Bond Dissociation Energies

3

The bond dissociation energy, D_e, is a critical parameter in thermodynamics, spectroscopy, and kinetics. For example, in thermodynamics, bond energies directly affect heats of formation and reaction. Dissociation energies thus also play key roles determining rates of reaction as a function of temperature. This chapter will give several examples of how spectroscopic information can reveal D_e (of ground and excited electronic states).

3.1 Birge–Sponer Method

A simple (but highly approximate) model, known as the Birge–Sponer method, can be used to directly convert spectroscopic parameters to dissociation energies [1]. It is based on a model of constant anharmonicity. If the anharmonicity is constant, the vibrational level spacing decreases to zero in the limit of dissociation.

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 \tag{3.1}$$

$$G(v + 1) = \omega_e(v + 3/2) - \omega_e x_e(v + 3/2)^2 \tag{3.2}$$

$$\Delta G(v) = G(v + 1) - G(v) = -2\omega_e x_e v + (\omega_e - 2\omega_e x_e) \tag{3.3}$$

The expression above [Eq. (3.3)] is linear with the form

$$\Delta G(v) = av + b \tag{3.4}$$

where the slope, a, is $-2\omega_e x_e$ and the intercept, b, is $\omega_e - 2\omega_e x_e$. ΔG, the separation between vibrational transitions, goes to zero when $v = v_D$, as shown in Fig. 3.1, and the corresponding dissociation energy is $G(v_D)$. (Note that $G(v_D)$ is also proportional to the integrated area under the curve of Fig. 3.1.)
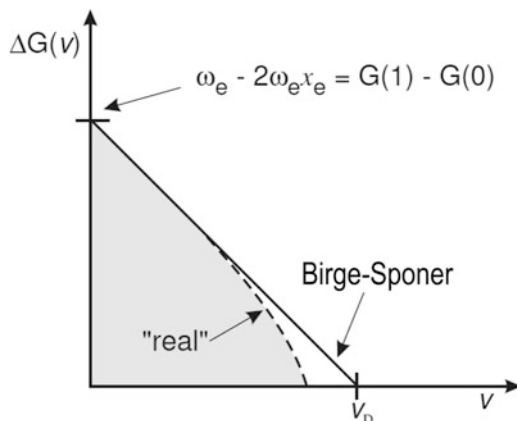
Fig. 3.1 Illustration of Birge–Sponer method for finding the dissociative vibrational level, v_D, and the dissociation energy, D_e

The "real" values of $\Delta G(v)$ are not perfectly linear with quantum number v because the anharmonicity of a real molecule tends to increase near the dissociation limit. The estimation by the Birge–Sponer method thus tends to overpredict the dissociation energy, D_e.

At the dissociation limit, $v = v_D$ and $\Delta G(v_D) = 0$.

$$\Delta G(v_D) = 0 = -2\omega_e x_e v_D + (\omega_e - 2\omega_e x_e) \tag{3.5}$$

Solving for v_D yields

$$\boxed{v_D = \frac{\omega_e}{2\omega_e x_e} - 1} \tag{3.6}$$

Substituting Eq. (3.6) into

$$D_e = \omega_e(v_D + 1/2) - \omega_e x_e(v_D + 1/2)^2 \tag{3.7}$$

gives

$$\boxed{D_e = \frac{\omega_e^2}{4\omega_e x_e} - \frac{\omega_e x_e}{4} \approx \frac{\omega_e^2}{4\omega_e x_e} = \frac{\omega_e}{4x_e}} \tag{3.8}$$

Example: HCl
For HCl, $\omega_e = 2990\,\mathrm{cm}^{-1}$ and $x_e = 0.0174$. Thus,

$$v_D = 27.7 \rightarrow 27 \text{ next lowest integer}$$

and

$$D_e = 513 \text{ kJ/mole}.$$

A more accurate value, based on known thermochemistry, is $D_e = 427 \text{ kJ/mole}$. Thus, Birge–Sponer gives a good first estimate, but overpredicts D_e by about 20 %.

3.2 Thermochemical Approach

The thermochemical approach is another method for finding D_e but can also depend indirectly on spectroscopic data. This method is based on evaluating the extent of a reaction as a function of temperature. For example, if the reaction were $I_2 \rightarrow 2I$, then the equilibrium constant is given by

$$K_p = \frac{P_I^2}{P_{I_2}}$$

and its change with temperature may be given by Van't Hoff's equation:

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H}{RT^2}$$

where

$$\Delta H = \sum v_i H_i = H_{\text{prod}} - H_{\text{react}} = D_e + 2 \int_I \hat{c}_p dT - \int_{I_2} \hat{c}_p dT$$

Thus, measurements of partial pressures can be used to infer $K_p(T)$ and hence both ΔH and D_e''. Partial pressures or species concentrations are often measured spectroscopically (e.g., by laser absorption) because these techniques provide an experimentalist with the ability to accurately measure a single species within a mixture.

3.3 Predissociation

Another way of establishing key energies is with the curve-crossing method, so named because it refers to a predissociative excited electronic state whose potential curve can cross the potential curve of the ground electronic state [1]. Two examples are shown below: HNO (nitroxyl) and N_2O (nitrous oxide).
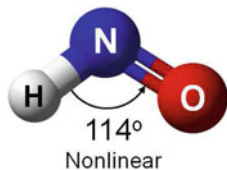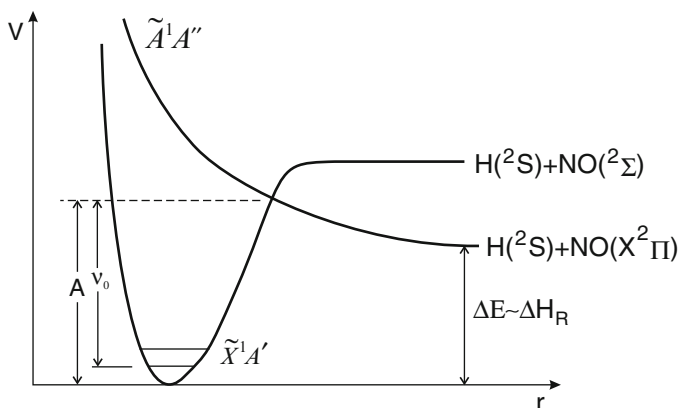
Fig. 3.2 HNO structure

Fig. 3.3 Curve-crossing method for HNO dissociation

3.3.1 HNO

Even though HNO is nonlinear (Fig. 3.2), we can plot its energy level diagram versus H–NO bond distance (i.e., for dissociation of HNO to H+NO) (Fig. 3.3).

$$\Delta E \approx \Delta H_R,$$

but

$$\Delta H_R = \Delta H_f^{\mathrm{H}} + \Delta H_f^{\mathrm{NO}} - \Delta H_f^{\mathrm{HNO}}$$

Therefore, we can solve for $\Delta H_f^{\mathrm{HNO}}$ from an estimate of ΔE, and knowledge of ΔH_f^{H} and ΔH_f^{NO}.

Recall: $1\,\frac{\mathrm{kcal}}{\mathrm{mol}} = 349.7\,\mathrm{cm}^{-1}$
$1\,\mathrm{cal} = 4.187\,\mathrm{J}$

Note: 1. Dissociation (without curve-crossing) of the ground state HNO leads to $NO(^2\Sigma)$, rather than the lower energy state $NO(^2\Pi)$.
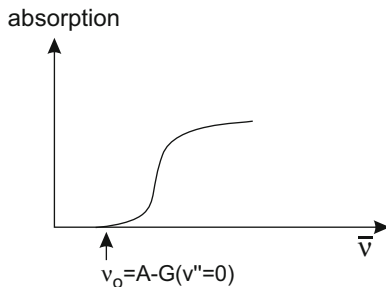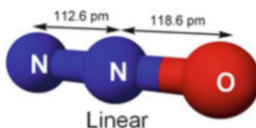
Fig. 3.4 Allowed absorption spectrum for HNO

Fig. 3.5 N_2O structure

2. Predissociation occurs at 590 nm ($17,000\,\mathrm{cm}^{-1}$) in absorption spectra, corresponding to $A \approx 49\,\mathrm{kcal/mol}$. This is then an upper bound on ΔH_R.
3. $\Delta H_R(0\ \mathrm{K}) \approx \Delta H_f^H + \Delta H_f^{NO} - \Delta H_f^{HNO}$, and hence we can use the upper bound value of ΔH_R, and known values for ΔH_f^H and ΔH_f^{NO} to establish a value for the heat of formation of HNO, ΔH_f^{HNO}.
4. Because both electronic states of HNO have the same multiplicity (singlet states with spin $= 0$), there is an allowed absorption spectrum (Fig. 3.4).
5. For polyatomic molecules, the electronic term symbols include a tilde ($\sim$) over the initial symbol; Roman symbols are used to denote the electronic structure (e.g., $^1A''$ and $^1A'$) unless the molecule is linear, in which case Greek symbols are used (e.g., $^1\Sigma$ or $^3\Pi$).

3.3.2 N_2O

Nitrous oxide is important in combustion chemistry and is linked to NO production and the greenhouse effect. N_2O is also a source of atomic oxygen in shock tube kinetics experiments (Fig. 3.5).

There are three relevant energies on the diagram in Fig. 3.6: the depth of the bound potential well, D_e''; the energy of the curve intersection, E_{act}; and the difference in energy between the repulsive state products and the bottom of the ground state potential well.
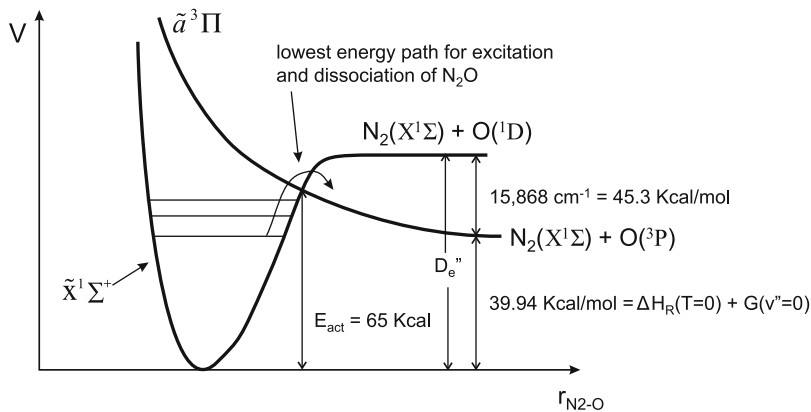
Fig. 3.6 Potential energy wells for N_2O

Note: 1. There is a spin change between the ground electronic state of N_2O and the excited repulsive state shown. As a result, there is no strong absorption process between these electronic states.
2. The dissociation products may result in either $O(^1D)$ or $O(^3P)$, but the latter is lower in energy, and hence more likely.
3. A measurement of the dissociation rate for

$$N_2O + M \rightarrow N_2 + O + M,$$
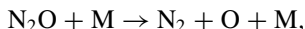
e.g. in a shock tube gives E_{act}, i.e. $k \propto \exp(-65\,[\text{kcal/mole}]/RT)$.
4. The observed activation energy of 65 kcal/mol provides a lower bound on the dissociation energy, D_e''.

3.4   Exercises

1. A banded structure is observed in the absorption spectrum of ground-state oxygen, which changes to a continuum at a wavelength corresponding to 7.047 eV. The upper electronic state of molecular oxygen dissociates into one ground state (^3P) atom and one excited (^1D) atom; the excitation energy of the (^1D) atom relative to the (^3P) atom is 1.967 eV. Determine D_o'' for O_2 in kcal/mole.
2. The zero-point energy of the ground state of O_2 is 793 cm^{-1}, and the difference in energy between the potential-energy minima of the two electronic states, T_e, of Problem 1 is 49,800 cm^{-1}. Determine D_e for the upper and ground states of O_2 in cm^{-1}.
3. Partial electronic band origin data for an absorption spectrum from the ground electronic state is listed below.

v'	$v'' = 0$
1	$31{,}800\,\text{cm}^{-1}$
2	$32{,}400\,\text{cm}^{-1}$
3	$32{,}800\,\text{cm}^{-1}$

    (a) Estimate the bond dissociation energy of the upper electronic state
    (b) If $G(v'' = 0)$ is $575\,\text{cm}^{-1}$, what is T_e in cm^{-1}?
4. Given the following band origin data (in cm^{-1}) for an electronic system:
    (a) Determine ω'_e, $\omega_e x'_e$, ω''_e, $\omega_e x''_e$
    (b) Calculate v'_D and D'_e using the Birge–Sponer method

v'	$v'' = 0$	$v'' = 1$	$v'' = 2$	$v'' = 3$
0	25,000			
1		24,700		
2	26,300			
3	26,800	25,800	24,800	23,800

Reference

1. C.N. Banwell, E.M. McCash, *Fundamentals of Molecular Spectroscopy*, 4th edn. (McGraw-Hill International (UK) Limited, London, 1994)