum of Iodine

Now, the actual emission spectrum can be evaluated. In order to get a spectrum with as little noise as possible, the discriminator was set to the low level of 300. Because of this, the signal overmodulated in the range of the laser peak, leading us to start the measurement behind the laser peak at $\lambda = 6400$ Å. Figure 12 shows the entire emission spectrum. As the peaks shown in the spectrum appear quite asymmetrical, we decided to approximate the position of each peak by hand rather than using a fit. In order to compensate for this, we tried to estimate the errors on the peak positions conservatively. The estimated peaks are shown alongside the spectrum in fig. 12. Table 2 shows the results from the estimation alongside the wave number $k_{\nu''}$ which was calculated for each estimated wavelength $\lambda_{\nu''}$ using

$$k_{\nu''} = \frac{1}{\lambda_{\nu''}}, \qquad s_{k_{\nu''}} = \frac{s_{\lambda_{\nu''}}}{\lambda_{\nu''}^2}.$$
(33)

By comparing the absolute wave number values with the literature values given in the staatsexamen [2], we found that the transitions

$$\nu' = 6 \rightarrow \nu'' = 5$$
 to $\nu' = 6 \rightarrow \nu'' = 16$

fit the measured wave numbers the best.

	Measu	Lit. Values	
ν''	$\lambda_{\nu^{\prime\prime}}$ [Å]	$k_{\nu''} [\mathrm{cm}^{-1}]$	$k_{\nu''} [{\rm cm}^{-1}]$
5	6510 ± 10	15361 ± 24	15394
6	6591 ± 10	15172 ± 23	15186
$\overline{7}$	6692 ± 5	14943 ± 11	14980
8	6776 ± 15	14760 ± 30	14776
9	6871 ± 10	14554 ± 21	14572
10	6964 ± 15	14360 ± 30	14370
11	7071 ± 12	14142 ± 24	14168
12	7165 ± 10	13957 ± 19	13969
13	7257 ± 25	13780 ± 50	13770
14	7375 ± 20	13560 ± 40	13572
15	7469 ± 25	13390 ± 50	13376
16	7594 ± 18	13170 ± 30	13181

Table 2: Measured wavelengths of the peaks in the emission spectrum (cf. fig. 12) alongside their respective wave numbers. Additionally, the literature values [2] of the wave numbers of the transition $\nu' = 6 \rightarrow \nu'' = 5$ to 16 are shown.

5 Discussion

5.1 Absorption Spectrum

Using a halogen lamp and a CCD detector in conjunction with the program Spectra-Suite, the absorption spectrum of the iodine molecule I₂ was measured. The expected absorption dips caused by the vibrational transitions were recognized and some of them attributed to specific vibrational transitions between the ground state $X^1 \Sigma_{0g}^+$ and the excited state $B^3 \Pi_{0g}^+$ of iodine. Using the Birch-Sponer method, a Birch-Sponer plot was created in order to find the molecular constants ω_e and $\omega_e x_e$ characterizing the molecule's potential in the excited state:

$$\omega_e = (133 \pm 3) \,\mathrm{cm}^{-1},$$

and $\omega_e x_e = (1.04 \pm 0.06) \,\mathrm{cm}^{-1}.$ (34)

The literature values of these constants are

$$\omega_e = 125.273 \,\mathrm{cm}^{-1},$$

and $\omega_e x_e = 0.7016 \,\mathrm{cm}^{-1},$ (35)

respectively [3]. Comparing the values determined by us with their respective literature values, one can see that our measurement of ω_e deviates by about 2.6 σ from the literature value, whereas $\omega_e x_e$ is off by about 5.6 σ . As the Birch-Sponer plot in fig. 7 is quite linear, it seems unlikely that our deviation from the literature values stem from a statistical misjudgement of the position of the dips in the spectrum. One could argue, however, that because the measurement of the absorption spectrum doesn't include a calibration as the emission measurement, we have no way of knowing that the wavelengths given by SpectraSuite correspond to the actual wavelength values: If the wavelength's scaling factor is off by a bit, the linearity of the dips won't be affected, but the slope and axis intercept would be affected. That way, the setup used to take the absorption measurement could be affected by a systematic error which explains the high deviation of the molecular constants.

Next, the potential wall depth D_0 was calculated using two methods: The first method consisted of approximating the sum of term differences by the area under the Birch-Sponer plot and gives a potential depth of

$$D'_{e,1} = (4250 \pm 290) \,\mathrm{cm}^{-1}.$$
 (36)

The second method used the properties of the Morse potential and yielded

$$D'_{e,2} = (4300 \pm 300) \,\mathrm{cm}^{-1}. \tag{37}$$

One can see that the error on both values is quite high, averaging about 7% of their values. Comparing both values with their literature value of $4391 \,\mathrm{cm}^{-1}$, we see that both values exist in a 1 σ -environment. However, this seems partly due to the large error as the values deviate by about 3%. Interestingly, the approximation used by the method with the Morse potential yields better results than the one which employed the Birch-Sponer plot. This could on the one hand again be due to a possible wavelength scaling issue by the program, but on the other hand due to the fact that we didn't sum up the term differences exactly, but rather approximated the sum using the area under the Birch-Sponer plot.

The dissociation energy $E_{\rm diss}$ was calculated to be

$$E_{\rm diss} = (19\,920 \pm 80)\,\rm cm^{-1} \tag{38}$$

using a visual analysis of the spectrum near the point where no more dips occur. The literature value is given as [3, p. 29]

$$E_{\rm diss} = 20\,014\,\rm cm^{-1},\tag{39}$$

meaning that our value deviates by about 1.2σ . As our spectrum doesn't show the low-wavelength peaks with a high enough precision, this could easily be due to the noise drowning out any peaks. Another possibility is that we didn't use the averaging function of the program appropriately, meaning that the missing peaks could have been simply averaged away.

Next, the energy difference between the potential minima of ground state and excited state T_e was determined using the dissociation energy. Our analysis showed the value to be

$$T_e = (15\,600 \pm 400)\,\mathrm{cm}^{-1},\tag{40}$$

which is in a 1σ -environment with regard to the literature value of $15\,770.59\,\mathrm{cm}^{-1}$ [3].

At last, the Morse potential was plotted using the values determined earlier. Although the constant $a = (19.8 \pm 1.1) \text{ nm}^{-1}$ deviates significantly from the one which can be calculated using the literature values of 1.62 nm^{-1} , the plot fits the expected Morse potential quite well (cf. fig. 9). As a was calculated using $\omega_e x_e$ which deviates significantly from the literature value, a high deviation of a isn't surprising.

5.2 Emission Spectrum

The second part of the experiment dealt with the emission spectrum of iodine: The spectrum could be measured by using a laser to excite the iodine and subsequently measuring the wavelength's intensities using a monochromator. By finding the location of each peak by hand and comparing its respective wave number to a table of literature values [2], the progression could be identified: The transition which occurred most likely was found to be

$$\nu' = 6 \to \nu'' = 5$$
 to $\nu' = 6 \to \nu'' = 16$

As one can see in table 2 the measured wave numbers coincide very well with the literature values, deviating below one standard deviation. As the relative error is of a magnitude of about 0.1%, the peaks locations could be identified with satisfying precision. However, the method relied on estimating the peaks position by hand. An analytical fit wasn't deemed useful by us, as the peaks appeared quite asymmetrical. Furthermore, the shape of each peak varies by quite a bit, meaning that it is hard to find an appropriate function to fit the peaks with. This issue could be solved by the use of a better monochromator unit. One can also criticise the experimental setup for a faulty measurement program as the program doesn't give the correct wavelengths. However, as shown in our calibration measurement (cf. fig. 10), by noting down start and end values of the wavelength, it was possible to extrapolate the correct wavelengths up to a satisfying degree. The figure shown there also supports the idea, that the measurement setup was not as well calibrated as we hoped it would: This can be seen in the peaks of the mercury lamp, which appear unusually wide, which could either be due to an imperfect optical path or even a fault in the monochromator's function.

A Appendix

List of Figures

1	Visualization of the Franck-Condon principle [4] on two separate en- ergetic states. The electron transition happens at a much shorter time scale than the nuclei's movements, meaning that the nuclear	
	coordinates don't change.	7
2	Setup of the first part of the experiment. 1: Halogen lamp, 2: Lens, 3: Mirror, 4: Tube containing iodine, 5: Mirror, 6: Lens, 7: Filter (not used), 9: Lamp power supply, 10: Mercury lamp, 11: Helium-Neon	
	laser, 12: Monochromator, 13: Photomultiplier	9
3	The setup used to measure the absorption spectrum of iodine. Lens 1 has a focal length of 150 mm and lens 2 a focal length of 70 mm. The	
	used spectrometer is a CCD.	9
4	The setup for measuring the emission spectrum. Lens 1 has a focal	
	length of 150 mm and lens 2 a focal length of 70 mm. A mercury lamp which is not shown in this figure was used for calibration during the	
	experiment	10
5	Absorption spectrum of iodine. The expected transition of $\nu'' = 0 \rightarrow \infty$	10
	$\nu' = 25$ is shown in red.	12
6	Closer view of the spectrum shown in fig. 5 with transition ν' values.	13
7	Birch sponer plot with the values shown in table 4	14
8	Crop of the absorption spectrum near the point where no more dips	
	sorption is observed anymore is marked by the red line. Its uncer	
	tainty is represented by the dotted lines	16
0	Morse potential determined by the molecular constants from the ab-	10
5	sorption spectrum plotted alongside the Morse potential obtained by	
	use of the literature values	17
10	Measured spectrum of the mercury lamp for calibration of the monochro-	±.
	mator wavelength. The intensity is given by the photomultiplier volt-	
	age U . In addition to the spectrum, the expected lines are also shown.	19
11	Measured spectrum of the laser as voltage U of the photomultiplier.	
	Additionally, the expected laser wavelength of $\lambda = 633$ nm is shown.	19
12	Measured emission spectrum of iodine with marked peaks. The dashed	
	lines show the estimated uncertainty of the location of each peak	20

List of Tables

1	Symbols used in this lab report. Quantities belonging to the ground	
	state are labelled using a single prime (\prime) ; quantities belonging to the	
	excited state are labelled using two primes $(\prime\prime)$	4
2	Measured wavelengths of the peaks in the emission spectrum (cf.	
	fig. 12) alongside their respective wave numbers. Additionally, the	
	literature values [2] of the wave numbers of the transition $\nu' = 6 \rightarrow$	
	$\nu'' = 5$ to 16 are shown.	21
3	Values of the transitional wavelengths and respective wave numbers	
	regarding ν' . The wavelengths are also shown in fig. 6	26
4	Differences in the transitional wave numbers of the transitions $\nu' + 1$	
	and ν' to be plotted in the birch sponer plot (cf. fig. 7)	26

ν'	$\lambda_{\nu'}$ [nm]	$k_{\nu'} [\mathrm{cm}^{-1}]$
37	522.65 ± 0.20	19133 ± 5
36	524.18 ± 0.20	19077 ± 5
35	525.78 ± 0.20	19019 ± 5
34	527.47 ± 0.20	18958 ± 5
33	529.18 ± 0.20	18897 ± 5
32	531.04 ± 0.20	18831 ± 5
31	532.94 ± 0.20	18764 ± 5
30	534.92 ± 0.20	18694 ± 5
29	537.08 ± 0.20	18619 ± 5
28	539.33 ± 0.20	18542 ± 5
27	541.47 ± 0.20	18468 ± 5
26	543.65 ± 0.20	18394 ± 5
25	545.87 ± 0.20	18319 ± 5
24	548.28 ± 0.20	18239 ± 5
23	550.80 ± 0.20	18155 ± 5
22	553.44 ± 0.20	18069 ± 5
21	556.22 ± 0.20	17978 ± 5
20	559.00 ± 0.20	17889 ± 5

Table 3: Values of the transitional wavelengths and respective wave numbers regarding ν' . The wavelengths are also shown in fig. 6.

		-		
$\nu' + \frac{1}{2}$	$\Delta G\left(\nu' + \frac{1}{2}\right)$	-	$\nu' + \frac{1}{2}$	$\Delta G\left(\nu'+\frac{1}{2}\right)$
36.5	56 ± 8	-	27.5	73 ± 7
35.5	58 ± 8		26.5	74 ± 7
34.5	61 ± 8		25.5	75 ± 7
33.5	61 ± 8		24.5	81 ± 7
32.5	66 ± 8		23.5	83 ± 7
31.5	67 ± 7		22.5	87 ± 7
30.5	69 ± 7		21.5	90 ± 7
29.5	75 ± 7		20.5	89 ± 7
28.5	78 ± 7			

Table 4: Differences in the transitional wave numbers of the transitions $\nu' + 1$ and ν' to be plotted in the birch sponer plot (cf. fig. 7).

Lab Notes



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