

1. In the infrared spectrum of H^{79}Br , there is an intense line at 2559 cm^{-1} . Calculate the force constant of H^{79}Br and the period of vibration of H^{79}Br .

Solution: The force constant is $k = \mu\omega^2 = \mu 4\pi^2\nu^2 = \mu 4\pi^2c^2\tilde{\nu}^2$ where $\tilde{\nu}$ is the symbol for the wavenumber of this vibrational transition. μ is the reduced mass:

$$\begin{aligned}\mu &= \frac{m_{\text{H}}m_{\text{Br}}}{(m_{\text{H}} + m_{\text{Br}})} \\ &= \frac{1 \times 79}{(1 + 79)} \times 1.672 \times 10^{-27} \text{ kg} = 1.651 \times 10^{-27} \text{ kg}\end{aligned}$$

Therefore, $k = 453.8\text{ N/m}$.

The period is $T = 1/\nu$ where ν is the frequency. Since $\nu = c\tilde{\nu}$ we have $\nu = 7.67 \times 10^{13}\text{ s}^{-1}$ and $T = 1.3 \times 10^{-14}\text{ s}$.

2. The force constant of $^{79}\text{Br}^{79}\text{Br}$ is 240 Nm^{-1} . Calculate the fundamental vibrational frequency and the zero-point energy.

Solution:

$$\mu = \frac{m_{\text{Br}}m_{\text{Br}}}{(m_{\text{Br}} + m_{\text{Br}})} = \frac{m_{\text{Br}}m_{\text{Br}}}{2m_{\text{Br}}} = \frac{m_{\text{Br}}}{2}$$

$$\omega = \sqrt{\frac{k}{\mu}} = \sqrt{\frac{240\text{ N/m}}{79/2 \times 1.672 \times 10^{-27}\text{ kg}}} = 6.02 \times 10^{13}\text{ s}^{-1}$$

The zero-point energy is:

$$\begin{aligned}E &= \frac{1}{2}\hbar\omega = 0.5 \times 1.054 \times 10^{-34}\text{ Js} \times 6.02 \times 10^{13}\text{ s}^{-1} \\ &= 3.17 \times 10^{-21}\text{ J}\end{aligned}$$

In wavenumbers this is $\tilde{\nu} = E/hc = 3.17 \times 10^{-21}\text{ J}/6.626 \times 10^{-34}\text{ Js} / 2.99 \times 10^{10}\text{ cm/s}$
 $\tilde{\nu} = 160\text{ cm}^{-1}$

3. The conjugate variables in the uncertainty principle are energy and time. Since $\Delta E \Delta t = h$, there is a lifetime broadening to an excited electron state. Imagine that the H_2^+ molecular ion is excited to the dissociative potential energy surface and flies apart. If this process occurs in 50 fs what is the linewidth for the absorption process? How does this time compare with the vibrational period of H_2^+ if we assume that the vibrational wavenumber is 3330 cm^{-1} ?

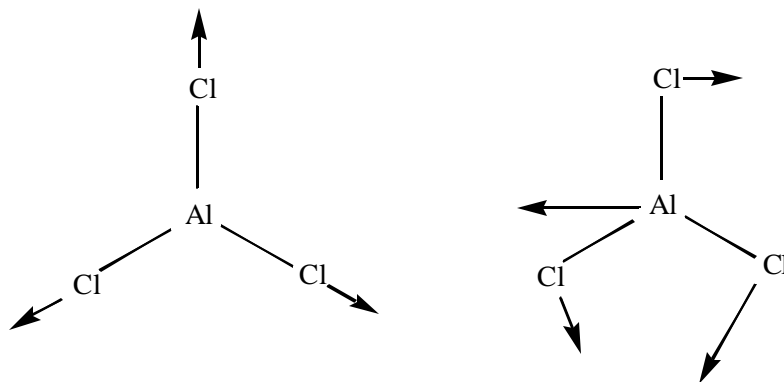
Solution:

The linewidth determined by the uncertainty principle is given by $\Delta E \Delta t = (2.6 \text{ cm}^{-1})(1 \text{ ps})$. Thus, if we are given $\Delta t = 50 \text{ fs} = 0.05 \text{ ps}$ we have $\Delta E = (2.6 \text{ cm}^{-1})(1 \text{ ps})/\Delta t = (2.6 \text{ cm}^{-1})(1 \text{ ps})/(0.05 \text{ ps}) = 53 \text{ cm}^{-1}$

A vibrational period for H_2^+ is

$T = 1/\nu = 1/c = 1/(3 \times 10^{10} \text{ cm/s} \times 3330 \text{ cm}^{-1}) = 1/10^{14} \text{ s}^{-1} = 10^{-14} \text{ s} = 10 \text{ fs}$. Thus, the molecule hangs together for five vibrational periods before dissociating.

4. We have learned that infrared activity depends on a change in the dipole moment of a molecule as it vibrates and that Raman activity results from a change in the polarizability of the molecule as it vibrates. Determine whether the following vibrational normal modes will be infrared or Raman active or both. Describe the motivation for your answer in terms of the dipole moment change of the molecule given the molecular symmetry.
- The symmetric stretch of CO_2 . **Raman active.**
 - The asymmetric stretch of CO_2 . **Infrared active.**
 - The bend of H_2S . **Infrared active (also Raman active since the molecule does not possess a center of symmetry).**
 - The symmetric breathing mode of CH_4 . A breathing mode consists of four simultaneous stretches in the C-H bonds. **Raman active.**
 - The following modes of AlCl_3 .



5. Polyenes can be treated as a particle-in-a-box problem. The longer the polyene molecule the closer the energy spacing and therefore the smaller the transition energy. This corresponds experimentally to the observation that the absorption spectra shift to lower energies (smaller wavenumber) as the length increases. Demonstrate the trend by calculating $h^2/8mL^2$ for the four polyenes shown given C-C = 154 pm and C=C = 135 pm. Note that the length of the box includes all of the bonds in the molecule plus one more C-C bond to account for the radius of carbon atoms at the end of the molecule.

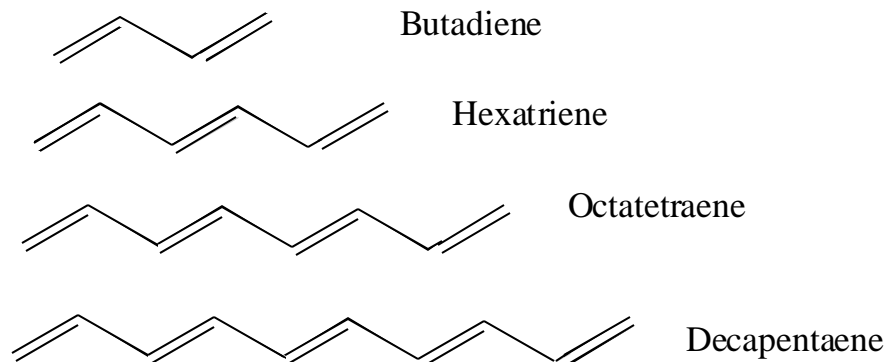
The distances are calculated as follows:

$$L(\text{butadiene}) = 2(\text{C}=\text{C}) + 2(\text{C}-\text{C}) = 2(135 \text{ pm}) + 2(154 \text{ pm}) = 578 \text{ pm}$$

$$L(\text{hexatriene}) = 3(\text{C}=\text{C}) + 3(\text{C}-\text{C}) = 3(135 \text{ pm}) + 3(154 \text{ pm}) = \dots$$

Note that in each case the number of π electrons is equal to the number of carbon atoms and further that according to the Pauli principle two electrons occupy each level of the "box".

- Using this model calculate the transition energy for each of the four polyenes.
- How many nodes are predicted for the HOMO of each of these molecules based on the particle in a box wave function?



Solution: The energy of the factor $h^2/8mL^2$ for octatetraene is

$$\frac{(6.626 \times 10^{-34} \text{ Js})^2}{8 \times 9.109 \times 10^{-31} \text{ kg} \times (11.56 \times 10^{-10} \text{ m})^2}$$

$$= 4.52 \times 10^{-20} \text{ J} \left(\frac{1 \text{ cm}^{-1}}{1.986 \times 10^{-23} \text{ J}} \right)$$

$$= 2280 \text{ cm}^{-1}$$

There are eight π electrons so quantum levels are filled through $n = 4$ and the lowest energy transition is from $n = 4$ to $n = 5$.

$$\Delta E = h^2/8mL^2(5^2 - 4^2) = 20,520 \text{ cm}^{-1}.$$

The energy of the factor $h^2/8mL^2$ for decapentaene is

$$\begin{aligned} & \frac{\left(6.626 \times 10^{-34} \text{ Js}\right)^2}{8 \times 9.109 \times 10^{-31} \text{ kg} \times \left(14.45 \times 10^{-10} \text{ m}\right)^2} \\ &= 2.89 \times 10^{-20} \text{ J} \left(\frac{1 \text{ cm}^{-1}}{1.986 \times 10^{-23} \text{ J}} \right) \\ &= 1460 \text{ cm}^{-1} \end{aligned}$$

There are ten π electrons so quantum levels are filled through $n = 5$ and the lowest energy transition is from $n = 6$ to $n = 5$.

$$\Delta E = h^2/8mL^2(6^2 - 5^2) = 16,060 \text{ cm}^{-1}.$$

Problem 1b. A node is a zero crossing of the wavefunction $\Psi = \sin(n\pi x/L)$ not counting the zero values at the walls. The number of nodes is $n_{\text{HOMO}} - 1$ where n is the quantum number of the HOMO.

For butadiene $n_{\text{HOMO}} = 2$ and the number of nodes is one.

For hexatriene $n_{\text{HOMO}} = 3$ and the number of nodes is two... etc.