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Band Spectra and Dissociation Energies

A Physical Chemistry Experiment

Physical chemistry now places increased stress upon the interpretation of chemical phenomena in terms of molecular energy levels. An experiment which has proved successful in introducing the spectroscopic determination of molecular energy levels and thermodynamic quantities is the analysis of the visible band spectrum of either iodine or bromine. In addition, this experiment introduces techniques now widely used in high temperature and astro-chemical studies.

While an experiment similar to this has been described by Davies (*1*), it was felt that publication of a revised procedure was in order. The present report[1] describes use of newer and more available equipment, changes the emphasis of the discussion, and lays stress on introducing the standard reference works on the spectroscopy of diatomic molecules.

Approximately four 3-hour laboratory periods are alloted for this experiment. The actual recording of the experimental data, using a recording spectrophotometer, is extremely simple and takes between one and two hours total. The remaining time is devoted to calculations and library work.

The experiment is divided into four parts, of which the last three are assigned at the discretion of the instructor.

(1) The visible absorption spectrum of one or several of the gaseous halogens, Cl_2, Br_2 or I_2 is observed using a recording spectrophotometer. The wavelengths and energies (in cm^{-1}) of the bands of either iodine or bromine) are tabulated and the dissociation energy ($D_0°$) is calculated using the graphical Birge-Sponer extrapolation and the known excitation energies of the product atoms.

(2) A formula is developed for the location of the band heads, and the spectroscopic parameters of the excited electronic state are calculated.

(3) The intensity distribution between the discrete and the continuous parts of the spectrum studied is explained in terms of the Franck-Condon principle and is compared with those of the other spectra taken.

(4) The heat of vaporization of I_2 is calculated from knowledge of the absolute absorption at a given temperature; this part of the experiment will be described in a following article. Normally parts (1) and (3) are assigned. Part (4) is treated as a separate short experiment. Part (2) is assigned to students with special interest in physical chemistry.

The computations for (1) and (2) may be done with the aid of an electronic digital computer. A fortran program for the IBM 709 is available (*2*).

If it is desired to assign only the calculation, without the experimental work, the necessary data may be obtained from Table 6 and Figure 8 of (*3*).

Introductory Information

Nomenclature. In Figure 1 the potential energy, E, is shown as a function of internuclear distance, r, for a diatomic system. This type of diagram is explained in detail in standard texts (*4–6*). The lower curve represents the combination of two halogen atoms in their lowest or *ground* electronic state, to form a stable molecule in the electronic state called X. The letter X is accepted nomenclature to indicate the lowest or *ground* electronic state of the molecule; the next levels in order of increasing energy are designated A, B, C.[2]

[1] A more extensive treatment and more detailed instructions to students are available from the author and will be sent to interested readers upon request.

[2] In addition to these letter symbols, atomic and molecular electronic energy levels are given special descriptive symbols. For instance, $^2P_{3/2}$ and $^2P_{1/2}$ represent the ground and first excited states of the halogen atoms. $^1\Sigma_g{}^+$ and $^2\Pi^+{}_{ou}$ represent what we have called the X and B states of the diatomic halogen molecules, and follow the rule that Roman letters represent atomic states; Greek letter, molecular states.

Quantum numbers for the upper state of a transition are denoted by a single prime (′) and indicated first; those for the lower state are indicated by a double prime (″) and indicated second. The direction of the transition is indicated by an arrow.

Two halogen atoms in the ground state may combine also with a slightly different electronic configuration to form another stable state. Since this is the first stable state above the ground state, it is given the prefix A. This state gives rise to an absorption spectrum lying toward the red side of the "visible" system which is not used in this experiment.

The upper curve indicates that a normal atom can combine with an excited atom I* of energy $E(\mathrm{I}^*)$ to form a stable configuration labeled B. The observed light absorption in the visible region to be studied involves this and the ground state. Therefore we designate this state by a single prime (′).

The important spectroscopic terms D_e and D_0 are defined in this diagram. A useful memnonic trick is that e stands for "extrapolated."

The difference in energy characteristic of the two states X and B is labeled ν_e. In each electronic level, the different vibrational levels are shown and are numbered $v = 0, 1, 2, \ldots$. The characteristic vibrational energies, grossly exaggerated in size, are labeled ω' and ω''. Associated with each vibrational level are many rotational levels whose spacing is much smaller than the ω and hence cannot be shown conveniently on this diagram. When indicated, they are almost always designated by a quantum number called J.

Spectra. One possible change in the molecule's internal energy is indicated in Figure 1 by the arrow labeled 1. The transition is to the second vibrational level of the B electronic state from the 0th vibrational level of the X state. This may be written in abbreviated form

$$(B,v' = 2 \leftarrow X, v'' = 0) \qquad (1)$$

where the direction of the arrow indicates absorption. If it is understood which two electronic states are involved, one may write $(2' \leftarrow 0'')$. The energy involved in this transition is

$$\Delta E = \Delta E(\text{electronic}) + \Delta E(\text{vibrational}) \qquad (2)$$

where the change in rotational energy has been omitted because it cannot be resolved in the present experiment. In the usually accepted spectroscopic notation (*4*), the symbols for the energy change and for electronic and vibrational energy (in cm^{-1}) are respectively ν, T_e, and $G(v)$. Equation (2) then becomes:

$$\nu = (T_e' - T_e'') + (G' - G'') \text{ (in cm}^{-1}) \qquad (2a)$$

It may happen that the change in energy occurs by

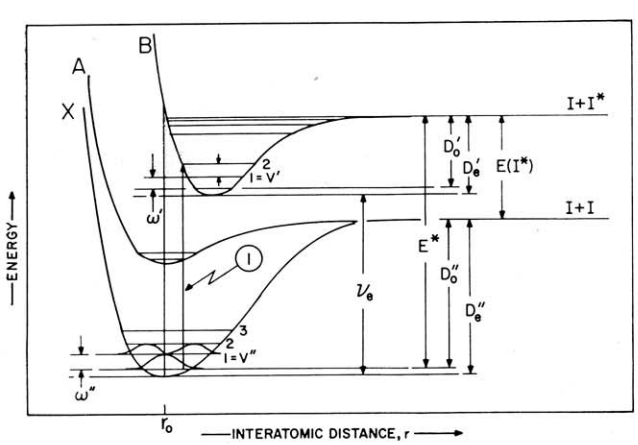

Figure 1. Representative potential energy curves for diatomic homonuclear halogens.

the emission or absorption of radiation resulting in a spectrum. A representative absorption spectrum, that of I_2 in the presence of air, is shown in Figure 2. Each small "bump," such as that indicated by the arrow 1, corresponds to a transition between two vibrational levels (v', v'') as indicated by the arrow 1 in Figure 1 and is called a *band*. When observed with a spectrograph of extremely high resolution these would be seen to consist of many fine lines, each corresponding to transitions between individual rotational levels. The maxima in this case are *band heads* and are due to a superposition of many rotational lines.

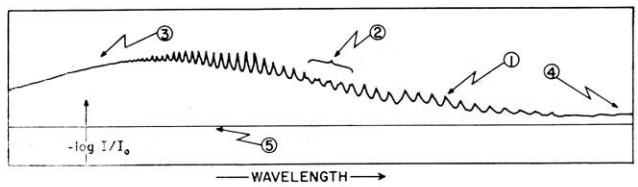

Figure 2. Spectrum of $I_2(g)$ taken in the presence of air with a Cary Model 11 Spectrophotometer. The scan is from 6500 to 4000 Å. Ordinates are $-\log I/I_0$ versus wavelength. (1) A band head. (2) Region where (v′, 1″) bands appear in the I_2 spectrum. (3) Region in which the convergence limit is located. (4) Start of the $(A - X)$ near-infrared bands (not used in this experiment). (5) "Base" line.

In the region marked 2 (iodine spectrum only), secondary maxima are observed and are bands due to absorption from vibrational level 1. The occurrence and location of these bands will be explained in terms of the Franck-Condon principle.

At a certain point, 3, called the *convergence limit*, the spacing between the bands becomes zero. The energy of the corresponding transition is shown as E^* in Figure 1 and corresponds to the formation of two free atoms, one of which is in an excited electronic state indicated by I*. Beyond the convergence limit the spectrum is continuous and corresponds to photodissociation yielding atoms with continuously variable amounts of kinetic energy. One of the aims of this work is to locate this convergence limit by means of the Birge-Sponer extrapolation.

Literature on Molecular Spectra. The appearance of molecular spectra is discussed in detail in the classic volume by Herzberg (*4*), chapter II. The theory of spectra is given by Herzberg and by Gaydon (*5*). Before reading these it might be well for students to read first a brief résumé in a text such as Pitzer (*6*), Moore (*7*), Barrow (*8*), or Glasstone (*9*). Photographs of the iodine spectrum are presented and discussed by Herzberg (ref. (*4*), Fig. 15) and Gaydon (ref. (*5*), Fig. 1). Gaydon also discusses Cl_2 and Br_2. Molecular parameters, including interatomic distances and vibration frequencies are given in ref. (*4*), Table 39, where the molecules are listed in approximately alphabetical order.

The Experiments

Instruments. Both the Beckman DK-2 and the Cary Model 11 have been used by our students. The DK-2 is of lower resolution and precision than the Cary. Also it is non-linear in both wavelength and energy, necessitating a more tedious reduction of the data. Data taken with the DK-2 give a Birge-Sponer extrapolation which has quite a bit of scatter, but which is

usable. Data from the Cary are easy to reduce because of the linear wavelength scale and give a very satisfactory B-S extrapolation. These spectrophotometers do have the advantage of being readily available in most laboratories and of eliminating the long work involved in exposing and processing photographic plate.

There is no change from instrumental procedure given by the manufacturers. The data obtained give the dissociation energy to $\pm 2\%$.

Reagents. Gaseous iodine is obtained by placing some iodine crystals in a 100 mm (or longer) absorption cell. Although a usuable absorption is obtained at room temperature, it is better to heat the cell to 35–40°C. Chlorine or bromine may be obtained "off the shelf." The spectrum of Cl_2 is taken only for discussion of the Franck-Condon principle. Its absorption is almost completely in the continuous part of the spectrum and cannot be used easily to determine a dissociation energy.

Observations of bands due to ICl and IBr was attempted (*5*, *6*). Cl_2 or Br_2 was mixed with I_2 over a platinum catalyst. Changes in the observed spectra indicated that reaction had occurred. However the data taken could not be used for determination of dissociation energies because spectra overlapped and resolving power was insufficient.

Calibration of Spectrophotometer. While most manufacturers sell special mercury lamps for calibration purposes, we have had good success using a simple Westinghouse or GE 4-watt germicidal lamp. (Total cost of lamp and ballast is less than $10.) In the case of the Cary, the tungsten lamp is pushed out of the way (to the hydrogen lamp operating position), and the germicidal lamp suspended in front of the opening to the spectrometer, approximately where the tungsten lamp had been. Even without collimating lenses, adequate intensity is obtained. In other instruments, similar techniques are possible. In all cases, the spectrophotometer is then run according to the instructions for "calibration," "emission," or "energy" supplied by the manufacturer.

Unless the calibration (*10*) shows drastic discrepancies, it is sufficient to correct only the wavelength at the start of the Birge-Sponer extrapolation. The calibration curve may be used to estimate the error or scatter expected in the data points.

If the heat of vaporization of iodine is to be calculated by the "absolute entropy" method, the temperature of the sample should be recorded, preferably at the time the region near 5200 Å is being scanned, and a blank run made to determine the zero line. These absolute entropy calculations are described in a following article (*11*).

Treatment of Experimental Data

The experimental data are the intensities of the bands and their position on the recording produced by the spectrophotometer. Figure 2 is a spectrum traced from student data.

First the bands are numbered. Detailed analyses of the I_2 and Br_2 spectra using very high resolution equipment have given the absolute values (*12*) of the v' for these bands. They may be assigned by using the figures given in Table 1. Any (v', 1'') bands, which for I_2 fall in the region marked 2 in Figure 2, should not be included in this numeration, but may be assigned their own numbers. The positions of the band heads are converted to wavelengths λ, then energies ν in cm^{-1}, and the first differences, $\Delta\nu$, taken. Data taken with a spectrophotometer are not sufficiently accurate to necessitate correction for the index of refraction of air.

Dissociation Energy. Of the different means available for obtaining dissociation energies from the spectroscopic data, the most widely used is the *Birge Sponer extrapolation* (Ref. (*5*), chapter 5). Starting with some band, v_0', the energy differences $\Delta\nu[= G(\nu' + 1) - G(\nu')]$ between successive band heads[3]

Table 1. Numbering of Band Heads in the (B-X) Visible Spectra of Br_2 and I_2 (12).

	v'	v''	λ
Br_2	15	0	5584.7
	16	0	5551.2
	17	0	5519.3
	21	0	5406.7
I_2	18	0	5677.9
	26	0	5468.2
	27	0	5434.7
	28	0	5411.8
	29	0	5398.9
	30	0	5368.7

with the same v'' are plotted against band number v'. This plot is then extrapolated to $\Delta\nu = 0$. When data for I_2 are taken with our spectrophotometer, the positions of the heads for $v' < 25$ apparently are perturbed by the (v', 1'') bands and by a systematic error in the wavelength drive cam causing $\Delta\nu$ for $v \approx 1$–10 to be too small, and $\Delta\nu$ for $v \approx 20$–24 to be too large. This has small effect on the results if the straight line is drawn through the center of gravity of these points.

A graphical Birge-Sponer extrapolation, from a student report, is shown in Figure (3).

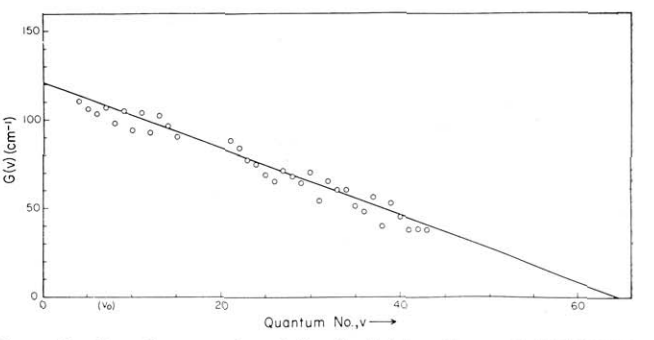

Figure 3. Birge-Sponer extrapolation for I_2 taken from a student report: $G(v' + 1) - G(v')$ versus quantum number, v. Data taken with Cary Model 11 Spectrophotometer with no correction for the wavelength calibration. Area from v_0 to $v = 64.5$ is 3105 cm^{-1}. For $v_0 = 7$, $\gamma_0 = 16{,}793$ cm^{-1}.

The energy in cm^{-1} of the band v_0' from which the extrapolation is started plus the area under the B-S curve is equal to the energy E^* (Fig. (1)) for the reaction of the type,

$$I_2 \rightarrow I + I^* \qquad E^*$$

[3] If sufficiently resolved spectra are available, the energy differences between the ($J' = 0$, $J'' = 0$) (missing) lines of each band are taken.

from which is calculated the dissociation energy to normal atoms;

$$D_0^\circ = E^* - E(\mathrm{I}^*)$$

where the second term on the right is the excitation energy of the atom for which the numerical values are 7598 and 3685 cm^{-1} respectively for iodine and bromine (*5*).

When data for I_2 are taken with a high resolution instrument it is possible to locate both the (v', $0''$) and (v', $1''$) bands very precisely. In this case a plot of $\Delta\nu$ *vs.* v can be used to give the lowest ground state vibrational energy spacing ($v'' = 1 - v'' = 0$). This may be obtained also from Raman or fluorescence spectra and is $\omega_0 \cong \omega_e = 215$ cm^{-1} for I_2 and 323 cm^{-1} for Br_2. This value may be used to compute.

$$D_e'' = D_0^0 + {}^1/_2\omega_e$$

The intercept of the Birge-Sponer curve with $v' = -1$ is ω_e' the vibration frequency extrapolated to the potential minimum.

Algebraic Representation of the Data. Spectroscopic Constants of the Upper State. It is useful to preserve the data contained in the original spectrum (wave number of band head as a function of band number) in the form of an equation. Spectroscopists have established conventions for the form of the equation and for the symbols used (Ref. (*4*), p. 149ff). Rewriting equation (2*a*), we have

$$\nu = (T_e' - T_e'') + [G(v') - G(v'')] \qquad (3)$$

Substituting the appropriate expressions for $G(v)$

$$\nu = \nu_e + [\omega_e'(v' + {}^1/_2) - \omega_e'x_e'(v' + {}^1/_2)^2 + \ldots] - [\omega_e''(v'' + {}^1/_2) - \omega_e''x_e''(v'' + {}^1/_2)^2 + \ldots] \qquad (3a)$$

where ν_e (*cf.* Fig. (1)) is the characteristic energy of the electronic transition and in this case equals T_e' because T_e'' for the ground state is defined equal to zero. Equation (3*a*) may now be used to represent the present experimental data. For the bands under consideration $v'' = 0$ and from independent measurements, (Ref. (*4*), Table 39, or Ref. (*12*)) $\omega_e'' = 215$ or 323 cm^{-1} and $\omega_e''x_e'' = 0.6$ or 1.07 cm^{-1} for I_2 or Br_2 respectively. When these values are substituted into the term in the second brackets it becomes a small constant correction term. The quantity $\omega_e'x_e'$, called the *anharmonicity* term, is simply related to the slope of the best straight line drawn through the points in the *B*-S extrapolation, and is given by

$$\omega_e'x_e' = {}^1/_2(\text{slope})$$

Finally, ω_e' from the $v' = -1$ intercept of the *B-S* curve, and some values of ν and v are substituted into (3*a*) and the equation is solved for ν_e. The dissociation energies for this upper state may be calculated from the relations (see Figure 1)

$$D_e' = E^* - \nu_e$$

$$D_0' = D_e' - {}^1/_2\omega_e'$$

Results and Discussion

The results of the experiment and calculations are ω_e', E^*, D_0° and D_e'' from part 1, and T_e ($=\nu_e$), D_e', D_0', and $\omega_e'x_e'$ from part 2. Values obtained by a student are given in Table 2.

Verma (*3*) reports observation of vibrational levels to $v'' = 114$ of the ground state of I_2 and determination of the dissociation energy to ± 1.5 cm^{-1} (± 0.003 kcal/mole). The present results and this may be compared to values obtained from thermochemical measurements which usually require meticulous care for accuracy better than 1 or 2 kcal/mole.

Table 2. Results

	Experimental (cm^{-1})	Accepted[a] (cm^{-1})	% Difference
E^*	19,898	20,040	1
D_0^0	12,300 (35.2 kcal/mole)	12,440 (35.6 kcal/mole)	1.2
D_e''	12,410	12,550	1.2
D_0'	4,195	4,335	3
D_e'	4,256	4,398	3
ω_e'	123	128	4
$\omega_e'x_e'$	0.94	0.834	13

[a] Values from (*4*) were used consistently.

Gaydon, Ref. (*5*), chapter 4, or Herzberg, Ref. (*4*), chapter 4.4a, gives detailed diagrams explaining how the Franck-Condon principle determines the intensity distribution in spectra. It is interesting to note which of the cases mentioned corresponds to the particular halogen studied. In the case of I_2 the occurrence of the (v', $1''$) bands is due to the fact that $\psi^*\psi$ for $v = 1$ is double humped with maxima near the extremes of the vibrational amplitude (Fig. 1). The most probable absorption occurs vertically from each maximum.

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