Properties of the iodine molecule observed by absorption spectroscopy

From absorption spectra in the visible properties of different electronic states of the iodine molecule will be determined. The spectra are recorded by a high resolution grating monochromator. For this purpose, the spectrograph has to be calibrated with a known light source.

Introduction

Iodine is in the gas phase a diatomic molecule (I_2). It has strong absorptions in the whole visible spectral range. These absorptions arise from transitions between the **electronic states**, the ground state labelled X and an excited electronic state labelled B. Furthermore, due to their internal degrees of freedom molecules have **vibrational and rotational structure**. Both are visible in absorption.

In this experiment the absorption of iodine vapour prepared in an iodine cell will be recorded and analyzed. As light source a broad band emitter, i.e. here a halogen lamp is employed. The transmitted light is dispersed by a high resolution grating spectrometer and allows for gaining spectral information on the absorption.

Molecular structure

The molecular ro-vibrational and electronic structure is usually described in the **Born-Oppenheimer approximation** [1,2]. The Born-Oppenheimer approximation is essentially based on the assumption, that the motion of the electrons is fast compared to the motion of the heavy nuclei. It separates the electronic from the vibrational and rotational motion, such that the energy of a rotational-vibrational level in an electronic state is given by $E = E_{elec} + E_{vib} + E_{rot}$. The energy scales are typically different such that $E_{elec} >> E_{vib} >> E_{rot}$ holds. Consequently, the electrons adapt immediately to the position, i.e. separation, of the nuclei and generate a force field that binds the atoms to a molecule. This is characterised by an electronic potential characteristic for a molecular electronic state.

Within this potential, the molecule may vibrate. Quantum mechanics shows that only distinct energies are possible. For a harmonic potential the level energies are given by

$$E_{vib} = \hbar\omega_e \cdot (\mathrm{v} + 1/2), \quad \mathrm{v} = 0, 1, 2, 3, ... \qquad (1)$$

where v is the vibrational quantum number and ω_e is the vibrational constant, $\hbar = h/2\pi$. The unit of frequency unit is chosen here to be a circular frequency. The real molecular potentials can be approximated by harmonic ones in the vicinity of their minimum. For higher v anharmonicities become visible. They can be taken into account by extending (1) into a power series of the vibrational energy ladder in (v + ½)

$$E_{vib} = \hbar\omega_e \cdot (\mathrm{v} + 1/2) - \hbar\omega_e x_e (\mathrm{v} + 1/2)^2 + \ldots, \quad \mathrm{v} = 0, 1, 2, 3, \ldots \tag{2}$$

where x_e is the first anharmonicity constant.
The rotational energy E_{rot} is given by a rotational constant B and the rotational quantum number J:

$$E_{rot} = \hbar B \cdot J \cdot (J+1) \tag{3}$$

Frequently, more constants are used in a combined power series of v and J. An often used compact representation is the so called Dunham series which has the general form

$$E(\gamma, \mathrm{v}, J) = \sum_{k,l \geq 0} Y_{kl} (\mathrm{v} + 1/2)^k (J(J+1))^l \tag{4}$$

The Dunham parameters Y_{kl} have the unit of energy. Comparing eq. 2 and eq. 4 one readily identifies $\omega_e = Y_{10}$ and $\omega_e x_e = -Y_{20}$. The label γ represents all other quantum numbers and labels necessary to characterize the electronic state.

Molecular electronic transitions from one electronic state to another allow for changes in v and J. The energy difference ΔE is carried by photons whose energy match the energetic separation of the two involved levels.

$$\Delta E = E(\gamma, \mathrm{v}', J') - E(\gamma, \mathrm{v}'', J'') = \sum_{k,l \geq 0} Y'_{kl} (\mathrm{v}' + 1/2)^k (J'(J'+1))^l - \sum_{n,m \geq 0} Y''_{n,m} (\mathrm{v}'' + 1/2)^n (J''(J''+1))^m$$

The energetic separation between neighbouring rotational transitions is too small to be resolved in this experiment. Nevertheless, the rotation together with the vibrational motion gives rise to distinct absorption bands with ‘band heads’, that appear as sharp ‘edges’ in the absorption spectra. The band heads appear due to selection rules for the transitions between rotational lines and different rotational constants for both involved electronic states [1,2].
Thus, the features in the absorption will be characterised by the vibrational quantum number v” in the lower electronic state X and in the excited B state (v’). Starting out from one level v”, a series of vibrational bands with different v’ according to eq. 2 is visible. Since a few levels v” in the X state are thermally populated, different series will appear.

Absorption

The reduction of the initial irradiance I_0 to I by an absorber is described by the **Lambert-Beer relation** for small concentrations k:

$$\ln(I_0/I) = l \cdot k \cdot \varepsilon \tag{5}$$

l is the length of the absorber, ε its extinction coefficient at a given wavelength. The extinction coefficient for a band is proportional to the number of molecules in v’’ and to the transition strength of the band. The first is given be **Boltzmann’s law**, the latter by the **Franck-Condon factor** of the band. The Franck-Condon factor *fcf* is the square of the overlap integral between the two vibrational wave functions of different electronic states $\Psi(v')$ and $\Phi(v'')$ involved in the transition

$$fcf = \left(\int_0^\infty dR\, \Psi(\mathrm{v}', R) \cdot \Phi(\mathrm{v}'', R) \right)^2 . \qquad (6)$$

Experimental set-up

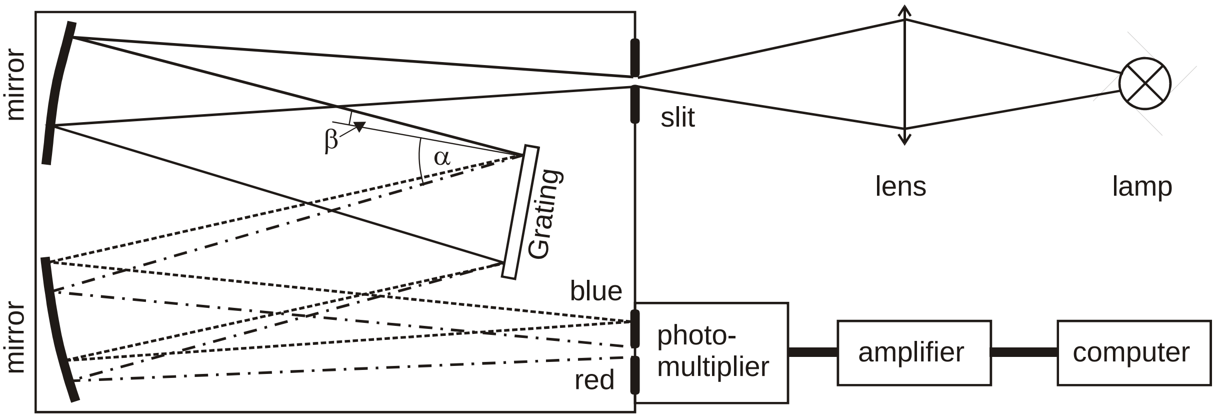

Figure 1: Schematics of monochromator, light source and detection.

This experiment uses a monochromator with a reflection grating [3]. Its operating principle is drawn in fig. 1. The entrance slit is imaged onto the grating by a concave mirror. The diffraction pattern is imaged by a second mirror on the exit plane. In this experiment typically the 1st diffraction order is used. A second slit cuts a small part of it. The width of both, entrance and exit slits is adjustable. The intensity of the light falling through the exit slit is measured by a photomultiplier tube, whose output current is converted with a current amplifier to an output voltage.

According to the grating formula [4]

$$\frac{1}{n} \cdot (\sin\beta \pm \sin\alpha) = m\lambda , \qquad (6)$$

this is only light of a narrow wavelength λ interval. n is the number of lines per millimetre, m the order of diffraction. The angles α, β are given in fig. 1 referred to the normal of the grating.

The angle of the grating can be adjusted by a motor to record spectra. To achieve a linear wavelength scale, a mechanical sine drive is implemented. The monochromator provides a mechanical counter indicating roughly the momentary wavelength in Ångstrøm (Å). Additionally, two electronic signals are provided, that give regular wavelength markers.

The spectrum and the markers can be recorded with a computer based data acquisition system.

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[1] W.A. Bingel: “Theory of Molecular Spectra”, *Chemical Topics for Students* J. Wiley & Sons, 1969

[2] H. Haken, H.C. Wolff: „Molekülphysik und Quantenchemie“, Springer 1997

[3] Alonso, Finn: Physics, Addison-Wesley 1993

[4] W. Demtröder: “Laser spectroscopy”, Springer 1993

Introductory questions

What are approx. the wavelength limits of visible light?

What is the energy interval of visible photons in cm^{-1}?

How does a grating work?

Are there other possibilities to disperse light?

Why are mirrors used in the monochromator instead of lenses?

Why is a lens used between the light source and the entrance slit?

Why are the slits of the monochromator adjustable?

Which line shape do you expect for wide slits (same widths) and a monochromatic light source? A narrow entrance slit and wide exit? And vice versa?

Why is a sine drive used to drive the grating?

What must be taken into account when comparing wavelengths?

What determines the number of molecules in the absorption cell?

What distinguishes molecular and atomic spectra?

Which values can a Franck-Condon factor have?

Which value do I get, when I sum over the fcfs belonging to the transitions from one v' to all v'' of another electronic state?

Which rules are to be accounted for understanding the spectra that you will observe?

Experiment

- Follow the description stepwise.
- Register the data and do the analysis immediately!
- Note the experimental conditions, steps and results of the analysis in the protocol. The protocol must contain everything that is necessary that another person can repeat the experiment and reproduce your results!
- For all results, the uncertainty or error must be considered.
- Comment on the questions in the experimental description below (not those above).
- **Have fun!**

Part 1: Calibration of the monochromator

1. Turn the grating by the handle and determine the number of electronic markers per Ångstrøm.
2. Turn on the high voltage supply of the photomultiplier; adjust the voltage to 300 V (not higher!). Image the light of the halogen lamp with the lens onto the entrance slit. Adjust the slit width to 200 µm. Monitor the signal around 5000 Å and optimise it by aligning the optical bench, lens etc.
3. Replace the halogen lamp by the mercury spectral lamp. Record a fast overview spectrum between 6000 Å and 4200 Å to identify the rough wavelength of the spectral lines.
4. Record each line with good signal to noise ratio. Mind the hysteresis of the mechanics!
5. Attribute the observed lines with the list of mercury lines given in the appendix. Interpolate linearly between the wavelength markers. Are all lines around 4330 Å visible? Do all lines belong to the mercury spectrum?
6. Use the attributed lines for a first calibration of the monochromator. Determine the wavelengths of the non-Hg lines. Assign them using the NIST wavelength data base (physics.nist.gov/cgi-bin/AtData/lines_form). Mind that the data in the appendix are for vacuum! To which element(s) belong the lines? Do the final calibration of monochromator with all lines. Compare a linear regression of the data with a quadratic one. Does the sine-drive do its job? Estimate the uncertainty of the calibration!
7. Chose one line and vary the entrance and exit slits. Record spectra under typical conditions and give quantitative explanations of the observations.

Part 2: Iodine absorption spectra

8. Replace the Hg lamp by the halogen lamp. Place the iodine cell between lamp and lens. Be careful with the cell!
9. Cool the 'side arm' of the cell with the temperature controller to -5°C. What will be the effect on the iodine gas? Record the spectrum from 6100 Å to 4800 Å.
10. Set the temperature to 20°C, but keep all settings for the remaining experimental work. Record the spectrum from 6100 Å to 4800 Å with the side arm at room temperature. In this scan, you have to identify the vibrational band given in the next point.
11. The vibrational band at ~5311 Å is the v” = 0 to v’ = 32 transition, called the 32-0 band. Assign the other vibrational levels starting from *v”* = 0, use the regular spacing to find your way through the different bands!
12. A commonly used unit of spectroscopists is cm^{-1}, thus inverse wavelength. It is called ‘Kayser’ or ‘wave number’. Why is this unit used instead of wavelengths? Plot the position of the band heads in cm^{-1} versus the vibrational quantum number. (Estimate the fractional part of the wavelength markers.) Fit the energies with an expression according to eq. 2. What is the physical meaning of the constants? Which is the energy reference point?
13. Plot the energy $\Delta v'_{i,i+1}$ differences of neighbouring v_i' and v'_{i+1} versus (v’ + ½). The value of $\Delta v'$ at $\Delta v'_{i,I+1} = 0$ gives an estimation of v'_{max}. The array bordered by the curve and the axes approximates the dissociation energy of the B state (see D_E in Appendix C). Can you give explanations for the deviations from the literature values?
14. Assign the bands starting from higher v”. Use the energy differences between the already attributed transitions from v” = 0 the find the assignment for v’. What is the vibrational spacing in the ground state?
15. Calculate the relative absorption of different transitions with the same upper level v’. Calculate the relative Franck-Condon factors assuming a Boltzmann distribution for the population in the X state. How can the -5°C spectrum be used? Compare your results with the Franck-Condon table in the appendix.
16. Heat the body of the cell to 250°C using the power supply. Record the absorption spectrum. Discuss the changes compared to your previous spectra!

Appendix A

Mercury lines from NIST atomic line database
(http://physics.nist.gov/cgi-bin/AtData/lines_form)

Wavelength Vacuum (A)	Rel. Int.
4340.44	250
4348.71	400
4359.55	4000
4884.36	5
4891.28	5
4917.44	80
4971.76	5
4982.03	5
5027.04	
5104.12	20
5122.07	40
5139.37	20
5292.21	20
5318.26	5
5355.54	60
5386.13	30
5462.26	1100
5551.17	30
5677.44	160
5771.2	240
5791.27	100
5792.27	280

Appendix B

Table of Franck-Condon factors between X and B state.

v'	v"=0	v"=1	v"=2	v"=3	v"=4
0	1.664E-09	4.225E-08	5.228E-07	4.214E-06	2.491E-05
1	2.412E-08	5.547E-07	6.184E-06	4.455E-05	2.330E-04
2	1.793E-07	3.735E-06	3.745E-05	2.403E-04	1.106E-03
3	9.120E-07	1.721E-05	1.548E-04	8.806E-04	3.541E-03
4	3.576E-06	6.100E-05	4.908E-04	2.464E-03	8.590E-03
5	1.152E-05	1.774E-04	1.273E-03	5.605E-03	1.677E-02
6	3.180E-05	4.409E-04	2.809E-03	1.078E-02	2.735E-02
7	7.725E-05	9.627E-04	5.423E-03	1.798E-02	3.808E-02
8	1.686E-04	1.884E-03	9.339E-03	2.651E-02	4.589E-02
9	3.360E-04	3.357E-03	1.456E-02	3.494E-02	4.807E-02
10	6.187E-04	5.510E-03	2.078E-02	4.155E-02	4.361E-02
11	1.063E-03	8.413E-03	2.737E-02	4.475E-02	3.367E-02
12	1.717E-03	1.204E-02	3.351E-02	4.368E-02	2.119E-02
13	2.628E-03	1.626E-02	3.832E-02	3.847E-02	9.752E-03
14	3.831E-03	2.084E-02	4.106E-02	3.022E-02	2.253E-03
15	5.347E-03	2.545E-02	4.129E-02	2.065E-02	1.406E-05
16	7.173E-03	2.973E-02	3.898E-02	1.163E-02	2.579E-03
17	9.286E-03	3.333E-02	3.447E-02	4.723E-03	8.158E-03
18	1.164E-02	3.596E-02	2.842E-02	8.265E-04	1.442E-02
19	1.417E-02	3.743E-02	2.164E-02	9.675E-05	1.931E-02
20	1.679E-02	3.764E-02	1.495E-02	2.036E-03	2.153E-02
21	1.941E-02	3.662E-02	9.076E-03	5.721E-03	2.080E-02
22	2.196E-02	3.451E-02	4.513E-03	1.008E-02	1.762E-02
23	2.433E-02	3.151E-02	1.525E-03	1.412E-02	1.303E-02
24	2.647E-02	2.787E-02	1.391E-04	1.712E-02	8.187E-03
25	2.830E-02	2.387E-02	1.910E-04	1.868E-02	4.058E-03
26	2.980E-02	1.975E-02	1.384E-03	1.873E-02	1.273E-03
27	3.093E-02	1.576E-02	3.355E-03	1.745E-02	6.485E-05
28	3.170E-02	1.206E-02	5.734E-03	1.518E-02	3.197E-04
29	3.210E-02	8.798E-03	8.187E-03	1.234E-02	1.692E-03
30	3.215E-02	6.050E-03	1.045E-02	9.326E-03	3.727E-03
31	3.189E-02	3.849E-03	1.232E-02	6.481E-03	5.969E-03
32	3.135E-02	2.192E-03	1.370E-02	4.046E-03	8.037E-03
33	3.056E-02	1.043E-03	1.454E-02	2.165E-03	9.662E-03
34	2.958E-02	3.470E-04	1.485E-02	8.867E-04	1.070E-02
35	2.843E-02	3.491E-05	1.470E-02	1.900E-04	1.112E-02
36	2.717E-02	3.351E-05	1.415E-02	1.294E-06	1.096E-02
37	2.582E-02	2.698E-04	1.329E-02	2.182E-04	1.034E-02
38	2.441E-02	6.757E-04	1.222E-02	7.279E-04	9.370E-03
39	2.298E-02	1.190E-03	1.103E-02	1.421E-03	8.190E-03
40	2.155E-02	1.762E-03	9.775E-03	2.201E-03	6.918E-03
41	2.014E-02	2.350E-03	8.525E-03	2.990E-03	5.650E-03
42	1.876E-02	2.919E-03	7.323E-03	3.727E-03	4.461E-03
43	1.742E-02	3.446E-03	6.201E-03	4.373E-03	3.399E-03
44	1.614E-02	3.915E-03	5.181E-03	4.902E-03	2.491E-03
45	1.493E-02	4.314E-03	4.271E-03	5.305E-03	1.745E-03
46	1.377E-02	4.640E-03	3.476E-03	5.582E-03	1.158E-03
47	1.269E-02	4.891E-03	2.793E-03	5.740E-03	7.156E-04
48	1.167E-02	5.070E-03	2.216E-03	5.791E-03	4.003E-04
49	1.072E-02	5.179E-03	1.735E-03	5.749E-03	1.914E-04
50	9.838E-03	5.226E-03	1.340E-03	5.631E-03	6.799E-05

Appendix C

Table of Dunham coefficients for X and B state. All values in cm^{-1}.
(B state: S. Gerstenkorn, P. Luc, Journal de Physique 46, 867-881 (1985),
X state: F. Martin, R. Bacis, S. Churassy, J. Vergès, J. Mol. Spectr. 116,, 71-100(1986))

	B state		X state	
	Y_{00}	15769.052		
	D_e	4381.244		
	Y_{k0}	Y_{0l}	Y_{k0}	Y_{0l}
1	1.2567E+02	2.9001E-02	2.1452E+02	3.7368E-02
2	-7.5040E-01	-1.4944E-04	-6.0792E-01	-1.1314E-04
3	-4.1440E-03	-1.2604E-06	-1.4186E-03	-8.6729E-07
4	2.2489E-04	3.6084E-08	3.8202E-05	1.9189E-07
5	-3.2287E-05	-1.1894E-08	-5.7356E-06	-3.6167E-08
6	2.8274E-06	1.6084E-09	4.2587E-07	4.0204E-09
7	-1.6976E-07	-1.4015E-10	-2.1521E-08	-2.8935E-10
8	7.2483E-09	8.1708E-12	7.5427E-10	1.4144E-11
9	-2.2367E-10	-3.2953E-13	-1.8694E-11	-4.8475E-13
10	5.0242E-12	9.3726E-15	3.2889E-13	1.1855E-14
11	-8.1832E-14	-1.8928E-16	-4.0667E-15	-2.0799E-16
12	9.5206E-16	2.6988E-18	3.4382E-17	2.5981E-18
13	-7.6838E-18	-2.6572E-20	-1.8807E-19	-2.2556E-20
14	4.0758E-20	1.7203E-22	5.9544E-22	1.2934E-22
15	-1.2753E-22	-6.5929E-25	-8.2184E-25	-4.4046E-25
16	1.7806E-25	1.1335E-27		6.7449E-28

Appendix D

In the following are three possible topics for an elaboration (Ausarbeitung). Other topics are possible, too.

Elaboration 1: Simulation of spectra

Write a program that simulates absorption spectra based on

- two sets of Dunham parameter,
- a corresponding table of Franck-Condon factors,
- an adjustable linewidth,
- an adjustable detection function, and
- the temperature of the sample.

Assume a light source with constant spectral power density and a detector without wavelength dependence. (The task is obviously **not** to simulate your recordings!)

Use the simulation for the B-X system of iodine to answer the following questions:

- What kind of monochromator would resolve rotational structures? What temperature of the sample would be allowed?
- At what temperature do the vibrational bands starting from $v''=0$ begin to overlap?
- What is the highest v'' that one can expect to measure with such an experiment just by heating the sample. Assume a cell resisting to any temperature and neglect black body radiation but consider the broadening of the bands due to the rotational temperature and Doppler broadening.
- What else can you figure out with the simulation? Just play around with the parameter!

Elaboration 2: Iodine in real science

The iodine molecules is one of the best known molecules (if not the best known) and used as a secondary frequency standard. Find at least four articles about spectroscopy of iodine. Discuss the following points to each publication:

- General information: authors, institute, year of publication, journal etc.
- What is the used experimental method?
- What are the observed transitions?
- What is the experimental uncertainty reached? What limits the precision? What errors are considered
- How are the observed transition frequencies reported? What is considered in the model of the molecule?

Compare the work and discuss how the spectroscopy has developed over the time. Make sure to choose articles that allow for comparison but also show the development over at least two decades.

Elaboration 3: Diatomic Molecules

Discuss some theory for diatomic molecules in your own words. Suggested topics are

- Born-Oppenheimer approximation
- Molecular quantum numbers
- Representations of potential energy curves
- Long-range interaction