Atomic and Laser Spectroscopy

Modern Physics, SH1012

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Contents

1   Introduction

In this lab exercise the goal is to determine the molecular vibrational constant and the Morse potential function for iodine molecules. This will be done by focusing a laser, namely a HeNe-laser, onto a canister supplied with the aforementioned matter.

The idea is to bring these iodine molecules to an excited energy state and detect the emitted photons, which are produced when the iodine molecules recede to a lower energy state. Naturally, a detector will be used in this stage of the exercise.

Firstly, a brief overview of the theory used in this lab exercise will be given. Thereafter, in spirit of scientific reproducibility, the experimental setup is explained in detail. This will be followed by a section containing all the achieved results and lastly this report will be concluded by a discussion about the results and possible error sources.

2   Theory

The potential in a diatomic molecule is given empirically by the Morse function

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

where a is a constant specific for the molecule in use, r the distance between the atoms and r_e the distance that minimizes the Morse function. This formula will take in account the effect of the bond, in the iodine molecule, breaking and forcing the molecule to dissociate into atoms. Therefore this Anharmonic Oscillator is used in liue of the simpler Harmonic Oscillator. D_e is the dissociation energy.

Now, if the Schrödinger equation is solved with the Morse function put in, vibrational energies of the ground state are found to be

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3, \quad v \in \mathbf{N}. \tag{2}$$

Here v is the vibrational quantum number; furthermore the vibrational energy levels for the excited state $B^3\Pi_0$ of iodine molecules are given by

$$F(u) = T_e + \omega_e'(u + 1/2) - \omega_e x_e'(u + 1/2)^2 + \omega_e y_e'(u + 1/2)^3, \quad u \in \mathbf{N}. \tag{3}$$

Notice that the primed values are different from the previously mentioned.

The laser's wavelength coincides with the vibrational energy level of $F(u = 26)$, which is the reason why the iodine always will transit from this level to the ground state, but with an unknown vibrational level. The energy difference between these levels equals the energy of the photon being emitted

$$\sigma_v = F(u = 26) - G(v). \tag{4}$$

Using (4) and taking the difference in wavenumber of two adjacent energy transitions and approximating yields

$$\Delta\sigma = \sigma_v - \sigma_{v+1} = \omega_e - 2\omega_e x_e - 2v\omega_e x_e. \tag{5}$$

Because $\omega_e \gg \omega_e x_e$ further approximation gives

$$\Delta\sigma = \omega_e - 2v\omega_e x_e. \tag{6}$$

By obtaining σ_v for different v, the data can be curve fitted to a linear polynomial and coefficients – ω_e, x_e – can be identified. Notice that $\sigma = \frac{1}{\lambda}$ so $\Delta\sigma$ can be calculated by

$$\Delta\sigma = \frac{1}{\lambda_v} - \frac{1}{\lambda_{v+1}}, \tag{7}$$

where λ_v is the wavelength of a photon corresponding to a transition from the excited state to the vibrational level, v, of the ground state.

A known approximate expression for D_e is

$$D_e = \frac{\omega_e^2}{4\omega_e x_e}. \tag{8}$$

The plot of (5) versus v is called a linear Birge-Sponer extrapolation. D_e is approximately the area under this plot. Approximating the Morse potential function with a harmonic oscillator around the equilibrium position results in

$$\omega_e x_e = \frac{ha^2}{16\pi^2 c\mu}, \tag{9}$$

where h is the Planck's constant, c the speed of light in vacuum and μ the reduced mass of the molecule. It is obvious that a can be calculated if ω_e and x_e are known. B_e is a constant that is given in the literature,

$$B_e = \frac{h}{8\pi^2 c\mu r_e^2}. \tag{10}$$

Solving for r_e is easy because everything is known. Consequently, by calculation of ω_e and x_e the Morse potential will be specified.

3   Experimental Setup

A computer is connected to a monochromator, which detects incoming photons that are collected by a lens and focused into it. The software shows the number of detections versus channel. Since channel isn't a physical quantity, it must be transformed into wavelength. This process is known as calibration.

In order to calibrate the spectrometer white light is guided into the lens by using a mirror. At front of the monochromator different filters are placed allowing only a certain wavelength to pass by. Data of channel and wavelength are collected. Every wavelength pertains to a specific channel and since this wavelength is known, a relationship between the two can be established by curve fitting the data obtained. The relationship is

$$\lambda = 740.4 + 5.185 x_{\text{ch}} \tag{11}$$

measured in Å. x_{ch} is the channel number.

λ [Å]	CH
4047	638
8094	1538
4358	696
8716	1418
5461	912
5782	973

Table 1: Wavelenght λ and Channel (CH)

Figure 1: Fitted curve.

Interference occurs when light is reflected in different atomic planes of the mirrors located inside the monochromator. This process is governed by Bragg's law

$$n\lambda = 2d\sin\theta, \tag{12}$$

where n is the order of the intensity maximum, θ is the angle of incidence and d is the distance between two adjacent atomic planes. For some filters it's possible to detect a second order diffraction peak corresponding to a wavelength of 2λ. Here λ is the wavelength of the light that is allowed to pass through the filter.

A HeNe laser is used with a wavelength of 5435 Å and is placed directly above the canister filled with iodine molecules. Florescent light is emitted by the iodine molecules and focused by the lens into the monochromator. The lens is adjusted until a reasonably strong signal is detected by the computer. Ambient light is removed artificially by software. This is done by measuring background light for an amount of time and averaging it over the measured intensity. This pattern is then subtracted from the original signal, i.e the laser plus ambient light.

The maximum energy an iodine molecule can emit depends solely on absorption of a photon from the laser, that has a wavelength of 5435 Å. This transition corresponds to going from the excited state to the ground state with $v = 0$. Since $E = hc/\lambda$, this is the smallest possible wavelength. Because (11) is monotonically increasing the smallest channel corresponds to the transition to $v = 0$. Therefore the peaks go from left to right with increasing quantum number beginning with $v = 0$. The lowest possible channel is calculated, 905.4, by putting in the laser's wavelength 5435 Å in the formula (11).

Some of the peaks are missing which makes interpolation come in handy. To obtain the interpolation formula (6) and (7) are exploited

$$\begin{cases} \sigma_v - \sigma_{v+1} = \omega_e - 2\omega_e x_e - 2v\omega_e x_e \\ \sigma_{v+1} - \sigma_{v+2} = \omega_e - 2\omega_e x_e - 2(v+1)\omega_e x_e. \end{cases} \tag{13}$$

Taking the difference yields

$$\sigma_v - 2\sigma_{v+1} + \sigma_{v+2} = 2\omega_e x_e \approx 0, \tag{14}$$

which, using $\sigma = \frac{1}{\lambda}$, leads to

$$\lambda_{v+1} = \frac{2\lambda_v \lambda_{v+2}}{\lambda_{v+2} + \lambda_v}. \tag{15}$$

4   Results

In the first table below the results of the experiment are shown. By using (11) the corresponding wavelengths are calculated. The second table shows the difference in wavenumber of two adjacent energy transitions.

v	CH	λ [Å]		v	CH	λ [Å]
0	901	5412		14	1093	6408
1	913	5474		15	1109	6491
2	925	5537		16	1125	6574
3	939	5609		17	1141	6656
4	–	5676*		18	–	6743*
5	965	5744		19	1175	6833
6	977	5806		20	1193	6926
7	991	5879		21	1209	7009
8	1005	5951		22	1227	7102
9	1019	6024		23	1245	7196
10	1033	6097		24	1263	7289
11	–	6174*		25	–	7386*
12	1063	6252		26	1301	7486
13	1079	6335		27	–	7583*
				28	1339	7683

Table 2: Quantum number v, channels CH and wavelength λ. * denotes interpolated peaks.

v	$\Delta\sigma$ [cm^{-1}]		v	$\Delta\sigma$ [cm^{-1}]
$1 \to 0$	210		$15 \to 14$	199
$2 \to 1$	205		$16 \to 15$	194
$3 \to 2$	234		$17 \to 16$	190
$4 \to 3$	212		$18 \to 17$	196
$5 \to 4$	207		$19 \to 18$	191
$6 \to 5$	187		$20 \to 19$	197
$7 \to 6$	213		$21 \to 20$	171
$8 \to 7$	207		$22 \to 21$	187
$9 \to 8$	202		$23 \to 22$	183
$10 \to 9$	198		$24 \to 23$	178
$11 \to 10$	207		$25 \to 24$	183
$12 \to 11$	201		$26 \to 25$	178
$13 \to 12$	209		$27 \to 26$	174
$14 \to 13$	179		$28 \to 27$	169

Table 3: Difference in wavenumber of two adjacent energy transitions.

Data from Table 3 is curve fitted to a linear function enabling coefficients to be identified and compared to (6).

Figure 2: Linear function fitted to data in table 3.

This gives $\omega_e = 215.5$ cm$^{-}1$ and $x_e = 0.0035$. Using these values and equations (9), (10) and (8) calculations can be made

D_e [cm^{-1}]	a [Å^{-1}]	r_e [Å]
$1.54 \cdot 10^4$	2.39	2.67

Table 4: Results.

The Morse function can now be plotted using (1) and is visualized below.

Figure 3: Morse potential function.

5   Discussion

When conducting the experiment, it's assumed that the vibrational level of the excited state in the iodine molecules is $u = 26$. As mentioned earlier, this has to do with the laser light's wavelength. Background radiation – e.g. gamma photons and black body radiation – could in principle excite the atom further and thus change the vibrational level. When the atom then recedes to its ground state a photon with an unexpected energy will be emitted. This situation can't be described by equation (6).

Between the canister and the detector lies air – which allows for photons, emitted by the iodine, to interact with its particles. Effects like Compton scattering will therefore be present and change the wavelength of said photon. This is accounted for when background radiation is removed artificially by computer software. However there is a risk that some of the emission pattern's peaks are weakened or removed when doing so. As the wavenumber grows it's harder to distinguish the peaks of the emission pattern as the transitions rate decreases with channel.

Interpolated peaks are also a source of error, it's hard to know where peaks have to be interpolated. Not all of the peaks can be seen on the screen.

In the calibration process interference is noticed. These effects should also be present when the light emitted by the iodine is detected. Measuring the detected wavelength might not correspond to the emitted wavelength. This would have an enormous effect on the data obtained and therefore on the Morse potential. Furthermore the detector in the monochromator isn't located strictly behind its opening making it harder to focus the light. This weakens the signal and it would be better if the detector was closer to the opening.

Since (11) is obtained by fitting a curve, there exists an error which is systemically forwarded to every single wavelength that has been calculated, affecting the fitted curve using the data in Table 3.

The opening of the monochromator which photons pass through is defined with an finite uncertainty. The Heisenberg uncertainty principle says it must exist an uncertainty in the wavelength of the photons incident to detector – since wavelength is inversely proportional to momentum. This effect may not even be detectable by the software used.

Obviously the approximations leading to (6) introduce an error as well.