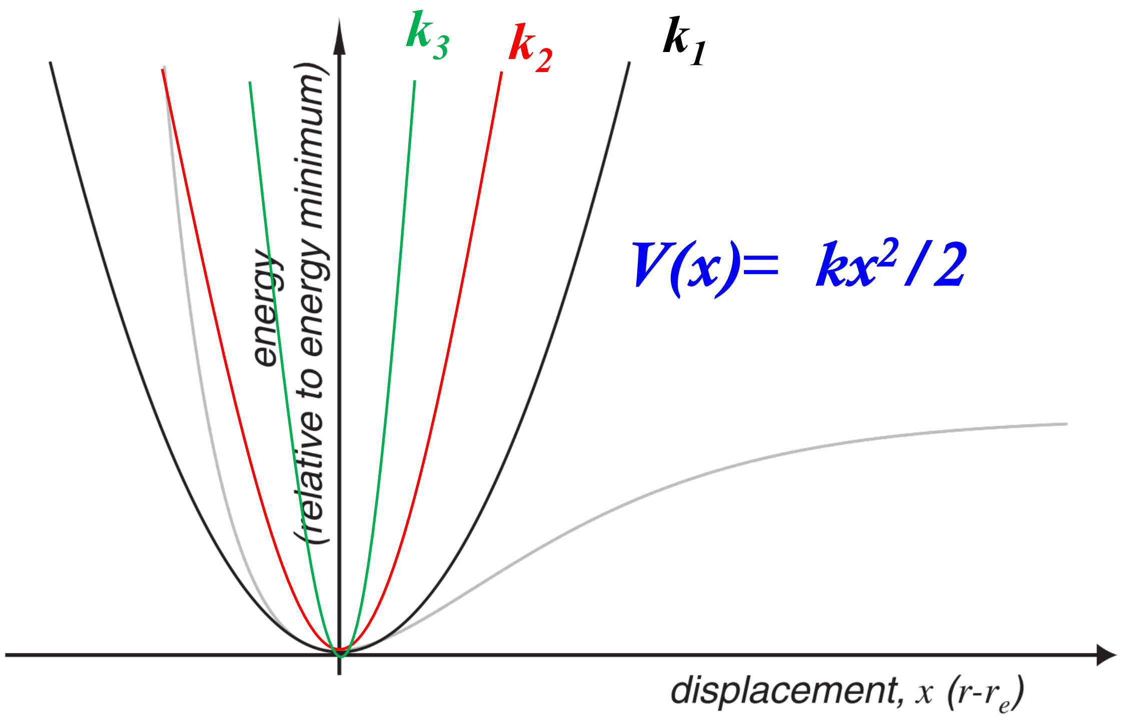
Molecular spectroscopy

Answers to the Questions1-5

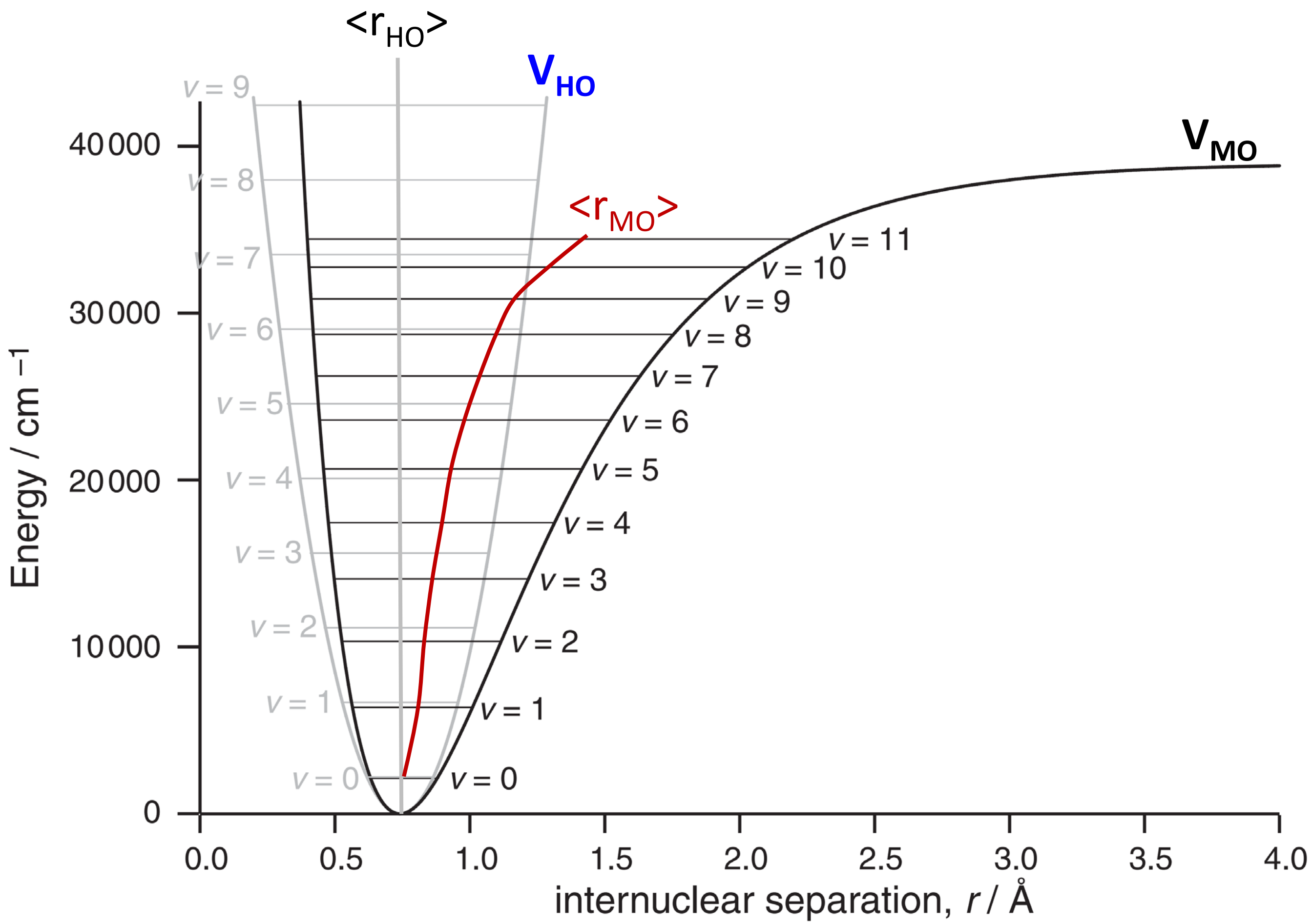
1. Sketch on the same graph the potential energy functions for the harmonic oscillator with three different values of k. How do you interpret the meaning of k?

A: $k_1<k_2<k_3$; k越大，越难以拉伸和压缩，势阱越狭窄！



2. Describe qualitatively how the average bond length changes with increasing vibrational energy for a vibrating diatomic using (a) the harmonic oscillator model and (b) the Morse model.

A: 谐振子每个量子态的平均键长均处于r_e；摩尔斯振子的平均键长随着能级的升高而增大



3. The far infrared spectrum of $^{39}K^{35}Cl$ has an intense line at 278.0 cm^{-1}. Calculate the force constant for KCl.

A: 分子的约化质量$\mu = m_K m_{Cl}(m_K+m_{Cl})^{-1}$

$= 39x35/(39+35)$ au = 18.446 au = 3.063×10^{-26} kg

谐振子模型下，v=0→v=1的跃迁最强，吸收光频率即为分子的特征波长，

即有：$\Delta\varepsilon_{1-0} = \tilde{\omega} = (2\pi\tilde{c})^{-1}\sqrt{k/\mu}$

$$k = \mu(2\pi\tilde{c}\Delta\varepsilon_{0-1})^2 = 83.99\ N\ m^{-1}$$

4. The force constant of $^{79}Br_2$ is 240 N m^{-1}. Calculate the fundamental vibrational frequency and the zero-point energy of $^{79}Br^2$.

A: 分子的约化质量 $\mu = m_{Br}/2 = 39.5$ au $= 39.5(\tilde{N}_0)^{-1} \times 10^{-3}$ kg

$$\tilde{\omega} = (2\pi\tilde{c})^{-1}\sqrt{k/\mu} = 321\ \mathrm{cm}^{-1}$$

由谐振子近似由: ZPE $= \tilde{\omega}/2 = 160.5\ \mathrm{cm}^{-1}$

5. From the data in the spectrum of carbon monoxide shown on page 12, determine ω and *xe* and hence k_M, D_e, D_0 and β, and explain what each of these terms means.

A: 已知 $\Delta\varepsilon_{1\text{-}0} = 2143.26\ \text{cm}^{-1} = \tilde{\omega} - 2\tilde{\omega}x_e$ $\Delta\varepsilon_{2\text{-}0} = 4260.04\ \text{cm}^{-1} = 2\tilde{\omega} - 6\tilde{\omega}x_e$

$$\tilde{\omega} = 3\Delta\varepsilon_{1\_0} - \Delta\varepsilon_{2\_0} = 2169.74\ \text{cm}^{-1}$$

$$2\tilde{\omega}x_e = 2\varepsilon_{1\text{-}0} - \varepsilon_{2\text{-}0} = 26.48\ \text{cm}^{-1} \qquad x_e = 2\tilde{\omega}x_e/(2\tilde{\omega}) = 0.006102$$

$$\tilde{\omega} = (2\pi\tilde{c})^{-1}\sqrt{k_M/\mu} \qquad k_M = \mu(2\pi\tilde{c}\tilde{\omega})^2 = 1902.0\ N/m$$

$$\tilde{D}_e\ (in\ cm^{-1}) = \tilde{\omega}(4x_e)^{-1} = 88924\ cm^{-1}$$

$$\tilde{D}_0\ (in\ cm^{-1}) = \tilde{D}_e - \varepsilon_0 = \tilde{D}_e - (\tilde{\omega}/2 - \tilde{\omega}x_e/4) = 87842\ cm^{-1}$$

$$\beta = \sqrt{2\mu x_e\omega/\hbar} = \sqrt{2\tilde{c}\mu x_e\tilde{\omega}/h} = 2.3207\times 10^{-10}\ m^{-1} = 2.32\ \text{Å}^{-1}$$