The Electronic Absorption Spectrum of Molecular Iodine: A New Fitting Procedure for the Physical Chemistry Laboratory

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The electronic absorption spectrum of molecular iodine has become a standard experiment in the undergraduate physical chemistry laboratory course (1–6). Observation of the vibrationally resolved spectrum in the visible region at low resolution ($\Delta\lambda \sim 0.5$ nm) affords students a good demonstration of the quantization of molecular energy levels, while the treatment of the spectral data gives them valuable experience in the determination of molecular constants. Students typically observe transitions from the $\upsilon'' = 0$, 1, and 2 levels in the ground electronic state to vibrational levels in the electronically excited B-state. Generally, they then analyze the transitions originating from the $\upsilon'' = 0$ level using a Birge–Sponer plot and thereby determine the various molecular constants and energies.

We use a different approach to data treatment that the students find more satisfying and that we believe has pedagogical advantages over the Birge–Sponer treatment. It involves simply fitting the transition frequencies to a second-order polynomial. This fit directly yields the important molecular constants and the various energy terms. With the availability of common graphing programs such as Excel, Kaleidagraph, and SigmaPlot, students can take advantage of more advanced fitting techniques and no longer have to rely on simple linear plots.

The Second-Order Polynomial Fit Treatment

The vibrational energy for a simple diatomic molecule is given (in cm^{-1}) by

$$G(\upsilon) = \omega_e(\upsilon + \tfrac{1}{2}) - \omega_e x_e(\upsilon + \tfrac{1}{2})^2 \qquad (1)$$

where ω_e is the fundamental vibrational frequency, $\omega_e x_e$ is the anharmonicity constant (or anharmonic correction term), and υ is the vibrational quantum number. For an optical transition from the ground electronic state to a vibrational level in an excited electronic state, the expression (in cm^{-1}) is

$$\nu = E_{el} + \omega_e'(\upsilon' + \tfrac{1}{2}) - \omega_e' x_e'(\upsilon' + \tfrac{1}{2})^2 - \omega_e''(\upsilon'' + \tfrac{1}{2}) + \omega_e'' x_e''(\upsilon'' + \tfrac{1}{2})^2 \ (2)$$

where ν is the observed transition frequency, E_{el} is the electronic energy separation from the equilibrium positions, and the primes and double primes refer to those values in the upper and lower electronic states, respectively (see Fig. 1). Rearrangement of eq 2 gives the frequency (in cm^{-1}) for transitions from the $\upsilon'' = 0$ vibrational level in the ground electronic state as

$$\nu = \{E_{el} - \omega_e''/2 + \omega_e'' x_e''/4\} + \omega_e'(\upsilon' + \tfrac{1}{2}) - \omega_e' x_e'(\upsilon' + \tfrac{1}{2})^2 \ (3)$$

This is simply the equation for a second-order polynomial in $(\upsilon' + \tfrac{1}{2})$, that is,

$$\nu = a + b(\upsilon' + \tfrac{1}{2}) + c(\upsilon' + \tfrac{1}{2})^2 \qquad (4)$$

where $a = \{E_{el} - \omega_e''/2 + \omega_e'' x_e''/4\}$, $b = \omega_e'$, and $c = -\omega_e' x_e'$. This expression represents the essence of the polynomial fit
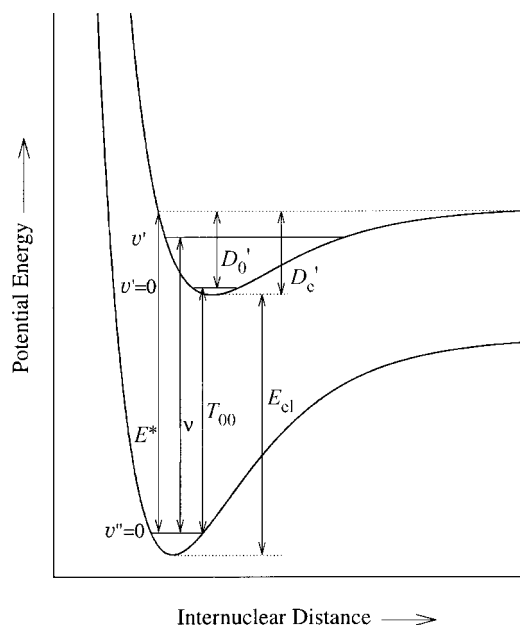

Figure 1. Potential energy diagram indicating the various energies and electronic transitions.
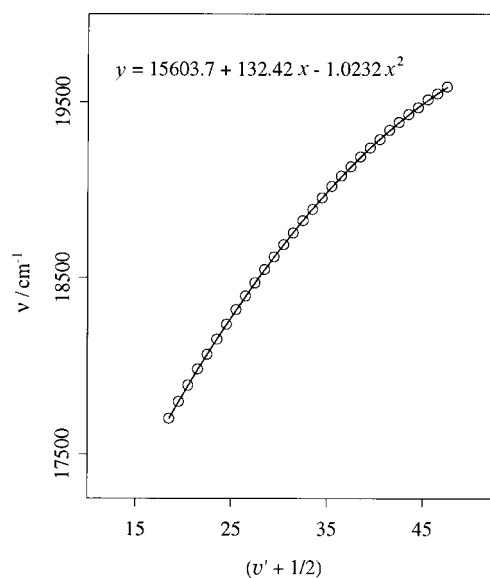

$$y = 15603.7 + 132.42\,x - 1.0232\,x^2$$

Figure 2. Typical student plot of data using a second-order polynomial fit.

treatment. The electronic band origin, T_{00}, is determined from eq 4 when $\upsilon' = 0$. That is:

$$T_{00} = a + b/2 + c/4 \qquad (5)$$

where $(b/2 + c/4) = (\omega_e'/2 - \omega_e'x_e'/4)$ is the zero-point vibrational energy in the excited electronic state.

A typical student plot of ν versus $(\upsilon' + 1/2)$ is shown in Figure 2. Notice how well the data are fit by a second-order polynomial over the observed range ($\upsilon' = 18$–47). From this plot students directly obtain ω_e', $\omega_e'x_e'$, and T_{00} (132.42 cm^{-1}, 1.0232 cm^{-1}, and 15669.6 cm^{-1}, respectively). Additionally, students can utilize their knowledge of limits to determine the convergence limit, E^*. By taking the first derivative of the polynomial (eq 4) with respect to $(\upsilon' + 1/2)$ and setting it equal to zero, they can solve for the asymptotic limit at $(\upsilon' + 1/2)_{max}$:

$$d\nu/d(\upsilon' + 1/2) = b + 2c(\upsilon' + 1/2)_{max} = 0 \qquad (6)$$

or

$$(\upsilon' + 1/2)_{max} = -b/2c \qquad (7)$$

Substituting this into eq 4 gives the convergence limit:

$$\nu_{max} = E^* = a - b^2/4c \qquad (8)$$

This assumes that the vibrational quantum number is a continuous function. (See Lessinger [6] for a discussion of the errors associated with this assumption.) Students can then calculate the well depth or dissociation energy in the excited electronic state from the $\upsilon' = 0$ vibrational level (see Fig. 1) according to

$$D_0' = E^* - T_{00} \qquad (9)$$

Finally, they can determine the well depth from the equilibrium position as

$$D_e' = D_0' + (\omega_e'/2 - \omega_e'x_e'/4) \qquad (10)$$

Typical student results from this treatment are shown in Table 1, along with a comparison to results from the Birge–Sponer treatment and some literature results.

The Birge–Sponer Treatment

For comparison purposes, we shall briefly review the Birge–Sponer treatment (7). The Birge–Sponer treatment involves using combination differences of two adjacent transitions originating from the same vibrational level with υ'' in the ground electronic state. That is,

$$\Delta\nu = \nu(\upsilon' + 1 \leftarrow \upsilon'') - \nu(\upsilon' \leftarrow \upsilon'') \qquad (11)$$

or, according to eq 2,

$$\Delta\nu = \omega_e' - 2\omega_e'x_e'(\upsilon' + 1) \qquad (12)$$

According to this treatment, students prepare a Birge–Sponer plot of $\Delta\nu$ versus $(\upsilon' + 1)$. The data show good linearity with a slope of $-2\omega_e'x_e'$ and an intercept of ω_e'. A typical student plot is shown in Figure 3. These are the same data as used for Figure 2. The scatter in the data appears greater in Figure 3 than in Figure 2 because of an expansion of the y-axis. The treatment presented here differs slightly from that in some of the literature (2, 6) in that others advocate a plot of $\Delta\nu$ vs υ' or $\Delta\nu$ vs $(\upsilon' + 1/2)$. We prefer the treatment presented here, which is consistent with ref 1, since the intercept is exactly ω_e' and not a combination of ω_e' and $\omega_e'x_e'$.

The area under this curve represents the well depth or dissociation energy in the excited electronic state from the

Table 1. Molecular Constants and Energies for Iodine

Constant	Student Results, Av of 5 Data Sets		Lit (5)[a]
	Polynomial Fit	Birge–Sponer	
ω_e'	131.9	133.4	132.11
$\omega_e'x_e'$	1.016	1.026	1.051
T_{00}	15,679	15,692	15,689
E^*	19,895	19,896	19,735
D_0'	4,216	4,204	4,046
D_e'	4,282	4,270	4,112

NOTE: All values are in units of cm^{-1}.
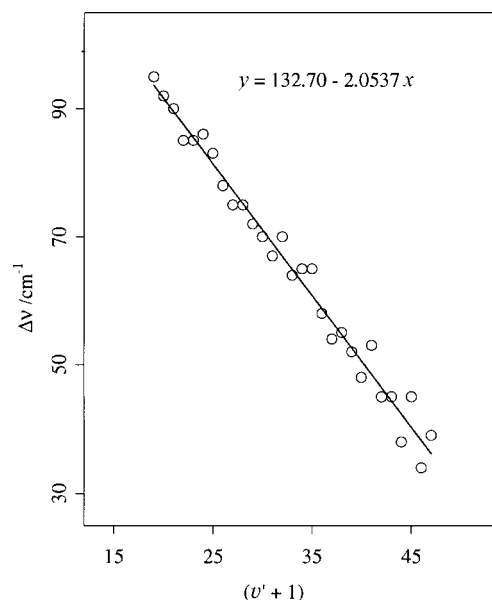[a]Based on band-head fitting. Includes the first anharmonic correction term only.

Figure 3. Typical student plot of data using the Birge–Sponer treatment and fitting to a line. (These data are the same as in Fig. 2. The scatter appears greater because of an expansion of the y-axis.)

$\upsilon' = 0$ vibrational level, D_0':

$$D_0' = {}^1\!/_2 \text{ base} \times \text{height} =$$
$${}^1\!/_2(\omega_e'/2\omega_e'x_e') \times (\omega_e') = \omega_e'^2/4\omega_e'x_e' \qquad (13)$$

The corresponding energy from the equilibrium position is then determined from D_0' and the zero-point energy according to eq 10. Finally, the convergence limit energy, E^*, and the electronic band origin, T_{00}, can be determined rather indirectly from one of the observed transition frequencies by adding and subtracting, respectively, a portion of the area under the Birge–Sponer plot (see 1). Typical student values using this treatment are given in Table 1.

Again, the Birge–Sponer treatment presented here does not include Lessinger's corrections for incorrectly treating the vibrational quantum number as a continuous function (6).

Discussion

As presented in Table 1, the molecular constants and energies for the two treatments are nearly identical. We are not advocating the second-order polynomial fit treatment

over the Birge–Sponer treatment because of superior results. Rather, we advocate this new treatment because students find it more understandable and straightforward. It is not uncommon for students to object to the Birge–Sponer treatment because, in their view, it is just a mathematical cookbook approach. They do not understand the Birge–Sponer plot or how the area under this plot is the dissociation energy. They quickly lose sight of the potentials and the associated energies, as presented in Figure 1. Additionally, the determination of E^* and T_{00} is somewhat cumbersome.

The polynomial treatment is more appealing because the students are plotting their "raw" data, usually after the conversion from λ (nm) to ν (cm^{-1}). They have the mathematical formula that expresses these data in terms of the molecular constants and energies (see eq 3). The fit to a second-order polynomial is very good (Fig. 2), and students immediately have ω_e', $\omega_e' x_e'$, and T_{00}. From this, determination of the other

energy terms is straightforward, as outlined above. Students therefore have a greater sense of satisfaction and appear to have gained a better understanding of vibrational quantum states, electronic potentials, and their associated energies.

Literature Cited

1. Sime, R. J. *Physical Chemistry: Methods, Techniques, and Experiments*; Saunders: Orlando, FL, 1990; pp 660–668.
2. Shoemaker, D. P.; Garland, C. W.; Nibler, J. W. *Experiments in Physical Chemistry*, 6th ed.; McGraw-Hill: New York, 1996; pp 425–434.
3. Stafford, F. E. *J. Chem. Educ.* **1962,** *39,* 626–629.
4. D'alterio, R.; Mattson, R.; Harris, R. *J. Chem. Educ.* **1974,** *51,* 282–284.
5. McNaught, I. J. *J. Chem. Educ.* **1980,** *57,* 101–105.
6. Lessinger, L. *J. Chem. Educ.* **1994,** *71,* 388–391.
7. Birge, R. T.; Sponer, H. *Phys. Rev.* **1926,** *28,* 259–283.