Laser-Induced Fluorescence (LIF) Spectroscopy of Molecular Iodine (I_2)

Advanced Lab Course in Physics

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1 Introduction

Elemental iodine in the gas phase exists as a diatomic molecule (I_2). It exhibits strong absorption resonances occurring across the entire visible spectral range. These absorption lines are caused by transitions between electronic states, with the ground state being denoted as X and an excited electronic state B, as well as additional states within the electronic manifolds. The latter arise as a consequence of the fact that molecules, in contrast to atoms, posses vibrational and rotational internal degrees of freedom which manifest themselves in a corresponding structure of the energy spectrum.

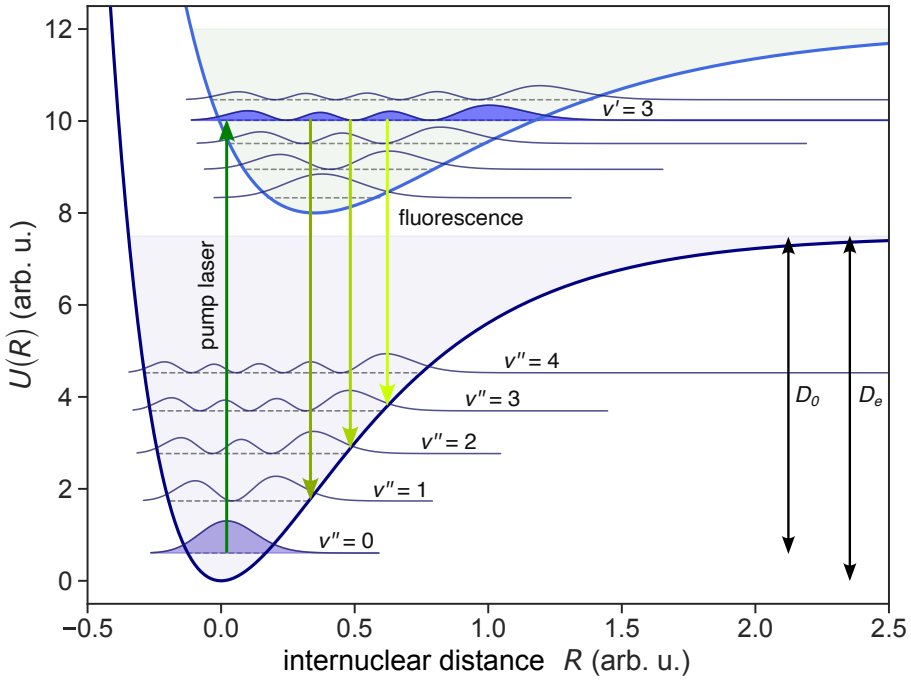

Figure 1: Working principle of Laser-Induced Fluorescence (LIF) spectroscopy for one electronic ground state (e.g. $X^1\Sigma_g^+$ in I_2) with vibrational sublevels v'' and an electronically excited state (e.g. BO_u^+) with sublevels v' (shown: energy $U(R)$ as a function of internuclear distance R; rotational structure neglected for simplicity). The molecule is excited by a pump laser from the vibronic ground state $\chi_1(v''=0)$ to the $\chi_2(v'=3)$ state of the excited electronic state (shown are $|\chi(v)|^2$). Spontaneous decay to any lower state v'' is possible, resulting in the emission of photons with an energy lower than that of the pump laser (since $v''=0$ these are the so-called Stokes lines). Spectrally resolved detection of fluorescence allows to measure the energies and relative intensities (determined by the overlap of the vibrational wavefunctions $\chi_1(v'', R)$ and $\chi_2(v', R)$, expressed as Franck-Condon factors) of all involved transitions, as well as the dissociation energies D_0 and D_e.

Such spectra can be obtained by both absorption and fluorescence detection methods. The focus of this Lab Course is on Laser-Induced Fluorescence (LIF) spectroscopy which allows to determine several important properties of the electronic ground state X including its vibrational structure, that is, the energetic spacing of sublevels described by the rotational quantum number v''. The basic working principle of this method is illustrated in Figure 1. In a first step, we optically excite a single transition between specific vibrational states of the electronic manifolds, specifically $X^1\Sigma_g^+, v'' = 0 \leftarrow BO_u^+, v' = 32$, which is referred to as the pumping transition. This is done by exposing molecular iodine contained in a vapor cell to the radiation of a suitable laser source operated at a wavelength of approximately $\lambda_p = 531$ nm. The fluorescence stemming from the spontaneous decay is then collected and detected in a spectrometer allowing us to determine the energies and intensities of the addressed transitions $X^1\Sigma_g^+, v'' \leftarrow BO_u^+, v' = 32$. This information is used to determine the characteristic Dunham coefficients Y_{j0} of the ground state, its approximate dissociation energy, and normalized Franck-Condon factors.

2 Molecular structure

The rovibrational and electronic structure of molecules is commonly described within the framework of the Born-Oppenheimer (BO) approximation [1, 2]. It is derived from the assumption that the wavefunctions of electrons and nuclei can be separated. In most cases, this is well justified because the nuclei are much heavier than the electrons, whose motion is consequently much faster. When considering the electronic, vibrational and rotational spectrum of a molecule within the BO approximation, the overall energy can be expressed as a sum of independent contributions:

$$E_{tot} = E_{el} + E_{vib} + E_{rot}. \tag{1}$$

Typically, the energy scales associated with these terms differ by orders of magnitude such that $E_{el} \gg E_{vib} \gg E_{rot}$. For each given separation of nuclei, the electrons adapt without any significant delay to the attractive forces between the electrons and the quasi-stationary nuclei as well to the repulsive forces between the nuclei. The resulting wavefunction with its corresponding characteristic eigenenergy provides a binding potential for the nuclei confined within it. The possible vibrations and rotations of the nuclei within the molecular potential are quantized and correpond to distinct energy levels. Close to the minimum of the potential, the vibrational eigenenergies can be approximated by the spectrum of a harmonic oscillator:

$$E_{vib} = \hbar\omega_e\,(v + 1/2)\,, \tag{2}$$

where $\hbar = h/(2\pi)$, ω_e and v denote the reduced Planck constant, the vibrational constant, that is, the vibration frequency times 2π, and the vibrational quantum number, respectively. For increasing v, the anharmonicities of the potential become significant and have to be taken into account. This can be done, e.g., by expanding Equation 1 into a power series of $(v + 1/2)$:

$$E_{vib} = \hbar\omega_e\,(v + 1/2) - \hbar\omega_e x_e\,(v + 1/2)^2 + \ldots\,, \quad v \in \mathbb{N}_0 \tag{3}$$

with x_e being the anharmonicity constant. The rotational energy is expressed in terms of the rotational constant B, which is a characteristic property of the molecule, and the rotational quantum number J:

$$E_{rot} = hB\,J\,(J+1)\,. \tag{4}$$

A general representation of the molecular energy structure containing all of the above contributions is the so-called Dunham series with coefficients Y_{kl} which have the unit of energy:

$$E(\gamma, v, J) = \sum_{k,l\geq 0} Y_{kl}\,(v+1/2)^k\,(J\,(J+1))^l\,. \tag{5}$$

The index γ is an abbreviation for all quantum numbers required to characterize the electronic state. By comparing Equations 3 and 5, we can identify Y_{10} as $\hbar\omega_e$ and Y_{20} as $-\hbar\omega_e x_e$.

In transitions between electronic manifolds, both the rotational and vibrational quantum numbers can change according to the corresponding selection rules, such that only transitions where $\Delta J = 0,\ \pm 1;\ (J' = 0 \nleftrightarrow J'' = 0)$ are allowed whereas $\Delta v = n,\ n \in \mathbb{N}_0$ is possible. However, the probability of vibronic transitions strongly depends on the combination of v' and v'' because it is determined by the overlap of the corresponding wavefunctions. Within the framework of the BO approximation and according to the Franck-Condon principle this dependence can be expressed using so-called Franck-Condon factors *FCF*. They are defined as the squares of the overlap integral between the wavefunctions $\chi(v, R)$, which describe the vibration of the nuclei in the molecular potential, of two electronic states with total wavefunctions $\Psi_1 = \psi_1(r, R)\chi_1(v', R)$ and $\Psi_2 = \psi_2(r, R)\chi_2(v'', R)$ involved in the transition [3, 2]:

$$FCF = \left(\int_0^\infty \chi_1(v', R)\chi_2(v'', R)\,dR\right)^2. \tag{6}$$

Here, $\psi(r, R)$ represents the contribution due to the motion of the electron with the coordinate r for fixed nuclear positions R.

The energy difference of two states participating in such rovibronic transitions is:

$$\begin{aligned}\Delta E_{rvc} &= E(\gamma', v', J') - E(\gamma'', v'', J'') \\ &= \sum_{k,l\geq 0} Y'_{kl}\,(v'+1/2)^k\,(J'\,(J'+1))^l - \sum_{m,n\geq 0} Y''_{mn}\,(v''+1/2)^m\,(J''\,(J''+1))^n\,.\end{aligned} \tag{7}$$

For transitions where the initial and final state remain in the rotational ground state $J = 0$, the energy difference according to Equations 7 and 3 becomes:

$$\Delta E_{rvc} = E(\gamma', v', 0) - E(\gamma'', v'', 0) = \sum_{k\geq 0} Y'_{k0}\,(v'+1/2)^k - \sum_{m\geq 0} Y''_{m0}\,(v''+1/2)^m\,. \tag{8}$$

This case is relevant in experiments where the spectral resolution is insufficient to observe the vibrational structure such as in the experimental setup used in the present Lab Course. In this scenario, Equation 8 gives a reasonable approximation of the rotational band heads which

appear as regions of maximal intensity in the measured rovibrational spectra [3].

3 Experimental setup

In this Lab Course, we use an experimental setup as summarized in Figure 2. It is used to excite molecular iodine contained within a sealed transparent vapor cell by exposing the molecules to the radiation of a laser operated at a wavelength of approximately $\lambda_p = 531$ nm which is resonant to the transition $X^1\Sigma_g^+, v'' = 0 \leftarrow BO_u^+, v' = 32$, that is, the 32-0 vibrational band. **CAUTION: The maximal output power of the laser module is approximately 50 mW (class 3B), so laser safety eyewear must be worn at all times!** The output power of the laser and its temperature can be adjusted with the connected control unit. Adjusting the temperature allows for changing the wavelength of the emitted radiation. This can be used to tune the laser into resonance with the pumping transition.

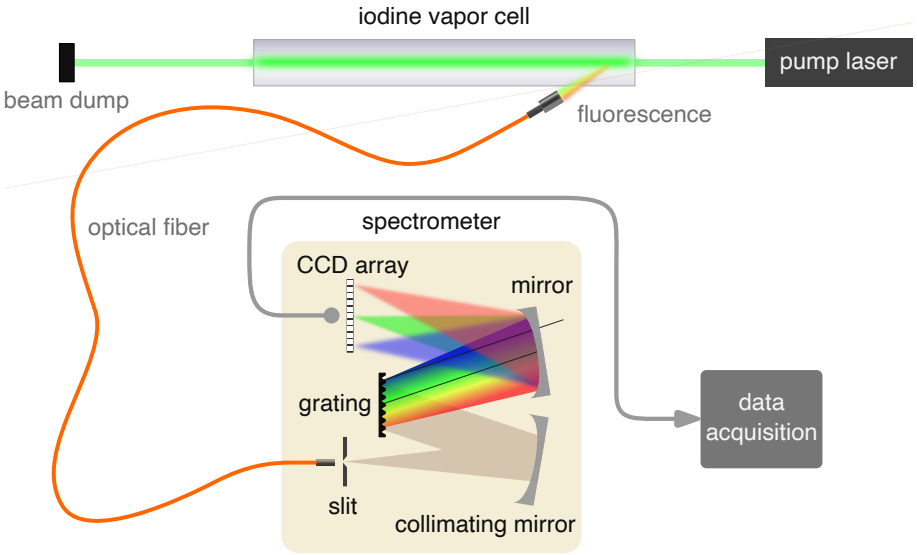

Figure 2: Simplified schematic of the experimental setup.

Absorption of the pump light followed by spontaneous decay from the excited electronic state causes fluorescence along the beam path within the cell. The emitted light is collected and coupled into a multimode optical fiber which is used to guide it into a spectrometer.

The vapor cell housing is equipped with heating elements and a locally placed Peltier element which allows to control the temperature of the molecular gas using a power supply for heating and a separate temperature controller for the Peltier element.

3.1 Calibration and operation of the spectrometer

The spectrometer is connected to a local computer equipped with a software interface which allows for data acquisition and setting of several parameters such as exposure time and averaging. A mercury lamp is used as a reference for calibrating the spectrometer. To this end,

the light emitted from the lamp is coupled into the optical fiber and the obtained spectra are recorded using the installed data acquisition software.
The spectral resolution of the instrument used in this experiment is 0.5 nm within the spectral operation range between $\lambda = 300$ and 980 nm. However, the sensitivity of the device is not uniform across the entire detection range, as shown in Figure 3. The data used to generate this Figure is given in Appendix B, Table 2. This means that transitions with wavelengths above 1100 nm cannot be effectively detected. In addition, even within regions where the sensitivity is sizable, e.g. between 532 nm and 800 nm, its dependence on λ has to be taken into account when the absolute intensity of the detected signals is evaluated at different wavelengths.

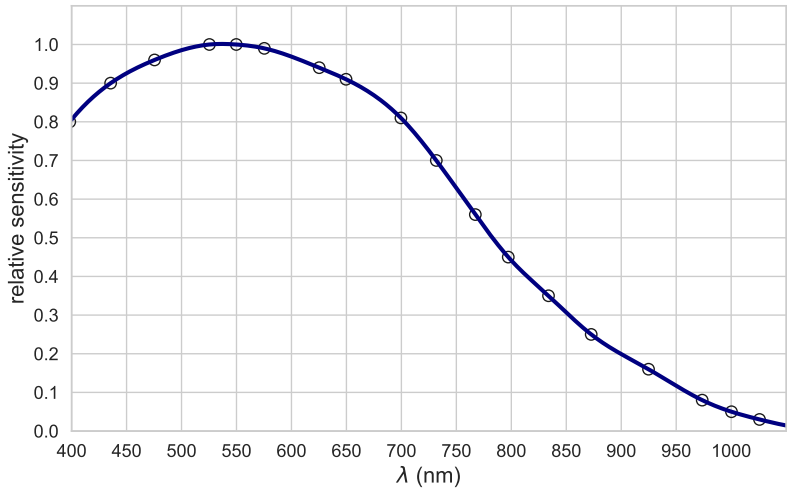

Figure 3: Relative spectral sensitivity of the CCD array sensor used in the spectrometer. The data (circles) is obtained from an approximate sampling of the manufacturer's data sheet, the solid line is the result of cubic spline interpolation of the data using the ScyPi package for python.

4 Questions to prepare for the Lab Course

Two-level system

- Which processes are possible during the interaction with a monochromatic light field?
- Which of these do we expect here?
- Does the excited state have a lifetime?
- What does the spectrum look like? What is the natural linewidth? How does it relate to the spectrum?

Harmonic oscillator

- What does the spectrum look like here?
- What is the energy of the ground state?

Multilevel atom

- What interactions with a monochromatic light field are possible?
- How is this reflected in the spectrum?

Diatomic molecules

- What potential do we expect as a function of the internuclear distance?
- Is the internuclear distance fixed? Which approximations can be made?
- What energy scales are there compared to the multilevel atom?
- How are the energy levels structured?
- What do the energy distances between vibrational states close to the ground state look like? What is the situation for higher excited vibrational states?
- How is the potential usually described/parameterized? What are the relevant quantum numbers?
- What is the difference between the parameters D_0 and D_e?
- What do the potentials of electronically excited states look like?
- Which interactions with a monochromatic light field are possible?
- Which transitions between electronic states are allowed? What is the situation for rotational states? What applies to vibrational states?
- What does this have to do with the shape of the potential of the electronic ground state and the excited electronic state?
- What does the fluorescence spectrum that we expect for molecules prepared in the state $B, v' = 32$ look like? Is the signal strength of a transition as detected with a spectrometer related to any quantitative features of the involved vibrational states?
- What do the energy differences of transitions $B, v' = 32 \rightarrow X, v'' = 0$ and $B, v' = 32 \rightarrow X, v''$ look like? How does this relate to equation 8?
- What do the energy differences between states X, v'' and $X, v'' + 1$ look like, up to 2nd order in $(v'' + 1/2)$?

5 Experiment

Carry out all of the following steps and document all information that is necessary to reproduce your results in the lab report which you will hand in along with your evaluation. This involves answering all questions in this section which are meant to guide you through the experiment,

making sure that you understand the steps, formulate expectations for their respective outcomes and can assess the plausibility of any individual measurement.

1. Activate the Hg spectroscopy lamp. **CAUTION: The Hg lamp emits significant amounts of radiation in the UV spectral range, suitable protection eyewear is required.** Position the coupler of the multimode fiber such that it collects light emitted by the Hg lamp. Start the control and data acquisition software on the computer connected to the spectrometer. Now, you should be able to see the characteristic fluorescence spectrum of the lamp. Adjust the exposure time (e.g. 100 ms) such that the signal is clearly visible but make sure that the strongest lines do not saturate the sensor. That is, the height of any peak should never exceed 65 536.

   Record a fluorescence spectrum of the mercury lamp. Identify visible lines and attribute them to transitions in mercury given in Appendix A, Table 1. To this end, use the characteristic spacing of 3 comparatively strong lines in the interval 2000 to 2300 px, which belong to Hg I with high confidence (double-peak above 2000 px and the adjacent line). Perform a rough calibration using a linear fit to this data[1].

   With this, you should be able to identify several additional Hg lines in the range above 2000 px. Perform an improved calibration using exclusively Hg lines of the extended data set. To this end, carry out both linear and 3rd order polynomial least square fits and compare quantitatively the fit statistics[2]. Which figure of merit is suitable for this task? Why is a linear fit inappropriate and why does polynomial regression provide a good approximation for grating-based spectrometers?

   With the improved calibration, identify the wavelengths of all lines in the measured spectrum. Note that on a linear plot of the fluorescence not all lines may be clearly visible at the same time. Do all lines belong to the mercury spectrum? If not, determine the wavelengths of transitions due to elements that are not Hg I. Assign them using the NIST Atomic Spectra Database [4]. NOTE: Keep in mind that the data listed in Table 1 are for a vacuum. Which element(s) do these lines most likely belong to[3]?

   Perform the final calibration of the spectrometer using all identified lines by means of a third order polynomial regression. Provide an estimate for the uncertainty of the calibration.

2. Next, set the temperature controller of the iodine cell to 20 °C and then position the fiber coupler as illustrated in Figure 2. **CAUTION: Laser protection eyewear is required for the next part of the experiment (laser power of 50 mW, laser class 3B)!** Turn on the

[1] For additional orientation, you can use a laser source at $\lambda \approx 532$ nm (laser pointer) as a rough reference (CAUTION: use only indirect scattering to avoid damage to the sensor; do not shine laser light into the fiber directly).

[2] As a cross-check, you should be able to confirm that the peak around 2849 px corresponds to an Hg I line at 4359.56 Å.

[3] Generally, almost every line could stem from transitions in a large number of atoms, ions and molecules, but not all assignments are plausible. It is worthwhile identifying the exact type of the lamp employed here using the manufacturer's datasheet (printout is available in the lab). Hints: (i) often, inert buffer gases are used in spectral lamps and (ii) the expected lifetime of the device is a key parameter for a Lab Course setup.

laser and set the current of the laser diode to $I_{LD} = 350$ mA (the activation of the controller requires a safety PIN). Set the temperature of the laser diode to about $T_{LD} = 27.5\,^{\circ}$C, then adjust it by slowly turning the jog dial in steps of 3 ticks in either direction within a range of $\pm 1\,^{\circ}$C while allowing the temperature to settle. Monitor the change of the fluorescence signal and repeat these steps to identify an optimal setpoint for T_{LD} by maximizing the fluorescence in the cell. This should take about 10 to 20 minutes.

3. Now, you should be able to see the characteristic fluorescence spectrum of molecular iodine. Adjust the position and pointing of the fiber coupler to maximize the fluorescence signal. Make sure that the signal-to-noise ratio (SNR) for peaks around 900 nm is at least 10 with integration times below 1 s. To estimate the RMS of the noise background, record a spectrum and evaluate the data subset below 315 nm. This spectral region is far from the laser-induced fluorescence after excitation at 531 nm, such that this data provides a reasonable approximation of the background noise. The amplitude of the weakest visible peak should then be $\geq$10 times the background RMS value.

4. Record a series of spectra (approximately 10 data sets) using the settings identified above. Convert the measured spectra to wavenumbers. Why is this preferable to wavelengths?

5. Plot a spectrum obtained by averaging over the data sets, use it to identify the transitions and plot it along with your assignment of the lines to vibrational quantum numbers v''. In an ideal experiment and neglecting the influence of finite temperature, how many transitions would you expect to observe and how many can you identify in your measurements? Is there a discrepancy between the expectation and your observations? If so, discuss how it comes about.

6. Determine the wavenumber of the $v' = 32 \rightarrow v'' = 0$ transition which approximates the photon energy of the pump laser E_p in units of cm^{-1}. Which terms in Equation 8 does this correspond to? What does Equation 8 look like for the specific transitions you probed in your experiments? Calculate $E_p - E(v'')$ as well as their statistic uncertainties and plot the results as a function of v''. Fit a function according to an appropriately adapted Equation 3 (up to third order) to the data, and extract the relevant Dunham parameters including their uncertainties. What is the physical meaning of these parameters? Compare your results with those reported in literature and discuss your findings.

7. Plot the energy spacing between neighboring vibrational states in the ground state, that is $\Delta E(v'') = E(v''+1) - E(v'')$, as a function of $v''+1/2$. Perform a linear fit to this data and calculate v_{max} where ΔE reaches zero, and the sum of all linearly extrapolated energy differences from $\Delta E(v''=0)$ to $\Delta E(v''_{max}) = 0$ (area enclosed by the fit function) to obtain an estimate for the dissociation energy. This is known as the Birge-Sponer extrapolation which we apply here for the ground state of I_2. Does this method provide an estimate for D_0 or D_e? Compare this result with literature (see, e.g., work cited in Appendix D) and

discuss the source of potential discrepancies[4].

8. Using the same data, perform a third order polynomial fit and estimate the dissociation energy by calculating the area enclosed by the fitted function. You can use the offset and linear coefficient from the previous linear approximation as fixed parameters. Discuss how this result compares with literature?

9. First, correct the measured fluorescence intensity at the peaks for the finite relative sensor sensitivity at the respective wavelengths using the data listed in Table 2 from Appendix B and a suitable interpolation method. To phenomenologically include the wavelength dependence of the fiber's collection efficiency, approximate this quantity by the number of guided modes $N \approx V^2/2$ (relative to the peak of the 32-0 band) using the normalized frequency $V \approx 2\pi a/\lambda$ where a is the radius of the fiber core. In a second step, normalize the fluorescence values to that of the $v'' = 4$ peak [5]. Lastly, calculate and plot the normalized peak fluorescence as a function of v''. For comparison, normalize the literature values FCF_{lit} for the $v' = 32 \rightarrow v''$ transition listed in Table 3 from Appendix C to the $FCF(v'' = 4)$ value and show your calculated normalized FCF_{exp}^{norm} and FCF_{lit}^{norm} in the same plot, including the uncertainties. Calculate the relative coefficients $FCF_{exp}^{norm}/FCF_{lit}^{norm}$ and show them in a separate plot. Discuss your findings and potential deviations from literature values.

[4] Hint: Considering the Dunham series in Equation 5 for $l = 0$, which terms does the Birge-Sponer approximation take into account and which ones are neglected? As a consequence, when considering how molecular iodine dissociates, what systematic deviation from an exact solution would you expect (see, e.g., chapter 5.3 of [1])?

Appendix A

Table 1: Hg I lines according to [4]. Shown are the line wavelengths λ (Å) in vacuum, the relative intensities, and the transition strengths A_{ik}. This compilation includes the strongest observed lines within the range 3000 to 8150 Å with $A_{ik} > 1 \times 10^4\,\mathrm{s}^{-1}$. It is not a complete set of all known transitions.

λ (Å)	rel. int.	A_{ki} (10^8 s^{-1})
3022.384	1200	51.00
3024.351	300	9.40
3028.371	60	1.98
3126.580	4000	66.00
3342.445	700	16.80
3651.198	9000	129.00
3655.883	3000	18.40
3663.930	500	3.60
4047.708	12 000	20.70
4078.988	1000	4.00
4109.213	70	2.20
4340.443	50	2.90
4348.717	150	8.40
4359.560	12 000	56.00
4917.440	20	5.80
5027.000	3	0.03
5462.268	6000	49.00
5771.210	1000	23.60
5791.300	30	0.60
5792.276	900	31.00
6074.320	30	0.06
6236.080	50	0.30
6718.190	600	0.24
6909.370	1000	1.60
7730.952	30	0.60

Appendix B

Table 2: Relative sensitivity of the CCD array sensor used in the spectrometer.

λ (nm)	rel. sensitivity
398.34	0.80
416.64	0.85
435.51	0.90
449.93	0.93
475.45	0.96
499.86	0.99
525.38	1.00
549.79	1.00
575.31	0.99
599.72	0.97
625.24	0.94
649.65	0.91
675.17	0.88
699.58	0.81
720.67	0.75
731.76	0.70
749.51	0.63
767.27	0.56
781.69	0.50
797.23	0.45
814.98	0.40
833.84	0.35
849.38	0.31
872.68	0.25
899.31	0.20
924.83	0.16
950.35	0.11
973.65	0.08
1000.28	0.05
1025.80	0.03
1042.44	0.02
1059.08	0.01
1074.62	0.01
1100.69	0.01

Appendix C

Table 3: Franck-Condon factors (FCF) for the transition series $B, v' = 32 \rightarrow X, v''$ observed in $^{127}I_2$ [6].

v''	$FCF \times 10^2$ $(B, v' = 32 \rightarrow X, v'')$
0	3.137
1	0.219
2	1.367
3	0.406
4	0.802
5	0.592
6	0.442
7	0.758
8	0.191
9	0.875
10	0.041
11	0.915
12	0.001
13	0.860
14	0.074
15	0.709
16	0.243
17	0.489
18	0.464
19	0.254
20	0.674
21	0.070
22	0.805
23	0.000
24	0.804
25	0.077
26	0.662
27	0.285
28	0.421
29	0.554
30	0.171
31	0.784
32	0.016
33	0.878
34	0.034
35	0.787
36	0.236
37	0.541
38	0.554
39	0.244
40	0.860

Appendix D

Spectroscopic data

Table 4: Dunham polynomial expansion coefficients up to 5^{th} order for the X and B states of $^{127}I_2$ as reported in [6].

i	$Y_{i,0}(X)$	$Y_{i,0}(B)$
0		$1.566\,194\,830\,000\,000 \times 10^4$
1	$2.145\,207\,97 \times 10^2$	$1.256\,703\,736\,408\,829 \times 10^2$
2	$-6.079\,223\,99 \times 10^{-1}$	$-7.526\,312\,444\,268\,988 \times 10^{-1}$
3	$-1.418\,587\,57 \times 10^{-3}$	$-3.127\,037\,525\,849\,298 \times 10^{-3}$
4	$3.820\,191\,43 \times 10^{-5}$	$-4.392\,558\,498\,456\,961 \times 10^{-6}$
5	$-5.735\,558\,41 \times 10^{-6}$	$-1.899\,435\,107\,249\,887 \times 10^{-6}$

Dissociation limit energies of the X and B states

The dissociation energy of the X state is $D_0 = 12440.9 \pm 1.1$ cm^{-1} as reported in [7].

The value for the B state is $D_e = 4381.249 \pm 0.001$ cm^{-1} [8].

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