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# *Determination of Vibrational and Electronic Parameters From an Electronic Spectrum of $I_2$ and a Birge-Sponer Plot*

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## Abstract

Using an electronic spectrum of $I_2$, Deslanders table and Birge-Sponer plots, vibrational and electronic parameters were calculated. The vibrational frequency, anharmonicity constant, dissociation energy and the equilibrium dissociation energy for the ground state were found to be 221.103 $cm^{-1}$, 0.0119 $cm^{-1}$, 12189 $cm^{-1}$ and 12300.2 $cm^{-1}$, respectively. The vibrational frequency, anharmonicity constant, dissociation energy and the equilibrium dissociation energy for the excited state were calculated to be 132.21 $cm^{-1}$, 0.00771 $cm^{-1}$, 4351.29 $cm^{-1}$ and 4284.93 $cm^{-1}$, respectively. The convergence limit, electronic energy of the B state and the energy of the excited iodine atom were calculated to be 19903.3 $cm^{-1}$, 15440.8 $cm^{-1}$ and 10174.89 $cm^{-1}$, respectively. The calculated parameters for the excited state were in good agreement to tabulated values. It was concluded that the excited state follows a harmonic oscillator better than the ground state and that the bond length in the excited state was longer than the ground state.

## Introduction

Upon heating, the excited vibrational levels of the ground state of $I_2$ become populated.[1,2] The vibronic spectrum that may be obtained by monitoring these excitations provides vibrational constants and dissociation energies of each electronic state.[3] The electronic transitions observed in the spectrum are the transitions between the lower levels, $X^1\Sigma^+$ (v"=0), and various excited vibrational levels of the $B^3\Pi$ (v') electronic state.[2,4] In this investigation, transitions from v"=0,1 and 2 states to v'=13, 14, 15, …,47 are investigated using an electronic spectrum of $I_2$ and a Birge-Sponer plot.

## Experimental[3]

A prepared 1 cm cuvette containing iodine crystals was heated until $I_2(g)$ was visible. The cuvette was placed into a Cary UV-Visible spectrophotometer and $I_2(g)$ was scanned from 500-600 nm. The settings on the spectrophotometer included an average time of 1 sec, average data interval of 0.1 nm, a band width of 0.2 nm and a double beam mode. The resulting spectrum was analyzed yielding the vibrational and electronic parameters $\tilde{\nu}_e'', \tilde{x}_e'', D_e'', D_0'', \tilde{\nu}_e', \tilde{x}_e', D_e', D_0', E^*, \tilde{T}_e'$ and $E(I^*)$. These parameters were calculated using Equations 1-5 and a Birge-Sponer plot.

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

$$D_0' = \Delta\tilde{\nu}(v'=0) + \Delta\tilde{\nu}(v'=1) + \Delta\tilde{\nu}(v'=2) + \ldots = A \qquad \text{Equation 2}$$

$$D_e' = D_0' + E_{vib}(v'=0) = D_0' + \frac{1}{2}\tilde{\nu}_e' - \frac{1}{4}\tilde{\nu}_e'\tilde{x}_e \qquad \text{Equation 3}$$

$$E^* = \tilde{\nu}(v'=b) + A' = D_o' + E(I^*) \qquad \text{Equation 4}$$

$$\tilde{T}_e' = D_e'' + E(I^*) - D_e' \qquad \text{Equation 5}$$

In these equations, $\tilde{\nu}$ is the vibrational frequency, $\tilde{x}_e$ is the anharmonicity constant, $D_0'$ is the dissociation energy, $A$ is the area under the Birge-Sponer plot, $D_e'$ is the equilibrium dissociation energy, $E^*$ is the convergence limit, $E(I^*)$ is the energy of the excited iodine atom, $\tilde{T}_e'$ is the electronic energy of the $B$ state, v'=b at the last transitions state before the bands become continuous and *A'* is the area under the Birge-Sponer plot from v'=b to the convergence point. A Birge-Sponer plot of (v'+1) vs. $\Delta\tilde{\nu}$ (v') was constructed to yield desired values in Equations 1-5. A two-point plot of (v"+1) vs. $\Delta\tilde{\nu}$ (v") was constructed to compare a calculated value of *E*(*I**) to the tabulated value of 7603.15 $\text{cm}^{-1}$ used in Equation 4.[3]

## Results

Each band on the $I_2$ electronic spectrum was labeled with its corresponding initial and excited state. Because of the small overlap between the shifted harmonic oscillator vibrational wave functions of the v“=0 and v'=0 states, tabulated values were used as a basis to start the band assignments.[3] The $I_2$ spectra with labeled transitions may be seen in Figure 1.

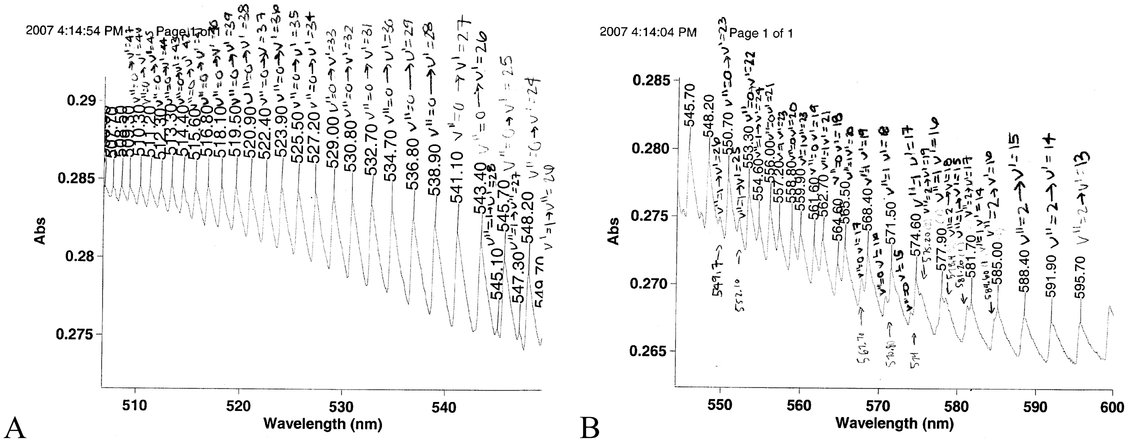

**Figure 1:** Electronic spectrum of $I_2(g)$. Figures A and B are enlarged versions of the original spectrum. Figure A includes 500 nm to 550 nm and Figure B includes 545 nm to 600 nm. Transitions were labeled based on values Table 1. v"=0 to v"=1 and v"1 to v"2 transitions occurred with increasing wavelength. v'=13, 14, 15,…,47 transitions occurred with decreasing wavelength.

Once the transitions were labeled, a Deslanders table was constructed (Table 1). Values from this table were constructed into a Birge-Sponer plot (Figure 2). Based on Equation 1, the linear regression of this plot, y = -2.0397×x + 132.21, reveals a y-intercept equal to $\tilde{\nu}_e'$, a slope equal to -2 $\tilde{x}_e'\tilde{\nu}_e'$ and an x-intercept equal to the convergence limit. Using this plot and Equations 1-5 the electronic parameters

$\tilde{\nu}_e'', \tilde{x}_e'', D_e'', D_0'', \tilde{\nu}_e', \tilde{x}_e', D_e', D_0', E^*, \tilde{T}_e'$ were calculated (Table 2). The values $\tilde{\nu}_e''$ and $\tilde{x}_e''$ were obtained with Equation 1, using values of v”=0 and v”=1 in place of the v’ values. An experimental value of $E(I^*)$ was calculated to be 10174.89 $\text{cm}^{-1}$using a two-point Birge-Sponer plot (Figure 2).

**Table 1:**Deslanders table of experimental data.

| v'/v" | 0 | | 1 | | 2 | Avg |
|---|---|---|---|---|---|---|
| 13.00 | | | | | 16786.97331 | |
| | | | | | (107.7724254) | 107.77242 |
| 14.00 | | | 17105.71 | [210.9676] | 16894.74573 | |
| | | | (100.0678) | | (100.4955984) | 100.2817 |
| 15.00 | 17421.6 | [215.821645] | 17205.78 | [210.5398] | 16995.24133 | |
| | (97.66841) | | (98.2507) | | (98.77576159) | 98.23162 |
| 16.00 | 17519.27 | [215.2393589] | 17304.03 | [210.0147] | 17094.01709 | |
| | (95.66627) | | (99.37923) | | (96.97482622) | 97.34011 |
| 17.00 | 17614.94 | [211.5263984] | 17403.41 | [212.4191] | 17190.99192 | |
| | (96.7168) | | (94.4017) | | (98.08138544) | 96.39996 |
| 18.00 | 17711.65 | [213.8414951] | 17497.81 | [208.7395] | 17289.07331 | |
| | (94.61354) | | (95.43142) | | (96.18399614) | 95.40965 |
| 19.00 | 17806.27 | [213.023612] | 17593.24 | [207.9869] | 17385.2573 | |
| | (89.22253) | | (90.22177) | | | 89.72215 |
| 20.00 | 17895.49 | [212.0243771] | 17683.47 | | | |
| | (90.12117) | | (87.99308) | | | 89.05713 |
| 21.00 | 17985.61 | [214.152474] | 17771.46 | | | |
| | (87.7664) | | (88.87317) | | | 88.31978 |
| 22.00 | 18073.38 | [213.0457122] | 17860.33 | | | |
| | (85.32919) | | (86.54504) | | | 85.93711 |
| 23.00 | 18158.71 | [211.8298567] | 17946.88 | | | |
| | (82.81059) | | (84.1361) | | | 83.47335 |
| 24.00 | 18241.52 | [210.5043513] | 18031.01 | | | |
| | (83.56935) | | (81.64741) | | | 82.60838 |
| 25.00 | 18325.09 | [212.4262943] | 18112.66 | | | |
| | (77.56294) | | (79.0802) | | | 78.32157 |
| 26.00 | 18402.65 | [210.909032] | 18191.74 | | | |
| | (78.22232) | | (79.77376) | | | 78.99804 |
| 27.00 | 18480.87 | [209.3575886] | 18271.51 | | | |
| | (75.44613) | | (73.74304) | | | 74.59459 |
| 28.00 | 18556.32 | [211.0606756] | 18345.26 | | | |
| | (72.59365) | | | | | |
| 29.00 | 18628.91 | | | | | |
| | (73.16386) | | | | | |
| 30.00 | 18702.08 | | | | | |
| | (70.21617) | | | | | |
| Avg | | [212.4830622] | | [210.1113] | | |

Values in [ ] are vibrational state separations in the ground state and values in ( ) are vibrational state separations in the excited state. All units are cm$^{-1}$.

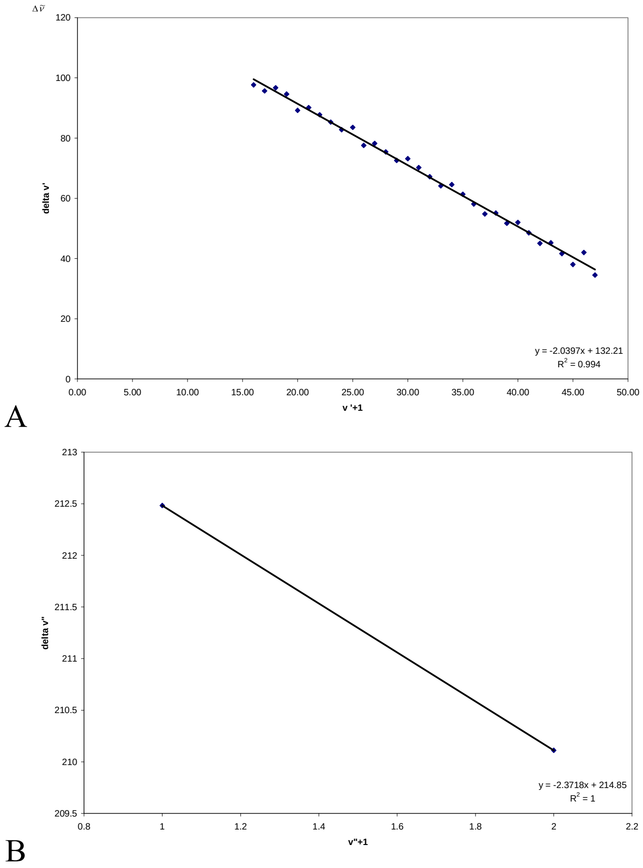

**Figure 2:** (A) Birge-Sponer plot of (v'+1) vs. $\Delta\tilde{\nu}$ (v') and (B) a two-point Birge-Sponer plot of (v"+1) vs. $\Delta\tilde{\nu}$ (v"). Using Figure A and Equations 1-5 the desired electronic parameters were calculated. Using Figure B an experimental calculation of *E*(*I**) was obtained.

**Table 2:** Calculated electronic parameters compared to tabulated values.

| | $\tilde{\nu}_e''$ (cm$^{-1}$) | $\tilde{x}_e''$ (cm$^{-1}$) | $D_e''$ (cm$^{-1}$) | $D_0''$ (cm$^{-1}$) | $\tilde{\nu}_e'$ (cm$^{-1}$) | $\tilde{x}_e'$ (cm$^{-1}$) | $D_e'$ (cm$^{-1}$) | $D_0'$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| Calculated | 221.103 | 0.0119 | 12189 | 12300.2 | 132.21 | 0.00771 | 4351.29 | 4284.93 |
| Tabulated | | | | | 125.69 | 0.00608 | 4391.0 | |

| | E* (cm$^{-1}$) | $\tilde{T}_e'$ (cm$^{-1}$) | $E(I^*)$ (cm$^{-1}$) |
|---|---|---|---|
| Calculated | 19903.3 | 15440.8 | 10174.89 |
| Tabulated | | 15768.3 | 7603.15 |

Tabulated values were obtained from NIST Webbook.[5]

## Discussion

Calculated constants were in good agreement with tabulated values. *D$_e$*' had the closest comparison to tabulated data, with an approximate 1% error. Tabulated values for the ground state were unable to found. From Table 2, it may be seen that the values for $\tilde{\nu}_e$, $\tilde{x}_e$, $D_e$ and $D_0$ were greater for the ground state than for the excited state. The correction for anharmonicity is greater for the ground state by 0.00423 cm$^{-1}$ because the potential energy well for the excited state follows the harmonic oscillator approximation better than the ground state, giving it a narrower well on a potential energy diagram.

Even though a majority of the data corresponded well with tabulated values, the calculated value of $E(I^*)$ did not. The large deviation in the two values is due to the use of a two-point plot. If more data points were obtained and used in the calculation, the two values would be in better agreement.

When comparing the dissociation energy, the energy was 8015.27 cm$^{-1}$greater for the ground state than for the excited state. This difference is associated to the varying bond strengths of the different states. The bond in the ground state is shorter and absorbs at shorter wavelengths. This indicates that the bond is stronger, therefore resulting in a higher bond dissociation energy. When the electrons of $I_2$ are promoted to an excited state both their energy and bond length increase. As seen in Figure 1, as the electrons move to higher energy levels they absorb at greater wavelengths. This is because as the bond increases in length it decreases in strength. Therefore, the bond length is greater in B, the excited state, than it is in X, the ground state.

## Conclusion

Calculated parameters $\tilde{\nu}_e'', \tilde{x}_e'', D_e'', D_0'', \tilde{\nu}_e', \tilde{x}_e', D_e', D_0', E^*, \tilde{T}_e'$ from an $I_2$ electronic spectrum and Birge-Sponer plot yielded good results when calculated values for the excited state were compared to tabulated values. $E(I^*)$, however, was obtained using a two-point Birge-Sponer plot and did not correspond well to tabulated results. When comparing the ground state to the excited state, the excited state better represents a harmonic oscillator and has a longer bond. This creates a smaller well for the potential energy and a smaller bond dissociation energy for the excited state.

## Resources

(1) University, T. A. Absorption and Laser Induced Fluorescence Spectra of Molecular Iodine, 2004.

(2) Chapman, D. The Electronic Spectrum of Iodine. In *SOU Chem 445*, 2007.

(3) Nienow, A. Lab #4: Spectrum And Dissociation Energies of I2, 2007.

(4) Steinfeld, J. I.; Zare, R. N.; Jones, L.; Lesk, M.; W, K. *J. Chem. Phys.* **1965**, *42*, 25.

(5) NIST. NIST Chemistry WebBook, 2005; Vol. 2007.