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Atomic and Laser Spectroscopy

*The aim of this exercise is to give an overview of the field of laser spectroscopy and to show modern spectroscopic methods used in atomic, molecular and chemical physics. In this laboratory characteristics of the iodine molecule will be studied by **laser spectroscopy**.*

I. Laser Induced Fluorescence on molecular iodine

Determination of the molecular vibrational constants and the Morse potential function of the molecular iodine, I_2 $X^1\Sigma$ ground state.

By using the HeNe 543.5 nm laser line excitation of molecular iodine, contained in a small glass cell, can be performed and laser induced fluorescence (LIF) can be detected by using a small monochromator observing the fluorescence. The HeNe laser line will produce a progression of fluorescence lines caused by transitions from the excited $B^3\Pi_0$ state to different vibrational states of the $X^1\Sigma$ ground state.

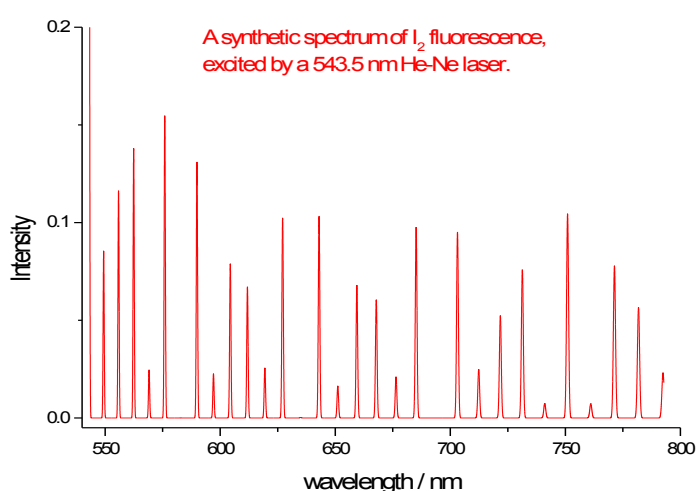


Fig.1: synthetically generated spectrum of molecular iodine in the 530-800 nm wavelength region; the intensity pattern of this spectrum is slightly different from the experimental one.

After analysis of the spectrum, the molecular vibrational constants ω_e and $\omega_e x_e$ can be determined. The dissociation energy, D_e , of the $X^1\Sigma$ ground state can be determined and the Morse potential function can be calculated.

1. Theory: the vibrational structure of diatomic molecules

1.1 The Harmonic Oscillator

Using classical mechanics and Hooke's law one can discuss the vibrations of a diatomic molecule by applying a simple model:

$$F = -kx = \frac{d^2x}{dt^2} m$$

where x is the displacement from the position of equilibrium and k is the force constant. The solution to this equation is a sinus function:

$$x = x_0 \sin(2\pi f t + \phi) \text{ with } f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where f is the vibrational frequency, x_0 is the vibrational amplitude and ϕ is a phase constant depending on the initial conditions. The potential energy of the harmonic oscillator is $V(x) = kx^2/2$. If we solve the Schrödinger equation for this potential energy considering the reduced mass μ of the system and with the equilibrium distance between the two masses as r_e we end up with the following energy eigenvalues depending on the vibrational quantum number v :

$$E_v = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} (v + 1/2) = hf_0 (v + 1/2) \quad \text{where } f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

This is the frequency obtained from a system with mass μ attached to a string with force constant k vibrating around its equilibrium position. The vibrational quantum number is v with the possible values 0, 1, 2,.... The zero point energy is $hf_0/2$ with $v = 0$. Thus, the molecule is still vibrating though the vibrational quantum number is $v = 0$. This is also the fact according to the Heisenberg uncertainty relation. We can now define the vibrational energy $G(v)$ in the following way:

$$G(v) = \frac{E_v}{hc} = \frac{f_0}{c} (v + 1/2) = \omega_e (v + 1/2)$$

where ω_e denotes the vibrational frequency in cm^{-1} and v is the vibrational quantum number.

In Fig.5, potential energy diagram is given showing both the vibrational energy levels as well as the potential curve.

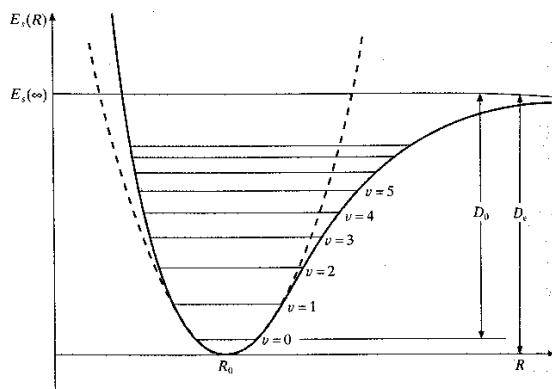


Fig. 5. The vibrational energy levels of a diatomic molecule.

If we have a transition between two vibrational states within the same electronic state the wavenumber $\sigma = 1/\lambda$ for the corresponding radiation is given by:

$$\sigma = \frac{E_{v'}}{hc} - \frac{E_{v''}}{hc} = G(v') - G(v'')$$

v' and v'' are the vibrational quantum numbers for the upper and lower vibrational levels.

1.2 The Anharmonic Oscillator.

The description of molecules by using the harmonic oscillator is merely a first order approximation of a more general case. If for instance the bond between the atoms is stretched there comes a point where it will break - the molecule then dissociates into atoms. Thus, for larger amplitudes of the extension of the bond a more complicated description has to be applied.

A purely empirical expression, which fits this curve to a good approximation, is the *Morse function*:

$$V(r) = D_e \left[1 - e^{a(r_e - r)} \right]^2$$

where a is a constant for a particular molecule and D_e is the dissociation energy.

If we now apply this energy function and use it in the Schrödinger equation the vibrational energy levels are found to be:

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3 \quad (v = 0, 1, 2, \dots)$$

The so called zero-point energy can be obtained by putting $v = 0$. Thus we obtain approximately $G(0) = \omega_e/2$ as the energy of the $v = 0$ level. This point lies $\omega_e/2$ units above the lowest part of the potential energy curve.

In this exercise, we use a laser line of the HeNe laser (543.5 nm). This wavelength **accidentally** coincides with the energy of the vibrational level $u = 26$ of the excited state $B^3\Pi_0$ of iodine. The fluorescence spectrum is collected when this state relaxes to the ground state. The excited state's vibrational levels are also found to be:

$$F(u) = T_e + \omega_e'(u + 1/2) - \omega_e x_e'(u + 1/2)^2 + \omega_e y_e'(u + 1/2)^3 \quad (u = 0, 1 \dots)$$

with different vibrational constants ω_e' , $\omega_e x_e'$, $\omega_e y_e'$.

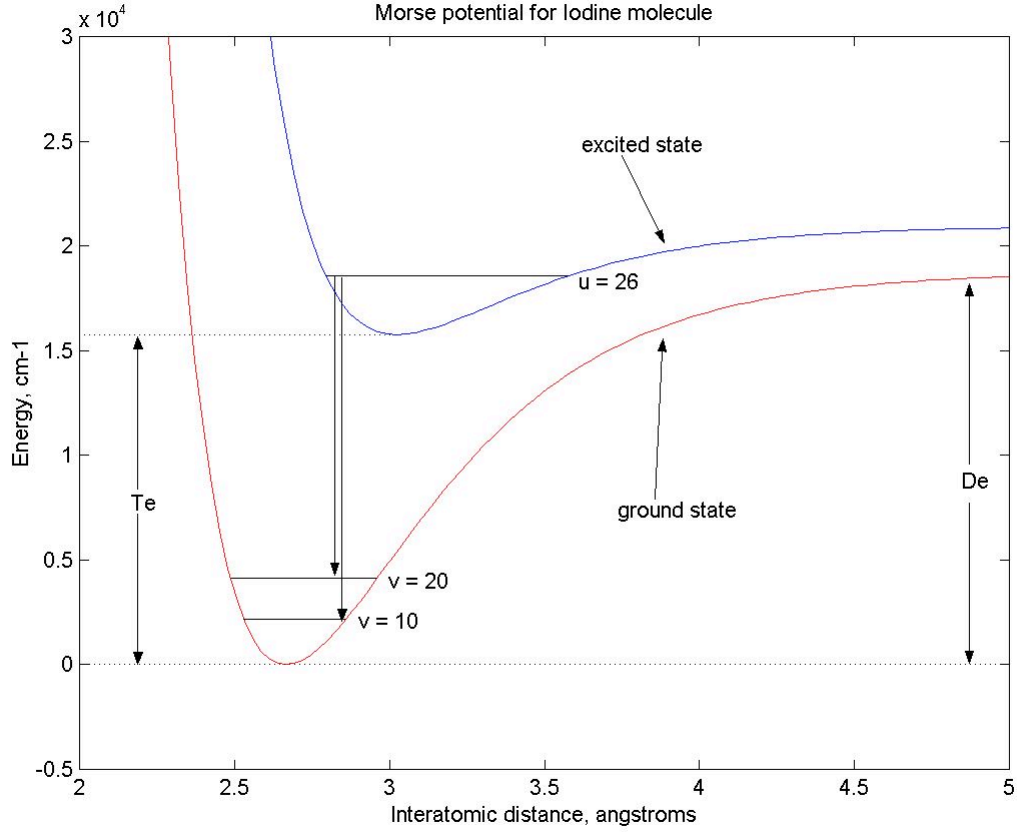


Fig. 6: Morse potential of both excited and ground states of the iodine molecule.

When the excited state $u = 26$ decays to any vibrational level of the ground state, the energy difference σ can be expressed as:

$$\sigma_v = F(u = 26) - G(v)$$

So, if we take the difference between two adjacent fluorescent emissions:

$$\sigma_v - \sigma_{v+1} = (F(u = 26) - G(v)) - (F(u = 26) - G(v+1)) = G(v+1) - G(v)$$

Let us now calculate this expression to obtain the vibrational constants of an unknown spectrum:

$$\Delta G(v+1/2) = G(v+1) - G(v) =$$

$$\omega_e - \omega_e x_e(2v + 2) + \omega_e y_e(3v^2 + 6v + 13/4) + \dots$$

In a spectrum where a vibrational progression can be seen, the separation between two adjacent vibrational lines is approximately given by:

$$\sigma_v - \sigma_{v+1} = G(v+1) - G(v) = \omega_e - 2\omega_e x_e - 2v\omega_e x_e$$

As $\omega_e \gg \omega_e x_e$, the separation is roughly around ω_e . Note that this expression is a linear function of v . The plot of $\sigma_v - \sigma_{v+1}$ versus v is called a linear Birge-Sponer extrapolation.

If we increase the quantum number v we will reach a point where the difference $\Delta G(v+1/2)$ between two successive levels becomes very small, i.e. at the energy equal to $V(\infty)$. The summation of the combination differences will give

$$D_0 = \sum_{v=0} \Delta G(v+1/2)$$

Birge and Sponer gave a graphical method to obtain this summation as is shown in Fig.6.

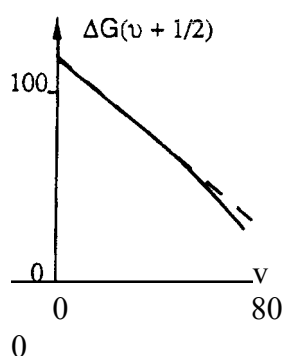


Fig.6. Linear Birge-Sponer extrapolation.

The area under the curve gives the value of D_0 , which is in our case approximately equal to D_e . When using the linear expression of $\Delta G(v+1/2)$ making the summation, one obtains the following expression:

$$D_e = \frac{\omega_e^2}{4\omega_e x_e}$$

Evaluation of this constant can then be used in order to obtain the Morse potential function described earlier:

$$V(r) = D_e \left[1 - e^{a(r_e - r)} \right]^2$$

This is just one of several empirical formulae proposed to give the molecular potential curve. If we simply expand the potential as a Taylor series in $(r - r_e)$, the following expression is obtained:

$$V(r) = V(r_e) + (r - r_e) V'(r_e) + \frac{(r - r_e)^2}{2!} V''(r_e) + \frac{(r - r_e)^3}{3!} V'''(r_e)$$

Classically we can compare this with the result obtained from the harmonic oscillator where Hooke's law $F = -k_e (r - r_e)$ gives

$$V(r) = k_e \frac{(r - r_e)^2}{2}$$

By comparing the expressions we see that the force constant $k_e = V''(r_e)$.

Taking the derivatives of the Morse equation we obtain at $r = r_e$

$$V(r_e) = 0; \quad V''(r_e) = 2a^2 D_e$$

This leads to the following equation

$$\omega_e x_e = \frac{ha^2}{16\pi^2 c \mu}$$

where μ is the reduced mass, h Planck's constant and c the speed of light

From the literature we can take the rotational constant B_e to obtain the equilibrium distance r_e by using the expression:

$$B_e = \frac{h}{8\pi^2 c \mu r_e^2}$$

Thus we can derive the Morse potential function knowing the experimentally derived constants ω_e , r_e and D_e .

2. Experimental part: task during the exercise

Calibration

Calibrate the spectrometer system by using 4 Hg filters and the light from the roof lamps. Use the mirror and the lens to focus the light into the spectrometer. In order to get good spectra, choose different exposure times of the monochromator-CCD setup. For some filters it is possible to see also the second order diffraction peak. Remember that diffraction is governed by the Bragg's law

$$n \cdot \lambda = 2 \cdot d \cdot \sin\theta$$

where n is the order of the intensity maximum, d is the lattice constant and θ is the angle at which occurs the maximum.

When the spectrum looks nice, take the value of the peak channel (first and second order diffraction peak), using the PEAK command: write these values in a table with the corresponding filter wavelengths, plot wavelengths versus channels and perform a linear least squares fit (you can use Excel or MatLab on the computer in the lab, or whatever other programs you have). The best fit equation gives you the calibration of the spectrometer.

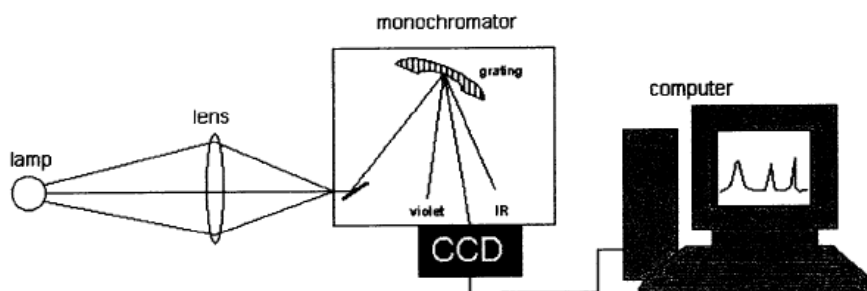


Fig. 2. Overview of the set-up needed in order to calibrate the spectrometer.

Laser Spectroscopy

The HeNe green laser is used to excite molecular iodine (I_2) from the $X^1\Sigma$ ground state to the $B^3\Pi$ excited state. The green HeNe laser line at 543.5 nm coincides (by accident) with a branch of the $B^3\Pi - X^1\Sigma$ I_2 transition. A monochromator equipped with a linear diode array consisting of 2048 diodes is used to record the spectra.

1. Switch on the laser by turning the key of the power supply and line up the optics. OBS!: the HeNe laser light has the power of 1.5 mW and can cause damage on the eye if you look directly into the laser.
2. Put the iodine cell below the laser and align the fluorescence light emitted by the gas into the entrance slit of the monochromator.

3. Use a piece of paper in front of the spectrometer to check if the fluorescence light is correctly aligned. In order to get good spectra it is necessary to use background subtraction and average several spectra (see below).
4. Record the channel number for each line of the I_2 *LIF* spectrum and then determine the wavelengths using the calibration equation; calculate the corresponding wavenumbers σ in cm^{-1} and $\Delta\sigma_{ij} = 1/\lambda_i - 1/\lambda_j$ between two adjacent lines. Note that each spectrum line corresponds to a particular vibrational quantum number v . OBS!: the I_2 spectrum lies between 500 nm and 900 nm and it is necessary to record up to 30 lines in order to have good results.
5. Plot $\Delta\sigma$ as a function of vibrational quantum number v . Perform a linear least squares fit (Birge-Sponer extrapolation) and determine ω_e and $\omega_e x_e$. Calculate also the dissociation energy D_e in cm^{-1} . Compare your values of ω_e and $\omega_e x_e$ with the theoretical ones you find on the NIST web page (see below “How to use the NIST chemistry webBook page”). **Observe that your D_e value is not the same as the D_e given at NIST web page. There, D_e is the distortion constant for rotational energy. It cannot be determined in the present experiment.**
6. Calculate the molecular constant a using the formula for $\omega_e x_e$, and the equilibrium distance r_e from the rotational constant B_e . You find the value of B_e on the NIST web page. Determine and plot the Morse potential function.

How to use the NIST Chemistry WebBook page...

First you go to the NIST link:

<http://webbook.nist.gov/chemistry/>

And let's say you are searching for the equilibrium internuclear distance r_e of the hydrogen (H_2) molecule in the excited state " $C^1\Pi_u\ 2p\pi$ ".

So...

In the *search options*, click on *formula*.¹

In the page, fill item "1" with " H_2 ". You are searching for something that belongs to the "*constants of diatomic molecules*" part, so that's what you select in the item "4".

In the following page a lot of data will appear, and when you scroll down you will see a table that looks like this:

State	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	γ_e	D_e	β_e	r_e	Trans.	v_{00}
$n\ ^3\Pi_u\ 5p\pi$	120952.9	2321.4	62.8 ₆		29.9 ₅	1.24 ₇		[0.023]		1.057	$n \rightarrow a$	24847.3 4
Richardson, 1934; Dieke, 1958												
$m\ ^3\Sigma_u^+ 4f\sigma$	(119317) 8	[2457.1]			6						$m \rightarrow a$	23295.1 9
Richardson, Yarrow, et al., 1934												
$s\ ^3\Delta_g\ 4d\delta$	118875.2	2291.7 10	62.4 ₄ 10		11						$s \rightarrow c$	22949.3 12
Richardson, 1934; Foster and Richardson, 1953; Dieke, 1958												
$r\ ^3\Pi_g\ 4d\pi$	118613.7	2280.3 13	57.9 ₆ 13		11						$r \rightarrow c$	22683.2 13
Richardson, 1934; Foster and Richardson, 1953; Dieke, 1958												

OK...

Here you have to search for the state you want ($C^1\Pi_u\ 2p\pi$), and take note of the value you want. **BUT, you have to be careful: the symbols may differ to the ones you use, or the units.** So how do you check this out?

If you look carefully in the initial page (<http://webbook.nist.gov/chemistry/>) you will see a title that says "**Documentation**". A few links are on display, among them "A Guide to the NIST Chemistry WebBook". Click on it. A lot of links will appear after the title "**Contents**".

In part "**iv. Data Available**" is the item "**k. Constants of Diatomic Molecules**". This is what you are searching for. When you click on it, an explanation of each symbol meaning will appear, sometimes with units. **The symbols that do not have units, are in the standard units, for example the energy and the wavenumber is in cm^{-1} .**

In this case, you search for "Internuclear distance in Å, r_e ".

So, in the page of the data of the hydrogen, you have to go to the table, search for the name of the state and find the value given after r_e , in this case the answer is: 1.0327 Å.

¹ If you want, you can use also **Name** and fill item "1" with "hydrogen".