

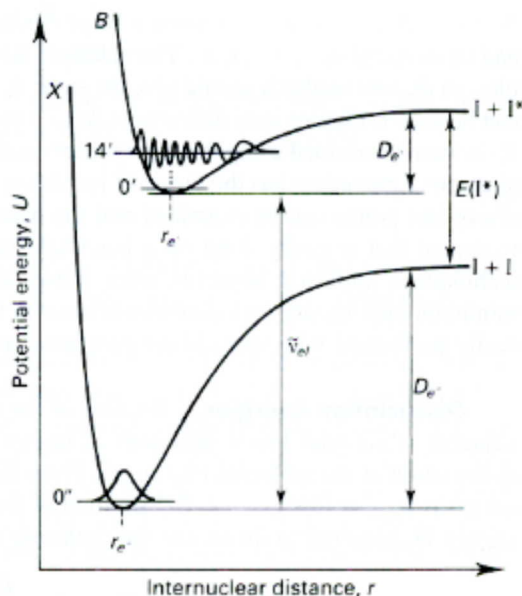
## EXPERIMENT 40

### Absorption and Emission Spectra of Molecular Iodine

Although the electronic spectra of condensed phases are typically quite broad and unstructured, the spectra of small molecules in the gas phase often reveal a wealth of resolved vibrational and rotational lines. Such spectra can be analyzed to give a great deal of information about the molecular structure and potential energy curves for ground and excited electronic states.<sup>1,2</sup> The visible absorption spectrum of molecular iodine vapor in the 490- to 650-nm region serves as an excellent example,<sup>3-5</sup> displaying discrete vibrational bands at moderate resolution and extensive rotational structure<sup>6</sup> at very high resolution. The latter structure is not seen at a resolution of  $\sim 0.2$  nm, a common limit for commercial ultraviolet-visible spectrophotometers, but the vibrational features can be easily discerned in both absorption and emission measurements. In this experiment, the absorption spectrum of  $I_2$  will be used to obtain vibrational frequencies, anharmonicities, bond energies, and other molecular parameters for the ground  $X^1\Sigma_g^+$  and excited  $B^3\Pi_{0u}^+$  states involved in this electronic transition. As an additional option, emission spectra<sup>7,8</sup> can be used to measure many more vibrational levels of the  $X$  state and hence to get improved values of the ground-state parameters.

#### THEORY

The relevant potential energy curves for  $I_2$  are depicted in Fig. 1, which also shows some of the parameters to be determined from the spectra. The spacings between levels in the two electronic states can be measured by either absorption or emission spectroscopy. Emission occurs following an absorption event if the upper state is not relaxed by a nonradiative collisional process (called *quenching*). The emission is termed *fluorescence*, and the transition between two states is said to be spin-allowed if the states have the same



**FIGURE 1**

Potential-energy diagram for molecular iodine. The energy zero has been arbitrarily set at the minimum of the ground-state potential.

spin multiplicity (e.g., both are singlets or both are triplets). Fluorescence intensities are usually high, and the lifetime of the emitting state is short ( $\sim 10^{-8}$  s). If the multiplicity changes in the transition, the emission is termed *phosphorescence*. In that case, the intensity is lower and the lifetime is longer ( $\sim 10^{-3}$  s), since the transition is "forbidden" by the spin-selection rules (which are only approximate owing to electron spin-orbit interactions). There is no strict selection rule for the change  $\Delta v$  in vibrational quantum number during an electronic transition; thus sequences of transitions are observed. Each band in the sequence contains rotational structure which, for  $I_2$ , is subject to the selection-rule constraint that  $\Delta J = \pm 1$ .<sup>9</sup>

As discussed in Exp. 39, the frequency  $\bar{\nu}$  (in wavenumbers) for a transition between vibrational levels  $v''$  and  $v'$  is given by<sup>9</sup>

$$\bar{\nu} = T' - T'' + G(v') - G(v'') + F(J') - F(J'') \quad (1a)$$

$$= \bar{\nu}_{el} + G(v') - G(v'') \quad (1b)$$

where  $\bar{\nu}_{el} = T' - T'' = T'$  since  $T'' = 0$  for the ground electronic state.  $G(v)$  is the vibrational term value, which, for an anharmonic oscillator, is

$$G(v) = \bar{\nu}_e(v + \frac{1}{2}) - \bar{\nu}_e x_e(v + \frac{1}{2})^2 + \bar{\nu}_e y_e(v + \frac{1}{2})^3 + \dots \quad (2)$$

The rotational-term difference  $F(v', J') - F(v'', J'')$  will be ignored, since the rotational structure is not resolved in this experiment. The cubic term in  $G(v)$  is also small and can be neglected in obtaining the transition frequency

$$\bar{\nu}(v', v'') = \bar{\nu}_{el} + \bar{\nu}'_e(v' + \frac{1}{2}) - \bar{\nu}'_e x'_e(v' + \frac{1}{2})^2 - \bar{\nu}''_e(v'' + \frac{1}{2}) + \bar{\nu}''_e x''_e(v'' + \frac{1}{2})^2 \quad (3)$$

If the quantum numbers  $v'$  and  $v''$  are known, the measured frequencies in an absorption or emission spectrum can then be used with a multiple linear least-squares technique (see Chapter XXII) to determine the parameters  $\bar{\nu}_{el}$ ,  $\bar{\nu}'_e$ ,  $\bar{\nu}'_e x'_e$ ,  $\bar{\nu}''_e$ , and  $\bar{\nu}''_e x''_e$ .

An alternative analysis procedure that is often used concentrates on the determination of  $\bar{\nu}_e$ ,  $\bar{\nu}_e x_e$  parameters within each electronic state. Differences between levels in the upper state are obtained from

$$\Delta\bar{\nu}(v') \equiv \bar{\nu}(v' + 1, v'') - \bar{\nu}(v', v'') = \bar{\nu}'_e - 2\bar{\nu}'_e x'_e(v' + 1) \quad (4)$$

A plot of  $\Delta\bar{\nu}(v')$  versus  $v'$ , termed a Birge-Sponer plot, will thus have a slope of  $-2\bar{\nu}'_e x'_e$  and an intercept of  $\bar{\nu}'_e - 2\bar{\nu}'_e x'_e$ . The values of  $\Delta\bar{\nu}(v')$  for all  $v''$  values are combined in this plot, so the two methods should give the same  $\bar{\nu}'_e$  and  $\bar{\nu}'_e x'_e$  parameters. A similar treatment can be used for lower-state differences  $\Delta\bar{\nu}(v'')$  to yield  $\bar{\nu}''_e$  and  $\bar{\nu}''_e x''_e$ . The electronic spacing  $\bar{\nu}_{el}$  is then determined using these parameters and the observed frequencies in Eq. (3). This alternative procedure has the virtue of providing a visual representation of the data so that discordant points can be examined and the data can be fitted with a single least-squares treatment that is easily done on a hand-held calculator. The multiple linear regression technique is preferred, however, since it uses all the data with equal weighting and has minimum opportunity for calculational error in forming differences. Such regressions are easily performed with spreadsheet programs, as discussed in Chapter III.

**Dissociation Energies.** Because of the anharmonicity term, the spacing between adjacent vibrational levels decreases at higher  $v$  values, going to zero at the point of dissociation of the molecule into atoms. From Eq. (4), the value of  $v = v_{\max}$  at which this occurs is  $v_{\max} = (1/2x_e) - 1$ . Substitution of this into Eq. (2) gives an expression for the energy  $D_e$  required to dissociate the molecule into atoms:

$$D_e = G(v_{\max}) = \frac{\bar{\nu}_e(1/x_e - x_e)}{4} \quad (5)$$

The energy  $D_0$  to dissociate from the  $v = 0$  level is smaller than  $D_e$  by the zero-point energy  $G(0) = \tilde{\nu}_e/2 - \tilde{\nu}_e x_e/4$ , so

$$D_0 = \frac{\tilde{\nu}_e(1/x_e - 2)}{4} \quad (6)$$

The expressions used in Eqs. (3) to (6) assume that  $\tilde{\nu}_e y_e$  and higher-order anharmonicity terms can be neglected, an approximation that is good for the  $B$  state of  $I_2$  but more typically leads to  $D_e$  values that are high by 10 to 30 percent. The error for the  $X$  ground electronic state is particularly large if only the absorption data are used to deduce  $\tilde{\nu}_e''$ ,  $\tilde{\nu}_e'' x_e''$ , and  $D_e''$  since only the  $v'' = 0, 1, 2$  levels are appreciably populated at room temperature. Extension to higher levels,  $v''$  up to  $\sim 30$ , is possible using the emission spectrum, so that improved values of  $\tilde{\nu}_e''$  and  $\tilde{\nu}_e'' x_e''$  are obtained. The value of  $D_e''$  remains poorly determined, however, since even the  $v'' = 30$  level is less than halfway to the dissociation limit.

A more accurate value of  $D_e''$  can be obtained by combining  $\tilde{\nu}_{el}$  and  $D_e'$  values with  $E(I^*)$ , the difference in electronic energy of the iodine atoms produced by dissociation from the  $X$  and  $B$  states. The value of  $E(I^*)$  is known to be  $7603 \text{ cm}^{-1}$  from atomic spectroscopy,<sup>10</sup> so that, as seen in Fig. 1,

$$D_e'' = \tilde{\nu}_{el} + D_e' - E(I^*) \quad (7)$$

**Potential Functions.** Near the minimum in the potential-energy curve of a diatomic molecule, the harmonic-oscillator model is usually quite good. Therefore, the force constant  $k_e$  can be calculated from the relation

$$k_e = \left( \frac{\partial^2 U}{\partial r^2} \right)_{r_e} = \mu (2\pi c \tilde{\nu}_e)^2 \quad (8)$$

where  $\mu$  is the reduced mass and  $c$  is the speed of light in  $\text{cm s}^{-1}$  units. The constant  $k_e$  is the curvature of the potential curve at the minimum distance  $r_e$  and, like the dissociation energy, serves as a measure of the bond strength.

At large displacements from the equilibrium position, the harmonic representation of the potential energy is invalid and a more realistic model is necessary. One simple function that is often employed is the Morse potential,

$$U(r - r_e) = D_e \{ \exp[-\beta(r - r_e)] - 1 \}^2 \quad (9)$$

which has the desired values of 0 at  $r = r_e$  and  $D_e$  at  $r = \infty$ . The parameter  $\beta$  is determined by equating  $k_e$  to the curvature of the Morse potential at  $r = r_e$ , yielding

$$\beta = \left( \frac{k_e}{2hcD_e} \right)^{1/2} \quad (10)$$

This three-parameter function provides a very good approximation to the real potential-energy curve at all distances except  $r \ll r_e$ , a region of no practical significance.

**Rotational Structure.** Although rotational structure is not resolved in the present  $I_2$  absorption experiment, each vibrational band consists of  $P$  ( $\Delta J = -1$ ) and  $R$  ( $\Delta J = +1$ ) branches as discussed in Exp. 37. For vibrational changes *within* a given electronic state, such as those measured for HCl in Exp. 37, the  $P$  and  $R$  branches are distinct, with a pronounced dip between them that characterizes the missing  $Q$  branch frequency for the "pure" vibrational transition (see Fig. 37-3). The spacing between lines in each branch is not constant, a slight asymmetry arising from a quadratic term [see Eqs. (37-9, 37-10; 38-11)],

$$\tilde{\nu} = \tilde{\nu}_0 + (B' + B'')m + (B' - B'')m^2 \quad (11)$$

This is a general equation for the transition frequencies in which  $m = -J$  for the  $P$  lines and  $m = J + 1$  for the  $R$  lines. For  $B' < B''$ , the  $m^2$  term causes a decrease (increase) in line spacing in the  $R(P)$  branch at high  $J$  values. The resultant asymmetry is small for HCl, since  $B' - B''$  is small.

If the upper and lower levels of a transition correspond to *different* electronic states,  $B' - B''$  is generally much larger and the corresponding quadratic term in Eq. (11) will often cause a frequency maximum ( $B' < B''$ ) in the  $R$  branch or a frequency minimum ( $B' > B''$ ) in the  $P$  branch. This reversal in the progression of lines at low values of  $J$  produces a sharp *band head*, which in the case of  $I_2$  occurs on the  $R$  branch edge at a  $J$  value as low as  $J = 2$ . The  $R$  branch thus folds back and merges with the  $P$  branch so that only a single band is seen for each transition to a vibrational level. A transition frequency measured at the intensity maximum of this band will be *lower* than the "pure" vibrational transition frequency assumed in Eq. (3). This error is not constant, varying from 20 to  $50 \text{ cm}^{-1}$  for  $I_2$  as  $v'$  increases from 0 to the dissociation limit. For this reason, in the present experiment, band-head frequencies, rather than band maxima, will be measured to obtain the best values of the transition frequencies and the vibrational spacings.

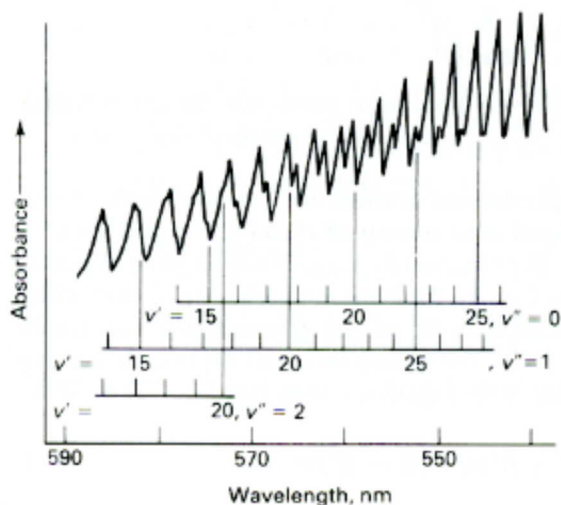
The *emission* of bands of  $I_2$  will also contain many rotational lines if the spectral width of the excitation source is broad enough to populate many upper-state levels. However, if the source is *monochromatic*, excitation to a single  $v'$ ,  $J'$  level can occur and the resultant spectral emission is greatly simplified. Assuming that there is no change to another level in the upper state owing to collisions, the emission to a given lower  $v''$  level will consist of only the two transitions corresponding to  $\Delta J = -1$  and  $\Delta J = +1$ . Since there is no restriction on  $\Delta v$ , one will observe sequences of doublets whose large spacings give the vibrational-level separations in the ground electronic state. The small spacing corresponds to  $2B''(2J' + 1)$ , the separation between the  $J'' = J' + 1$  and  $J'' = J' - 1$  levels in the lower  $v''$  state. If a doublet of known  $J'$  value can be resolved, the splitting can be used to determine the rotational constant  $B''(v'')$ .

## EXPERIMENTAL

**Absorption Spectrum.** The absorption spectrum of  $I_2$  vapor is easily obtained with any commercial visible spectrometer having a resolution of about 0.2 nm or better; see Fig. 2. A general description of such spectrometers is given in Chapter XX, and the

**FIGURE 2**

A portion of the medium-resolution spectrum of the visible  $B \leftarrow X$  iodine absorption spectrum with assignments for the overlapping progressions for  $v'' = 0, 1, 2$ . The upper-state  $v'$  values are indicated at the estimated band-head positions on the short-wavelength side of each transition; the band maxima are at the *top* of the figure.



instrument manual of the instrument to be used should be consulted for specific operational details. Follow the guidelines provided by the instructor in recording the spectra at the highest resolution possible with the instrument. Calibration corrections to the wavelength readout should be provided or made as described in Chapter XX. Unless these are quite variable over the 450- to 650-nm range, a single correction value is sufficient.

Crystals of  $I_2$  can be placed in a conventional glass cell of 100-mm length which is then closed with a Teflon stopper. A usable spectrum can be obtained at room temperature (vapor pressure of  $I_2 \sim 0.2$  torr), although the absorption is much more intense if the cell is wrapped with heating tape to raise the temperature to  $\sim 40^\circ\text{C}$  (vapor pressure  $\sim 1$  Torr). In this case, to avoid condensation of  $I_2$ , the windows should be heated to a higher temperature by wrapping the ends of the cell with extra coils of heating tape.