

Steven Labalme

TA: Rowan Simonet

Lab partners: Eric Yuan and Kate Kaplin

12 January 2023

10 February 2023

3 UV-VIS ANALYSIS OF IODINE

Abstract

The goal of this experiment is to determine several spectroscopic constants of iodine and use them to calculate the potential energy surface, approximated as a Morse potential, of the ground and second excited states. Additionally, it is desired to compare solution-phase and gas-phase data to obtain insight into how phase changes alter molecular dynamics.

As a result of both gas- and solution-phase analyses, the fundamental vibrational frequency, first anharmonicity constant, well depth, dissociation energy (from the zero point energy), difference in energy between the X and B states, and Morse constant β were calculated.

The aim is to provide an experimental verification of the basic quantum mechanical theory of molecular transition mechanics.

Introduction

The experiment described herein has two main parts. The primary purpose of the first of these is to determine several spectroscopic constants of diatomic iodine (I_2) from the gas-phase ultraviolet-visible (UV-Vis) absorption spectrum and use them to calculate the potential energy surface, approximated as a Morse potential, of the ground ($^1\Sigma_g^+$) and second excited ($^3\Pi_{ou}^+$) states^{1,2}. The primary purpose of the second of these is obtain a solution-phase UV-Vis absorption spectrum and, from it, calculate the molar extinction coefficient.

From the gas-phase data in particular, we can obtain the frequencies, anharmonicities, and magnitudes of each electronic state, the dissociation energies of each electronic state, and more, but we will only focus on the first two herein². From the solution-phase data, we can only obtain the frequency and magnitude of the transition.

As mentioned above, we will collect our data via UV-Vis spectroscopy (gas phase and solution phase). We will analyze anharmonicity (and its derived constants) using a linear model and hence linear regression. All theoretical calculations build up to the construction of a Morse potential.

The main theoretical idea behind the experiment is that incoming radiation couples to the eigenstates of the system. Specifically, frequencies of radiation that (nearly) exactly match the difference in energy between two quantum states are capable of causing a transition. In the UV-Vis range, this excitation occurs between vibronic energy levels. The electronic energy levels are represented by discrete potential energy surfaces (PES's), and the vibrational energy levels occur as sublevels within the larger electronic levels. If we approximate the electronic potential wells as parabolas (corresponding to a harmonically oscillating molecule), we can prove via quantum mechanics that the energies of the vibrational sublevels depend on an indexing parameter v via

$$E_v = \bar{\nu}_e \left(v + \frac{1}{2} \right)$$

where $\bar{\nu}_e$ is the fundamental vibrational frequency. Realizing that a harmonic oscillator is not a good approximation, we can introduce anharmonicity into the math by expanding the above energy levels as a power series in $v + 1/2$. Using this energy function to second order, we can derive a formula for the spacing between adjacent vibrational energy levels that is linear. This formula comes in two flavors, one for changes in the vibrational energy level to which an electron is excited and one for changes in the ground state vibrational energy level (i.e., fundamental transitions vs. hot bands). Both are listed below.

$$\Delta\bar{\nu}(v') = \bar{\nu}'_e - 2\bar{\nu}'_e x'_e (v' + 1) \qquad \Delta\bar{\nu}(v'') = \bar{\nu}''_e - 2\bar{\nu}''_e x''_e (v'' + 1)$$

In the above equations, x_e is the first anharmonicity constant, and the other variables are as defined above.

Thus, fitting the peaks on a UV-Vis spectrum (which correspond to distinct vibronic transitions) allows us to reverse engineer the fundamental frequency and anharmonicity parameters. These parameters give information on the shape of the potential well that can be fit to a Morse potential via¹

$$D_e \approx \frac{\bar{\nu}_e}{4x_e} \qquad \beta = \bar{\nu}_e \pi \cdot \sqrt{\frac{2c\mu}{hD_e}}$$

In the above equations, $c = 2.998 \times 10^8 \text{ m s}^{-1}$ is the speed of light, $\mu = 1.06 \times 10^{-25} \text{ kg}$ is the reduced mass of I_2 , $h = 6.626 \times 10^{-34} \text{ J s}$ is Planck's constant, and all other variables are as defined above.

Per Verma [3], the Morse potential is an excellent approximation for the PES of I_2 , even among similar diatomics, so we can expect physically comparable results from the following equation even using such a crude experiment and theoretical model.

$$U(r) = D_e(e^{-\beta(r-r_e)} - 1)^2$$

In the above equation, U is the potential energy, r is the bond distance on which U depends, β is the Morse constant, r_e is the equilibrium constant, and e is Euler's number.

Experimental

To collect the gas-phase spectrum, an apparatus centered around a SPEX 500M monochromator was used. Said apparatus also included a light source, the I_2 sample, a light shutter, and an RCA 6217 photomultiplier tube (PMT) which functioned as a detector. Removal of external light was accomplished by carrying out the experiment in a darkened room and shrouding the PMT in an additional blanket. Data collection was performed in LabView from National Instruments¹. During the post-collection analysis phase, extra care was taken at the lower ends of $(v', 0)$, $(v', 1)$, and $(v', 2)$ peaks since hot bands eventually outweigh other data. However, the hot bands were still analyzed as they actually make it possible to obtain much more data from the excited-state Birge-Sponer plot, and data at all for a ground-state Birge-Sponer plot².

To collect the solution-phase spectrum, an Ocean Optics USB4000 spectrometer was connected to a standard desktop computer running OceanView. The solvent used for I_2 was chloroform (CHCl_3). An extremely dilute sample was used to bring the data in to the Beer's Law region (to allow for calculation of the molar extinction coefficient, as previously mentioned). Beer's law is given by

$$A = \epsilon b C$$

where A is absorbance, ϵ is the molar extinction coefficient, b is the path length (1 cm in this case since that's the width of the cuvette), and C is the concentration of the dilution ($2.8 \times 10^{-4} \text{ M}$ in this case).

The overall procedure was as follows. First, a broad-spectrum scan of the gas-phase sample was collected to identify the region of interest. Next, a narrow-range spectrum was collected to far greater accuracy, allowing for the resolution of vibrational transitions. A subsequent calibration step (using a mercury lamp that emits at one known characteristic wavelength) was performed to account for any error in the monochromator. For the solution, a chloroform and cuvette background, and a dark background were taken. Then, the sample was diluted using 0.7 mL of a 0.01 M stock solution and an additional 24.3 mL of pure chloroform; the result was a $2.8 \times 10^{-4} \text{ M}$ solution of I_2 in CHCl_3 . Lastly, a UV-Vis absorption spectrum of this sample was taken.

Safety goggles and nitrile gloves were used at all times when handling chloroform-containing samples.

Results

As determined by the initial broad-spectrum scan, the gas-phase spectrum was collected between 5000-6500 Å. It is plotted below in Figure 1. Note that the colored numbers correspond to the wavelengths of certain vibrational transitions (green for ground state, orange for the first hot band, red for the second hot band).

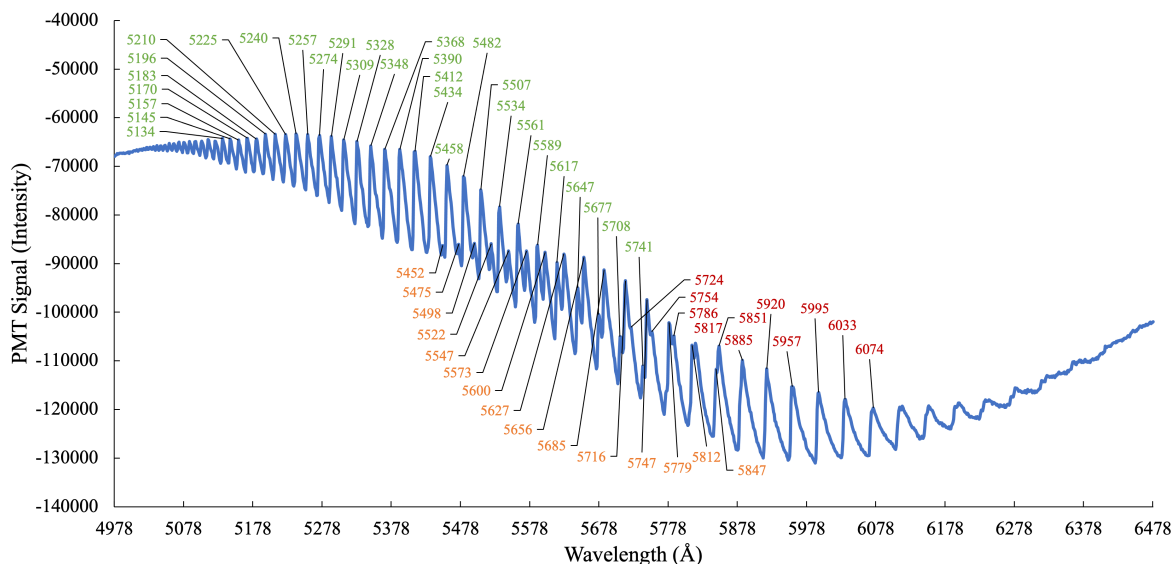


Figure 1: The absorption spectrum of gaseous I_2 between $\lambda = 5000 - 6500 \text{ \AA}$.

Since the PMT is not capable of measuring absorption directly and unforeseen circumstances prevented the collection of a background spectrum in a timely manner, the spectrum is plotted in *intensity* vs. wavelength instead of the standard *absorption* vs. wavelength. Support for an accurate measurement of the wavelength comes from the aforementioned mercury lamp calibration step, and steps have been taken to ensure that the PMT intensity (as described above) is also accurate.

The overall trend observed in Figure 1 is representative of the electronic absorption band, while the fine structure is vibrational in nature. The variable peak spacing is representative of anharmonicity and is characterized below in Figure 2.

First, though, the peaks labeled in Figure 1 are tabulated and assigned to vibronic transitions using known reference values. The result is as follows. Note that wavelength has been converted to wavenumber.

v'	v''	$\omega \text{ (cm}^{-1}\text{)}$	v'	v''	$\omega \text{ (cm}^{-1}\text{)}$	v'	v''	$\omega \text{ (cm}^{-1}\text{)}$
						10	2	16464
						11	2	16576
						12	2	16681
						13	2	16787
			14	1	17103	14	2	16892
15	0	17419	15	1	17206	15	2	16992
16	0	17519	16	1	17304	16	2	17091
17	0	17615	17	1	17400	17	2	17191
18	0	17709	18	1	17495	18	2	17283
19	0	17803	19	1	17590	19	2	17379
20	0	17892	20	1	17680	20	2	17470
21	0	17982	21	1	17771			
22	0	18070	22	1	17857			
23	0	18159	23	1	17944			
24	0	18242	24	1	18028			
25	0	18322	25	1	18109			
26	0	18402	26	1	18188			
27	0	18477	27	1	18265			
28	0	18553	28	1	18342			
29	0	18629						
30	0	18699						
31	0	18769						
32	0	18836						
33	0	18900						
34	0	18961						
35	0	19022						
36	0	19084						
37	0	19139						
38	0	19194						
39	0	19246						
40	0	19294						
41	0	19342						
42	0	19391						
43	0	19436						
44	0	19478						

Table 1: Peaks and their corresponding transitions.

Using the data in Table 1 and the $\Delta\bar{\nu}(v')$ equation from the introduction, it is possible to construct and characterize a Birge-Sponer plot (Figure 2) to determine both the fundamental vibration frequency and the first anharmonicity constant. All three data sets ($v'' = 0, 1, 2$) are plotted on top of each other, and are plotted versus the change in wavenumber.

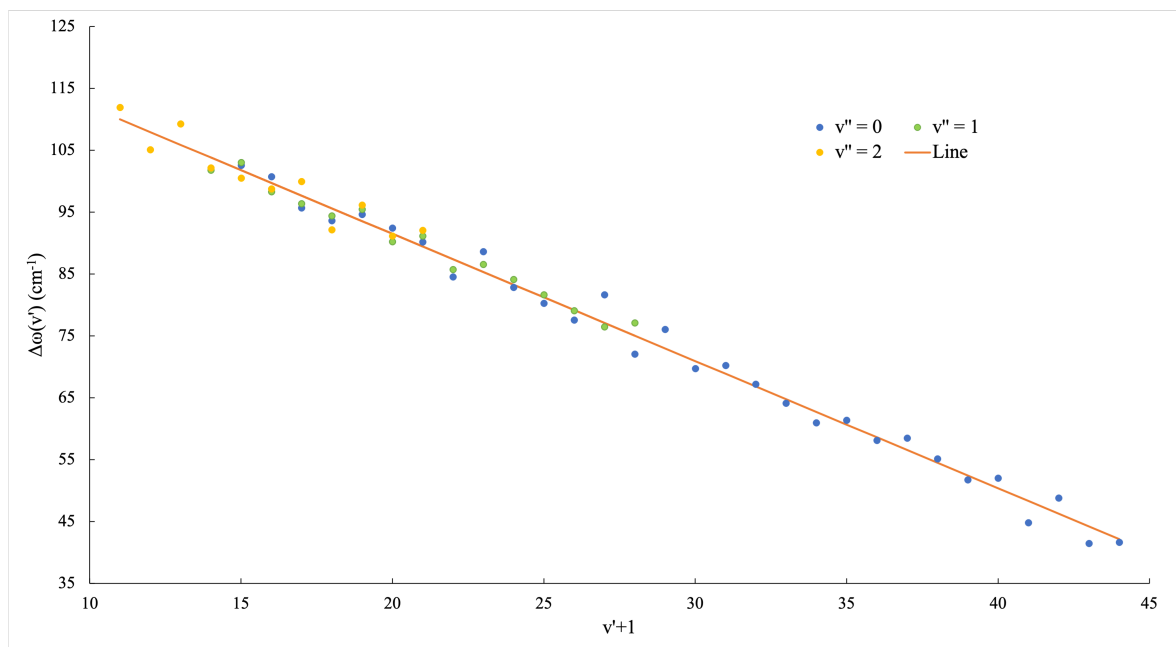


Figure 2: Birge-Sponer plot for the B state.

Evidently, the linear analysis provides a remarkable fit to the data, and it is not immediately obvious that a higher-order energy equation (e.g., cubic, quartic, etc.) would have been necessary to account for additional anharmonicity.

The above analysis was repeated for the $\Delta\bar{\nu}(v'')$ data. From $\bar{\nu}'_e$, $\delta\nu'_e x'_e$, $\bar{\nu}''_e$, and $\delta\nu''_e x''_e$, the ground and excited state dissociation energies from both the bottom of the energy well and the zero point energy can be calculated: D'_e , D'_0 , D''_e , and D''_0 . The calculation of the energy gap between electronic levels T_e followed from the previous data and additional information on the hypothetical energy of a dissociated excited I_2 molecule. All constants are summarized below.

	$\bar{\nu}'_e$	$\bar{\nu}'_e x'_e$	D'_e	D'_0	$\bar{\nu}''_e$	$\bar{\nu}''_e x''_e$	D''_e	D''_0	T_e
Calculated values	132.22	1.019	4288.6	4222.7	214.97	0.912	12 672	12 564	15 986.11
Literature values	125.69 ⁴	0.764 ⁴	5169.3	5106.6	214.50 ⁴	0.614 ⁴	18 734	18 627	15 769.01 ⁴

Table 2: Calculated spectroscopic constants and their reported values.

Note that the unit for all values in Table 2 is cm^{-1} . Also note that the D_e and D_0 values were calculated from the NIST $\bar{\nu}'_e$ and $x'_e = \bar{\nu}'_e x'_e / \bar{\nu}'_e$ values using Equations 9 and 12 in Lant [1], respectively.

The experimental values in Table 2 may be plugged into two Morse potential equations as follows. D_e values go in directly. β values must be calculated as in the introduction. Equilibrium bond length values are found in Lant [1]. And T_e gives the vertical offset between the two equations (the zero of energy was arbitrarily defined to be the bottom of the ground (X) state potential well).

Additionally, as wavenumbers have been used throughout the analysis, they are used as the unit of energy on the y -axis of Figure 3 below. Lastly, angstroms are a natural scale on which to discuss molecules, so bond length (the x -axis below) is given in terms of it. All above determinations of error suggest that the variables are being measured largely accurately.

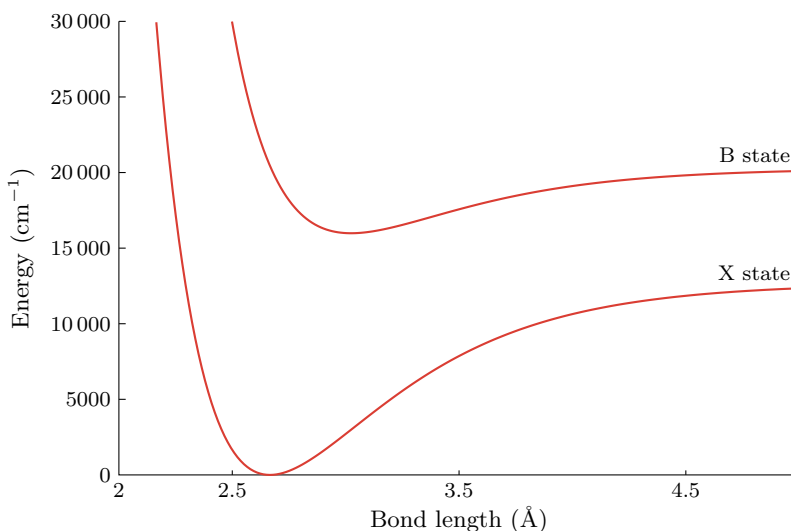


Figure 3: Morse potential curves.

From the above plot, it can be seen that the excited state has a slightly longer average bond length (as is to be expected for a molecule that is vibrating more extremely). Additionally, the ground state energies are generally more concentrated in one area, whereas the excited state ones are more spread out.

Lastly, all of the gas-phase analysis above is compared to the solution phase data. Both the initial data from Figure 1 (or rather a separate data set in terms of the molar extinction coefficient, which is closely related to absorption, obtained from Saiz-Lopez et al. [5]) and the solution-phase data are plotted in Figure 4 on the same set of axes. Expressing the data in terms of molar extinction coefficient is driven by the nature of the data from Saiz-Lopez et al. [5]; data from the solution-phase experiment performed by the authors is readily converted from absorption to molar extinction coefficient using Beer's law (per the introduction). Wavelength has been adjusted for as previously mentioned.

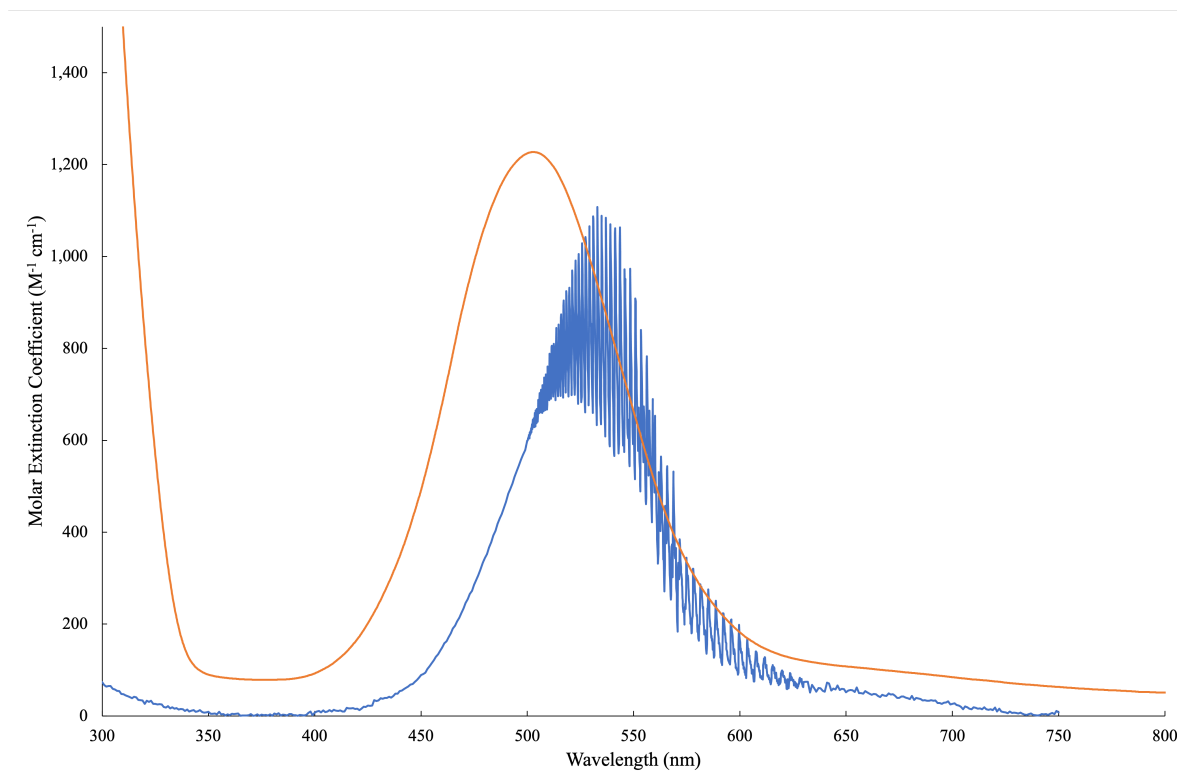


Figure 4: The absorption spectrum (in terms of the directly proportional molar extinction coefficient) of gaseous⁵ (blue) and chloroform-based (orange) I_2 between $\lambda = 300 - 800$ nm.

The maximum of the gas-phase electronic band is $1089 \text{ M}^{-1} \text{ cm}^{-1}$ and occurs at $\lambda = 534.9$ nm. The maximum of the solution-phase electronic band is $1227 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 502.7$ nm.

Half the gas-phase electronic maximum is $544.5 \text{ M}^{-1} \text{ cm}^{-1}$. The line $\epsilon = 544.5 \text{ M}^{-1} \text{ cm}^{-1}$ intersects the left side of the peak at $\lambda = 496$ nm and the right side between $\lambda = 548.1 - 565.8$ nm. Taking the average yields

$$\frac{548.1 + 565.8}{2} = 557.0$$

Thus, the full width of the absorption band at half the maximum height (FWHM) is

$$\text{FWHM} = 557.0 - 496 = 61 \text{ nm}$$

Half of the solution-phase electronic maximum is $613.5 \text{ M}^{-1} \text{ cm}^{-1}$. The line $\epsilon = 613.5 \text{ M}^{-1} \text{ cm}^{-1}$ intersects the left side of the peak at $\lambda_1 = 456.7 \text{ nm}^{-1}$ and the right side at $\lambda_2 = 553.19 \text{ nm}^{-1}$. Therefore, the FWHM is

$$\text{FWHM} = 96.5 \text{ nm}$$

The molar extinction coefficient can be read off the graph above as the electronic maximum, yielding $1227 \text{ M}^{-1} \text{ cm}^{-1}$.

Discussion

Assuming that each vibrational peak corresponds to a Lorentzian lineshape, the “disappearance” of vibrational peaks in the solution phase likely is actually representative of extreme flattening of the peaks. Molecularly, this corresponds to heightened damping of the oscillator, which would make sense in solution as all I_2 molecules will be restricted in motion by the surrounding solvent molecules. Additionally, the electronic blue shift means that more energy in general is required to excite the molecule in solution. One possible factor that could account for the shift in wavelength is that effective wavelength is shortened in substances

(including chloroform) due to their index of refraction. However, this effect is more an empirical one than an actual one (light is just bouncing around more and thus “looks” slower), so this could probably not explain the corresponding energy shift. A better theory is that the ground and excited states actually get farther apart in solution. One potential cause of this is stabilization of the ground state due to solvent effects. This stabilization would not similarly apply to the excited state since by the Born-Oppenheimer approximation, solvent molecules will not have time to rearrange on the timescale of the transition.

For free molecular dynamics, though, it is far more instructive to look at the gas phase. The light excites an electron from its ground electronic state and a ground (or slightly excited) vibrational state to an excited electronic state and a much higher vibrational state in a vibronic transition.

Theory and measured literature values are generally pretty close, and always on the same order of magnitude (sometimes much better). A precise quantitative treatment was not performed, but it can be assumed that this is pretty close, given the crudeness of the setup.

Throughout the experiment, steps were taken to collect baselines and correct for instrumental error. To calibrate the SPEX 500M monochromator, a mercury lamp that emits strongly at one characteristic frequency was used. This known frequency was compared against that recorded by the monochromator and PMT to determine an offset in the values. With the solution-phase setup, both a dark baseline (for system error) and a chloroform/cuvette baseline (for setup error) were subtracted from our final data to hopefully isolate the UV/Vis absorption due to I_2 alone.

However, some error likely remained. For example, the gas-phase spectrum was only measured to 1 Å resolution. The machine was capable of going further, and doing so could have yielded more exact peak assignments. Given that even 1 Å shifts in a few peaks can have a remarkable effect on the ultimate analysis, it is certainly possible that being exact to decimal angstroms could have been helpful. Additionally, the monochromator itself is very old and likely has become less exact with age in ways that even mercury calibration cannot fully account for. The not-super-rigorous exclusion of external light sources could also have lead to error in peak height analysis, perhaps affecting calculations of the electronic band maxima. Possible error could have also come from sublimed iodine on the surface of the tube windows². Human error in the chloroform setup included the fact that the instrument was manually put together and the shield, for instance, could have been in slightly different places each time. Additionally, the dilution was carried out by hand, so there could have been error in the calculation of the concentration of the solution. Moreover, chloroform is very volatile, so subtle concentration changes likely occurred throughout the experiment due to evaporation. On the data-analysis side of things, the Morse potential in and of itself is a crude model. Using the Lennard-Jones potential, for instance, would have been more accurate. Additionally, the anharmonicity was only approximated to first order, not to higher order as it certainly could have been. Thus, the PES's in Figure 3 and data in Table 2 may not even be entirely representative of the data collected.

However, given the remarkable closeness to literature values, the data was likely pretty good with a few of the aforementioned sources of error disproportionately affecting the overall data quality.

Conclusion

The most important results are that solvent effects blue shift the overall transitions between solution-phase and gas-phase data, and that there is an experimental basis for anharmonicity. From Figure 2, a linear fit is not a bad approximation of anharmonicity, so the Morse potential is at least somewhat justified. Further evidence for this justification comes from Verma [3].

The goal of this experiment was to determine several spectroscopic constants of I_2 and use them to calculate the potential energy surface, approximated as a Morse potential, of the ground and second excited states. This was achieved. Additionally, the researchers sought to compare solution-phase and gas-phase data to obtain insight into how phase changes alter molecular dynamics. This was also achieved.

The result is a verification of the quantum-mechanical theory of light absorption. Additionally, this experiment shows that even simple models like the Morse potential can have real predictive power. Separately, it shows that molecular interaction effects in condensed phases (and the lack thereof in expanded phases) have identifiable optical effects.

References

- (1) Lant, H. Electronic Spectroscopy: Absorption Spectra of Molecular Iodine in the Gas Phase, Rev. 1-21-23, 2023.
- (2) McNaught, I. J. The Electronic Spectrum of Iodine Revisited. *J. Chem. Educ.* **1980**, *57*, 101–105.
- (3) Verma, R. D. Ultraviolet Resonance Spectrum of the Iodine Molecule. *J. Chem. Phys.* **1960**, *32*, 738–749.
- (4) Huber, K. P.; Herzberg, G. H. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Linstrom, P. J., Mallard, W. G., Eds., <https://doi.org/10.18434/T4D303>; National Institute of Standards and Technology: Gaithersburg MD, 20899; Chapter Constants of Diatomic Molecules.
- (5) Saiz-Lopez, A.; Saunders, R. W.; Joseph, D. M.; Ashworth, S. H.; Plane, J. M. C. Absolute absorption cross-section and photolysis rate of I₂. *Atmos. Chem. Phys.* **2004**, *4*, 1443–1450.