## 6.1.4 Dissociation Energy and Dissociation Products

Figure 6.4(a) and (b) shows two of the ways in which electronic excitation can lead to dissociation (a third way called *predissociation*, will be considered in Sec. 6.1.7). Part (a) of the figure represents the case, previously discussed, where the equilibrium nuclear separation in the upper state is considerably greater than that in the lower. The dashed line limits of the Morse curves represent the dissociation of the normal and excited molecule into atoms, the dissociation energies being $D_0''$ and $D_0'$ from the $v = 0$ state in each case. We see that the total energy of the dissociation products (i.e., atoms) from the upper state is greater by an amount called $E_{ex.}$ than that of the products of dissociation in the lower state. This energy is the *excitation energy* of one (or rarely both) of the atoms produced on dissociation.

We saw in the previous section that the spectrum of this system consists of some vibrational transitions (quantized) followed by a continuum (non-quantized transitions) representing dissociation. The lower wavenumber
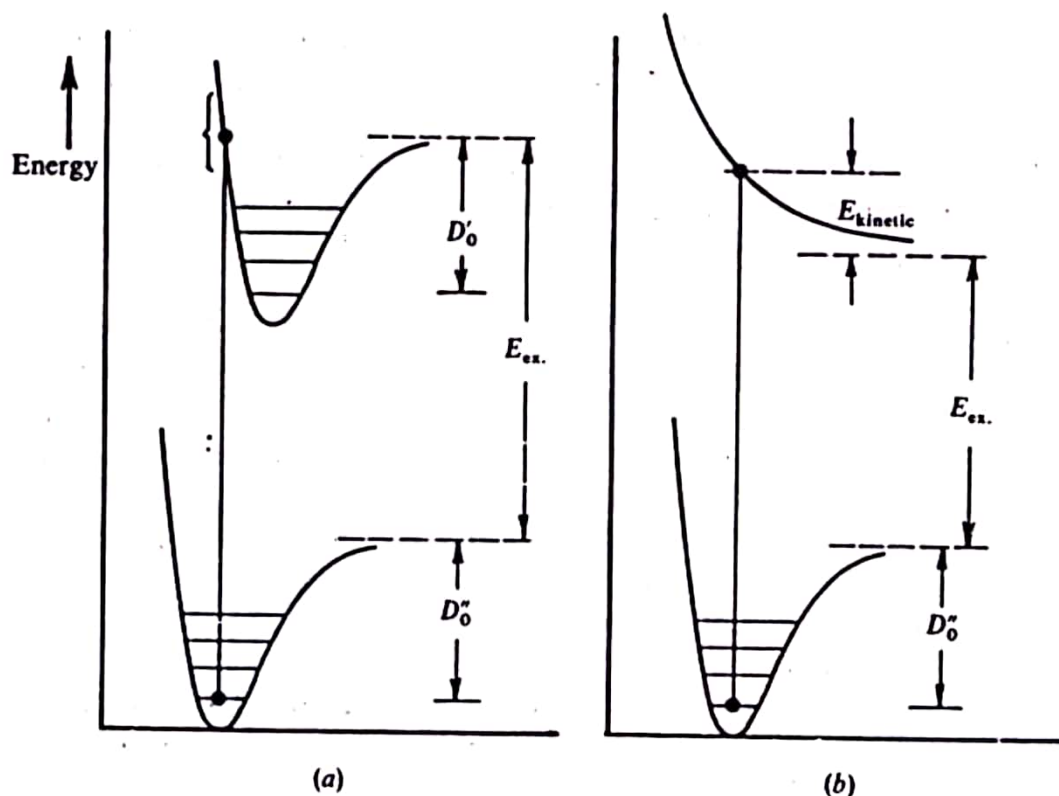
**Figure 6.4** Illustrating dissociation by excitation into (a) a stable upper state, and (b) a continuous upper state.

limit of this continuum must represent just sufficient energy to cause dissociation and no more (i.e., the dissociation products separate with virtually zero kinetic energy) and thus we have

$$\bar{v}_{(\text{continuum limit})} = D_0'' + E_{\text{ex.}} \quad \text{cm}^{-1} \qquad (6.7)$$

and we see that we can measure $D_0''$, the dissociation energy, if we know $E_{\text{ex.}}$, the excitation energy of the products, whatever they may be. Now, although the excitation energy of atoms to various electronic states is readily measurable by atomic spectroscopy (cf. Chapter 5), the precise *state* of dissociation products is not always obvious. There are several ways in which the total energy $D_0'' + E_{\text{ex.}}$ may be separated into its components, however; here we shall mention just two.

Firstly, thermochemical studies often lead to an approximate value of $D_0''$ and hence, since $D_0'' + E_{\text{ex.}}$ is accurately measurable spectroscopically, a rough value for $E_{\text{ex.}}$ is obtained. When the spectrum of the atomic products is studied, it usually happens that only one value of excitation energy corresponds at all well with $E_{\text{ex.}}$. Thus the state of the products is known, $E_{\text{ex.}}$ measured accurately, and a precise value of $D_0''$ deduced.

Secondly, if more than one spectroscopic dissociation limit is found, corresponding to dissociation into two or more different states of products with different excitation energies, the separations between the excitation energies are often found to correspond closely with the separations between

only one set of excited states of the atoms observed spectroscopically. Thus the nature of the excited products and their energies are immediately known.

In Fig. 6.4(b) we illustrate the case in which the upper electronic state is *unstable*: there is no minimum in the energy curve and, as soon as a molecule is raised to this state by excitation, the molecule dissociates into products with total excitation energy $E_{ex.}$. The products fly apart with kinetic energy $E_{kinetic}$ which represents (as shown on the figure) the excess energy in the final state above that needed just to dissociate the molecule. Since $E_{kinetic}$ is not quantized the whole spectrum for this system will exhibit a continuum the lower limit of which (if observable) will be precisely the energy $D_0'' + E_{ex.}$. As before, if $E_{ex.}$ can be found from a knowledge of the dissociation products, $D_0''$ can be measured with great accuracy.

We shall see in Sec. 6.2.1 what sort of circumstances lead to the minimum in the upper state (Fig. 6.4(a)) on the one hand, or the *continuous* upper state (Fig. 6.4(b)) on the other.

In many electronic spectra no continua appear at all—the internuclear distances in the upper and lower states are such that transitions near to the dissociation limit are of negligible probability—but it is still possible to derive a value for the dissociation energy by noting how the vibrational lines converge. We have already seen in Chapter 3 (cf. Eq. (3.12)), that the vibrational energy levels may be written:

$$\varepsilon_v = (v + \tfrac{1}{2})\bar{\omega}_e - x_e(v + \tfrac{1}{2})^2\bar{\omega}_e \quad \text{cm}^{-1} \tag{6.8}$$

and so the separation between neighbouring levels, $\Delta\varepsilon$, is plainly:

$$\Delta\varepsilon = \varepsilon_{v+1} - \varepsilon_v$$
$$= \bar{\omega}_e\{1 - 2x_e(v + 1)\} \quad \text{cm}^{-1} \tag{6.9}$$

This separation obviously decreases linearly with increasing $v$ and the dissociation limit is reached when $\Delta\varepsilon \to 0$. Thus the maximum value of $v$ is given by $v_{max.}$, where:

$$\bar{\omega}_e\{1 - 2x_e(v_{max.} + 1)\} = 0$$

i.e.,

$$v_{max.} = \frac{1}{2x_e} - 1 \tag{6.10}$$

We recall that the anharmonicity constant, $x_e$, is of the order $10^{-2}$, hence $v_{max.}$ is about 50.

We saw in Sec. 3.1.3, that two vibrational transitions (in the infra-red) were sufficient to determine $x_e$ and $\bar{\omega}_e$. Thus, an example given there for HCl yielded $\bar{\omega}_e = 2990$ cm$^{-1}$, $x_e = 0\cdot0174$. From Eq. (6.10) we calculate $v_{max.} = 27\cdot74$ and the next lowest integer is $v = 27$. Replacing $v = 27$, $\bar{\omega}_e = 2990$ cm$^{-1}$ and $x_e = 0\cdot0174$ into Eq. (6.8) gives the maximum value of the

vibrational energy as $42\,890$ cm$^{-1}$ or $513{\cdot}0$ kJ mol$^{-1}$. This is to be compared with a more accurate value of $427{\cdot}2$ kJ mol$^{-1}$ evaluated thermochemically.

The discrepancy between these two figures arises from two causes. Firstly, the infra-red data only allows us to consider two or three vibrational transitions (the fundamental plus the first and second overtones). The electronic spectrum, as we have seen, shows many more vibrational lines (in fact the number is limited not by quantum restrictions, but by the Franck–Condon principle) and we shall get a better value of $D_0''$ if we make use of this extra data. Secondly, we have assumed that Eq. (6.8) applies exactly even at high values of $v$; this is not true because cubic and even quartic terms become important at this stage. Because of these, $\Delta\varepsilon$ decreases more rapidly than Eq. (6.9) suggests.

Both these points may be met if we plot the *separation* between vibrational transitions, $\Delta\varepsilon$, as observed in the electronic spectrum, against the
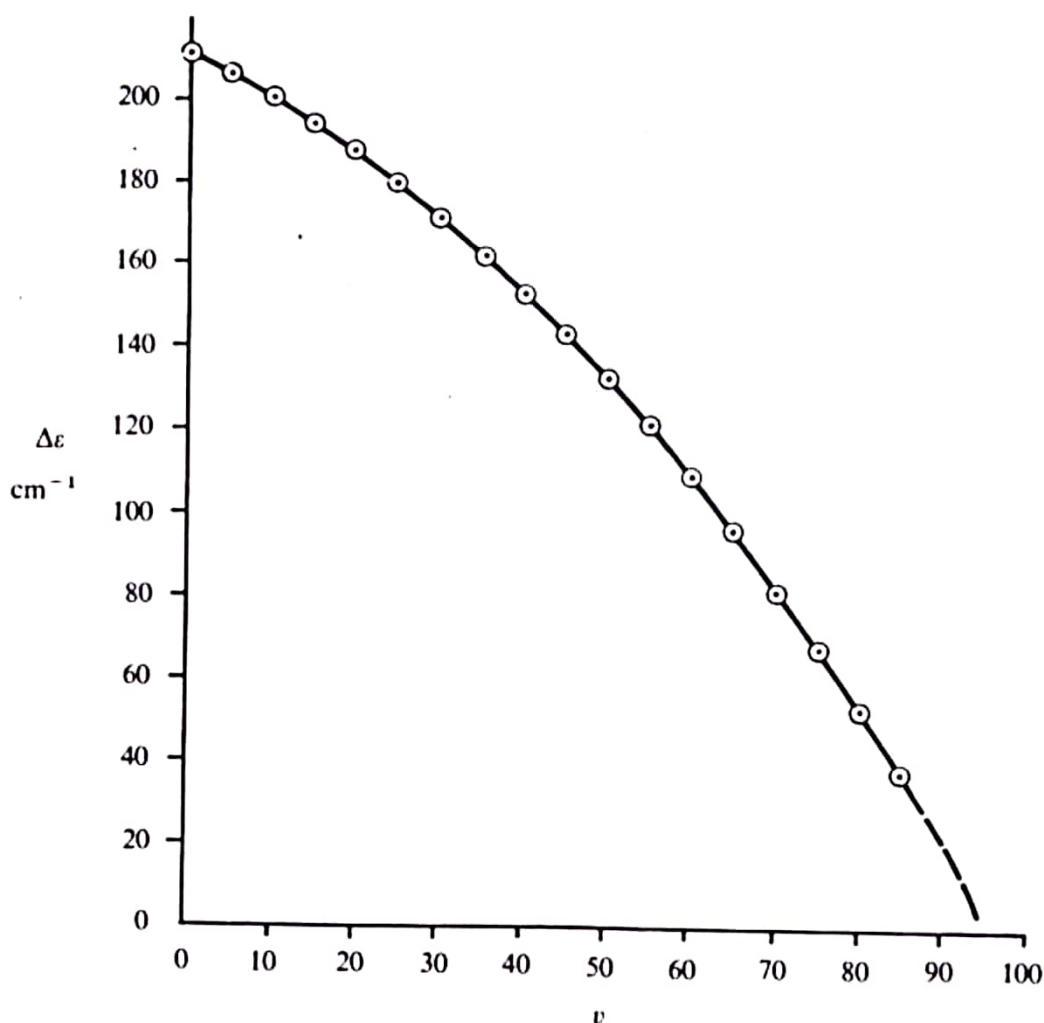


**Figure 6.5** Birge–Sponer extrapolation to determine the dissociation energy of the iodine molecule, I$_2$. *(Taken from the data of R. D. Verma, J. Chem. Phys., vol. 32, p. 738 (1960), by kind permission of the author.)*

vibrational quantum number. Initially, Eq. (6.9) will apply quite accurately and the graph will be a straight line which may be extrapolated either to find $v_{max.}$ or, since the dissociation energy itself is simply the sum of all the increments $\Delta\varepsilon$ from $v = 0$ to $v = v_{max.}$, the *area* under the $\Delta\varepsilon$ versus $v$ graph gives this energy directly. Such a linear extrapolation was first suggested by Birge and Sponer and is usually given their name.

On the other hand, if extensive data are available about a set of electronic–vibration transitions, the graph of $\Delta\varepsilon$ versus $v$ will, at high $v$, begin to fall off more sharply as cubic and quartic terms become significant. In this case the most accurate determination of dissociation energy is obtained by extrapolating the smooth curve and finding the area beneath it. Figure 6.5 shows this process for data on iodine vapour given by R. D. Verma, *J. Chem. Phys.*, **32**, 738 (1960).

In absorption spectra it is normally the series of lines originating at $v'' = 0$ which is observed (cf. Fig. 6.1). Thus the convergence of the levels in the upper state and hence the dissociation energy of that state is normally found. While this in itself is of great interest, particularly since molecules in excited states usually revert to the ground state within fractions of a microsecond, the dissociation energy in the ground state can be found quite easily provided, as before, the dissociation products and their excitation energy are known. Thus, in Fig. 6.4(a), if we know $E_{ex.}$ (from atomic spectroscopy), and $D'_0$ (from Birge–Sponer extrapolation), and if we can measure the energy of the (0, 0) transition either directly or by calculation from the observed energy levels, we have:

$$D''_0 = \text{energy of } (0, 0) + D'_0 - E_{ex.} \quad \text{cm}^{-1} \qquad (6.11)$$