Absorption and Fluorescence of Molecular Iodine

Kaitlyn King,[*] **Chelsea Arnold,**[a]

Physical Chemistry Laboratory, 4014 Malott Hall, Department of Chemistry, University of Kansas

[*]*Corresponding author: Kaitlyn.d.king@gmail.com,* [a]*Lab group member*

The UV-Vis absorption spectrum and LIF emission spectrum of I_2 were found for the purpose of gaining information about the energy of the ground $X(^1\Sigma_g^+)$ and excited $B(^3\Pi_{0u}^+)$ states. This information was compared to information obtained from the Gaussian program which uses quantum mechanical calculations and numerical approximations to predict electronic energy levels. The iodine molecule was found to be approaching its convergence limit near 500nm. The Gaussian program predicted this to occur at a much higher energy. Gaussian also predicted the term value and the energy gap $\Delta E(I^*)$ from $X(^1\Sigma_g^+)$ to $B(^3\Pi_{0u}^+)$ to be much greater than accepted literature values. This indicates that Gaussian is insufficient at predicting relative energy levels. Gaussian was however able to predict reasonable values for the equilibrium bond lengths indicating that it may be suitable for determining the shape of potential energy curve. The Morse potential energy curves provided a more accurate representation of the iodine molecule than the harmonic oscillator model. The harmonic oscillator model is only valid very near the equilibrium bond length. The most intense transitions occurred from the v"=0 level to the v'=34-36 range as predicted by the Franck-Condon principle. The comparative values of the force constant, equilibrium bond length, and potential energy curve well depth indicate that the bond strength is greater in the ground state than in the excited state. The experimentally determined values of equilibrium vibrational frequency were slightly higher than the literature values.

I. Introduction

Molecular Iodine is of interest because it is a heavy common halogen with many electrons. And, accurate modeling of iodine's excited electronic states is an ongoing area of research[1]. For this reason, it is of value to examine the absorption and emission spectra of I_2 in the gas phase. This provides information about the energy of the ground and excited states of the molecule which can be compared to the information garnered from theoretical calculations[1].

Laser induced fluorescence (LIF) and UV-Vis spectroscopy were used because the I_2 has a colored vapor which allows for visible absorption. The UV-Vis absorption and the LIF provide complementary information. The absorption spectrum provides information about the transition from the ground to the excited electronic state. The LIF spectrum provides information about the relaxation from the excited state back to the ground state. Conventional IR spectroscopy cannot be used to study I_2 because it is a diatomic molecule and therefore has no dipole moment. A dipole moment is necessary to determine the vibrational frequencies using IR spectroscopy[2].

The electronic transition of the absorption of I_2 is from the singlet ground state, $X(^1\Sigma_g^+)$, to an excited triplet state, $B(^3\Pi_{0u}^+)^3$. This transition is considered forbidden because the total spin angular momentum quantum number of the excited state is equal to 1. This occurs when the spins of two electrons are unpaired. This arrangement is considered highly improbable.

Neglecting the rotational-term difference and the cubic term, the transition frequency may be described by equation 1[1] below. With known transition frequencies and vibrational levels (v), this equation can be used to determine the values of the equilibrium vibrational frequencies ($\tilde{\nu}_e$) and the anharmonicity constants (x_e).

Equation 1:

$$\tilde{\nu}(v',v") = \tilde{\nu}_{el} + \tilde{\nu}_e'\left(v'+\frac{1}{2}\right) - \tilde{\nu}_e'x_c'\left(v'+\frac{1}{2}\right)^2 - \tilde{\nu}_e"\left(v"+\frac{1}{2}\right) - \tilde{\nu}_e"x_c"\left(v"+\frac{1}{2}\right)^2$$

Potential energy curves describe the electronic energy of the molecule in the specified state as a function of bond length[3]. The potential energy curves can be used to determine properties of the molecule such as the equilibrium bond length, the allowed energy levels, the term value, and the dissociation energy. The equilibrium bond length is the bond distance between the two atoms in the diatomic molecule that corresponds to the lowest energy. The term value is the energy difference between the bottom of the ground state potential energy

curve and the bottom of the excited state potential energy curve in wavenumbers[3].

The dissociation energy, D_e, is the energy at which the molecule dissociates into atoms[1]. This can be seen on a potential energy curve as the point at which the energy no longer changes as a function of the bond length. This may also be determined from the equilibrium vibrational frequency, $\tilde{\nu}_e$, and and the anharmonicity constant, x_e using equation 2[1] below for the excited state.

$$\text{Equation 2:} \quad D_e = \frac{\tilde{\nu}_e\left(1/x_e - x_e\right)}{4}$$

The ground state dissociation energy may be found from equation 3[1] which follows, the electronic frequency, $\tilde{\nu}_{el}$, and the difference in the electronic energy of the atoms produced by dissociation from the ground and excited states, $\Delta E(I^*)$.

$$\text{Equation 3:} \quad D_e{}'' = \tilde{\nu}_{el} + D_e{}' - E(I^*)$$

D_o is the energy required for the molecule to dissociate from the v=0 vibrational level. This may be found from Equation 4[1] below.

$$\text{Equation 4:} \quad D_o = \frac{\tilde{\nu}_e\left(1/x_e - 2\right)}{4}$$

The Franck-Condon Principle states that vibronic transitions are more likely if the vibrational wavefunctions overlap significantly. The intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition[4]. The Boltzmann distribution predicts that the majority of the iodine molecules will be in the ground state at v"=0. The Franck-Condon principle states that the transition will be much more likely if the wavefunctions overlap. For I_2 the wavefunctions don't significantly overlap with the ground state wavefunction until the v'=20 to 50 range of vibrational states in the B(3Π0u+) excited electronic state. At lower vibrational states the wavefunctions do not overlap because the equilibrium bond lengths (r_e) are greater than the equilibrium bond length of the ground state.

The comparative bond strengths of the ground and excited electronic states may be determined by r_e, the well depth of the potential energy curves, and the force constants. The bond strength is greater at shorter equilibrium bond lengths. A deeper well on the potential energy curve also indicates greater bond strength. The force constant, k_e, is a measure of the restoring force that resists stretching of the bond. The stronger the bond is, the greater it will resist stretching and the greater the force constant will be. The force constant

may be calculated using equation 5[1] below where μ is the reduced mass and c is the speed of light.

$$\text{Equation 5:} \quad k_e = \mu\left(2\pi c\, \tilde{\nu}_e\right)^2$$

The convergence limit is the point at which the spacing between the bands on the absorption spectrum decreases to zero. Beyond this point, the molecule is not bound in the excited state and the spectrum is continuous. This is the dissociation energy of the $B(^3\Pi_{0u}{}^+)$ excited state. Beyond this limit, the absorption of light is continuous. The gaps between the v' vibrational levels become closer together near the convergence limit because the potential energy curve well broadens since it is an anharmonic oscillator. If I_2 were harmonic, the well would be a parabola and the molecule would never dissociate.

Stokes shift is a phenomenon that occurs when the photons emitted have lower energy, higher wavelengths, than the photons absorbed. This occurs when there is rapid internal conversion from higher vibrational states to the lowest vibrational energy level which does not emit light. This nonradiative internal decay occurs when energy is dissipated by heat or when energy is transferred through collisions. Nonradiative relaxation is much faster than radiative and occurs when the energy level differences are small.

The Morse potential is often used when the harmonic oscillator is not adequate at large distances from the equilibrium bond length[1]. The Morse potential may be calculated from equation 6[1] below.

$$\text{Equation 6:} \quad U\left(r - r_e\right) = D_e\left(e^{[-\beta(r-r_e)-1]}\right)^2$$

β in equation 6 may be found from the force constant and equation 7[1] which follows.

$$\text{Equation 7:} \quad \beta = \left(\frac{k_e}{2hcD_e}\right)^{1/2}$$

The value of r_e for the excited state can be determined by finding the transition of greatest intensity from v"=0. This transition intersects the Morse potential curve at r'=r_e"[1]. This gives equation 8[7] below.

Equation 8:

$$r_e{}' = r_e{}'' + \frac{1}{B'}\left\{\ln\left(1 + \sqrt{\frac{(\tilde{\nu}(v^*) + 1/2\,\nu_e{}' - (D_e{}' - D_e{}''))r_e{}''}{D_e{}'}}\right)\right\}$$

II. Experimental Approach

The UV-Vis absorption spectrum was obtained using a Cary-100 Bio UV-Vis Spectrophotometer over a range of 450 to 650nm. The sample consisted of a few

crystals of I_2 in a 10cm cell. The absorption spectrum was used to determine the frequencies of the vibronic transitions. This was then used to create a Deslandres table.

The emission spectrum of the I_2 vapor was found using laser induced fluorescence. The laser used was a Class IIIB argon ion laser. The sample was excited at 514.5nm. The fluorescence signal was strengthened with a photomultiplier tube and averaged using a box-car integrator. The fluorescence intensity was recorded as a function of the wavelength using a scanning monochromator. The spectrum was recorded from 600 to 520nm using PChem pScan Scanner Version 0.5.1software.

III. Computational Methods

The Gaussian program was used to create the potential energy curves for the ground state, the lowest three singlet excited electronic states, and the lowest four triplet excited electronic states. The program calculates the allowed electronic energy levels using numeric approximations. Gaussian uses basis sets and the principle of superposition to arrange the wavefunctions as linear combinations, called Gaussians[3]. The program uses the Moller-Plesset second-order perturbation theory (MP2) to calculate the ground state potential energy curve. And it uses the Configuration Interaction-Singles (CIS) theory to calculate the excited state potential energy curves. CIS theory is an extension of the Hartree-Fock approximation[3].

IV. Results and Analysis

A. UV-Vis Absorption

The absorption spectrum over the range of 500 to 625nm is shown in Figure 1 which may be seen in the following column. The spectrum may be seen approaching the convergence limit near 500nm where the vibrational energy levels become so close that the peaks are no longer distinguishable.
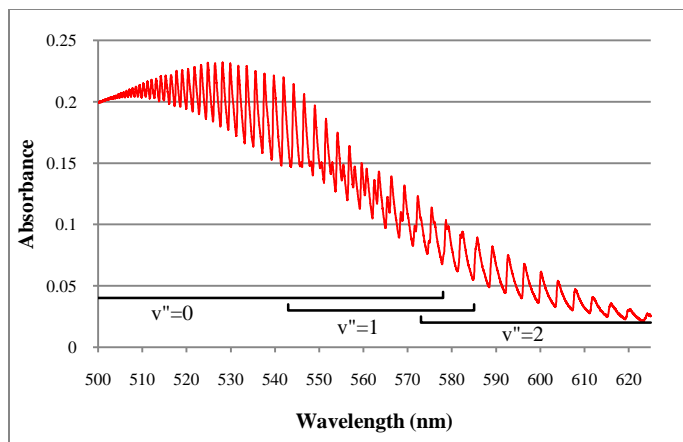

Figure 1: I_2 Absorption spectrum with designated regions of transitions from the v''= 0, 1, and 2 vibrational states.

The absorption spectrum was used to determine the transition frequencies from the ground state vibrational levels to the $B({}^3\Pi_{0u}{}^+)$ excited state vibrational levels. This data was used to create a Deslandres table. The Deslandres table was used to verify the assignments of vibrational levels for the transition frequencies. The Deslandres table shows that the differences between the rows are relatively constant for each column. This implies that the assignment of the vibrational levels is correct. Table 1 which follows is the Deslandres table.

Table 1: Deslandres Table (Band-head frequencies in cm^{-1}, differences between entries in red) for I_2

v'	v''=0	v''=1	v''=2	Average Differences
14	17301.0	17099.9	16889.0	
	97.8	97.0	104.5	99.8
15	17398.9	17196.9	16993.5	
	108.1	104.1	106.4	106.2
16	17507.0	17301.0	17099.9	
	95.5	97.8	97.0	96.8
17	17602.5	17398.9	17196.9	
	96.6	83.6	104.1	94.8
18	17699.1	17482.5	17301.0	
	93.2	107.6	90.3	97.0
19	17792.3	17590.1	17391.3	
	91.0	77.7	---	84.3
20	17883.3	17667.8	---	
	90.6	94.1	---	92.4
21	17974.0	17762.0	---	
	86.3	95.2	---	90.8
22	18060.3	17857.1	---	
	85.9	64.0	---	74.9
23	18146.2	17921.1	---	
	83.4	96.9	---	90.1
24	18229.5	18018.0	---	
	81.4	81.5	---	81.5
25	18311.0	18099.5	---	
	84.2	82.3	---	83.2
26	18395.2	18181.8	---	
	74.1	66.4	---	70.2
27	18469.3	18248.2	---	
	74.7	66.8	---	70.8
28	18543.9	18315.0	---	

Multiple variable linear regression was performed using Excel on the transition frequency data to determine values for the electronic frequency, $\tilde{v}_{el}$, the equilibrium vibrational frequencies for the ground and excited states, $\tilde{v}_e''$ and $\tilde{v}_e'$, and the anharmonicity constants for the ground and excited states, x_e'' and x_e'. The regression was performed by fitting a curve to equation 5 for the transition frequency.

Table 2 below shows the output from the regression. The uncertainty is given in percent relative standard deviation.

Table 2: Multiple Linear Regression Output for Frequency Data Determined from the Absorption Spectrum of I2

	cm^{-1}	St. Dev.	%RSD
$\tilde{v}_{el}$:	15683.71	24.6163	0.2%
$\tilde{v}_e'$:	135.2955	2.34953	1.7%
$\tilde{v}_e' x_e'$:	1.093409	0.054018	4.9%
$\tilde{v}_e''$:	228.5318	5.946893	2.6%
$\tilde{v}_e'' x_e''$:	8.328487	2.110188	25.3%

The data in table 2 was used to determine the dissociation energies for the ground and excited states with equations 2-4. The value of $\Delta E(I^*)$ used was the known literature value[1] of 7603cm^{-1}. The calculated dissociation energies may be seen in Table 3 which follows.

Table 3: Dissociation Energies for the Ground and Excited States of I$_2$

	Energy (cm^{-1})
D_e':	4185.0
D_o':	4117.6
D_e'':	12265.7
D_o'':	1453.4

The information in Table 2 was also used to calculate the force constant, k_e for states $X(^1\Sigma_g^+)$ and $B(^3\Pi_{0u}^+)$ with equation 5. The reduced mass, μ, was taken to be $1.05e^{-25}$ kg and c was $3.0e^{10}$cm/s. Table 4 below is a summary of the force constants for the two states.

Table 4: Force Constants for the Ground and Excited States of I$_2$

k_e' (kg/s^2)	68.39
k_e'' (kg/s^2)	195.14

The force constant for the ground state, k_e'' is greater than the force constant for the excited state, k_e'. This

indicates that the bond strength is greater in the ground state than in the excited state.

The Morse potential parameters were then determined using the force constants and equation 7. Table 5 which follows displays the calculated Morse potentials.

Table 5: Morse Potential Parameters for the Ground and Excited States of I$_2$

β' (nm^{-1})	20.28
β'' (nm^{-1})	20.01

The Morse curves were developed from the calculated Morse potentials and equation 6. The accepted literature value of r_e'' was used and is equal to 0.2666nm[1]. The value of r_e' was calculated using Equation 8. The value of the frequency of the most intense transition was found to be 18933.7cm^{-1} from the absorption spectrum. This transition was from the $v''=0$ ground state vibrational level to the $v'=34$ excited state vibrational level. The value of r_e' was found to be 0.308nm. The calculated force constants and the harmonic oscillator model were also used to create a potential energy curve for comparison to the Morse potentials. These curves may be seen in Figure 2 below.
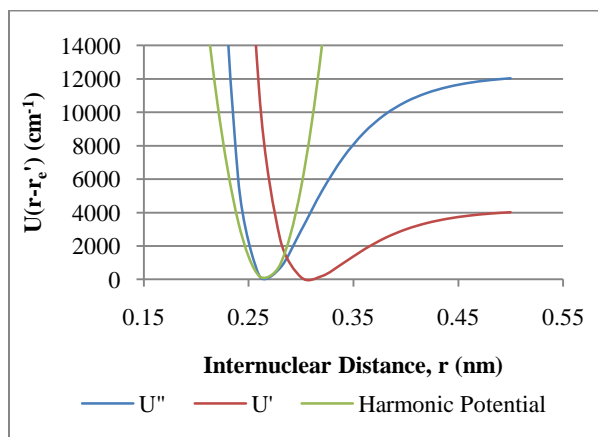

Figure 2: Morse curve for ground and excited electronic states and Harmonic Oscillator potential of the ground state for I$_2$

B. LIF Emission

The LIF spectrum was recorded between 600 and 520 nm. The monochromator slit width was 0.25mm. The sample was excited at 514.5nm. The spectrum may be seen in figure 3 which follows.
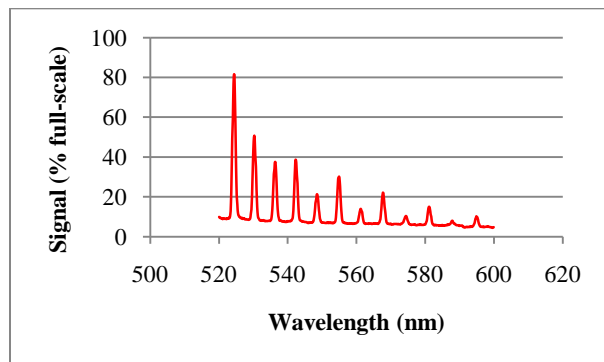

Figure 3: LIF Spectrum of I$_2$ from PChem pScan Scanner Version 0.5.1.

The vibrational level of the excited state is v'=43. There are two possible rotational levels, j'=13 and j'=15. The emission spectrum displays the intensity of the fluorescence from the relaxation of electrons from the v'=43 vibrational level to the ground state. The wavelengths of the transition peaks may be seen in Table 6 below.

Table 6: LIF Emission Band Wavelengths

Band	Wavelength (nm)
12	524.4
11	530.3
10	536.3
9	542.3
8	548.5
7	554.9
6	561.3
5	567.7
4	574.4
3	581.1
2	587.9
1	594.9

The most intense fluorescence band was observed at 524.4nm. The most intense absorption band occurs at approximately 528nm.

The Stokes shift phenomenon was not observed in the iodine absorption experiment. This indicates that there is no rapid internal conversion from higher vibrational states to the lowest vibrational energy level that does not emit light.

C. Gaussian Calculations

Potential energy curves were created from the data obtained by running the Gaussian program. The curves were created for the ground state, the three lowest energy excited singlet states, and the four lowest energy excited triplet states. The following figure shows the potential energy curves.
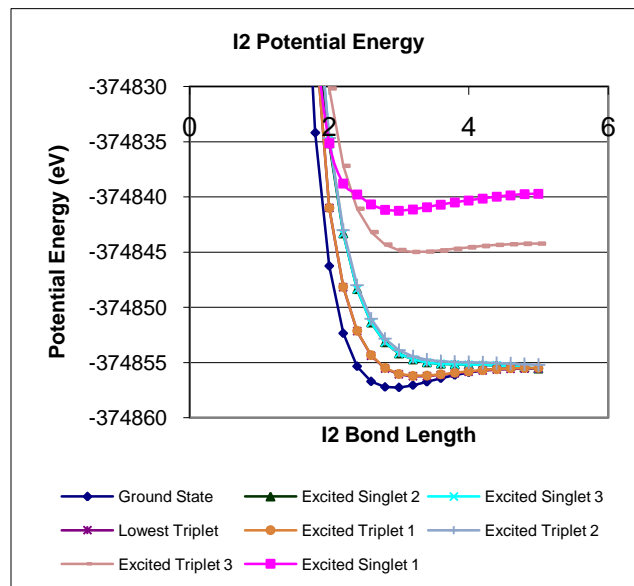

Figure 4: Potential energy curves for the ground state, first three excited singlet states and lowest four triplet states of I$_2$.
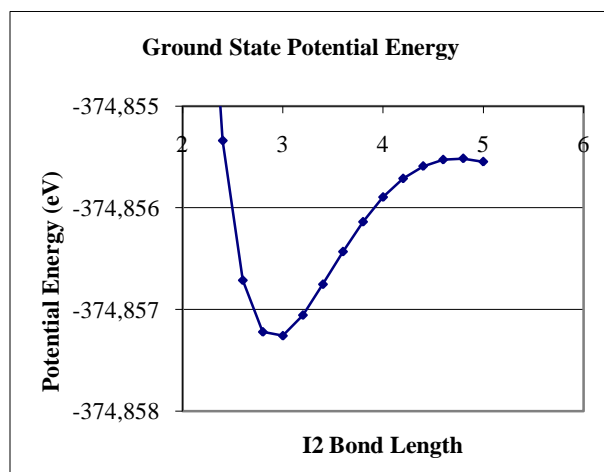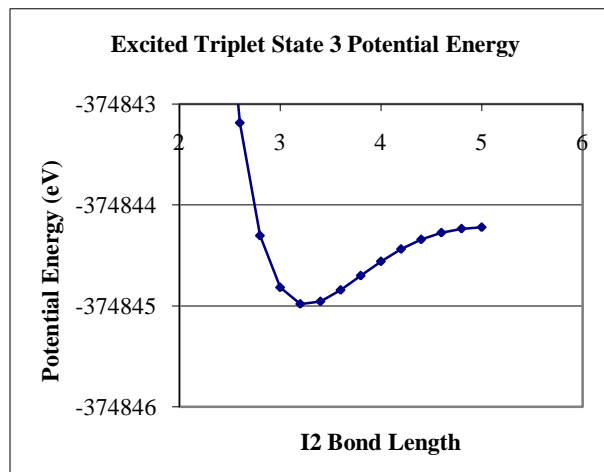
From the potential energy curves it was found that the ground state, the first singlet excited state, the lowest triplet state, and the first and third excited triplet states are bound. The remaining three states are purely dissociative. The third excited triplet state is the $B(^3\Pi_{0u}^{+})$ state. $\Delta E(I^*)$ was found to be 91356cm^{-1} from the Gaussian data for the $X(^1\Sigma_g^{+})$ and $B(^3\Pi_{0u}^{+})$ states.

Equilibrium bond lengths were predicted from the potential energy curves for the $X(^1\Sigma_g^{+})$ and $B(^3\Pi_{0u}^{+})$ states. r_e" was found to be 3.0Å on the curve and r_e' was found to be 3.2Å. This indicates that the bond strength is greater in the ground state compared to the excited state. This is because bond length is inversely related to bond strength. The longer the bond length, the lower the dissociation energy and the weaker the bond is. The well depths of the potential energy curves were also determined for the $X(^1\Sigma_g^{+})$ and $B(^3\Pi_{0u}^{+})$ states. Table 7 on the following page displays the well depths for the two states.

Table 7: Comparison of Well Depth, De, for the ground and Excited States

	Well Depth, D_e (eV)
Ground State	1.71
Excited State	0.76

The depth of the well is equal to the bond energy. The greater well depth of the ground state further suggests that the bond strength is stronger in the ground state. This is in agreement with the finding from the force constants calculated from the absorption data. The following two figures demonstrate the difference in well depth of the two states.

Figure 5: Ground State Potential Energy Curve Well.

Figure 6: $B(^3\Pi_{0u}^+)$ Excited State Potential Energy Curve Well.

The energy at the bottom of the ground state curve was found to be 374,857eV. The energy at the bottom of the $B(^3\Pi_{0u}^+)$ excited state curve was found to be 374,845eV. From this data the electronic term value, T_e, was calculated to be 12.28 eV.

D. Comparison to Literature

The term value, T_e, obtained from the Gaussian potential energy curves was compared to literature values from de Jong et al.[5], and accepted values[3]. Table 8 following shows the comparison of the values.

Table 8: Comparison of Literature Term Values to the Calculated Term Value from Gaussian Data

	T_e (eV)	T_e (cm^{-1})
Potential Energy Curve	12.28	99029.1
Literature Value[3]		15769.01
de Jong Value[5]	2.009	

The value predicted from the computational results was much higher than the values from the literature.

The equilibrium bond length calculated from equation 8 for the $B(^3\Pi_{0u}^+)$ excited state and the equilibrium bond lengths predicted from Gaussian for the ground and $B(^3\Pi_{0u}^+)$ states were also compared to literature. Table 9 below compares the equilibrium bond length values.

Table 9: Comparison of Equilibrium Bond Lengths for Ground and Triplet Excited States of I2.

	r_e'' (Å)	r_e' (Å)
Calculated (Eq. 8)		3.08
Potential Energy Curve	3.0	3.2
Literature Value[3]	2.666	3.024
de Jong Value[5]	2.666	3.07

The values predicted from the potential energy curves created from Gaussian data are higher than the values found in literature for both the ground state and the $B(^3\Pi_{0u}^+)$ excited electronic state and higher than the calculated value or r_e' from experimental data. The predicted r_e'' value is approximately 12.5% higher than the values from literature and de Jong et al. The value for r_e' is approximately 5.8% higher than the accepted literature values and 4.2% higher than the value from de Jong et al. The predicted excited state equilibrium bond length is closer to the accepted literature values than the predicted ground state equilibrium bond length.

The value of $\Delta E(I^*)$ between the $X(^1\Sigma_g^+)$ and $B(^3\Pi_{0u}^+)$ states predicted by the Gaussian potential energy curves was also compared to the accepted literature value[3]. Table 10 below compares the values.

Table 10: Comparison of $\Delta E(I^*)$ values predicted by Gaussian to the accepted literature value.

	$\Delta E(I^*)$ (cm^{-1})
Potential Energy Curve	91356
Literature Value[1]	7603

The value of $\Delta E(I^*)$ predicted by Gaussian was significantly higher than the accepted literature value. This indicates that Gaussian may not be a good predictor of energy differences between states.

The experimentally determined values of the equilibrium $X(^1\Sigma_g^+)$ and $B(^3\Pi_{0u}^+)$ vibrational frequencies were also compared to values from the de Jong et al.[5] study and the McNaught[6] study. Table 11 below is a comparison of the values. The uncertainty reported in the experimental values is in percent relative standard deviation.

Table 11: Comparison of vibrational frequencies between experimental and literature values.

	$\tilde{\nu}_e''$ (cm^{-1})	$\tilde{\nu}_e'$ (cm^{-1})
de Jong Values[1]	214.5	119.3
McNaught Values[4]	213.36 ($\pm$0.87)	132.11 ($\pm$0.24)
Experimental Values	228.5 ($\pm$2.6%)	135.3 ($\pm$1.7%)

The experimental values of equilibrium vibrational frequency were higher than the literature values. The experimental values were determined using linear regression on equation 1. The experimentally determined values may be different from the literature values because this equation neglects the rotational-term difference and the cubic term.

V. Discussion

The spectrum was seen to be approaching the convergence limit near 500 nm. From this it can be predicted that at higher energies, wavelengths less than 500 nm, the excited state $B(^3\Pi_{0u}^+)$ is no longer bound. This corresponds to an energy of approximately 20,000cm^{-1}. The Gaussian program predicted this value to be greater than 90,000cm^{-1}. This indicates that while the Gaussian program may be able to predict the shape of the potential energy curves, it is inadequate at predicting the relative energy levels of the various states

for heavy, many electron molecules such as molecular iodine.

The Morse potential energy curves showed the curves leveling off at the dissociation energy. The harmonic oscillator curve was a parabola. This shows that if this model were correct, the molecule would never dissociate. This demonstrates that the harmonic oscillator model is not adequate for this system overall. However, the harmonic oscillator model was very close to the Morse curve at low energies near the equilibrium bond length. Therefore it can reasonably be concluded that the harmonic oscillator model is good at distances very near the equilibrium bond length.

The value of the frequency of the most intense excitation transition was found to be 18933.7cm^{-1} (528.2nm) from the absorption spectrum. This transition was from the v''=0 ground state vibrational level to the v'=34 excited state vibrational level. This is in the range predicted by the Franck-Condon principle. The most intense fluorescence band was observed at 524.4nm which corresponds to approximately 19069cm^{-1}. This would correspond to a transition from approximately the v'=36 level to the v''=0 level. Again, this is supported by the Franck-Condon principle.

The Stokes shift was not observed in I_2. This is likely because the iodine vapor is at a low pressure which means there will be few atomic collisions to dissipate energy. Additionally, there is a large energy gap between the $B(^3\Pi_{0u}^+)$ excited state and the lowest excited vibrational state. This may be too large of an energy gap for the energy to be dissipated between the atoms with nonradiative relaxation.

The comparative values of the force constant determined from experimental data indicate that the bond strength is greater in the ground state than in the $B(^3\Pi_{0u}^+)$ excited state. The Gaussian potential energy data further supported this finding. The relative values of the equilibrium bond length and the well depth are evidence that the bond strength is greater in the ground state. The agreement of the Gaussian finding to the experimental finding in terms of bond strength indicates that while the Gaussian program is inadequate at determining relative energies, it may be suitable for determining other characteristics of iodine. This is further suggested by the closeness of the comparison of the equilibrium bond length predicted by the potential energy curves to the literature values.

The term value, T_e, predicted from the computational results was substantially higher than the values from the literature. Likewise, the value of $\Delta E(I^*)$ predicted by Gaussian was significantly higher than the

accepted literature value. Again, this leads to the conclusion that the computational analysis is not a good predictor of the energy differences between the states for iodine.

The values of the equilibrium bond lengths predicted from the potential energy curves were higher than literature or experimental data. The value of r_e' determined from experimental values and from calculations was very near the reported literature values. The potential energy curve values may have been consistently higher because the Gaussian potential energy curves do not take into account relativistic and spin-orbit coupling effects. The de Jong et al. study also included corrections from experimental data. A more rigorous numerical approximation may correct for this discrepancy.

The experimental values of equilibrium vibrational frequency were slightly higher than the literature values. This is likely due to the fact that the equation used in the multiple variable linear regression does not take into account the rotational-term difference and the cubic term. A more rigorous approach may be to perform iterations on the calculations by first using equation 1 to calculate the equilibrium vibrational frequencies and anharmonicity constants as was done here. Then, the rotational term difference and cubic term could be determined from the more rigorous equation with these included. With those values known, one could then perform the linear regression with the more rigorous equation to get more accurate values of vibrational frequency.

VI. Conclusions

The iodine molecule was found to be approaching its convergence limit near 500nm. The Gaussian program predicted this to occur at a much higher energy. Gaussian also predicted the term value and the energy gap $\Delta E(I^*)$ from $X(^1\Sigma_g^+)$ to $B(^3\Pi_{0u}^+)$ to be much greater than accepted literature values. This indicates that Gaussian is insufficient at predicting relative energy levels. Gaussian was however able to predict reasonable values for the equilibrium bond lengths indicating that it may be suitable for determining the shape of potential energy curve. However, these values were slightly high due to the neglect of relativistic and spin-orbit coupling effects. The Morse potential energy curves provided a more accurate representation of the iodine molecule than the harmonic oscillator model. The harmonic oscillator model is only valid very near the equilibrium bond length. The most intense transitions occurred from the v"=0 level to the v'=34-36 range as predicted by the Franck-Condon principle. The Stokes shift was not observed in I_2. The comparative values of the force constant, equilibrium bond

length, and potential energy curve well depth indicate that the bond strength is greater in the ground state than in the excited state. The experimentally determined values of equilibrium vibrational frequency were slightly higher than the literature values. This is likely due to the fact that the calculations do not take into account the rotational-term difference and the cubic term. A more rigorous approach may be to perform iterations on the calculations using the more rigorous equation to get more accurate values of vibrational frequency.

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