Teaching the Rovibronic Spectroscopy of Molecular Iodine

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The spectroscopy of molecular iodine has been discussed in the pedagogical literature for over fifty years (1–15). Iodine has a low-lying bound excited state, the \( ^3\Pi_{\text{g}} \) B state, which is accessible from the ground \( ^1\Sigma_{\text{u}} \) X state by visible photons (Figure 1). Both absorption and fluorescence spectra of molecular iodine can be collected with instruments of modest resolution, common to teaching laboratories, and sample preparation is simple. The ease with which students may observe evidence of quantized electronic and molecular behavior in iodine spectra is thus the primary attraction of the experiment. Students can determine many electronic potential parameters for both the B state and the X state using straightforward spectral analysis, and students can use their potential parameters for both the B state and the X state using the experiment. Students can determine many electronic potential parameters for both the B state and the X state using the experiment. Brief explanations are provided for subtle features of the molecular iodine spectra, such as the aforementioned extrapolation error intrinsic to the determination of \( \tilde{\nu}_{\text{e}} \). A more thorough discussion is available for the interested reader in the accompanying Supplemental Material.

One would hope that students could find affirmation of quantum mechanical theory by determining a precise and accurate value of \( \tilde{\nu}_{\text{e}} \) from the spectrum. A survey of molecular iodine articles published in this journal and elsewhere, however, does not show such corroboration (Table 1). Reported values for \( \tilde{\nu}_{\text{e}} \) are found to fall into two groups, clustered around either \( 125 \text{ cm}^{-1} \) (2, 4, 5, 10) or \( 132 \text{ cm}^{-1} \) (6, 11, 15). The first group of values is in good agreement with the accepted value for \( \tilde{\nu}_{\text{e}} \) of \( 125.6687 \text{ cm}^{-1} \) (20). Unfortunately, though, refs 2, 4, 5, and 10 all contain mistakes in the interpretation of the molecular iodine absorption spectrum, as does the article reporting a value of \( 130 \text{ cm}^{-1} \). Only refs 6 and 15 analyze the spectrum correctly! As will be explained below, the value of \( \tilde{\nu}_{\text{e}} \) can only be determined to two significant figures of accuracy from analysis of the visible absorption spectrum in the undergraduate experiment. This is due to an unavoidable extrapolation error.

Evaluation of refs 1–15 has found that at least half contain mistakes of various types. The intent of this article is to clear up the confusion by reviewing which molecular iodine potential parameters may be determined from the absorption and fluorescence spectra, specifying how the spectra are properly analyzed, and summarizing how well the determined values can be expected to agree with accepted literature values. The article is broken into three sections: (i) finding B-state potential constants from the absorption spectrum, (ii) finding X-state potential constants from fluorescence spectra, and (iii) combining data from both types of experiments to gain additional insight into the system. Each section is subdivided into basic analysis, clarifications, and possible supplementary projects for students with more time to devote to the experiment. Brief explanations are provided for subtle features of the molecular iodine spectra, such as the aforementioned extrapolation error intrinsic to the determination of \( \tilde{\nu}_{\text{e}} \). A more thorough discussion is available for the interested reader in the accompanying Supplemental Material.

![Figure 1. X-state and B-state potential energy curves for molecular iodine. The shape and placement of potential energy curves are quantitatively accurate, using data compiled from primary literature sources (20, 24–26, 31). Tick marks on the left edges of the potential wells indicate the locations of every tenth vibrational level. The arrow labeled \( \tilde{\nu}_{\text{e}} \) shows the energy change when X-state iodine at \( \nu = 0 \) absorbs a photon and is excited to an arbitrary high vibrational level (\( \nu = 35 \)) of the B state.](image)

### Table 1. Reported Molecular Iodine \( \tilde{\nu}_{\text{e}} \) Values

<table>
<thead>
<tr>
<th>( \tilde{\nu}_{\text{e}} )/\text{cm}^{-1}</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>123</td>
<td>2</td>
</tr>
<tr>
<td>123.4</td>
<td>5</td>
</tr>
<tr>
<td>125</td>
<td>10</td>
</tr>
<tr>
<td>126.5</td>
<td>4</td>
</tr>
<tr>
<td>130</td>
<td>11</td>
</tr>
<tr>
<td>132.1</td>
<td>5</td>
</tr>
<tr>
<td>133.4</td>
<td>15</td>
</tr>
<tr>
<td>Accepted</td>
<td>125.67</td>
</tr>
</tbody>
</table>

**Note:** Values reported in pedagogical discussions on the visible absorption experiment. Comparison is made to the most recent accepted literature value.
Clarifications

Four clarifications are in order with respect to analysis of the absorption spectrum. First, the absorption peak locations used in the plot of $\tilde{\nu}_{ab}$ versus $v' + \frac{1}{2}$ are best assigned to the valleys on the high-energy side of each peak (18, 21, 22), and not the peak maxima. Each peak is wide owing to many unresolved rotational transitions. Rotational energy changes are neglected in eq 2, so the proper “center” of the peak for this analysis would be the Q branch. Q branches do not appear in the rovibronic peaks because $\Delta \tilde{J} = 0$ is forbidden for the $B \leftrightarrow X$ transition of molecular iodine. If Q branches were present, though, they would be located near the edges on the high energy sides of each peak. This is because the average internuclear distances of the X state and the B state are significantly different, leading to different rotational constants and to superposition of the R branch over the P branch (21).

The second clarification has to do with the accuracy to which the coefficients in eq 2 may be determined. The typical range of $v'$ for which absorption peaks can be identified in Figure 2 is from 15 to ~52. The upper limit on $v'$ has some play: peaks get closer together and Franck-Condon overlap gets progressively poorer on the high-energy side of the cold band, so instrumental resolution and signal averaging determine the actual upper limit for $v'$. The lower limit on $v'$, however, is constrained by the onset of hot band peaks that overwhelm the cold band peaks around 575 nm. Without data below $v' = 15$, two problems arise in the fit. First, the coefficients will be highly dependent upon the order of the polynomial fit even though the $R^2$ for the fit may be almost exactly one. For example, a third-order fit and a fourth-order fit on the same set of data can give values of $\tilde{\nu}_{e}$ that differ by 10 cm$^{-1}$. Second, the true energy spacings of B-state vibrational levels change more slowly below $v' = 12$ than above $v' = 12$. This behavior cannot be predicted from the collected data, so the value of $\tilde{\nu}_{e}$ found by undergraduates is systematically too high, usually by 5 to 10 cm$^{-1}$.

For similar reasons, the value of $E^*$ found from extrapolation of the polynomial fit to a maximum will be systematically too low by 50 to 200 cm$^{-1}$. In this case the actual spacings of the vibrational energy levels decrease more slowly beyond $v' = 55$ than would be expected based on data prior to $v' = 55$. The experimental value of $D_{e}$ will also be systematically lower than the literature value.

The third clarification is with respect to the hot band region of the absorption spectrum. Although the hot band region looks as simple as the cold band (Figure 1), the hot band region is actually an intricate mixture of unresolved and overlapping contributions originating from $v' = 0$ through at least $v' = 5$ of the ground electronic state. Undergraduates should be instructed to ignore this portion of the spectrum when characterizing molecular iodine because much higher instrumental resolution is necessary to track the high-resolution features.
bands correctly. The five lowest values of \( v'_1 \) listed in Table 1 all come from erroneous hot band assignments.

As a final point, students must be provided the assignment of \( v' \) for one absorption peak in order to carry out their polynomial fit. If students also measure the fluorescence spectrum generated from the 514.5 nm line of an argon ion laser, then there is a context for providing this extra information. The 514.5 nm line excites molecular iodine from \( v'' = 0 \) to \( v'' = 43 \), and students can make the assignment to the appropriate peak in the absorption spectrum (Figure 2).

**Supplementary Analysis**

Students may wonder about the number of terms to include in a polynomial fit (eq 2). Analysis of the molecular iodine absorption spectrum provides students with an excellent opportunity to learn how the order of a fit is limited by the noise and span of the data. Programs such as PeakFit (Systat Software) calculate \( P \) values automatically for each fitting parameter, or students may evaluate the statistical merits of higher-order terms using \( F \) tests. An excellent discussion on this latter topic is found in Garland et al. (18).

A second project would be for students to explore why the best assignment of an absorption peak location is on the high-energy side of the peak. Students can use the rotational constants for the two states to find the value of \( J \) at which the R branch turns around and heads towards overlap with the P branch (21). They can then compare this value of \( J \) with the room temperature rotational population distribution predicted by the Boltzmann equation.

**Determination of X-State Potential Constants**

**Basic Analysis**

Characteristics of the X-state potential surface can be determined by exciting molecular iodine to a specific vibrational level in the B state and then collecting the resulting fluorescence spectrum. Excitation sources used in undergraduate laboratories include mercury lamps (3), helium–neon lasers (7, 11, 14), and argon-ion lasers (13). The argon ion 514.5 nm laser-induced fluorescence (LIF) spectrum shown in Figure 3 consists of a series of spikes to the red of the laser line that gradually diminish in intensity. The 514.5 nm line excites molecular iodine to \( v' = 43 \) in the B state, and each successive spike away from the laser line corresponds to relaxation from \( v' = 43 \) down to progressively higher values of \( v'' \) in the X state. The overall intensity envelope of the fluorescence depends on instrumental sensitivity and Franck–Condon overlap between \( v' = 43 \) and the X-state vibrational levels.

The energy difference \( \Delta \nu \) between the excitation photon \( \nu_{\text{laser}} \) and the fluorescence photon \( \nu_{\text{ani}} \) is equal to the energy difference between the initial and final X-state vibrational levels:

\[
\Delta \nu = \nu_{\text{laser}} - \nu_{\text{ani}}(v' = 43, v'')
\]

When \( \nu_{\text{ani}}(v'') \) is written as a series expansion in \( v'' + \frac{1}{2} \), then \( \Delta \nu \) becomes:

\[
\Delta \nu = -\nu_{\text{ani}}(0) + \nu_{\text{ani}}(v'' + \frac{1}{2}) - \nu_{\text{ani}}(v'' + \frac{1}{2}) + \nu_{\text{ani}}(v'' + \frac{1}{2})^3 + \ldots
\]

Students find \( \Delta \nu \) values by subtracting the photon energies of their fluorescence peaks from \( \nu_{\text{ani}} \), which is 19429.7694 cm\(^{-1}\) for Ar\(^+\) 514.5 nm laser output (23). The coefficients in eq 5 are then determined by plotting \( \Delta \nu \) for each peak as a function of \( v'' + \frac{1}{2} \) and fitting the data to a polynomial of appropriate order. With 514.5 nm excitation, the data usually warrant a polynomial of order three or four. Extrapolation of the data points to their maximum yields \( D_{0}'' \), the energy required to take molecular iodine from the lowest vibrational level of the ground state to the dissociation limit (Figure 1).

**Clarifications**

In contrast to the B-state analysis, excellent quantitative agreement is obtained between experimental and literature values of \( \nu_{\text{ani}}'' \), \( \nu_{\text{ani}}'x' \), and \( \nu_{\text{ani}}''x'' \) because the data begin at the lowest vibrational level and there is no extrapolation to small \( v'' \). Calculated values of \( \nu_{\text{ani}}'y' \) and \( \nu_{\text{ani}}''y'' \) show only qualitative agreement with literature values, but these terms are more heavily influenced by the span of the data and the overall order of the polynomial fit.

Determination of the X-state spectroscopic well depth \( D_{0}'' \) depends on a lengthy extrapolation. The last detected Ar\(^+\) 514.5 nm LIF line typically occurs at 858 nm (\( v'' = 42 \), but the highest bound X-state vibrational level is reported to be \( v'' = 113 \) (24). Still, an extrapolation based on a fourth-order polynomial fit to these data predicts the X-state vibrational level spacing at high \( v'' \) well enough to match the literature value of 12440.2 cm\(^{-1}\) (25, 26) to within one to two percent. With fewer data points and a lower order polynomial fit, though, \( D_{0}'' \) will be overestimated by 1000 cm\(^{-1}\) or more.
Table 2. Summary of X-State and B-State Potential Energy Parameters Determined by the Visible Absorption and 514.5 nm Ar⁺ LIF Experiment

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Literature</th>
<th>This Work</th>
<th>Precision</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G(0) ) (cm⁻¹)</td>
<td>107.11</td>
<td>107.28 ± 0.27</td>
<td>4</td>
<td>Ar⁺ and HeNe LIF data yield a value precise to four significant figures. Absorption spectrum hot band analysis is precise to three.</td>
</tr>
<tr>
<td>( \nu_x / \text{cm}^{-1} )</td>
<td>214.53</td>
<td>214.36 ± 0.09</td>
<td>4</td>
<td>Same as ( G(0) ).</td>
</tr>
<tr>
<td>( \nu_y / \text{cm}^{-1} )</td>
<td>0.6130</td>
<td>0.603 ± 0.008</td>
<td>2</td>
<td>Systematically low by 0.01 to 0.05 cm⁻¹.</td>
</tr>
<tr>
<td>( \nu_z / \text{cm}^{-1} )</td>
<td>-1.03 × 10⁻⁴</td>
<td>([-1.0 ± 0.3] \times 10⁻³) Qual</td>
<td>Highly dependent on order of polynomial fit.</td>
<td></td>
</tr>
<tr>
<td>( \nu_x \nu_z / \text{cm}^{-1} )</td>
<td>-1.43 × 10⁻⁴</td>
<td>([-1.8 ± 0.3] \times 10⁻⁵) Qual</td>
<td>Most likely not statistically valid with HeNe LIF experiment.</td>
<td></td>
</tr>
<tr>
<td>( D_0 / \text{cm}^{-1} )</td>
<td>12440.2</td>
<td>12440 ± 110</td>
<td>3</td>
<td>Value for a fourth-order fit to eq 5. Lower-order fits will overestimate the true value.</td>
</tr>
<tr>
<td>( D_0 / \text{cm}^{-1} )</td>
<td>12547.3</td>
<td>12547 ± 110</td>
<td>3</td>
<td>Accuracy and precision depend on ( D_0 ).</td>
</tr>
<tr>
<td>( B / \text{cm}^{-1} )</td>
<td>0.037368</td>
<td>0.0372 ± 0.0007</td>
<td>3</td>
<td>Dependent on monochromator. Quoted precision is for 0.025 nm resolution.</td>
</tr>
<tr>
<td>( R / \text{pm} )</td>
<td>1.138 × 10⁻⁴</td>
<td>((1.17 ± 0.04) \times 10⁻⁴)</td>
<td>2</td>
<td>See Supplemental Material.</td>
</tr>
<tr>
<td>( R / \text{pm} )</td>
<td>266.64</td>
<td>267.2 ± 2.5</td>
<td>3</td>
<td>Accuracy and precision depend on ( B / \text{cm}^{-1} ).</td>
</tr>
<tr>
<td>( \nu_x / \text{cm}^{-1} )</td>
<td>125.67</td>
<td>128 ± 3</td>
<td>2</td>
<td>Systematic error due to extrapolation. Magnitude of error depends on order of fit. Most likely to be 5–10 cm⁻¹ too high.</td>
</tr>
<tr>
<td>( \nu_y / \text{cm}^{-1} )</td>
<td>0.7504</td>
<td>0.79 ± 0.15</td>
<td>Qual</td>
<td>Highly dependent on order of polynomial fit.</td>
</tr>
<tr>
<td>( \nu_z / \text{cm}^{-1} )</td>
<td>-4.14 × 10⁻³</td>
<td>([-6 ± 3] \times 10⁻³) Qual</td>
<td>Highly dependent on order of polynomial fit.</td>
<td></td>
</tr>
<tr>
<td>( E / \text{cm}^{-1} )</td>
<td>20043.2</td>
<td>19981 ± 25</td>
<td>3</td>
<td>Systematic error due to extrapolation. Likely to be underestimated by 50–200 cm⁻¹.</td>
</tr>
<tr>
<td>( T / \text{cm}^{-1} )</td>
<td>15769.1</td>
<td>15757 ± 26</td>
<td>4</td>
<td>Systematic error due to extrapolation dependent on order of fit.</td>
</tr>
<tr>
<td>( D / \text{cm}^{-1} )</td>
<td>4381.2</td>
<td>4330 ± 40</td>
<td>2</td>
<td>Affected by systematic errors in ( E / \text{cm}^{-1} ) and ( T / \text{cm}^{-1} ). Likely to be underestimated by 50–200 cm⁻¹.</td>
</tr>
<tr>
<td>( E(1) / \text{cm}^{-1} )</td>
<td>4318.6</td>
<td>4270 ± 40</td>
<td>2</td>
<td>Same as ( D / \text{cm}^{-1} ).</td>
</tr>
<tr>
<td>( R / \text{pm} )</td>
<td>302.67</td>
<td>298.7 ± 2.7</td>
<td>3</td>
<td>See Supplemental Material.</td>
</tr>
<tr>
<td>( R / \text{pm} )</td>
<td>0.029901</td>
<td>0.0298 ± 0.0004</td>
<td>2</td>
<td>Calculated from value of ( R / \text{pm} ).</td>
</tr>
</tbody>
</table>

Atomic iodine (32)

| \( E(1) / \text{cm}^{-1} \) | 7602.98 | 7540 ± 110 | 2 | Affected by systematic errors in \( D_0 / \text{cm}^{-1} \) and \( E / \text{cm}^{-1} \). |

Supplementary Analysis

Students can obtain the equilibrium internuclear distance \( R_0 / \text{pm} \) of ground-state molecular iodine from the Ar⁺ 514.5 nm LIF spectrum by using rotational splitting in the spectrum to calculate the rotational constant, \( B / \text{cm}^{-1} \). The 514.5 nm line accesses several specific rovibronic transitions (20, 24, 27). The 43 ← 0 vibronic transition has already been mentioned, but the rotational splitting associated with this transition is difficult to resolve. The 514.5 nm line will also access a weak hot band transition, \( v'' = 1 \) to \( v' = 58 \), in which the rotational quantum number changes from \( J'' = 98 \) to \( J' = 99 \) (28). Upon relaxation from the B state back to the X state, the molecule ends up as either \( J'' = 98 \) again or \( J'' = 100 \), so each vibronic line will be split into two. With minor theoretical approximations, the energy difference of these two lines is equal to \((4J'' + 6)B / \text{cm}^{-1} \), or 398B / \text{cm}⁻¹. Thus if students are able to resolve the doublet, they can calculate \( B / \text{cm}^{-1} \) and then \( R / \text{pm} \) since

\[
B'' = \frac{h}{8 \pi^2 \epsilon \mu R''^2}
\]

In eq 6, \( h \) is Planck's constant, \( \epsilon \) is the speed of light, and \( \mu \) is the reduced mass of \( ^{127}\text{I}_2 \).

The 58 ← 1 rotational doublets are buried in most of the LIF spectrum because the transition is about two orders of magnitude weaker than the 43 ← 0 transition. However, since the transition starts from \( \nu'' = 1 \) and relaxation back down to \( \nu'' = 0 \) will release more energy than was absorbed, and one emission doublet can be found to the blue of the lasing wavelength in a relatively uncluttered region of the spectrum. The energy difference for this pair of peaks is 14.81 cm⁻¹, and the rotational doublet is distinct at 0.25 nm resolution (inset in Figure 3).

If students have LIF instrumentation capable of 0.025 nm resolution, they might also investigate one of the 43 ← 0 fluorescence lines more closely. Each line in Figure 3 has substantial structure. The strongest portion of the signal is due to an overlapped pair of closely spaced rotational doublets because the Ar⁺ 514.5 nm line actually accesses two 43 ← 0 rovibronic transitions: \( J'' = 15 \) to \( J' = 16 \) and \( J'' = 13 \) to \( J' = 12 \). There is also low-lying structure in the signal that has been attributed to changes in \( f \) caused by collisions prior to relaxation (21, 29).
Combining Absorption and Fluorescence Data

**Basic Analysis**

After collecting and analyzing fluorescence data, students may return to their absorption spectrum data and calculate $\tilde{D}_c$ from the constant term in the polynomial fit of eq 2. They may also calculate $E(I^*)$, the excitation energy corresponding to the lowest $^3P_{1/2} \leftrightarrow ^3P_{3/2}$ transition of atomic iodine (Figure 1):

$$E(I^*) = E^* - \tilde{D}_0''$$  

(7)

**Supplementary Analysis**

Reinforcement of how the energy of molecular iodine changes during both the visible absorption experiment and the laser-induced fluorescence experiment comes about by having students plot approximate potential energy surfaces for the X state and the B state. The simplest approximation is a Morse potential (30), for which students must provide $\tilde{D}_0$, $\tilde{\nu}_e$, $R_e$, and $\tilde{T}_e$:

$$E = \tilde{T}_e + \tilde{D}_0 \left( 1 - e^{-x} \right)^2$$

where $x = \beta(R - R_e)$; $\beta = \tilde{\nu}_e \pi \frac{2\mu}{\hbar \tilde{b}}$  

(8)

Results from the Ar* 514.5 nm LIF experiment give students all the information they need to plot the X state as a Morse potential. Combining the visible absorption and LIF data yields all of the B-state parameters except $R_e'$. Students can either be given this value or else they can follow a method described by D’alterio for estimating $R_e'$ from the visible absorption spectrum (5).

**Conclusion**

Exploration of the visible spectroscopy of molecular iodine provides students with a wonderful opportunity to test many key quantum mechanical concepts they have learned in physical chemistry. This article has presented guidelines for molecular iodine spectral analysis to assist instructors and students in reaching their experimental objectives correctly. One major objective of this article has been to clearly identify the accuracy and precision in potential parameters that students may expect to obtain from their measurements. Table 2 summarizes the results, listing recent primary literature values, the corresponding experimental values determined from the spectra presented in this article, and brief commentary on each one. Expanded theoretical development and further clarification on how to interpret the spectra are available online in the Supplemental Material.

**Acknowledgments**

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**Supplemental Material**

Expanded theoretical development, further clarification on how to interpret the spectra, and a flowchart for students showing the main analysis steps necessary to calculate model potential energy curves from the collected spectra are available for the interested reader in this issue of JCE Online.

**Literature Cited**