Bond vibrational energies and stable isotope fractionation

ESS 312 - Spring 2013

In class we looked at a highly simplified explanation for stable isotope fractionation between compounds at equilibrium.

Starting from a bond-energy diagram like the one shown in Fig. 1 (next page), we derived an expression for the *molecular dissociation energy*, which is a measure of the *bond strength* . The ground-state vibrational energy E of the bond is given by:

$$E = \frac{1}{2} h \nu \tag{1}$$

where ν the vibrational frequency can be approximated using Hooke's Law as:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \tag{2}$$

Here μ is the "reduced mass", which depends on the masses m_1 and m_2 of the two atoms bonded to one another:

$$\mu = (\frac{m_1 \times m_2}{m_1 + m_2}) \tag{3}$$

Putting all this together we get an expression for E, the bond strength:

$$E = \frac{h \sqrt{k}}{4 \pi} \sqrt{\frac{1}{\mu}} \tag{4}$$

which evidently is proportional to $\sqrt{\frac{1}{\mu}}$. This predicts that there should be a small difference in bond vibrational frequency and bond strength between isotopically-substituted variants of a molecule. For example, in the simple case of H_2 vs HD, or $^{16}O_2$ vs $^{16}O^{18}O$, the variant containing the heavy isotope should have a slightly stronger bond. In the case of molecular oxygen, the difference in bond strength is:

$$\frac{ZPE_{^{16}O^{18}O}}{ZPE_{^{16}O^{16}O}} = \frac{(\sqrt{\frac{16 + 18}{16 \times 18}})}{(\sqrt{\frac{16 + 16}{16 \times 16}})} = 0.972 \tag{5}$$

Note that the term under each of the square root signs is the *inverse* of the reduced mass which we defined in equation (3) above.

Referring to Fig. 1, this difference in bond strength corresponds to a difference in the zero-point vibrational energies (ZPE) of isotopically-substituted molecules. The difference in ZPE is referred to as an "isotopic shift". When compounds equilibrate with one another, the overall energy of the system is minimized by a small degree of preferential substitution of heavy isotopes into the compound whose bonds have the greater isotopic shift. This is the basis of *stable isotope fractionation* between compounds at equilibrium.
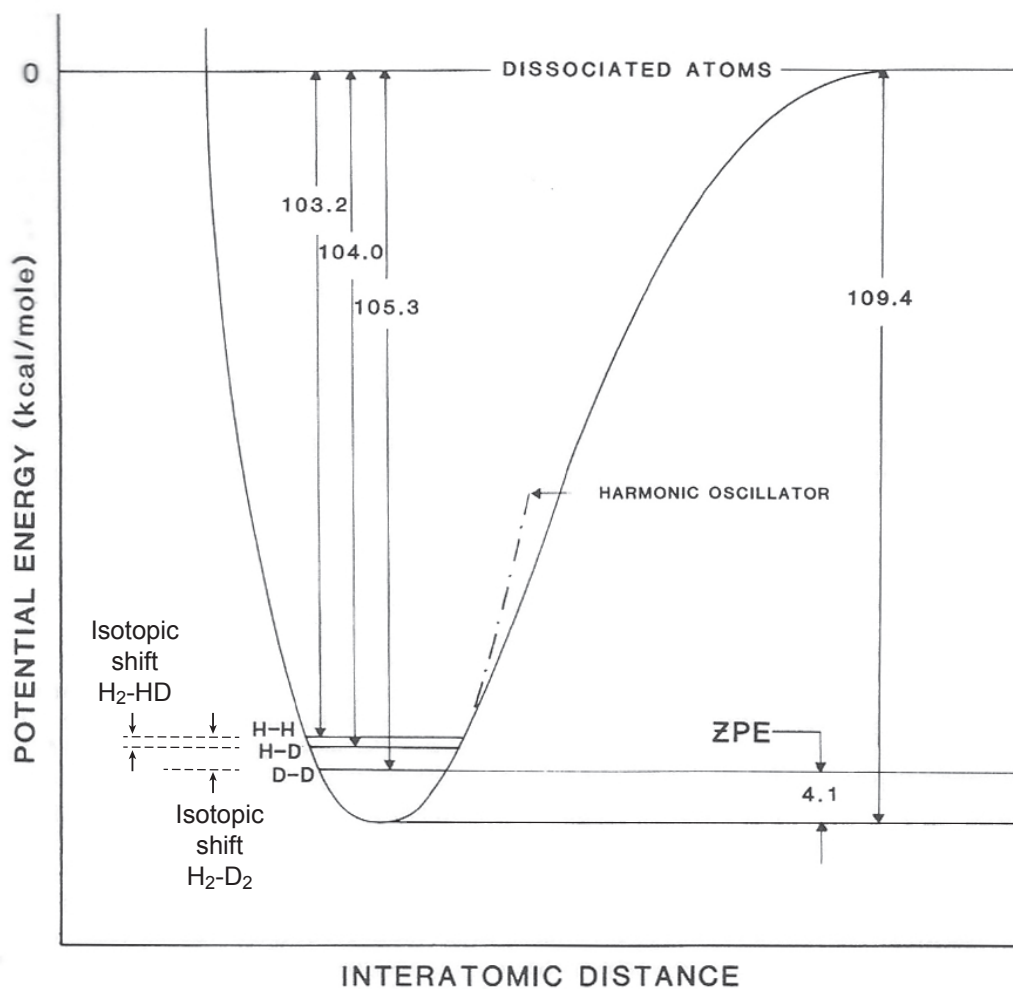
POTENTIAL ENERGY (kcal/mole)

0 — DISSOCIATED ATOMS —

103.2

104.0

105.3

109.4

HARMONIC OSCILLATOR

Isotopic
shift
H_2-HD

H–H
H–D
D–D

ZPE

4.1

Isotopic
shift
H_2-D_2

INTERATOMIC DISTANCE

Figure 1. Schematic potential energy diagram for the hydrogen molecule with scale at bottom of the curve exaggerated to show relation between n = 0 vibrational energy levels of the three isotopic forms of the molecule. The fundamental vibrational frequencies are: H_2, 4405 cm^{-1}; HD, 3817 cm^{-1}; D_2, 3119 cm^{-1}. With increasing temperature, vibrations of all molecules become increasingly anharmonic and the spacings between energy levels (not shown) become smaller and smaller until dissociation occurs. All isotopic forms of hydrogen have the same spectroscopic dissociation energy (109.4 kcal/mole) but chemical dissociation energies and zero point energies (ZPE) that differ by up to 2 kcal/mole. Note that molecules containing the heavy isotope are more stable (have higher dissociation energies) than molecules with the light isotope. Isotopic fractionations between molecules are explained by differences in their ZPE.

Figure 1: Schematic bond potential energy diagram for the hydrogen molecule, showing zero-point energies and molecular dissociation energies for the three isotopic variants of hydrogen: H_2, HD and D_2.