

I_2 -Molecule

September 16 and 17, 2014

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All calculations in this protocol were performed either with Python 2.7 using the following libraries:

- PyROOT (<http://root.cern.ch/drupal/content/pyroot>)
- NumPy (<http://www.numpy.org/>)

or with Mathematica 9.0 and 10.0 (<http://www.wolfram.com/mathematica/>).

All graphics were drawn with Inkscape (<http://www.inkscape.org>).

The python-scripts, L^AT_EX-scripts, Mathematica notebooks and svg-graphics can be accessed online under <https://github.com/Bigben37/FP1/tree/master/0916-I2>.

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1. Aim of the experiment

In this experiment the transmission spectrum of iodine will be recorded. This data provides information about vibrational transitions which accompany the electronic transition from $^1\Sigma_{0g}^+$ to $^3\Pi_{0u}^-$. Analysis of the vibrational transitions reveals information about fundamental constants to describe the I_2 -molecule: Vibration constants of ground and excited electronic state, dissociation energies and the shape of the potential of the nuclei.

2. Physical Principles

The formulas and explanations in this section are based on [1] (p. 6 - 20)

2.1. Born-Oppenheimer approximation

Since molecules have a much more complicated Hamiltonian than a hydrogen atom, it is not possible to solve the Schrödinger equation analytical. But there are ways to solve the Schrödinger equation for this problem anyway, if you use approximations for the wave function. A good approximation for molecules is the *Born-Oppenheimer approximation*. The reasoning is in the following way: The nuclei are much heavier than the electrons of the molecule ($m_{\text{nucleus}} \gg m_{\text{electron}}$). Thus the electrons have a much shorter time scale in which they react to changes of the potential of the molecule than the nuclei. Also they are only minimally affected by the proper motion of the nuclei. According to the *Born-Oppenheimer approximation* you can write the whole wave function as a product of the wave functions of the nuclei and the electrons:

$$\Psi_{\text{total}} = \Psi_{\text{electrons}} \cdot \Psi_{\text{nuclei}} \quad (2.1)$$

2.2. Energy levels of vibration

In a two atomic molecule the two nuclei interact with each other in a mutual potential, which is a function of the internuclear distance. In analogy to the two-body problem in classical mechanics you can reduce the problem to a problem with only one particle with a reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$ and an effective potential $V(r)$. The Schrödinger equation is

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + V(r) \right) \Psi(r) = E\Psi(r). \quad (2.2)$$

For small vibrations around the minimum of the potential ($r = r_e$), the two nuclei are in equilibrium and you can perform a series expansion on the potential $V(r)$:

$$\begin{aligned} V(r) &= V(r_e) + \underbrace{\frac{\partial V(r)}{\partial r} \Big|_{r=r_e}}_{=0} (r - r_e) + \frac{1}{2} \frac{\partial^2 V(r)}{\partial r^2} \Big|_{r=r_e} (r - r_e)^2 \\ &\quad + \frac{1}{6} \frac{\partial^3 V(r)}{\partial r^3} \Big|_{r=r_e} (r - r_e)^3 + \dots \\ &=: V(r_e) + \frac{1}{2} V''(r_e)(r - r_e)^2 + \frac{1}{6} V'''(r_e)(r - r_e)^3 + \dots \end{aligned} \quad (2.3)$$

If you approximate the potential only up to second order the potential equals the potential of a harmonic oscillator with known frequency and eigenenergies:

$$\omega = \sqrt{\frac{V''(r_e)}{m}} \quad (2.4)$$

$$E(\nu) = \hbar\omega \left(\nu + \frac{1}{2} \right), \quad \nu = 0, 1, 2, \dots \quad (2.5)$$

For higher energy levels this approximation is not good enough, since the potential is not symmetric around r_e , and you need to consider higher orders of the series expansion. You can solve the Schrödinger equation with perturbation theory and it yields the eigenenergies of an inharmonic oscillator:

$$G(\nu) = \omega_e \left(\nu + \frac{1}{2} \right) - \omega_e x_e \left(\nu + \frac{1}{2} \right)^2 + \omega_e y_e \left(\nu + \frac{1}{2} \right)^3 + \dots, \quad \nu = 0, 1, 2, \dots \quad (2.6)$$

The factor ω_e corresponds to the oscillation frequency of the harmonic oscillator, the factors $\omega_e x_e$, $\omega_e y_e$, \dots describe the inharmonicity of the potential. The order of magnitudes decrease with higher powers of ν

$$\omega_e \gg \omega_e x_e \gg \omega_e y_e \gg \dots \quad (2.7)$$

The difference between two adjacent eigenenergies is

$$\Delta G \left(\nu + \frac{1}{2} \right) = G(\nu+1) - G(\nu) = \omega_e - \omega_e x_e (2\nu+2) + \omega_e y_e \left(3\nu^2 + 6\nu + \frac{13}{4} \right) + \dots \quad (2.8)$$

Provided that $\omega_e x_e$ is positive (and it is for the I_2 -molecule) there is a ν_{diss} with $\Delta G(\nu_{\text{diss}} + \frac{1}{2}) = 0$. If the energy of the molecule is above this energy level it is in a dissociated state, the atoms split into two ions.

The dissociation energy from the lowest energy level is

$$D_0 = \sum_{\nu=0}^{\nu_{\text{diss}}} \Delta G \left(\nu + \frac{1}{2} \right), \quad (2.9)$$

and from the minimum of the potential

$$D_e = G(0) + D_0 \quad (2.10)$$

Since $\hbar\omega = hf$, $f = \frac{c}{\lambda}$ and $\lambda = \frac{1}{\bar{\nu}}$ the energy of vibrational states and dissociation often is denoted in wavenumbers $\bar{\nu}$ (in multiples of hc , because $E = hc\bar{\nu}$) with the dimension cm^{-1} .

2.3. Morse potential

A good approximation of the real potential of a two atomic molecule is the *Morse potential*

$$V(r) = D_e (1 - e^{-a(r-r_e)})^2 \quad (2.11)$$

with dissociation energy (from the minimum of the potential) D_e , a molecule specific constant a and the internuclear distance r_e .

For small distances, the Morse potential describes a strong repulsion (Coulomb force). For higher distances it depicts attraction due to the van der Waals force. The potential minimum, where the two forces are in balance, is the position of the equilibrium distance of the nucleus.

The Schrödinger equation for this potential yields for the constants in [Equation 2.6](#):

$$w_e = a \sqrt{\frac{\hbar D_e}{\pi c \mu}} \quad (2.12)$$

$$w_e x_e = \frac{\hbar a^2}{4\pi c \mu} \quad (2.13)$$

The dissociation energy can be calculated with those two constants:

$$D_e = \frac{\omega_e^2}{4\omega_e x_e} \quad (2.14)$$

2.4. Absorption of radiation

In the beginning the molecule is in the electronic ground state with vibration quantum number ν'' . If now light with a continuous spectrum is irradiated, a electron can be lifted into an excited state with vibration quantum number ν' . Since the spectrum of the used light is continuous, there is not only one absorption line but many. The lines in their entirety are called a *bond*, where every transition $\nu'' \leftrightarrow \nu'$ corresponds to a definite wavelength. All transitions from the same ground state level ν'' are summarized as a *progression*.

The probability α , which is in accordance with the intensity and can also be found under

the name of *Franck-Condon factor*, of a transition is calculated via the *Franck-Condon principle*:

$$\alpha = \left| \int \Psi_{\nu'}(R) \Psi_{\nu''}(R) dV \right|^2 \quad (2.15)$$

with wave functions of the electronic ground state $\Psi_{\nu''}$ and the excited state $\Psi_{\nu'}$. This integral is also called an overlap integral, because it describes the concentration of the two states in the same space.

2.5. Allowed transitions

Basically there is an infinite number of possible transitions into higher states, but not all are allowed. The theoretical foundation is provided by *Fermi's golden rule*, which leads to specific transition rules depending on which multipole for approximation is used. In this case the consideration of the electric dipole is enough and leads to following rules:

- $g \leftrightarrow u, g \nleftrightarrow g, u \nleftrightarrow u$
- $\Delta M_j = 0, \pm 1$
- $\Delta \Lambda = 0, \pm 1$
- $\Delta S = 0$

M_j is the magnetic quantum number, Λ the total angular momentum and S the total spin of the molecule. The parity is described with g (even = “gerade”) and u (odd = “ungerade”). The ground state of I_2 is $^1\Sigma_{0g}^+$. If you use the transition rules onto this state, there are only two excited states which are allowed: $^3\Pi_{0u}^-$ and $^3\Pi_{2u}$. But the transition to the second excited state is very weak so that only the transition to the first one can be measured in this experiment.

2.6. Rotation

While the molecule is vibrating it can also rotate around its center of mass. The quantum-mechanical consideration of the angular momentum operator \hat{L}^2 yields a correlation between the rotational constant B_e ¹, the reduced mass μ and the equilibrium distance r_e of the two nuclei:

$$B_e = \frac{\hbar^2}{4\pi\mu r_e^2} \quad (2.16)$$

¹With this rotational constant you can write the eigenenergies \hat{L}^2 as $E_l = Bhcl(l+1)$, where l are the eigenvalues of \hat{L}^2 . But since this experiment does not include the experimental measurement of this constant, the theory has been kept to minimum.

2.7. Statistics

2.7.1. Weighted mean

Different values x_i with individual errors s_i are given. The weighted (arithmetic) mean and its error is:

$$\bar{x} = \frac{\sum_i \frac{x_i}{s_i^2}}{\sum_i \frac{1}{s_i^2}}, \quad s_{\bar{x}}^2 = \frac{1}{\sum_i \frac{1}{s_i^2}} \quad (2.17)$$

3. Experimental Setup

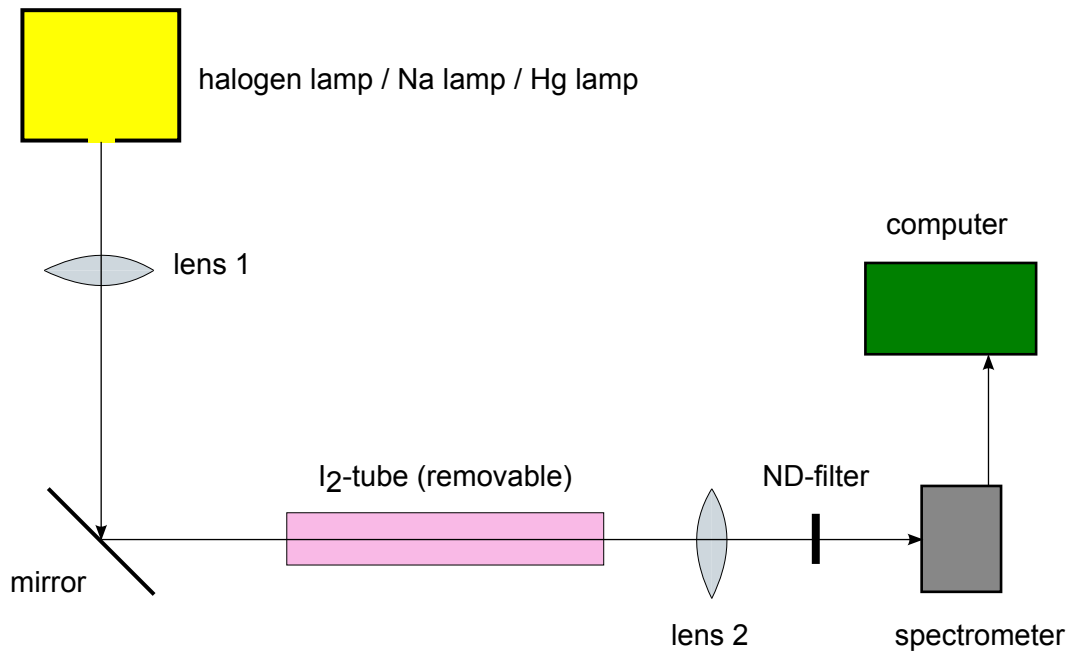


Figure 3.1: Experimental setup for measuring the emission spectra of different lamps and the transmission spectrum of I₂.

Figure 3.1 shows the experimental setup which has been constructed on an optical bench. As a light source, two lamps with discrete spectra (Na and Hg lamp) or a halogen lamp with continuous spectrum can be mounted. The light from the lamp is collimated by lens 1 and then reflected by 90° with a mirror. To measure the absorption of I₂, a glass tube filled with grains of solid iodine can be inserted in the optical path. Before the light enters the spectrometer, it is focused with lens 2 and its intensity reduced with a exchangeable neutral density filter. The data from the spectrometer *ocean optics USB2000+* is then captured on a computer.

4. Experimental Procedure

4.1. Calibration of the setup with spectra of sodium and mercury

To verify the data delivered by the spectrometer, as a first measurement the Na lamp and the Hg lamp have been used in the setup without I₂-tube. Lens 1 was positioned in a way that after the mirror a beam of constant diameter was formed. With lens 2 the beam was focused on the entrance slit of the spectrometer.

For the Na measurement, the NGG13² filter has been used. The signal was integrated for 2 ms in the spectrometer and 10 measurements were averaged.

The Hg measurement was conducted with the NGG11 filter, 10 ms integration time and also an averaging of 10 measurements.

4.2. Spectrum of the halogen lamp

Then the lamp was replaced by the halogen lamp and its spectrum was measured. The NGG10 was used, 10 ms integration time and an averaging of 100 measurements.

4.3. Spectrum of iodine

For the last measurement, the iodine tube was inserted in the optical path and the spectrum was captured with the same settings as for the spectrum of the halogen lamp.

5. Measurement Results and Evaluation

5.1. Calibration of the setup with spectra of sodium and mercury

The calibration of the setup has been carried out measuring the positions of known lines of Sodium and Mercury ([Figure 5.1](#) and [Figure 5.2](#)).

²During the measurement an inconsistency in the naming of the ND filter has been determined: A 100 times stronger absorption of the NGG13 compared to the NGG11 (as their names suggest) does not seem to occur. The NGG12 provides stronger absorption than NGG13.

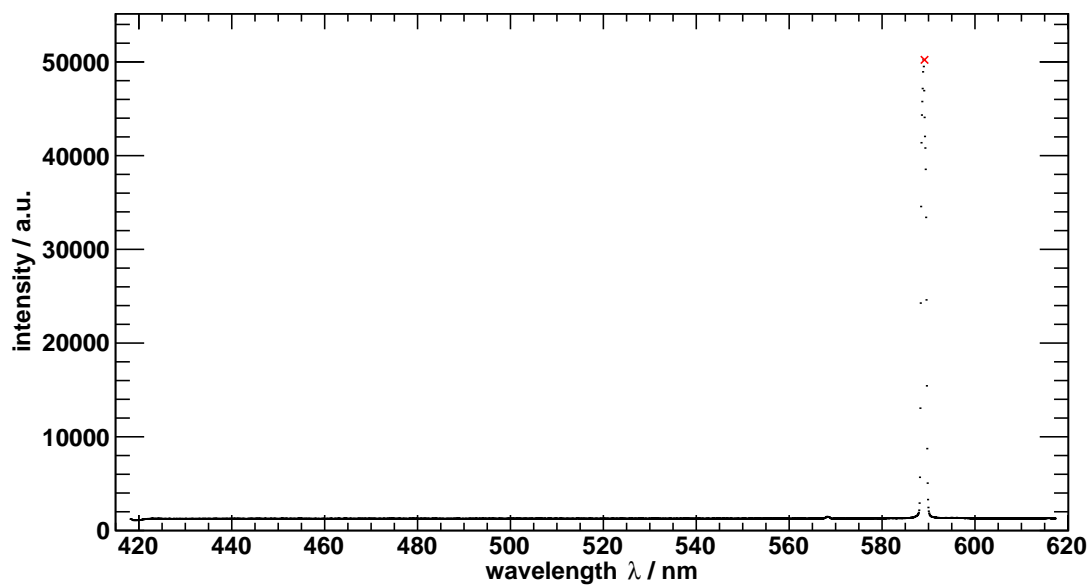


Figure 5.1: Emission spectrum of Sodium with D-line at 589.20 nm.

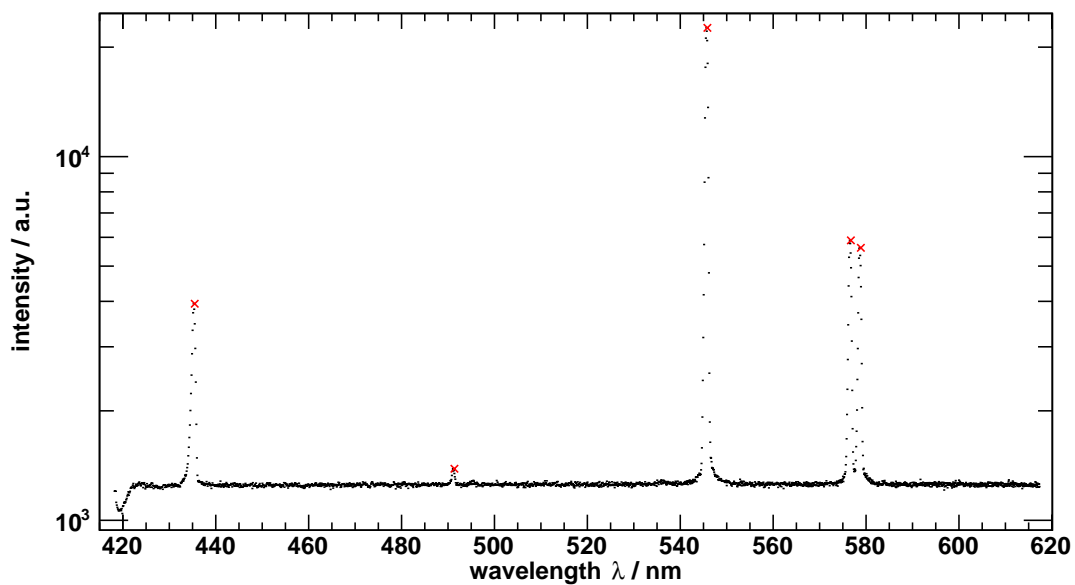


Figure 5.2: Emission spectrum of Mercury with g-line at 435.83 nm, e-line at 546.07 nm and orange double lines at 576.96 nm and 579.07 nm.

Table 5.1: Measured and literature values for known lines of Mercury and Sodium.

Element	λ_{exp} / nm	λ_{lit} / nm
Hg	435.47	435.83
Hg	491.38	491.61 ³
Hg	545.84	546.07
Hg	576.73	576.96
Hg	578.88	579.07
Na	589.14	589.20 ⁴

As you can see in [Table 5.1](#) the measured data matches the literature values already well. However, as a small offset is visible over the measured range, a linear fit has been done to correct the data of the iodine absorption:

$$\lambda_{\text{lit}} = a + b \cdot \lambda_{\text{exp}} \quad (5.1)$$

The fit and the fitting parameters are shown on [Figure 5.3](#).

Now an arbitrary measured wavelength λ and its error can be corrected ⁵:

$$\lambda_{\text{corr}} = a + b \cdot \lambda, \quad s_{\lambda_{\text{corr}}}^2 = s_a^2 + \lambda^2 \cdot s_b^2 + b^2 \cdot s_{\lambda}^2 + 2 \cdot \lambda \cdot \rho \cdot s_a \cdot s_b \quad (5.2)$$

³Found at <http://physics.nist.gov/ASD>

⁴This is the weighted mean over the D_1 - and D_2 -line of Sodium, the weights are the relative intensities, also found at NIST

⁵The correlation coefficient between a and b is $\rho \approx -0.995$

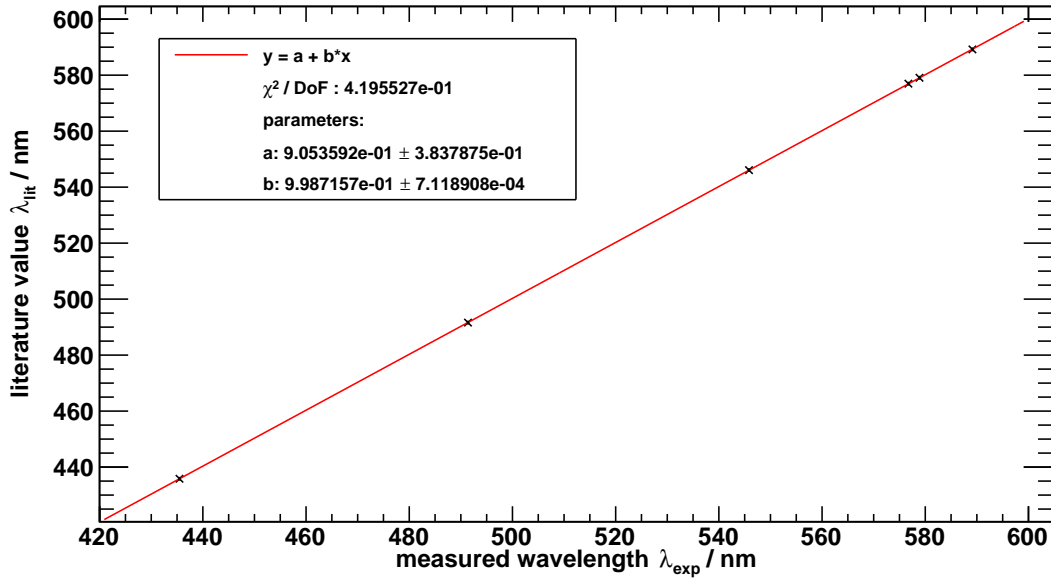


Figure 5.3: Measured values for the lines of sodium and mercury versus literature values. The constant offset a and the linear offset b are used later to adjust the data of the iodine spectrum.

Furthermore the shortening of the measured wavelengths, which is caused by air, needs to be considered.

$$\lambda_{\text{vac}} = n(\lambda_{\text{air}}) \cdot \lambda_{\text{air}} \quad (5.3)$$

Hence a linear fit on the literature values of the refractive index of air has been done (see [Figure 5.4](#)) and provides another correcting function which is applied on the measured data for iodine:

$$n(\lambda) = a + b \cdot \lambda \quad (5.4)$$

With this correction a measured wavelength λ in air can now be calculated as a vacuum wavelength⁶:

$$\begin{aligned} \lambda_{\text{vac}} &= a \cdot \lambda + b \cdot \lambda^2, \\ s_{\lambda_{\text{vac}}}^2 &= \lambda^2 \cdot s_a^2 + \lambda^4 \cdot s_b^2 + (a + 2 \cdot b\lambda)^2 s_\lambda^2 + 2 \cdot \lambda^3 \cdot \rho \cdot s_a \cdot s_b \end{aligned} \quad (5.5)$$

⁶The correlation coefficient between a and b is $\rho \approx -0.993$

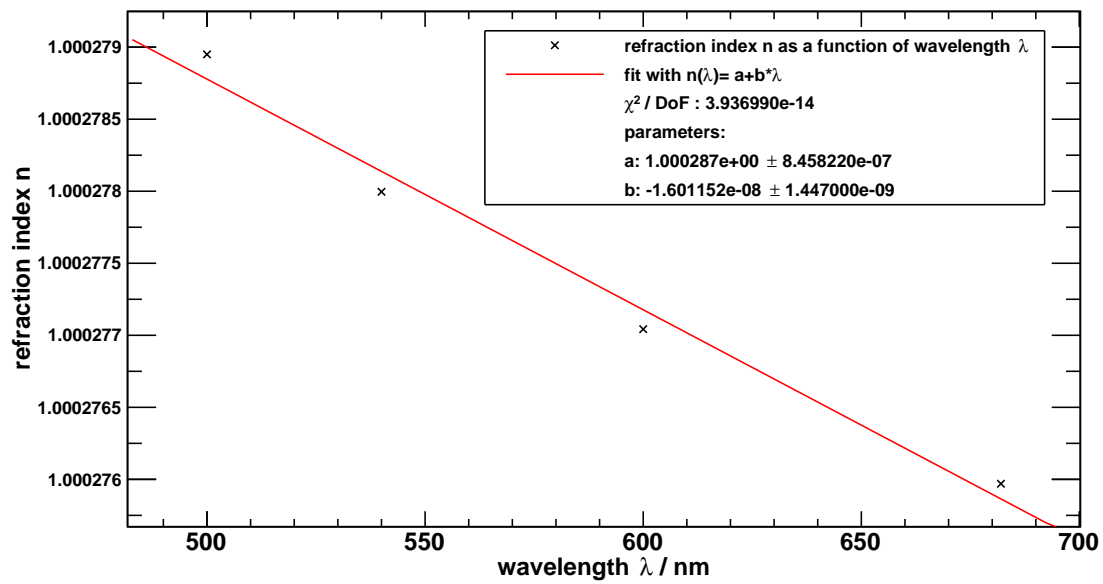


Figure 5.4: Linear fit on the refractive index of air to obtain a function for adjusting the measured wavelengths to their vacuum value.

5.2. Spectrum of the halogen lamp

Figure 5.5 shows the spectrum of the halogen lamp. The spectrum looks smooth and no absorption lines are visible. An approximation with the model of a black body gives no good description of the data, so probably the emissivity of the lamp changes for different wavelengths.

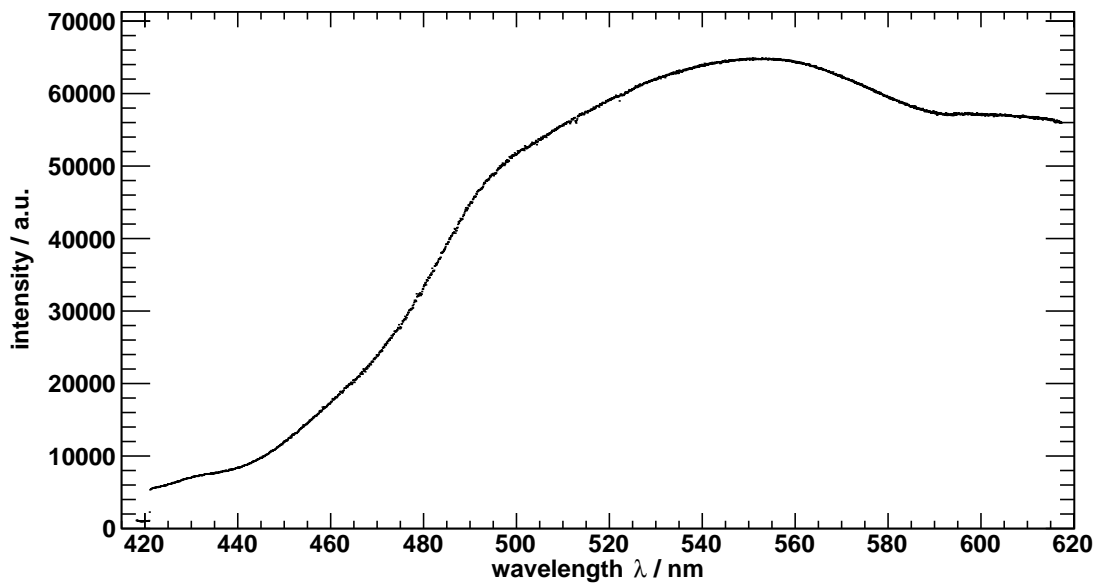


Figure 5.5: Spectrum of the halogen lamp.

5.3. Identification of the 3 progressions in the spectrum of iodine

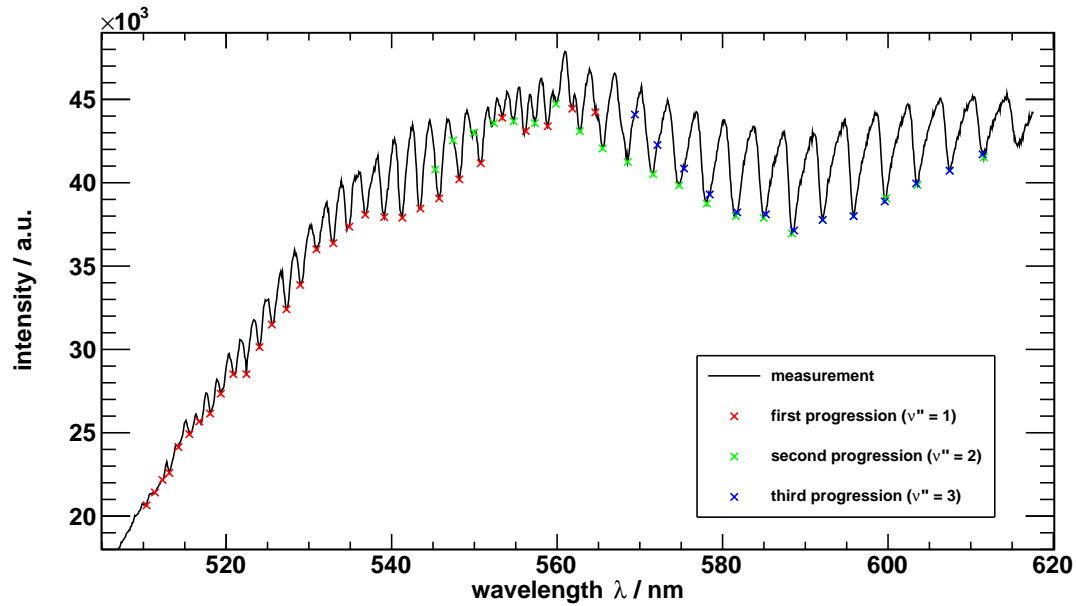


Figure 5.6: Transmission spectrum of iodine and identification of absorption peaks due to electronic-vibronic transitions.

Figure 5.6 shows the measured transmission spectrum of a halogen lamp through iodine. The first three progressions (minima of transmission due to simultaneous electronic and vibronic excitation of iodine molecules) could be identified and are marked in the figure⁷. A closer look at the shape of those "dips" yields information about the ratio of the rotation constants of the ground state and the excited electronic state: The dips are slightly asymmetric and steeper on their left side. This so called "red-shadowing" appears, when the rotation constant of the excited state is *smaller* than the one of the ground state. As the constants are closely related to the equilibrium distance between the nuclei, one can see that on excitation the nuclei move away from each other.

5.4. Evaluation of the vibration constants ω'_e and $\omega'_e x'_e$ for the excited state via Birge-Sponer plots

To make the Birge-Sponer plots, the difference $\Delta G(\nu' + 1/2)$ between two energy levels of one progression, between $G(\nu' + 1/2)$ and $G(\nu' + 3/2)$, has been calculated with

$$\Delta G(\nu' + 1/2) = \frac{1}{\lambda_{\text{cor}}(\nu' + 1)} - \frac{1}{\lambda_{\text{cor}}(\nu')} \quad (5.6)$$

and

$$s_{\Delta G(\nu'+1/2)} = \sqrt{\frac{s_{\lambda_{\text{cor}}(\nu'+1)}^2}{\lambda_{\text{cor}}^4(\nu' + 1)} + \frac{s_{\lambda_{\text{cor}}(\nu')}^2}{\lambda_{\text{cor}}^4(\nu')}} \quad (5.7)$$

The theoretical model for $\Delta G(\nu' + 1/2)$ is given in Equation 2.8:

$$\Delta G(\nu' + \frac{1}{2}) = \omega'_e - \omega'_e x'_e (2\nu' + 2) + \omega'_e y'_e (3\nu'^2 + 6\nu' + \frac{13}{4}) \quad (5.8)$$

This model was fitted on the data for the three progressions, as shown in Figure 5.7, Figure 5.8 and Figure 5.9.

With the 2nd-order model, there seems to appear a problem of overfitting, particularly for the third progression. So we decided to set the factor $\omega'_e y'_e$ to 0 and to use linear 1st-order models for further calculations. The fitting parameters ω'_e and $\omega'_e x'_e$ we obtained from the three fits are shown in Table 5.2.

Table 5.2: Oscillation constants for first order fit of Birge-Sponer plots

ν''	ω'_e/cm^{-1}	$s_{\omega'_e}/\text{cm}^{-1}$	$\omega'_e x'_e/\text{cm}^{-1}$	$s_{\omega'_e x'_e}/\text{cm}^{-1}$
0	133.3	3.6	1.024	0.053
1	126.9	2.8	0.877	0.075
2	128.0	5.3	0.865	0.165

⁷The exact positions of the lines and their corrected values (with calibration data of the setup and refraction index of air) are shown in the appendix, Table A.1, Table A.2 and Table A.3.

The weighted means (Equation 2.17) of the values are

$$\begin{aligned}\overline{\omega'_e} &= (129.1 \pm 2.0) \text{ cm}^{-1} \\ \overline{\omega'_e x'_e} &= (0.97 \pm 0.04) \text{ cm}^{-1}\end{aligned}\quad (5.9)$$

The literature values [3] amount to

$$\begin{aligned}\omega'_{e,\text{lit}} &= 125.27 \text{ cm}^{-1} \\ \omega'_{e x'_{e,\text{lit}}} &= 0.702 \text{ cm}^{-1}\end{aligned}\quad (5.10)$$

The first vibration constant $\overline{\omega'_e}$ includes the literature value within its $2\text{-}\sigma$ -interval, but $\overline{\omega'_e x'_e}$ lies far away from the literature value. This could be caused by the rough modelling in combination with not enough data points for the fit.

The classical oscillation frequency f'_c we get from our values amounts to

$$f'_c = \overline{\omega'_e} \cdot c = (387 \pm 6) \cdot 10^{10} \text{ s}^{-1} \quad (5.11)$$

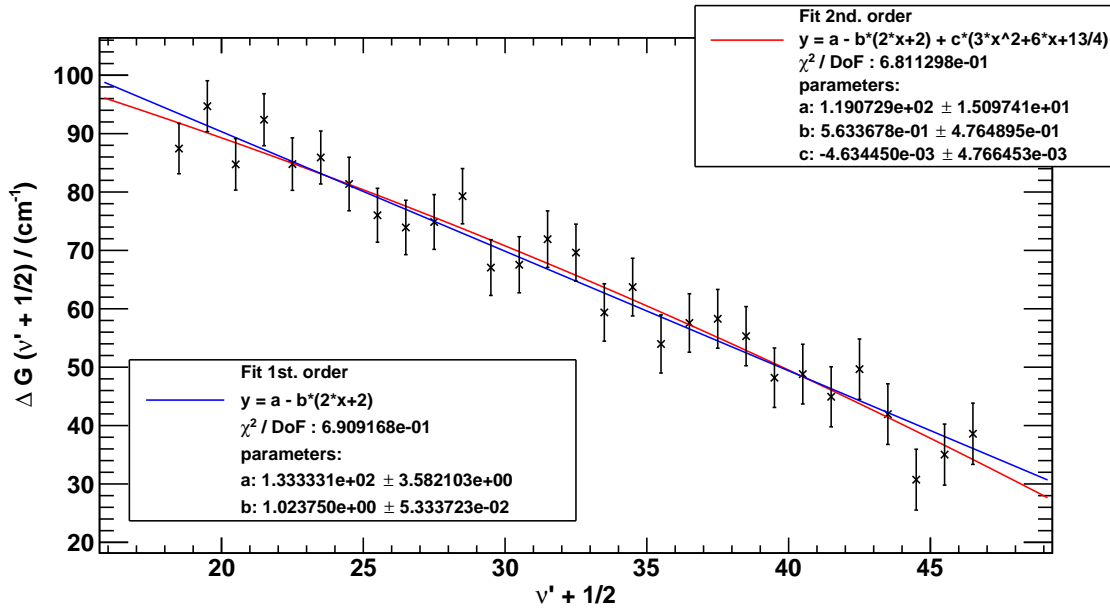


Figure 5.7: Birge-Sponer plot for the first progression and fits with models of linear and quadratic order.

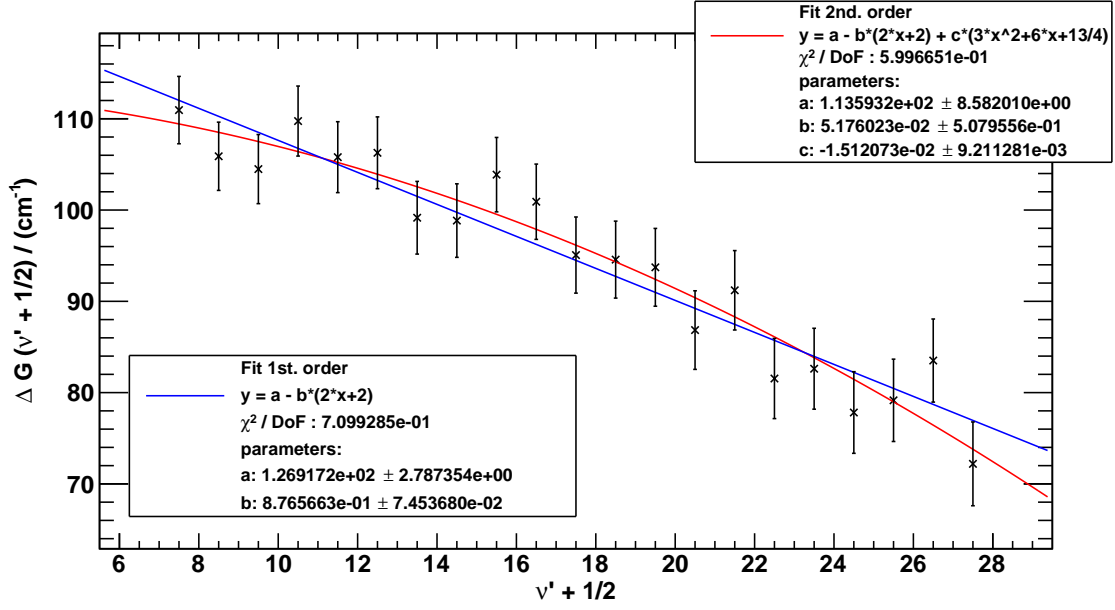


Figure 5.8: Birge-Sponer plot for the second progression and fits with models of linear and quadratic order.

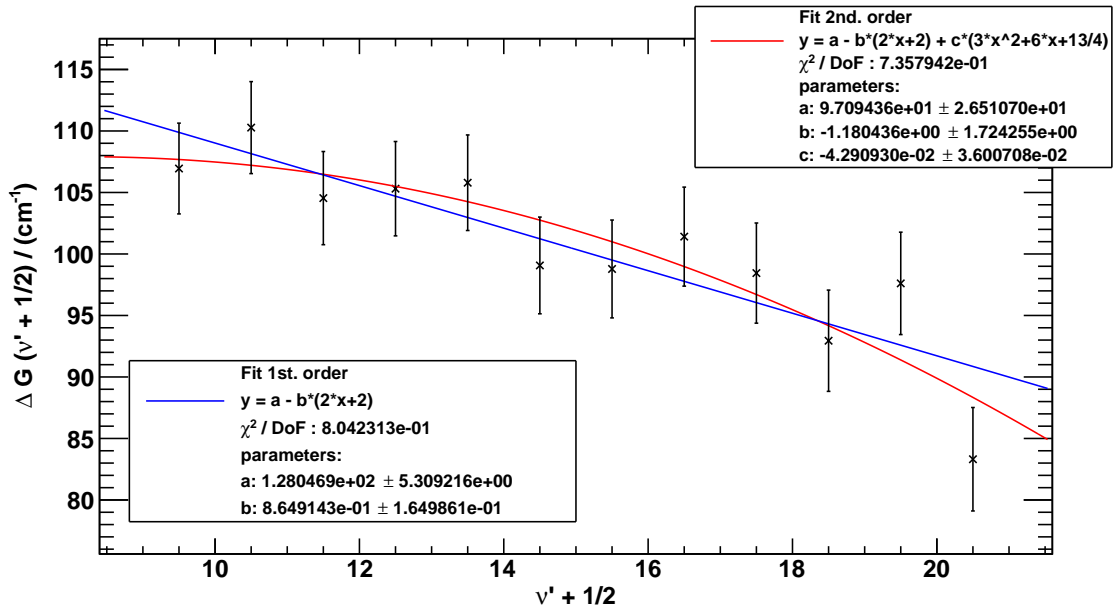


Figure 5.9: Birge-Sponer plot for the third progression and fits with models of linear and quadratic order.

5.5. Evaluation of the vibration constants ω_e'' and $\omega_e''x_e''$ for the ground state

Equation 2.8 states for the energy level G'' of the ground state

$$G''\left(\nu'' + \frac{1}{2}\right) = \omega_e''\left(\nu'' + \frac{1}{2}\right) - \omega_e''x_e''\left(\nu'' + \frac{1}{2}\right)^2 \quad (5.12)$$

Due to the Boltzmann statistics, we only have data for the three lowest ground state levels ($\nu'' = 0, \nu'' = 1, \nu'' = 2$), which is not enough for a proper fit like we could do with the excited state. But we can express the energy differences between those levels by data we obtained from transitions to the excited electronic state with the energy level ν' :

$$\begin{aligned} \Delta G''\left(\frac{1}{2}\right) &= G''\left(\frac{3}{2}\right) - G''\left(\frac{1}{2}\right) \\ &= \left[G'\left(\nu' + \frac{1}{2}\right) - G''\left(\frac{1}{2}\right)\right] - \left[G'\left(\nu' + \frac{1}{2}\right) - G''\left(\frac{3}{2}\right)\right] \\ &= \omega_e'' - 2\omega_e''x_e'' \\ \Delta G''\left(\frac{3}{2}\right) &= G''\left(\frac{5}{2}\right) - G''\left(\frac{3}{2}\right) \\ &= \left[G'\left(\nu' + \frac{1}{2}\right) - G''\left(\frac{3}{2}\right)\right] - \left[G'\left(\nu' + \frac{1}{2}\right) - G''\left(\frac{5}{2}\right)\right] \\ &= \omega_e'' - 4\omega_e''x_e'' \end{aligned} \quad (5.13)$$

We calculate the weighted mean (Equation 2.17) of the values we get for all the pairs in different progressions with the same ν' in our measured data:

$$\begin{aligned} \overline{\Delta G''(1/2)} &= (211.83 \pm 1.34) \text{ cm}^{-1} \\ \overline{\Delta G''(3/2)} &= (208.87 \pm 1.11) \text{ cm}^{-1} \end{aligned} \quad (5.14)$$

Multiplying and adding the two expressions in Equation 5.13 gives us a way to calculate the two vibration constants:

$$\begin{aligned} \omega_e'' &= 2\overline{\Delta G''(1/2)} - \overline{\Delta G''(3/2)} \\ \omega_e''x_e'' &= \frac{1}{2}(\overline{\Delta G''(1/2)} - \overline{\Delta G''(3/2)}) \end{aligned} \quad (5.15)$$

To determine the errors we use the law of error propagation

$$\begin{aligned} s_{\omega_e''} &= \sqrt{4s_{\overline{\Delta G''(1/2)}}^2 + s_{\overline{\Delta G''(3/2)}}^2} \\ s_{\omega_e''x_e''} &= \frac{1}{4}\sqrt{s_{\overline{\Delta G''(1/2)}}^2 + s_{\overline{\Delta G''(3/2)}}^2} \end{aligned} \quad (5.16)$$

The two equations above yield the results

$$\begin{aligned} \omega_e'' &= (215 \pm 3) \text{ cm}^{-1} \\ \omega_e''x_e'' &= (1.5 \pm 0.9) \text{ cm}^{-1} \end{aligned} \quad (5.17)$$

The literature values [2] are

$$\begin{aligned}\omega_{e,\text{lit}}'' &= 214.5 \text{ cm}^{-1} \\ \omega_e'' x_{e,\text{lit}}'' &= 0.61 \text{ cm}^{-1}\end{aligned}\tag{5.18}$$

Our results match the literature values well. The high error on the second vibration constant arises, because we use quite a crude way to get information about a subtle constant.

The classical oscillation frequency f_c'' we get from our values amounts to

$$f_c'' = \omega_e'' \cdot c = (645 \pm 9) \cdot 10^{10} \text{ s}^{-1}\tag{5.19}$$

5.6. Determination of the dissociation energies

5.6.1. Via Morse-Approximation for ground state and excited state

Having evaluated the vibration constants in the last two sections, Equation 2.14 gives us now a way to calculate the dissociation energies for the ground state D_e'' and the excited state D_e' .

$$D_e'' = \frac{\omega_e''^2}{4\omega_e'' x_e''} = (8 \pm 5) \cdot 10^3 \text{ cm}^{-1}\tag{5.20}$$

$$D_e' = \frac{\omega_e'^2}{4\omega_e' x_e'} = (43 \pm 2) \cdot 10^2 \text{ cm}^{-1}\tag{5.21}$$

For the errors the following equation has been employed

$$s_{D_e} = \frac{\omega_e \sqrt{4(\omega_e x_e)^2 s_{\omega_e}^2 + \omega_e^2 s_{\omega_e x_e}^2}}{4(\omega_e x_e)^2}\tag{5.22}$$

The literature values (from [1] and [3]) for the dissociation energies are the following:

$$D_{e,\text{lit}}'' = 12560 \text{ cm}^{-1}\tag{5.23}$$

$$D_{e,\text{lit}}' = 4391 \text{ cm}^{-1}\tag{5.24}$$

Our results match with the literature values. The high error on the dissociation energy of the ground state is caused by the uncertainty on the second vibration constant.

5.6.2. Graphically from the Birge-Sponer plot for the excited state (D'_0)

Calculating the dissociation energy D'_0 of the excited state is also possible with the data shown in [Figure 5.7](#): Summing up over all the the energy differences $\Delta G'$ ([Equation 2.9](#)) from the non-vibrating state ($\nu' = 0$) up to the last vibrational state ($\nu' = \nu'_{\text{diss}}$), from which, by further excitation, the molecule will separate.

$$D'_0 = \sum_{\nu'=0}^{\nu'_{\text{diss}}} \Delta G' \left(\nu' + \frac{1}{2} \right), \quad (5.25)$$

As we do not have measurement values for $\nu' < 18$ and $\nu' > 47$, we are forced to extrapolate to those values using our fitted model. And since the fit was calculated with a least-square-approximation, integrating the model over the range of the measured points should give a value very close to the sum of the measured points. So the equation above can be transformed into an integral form:

$$D'_0 = \int_0^{\nu'_{\text{diss}}} \Delta G' \left(\nu' + \frac{1}{2} \right) d\nu' \quad (5.26)$$

Using our 1st-order model, we get

$$D'_0 = \int_0^{\nu'_{\text{diss}}} \omega'_e - \omega'_e x'_e (2\nu' + 2) d\nu' \quad (5.27)$$

To find the ν'_{diss} , we solve the equation

$$\omega'_e - \omega'_e x'_e (2\nu'_{\text{diss}} + 2) = 0 \quad \Leftrightarrow \quad \nu'_{\text{diss}} = \frac{\omega'_e}{2\omega'_e x'_e} - 1 \quad (5.28)$$

This result is used to solve the integral:

$$D'_0 = \frac{(\omega'_e - 2\omega'_e x'_e)^2}{4\omega'_e x'_e} \quad (5.29)$$

From the error propagation law we get

$$s_{D'_0} = \frac{(\omega'_e - 2\omega'_e x'_e) \sqrt{4(\omega'_e x'_e)^2 s_{\omega'_e}^2 + (\omega'_e + 2\omega'_e x'_e)^2 s_{\omega'_e x'_e}^2}}{4(\omega'_e x'_e)^2} \quad (5.30)$$

Using the data for the first progression ([Table 5.2](#)), we obtain the following value:

$$D'_0 = (42 \pm 3) \cdot 10^2 \text{ cm}^{-1} \quad (5.31)$$

5.6.3. Analytical determination for the ground state

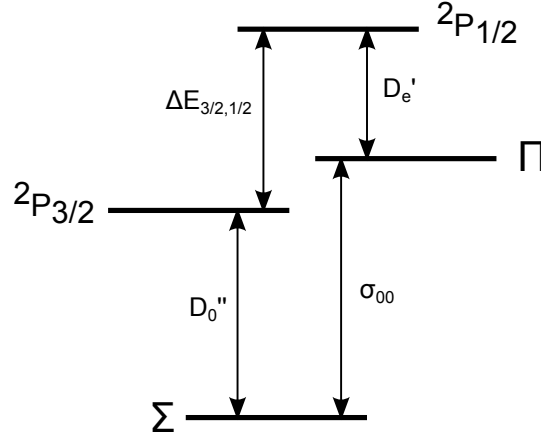


Figure 5.10: Term diagram for excitation and dissociation of I₂.

Figure 5.10 shows another way to calculate the dissociation energy D_0'' of the ground state: The energy for electronic excitation σ_{00} to the Π -state and the dissociation energy of the excited state D_e' are known. We also know that after dissociation of the two atoms from the ground state, they are both in the state $^2P_{3/2}$, whereas after dissociation of the excited state one atom is in the state $^2P_{1/2}$. The energy difference $\Delta E_{3/2,1/2}$ of those two states is 7603 cm^{-1} . So we have the following relation:

$$D_0'' = \sigma_{00} + D_e' - \Delta E_{\frac{3}{2}, \frac{1}{2}} \quad (5.32)$$

$$s_{D_0''} = \sqrt{s_{\sigma_{00}}^2 + s_{D_e'}^2} \quad (5.33)$$

With our data we obtain a value of

$$D_0'' = (12.4 \pm 1.5) \cdot 10^3 \text{ cm}^{-1} \quad (5.34)$$

5.7. Determination of the energy for electronic excitation σ_{00}

An approximation of the energy σ_{00} which is necessary for the electric excitation is given by the following equation:

$$\sigma_{00} = G'(\nu' = 0) \approx G'(\nu' = n) - \frac{\Delta G'(\frac{1}{2}) + \Delta G'(n + \frac{1}{2})}{2} \quad (5.35)$$

To get the best approximation, we use the lowest point we could measure in the first progression ($\nu' = 18$). The values for $\Delta G'(\frac{1}{2})$ and $\Delta G'(18\frac{1}{2})$ are taken from the linear

model:

$$\Delta G'(\nu' + \frac{1}{2}) = \omega'_e - \omega'_e x'_e (2\nu' + 2) \quad (5.36)$$

With the expressions for the errors

$$s_{\sigma_{00}} = \sqrt{s_{G'(n)}^2 + \frac{s_{\Delta G'(\frac{1}{2})}^2 + s_{\Delta G'(n+\frac{1}{2})}^2}{4}} \quad (5.37)$$

$$s_{\Delta G'(\nu'+\frac{1}{2})} = \sqrt{s_{\omega'_e}^2 + 4 \cdot (n+1) \cdot \rho \cdot s_{\omega'_e} \cdot s_{\omega'_e x'_e} + 4 \cdot ((n+1) \cdot s_{\omega'_e x'_e})^2} \quad (5.38)$$

and our values we get for the energy of electronic excitation

$$\sigma_{00} = (15.7 \pm 1.5) \cdot 10^3 \text{ cm}^{-1} \quad (5.39)$$

This also meets well the literature value of [3]

$$\sigma_{00,\text{lit}} = 15771 \text{ cm}^{-1} \quad (5.40)$$

5.8. Calculation of the energy E_{Diss} of the dissociated iodine molecule in the experiment

The dissociation energy E_{Diss} can be calculated with:

$$E_{\text{Diss}} = \sigma_{00} - G''(0) + D'_e \quad (5.41)$$

in which σ_{00} was calculated in 5.7 and D'_e in 5.6.1. $G''(0)$ is given with Equation 2.6 to first order:

$$G''(0) \approx \frac{\omega_e''}{2} + \frac{\omega_e'' x_e''}{4} \quad (5.42)$$

with ω_e'' and $\omega_e'' x_e''$ from Equation 5.17. Therefore the dissociation energy E_{Diss} is

$$E_{\text{Diss}} = (20.0 \pm 1.5) \cdot 10^3 \text{ cm}^{-1} \quad (5.43)$$

5.9. Morse potential for the excited state

The formula for the Morse potential of the excited state is according to Equation 2.11:

$$V(r) = D'_e \left(1 - e^{-a'(r-r_e)}\right)^2 \quad (5.44)$$

The dissociation energy D'_e has following value

$$D'_e = (43 \pm 2) \cdot 10^2 \text{ cm}^{-1}, \quad (5.45)$$

which was calculated in [Equation 5.21](#).

The molecular specific constant a' can be calculated with [Equation 2.13](#) and [Equation 2.14](#):

$$a' = \omega'_e \cdot \sqrt{\frac{\pi c \mu}{\hbar D'_e}}, \quad s_{a'} = a' \cdot \sqrt{\left(\frac{s_{\omega'_e}}{\omega'_e}\right)^2 + \left(\frac{s_{D'_e}}{2D'_e}\right)^2} \quad (5.46)$$

With the reduced mass $\mu = \frac{1}{2} \cdot 126.9 \cdot 1.66 \cdot 10^{-27} \text{ kg}$ of I_2 the constant a' is:

$$a' = (1.91 \pm 0.06) \frac{1}{\text{\AA}} \quad (5.47)$$

The distance r_e of the equilibrium position can be calculated with the given rotational constant $B'_e = 0.029 \text{ cm}^{-1}$ using [Equation 2.16](#):

$$r_e = 3.027 \text{ \AA} \quad (5.48)$$

The Morse potential with these values is shown in [Figure 5.11](#)

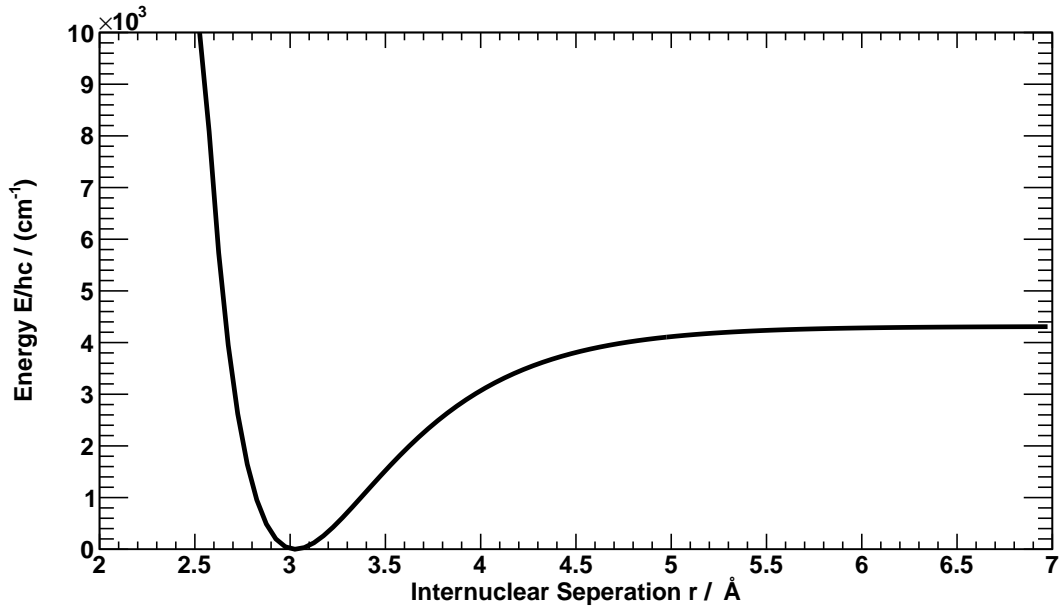


Figure 5.11: Morse potential of the excited state

6. References

- [1] Bitsch, K. *Aufbau einer Apparatur fürs Fortgeschrittenen-Praktikum: "Untersuchung der Schwingungsstruktur des $B^3\Pi_{0u}^+ \leftarrow X^1\Sigma_g^+$ -Übergangs beim I_2 -Molekül"; Staatsexamensarbeit.* Freiburg, 1977.
- [2] Rank, D.H. and Rao, B.S. *Molecular Constants of the Ground State of I_2 .* Journal of Molecular Spectroscopy 13, 1964.
- [3] Steinfeld, J. et al. *Spectroscopic Constants and Vibrational Assignment for the $B^3\Pi_{0u}^+$ State of Iodine.* Journal of Chemical Physics 42, 1965.

A. Tables

A.1. Progressions

Table A.1: Measured position of transmission minima in I_2 -spectrum and corrected values of progression 1.

ν'	$\lambda_{\text{exp}} / \text{nm}$	$\lambda_{\text{cor}} / \text{nm}$	$s_{\lambda_{\text{cor}}} / \text{nm}$
47	510.38	510.77	0.09702626
46	511.39	511.78	0.09702626
45	512.31	512.70	0.09702625
44	513.12	513.51	0.09702625
43	514.23	514.62	0.09702625
42	515.55	515.94	0.09702624
41	516.75	517.14	0.09702624
40	518.06	518.44	0.09702623
39	519.36	519.74	0.09702623
38	520.86	521.24	0.09702622
37	522.45	522.83	0.09702622
36	524.03	524.41	0.09702621
35	525.52	525.90	0.09702621
34	527.29	527.66	0.09702620
33	528.95	529.32	0.09702620
32	530.91	531.28	0.09702619
31	532.95	533.32	0.09702618
30	534.88	535.25	0.09702618
29	536.81	537.18	0.09702617
28	539.11	539.47	0.09702616
27	541.30	541.66	0.09702616
26	543.48	543.84	0.09702615
25	545.74	546.10	0.09702614
24	548.18	548.53	0.09702613
23	550.78	551.13	0.09702612
22	553.37	553.72	0.09702612
21	556.22	556.57	0.09702611
20	558.86	559.20	0.09702610
19	561.84	562.18	0.09702609
18	564.62	564.96	0.09702608

Table A.2: Measured position of transmission minima in I_2 -spectrum and corrected values of progression 2.

ν'	$\lambda_{\text{exp}} / \text{nm}$	$\lambda_{\text{cor}} / \text{nm}$	$s_{\lambda_{\text{cor}}} / \text{nm}$
28	545.27	545.63	0.09702614
27	547.43	547.78	0.09702614
26	549.95	550.30	0.09702613
25	552.36	552.71	0.09702612
24	554.75	555.10	0.09702611
23	557.31	557.65	0.09702610
22	559.86	560.20	0.09702610
21	562.74	563.08	0.09702609
20	565.51	565.85	0.09702608
19	568.53	568.86	0.09702607
18	571.61	571.94	0.09702606
17	574.74	575.07	0.09702605
16	578.10	578.42	0.09702604
15	581.60	581.92	0.09702603
14	584.97	585.29	0.09702602
13	588.39	588.70	0.09702601
12	592.10	592.41	0.09702600
11	595.84	596.15	0.09702599
10	599.77	600.07	0.09702597
9	603.56	603.86	0.09702596
8	607.45	607.74	0.09702595
7	611.58	611.87	0.09702594

Table A.3: Measured position of transmission minima in I_2 -spectrum and corrected values of progression 3.

ν'	$\lambda_{\text{exp}} / \text{nm}$	$\lambda_{\text{cor}} / \text{nm}$	$s_{\lambda_{\text{cor}}} / \text{nm}$
21	569.41	569.74	0.09702607
20	572.13	572.46	0.09702606
19	575.35	575.68	0.09702605
18	578.45	578.77	0.09702604
17	581.77	582.09	0.09702603
16	585.23	585.55	0.09702602
15	588.64	588.95	0.09702601
14	592.10	592.41	0.09702600
13	595.84	596.15	0.09702599
12	599.61	599.91	0.09702597
11	603.40	603.70	0.09702596
10	607.45	607.74	0.09702595
9	611.43	611.72	0.09702594