4. *Ibid.*, pp. 40–42.
5. *Ibid.*, p. 161.
6. A. Gatterer, "Grating Spectrum of Iron," Specola Vaticana, Vatican City (1951); C. E. Moore, "Atomic Energy Levels," vol. II, p. 49*ff*, Natl. Stand. Ref. Data Ser.-Natl. Bur. Stand. 35, U.S. Government Printing Office, Washington, D.C. (1971).
7. G. Herzberg, *op. cit.*, p. 32.
8. K. P. Huber and G. Herzberg, "Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules," Van Nostrand-Reinhold, New York (1979); R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra," 4th ed., p. 217*ff*, Chapman and Hall, London (1976).
9. G. Herzberg, *op. cit.*, p. 46.

GENERAL READING

G. Herzberg, *op. cit.*, chap. IV.
J. M. Hollas, "Modern Spectroscopy," Wiley, New York (1987).
J. I. Steinfeld, *op. cit.*, chap. 5.

EXPERIMENT 42
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.[1,2] The visible absorption spectrum of molecular iodine vapor in the 490 to 650 nm region serves as an excellent example,[3–5] displaying discrete vibrational bands at moderate resolution and extensive rotational structure[6] at very high resolution. The latter structure is not seen at a resolution of ~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[7,8] 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

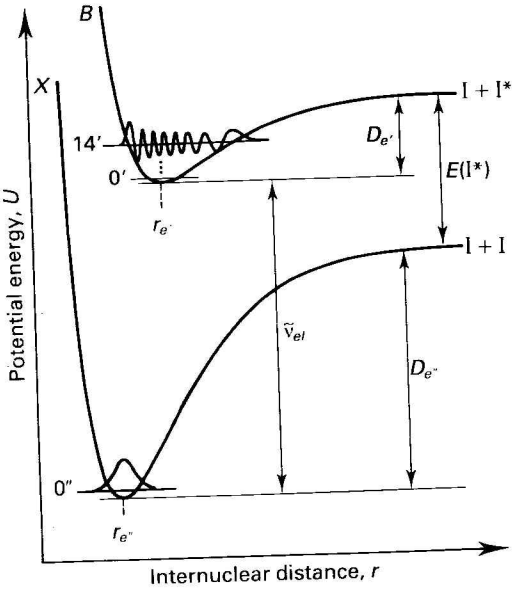

FIGURE 1
Potential energy diagram for molecular iodine. The energy zero has been arbitrarily set at the minimum of the ground state potential.

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 non-radiative 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 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 Δv 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 $\Delta J = \pm 1$.[9]

As discussed in Exp. 41, the frequency $\tilde{\nu}$ (in wavenumbers) for a transition between vibrational levels v'' and v' is given by,[9]

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

$$\simeq \tilde{\nu}_{el} + G(v') - G(v'') \tag{1b}$$

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

$$G(v) = \tilde{\nu}_e(v + \tfrac{1}{2}) - \tilde{\nu}_e x_e(v + \tfrac{1}{2})^2 + \tilde{\nu}_e y_e(v + \tfrac{1}{2})^3 + \cdots \tag{2}$$

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

$$\tilde{\nu}(v', v'') = \tilde{\nu}_{el} + \tilde{\nu}_e'(v' + \tfrac{1}{2}) - \tilde{\nu}_e'x_e'(v' + \tfrac{1}{2})^2 - \tilde{\nu}_e''(v'' + \tfrac{1}{2}) + \tilde{\nu}_e''x_e''(v'' + \tfrac{1}{2})^2 \quad (3)$$

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 XX) to determine the parameters $\tilde{\nu}_{el}$, $\tilde{\nu}_e'$, $\tilde{\nu}_e'x_e'$, $\tilde{\nu}_e''$, and $\tilde{\nu}_e''x_e''$.

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

$$\Delta\tilde{\nu}(v') \equiv \tilde{\nu}(v' + 1, v'') - \tilde{\nu}(v', v'') \simeq \tilde{\nu}_e' - 2\tilde{\nu}_e'x_e'(v' + 1) \quad (4)$$

A plot of $\Delta\tilde{\nu}(v')$ versus v', termed a Birge–Sponer plot, will thus have a slope of $-2\tilde{\nu}_e'x_e'$ and an intercept of $\tilde{\nu}_e' - 2\tilde{\nu}_e'x_e'$. The values of $\Delta\tilde{\nu}(v')$ for all v'' values are combined in this plot so that the two methods should give the same $\tilde{\nu}_e'$ and $\tilde{\nu}_e'x_e'$ parameters. A similar treatment can be used for lower-state differences $\Delta\tilde{\nu}(v'')$ to yield $\tilde{\nu}_e''$ and $\tilde{\nu}_e''x_e''$. The electronic spacing $\tilde{\nu}_{el}$ 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 to be preferred, however, since it uses all the data with equal weighting and has minimum opportunity for calculational error in forming differences. Such regressions are only slightly more complicated on a hand-held calculator, and they are particularly simple on a computer if a spreadsheet program (such as Lotus 1-2-3™ or Symphony™) or a fitting program is available.

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:

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

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 that

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

The expressions used in Eqs. (3)–(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%.