

1. Both ^{31}P and ^{19}F have 100% natural abundance with nuclear spin 1/2. Discuss the structure and the spectra of ^{31}P , ^{19}F NMR for PF_5 . (10%)

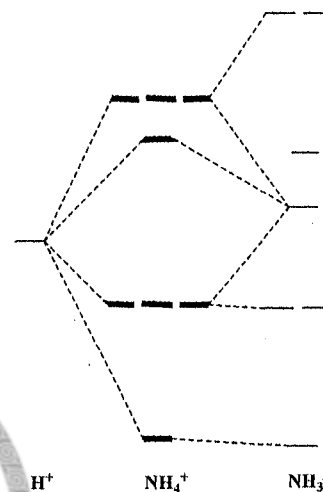
2. How do you distinguish the isomers of $\text{Pt}(\text{CO})_2\text{Br}_2$ experimentally? (10%)

3. The MO energy diagrams of H^+ , ammonium and ammonia is shown below.

(a) Filled in the electrons and label the frontier orbitals of ammonium ion. (5%)

(b) Does ammonia meets the requirement of Lewis base or Lewis acid? (5%)

(c) Explain the acid-base chemistry of ammonia with the MO theory. (10%)



4. The substitution reaction of $\text{Cr}(\text{CO})_6$ with PPh_3 follows the rate law below.

$$-\frac{d[\text{Cr}(\text{CO})_6]}{dt} = a[\text{PPh}_3][\text{Cr}(\text{CO})_6] / \{b[\text{CO}] + c[\text{PPh}_3]\}$$

(a) Describe the point group and the carbonyl vibration modes of the product. (5%)

(b) Propose a mechanism and prove it matches with the given rate law. (10%)

5. Heck coupling reaction of PhI with $\text{CH}_2=\text{CHPh}$ yields stilbene, $\text{PhCH}=\text{CHPh}$, is catalyzed by $\text{Pd}(0)$ complex. The reaction is known to first undergo a reaction of oxidative addition.

(a) Draw a catalytic cycle of three fundamental steps to describe the Heck reaction, and why the first step is called oxidative addition? (10%)

(b) What kind of reactions the 2nd and the 3rd steps belong to? (5%)

6. Discuss the stability of Li_2O , CaO , and CsO_2 and explain. (10%)

7. The structure of heme is shown below

(a) How many sp^2 carbon atoms in heme? (5%)

(b) Draw the simplified MO diagram of $\text{Fe}(\text{III})\text{N}_6$. (10%)

(c) What is the low-spin electronic configuration of the iron center and predict its energy difference of d-d transition in terms of cm^{-1} . (5%)

