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Potential Curves for the I_2 Molecule

An undergraduate physical chemistry experiment

A study of the visible absorption spectrum of I_2 vapors at low resolution ($\Delta\lambda \approx 0.2$ nm) has become a classic molecular spectroscopy experiment in the undergraduate physical chemistry laboratory. Stafford (*1*) has described an experiment in which the spectroscopic constants $\tilde{\omega}_e$, $\tilde{\omega}_e x_e$, and $\tilde{D}_e$ for the B state of I_2 are obtained from an analysis of the vibrational structure of the spectrum. In a subsequent article (*2*) it was shown how these spectroscopic constants may be utilized to predict thermodynamic properties of the element. In this communication it is shown how a vibrational analysis of the absorption spectrum may be used to predict the equilibrium bond length R_e' of the molecule in the B electronic state ($^3\Pi_{og}$). The value of R_e' is then employed in the construction of an appropriate potential energy curve for this excited state. Our method of analysis makes use of the Franck-Condon principle (*3*), and it is assumed that the potential energy curve of the excited state is well represented by a Morse function (*4*) at small internuclear distances.

Theory

The vibrational-electronic spectrum of I_2 in the region from 640–490 nm displays a large number of well-defined bands, which, for the most part, correspond to $v' \leftarrow 0$ transitions connecting the $v'' = 0$ vibrational level of the ground electronic state (X state) to many different vibrational levels of the B electronic state.[1] Under the conditions of this experiment, the rotational lines within each band are not resolved. However, the peaks may be identified as R-branch band heads (*5*). For a molecule as heavy as I_2, the position of each band head is within a few tenths of one cm^{-1} of the band origin (*6*), and, for the purposes of this experiment, the distinction between the two may be ignored.

Franck-Condon Principle

The relative intensities of the band peaks are related to the vibrational wave functions of the connected states by (*6*)

$$I(\nu) \propto \nu|\int \psi_{v''}\psi_{v'}d\tau|^2 \qquad (1)$$

where ν is the frequency at which the $v' \leftarrow v''$ transition is observed. The lower vibrational state is either the $v'' = 0$ or $v'' = 1$ state in these experiments, whereas v' may run as high as 60.[2] Vibrational energy levels with large quantum numbers ($v' \geq 10$) are characterized by wave functions which tend to localize the oscillator at the inner and outer classical turning points (*7*), $R_{v'}{}^i$ and $R_{v'}{}^o$ (see Figure 1). For large values of the quantum number v', therefore, the major contributions to the integral in eqn. (1) come from small intervals δR about $R_{v'}{}^i$ and $R_{v'}{}^o$. In this approximation the absorption intensity is

$$I(\nu) \propto \nu|\psi_{v''}(R_{v'}{}^i)\psi_{v'}(R_{v'}{}^i) + \psi_{v''}(R_{v'}{}^o)\psi_{v'}(R_{v'}{}^o)|^2\delta R^2 \qquad (2)$$

The physical interpretation of eqn. (2) is usually given in the form of the Franck-Condon principle, which states that the molecule undergoes "vertical" transitions, as indicated in Figure 1. This figure depicts the commonly occurring case in which the potential energy curve of the excited electronic state is displaced toward larger internuclear distances with respect to the ground state, due to the weakening of the chemical bond. At the large internuclear distances of the outer turning points the lower state vibrational wave function is vanishingly small, and the intensity function reduces to

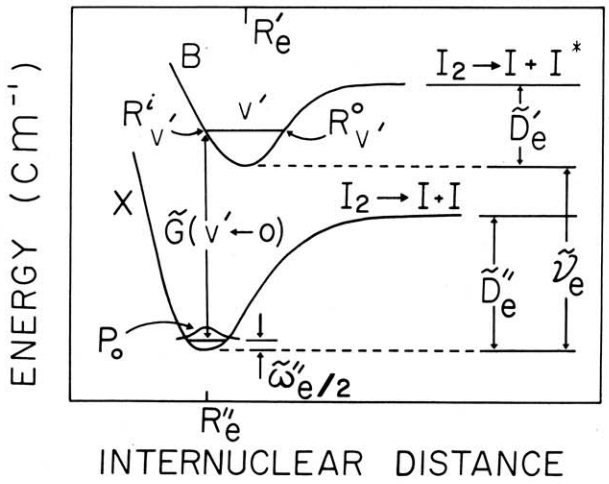

Figure 1. Schematic representation of the potential energy curves for the X and B electronic states of I_2.

$$I(\nu) \propto \nu(\psi_{v''}{}^2(R_{v'}{}^i)\delta R)(\psi_{v'}{}^2(R_{v'}{}^i)\delta R) \qquad (3)$$

which is the product of the probabilities of finding the molecule near the internuclear distance $R_{v'}{}^i$ when it is in the v'' and v' vibrational-electronic states, respectively. It was noted above, however, that for the upper state (v') there is a 50% probability of finding the molecule at each of its classical turning points. That is, $\psi^2{}_{v'}{}^2(R_{v'}{}^i)\delta R = 0.5$. Substituting this relation into eqn. (3) one obtains the following expression for the absorption intensity

$$I(\nu) \propto \nu\psi_{v''}{}^2(R_{v''}{}^i)\delta R \qquad (4)$$

Morse Potential

Even in the Born-Oppenheimer approximation (*8*), it is not possible to solve the Schroedinger equation for the electronic motion in diatomic molecules which have more than a few electrons. However, it has been empirically determined that potential energy curves for the low lying electronic states of diatomics can be described with re-

[1]Following standard spectroscopic notation, we denote any quantities pertaining to the upper electronic state with a superscript prime (′); any quantities pertaining to the lower electronic state are denoted with superscript double-prime (″).

[2]The experimental results given in Ref. (*1*) indicate that there may be as many as 65 vibrational levels in the B state.

markable accuracy by the simple three-parameter function of Morse (*4*)

$$U(R) = D_e\{1 - e^{-b(R - R_e)}\}^2 \tag{5}$$

The parameter b measures the curvature of the potential in the neighborhood of its equilibrium position R_e, and this particular version of the Morse function has a zero of energy at $R = R_e$.

The exponential form of the Morse function cannot properly describe the long-range dispersion forces between atoms (*9*); however, it is generally recognized that this potential function gives a quantitative representation of the electronic eigenvalues at small internuclear distances. In particular, Verma (*10*) has found that the Morse function works well for the ground state of I_2. It is therefore reasonable to assume that a Morse function, with appropriate parameter values, can give an accurate description at small internuclear distances of the potential energy curve for the B state of I_2.

Determination of $\tilde{D}_e'$, b', and R_e'

The potential parameters $\tilde{D}_e'$ and b' for the B state are readily determined from a Birge-Sponer plot for the $v' \leftarrow 0$ transitions (*1*). More precisely, one first obtains the spectroscopic constants $\tilde{\omega}_e'$ and $\tilde{D}_e'$ as outlined in Ref. (*6*), Chapter III, and then b' is computed from the relation

$$b' = \tilde{\omega}_e'\left(\frac{2\pi^2\mu c}{\tilde{D}_e' h}\right)^{1/2} 10^{-8}\ (\text{Å}^{-1}) \tag{6}$$

where $\tilde{\omega}_e'$ and $\tilde{D}_e'$ are in units of cm^{-1}. The remaining parameter R_e' can then be obtained from eqn. (5) above if the value of U can be determined at one particular value of R.

Inspection of Figure 1 reveals that it is possible to determine the value of U at $R = R_e''$, the equilibrium position for the ground electronic state potential energy curve. According to the Franck-Condon principle, as expressed through eqn. (4), the probability distribution P_0 for the $v'' = 0$ level is related to the measured intensities of the peaks in the spectrum by

$$P_0(R) \equiv |\psi_{v''=0}(R)|^2 \delta R \propto \frac{I(\nu)}{\nu} \tag{7}$$

where ν is the frequency of the vertical transition originating from the internuclear distance R. Since the maximum in P_0 occurs at $R = R_e''$, the vertical transition corresponding to the maximum in the function $I(\nu)/\nu$ originates from $R = R_e''$. This transition energy is denoted by $\tilde{G}(v' \leftarrow 0)$ in Figure 1. The electronic transitions leave the system in the B state with potential energy $U(R_e'')$, relative to the minimum in the B state potential energy curve. The relationship between the measured quantity $\tilde{G}(v' \leftarrow 0)$ and the potential energy is given by

$$U(R_e'') = \tilde{G}(v' \leftarrow 0) + \frac{\tilde{\omega}_e''}{2} - \tilde{\nu}_e \tag{8}$$

where ω_e'' and $\tilde{\nu}_e$ are defined in Figure 1. The value of $\tilde{\omega}_e''$ is given in the Appendix to Reference (*6*) as 214.6 cm^{-1}. Solving eqn. (5) for R_e', one obtains[3]

$$R_e' = R_e'' + \frac{1}{b'}\left\{\ln\left(1 + \sqrt{\frac{U(R_e'')}{\tilde{D}_e'}}\right)\right\} \tag{9}$$

Experimental

Suitable low resolution visible spectra of I_2 vapors in air were obtained on a Varian Techtron 635 spectrophotometer. The cell path length was 100 mm, and the cell was at room temperature. The output was recorded on a Heath-Schlumberger EU-205-11 multispeed recorder which was equipped with a potentiometric amplifier and a DC offset module. The wave length drive was calibrated by a factory representative, and both it and the stepmotor were sufficiently linear that further calibrations were found to be unnecessary. A scan rate of 12 nm/min was used. At long wave lengths the chart speed was set to record the spectrum at a rate of 4 nm/in. In the band convergence region ($\lesssim$520 nm) the signal was amplified, and the chart speed was increased to record at 2 nm/in. With the optical resolution set at 0.2 nm, it was possible to observe as many as 60 $v' \leftarrow 0$ transitions. Spectral assignments were based on the analysis of high resolution I_2 spectra by Steinfeld (*11*), which indicated a wave length accuracy of ±0.3 nm using the above equipment.

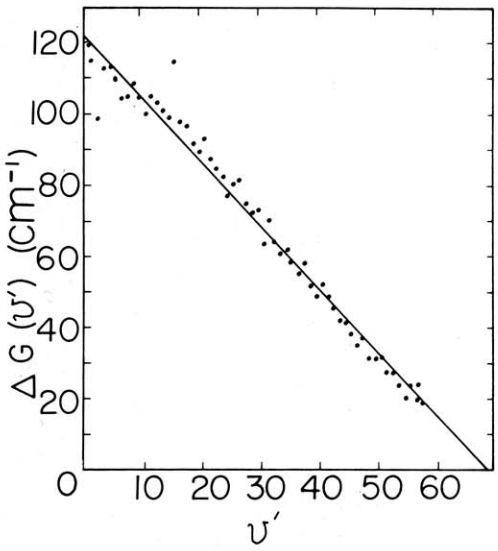

Figure 2. Birge-Sponer plot for $v' \leftarrow 0$ transitions in the visible spectrum of I_2. The slope of the line, as determined by the method of least squares, is $-1.780\ cm^{-1}$. The x-axis intercept is at $v' = 68.3$, and the y-intercept is at $\Delta G(0) = 121.6\ cm^{-1}$.

Spectroscopic Constants and Potential Parameters[a]

	Experimental	Accepted[b]
$\tilde{\omega}_e'$	123.4	128.0
$\tilde{\omega}_e' x_e'$	0.890	0.834
$\tilde{D}_e'$	4,216	4,398
b'	1.844	1.873
$\tilde{\nu}_e$	15,840	15,642
R_e'	3.002	3.016

[a] All quantities are in units of cm^{-1} except for b' and R_e', which are given in $Å^{-1}$ and Å, respectively.
[b] The accepted values were obtained from Ref. (*6*).

Results and Discussion

A Birge-Sponer plot for the $v' \leftarrow 0$ transitions, taken from a student report, is shown in Figure 2. The data is nearly linear, and the best (least squares) straight line was found to have a slope of $-1.780\ cm^{-1}$. In addition to simplifying the numerical analysis of the spectrum, a linear Birge-Sponer plot has a second important consequence: the vibrational spectrum can be rigorously derived from a Morse potential. That is, the data implies that the Morse functional form may be valid for the B state of I_2 except, of course, at very large internuclear distances. See Ref. (*6*), pp. 101–102 for a discussion of this point.

The values of $\tilde{\omega}_e'$, $\tilde{\omega}_e' x_e'$, and $\tilde{D}_e'$ obtained from this Birge-Sponer plot are listed in the table. For this particular run, the student's results were within about 5% of the accepted values of these spectroscopic constants. Similar accuracy was obtained in a number of other runs. The experimental value of the Morse function parameter b', also listed in the table, was found to be within 2% of the accepted value.

The experimentally determined probability distribution

[3] In the derivation of eqn. (9), the negative root of U/D_e' is used. The positive root does not appear to have physical meaning.

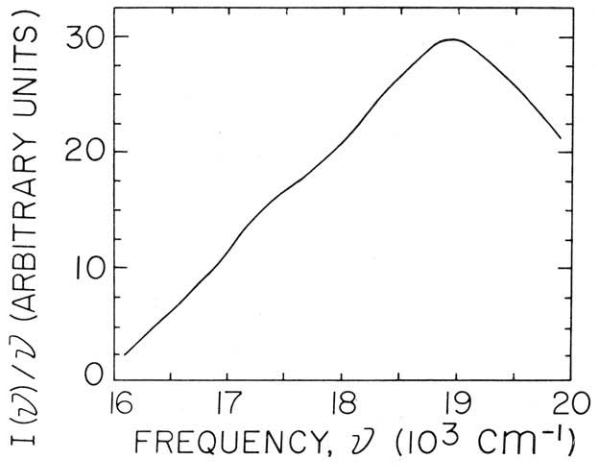

Figure 3. Experimental probability distribution for the I_2 molecule in X electronic state. The Gaussian shape near the maximum indicates that most of the molecules are in the $v'' = 0$ vibrational level. The small "hump" on the low energy side is the contribution from molecules in the $v'' = 1$ state.

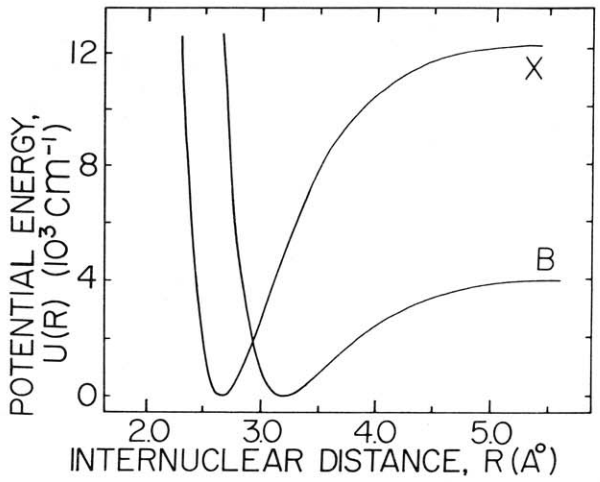

Figure 4. Morse potential energy curves for the X and B states of the I_2 molecule.

P_0 is shown in Figure 3. The data yields a set of discrete points through which a smooth curve has been drawn. The experimental curve has the expected Gaussian shape near its maximum, but there is a hump on the low energy side of the curve due to the superposition of the signal from $v' \leftarrow 1$ transitions. In this particular run, the maximum in the curve was found at 18,903 cm^{-1}, which corresponds to the $33 \leftarrow 0$ transition. Using for $\tilde{\nu}_e$ the experimental value[4] of 15,840 cm^{-1} and for R_e'' the literature value of 2.666 Å, the equilibrium position for the B state potential curve was found to be 3.002 Å. This is in excellent agreement with the literature value (see the table).

The experimental potential parameters listed in the table were used to construct the B state potential energy curve shown in Figure 4. The Morse potential curve for the X state was taken from Ref. (*10*). The curves are displayed side-by-side to emphasize three effects which the electronic transition has on the I_2 chemical bond. There is a decrease in the dissociation energy, there is an increase in bond length, and the "spring" constant (curvature) is smaller.

[4]The frequency ν_e is related to the $0 \leftarrow 0$ transition through the relation $\nu_e = G(0 \leftarrow 0) + \omega_e''/2 - \omega_e'/2$. (See Figure 1.)

Literature Cited

(1) Stafford, F. E., J. CHEM. EDUC., **39,** 626 (1962).
(2) Stafford, F. E., J. CHEM. EDUC., **40,** 249 (1963).
(3) Condon, E. U., *Phys. Rev.*, **32,** 858 (1928).
(4) Morse, P. M., *Phys. Rev.*, **34,** 57 (1929).
(5) Barrow, G., "Introduction to Molecular Spectroscopy," McGraw-Hill Book Co., New York, **1962,** Chap. 10, pp. 238–244.
(6) Herzberg, G. "Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Co., **1950,** p. 171.
(7) Schiff, L. I., "Quantum Mechanics," McGraw-Hill, Book Co., New York, 2nd Ed., **1955,** pp. 65–67.
(8) Born, M., and Oppenheimer, J. R., Ann. Phys., **84,** 457 (1927).
(9) For a discussion of long-range dispersion forces see, Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., "Molecular Theory of Liquids and Gases," John Wiley & Sons, Inc., New York, **1954,** Chap. 12 and 13.
(10) Verma, R. D., *J. Chem. Phys.*, **32,** 738 (1960).
(11) Steinfeld, J., Zare, R., Jones, F., Lesk, M., and Klemperer, W., *J. Chem. Phys.*, **42,** 25 (1965).