

### Problem 5.3

Chlorine has two naturally occurring isotopes,  $\text{Cl}^{35}$  and  $\text{Cl}^{37}$ . Show that the vibrational spectrum of HCl should consist of closely spaced doublets, with a splitting given by  $\Delta\nu = 7.51 \times 10^{-4}\nu$ , where  $\nu$  is the frequency of the emitted photon. *Hint:* Think of it as a harmonic oscillator, with  $\omega = \sqrt{k/\mu}$ , where  $\mu$  is the reduced mass (Equation 5.15) and  $k$  is presumably the same for both isotopes.

[**TYPO: This is an ambiguous pronoun: What does “it” refer to?**]

#### Solution

Suppose an HCl molecule undergoes a transition from  $n_i$  to  $n_f$ , where  $n_i > n_f$ . A photon is generated as a result with energy  $E_\gamma = h\nu$ .

$$E_\gamma = E_i - E_f$$

$$h\nu = E_i - E_f$$

Assume the HCl molecule behaves as a harmonic oscillator. Then the  $n$ th state has energy  $E_n = (n + 1/2)\hbar\omega$  with  $n = 0, 1, 2, \dots$

$$\begin{aligned} h\nu &= \left(n_i + \frac{1}{2}\right)\hbar\omega - \left(n_f + \frac{1}{2}\right)\hbar\omega \\ &= (n_i - n_f)\hbar\omega \\ &= (n_i - n_f) \left(\frac{h}{2\pi}\right) \sqrt{\frac{k}{\mu}} \end{aligned}$$

Divide both sides by  $h$  to solve for  $\nu$ .

$$\nu = \frac{n_i - n_f}{2\pi} \sqrt{\frac{k}{\mu}}$$

Take the derivative of both sides.  $n_i$ ,  $n_f$ , and  $k$  are constants.

$$\begin{aligned} \frac{d\nu}{d\mu} &= \frac{n_i - n_f}{2\pi} \left(-\frac{1}{2}\mu^{-3/2}\right) \sqrt{k} \\ &= -\frac{1}{2\mu} \left(\frac{n_i - n_f}{2\pi} \sqrt{\frac{k}{\mu}}\right) \\ &= -\frac{\nu}{2\mu} \end{aligned}$$

Multiply both sides by  $d\mu$ .

$$d\nu = -\frac{\nu}{2} \left( \frac{d\mu}{\mu} \right)$$

$$d\nu = -\frac{\nu}{2} d(\ln \mu)$$

There are only two isotopes of chlorine, so replace the differentials with differences.

$$\Delta\nu = -\frac{\nu}{2} \Delta(\ln \mu)$$

$$\nu_{35} - \nu_{37} = -\frac{\nu}{2} (\ln \mu_{35} - \ln \mu_{37})$$

$$= -\frac{\nu}{2} \ln \frac{\mu_{35}}{\mu_{37}}$$

$$= \nu \ln \sqrt{\frac{\mu_{37}}{\mu_{35}}}$$

$\nu_{35}$  represents the frequency of the HCl molecule with the  $^{35}\text{Cl}$  isotope, and  $\mu_{35}$  represents the reduced mass of the HCl molecule with the  $^{35}\text{Cl}$  isotope.  $\nu_{37}$  and  $\mu_{37}$  are defined similarly for the HCl molecule with the  $^{37}\text{Cl}$  isotope. The reduced mass for an HCl molecule is

$$\mu = \frac{m_{\text{H}}m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}}.$$

The chemical bond between the hydrogen and chlorine atoms is polar covalent; that is, the valence electrons of both atoms are shared. However, since chlorine has a significantly higher electronegativity than hydrogen, the hydrogen's electron is mostly in the vicinity of the Cl atom. As a result, the mass of hydrogen is just that of its proton, and the mass of the chlorine atom is the sum of its protons' masses, its neutrons' masses, and the masses of all electrons of both atoms.

$$\mu_{35} = \frac{m_p(17m_p + 18m_n + 18m_e)}{m_p + (17m_p + 18m_n + 18m_e)}$$

$$\mu_{37} = \frac{m_p(17m_p + 20m_n + 18m_e)}{m_p + (17m_p + 20m_n + 18m_e)}$$

Therefore, the splitting of the doublets in the vibrational spectrum of HCl is

$$\begin{aligned} \Delta\nu &= \nu \ln \sqrt{\frac{\mu_{37}}{\mu_{35}}} \\ &= \nu \ln \sqrt{\frac{17m_p + 20m_n + 18m_e}{18m_p + 20m_n + 18m_e} \times \frac{18m_p + 18m_n + 18m_e}{17m_p + 18m_n + 18m_e}} \\ &\approx 7.50869 \times 10^{-4} \nu. \end{aligned}$$