Chem 332 **Assignment #8** (due* Monday 29 March, in class)

*You might still be studying for the test, so this assignment is *optional*. No marks lost if it is not handed in.

Q1. This questions refers to the **spectroscopic selection rules** for free particles.

A **free electron** with kinetic energy $T = \frac{1}{2} m_e v_e^2$ moving in the positive x-direction is described by the wave function

$$\psi(x) = A e^{i\sqrt{2m_e T}\, 2\pi x/h}$$

A is a normalization constant and m_e is the electron mass.

a) Use $\lambda = h/m_e v_e$ for the electron **de Broglie wavelength** to show $\psi(x)$ simplifies to

$$\psi(x) = A e^{i 2\pi x/\lambda}$$

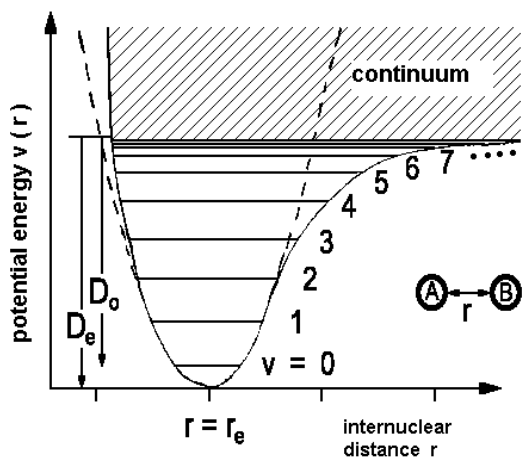
[5] **b)** Radiation of wavelength λ_{rad} provides the oscillating electric potential $\varphi(x) = \varphi_0 \cos(2\pi x/\lambda_{rad})$ in volts along the x-axis. Show the **transition dipole moment** for the spectroscopic transition of an electron with initial energy state T_i to the final energy state T_f is

$$(\mu_z)_{i\to f} = -e\varphi_0 \int \psi_i(x)^* \cos(2\pi x/\lambda_{rad}) \psi_f(x) dx = -e\varphi_0 A^2 \int e^{-i2\pi x/\lambda_i} \cos(2\pi x/\lambda_{rad}) e^{i2\pi x/\lambda_f} dx$$

c) Use the expression for the transition dipole moment to derive the spectroscopic selection rules for free electrons. *Hint*: $\cos u = (e^{iu} + e^{-iu})/2$

Q2. The potential energy curve and vibrational energy levels of diatomic molecule AB are sketched below. No energy levels are marked in the "continuum" region. Explain. *Hint*: See Q1.

[2]



Q3. What are **free electron lasers**? How do they differ from ordinary lasers? Give two advantages of
[3] free electron lasers for spectroscopic measurements.

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Q4. The probability P_J that a rigid rotor has energy E_J is proportional to the Boltzmann factor

$$P_J \propto (2J+1)e^{-BJ(J+1)/kT}$$

[2] Derive an expression in terms of B and k for the most probable value of J at temperature T.

Q5. **a)** Diatomic O_2 and triatomic CO_2 molecules have *identical* rotational reduced masses μ! Why?

$$\mu = m_O m_O/(m_O + m_O) = m_O/2$$

b) Calculate the rotational B coefficient of CO_2.

[3] **c)** High-resolution microwave emission spectra measured for CO_2 in the atmosphere of a distant planet indicate maximum intensity for the $J = 4$ to $J = 3$ transition. Calculate the temperature of the atmosphere.

Data: $m_O = 2.657 \times 10^{-26}$ kg C=O bond length is 0.116 nm

Q6. The moments of inertia of the ammonia molecule (NH_3, a symmetric top) are

$$I_{\parallel} = 2m_H R^2(1-\cos\theta)$$

$$I_{\perp} = m_H R^2(1-\cos\theta) + \frac{m_N m_H}{m_N + 3m_H} R^2(1+2\cos\theta)$$

[5]

R is the N−H bond length (0.1012 nm) and θ is the H−N−H bond angle (106.67°).

The masses of the rotating nuclei are $m_H = 1.672622 \times 10^{-27}$ kg and $m_N = 2.324000 \times 10^{-26}$ kg.

a) Calculate the moments of inertia of the NH_3 molecule.

b) Is NH_3 a prolate symmetric top? Explain.

c) The rotational energy levels of NH_3 (assumed to be a rigid rotor) are

$$\tilde{E}_J = \tilde{B}J(J+1) + (\tilde{A}-\tilde{B})K^2 \qquad J = 0, 1, 2, 3, \ldots \quad K = 0, \pm1, \pm2, \pm3, \ldots \pm J$$

with rotational constants (in wavenumbers)

$$\tilde{A} = \frac{\hbar}{4\pi c I_{\parallel}} \qquad \tilde{B} = \frac{\hbar}{4\pi c I_{\perp}}$$

Calculate the frequencies of the first four lines in the microwave absorption spectrum of NH_3.

Hint: The selection rules in this case are $\Delta J = 1$ and $\Delta K = 0$.