Structure of matter: Homework to exercise 13

Due on january 23rd 2024 at noon

Spectra of MOLECULES

1. Multiple-choice test: Please tick the box(es) with the correct answer(s)!
   (correctly ticked box: +1/2 point; wrongly ticked box: -1/2 point)

In a C_{60} molecule, the number of vibrational degrees of freedom is equal to	180	
	186	
	174	✓
In an anharmonic oscillator, vibrational overtone absorption	Is strongly forbidden	
	May be observed	✓

2. True or wrong? – make your decision!

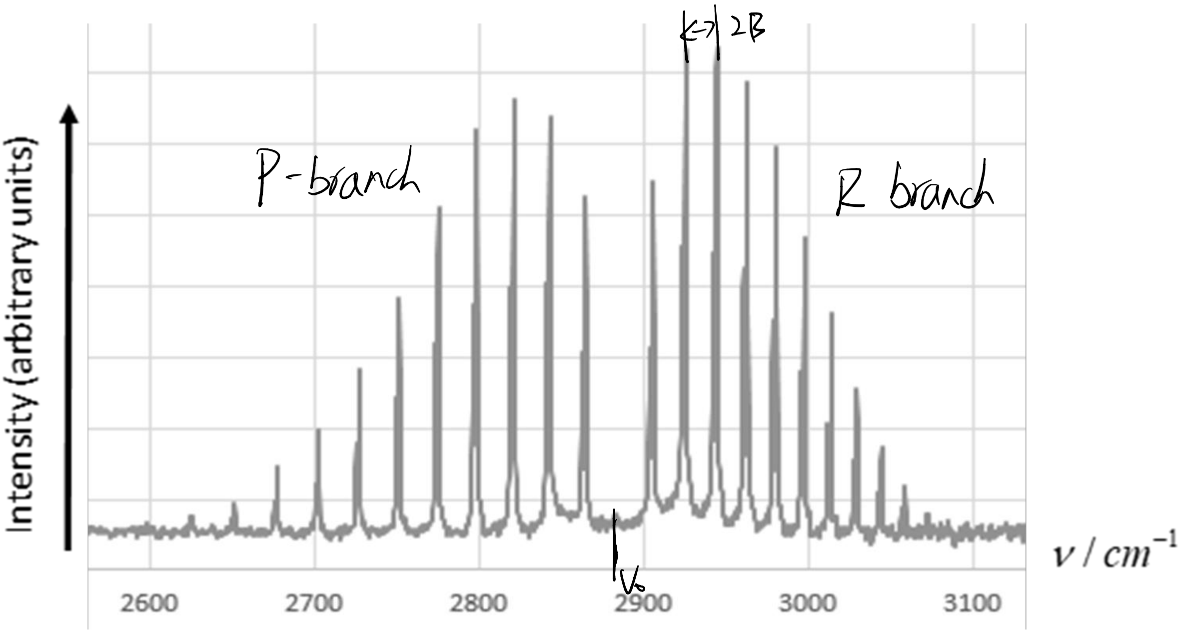
(2 points): 1 point per correct decision, 0 points per wrong or no decision

Statement	true	wrong
While fundamental molecular vibration modes lead to absorptions in the MIR, overtones may also contribute to absorption phenomena in the NIR.	✓	
The selection rules relevant for Raman spectra are identical to those relevant for infrared absorption.		✓

3. Hydrogen has three isotopes - the "normal" hydrogen H, deuterium D and tritium - the later ones being much rarer than H. Let us consider the molecules H_2, HD and D_2.
   We can assume that the distance between the nuclei r_0 is the same in all three cases (r_0 = 0.74 *10^{-10} m) and the force constant κ shall be the same, too. For the H_2-molecule the energy difference between the ground state and the first excited oscillation mode is 0.546 eV. Please calculate
   (a) the force constant κ (assume a harmonic oscillator),
   (b) the energy difference between the ground level and the first excited oscillation level for HD and D_2, respectively
   (c) the energy difference between the rotational levels J = 3 und J = 2 in all three cases.

   6 points

4. The figure below sketches the measured middle infrared spectrum of a HCl gas held at room temperature.



a) Indicate P- and R-branch of the spectrum in the figure, as well as the resonance wavenumber ν_0 corresponding to pure vibration of the molecule. (1.5 point) $\nu_0 = \frac{\omega_0}{2\pi c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = \sqrt{\frac{k}{4\pi^2 c^2 \mu}}$

b) What is the rotational constant B, provided that the spacing between adjacent rotation lines is approximately $20 cm^{-1}$? (0.5 point)

$$\nu_0^2 = \frac{1}{4\pi^2 c^2}\frac{k}{\mu}$$

Assuming B, ν_0 as well as the masses of the Cl-atom m_{cl} (assume a mass number = 35) and of the H-atom m_H (mass number = 1) as known, write down explicit equations for estimating

c) the force constant κ relevant for small vibrations of the molecule (2 points) $k = 4\pi^2 c^2 \mu \nu_0^2$

d) the equilibrium interatomic distance r_0 between the Cl and H nuclei (2 points)

e) Finally, estimate the numerical values for κ and r_0 from the known data! (2 points)

5. Imagine that you have recorded the Raman spectrum of a C_{60} fullerite sample by means of an Argon ion laser, operating at an excitation wavelength of 514nm. You observe a strong Stokes line at a wavelength of 556nm. At which wavelength you will observe that Stokes line, when the excitation wavelength is changed to 488nm? (2 points)

6. Consider a Fulleren C_{60} molecule. Estimate its mass moment of inertia (for rotation around a central axis), assuming the molecule as a hollow sphere with very thin walls and a diameter of 0.71nm. Start from the expression for the mass moment of inertia of a homogenous sphere! (4 points)

3. Hydrogen has three isotopes - the "normal" hydrogen H, deuterium D and tritium - the later ones being much rarer than H. Let us consider the molecules H_2, HD and D_2.
We can assume that the distance between the nuclei r_0 is the same in all three cases (r_0 = 0.74 *10^{-10} m) and the force constant ~~κ shall be~~ the same, too. For the H_2-molecule the energy difference between the ground state and the first excited oscillation mode is 0.546 eV. Please calculate
(a) the force constant κ (assume a harmonic oscillator),
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(c) the energy difference between the rotational levels J = 3 und J = 2 in all three cases.

$$W_0 = \frac{0.546}{\hbar} = \sqrt{\frac{k}{\mu}} \Rightarrow k = \frac{(0.546)^2}{\hbar^2}\cdot\frac{1}{2}\times 1.672$$

(a) $E_{vib} = \hbar w_0 (v+\frac{1}{2})$ $\quad \Delta E = \hbar w_0\left((1+\frac{1}{2})-\frac{1}{2}\right) = \hbar w_0 = 0.546\,eV \Rightarrow w_0 = \frac{0.546\times 1.602\times 10^{-19}\,eV}{1.054\times 10^{-34}\,J\cdot s}$

$\Rightarrow w_0 \approx 8.3\times 10^{14}\,s^{-1}$ $\quad \sqrt{\frac{k}{\mu}} = w_0 \Rightarrow k = \mu w_0^2 = \frac{1}{2}\times 1.672\times 10^{-27}\,kg\cdot 8.3^2\times 10^{28}\,s^{-2} = 575.9\,N/m$

(b) $E_t = E_{vibr} + E_{rot} = -D + \hbar w_0(v+\frac{1}{2}) + \frac{\hbar^2}{2I}J(J+1) = U_0 + \hbar\sqrt{\frac{k}{\mu}}(v+\frac{1}{2}) + \frac{\hbar^2}{2\mu r_0^2}J(J+1)$

$\mu_{HD} = \frac{m_1 m_2}{m_1+m_2} = \frac{m_p\cdot 2m_p}{m_p+2m_p} = \frac{2}{3}m_p$ $\quad \mu_{D_2} = \frac{2m_p\cdot 2m_p}{2m_p+2m_p} = m_p$

For HD $\quad E_{c.ground} = U_0 + \frac{\hbar}{2}\sqrt{\frac{k}{\frac{2}{3}m_p}}$ $\quad E_{c.1} = U_0 + \frac{3}{2}\hbar\sqrt{\frac{k}{\frac{2}{3}m_p}} + \frac{\hbar^2}{\mu r_0^2}$

$$\Rightarrow \Delta E = \hbar\sqrt{\frac{3k}{2m_p}} + \frac{3\hbar^2}{2m_p r_0^2} = 1.054\times 10^{-34}\,W\cdot s^2\sqrt{\frac{3\times 575.9\,N/m}{2\cdot 1.672\times 10^{-27}\,kg}} + \frac{3\times 1.054^2\times 10^{-68}\,W^2 s^4}{2\cdot 1.672\times 10^{-27}\,kg\cdot 0.74^2\times 10^{-20}\,m^2}$$

$$= 5.36\times 10^{-20}\,J + 1.82\times 10^{-21} = 5.54\times 10^{-20}\,J$$

For D_2 $\quad E_{c,g} = U_0 + \frac{\hbar}{2}\sqrt{\frac{k}{m_p}}$ $\quad E_{c.1} = U_0 + \frac{3}{2}\hbar\sqrt{\frac{k}{m_p}} + \frac{\hbar^2}{m_p r_0^2}$

$$\Delta E = \hbar\sqrt{\frac{k}{m_p}} + \frac{\hbar^2}{m_p r_0^2} = 1.054\times 10^{-34}\,W\cdot s^2\sqrt{\frac{575.9\,N/m}{1.672\times 10^{-27}\,kg}} + \frac{(1.054)^2\times 10^{-68}\,W^2 s^4}{1.672\times 10^{-27}\,kg\cdot 0.74^2\times 10^{-20}\,m^2}$$

$$= 6.2\times 10^{-20}\,J + 1.213\times 10^{-21}\,J = 6.32\times 10^{-20}\,J.$$

(c) $E_{rot} = \frac{\hbar^2}{2\mu r_0^2}J(J+1)$ $\quad \Delta E = E_{J=3} - E_{J=2} = \frac{3\hbar^2}{\mu r_0^2}$

For H_2 $\quad \mu = \frac{m_p\cdot m_p}{m_p+m_p} = \frac{1}{2}m_p \Rightarrow \Delta E_{H_2} = \frac{6\hbar^2}{m_p r_0^2} = \frac{6\times(1.054)^2\times 10^{-68}\,W^2 s^4}{1.672\times 10^{-27}\,kg\cdot 0.74^2\times 10^{-20}\,m^2} = 7.28\times 10^{-21}\,J$

For HD $\quad \Delta E_{HD} = \frac{9\hbar^2}{2\mu r_0^2} = \frac{9\times 1.054^2\times 10^{-68}\,W^2 S^4}{2\times 1.672\times 10^{-27}\,kg\cdot 0.74^2\times 10^{-20}\,m^2} = 5.46\times 10^{-21}\,J$

For D_2 $\quad \Delta E_{D_2} = \frac{\hbar^2}{\mu r_0^2} = \frac{1.054^2\times 10^{-68}\,W^2\cdot s^2}{1.672\times 10^{-27}\,kg\cdot 0.74^2\times 10^{-20}\,m^2} = 1.213\times 10^{-21}\,J$

b) What is the rotational constant B, provided that the spacing between adjacent rotation lines is approximately 20cm^{-1}? (0.5 point)

Assuming B, ν_0 as well as the masses of the Cl-atom m_{Cl} (assume a mass number = 35) and of the H-atom m_H (mass number = 1) as known, write down explicit equations for estimating

c) the force constant κ relevant for small vibrations of the molecule (2 points)

d) the equilibrium interatomic distance r_0 between the Cl and H nuclei (2 points)

e) Finally, estimate the numerical values for κ and r_0 from the known data! (2 points)

(4) (b) $2B = 20\,cm^{-1} \Rightarrow B = 10\,cm^{-1} = 1000\,m^{-1}$

(c) $\nu_0 = \frac{w_0}{2\pi c} = \sqrt{\frac{k}{\mu}}\cdot\frac{1}{2\pi c} \Rightarrow 4\pi^2 c^2 \nu_0^2 \mu = k$

(d) $B = \frac{\hbar}{4\pi c I} = \frac{\hbar}{4\pi c \mu r_0^2} \Rightarrow r_0 = \sqrt{\frac{\hbar}{4\pi c \mu B}}$

(e) $\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{35}{36} m_H = \frac{35}{36} \times 1.672 \times 10^{-27}\,kg$

$$r_0 = \sqrt{\frac{1.054\times10^{-34}\,W\cdot s^2}{4\times3.14\times3\times10^8\,m/s\times\frac{35}{36}\times1.672\times10^{-27}\,kg\cdot10^3\,m^{-1}}} \approx 0.131\times10^{-9}\,m = 0.131\,nm$$

$V_0 \approx 2880\,cm^{-1} = 2.88\times10^5\,m^{-1}$

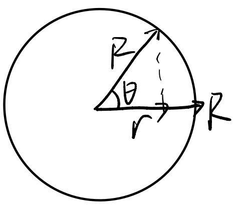
$$K = 4\pi^2 c^2 V_0^2 \mu = 4\times3.14^2\times9\times10^{16}\,m^2/s^2\cdot2.88^2\times10^{10}\,m^{-2}\times\frac{35}{36}\times1.672\times10^{-27}\,kg = 478.57\,N/m$$

5. Imagine that you have recorded the Raman spectrum of a C_{60} fullerite sample by means of an Argon ion laser, operating at an excitation wavelength of 514nm. You observe a strong Stokes line at a wavelength of 556nm. At which wavelength you will observe that Stokes line, when the excitation wavelength is changed to 488nm? (2 points)

$\because\ \Delta V = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1}\right) = \left(\frac{1}{514} - \frac{1}{556}\right) nm^{-1}$

$\Delta V = \left(\frac{1}{\lambda_0'} - \frac{1}{\lambda_1'}\right) \Rightarrow \left(\frac{1}{514} - \frac{1}{556}\right) = \left(\frac{1}{488} - \frac{1}{\lambda_1'}\right) \Rightarrow \frac{1}{\lambda_1'} = \frac{1}{488} + \frac{1}{556} - \frac{1}{514} \Rightarrow \lambda_1' \approx 525.7\,nm$

6. Consider a Fulleren C_{60} molecule. Estimate its mass moment of inertia (for rotation around a central axis), assuming the molecule as a hollow sphere with very thin walls and a diameter of 0.71nm. Start from the expression for the mass moment of inertia of a homogenous sphere! (4 points)



$I = mr^2 \quad \sigma = \frac{M}{4\pi R^2} \Rightarrow I = \iint r^2 \sigma\, ds = \iint R^2 \sin^2\theta \cdot \frac{M}{4\pi R^2} R^2 \sin\theta\, d\theta\, d\varphi$

$\Rightarrow I = \frac{MR^2}{4\pi}\int_0^{2\pi} d\varphi \int_0^{\pi} \sin^3\theta\, d\theta = \frac{1}{2}MR^2 \int_0^{\pi} \sin^3\theta\, d\theta$

$\int_0^{\pi} \sin^3\theta = -\int_0^{\pi} \sin^2\theta\, d\cos\theta = -\int_0^{\pi}(1-\cos^2\theta)\, d\cos\theta$

$= -\int_0^{\pi} d\cos\theta + \int_0^{\pi} \cos^2\theta\, d\cos\theta = -\cos\theta\Big|_0^{\pi} + \frac{1}{3}\cos^3\theta\Big|_0^{\pi} = \frac{4}{3}$

$\Rightarrow I = \frac{1}{2}MR^2 \cdot \frac{4}{3} = \frac{2}{3}MR^2$

$M = 60\times12\times1.672\times10^{-27}\,kg = 1.203\times10^{-24}\,kg$

$\Rightarrow I = 1.203\times10^{-24}\,kg \times \frac{2}{3} \times \frac{0.71^2}{4}\times10^{-18}\,m^2 \approx 1.01\times10^{-43}\,kg\cdot m^2$