5.05 2005 Exam 3. April 12, 2005

Instructions: This exam is closed-book. Please write on the exam paper your start and end time and do not exceed 2 h total. Write your name on the exam. Illegible answers will not be credited, so please write clearly.

1. **Spin-orbit effects in main group chemistry.** Based *in part* on your scrutiny of the Pyykkö paper,[1]
    a. describe each of the three terms that determine the ^{13}C NMR shielding for a compound such as iodomethane, and
    b. make a prediction as to what molecule has the largest negative ^{13}C NMR shift (δ, ppm) of all, and explain your reasoning.
2. **The remarkable chemistry of gold.**
    a. What is the solvent system used in the synthesis of $[AuXe_4]^{2+}$ and why is the solvent choice crucial?
    b. Write down a balanced chemical equation corresponding to the synthesis of $[AuXe_4]^{2+}$. Draw structures of all the xenon-containing products with stereochemistry clearly indicated.
    c. The synthesis of $[N(AuPPh_3)_5]^{2+}$ proceeds in two stages. Write balanced chemical equations corresponding to these stages and discuss briefly the structural chemistry of the key molecules.
    d. What interatomic distance is typical of an aurophilic interaction?
    e. In no more than one paragraph describe the origin of the aurophilicity phenomenon.
3. **Noble gas chemistry.** Write down equations showing the product(s) of reaction of 1.0 KrF_2 with each of the following:
    a. 2/7 Au.
    b. 1/7 I_2.
    c. 1/3 Xe.
    d. 2/3 $B(OTeF_5)_3$.
    e. 2 SbF_5.
4. **Noble gas chemistry.** The synthesis of KrF_2 must overcome what two (interrelated) main obstacles? Contrast the situation with the requirements for XeF_2 synthesis.
5. **Noble gas chemistry.** How does the MO picture for the bonding in KrF_2 contrast with the simple VSEPR approach to its electronic structure?
6. **Inert pair effect.** Who coined this term and what does it mean?
7. **Polynitrogen compounds.** In the synthesis of $[N_5][Sb_2F_{11}]$,
    a. what material is the reaction vessel made of and,
    b. what material is the vacuum line made of?
    c. Explain your answers to both (a) and (b).
    d. Describe the protocol followed for preparing the reaction vessel prior to carrying out the synthesis.
8. **Polynitrogen compounds.** Contrast the structures of N_5^+ and N_5^-, and discuss what has been the closest approach to date to synthesizing the latter.

[1] Spend no more than 10-15 minutes on this question. The Pyykkö paper is exempt from closed-book status for the purposes of this exam.

Please refer to the following Pyykkö paper for problem 1:

Kaupp, Martin, Olga L. Malkina, Vladimir G. Malkin, and Pekka Pyykkö. "How Do Spin -Orbit-Induced Heavy-Atom Effects on NMR Chemical Shifts Function? Validation of a Simple Analogy to Spin - Spin Coupling by Density Functional Theory (DFT) Calculations on Some Iodo Compounds." *Chem. Eur. J.* 4, no. 1 (1998): 118-126.