

## BAND SPECTRA AND DISSOCIATION ENERGIES

The colors of room temperature objects such as plants, animals, clothes, and paints are determined by the electronic absorption spectra of the pigments underneath the surface. The colors of hot objects such as flames, lightning, and stars are determined by electronic emission spectra. Electronic spectra are used to obtain information about the chemical composition of plasmas used in semiconductor processing, interplanetary clouds, and the level of oxygen in blood during surgery. In chemistry, electronic spectra of the excited states of stable molecules have helped to predict the geometries of unstable reactive intermediates. Because electronic spectra depend on the instantaneous molecular shape, they can be used to follow the pathways of chemical reactions even down to the motions of the atoms across the transition state. Electronic spectra also provide the most accurately known molecular dissociation energies.  $I_2$  is one of the smallest stable molecules with a visible electronic absorption spectrum, so the spectrum of  $I_2$  was used to unravel the molecular factors controlling electronic spectra. This experiment provides an introduction to electronic spectroscopy.

### THEORY

In spectroscopy, a transition between two of the allowed states of a molecule is observed. Unlike the single sharp lines observed in atoms, the transition between two electronic levels of a molecule is broadened because the electronic energy is a function of bond length. Quantum mechanically, the spectrum consists of many lines because each electronic level has a number of vibrational sublevels, and every one of these vibrational sublevels has rotational sublevels (see the HCl lab write-up for a discussion of rotational and vibrational levels on the ground electronic state).

A diagram illustrating two electronic states in a diatomic molecule is shown in Fig. 1. The ground or lowest energy state is designated by X and the excited state is designated by B. There are several lower lying excited states for halogens which are not shown in Fig.1. (Ordinarily, the first excited state is labelled A, the second B, etc. but often some states were missed and the “wrong” labels have stuck.) If we bring two ground state halogen atoms together, the orbital overlap between these atoms can be either bonding, non-bonding, or anti-bonding depending on the orientation of the

occupied orbitals. The X curve represents the energy of the electrons as a function of internuclear distance in the case of a bonding overlap between ground state halogen atoms with their half occupied p orbitals aligned along the line between the two atoms and antiparallel electron spins: the two atoms combine to form a stable molecule. The bond length is the equilibrium internuclear distance  $r_e$  at the minimum of the electronic energy curve. The curve B represents the electronic energy of two halogen atoms where one atom is in the ground state and one atom is in the first excited state. The two atoms combine to form a halogen molecule in an excited state. The half occupied p orbital of one atom lies at a right angle to the internuclear axis, which reduces the bonding overlap with the orbital along the bond axis and lengthens the equilibrium internuclear distance.

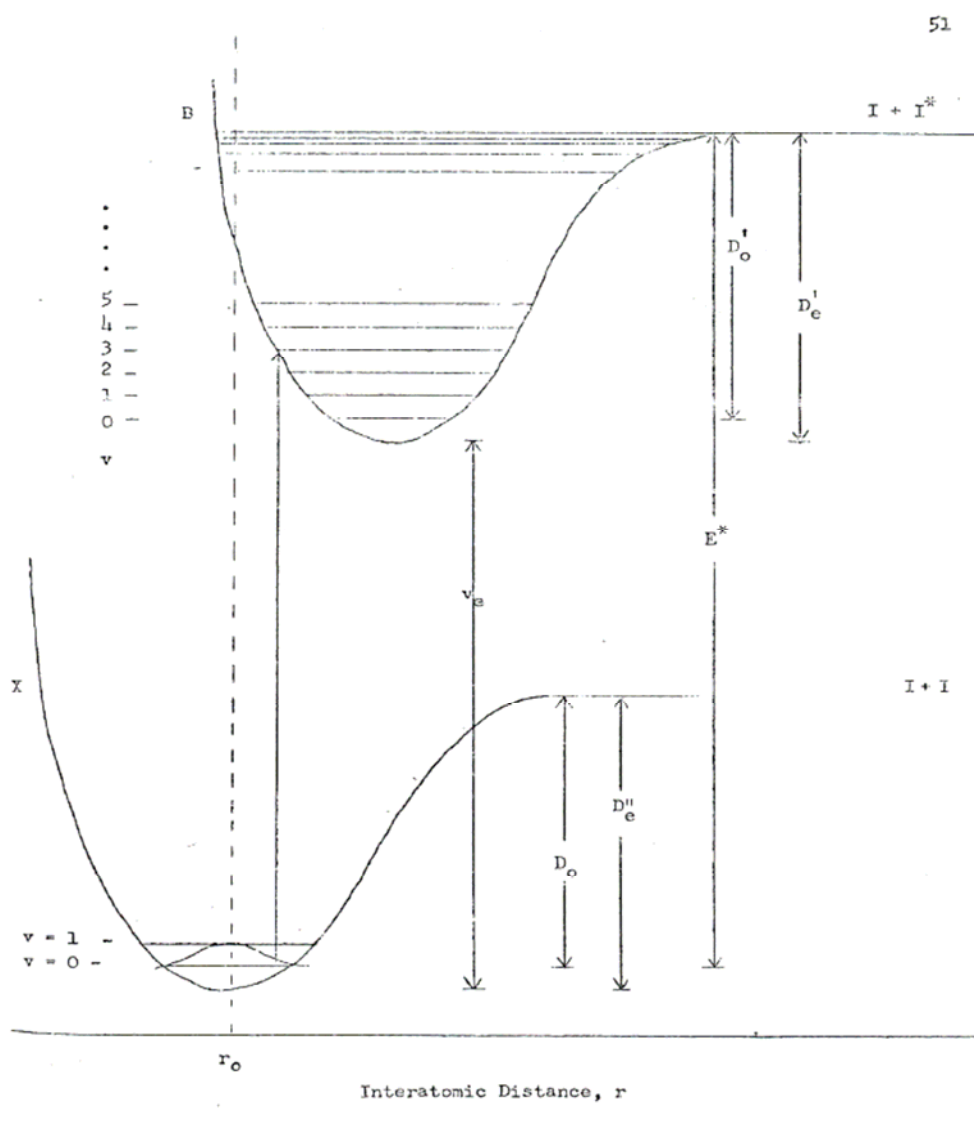


Figure 1. Illustration of the two electronic state in a diatomic molecule

This longer internuclear distance reduces the equilibrium rotational constant  $B_e$ . In the excited state, the shape and depth of the potential well also change because the bond is weakened. This lowers the vibrational frequency  $\omega_e$  and alters the anharmonicity constant  $\omega_e x_e$ . We need a different set of vibrational constants for each electronic state (and a different rotational constant for every vibrational sublevel on each state). Each electronic state has a set of vibrational sub-levels labeled according to their vibrational quantum number in figure 1, and each of these vibrational states has a set of rotational sub-levels. These rotational sub-levels are not shown in figure 1 because the spacing is too small to be observed in this experiment. The maxima observed in this experiment correspond to rotational “band heads” where the sum of these unresolved rotational-vibrational-electronic line intensities are strongest. These band heads occur because the change in  $B$  upon electronic excitation is so great that the R branch actually turns back on itself rather than just growing closer together as in the HCl experiment.

To a good approximation, the total internal energy of a diatomic molecule can be regarded as a sum of the electronic, vibrational, and rotational energies for that state.

Thus we can write

$$E(n,v,J) = E^{\text{elec}}(n) + E_n^{\text{vib}}(v) + E_{n,v}^{\text{rot}}(J) \quad (1)$$

where  $n$ ,  $v$ ,  $J$  refer to the electronic, vibrational, and rotational quantum numbers of the particular state. The subscripts are used as a reminder that the constants in the vibrational energy depend on the electronic state  $n$ , and that those in the rotational energy depend on both the electronic ( $n$ ) and vibrational ( $v$ ) states. We now introduce some spectroscopic notation:

' (single prime) - designates the upper state

" (double prime) - designates the lower state

$T_e$  - designates electronic energy at the equilibrium bond length

(by convention  $T_e = 0$  for the ground electronic state)

$\nu_e$  - electronic transition energy  $T_e' - T_e''$  ( $\text{cm}^{-1}$ )

$G(v)$  - designates the vibrational energy above  $T_e$

$\omega_e$  - fundamental vibration frequency

$\omega_e x_e$  - anharmonicity constant

Electronic transitions can occur between populated vibrational states of the ground state and various vibrational states of the excited states. These transitions are governed by the Frank-Condon principle, which states that electronic transitions occur so rapidly that the nuclei cannot change configuration during a transition. This means that only transitions corresponding to vertical lines in figure 1 can occur. Such a transition [the ( $3' \leftarrow 0''$ ) transition] is shown in Figure 1. There will be a series of such transitions allowed for a halogen molecule corresponding to different values of  $v'$ . These transitions give rise to a set of overlapping bands in the violet or visible region -- hence the name band spectra. The energies of these transitions are given by the formula

$$\hbar\omega = E_{upper} - E_{lower} = [T'_e + G'(v')] - [T''_e + G''(v'')] \quad (2)$$

Since this experiment uses vibrational energy levels up to the dissociation limit, an anharmonic oscillator equation must be used for accurate vibrational energies

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e (v + 1/2)^2 \quad (3)$$

Substituting Eq. (3) and  $\tilde{\nu}_e$  for  $T_{e'} - T_{e''}$  into eq. (2), we have

$$\begin{aligned} \tilde{\nu}(v' \leftarrow v'') = \tilde{\nu}_e + [\omega_e'(v'+1/2) - \omega_e x_e'(v'+1/2)^2] \\ - [\omega_e''(v''+1/2) - \omega_e x_e''(v''+1/2)^2] \end{aligned} \quad (4)$$

Due to the anharmonicity of the potential in the excited state, the spacing of the vibrational substructure on the band becomes progressively smaller as  $\omega$  increases until finally, at the convergence limit, the halogen molecule dissociates into a pair of halogen atoms, one in the ground state and one in an excited state. At higher energies, the absorption of light is continuous since the iodine atoms can be dissociated with any amount of excess kinetic energy. The transition corresponding to the convergence limit is designated as  $E^*$  in figure 1.

There are two ways of specifying the dissociation energy. The first refers to the energy required to dissociate a molecule from the  $v = 0, J = 0$  level into atoms with zero velocity. This experimentally measured dissociation energy is called  $D_0$  where the subscript '0' refers to the initial zero point level. Because the dissociation energy  $D_0$  is measured starting from the zero point level, it depends on the isotope dependent zero point energy. The Born-Oppenheimer approximation indicates that the total depth of the potential well does not depend on the isotope. In other words, the sum of the

experimental dissociation energy ( $D_0$ ) and the vibrational zero point energy [ $G(v=0)$ ] should be isotope independent.

$$D_e = D_0 + G(v=0) \quad (5)$$

This dissociation energy  $D_e$  is called the “equilibrium dissociation energy”. It is an isotope independent property of the potential surface.

## EXPERIMENTAL

A vapor phase spectrum of either iodine or bromine will be run using a 10 cm cell in the CARY 219 ultraviolet-visible spectrophotometer. The wavelength of each band head is recorded and then the band heads are numbered according to the value of  $v'$ . To do this, one or more band heads are identified using the data of Table 1.

Molecule	$v'$	$v''$	Wavelength (nm)
Bromine	15	0	558.47
	16	0	555.12
	17	0	551.93
	21	0	540.67
Iodine	17	0	567.79
	25	0	545.82
	26	0	543.47
	27	0	541.18
	28	0	538.99
	29	0	536.87

Table 1. Numbering of band heads in the (B-X) visible spectra of Bromine and Iodine.

## CALCULATIONS

1. Find the transition energy in wavenumbers for each band head, use table one to help you find the correct transition.

2. Calculated the first differences of transition energies for each pair of lines [i.e.  $\omega(v'+1 \leftarrow 0'') - \omega(v' \leftarrow 0'')$ ]. Use Eq. (4) to derive an analytical expression for these first differences.

3. The next step is to calculate the dissociation energy  $D_0''$ . This is done by making use of a procedure called the Birge-Sponer (B-S) extrapolation. To make such an extrapolation, the first differences calculated in step 3 are plotted versus the band number  $v'$ , starting with some  $v'$  called  $v'_0$ . A least squares procedure should be used to draw the best straight line through the data and the line should be extrapolated to  $\Delta v = 0$ . The energy in  $\text{cm}^{-1}$  of the band  $v'_0$  from which the extrapolation is started plus the area under

the B-S curve (from  $v' = v_0'$  to  $v' = v_{\max}'$ ) is equal to the energy  $E^*$  of Fig. 1. This is the energy of the reaction



The dissociation energy of the halogen to atoms in the ground state can be determined from  $E^*$  if the energy of the atomic excitation  $\text{X} \longrightarrow \text{X}^*$  is known. This energy is 7598  $\text{cm}^{-1}$  for iodine and 3685  $\text{cm}^{-1}$  for bromine.

4. What is the slope of the Birge-Sponer line? Use this slope to calculate  $\omega_e x_e'$ .
5. The vibrational frequency  $\omega_e'$  in the excited B state can also be obtained from the Birge-Sponer plot if the vibrational quantum numbers  $v'$  are known. How is it obtained and what is its value?
6. From high resolution data,  $\omega_e''$  and  $\omega_e x_e''$  can also be determined. Our data is not this good, however, and we will use the literature values which are

	Br <sub>2</sub>	I <sub>2</sub>
$\omega_e''$ ( $\text{cm}^{-1}$ )	323	214.5
$\omega_e x_e''$ ( $\text{cm}^{-1}$ )	1.07	0.614

7. Using several values of  $v'$  and the appropriate quantities determined above, calculate  $v_e$  from Eq. 4.
8. Calculate the equilibrium dissociation energy of the upper state,  $D_e'$ .

**\*NO ERROR PROPOGATION IS NECESSARY!\***

## DISCUSSION

- Do the simple models we use do a good job of representing our system?
- Where do they fail?

	Bromine ( $\text{cm}^{-1}$ )	Iodine ( $\text{cm}^{-1}$ )
$E^*$	19,583	20,040
$D_0$	15,898	12,440
$D_e''$	16,060	12,550
$D_0'$	3,769	4,335
$D_e'$	3,854	4,398
$\omega_e'$	170	125.69
$\omega_e' x_e'$	1.913	0.764

Table 2. Experimental values of spectroscopic constants for iodine and bromine.

## REFERENCES

1. F. E. Stafford, "Band Spectra and Dissociation Energies", J. Chem. Ed., 29, 626 (1962).

2. G. Herzberg, *Molecular Spectra and Molecular Structure, I: Spectra of Diatomic Molecules*, 2nd Ed. D. Van Nostrand, Princeton, New Jersey (1950) pp. 14a ff.
3. K.P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, IV: Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York (1979). [The revised spectroscopic constants for the B state vibrational levels in Huber and Herzberg are based on an isotopic determination of the absolute vibrational numbering which was not available when references 1 and 2 were written. This revised absolute numbering is used here in Table 1.]

<http://www.chemistry.gatech.edu/class/pchem/expt6m.pdf>

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