

# The Electronic Spectrum of Iodine Revisited

When experimental data are obtained from expensive equipment it is desirable to extract as much information as possible from those data. It is also desirable to make the analysis as self-contained as possible by minimizing the need to use literature values for quantities unobtainable by the experimental design.

The electronic spectrum of iodine has played a central role in testing the consistency of quantum mechanics and observed spectroscopic fine structure. The results have been summarized in a masterly fashion by Mulliken (1). The analysis of the low resolution electronic spectrum of  $I_2$  has become a classic advanced undergraduate experiment, particularly since the expository paper of Stafford (2) and its extension by D'alterio et al. (3). The ready availability of minicomputers and programmable calculators means that it is possible for students to perform much more sophisticated analyses of experimental data than has previously been the case. Stafford's analysis is quite restricted; with no more experimental work it is possible to extract very much more information on the spectroscopic constants of the iodine molecule and gain significant insight into a range of spectroscopic and quantum mechanical concepts.

The data that can be obtained include

- the separation between the minima of the potential curves,  $\sigma_e$ ,
- the frequencies and anharmonicities in each electronic state,  $\omega_e, \omega_e x_e$ ,
- the dissociation energies in each electronic state,  $D_e, D_0$ ,
- the differences in equilibrium bond lengths,
- maximum intensity transitions as well as information on the vibrational wavefunctions.

## Spectroscopic Introduction

The variation of potential energy of a diatomic molecule with internuclear distance is conveniently represented on a potential energy diagram. Figure 1 shows the variation in potential energy for the iodine molecule in its ground (X) electronic state and its second (B) excited electronic state. This figure illustrates the parameters to be calculated and uses the standard spectroscopic notation (4).

The iodine molecule gives rise to well resolved vibronic bands between 500 nm and 620 nm. However, as can be seen from Figure 2, there is significant overlap between  $(v', 0)$ ,  $(v', 1)$  and  $(v', 2)$  in the middle of this region. This makes the Birge-Sponer plots (4, p. 438) of both Stafford and D'alterio

et al. suspect at lower values of the vibrational quantum number as it is clear that the  $(v', 0)$  bands for  $v'$  less than 14 are swamped by the intensity of the  $(v', 1)$  and  $(v', 2)$  bands. Therefore, particular care must be taken in analyzing this region. Fortunately, the existence of these hot bands makes it possible, as will be shown below, to obtain much more information than is usually done.

## Experimental Details

The spectrometer used was a Unicam SP 1750 run at  $0.2 \text{ nm s}^{-1}$  with a band width of  $0.2 \text{ nm}$ , the spectrum being recorded on an AR 55 recorder. The spectrometer was calibrated as suggested by Stafford (2). The spectrum of gaseous iodine was run at room temperature after placing several crystals in a 10-cm cell. It was found unnecessary to use higher temperatures provided that the sublimed iodine was removed from the windows prior to a run.

## Treatment of Experimental Data

The first problem is to assign vibrational quantum numbers to the bands. The numbering given in Table 1 is based on that proposed by Steinfeld et al. (5) on the basis of intensity distributions and proved by Brown and James (6) from an analysis of the isotope effect.

In order to ensure that the assignments are consistent, it is useful to prepare a Deslandres table (4, p. 40) as in Table 2. An inconsistency in the numbering will show up as an inconsistency in the differences between rows or columns. This technique will not show up a consistent numbering error.

Table 1. Numbering of Band Heads for Iodine

$v'$	$v''$	$\lambda/\text{nm}$	$v'$	$v''$	$\lambda/\text{nm}$	$v'$	$v''$	$\lambda/\text{nm}$
27	0	541.2	18	1	571.6	13	2	595.7
28	0	539.0	19	1	568.6	14	2	592.0
29	0	536.9	20	1	565.6	15	2	588.5

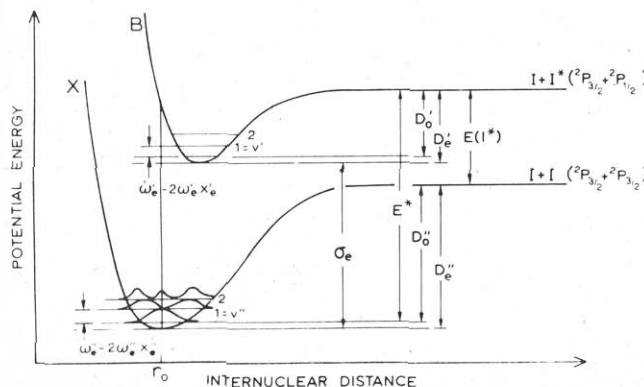


Figure 1. Potential energy diagram for iodine.

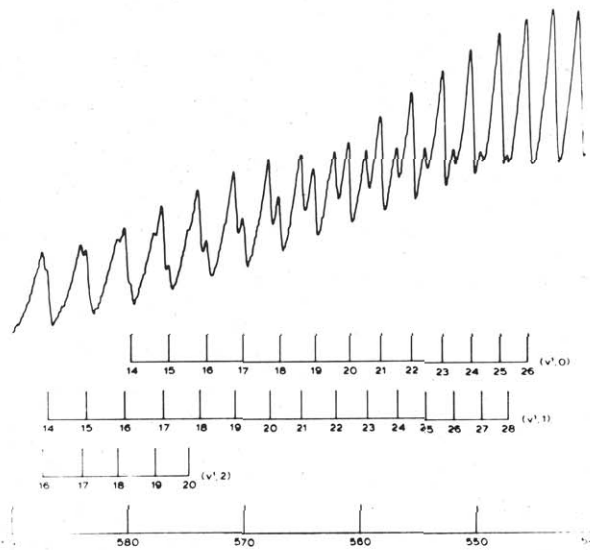


Figure 2. Overlapping of  $(v', 0)$ ,  $(v', 1)$  and  $(v', 2)$  bands in iodine.

## Directly Derived Parameters

If  $T'$  and  $T''$  represent the electronic term energies of the two states while  $G(v')$  and  $G(v'')$  represent their vibrational energies then, ignoring rotational energy changes, the energy of a transition will be given by

$$\sigma = T' - T'' + G(v') - G(v'') \quad (1)$$

For the case studied here  $T''$  is zero, because it refers to the ground electronic state while  $T'$  equals  $\sigma_e$ , the frequency of the hypothetical transition between the two minima of the potential curves (Fig. 1).

The vibrational term values can be written as

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3 + \dots \quad (2)$$

where  $\omega_e$  is the frequency for infinitesimal amplitudes of vibration and  $\omega_e x_e$ ,  $\omega_e y_e$  etc. are anharmonicity constants. If only the first two terms in this expression are taken, i.e.

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 \quad (3)$$

then the transition frequency is given by

$$\sigma = \sigma_e + \omega_e(v' + 1/2) - \omega_e x'_e(v' + 1/2)^2 - \omega_e(v'' + 1/2) + \omega_e x''_e(v'' + 1/2)^2 \quad (4)$$

The usual procedure from this point (2) is to use a Birge-Sponer plot to obtain  $\omega_e$  and  $\omega_e x'_e$ , then to use literature values for  $\omega_e$ ,  $\omega_e x''_e$  along with the observed  $\sigma$  to determine  $\sigma_e$ .

A much better way is to use the technique of multiple linear regression (7) to determine  $\sigma_e$ ,  $\omega_e$ ,  $\omega_e x'_e$ ,  $\omega_e x''_e$  and  $\omega_e y_e$  directly from  $\sigma$ ,  $v'$  and  $v''$ .

## Indirectly Derived Parameters

### Convergence Limit $E^*$

$E^*$  is the energy of the transition from  $v'' = 0$  to the top of the upper state potential well, i.e., the energy at which the vibrational structure joins the continuum. It is calculated as the energy of a transition ending on level  $v$  plus the sum of all the vibrational quanta above  $v$  to the maximum  $v_{\max}$ . The energy of the vibrational quanta is given by  $G(v + 1) - G(v)$ , so that

$$E^* = \sigma_v + \sum_v (G(v + 1) - G(v)) \quad (5)$$

Retaining only quadratic terms in  $G(v)$  gives

$$G(v + 1) - G(v) = \omega'_e - 2\omega'_e x'_e(v + 1) \quad (6)$$

It follows from this equation that  $v_{\max}$  (i.e., that  $v$  for which  $G(v + 1) - G(v) = 0$ ) is given by

$$v_{\max} = \omega'_e / (2\omega'_e x'_e) - 1 \quad (7)$$

Therefore

$$E^* = \sigma_v + 1/2[\omega'_e - 2\omega'_e x'_e(v + 1)](v_{\max} - v) \quad (8)$$

This equation is just the analytical form of the Birge-Sponer technique. Its advantage is that all the observed values of  $\sigma_v$  due to transitions from  $v'' = 0$  can be used to produce many independent values of  $E^*$ , these values can then be used to obtain some estimate of the error in  $E^*$ . The graphical technique is a one point method which gives no indication of the precision of the determined  $E^*$ .

This analytical technique assumes a linear Birge-Sponer extrapolation, a valid assumption for the data obtained in this experiment.

### Dissociation Energy $D_e$

The dissociation energy is the energy required to dissociate the molecule into atoms. (Dissociation into positive and negative ions is also possible; however, it does not happen in this case (4, p. 390)). If radiation of energy  $E^*$  is absorbed, the atom will dissociate into the upper state products. When separated the atoms have zero relative velocity. Increasing the energy above  $E^*$  will give atoms having increasing relative velocity and kinetic energy. It is this process which gives rise

to the continuum observed in this experiment at short wavelengths.

The ground state dissociation energy measured from the lowest vibrational level is given by

$$D_0^* = E^* - E(I^*) \quad (9)$$

where  $E(I^*)$  is the difference in energy between a ground state iodine atom ( $^2P_{3/2}$ ) and the first excited state of the iodine atom ( $^2P_{1/2}$ ). It has a value of  $7589 \text{ cm}^{-1}$  (8). The ground state dissociation energy measured from the bottom of its potential well differs from this value by the zero point energy, which in the approximation used here is  $(\omega_e''/2) - (\omega_e x''_e/4)$  i.e.

$$D_e^* = D_0^* + \frac{\omega_e''}{2} - \frac{\omega_e x''_e}{4} \quad (10)$$

The excited state dissociation energy measured from the bottom of its potential well is

$$D_e' = E^* - \sigma_e + \frac{\omega_e''}{2} - \frac{\omega_e x''_e}{4} \quad (11)$$

### Force Constants $k_e$

When a bond is stretched there arises a restoring force which resists the stretching force. Within the simple harmonic oscillator approximation this restoring force is given by (4, p. 74)

$$F = -k_e(r - r_e) \quad (12)$$

where  $r - r_e$  is the extension and  $k_e$  is the force constant. The greater the force constant the more difficult it is to stretch the bond. The force constant is related to the curvature of the potential well and can be calculated from (4, p. 98)

$$k_e = 4\pi^2 c^2 \mu \omega_e^2 \quad (13)$$

### Morse Curve

If the simple harmonic oscillator model did apply, the potential energy curve would be a parabola, i.e. its dissociation energy would be infinite. A more realistic potential energy curve is that introduced by Morse (9)

$$U(r - r_e) = D_e(e^{-\beta(r - r_e)} - 1)^2 \quad (14)$$

where

$$\beta = \pi \omega_e (2\mu c / D_e h)^{1/2} \quad (15)$$

The importance of this potential function is that it is possible to solve the Schrödinger equation for this potential and obtain the vibrational energy wavefunctions. These wavefunctions are finite and give eqn. 3 when appropriate identifications are made.

If  $r - r_e$  is denoted by  $u$  then these wavefunctions  $R_n(u)$  can be written (10)

$$R_n^2(u) \propto e^{-kz} (kz)^{k-2n-1} L_{kn}^2(kz) \quad (16)$$

where

$$z \equiv e^{-\beta u}, k \equiv 4D_e/\omega_e$$

Table 2. Deslandres Table for Iodine<sup>a</sup>

$v'/v''$	0	1	2
19	17799 93	213 93	17586 93
18	17706 94	213 94	17493 94
17	17612 97	213 97	17399 97
16	17515 99	213 98	17302 98
15	17416	212	17204
			16992

<sup>a</sup> All entries in  $\text{cm}^{-1}$ , corrected for vacuum (13). The difference between rows equals  $\omega'_e - 2\omega'_e x'_e(v + 1)$  while the difference between columns equals  $\omega_e'' - 2\omega_e x''_e(v + 1)$  where  $v$  is the lower of the two vibrational quantum numbers.

$$L_{kn}(kz) = (kz)^n - n(k-n-1)(kz)^{n-1} + \frac{1}{2}n(n-1)(k-n-1)(k-n-2)(kz)^{n-2} \dots \quad (17)$$

where  $n$  is the vibrational quantum number. In this experiment we are interested in transitions from  $n = 0, 1$ , and  $2$ . The required probability density distributions are given by

$$R_0^2(u) \propto e^{-kz} (kz)^{k-1} \quad (18)$$

$$R_1^2(u) \propto e^{-kz} (kz)^{k-3} [kz - (k-2)]^2 \quad (19)$$

$$R_2^2(u) \propto e^{-kz} (kz)^{k-5} [(kz)^2 - 2(k-3)kz + (k-3)(k-4)]^2 \quad (20)$$

However, for numerical evaluation these expressions are not very useful (they contain terms like  $200^{200}$ ), so a scaled probability density distribution can be introduced,

$$R_n^2(u) \equiv (R_n(u)/R_n(0))^2 \quad (21)$$

Explicitly the scaled probability density distributions used here are

$$R_0^2(u) = e^{-k(z-1)z} k^{-1} \quad (22)$$

$$R_1^2(u) = e^{-k(z-1)z} k^{-3} [kz - (k-2)]^2 \quad (23)$$

$$R_2^2(u) = e^{-k(z-1)z} k^{-5} [(kz)^2 - 2(k-3)kz + (k-3)(k-4)]^2 \quad (24)$$

Figure 3 shows these functions superimposed on the Morse curve for the ground state of iodine. Also plotted are the squares of the wavefunctions for the harmonic oscillator. The harmonic oscillator probability density distributions are presented by (4, p. 78)

$$\psi_0^2 \propto e^{-au^2} \quad (25)$$

$$\psi_1^2 \propto au^2 e^{-au^2} \quad (26)$$

$$\psi_2^2 \propto (2au^2 - 1)^2 e^{-au^2} \quad (27)$$

where  $a \equiv 4\pi^2 c \mu \omega_e / h$ . It is clear from Figure 3 that as the vibrational quantum number increases, the difference in bond length between the maxima for the harmonic and anharmonic oscillators becomes more pronounced. This is important in determining the expected intensity distribution in the vibronic bands.

#### Anharmonic Oscillator Maxima $u_i^{\max}$

The maxima in the anharmonic oscillator distributions can be calculated from the following formulae, where in each case  $z$  is related to  $u$  by the equation

$$u = -\frac{1}{\beta} \ln z \quad (28)$$

$$u_0^{\max}: z = (k-1)/k \quad (29)$$

$$u_1^{\max}: z = [(2k-3) \pm \sqrt{8k-15}]/2k \quad (30)$$

$$u_2^{\max}: (kz)^3 - (3k-7)(kz)^2 + (k-3)(3k-10)kz - (k-3)(k-4)(k-5) = 0 \quad (31)$$

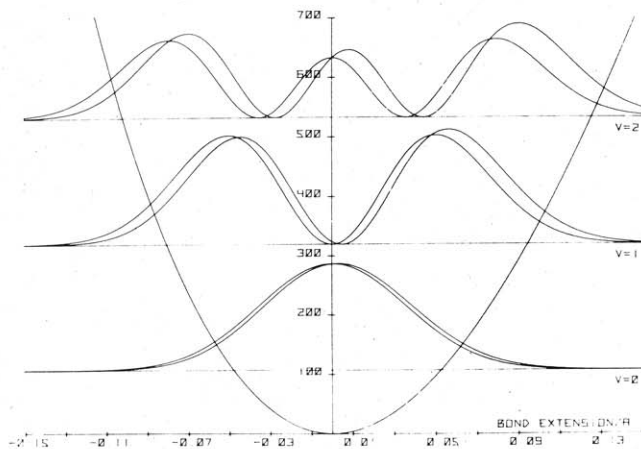


Figure 3. Harmonic and anharmonic probability density distributions for iodine.

Although an analytical solution for eqn. (31) is obtainable, it is easier to solve the equation numerically.

The classical turning points,  $u$ , for each of the three vibrational levels can be obtained by solving the equation

$$\omega_e''(v + \frac{1}{2}) - \omega_e''x_e''(v + \frac{1}{2})^2 = D_e''(e^{-\beta''u} - 1)^2 \quad (32)$$

#### Difference in Equilibrium Bond Lengths, $r_e' - r_e''$

As has been discussed by D'alterio et al. (3), it is possible to use the intensities of the  $(v', 0)$  bands to estimate the difference between the equilibrium bond lengths in the two states. Because of the problem of overlapping bands mentioned earlier, a simpler approach has been taken here. It is considered sufficient merely to take the energy corresponding to the most intense transition,  $\sigma_{int}$ . By the Franck-Condon principle (4, p. 194), this transition will originate and end at the internuclear distance  $r_0''$  (not  $r_e''$  as claimed by D'alterio et al.). It is clear from Figure 1 that

$$U'(u_0^{\max} + r_e'' - r_e') = \sigma_{int} - \sigma_e + \frac{\omega_e''}{2} - \frac{\omega_e''x_e''}{4} \quad (33)$$

$$= D_e'(e^{-\beta'u} - 1)^2 \quad (34)$$

$$\text{i.e., } r_e' - r_e'' = u_0^{\max} + \frac{1}{\beta'} \ln(1 \pm \sqrt{U'(u_0^{\max} + r_e'' - r_e')/D_e'}) \quad (35)$$

The plus sign is chosen if the bands are red degraded, i.e.,  $r_e' > r_e''$ , the negative sign if the bands are violet degraded, i.e.,  $r_e' < r_e''$ .

#### Transitions of Maximum Intensity

Provided that the vibrational quantum number is greater than about 10, the probability maxima lie close to the potential curve (11). Assuming that it lies at the same internuclear distance as the curve, and that the Franck-Condon principle holds, it is possible to predict the most intense  $(v', 0)$ ,  $(v', 1)$  and  $(v', 2)$  transitions. They are obtained by solving the following equation for  $v'$

$$U'(u) = \omega_e'(v' + \frac{1}{2}) - \omega_e'x_e'(v' + \frac{1}{2})^2 = D_e'(e^{-\beta'u} - 1)^2 \quad (36)$$

where

$$u = u_1^{\max} + r_e'' - r_e'$$

It should be noted that this calculation (where  $r_e'' - r_e'$  is used to calculate the maximum intensity) is *not* related in a circular way to the calculations in eqns. 33–35 (where the maximum intensity  $v'$  is used to calculate  $r_e' - r_e''$ ) as it brings in  $\omega_e'$  and  $\omega_e'x_e'$  which are independent of the parameters in those three equations. The calculations serve as a good check on the internal consistency of the experimental data.

If a plotter is available the relationship between the Morse curves and the vibrational wavefunctions can be shown as in Figure 4. Drawing a vertical transition from the maximum gives the value of  $U'(u)$ , it is instructive then to draw in the appropriate upper state vibrational levels using eqn. (3).

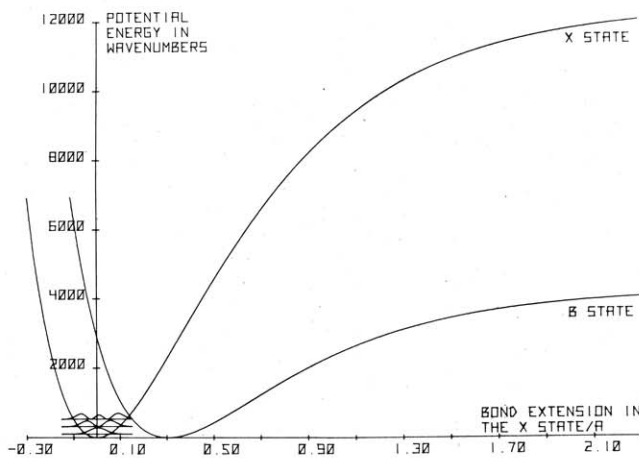


Figure 4. Derived potential curves for iodine.

Table 3. Parameters for Iodine <sup>a</sup>

	Equation (4)	Equation (42)
$\sigma_e$	15 730 ± 3	15 766 ± 4
$\omega_e$	132.11 ± 0.24	126.04 ± 0.69
$\omega_e x_e$	1.051 ± 0.006	0.735 ± 0.036
$\omega_e y_e$	—	-0.0052 ± 0.0006
$\omega_e x_e''$	213.36 ± 0.87	214.44 ± 0.44
$\omega_e x_e'''$	0.14 ± 0.32	0.67 ± 0.16
$E^*$	19 735 ± 2	19 464 ± 3
$D_0''$	12 137 ± 2	11 866 ± 3
$D_0'$	12 244 ± 3	11 973 ± 3
$D_0$	4 112 ± 6	3 805 ± 7
$k'$	4046 ± 6	3 742 ± 7
$k''$	124.5 ± 0.4	120.8 ± 0.9
$\beta'/\text{\AA}^{-1}$	229.5 ± 1.0	223.3 ± 0.5
$\beta''/\text{\AA}^{-1}$	1.998 ± 0.005	1.982 ± 0.012
$\beta'''/\text{\AA}^{-1}$	1.870 ± 0.008	1.901 ± 0.004
$a'/\text{\AA}^{-2}$	248.6 ± 0.5	237.2 ± 1.3
$a''/\text{\AA}^{-2}$	401.5 ± 1.6	403.6 ± 0.8
$10^2 u_0^{\text{max}}/\text{\AA}$	0.23	0.24
$10^2 u_1^{\text{max}}/\text{\AA}$	-4.43, 5.60	-4.41, 5.60
$10^2 u_2^{\text{max}}/\text{\AA}$	-6.95, 0.80, 8.97	-6.92, 0.81, 8.96
$(r_e'' - r_e')/\text{\AA}$	0.305 ± 0.001	0.315 ± 0.002
$10^2 B_e$	3.010 ± 0.002	2.990 ± 0.004
$r_e'/\text{\AA}$	2.971 ± 0.001	2.981 ± 0.002
$10^4 \alpha_e'$	2.020 ± 0.004	2.089 ± 0.010
$10^4 \alpha_e''$	1.564 ± 0.001	1.591 ± 0.001
$r_e''/\text{\AA}$	2.669	2.669
$r_1/\text{\AA}$	2.674	2.674
$r_2/\text{\AA}$	2.680	2.680
$10^{-5} k_e'/\text{dyne cm}^{-1}$	0.65	0.59
$10^{-5} k_e''/\text{dyne cm}^{-1}$	1.70	1.72
$v \text{ max. intens.}$	27, 14, 9	26, 14, 10

<sup>a</sup> All values in  $\text{cm}^{-1}$  except where indicated.

### Rotational Constants $B_v$

If the literature value for  $r_e''$  is assumed then it is possible to determine  $r_e'$  and from these the rotational constants in both states as well as their variation with vibrational quantum number. The equilibrium rotational constants are determined from

$$B_e = h/(8\pi^2 c \mu r_e'^2) \quad (37)$$

The rotational constant in a given vibrational level is related to  $B_e$  by the equation (4, p. 106)

$$B_v = B_e - \alpha_e(v + 1/2) \quad (38)$$

where  $\alpha_e$  can be determined from (4, p. 108)

$$\alpha_e = 3B_e(\sqrt{B_e/D_e} - 2B_e/\omega_e) \quad (39)$$

Equation (37) can be used to verify that the difference between the band head and band origin can be ignored within the accuracy of these data.

Equations (37)–(39) permit the calculation of the bond lengths  $r_0$ ,  $r_1$  and  $r_2$  in each of the three lowest vibrational levels.

### Choice of Equations

Equation (39) is a modification of the one quoted by Herzberg; the equation there involves the anharmonicity constant and therefore can have large error limits when determined from such low resolution data as obtained in this experiment. The transformation uses the relationship  $\omega_e x_e = \omega_e^2/4D_e$  (4, p. 100). Similarly, the literature contains a number of different equations from those used here, the criterion of choice for this paper being those equations that contained precisely obtainable parameters. For example, alternative equations for some of the parameters are

$$\beta = (8\pi^2 c \mu \omega_e x_e/h)^{1/2} (9) \quad (40)$$

$$k = \frac{1}{x_e} \quad (10) \quad (41)$$

Equations (40) and (41) involve the anharmonicity, for the

Table 4. Summary of Relations

$\sigma_e$	multiple linear regression
$\omega_e$	multiple linear regression
$\omega_e x_e$	multiple linear regression
$\omega_e y_e$	multiple linear regression
$\omega_e x_e''$	multiple linear regression
$\omega_e x_e'''$	multiple linear regression
$E^*$	$v_{\text{max}} = \omega_e/(2\omega_e x_e) - 1$ $E^* = \sigma_v + 1/2[\omega_e - 2\omega_e x_e(v + 1)][v_{\text{max}} - v]$
	Calculate for all $\sigma_v$ originating from $v'' = 0$ . Find the average and standard deviation.
$D_0''$	$D_0'' = E^* - E(I^*)$ $E(I^*)$ from literature
$D_0'$	$D_0' = D_0'' + 1/2\omega_e - 1/4\omega_e x_e''$
$D_0$	$D_0 = E^* - \sigma_e + 1/2\omega_e - 1/4\omega_e x_e''$
$k$	$k = 4D_e/\omega_e$
$\beta$	$\beta = \pi\omega_e(2c\mu/D_e h)^{1/2}$
$a$	$a = 4\pi^2 c \mu \omega_e/h$
$u_0^{\text{max}}$	$z = (k - 1)/k, u = -\frac{1}{\beta} \ln z$
$u_1^{\text{max}}$	$z = [(2k - 3) \pm \sqrt{8k - 15}]/2k, u = -\frac{1}{\beta} \ln z$
$u_2^{\text{max}}$	$(kz)^3 - (3k - 7)(kz)^2 + (k - 3)(3k - 10)kz - (k - 3)(k - 4)(k - 5) = 0$
$r_e' - r_e''$	$r_e' - r_e'' = u_0^{\text{max}} + \frac{1}{\beta'} \ln(1 + \sqrt{U'(u_0^{\text{max}} + r_e'' - r_e')/D_e})$ $U'(u_0^{\text{max}} + r_e'' - r_e') = \sigma_{\text{int}} - \sigma_e + 1/2\omega_e - 1/4\omega_e x_e''$
$B_e''$	$B_e'' = h/(8\pi^2 c \mu r_e'^2)$ $r_e''$ from literature
$B_e$	$B_e = h/(8\pi^2 c \mu r_e'^2)$
$\alpha_e$	$\alpha_e = 3B_e \left( \sqrt{\frac{B_e}{D_e}} - \frac{2B_e}{\omega_e} \right)$
$r_1$	$r_1 = \sqrt{h/8\pi^2 c \mu B_1}$
$k_e$	$k_e = 4\pi^2 c^2 \mu \omega_e^2$

ground state this is the least precisely determined parameter (see Table 3). Equation (41) does have the useful feature of showing that as the anharmonicity increases the value of  $k$  decreases.

### Results

The results of a typical careful run are collected together in Table 3.

The quoted errors are standard deviations.

### Comparison with the Literature

It is common practice to compare results with well tabulated literature values. Such a comparison must be approached cautiously for two reasons. The first reason is that new experimental data or reinterpretation of accepted data may lead to marked changes in the values.

The second and more important reason is that present literature values are usually obtained using much more sophisticated term functions, e.g., eqn. (2) is usually expanded to higher powers in  $(v + 1/2)$ , (for instance Le Roy (12) fitted the experimental data to an expansion up to  $(v + 1/2)^{10}$ ), thereby affecting the coefficients of the lower powers. This can have a marked effect, as can be seen in Table 3. The second column of figures was obtained from the same experimental data using eqn. (42) in place of eqn. (4)

$$\sigma = \sigma_e + \omega_e'(v' + 1/2) - \omega_e'x_e'(v' + 1/2)^2 + \omega_e'y_e'(v' + 1/2)^3 - \omega_e''(v'' + 1/2) + \omega_e''x_e''(v'' + 1/2)^2 \quad (42)$$

It is clear that the more sophisticated expression produces marked changes in the parameters and, in general, brings them closer to the accepted values.

Because of these problems, the emphasis should be on precision (internal consistency, standard deviation) in evaluating reports rather than accuracy (closeness to some tabulated accepted value). It is one of the advantages of multiple linear regression that error estimates of the parameters can be obtained easily, careful work produces small standard de-

viations and should be treated as more desirable than work that produces a mean value close to the accepted value but which has a large standard deviation.

Table 4 summarizes the method of calculation of the parameters in a logical order.

### Conclusion

This paper presents equations and techniques for calculating and interpreting many of the spectroscopically important parameters associated with the ground ( $^1\Sigma_g^+$ ) and second excited ( $^3\Pi_{ou}^+$ ) states of the iodine molecule. It also shows students that in physical chemistry the obtaining of experimental data in the laboratory is often only a small part of the total time commitment compared to the detailed analysis of data.

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