

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	<input checked="" type="checkbox"/>
	186	<input type="checkbox"/>
	174	<input type="checkbox"/>
In an anharmonic oscillator, vibrational overtone absorption	Is strongly forbidden	<input checked="" type="checkbox"/>
	May be observed	<input checked="" type="checkbox"/>

2. True or wrong? – make your decision!

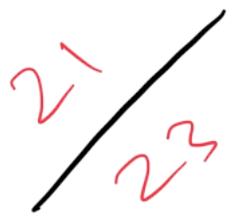
(2 points): 1 point per correct decision, 0 points per wrong or no decision

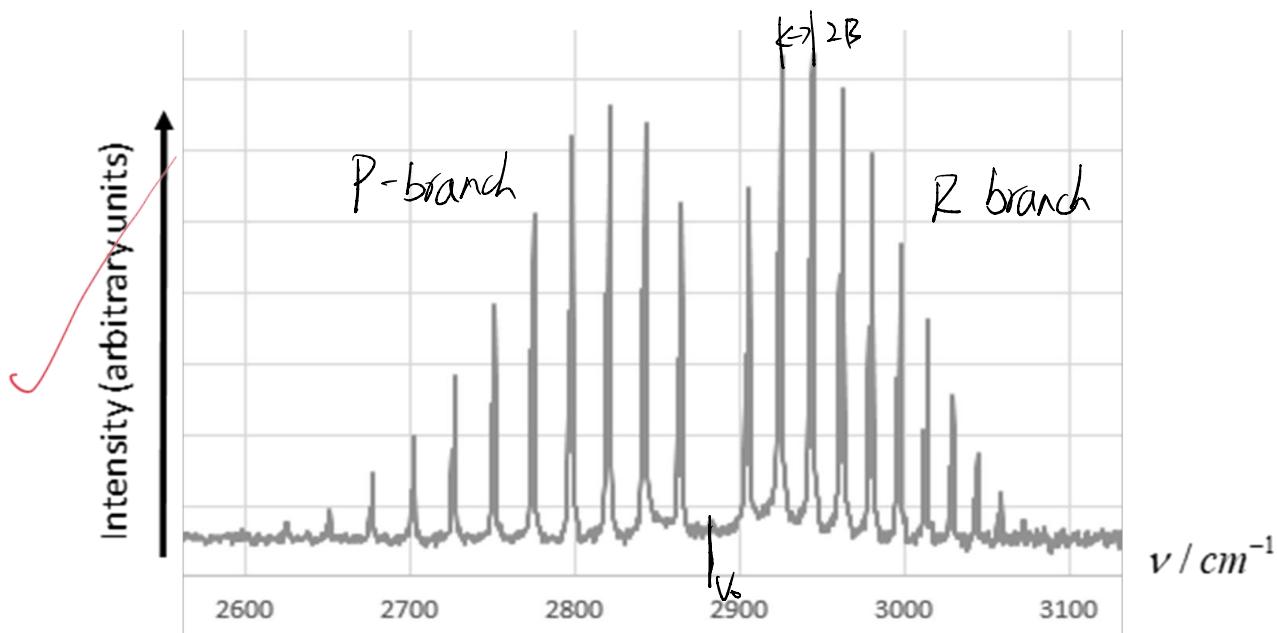
Statement	true	wrong
While fundamental molecular vibration modes lead to absorptions in the MIR, overtones may also contribute to absorption phenomena in the NIR.	<input checked="" type="checkbox"/>	<input type="checkbox"/>
The selection rules relevant for <u>Raman spectra</u> are identical to those relevant for infrared absorption.	<input type="checkbox"/>	<input checked="" type="checkbox"/>

3. Hydrogen has three isotopes - the "normal" hydrogen H, deuterium D and tritium - the latter ones being much rarer than H. Let us consider the molecules H₂, HD and D₂. We can assume that the distance between the nuclei r_0 is the same in all three cases ($r_0 = 0.74 \cdot 10^{-10}$ m) and the force constant κ shall be the same, too. For the H₂-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 D₂, 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)
- $$V = \frac{\omega_0}{2\pi c} = \frac{1}{2\pi c \mu} \sqrt{k} = \sqrt{\frac{k}{4\pi^2 c^2 \mu}}$$
- b) What is the rotational constant B, provided that the spacing between adjacent rotation lines is approximately 20cm^{-1} ? (0.5 point)
- $$b^2 = \frac{1}{4\pi^2 c^2} \frac{k}{\mu}$$
- 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)
- $$K = 4\pi^2 c^2 \mu b^2$$
- 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 latter ones being much rarer than H. Let us consider the molecules H₂, HD and D₂. We can assume that the distance between the nuclei r_0 is the same in all three cases ($r_0 = 0.74 \times 10^{-10}$ m) and the force constant κ shall be the same, too. For the H₂-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 D₂, respectively
- (c) the energy difference between the rotational levels J = 3 and J = 2 in all three cases.

$$(a) E_{vibr} = \hbar \omega_0 (v + \frac{1}{2}) \quad \Delta E = \hbar \omega_0 (1 + \frac{1}{2} - \frac{1}{2}) = \hbar \omega_0 = 0.546 \text{ eV} \Rightarrow \omega_0 = \frac{0.546 \times 10^3 \text{ eV}}{1.054 \times 10^{-34} \text{ J} \cdot \text{s}} = 5.2 \times 10^{14} \text{ s}^{-1}$$

$$\Rightarrow \omega_0 \approx 8.3 \times 10^{14} \text{ s}^{-1} \quad \sqrt{\frac{k}{\mu}} = \omega_0 \Rightarrow k = \mu \omega_0^2 = \frac{1}{2} \times 1.672 \times 10^{-27} \text{ kg} \cdot 8.3^2 \times 10^{28} \text{ s}^{-2} = 575.8 \text{ N/m}$$

$$(b) E_t = E_{vibr} + E_{rot} = -D + \hbar \omega_0 (v + \frac{1}{2}) + \frac{\hbar^2}{2J} J(J+1) = U_0 + \hbar \sqrt{\frac{k}{\mu}} (v + \frac{1}{2}) + \frac{\hbar^2}{2\mu R^2} J(J+1)$$

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

$$\text{For HD} \quad E_{C, \text{ground}} = U_0 + \frac{\hbar}{2} \sqrt{\frac{k}{\mu}} \quad E_{C, 1} = U_0 + \frac{3}{2} \hbar \sqrt{\frac{k}{\mu}}$$

$$\Delta E = \hbar \sqrt{\frac{3k}{2\mu}} = 1.054 \times 10^{-34} \text{ W} \cdot \text{s}^2 \cdot \sqrt{\frac{3 \times 575.8 \text{ N/m}}{2 \cdot 1.672 \times 10^{-27} \text{ kg}}} \\ = 5.36 \times 10^{-20} \text{ J}$$

0.472 ✓

$$\text{For D}_2 \quad E_{C, 0} = U_0 + \frac{\hbar}{2} \sqrt{\frac{k}{\mu}} \quad E_{C, 1} = U_0 + \frac{3}{2} \hbar \sqrt{\frac{k}{\mu}}$$

$$\Delta E = \hbar \sqrt{\frac{k}{\mu}} = 1.054 \times 10^{-34} \text{ W} \cdot \text{s}^2 \cdot \sqrt{\frac{575.8 \text{ N/m}}{1.672 \times 10^{-27} \text{ kg}}} \\ = 6.2 \times 10^{-20} \text{ J}$$

$$(c) E_{rot} = \frac{\hbar^2}{2\mu R^2} J(J+1) \quad \Delta E = E_{J=3} - E_{J=2} = \frac{3\hbar^2}{\mu R_0^2}$$

$$\text{For H}_2 \quad \mu = \frac{m_p \cdot m_p}{m_p + m_p} = \frac{1}{2} m_p \Rightarrow \Delta E = \frac{6\hbar^2}{m_p R_0^2} = \frac{6 \times (1.054)^2 \times 10^{-68} \text{ W}^2 \cdot \text{s}^4}{1.672 \times 10^{-27} \text{ kg} \cdot 0.74^2 \times 10^{-20} \text{ m}^2} = 7.28 \times 10^{-21} \text{ J}$$

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

$$\text{For D}_2 \quad \Delta E = \frac{\hbar^2}{\mu R^2} = \frac{(1.054)^2 \times 10^{-68} \text{ W}^2 \cdot \text{s}^4}{1.672 \times 10^{-27} \text{ kg} \cdot 0.74^2 \times 10^{-20} \text{ m}^2} = 1.213 \times 10^{-21} \text{ J}$$

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

Assuming B, v_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)

$$(d) \quad 2B = 20 \text{ cm}^{-1} \Rightarrow B = 10 \text{ cm}^{-1} = 1000 \text{ m}^{-1}$$

✓

$$(e) \quad V_0 = \frac{\omega_0}{2\pi c} = \sqrt{\frac{k}{\mu}} \cdot \frac{1}{2\pi c} \Rightarrow 4\pi^2 c^2 V_0^2 \mu = K$$

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

(c)

$$(e) M = \frac{m_H m_e l}{m_H + m_e} = \frac{35}{36} m_H = \frac{35}{36} \times 1.672 \times 10^{-27} \text{ kg}$$

$$r_0 = \sqrt{\frac{1.054 \times 10^{-34} \text{ W.S}^2}{4 \times 3.14 \times 3 \times 10^8 \text{ m/s} \times \frac{35}{36} \times 1.672 \times 10^{-27} \text{ kg} \cdot 10^3 \text{ m}^{-1}}} \approx 0.151 \times 10^{-9} \text{ m} = 0.151 \text{ nm}$$

$\sim \text{Lektor}$

$$V_0 \times 2880 \text{ cm}^{-1} = 2.88 \times 10^5 \text{ m}^{-1}$$

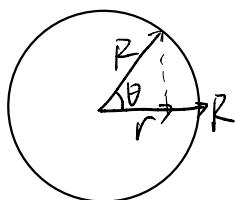
$$K = 4\pi^2 C^2 V_0^2 \mu = 4 \times 3.14^2 \times 8 \times 10^{16} \text{ m}^2/\text{s}^2 \cdot 2.88^2 \times 10^{10} \text{ m}^{-2} \times \frac{35}{36} \times 1.672 \times 10^{-27} \text{ kg} = 478.57 \text{ N/m}$$

5. Imagine that you have recorded the Raman spectrum of a C₆₀ 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 will you observe that Stokes line, when the excitation wavelength is changed to 488nm? (2 points)

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

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

6. Consider a Fullerene C₆₀ 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)



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

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

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

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

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

(d)

$$M = 60 \times 1.672 \times 10^{-27} \text{ kg} = 1.23 \times 10^{-24} \text{ kg}$$

$$\Rightarrow I = 1.23 \times 10^{-24} \text{ kg} \times \frac{2}{3} \times \frac{0.71^2}{4} \times 10^{-18} \text{ m}^2 \approx 1.0 \times 10^{-43} \text{ kg.m}^2$$

