7 Electronic Absorption Spectrum of Iodine

Purpose

The purpose of this experiment is to determine the properties of the ground and first excited electronic states of the Iodine molecule by determining the molecular potential parameters from the UV-Visible absorption spectrum of Iodine in the vapor phase.

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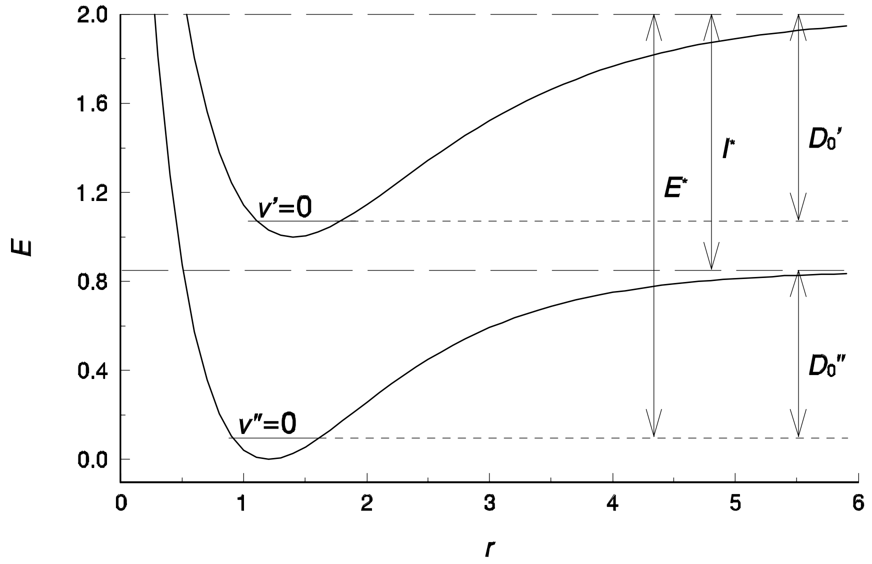

Figure 5: Variation of electronic energy with internuclear distance for the ground and first excited electronic states of a diatomic molecule (schematic).

Theory

In solving the Schrödinger equation for molecules, the Born-Oppenheimer approximation is invoked to separate the electronic part of the Hamiltonian from the part that describes the relative motion of the nucleii. Since the electrons in a molecule move many times faster than the nucleii, we usually solve the electronic problem for fixed (frozen) nuclear positions. Thus for each position of the nucleii, the solution yields the energy of the electrons. For a diatomic molecule, the collection of such energies make up what are usually refered to as the electronic energy curves. These curves now act as effective potentials for the movement of the nucleii, and for this reason, they are also called the molecular potential energy curves. Typical electronic energy curves for the ground and an excited state of a diatomic molecule are shown in Fig. 5. The purpose of this experiment is to determine these curves for the Iodine molecule from the analysis of the UV-Visible absorption spectrum of the molecule in a wavelength range which causes transitions from the vibrational states of the ground electronic state to those of the excited electronic state.

It is the convention in spectroscopy to denote all variables associated with the ground state using double primes (eg., v'') and variables associated with the excited state using single primes (eg., v'). The figure shows the zero point vibrational energies as well as the spectroscopic dissociation energies (D_0) for the two electronic states. The dissociation energy D_e for a particular electronic state is the energy difference between the minimum of the electronic energy curve and the electronic energy as $r \to \infty$ for that state.

The experimental part consists simply of recording the UV-Visible absorption spectrum of Idoine vapor in the range 500−650 nm. For the I_2 molecule, radiation in this energy range causes transitions from the $v'' = 0, 1$ and 2 states (vibrational states associated with the ground electronic state) to several v' states (vibrational states associated with the first excited electronic state). The spectrum therefore consists of three series (or progressions) of closely spaced lines corresponding to the $v'' = 0 \to$ various v', the $v'' = 1 \to$ various v', and $v'' = 2 \to$ various v' transitions. These progressions overlap at certain regions of the spectrum, and therefore, the analysis of the spectrum depends on correctly identifying and labeling the lines. The lines due to transitions between rotational states are also present, superimposed on the vibrational lines (recall the structure of the HCl spectrum which consisted of a single vibrational transition *viz.*, $v'' = 0 \to v' = 1$), but the resolution of the spectrophotometer in the present experiment cannot resolve these transitions. Therefore, in the following discussion, we will ignore all rotational energy levels and transitions between them.

The frequencies (in cm^{-1}) of the various peaks appearing in the spectrum are approximately given by the following relationship, which is simply the difference in energies between the energy levels in question, expressed in frequency units:

$$\begin{aligned} \omega_{v' \leftarrow v''}\ (\text{cm}^{-1}) &= \sigma_e + \left[\omega'_e\left(v' + \frac{1}{2}\right) - \omega'_e x'_e\left(v' + \frac{1}{2}\right)^2 + \ldots\right] \\ &\quad - \left[\omega''_e\left(v'' + \frac{1}{2}\right) - \omega''_e x''_e\left(v'' + \frac{1}{2}\right)^2 + \ldots\right] \end{aligned} \qquad (36)$$

where σ_e is the energy difference between the minima of the two electronic energy curves (taking the minimum of the ground state curve to be zero), the ω_e, $\omega_e x_e$ etc.. are respectively the fundamental frequency and the anharmonicity constant for the electronic states. The approximate nature of Eq. (36) is a result of truncating the expansion at the quadratic term in each electronic state, and also, as pointed out above, from ignoring the effects of rotational energy.

Note that there are five unknown parameters $(\sigma_e, \omega'_e, \omega'_e x'_e, \omega''_e$ and $\omega''_e x''_e)$ in Eq. (36), whose right hand side depends on two variables, namely, v' amd v''. This equation is therefore, of the form

$$z = f\left(x, y; a_1, a_2, ..., a_5\right). \tag{37}$$

The method of *multiple regression* can be used to simultaneously evaluate all five parameters that best fit the spectroscopic frequencies (the left hand side).[2]

Three additional quantities have to be indirectly derived (from the spectral data and from the literature) before we can reliably determine the nature of the potential energy curves for the molecule. The first of these is the quantity labeled as E^* in the figure on the previous page, which is the energy required to excite the molecule from the ground vibrational state ($v'' = 0$) to the dissociation energy of the upper electronic state. This is given by

$$E^*(\text{cm}^{-1}) = \omega_{v' \leftarrow 0} + \frac{1}{2}\left[\omega'_e - 2\omega'_e x'_e \left(v' + 1\right)\right]\left(v'_{\max} - v'\right), \tag{38}$$

where $v'_{\max} = \left(\omega'_e / 2\omega'_e x'_e\right) - 1$ is the quantum number of the highest vibrational level supported by the excited state electronic potential. Increasing the energy beyond the energy of this state results in the molecule dissociating, leading to Iodine atoms in the excited electronic state. The second and third quantities, which we shall get from the literature, are I^*, the energy difference between the ground and excited electronic states of the molecule as $r \to \infty$ (known to be 7589 cm^{-1}) and the equilibrium bond distances of the molecule in the ground and excited states: ($r''_e = 2.666 \times 10^{-8}$cm, $r'_e = 2.981 \times 10^{-8}$cm). The five parameters obtained from multiple regression and the three quantities above are sufficient to generate potential energy curves of the ground and first excited electronic states of the iodine molecule.

The spectroscopic dissociation energy, or the energy difference between the ground vibrational state and the energy of two separated Iodine atoms in the ground electronic state is given by

$$D''_0 = E^* - I^*. \tag{39}$$

The dissociation energy measured from the minimum of the electronic energy curve can now be found as

$$D''_e = D''_0 + \frac{\omega''_e}{2} - \frac{\omega''_e x''_e}{4}. \tag{40}$$

The analogous quantity for the excited electronic state is given by

$$D'_e = D'_0 + \frac{\omega'_e}{2} - \frac{\omega'_e x'_e}{4}. \tag{41}$$

We shall now approach the problem of determining the molecular potential from the information we have obtained above. The simplest (and most approximate) form of the molecular potential is given by the harmonic oscillator form of the potential, which is

$$V_h(r) = \frac{1}{2} k \left(r - r_e\right)^2, \tag{42}$$

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[2] We will use the Statistical Analysis System (SAS) on the mainframe computer to do this.

where r is the interatomic distance, r_e is the equilibrium bond distance, and k is the force constant. The force constant is related to the vibrational frequency through the relationship

$$\omega_e(\mathrm{cm}^{-1}) = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}, \ (c \text{ in cm s}^{-1}) \tag{43}$$

where μ is the reduced mass of the molecule (if the units of kg molecule $^{-1}$ are used for the mass, the force constant will have units of N m^{-1}). The harmonic approximation to the molecular potential is very poor except for low energies near the equilibrium geometry.

A more sophisticated model for the molecular potential which is valid over a large range of r, is the Morse potential

$$V_M(r) = D_e\left\{1 - \exp\left[-\beta\left(r - r_e\right)\right]\right\}^2, \tag{44}$$

where the parameter D_e has been found above for the ground and excited electronic states, and β can be evaluated from experimental data as follows. First, we expand the potential of Eq. (44) in a Taylor's series, about $r = r_e$. This gives us

$$\begin{aligned} V(r) \ \simeq \ & V_M(r_e) + \left.\frac{\partial V_M}{\partial r}\right|_{r=r_e}(r - r_e) + \frac{1}{2!}\left.\frac{\partial^2 V_M}{\partial r^2}\right|_{r=r_e}(r - r_e)^2 \\ & + \frac{1}{3!}\left.\frac{\partial^3 V_M}{\partial r^3}\right|_{r=r_e}(r - r_e)^3 + \ldots. \end{aligned} \tag{45}$$

where the first term is zero for the ground state (and equal to σ_e for the first excited state), and the second term vanishes because $r = r_e$ is the minimum of the potential. This means that if we ignore all terms higher than the quadratic term,

$$V(r) \simeq \frac{1}{2}\left(2D_e\beta^2\right)(r - r_e)^2. \tag{46}$$

Comparing Eq. (46) with the harmonic form of the potential in Eq. (42) and the relationship of Eq. (43), we get

$$k = 2D_e\beta^2 = (2\pi c\omega_e)^2\mu, \tag{47}$$

from which the parameter β can be found ($\beta = 2\pi c\omega_e\sqrt{\mu/2D_e}$). Now, substituting these values into the Morse function of Eq. (44), we get

$$V_M''(r) = D_e''\left\{1 - \exp\left[-\beta''\left(r - r_e''\right)\right]\right\}^2 \tag{48}$$

for the ground electronic state and

$$V_M'(r) = \sigma_e + D_e'\left\{1 - \exp\left[-\beta'\left(r - r_e'\right)\right]\right\}^2. \tag{49}$$

for the excited electronic state. Thus, analysis of the UV-Visible spectrum for a diatomic molecule yields several of the parameters required to evaluate the molecular potential.

Apparatus and Chemicals

A few crystals of Iodine, a quartz cell with a sealable side arm that can be connected to a vaccum pump and a UV-Visible spectrophotometer.

Procedure

A few iodine crystals are taken in a special quartz cell which is then connected to a vacuum pump and evacuated. The iodine sublimes and the cell now contains a sufficient amount of faintly purple iodine vapor. The cell is introduced into the UV-Visible spectrophotometer, and a spectrum is run at 0.2 nm bandpass (slit-width) at a scan rate of 10 nm/min in the wavelength range 500 nm–650 nm. A typical spectrum is shown in Fig. 6

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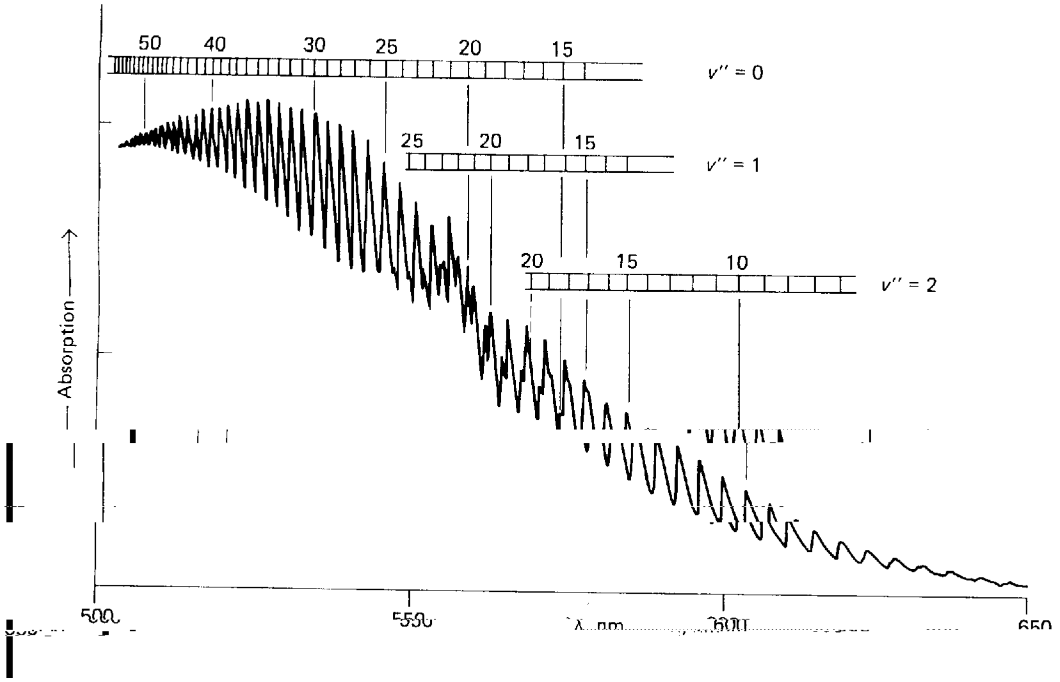

Figure 6: A typical absorption spectrum of the iodine molecule. The positions of various peaks are marked and labeled by the v' and v'' quantum numbers.

Treatment of Data

1. Assign vibrational quantum numbers to each of the peaks in the recorded spectrum, and convert the wavelengths (which are typically in nm) to frequencies (cm^{-1}).
2. Using the SAS package on the mainframe (or some other statistical analysis package), evaluate all five parameters in Eq. (36) and the errors associated with them.
3. Find E^* as the mean value of several values evaluated using Eq. (38).
4. Using Eqs. (40) and (41), respectively, find D_e'' and D_e'. Using the values of ω_e'' and ω_e' found step 2, find the parameters β'' and β' for the ground and excited electronic states [see Eq. (47)].

5. Compare all parameters evaluated in this experiment to literature values.
6. Plot the Morse and harmonic potentials for the two electronic states on the same graph and compare them.