CHEM 5620, Physical Methods in Chemistry; Spring 2003, Dr. Omary
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Homework set #4 *Magnetism* ***Due in class Monday, April 21.***

(1) Use your class notes and the paper by Clark and Franks (JACS 1975, 97, 2691) to answer the following questions:

a) Draw an energy-level diagram showing and labeling the molecular orbitals for the quaruply Mo-Mo bonded complex ion $Mo_2Cl_8^{4-}$. Explain why the ground-state is a singlet and not a triplet as the case would be for the gas phase Mo_2^{4+} dimer without ligands.

b) Explain why resonance Raman spectra are obtained with the argon ion laser lines 514.5 nm and 488.0 nm while exciting with the 641.1 nm line attains a normal Raman spectrum.

c) Elaborate on why only certain Raman modes were enhanced when running the resonance Raman spectra while other modes were not enhanced. Identify which modes were enhanced.

d) Give two reasons that explain why the ν_1 vibration (~ 350 cm^{-1}) may not be easily obtained in infrared spectroscopy, which necessitates its study using Raman spectroscopy.

e) Explain why the average vibronic spacing in the diffuse reflectance spectra (Figure 7 and Table VII) does not correspond to any of the vibrational modes of the $Mo_2Cl_8^{4-}$ ion like would have been the case if the vibronic progression was seen in luminescence spectra instead of absorption or diffuse reflectance spectra.

(2) Answer the following questions regarding the benefits and limitations of MW spectroscopy:

a) MW spectroscopy is a much more effective finger-printing tool compared to vibrational or electronic spectroscopy.

b) Structure determinations of transition complexes are usually accomplished with single-crystal X-ray crystallography despite being a much less accurate method for measuring interatomic distances and angles compared to MW spectroscopy.

c) The pure rotational spectrum can be determined for HCl but not Cl_2.

d) Although the pure rotational spectrum cannot be determined for Cl_2, the rotational levels can be characterized by Raman-MW spectroscopy.

(3) Answer the following questions regarding the P-, Q-, and R- branches in vibrational-rotational spectra.

a) Sketch a transition that corresponds to each of these branches on a suitable diagram.

b) Derive the energy of each transition.

c) Explain why transitions corresponding to the Q-branch cannot be seen in the vibrational-rotational spectrum of CO but can be seen for CO_2.

(4) The MW spectrum of $^{14}N^{16}O$ shows lines separated by 102.1690 GHz shows lines separated by 102.1690 GHz. Calculate the equilibrium internuclear distance (r_e).

(5) Use your class notes and the papers posted on the course web page about MW spectroscopy (by Gerry et al.) to answer the following questions:

a) Why were the 3-2 and 2-1 transitions so often observed experimentally in these papers in addition to the 1-0 transition despite the fact that the J=0 level should have a greater Boltzman population that the J=1 and J=2 levels?

b) Explain the presence of "D" terms in some expressions of the rotational energies.

c) Explain the presence of significant hyperfine structure in most papers posted.

d) Give two factors that might lead to the splitting of a give J level.

e) Explain briefly how the papers about the bonding of Noble gases to gold, silver and copper halides demonstrated the following:

i) What makes the bonding possible for a Noble gas with a metal?

ii) How the strength of the bonding changed upon varying the coinage metal while fixing the Noble gas?

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