

CHEM352: PHYSICAL CHEMISTRY II
HOMEWORK SET II - DUE 15th OF MARCH, 5.00 PM
Each problem is worth 5 points, 25 pts in total.

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Problem I

1. Show that first four eigenfunctions of the harmonic oscillator are orthonormal.
2. Show that first four eigenfunctions of the rigid rotator are orthonormal.

Problem II

The $J = 2 \leftarrow 1$ transition for AlH molecule in an electronic ground state ($X^1\Sigma^+$) has a frequency of 755199.790 MHz, whereas $J = 4 \leftarrow 3$ for AlD ($X^1\Sigma^+$) is 786755.93 MHz. Compute the bond distance for both molecules. The data comes from doi: 10.1088/0004-637X/791/1/65

Problem III

1. A common practice in identification of bands in vibrational spectroscopy is an isotopic substitution in specific groups that shifts the position of the band but do not alter the electronic structure (force constant) of the bond. Verify this for series of isotopes of $C = O$: $^{12}C = ^{16}O$ - $\omega = 2148.21 \text{ cm}^{-1}$, $C = O$: $^{13}C = ^{16}O$ - $\omega = 2091.7 \text{ cm}^{-1}$ and $C = O$: $^{12}C = ^{18}O$ - $\omega = 2087 \text{ cm}^{-1}$, vibrational values correspond to the electronic ground state ($X^1\Sigma^+$). Data comes from Ar-matrix measurements in doi: 10.1063/1.1725508 so it can differ from gas-phase value of 2170 cm^{-1} .
2. The excitation from singlet to triplet state ($a^3\Sigma^+$) for C=O shifts the vibrational frequency to 1218 cm^{-1} . Using your chemical intuition and IR band positions tables, rationalize this result. You can assume that the bond length in the excited molecule does not change.
3. Repeat the same computations as in point 1 for HBr and DBr.

Problem IV

1. Calculate $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p \rangle$ and $\langle p^2 \rangle$ for the $\theta=3$ state of the harmonic oscillator. Compute the standard deviation.

Problem V

For electric dipole transitions, analyzed in spectroscopy, the intensity of the absorption band is proportional to:

$$\int_{-\infty}^{\infty} \psi_{\theta}^*(x) \hat{x} \psi_{\theta}(x) dx$$

Calculate the transition dipole moments for $\psi_1 \rightarrow \psi_2$, $\psi_1 \rightarrow \psi_3$, $\psi_2 \rightarrow \psi_4$ and $\psi_3 \rightarrow \psi_4$ transitions, where $\psi_{\theta}(x) = H_{\theta}(x) \exp(-x^2/2)$. Do you recover the selection rules?