

Absorption spectrum of iodine vapor—An experiment

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(Received 20 July 1987; accepted for publication 25 November 1988)

The absorption spectrum of iodine was photographed in the visible region using a 3.4-m Ebert plane-grating spectrograph. An evacuated glass envelope containing a small amount of iodine was used as the absorption cell while a tungsten filament lamp served as the continuous source. A number of band heads were identified and these measurements led to the determination of the dissociation limit, the dissociation energy, the force constant, and the fundamental vibrational frequency of the iodine molecule. Such an experiment will provide the physics major with an introduction to molecular spectra and, in light of the discovery of molecular lasers, it is recommended that such an experiment be included in the undergraduate physics curriculum.

I. INTRODUCTION

The spectra emitted by atoms as a result of energy changes in their electronic system are known as line or atomic spectra. There is another class of spectra, known as band or molecular spectra, emitted by molecules, i.e., when the emitting element is in the molecular state. The fact that spectra of this type are actually due to molecules is readily established by the disappearance of the bands when the emitter is heated to temperatures at which the molecules dissociate into atoms. Three different types of band systems exist in molecules and they are classified as (1) rotation bands caused by the rotation of the molecules; (2) rotation-vibration bands due to the vibrations of the atoms inside the molecules with the superposition of rotational bands; and (3) electronic bands connected with electronic transitions over which are superposed molecular vibrations and rotations. Molecular spectra will be more complicated than atomic spectra because of the additional degrees of freedom of the molecules.

The main purpose of the present experiment is to study one of the band systems of the iodine molecule and to use the data to obtain the dissociation limit, the dissociation energy, and the force constant from the fundamental vibrational frequency of the molecule. These quantities can further be used to study the nature of potential energy curves of various electronic states.

II. THEORY

Absorption or emission of radiation from molecules can occur as a result of changes in their rotational, vibrational, and electronic energies. The energy changes involved in a transition from one electronic state to another are usually large and correspond to radiations in the visible or ultraviolet regions. During these transitions, the vibrational and rotational energies also change, leading to broad emission or absorption lines. An investigation of the structure of these bands enables the determination of molecular constants and dissociation energies in various electronic states.

The variation of the potential energy of a diatomic molecule as a function of internuclear distance for two different electronic states is given in Fig. 1. The curves indicate that, for each of the electronic states, the horizontal lines represent the energies of the allowed vibrational levels.¹ We consider transitions between two vibrational levels belonging

to different electronic states, represented by vertical lines. Detailed theoretical treatments can be found in textbooks^{2,3} and an outline of the methods is presented here.

III. VIBRATIONAL STRUCTURE

Since the energies of the electronic rearrangements and the vibrational motions are so different, the diatomic molecule may be considered to execute vibrations and electronic transitions independently. The total energy of the molecule in the Born-Oppenheimer approximation is given by

$$E = T_e + G(v), \quad (1)$$

where T_e and $G(v)$ are the electronic and vibrational energies in cm^{-1} and are called the electronic and vibrational term values, respectively.⁴ Considering the molecule as an anharmonic oscillator, the vibrational term value is given by

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e X_e(v + \frac{1}{2})^2 + \cdots, \quad (2)$$

where ω_e is the fundamental vibrational frequency, X_e represents anharmonicity, and v can have values 0, 1, 2, 3, ... corresponding to the allowed vibrational levels in an electronic state. It is customary to designate the various vibrational levels in the lower electronic state by v'' and those in the upper electronic state by v' . Since the equilibrium internuclear distances and the nature of the potential energy curves (Fig. 1) may be different in the two electronic

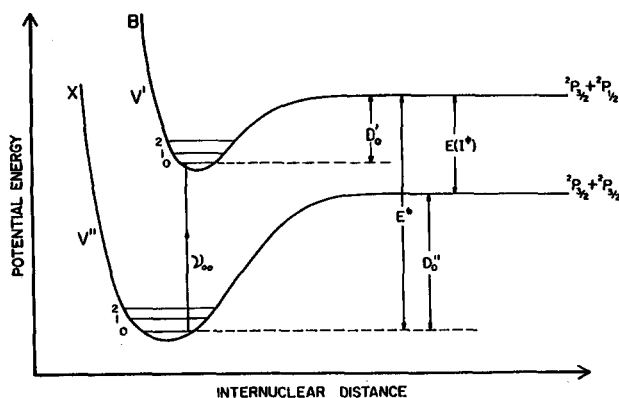


Fig. 1. Potential energy diagram for iodine.

states, we designate by ω_e'' , X_e'' , and ω_e' , X_e' ,... the corresponding fundamental frequencies and anharmonicity constants.

Considering an electronic transition from a vibrational level v'' of lower state to a v' of the upper state, the change in energy involved is

$$\Delta\epsilon = (T_e' - T_e'') + (v' + \frac{1}{2})\omega_e' - (v' + \frac{1}{2})^2\omega_e'X_e' - (v'' + \frac{1}{2})\omega_e'' + (v'' + \frac{1}{2})^2\omega_e''X_e'', \quad (3)$$

where we have neglected the cubic and higher anharmonic terms in $G(v)$. The frequency of the radiation associated with this transition is given by

$$\nu = \nu_e + (v' + \frac{1}{2})\omega_e' - (v' + \frac{1}{2})^2\omega_e'X_e' - (v'' + \frac{1}{2})\omega_e'' + (v'' + \frac{1}{2})^2\omega_e''X_e'', \quad (4a)$$

where

$$\nu_e = (T_e' - T_e''). \quad (4b)$$

In absorption or emission spectra, the spacings and the differences in spacings between successive vibrational bands give us information about the fundamental vibrational frequencies and anharmonicity constants. The frequencies of the transitions from $v'' = 0$ of the lowest state to various v' levels of the upper state in an absorption process are given by

$$\nu = \nu_e + G(v') - G(0). \quad (5)$$

Therefore, the frequencies of two adjacent bands starting from $0 \rightarrow v'$ and $0 \rightarrow v' + 1$ can be written as $\nu_{v'} = \nu_e + G(v') - G(0)$ and $\nu_{v'+1} = \nu_e + G(v' + 1) - G(0)$. Their separation $\Delta\nu$ then becomes

$$\Delta\nu = G(v' + 1) - G(v'). \quad (6)$$

We define the first and second differences $\Delta^1G(v')$ and $\Delta^2G(v')$ for the v' progression with $v'' = 0$, as

$$\begin{aligned} \Delta^1G(v') &= \Delta\nu = G(v' + 1) - G(v'), \\ \Delta^2G(v') &= \Delta^1G(v') - \Delta^1G(v' + 1). \end{aligned} \quad (7)$$

Substituting for $G(v')$, we find that

$$\Delta^1G(v') = \omega_e' - 2(v' + 1)\omega_e'X_e', \quad (8a)$$

$$\Delta^2G(v') = 2\omega_e'X_e'. \quad (8b)$$

We can similarly define

$$\Delta^1G(v'') = \omega_e'' - 2(v'' + 1)\omega_e''X_e'', \quad (9a)$$

$$\Delta^2G(v'') = 2\omega_e''X_e''. \quad (9b)$$

for the v'' progressions observed in an emission experiment, from $v' = 0$ to various v'' levels. For an ideal harmonic oscillator, the anharmonicity constants X_e are zero and hence the band progressions will correspond to equally spaced bands [Eqs. (8) and (9)].

IV. BIRGE-SPONER PLOTS

Absorption and emission spectra thus give us the fundamental frequencies and anharmonicity constants. However, due to anharmonicity, the first differences $\Delta^1G(v')$ or $\Delta^1G(v'')$ will tend to decrease as v' or v'' increase and, at the dissociation limit starting the continuum of levels, $\Delta^1G(v)$ will become zero. Hence,

$$\omega_e - 2(v + 1)\omega_eX_e = 0 \quad (10)$$

gives us the vibrational quantum number $v = v_m$ for the dissociation limit in a given electronic state, as

$$v_m = (1/2X_e) - 1. \quad (11)$$

The dissociation energy (in cm^{-1}) can then be obtained from

$$D = G(v_m) \quad (12)$$

using Eq. (2).

If we now plot a graph of $\Delta G(v)$ vs v for a given progression [Eq. (8a) or (9a)], it will be a straight line with a slope $-2\omega_eX_e$ and an intercept at $v = -1$, equal to ω_e . The straight line can be extrapolated to find v_m or, since the dissociation energy itself is simply the sum of all the increments $\Delta^1G(v)$ from $v = 0$ to $v = v_m$, the area under the graph will give the dissociation energy directly.

However, the cubic and quadratic anharmonic terms in the expansion of $G(v)$ [Eq. (2)] will become very important for large values of v leading to a steeper decrease in $G(v)$ as v increases. With the extensive data available on $\Delta^1G(v)$ vs v in electronic absorption or emission spectra, a graph of $\Delta^1G(v)$ vs v with $\Delta^1G(v)$ falling off more rapidly with v can be plotted and the accurate determination of dissociation energy is obtained by extrapolating the smooth curve and finding the area underneath. This is the principle of the Birge-Sponer extrapolation method.²

The measurements on the bands of v' progression in absorption enable an estimate of ω_e' , $\omega_e'X_e'$, and D_0' . Similarly, measurements on the bands of v'' progression in emission lead to a determination of ω_e'' , $\omega_e''X_e''$, and D_0'' corresponding to the lower electronic state. From our absorption experiments, we can estimate D_0'' using the fact

$$D_0'' = E^* - E(I^*), \quad (13)$$

where 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. $E(I^*)$ is the difference in energy between a ground-state iodine atom ($2P_{3/2}$) and the first excited state of the iodine atom. This value⁴ is taken as 7589 cm^{-1} .

From Fig. 1, we also see that

$$D_0'' + E(I^*) = \nu_{00} + D_0', \quad (14)$$

where ν_{00} is the energy associated with the $0 \rightarrow 0$ transition.⁵

The molecular constants estimated from the vibrational structure can be employed to construct the Morse potential¹ for the given electronic state using

$$U(r - r_e) = D_e(1 - e^{-\beta(r - r_e)})^2, \quad (15)$$

where r_e is the equilibrium internuclear distance,

$$\beta = \omega_e(2\mu c/D_e h)^{1/2}, \quad (16)$$

where c is the velocity of light and μ is the reduced mass of the molecule.

V. EXPERIMENT

The absorption spectrum of iodine was photographed in the visible region using a 3.4-m Ebert plane-grating spectrograph (see Fig. 2). The reciprocal linear dispersion of the spectrograph was about 5 Å/mm . The spectrum can also be recorded employing a simple constant deviation



Fig. 2. The absorption spectrum of I_2 vapor. The left-hand side is about 5383 Å and to the right is the region where the convergence limit of the bands is located (4995 Å).

spectrograph, as is done in the second author's laboratory. Such spectrographs are available in many physics laboratories and have a linear dispersion of about 12 Å/mm. An evacuated glass cell (length about 30 cm and diameter about 1.5 cm) containing a small amount of iodine crystals was used as the absorbing medium. A tungsten filament lamp served as the continuous source. The cell was heated to about 40 °C. An iron arc spectrum was superimposed for calibration. The exposure time was about 10 s for each spectrum. Two 2 × 10-in. Kodak spectroscopic plates (one type O and the other F) were used. Experiments dealing with the iodine spectrum can be found in Refs. 6–9.

VI. RESULTS AND DISCUSSION

In an absorption experiment, the temperature is often near room temperature and the vibrational level $v'' = 0$ is most populated. Hence, we can expect a progression of bands due to transitions $v'' = 0$ to v' varying from zero to larger values. If the vibrational quantum of energy in the lowest state ω_e'' is small (215 cm^{-1} for iodine) or generally if the temperature is high, the number of molecules in the first excited vibrational level becomes significant and this leads to the appearance of band progressions from $v'' = 1$ to various v' values, although with smaller intensities compared to the $v'' = 0$ progressions. However, the separation between the bands in both $v'' = 0$ and $v'' = 1$ progressions will be the same as in Eq. (6).

The vibrational electronic spectrum of iodine in the wavelength region of 4900–6300 Å exhibits a large number of well-defined bands. These bands mostly correspond to $v' \leftarrow 0$ transitions connecting the $v'' = 0$ level of the ground electronic state (X state) to many different vibrational levels v' of the excited electronic state (B state). Some of the bands correspond to transitions between $v'' = 1$ to various v' levels and these have the same separation between them as $v'' = 0$ bands. The wavenumbers of a number of band heads were measured and a large number of pairs identified giving a constant difference of about 125 cm^{-1} , which is the fundamental vibrational frequency of the molecule in the excited electronic state (B state) from Eq. (8a). Detailed analysis of the iodine spectrum using very high-resolution equipment has given the absolute values of v' for these bands.⁵ From the first and second differences $\Delta^1 G(v')$ and $\Delta^2 G(v')$ for the v' progressions with $v'' = 0$, and the absolute values of v'' , the molecular constants ω_e' and $\omega_e' X_e'$ are obtained. The fundamental frequency ω_e'' in the ground electronic state can then be obtained⁵ using Eq. (5).

To obtain the dissociation limit, the Birge–Sponer extrapolation method was used (Fig. 3). Starting with some band head v' , the energy differences $\Delta^1 G(v')$ between successive bands with $v'' = 0$ are plotted against the band number v' . With linear extrapolation to $\Delta^1 G(v') = 0$, the band number v_m' corresponding to the dissociation limit

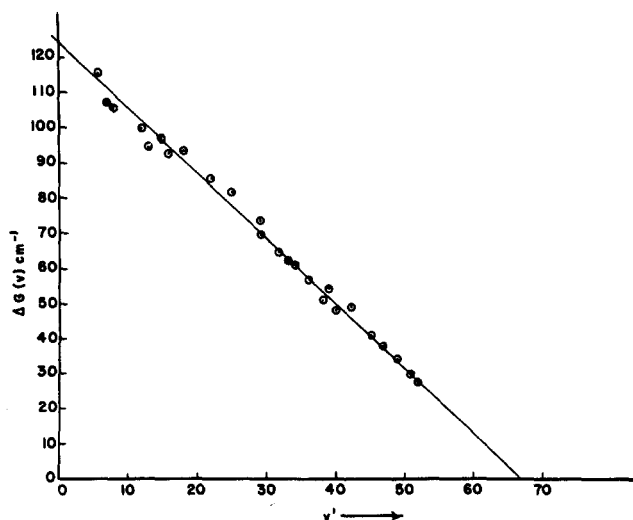


Fig. 3. Birge–Sponer plot for $v' \leftarrow 0$ transitions in I_2 .

was obtained. The dissociation energy (D_0') in the excited state corresponds to an energy $G(v_m')$. The energy of transition from $v'' = 0$ level to the top of the upper state continuum is given by Eq. (14),

$$E^* = \nu_{00} + D_0'.$$

This gives $E^* = 19\,948\text{ cm}^{-1}$. Hence, the dissociation energy D_0'' of the molecule in the ground state calculated from Eq. (13) is $D_0'' = 12\,359\text{ cm}^{-1}$.

The anharmonicity term $\omega_e' X_e'$ for the upper state can be further estimated from the slope of the best straight line drawn through the points in the linear Birge–Sponer curve. This slope gives $\omega_e' X_e' = 0.93$ and the intercept $v' = -1$ gives $\omega_e' = 125$, the vibrational frequency extrapolated to the potential minimum. The force constant k_e' can be obtained from $k_e' = 4\pi^2 c^2 \mu \omega_e'^2$, where μ is the reduced mass of the molecule. The value of $k_e' = 1.73 \times 10^5\text{ dyn/cm}$ compares favorably with the value $1.72 \times 10^5\text{ dyn/cm}$ given in Herzberg.² Other results are tabulated in Table I. The accepted values are taken from Stafford.⁷

The present experiment demonstrates that extensive information on the molecular constants and dissociation energies of the iodine molecule for the first excited state can be obtained from absorption measurements. With the results of high-resolution and emission data, a complete set of molecular constants, dissociation energies, and potential energy curves of diatomic molecules can be accurately estimated for various interacting electronic states.

Table I. Parameters for iodine.

Parameters	Experimental (cm^{-1})	Accepted (cm^{-1})	% difference
E^*	$19\,948 \pm 50$	20 040	0.5
D_0''	$12\,359 \pm 55$	12 440	0.8
ω_e''	214 ± 2	213	0.5
ω_e'	125 ± 3	128	2.3
$\omega_e' X_e'$	0.93 ± 0.04	0.834	12

ACKNOWLEDGMENTS

One of the authors (SG) wishes to acknowledge the help of two of his students: Mark Warner, for taking the spectrogram, and Dale Stanbridge, for making some calculations. He is also grateful to Professor Peter Baine of the Chemistry Department for some helpful comments.

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PROBLEM: THEVENIN EQUIVALENT FOR A CIRCUIT WITH N LOOPS

In Fig. 1 is shown a circuit with an even number of loops, N . All resistances have the same value R_0 , and all sources have an emf of value V_0 . Find the Thevenin equivalent of the circuit between points a and b.

Do the same when the number of loops is $N + 1$, with $N + 1$ an odd number. (Solution is on p. 857.)

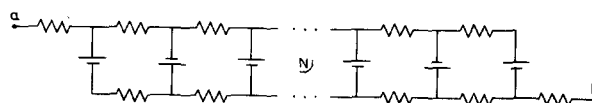


Fig. 1. A circuit with an even number N of loops.