

PROBLEM 2.

Find the ratio of frequencies ω and ω' of the oscillations of two diatomic molecules consisting of atoms of different isotopes, the masses of the atoms being m_1, m_2 and m'_1, m'_2 .

SOLUTION: Within the harmonic approximation, isotopic substitution changes the masses while leaving the interatomic potential, and hence its curvature k at equilibrium, unchanged.

Let u_1 and u_2 be the displacements of the atoms from their equilibrium positions along the molecular axis, with atom 2 on the positive side of atom 1. We define the centre-of-mass displacement X and the change q in interatomic separation from equilibrium by

$$X = \frac{m_1 u_1 + m_2 u_2}{m_1 + m_2}, \quad q = u_2 - u_1.$$

Inverting these relations gives

$$u_1 = X - \frac{m_2}{m_1 + m_2} q, \quad u_2 = X + \frac{m_1}{m_1 + m_2} q.$$

Substituting them into the kinetic energy, the cross terms in $\dot{X}\dot{q}$ cancel, and we get

$$T = \frac{1}{2} m_1 \dot{u}_1^2 + \frac{1}{2} m_2 \dot{u}_2^2 = \frac{1}{2} (m_1 + m_2) \dot{X}^2 + \frac{1}{2} \frac{m_1 m_2}{m_1 + m_2} \dot{q}^2.$$

The first term describes the free translation of the molecule as a whole, and the second describes its vibration. The potential energy depends only on the interatomic separation, and hence only on q ; in the harmonic approximation, it is $\frac{1}{2} k q^2$. Dropping the translational term, the vibrational Lagrangian is

$$L_{\text{vib}} = \frac{1}{2} \mu \dot{q}^2 - \frac{1}{2} k q^2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}.$$

The equation of motion is

$$\mu \ddot{q} + k q = 0,$$

so that

$$\omega = \sqrt{\frac{k}{\mu}}.$$

For the isotopically substituted molecule,

$$\mu' = \frac{m'_1 m'_2}{m'_1 + m'_2}, \quad \omega' = \sqrt{\frac{k}{\mu'}}.$$

Taking the ratio eliminates the common force constant.

ANSWER TO PROBLEM 2.

$$\frac{\omega'}{\omega} = \sqrt{\frac{\mu}{\mu'}} = \sqrt{\frac{m_1 m_2 (m'_1 + m'_2)}{m'_1 m'_2 (m_1 + m_2)}}$$