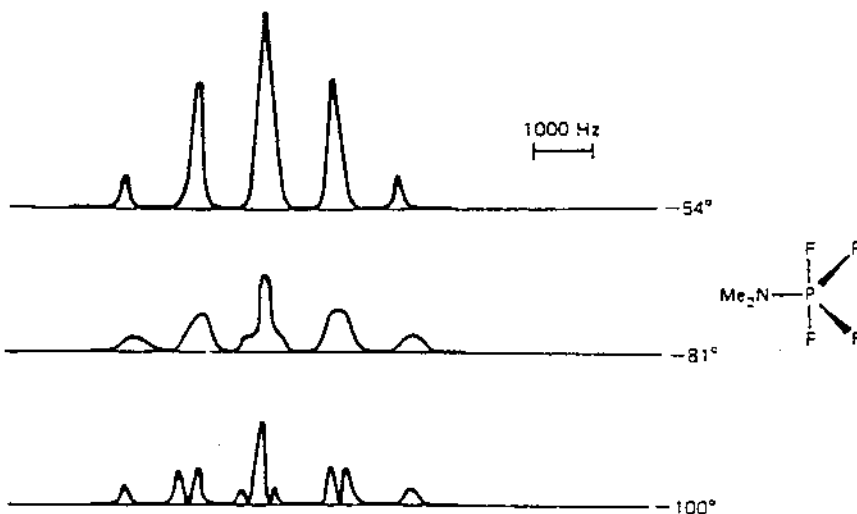


- 注意事項：1. 答案一律寫在答案卷上，否則不予計分。
2. 請標明題號依序作答，不必抄題。
3. 試題應隨同試卷繳回，不得攜出試場。

1. (a) The hydride ion (H^-) and methoxide ion (CH_3O^-) have much greater affinities for H^+ than the OH^- ion does. Write equations for the reactions that occur when NaH and NaOCH_3 are dissolved in water. (6 %)
- (b) You are given a compound that is either iron(II) sulfate or iron(III) sulfate. How could you determine the identity of the compound by using a dilute solution of potassium permanganate? (6 %)
2. (a) What do we mean when we say that a 4s electron is more penetrating than a 3d electron? (4 %)
- (b) Explain why a graph of ionization energy versus atomic number (across a row) is not linear. Where are the exceptions? Explain why they occur. (8 %)
3. Determine the point group for each of the following species. (8 %)
- (a) CH_2FCl (b) NSF_3 (c) ClOF_4^- (d) IO_2F_2
4. The following are ^{31}P nmr spectra of $\text{PF}_4(\text{NMe}_2)$, $I_P = I_F = 1/2$. No J_{P-H} coupling is ever resolved.



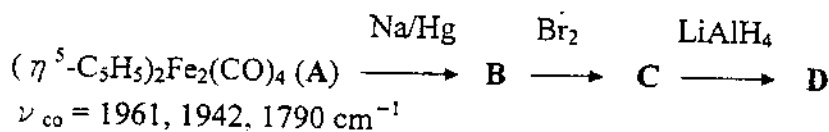
- (a) Explain the low temperature spectrum. (4 %)
- (b) Explain the high temperature spectrum. (2 %)
- (c) On the basis of these spectra, what can you say about the mechanism of exchange? (6 %)

(背面仍有題目.請繼續作答)

5. The ion H_3^+ has been observed, but its structure has been the subject of some controversy. Prepare molecular orbital energy level diagrams for H_3^+ , assuming a cyclic structure. (8 %)

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
A_2'	1	1	-1	1	1	-1		(x, y)
E'	2	-1	0	2	-1	0	z	
A_1''	1	1	1	-1	-1	-1		(R_x, R_y)
A_2''	1	1	-1	-1	-1	1		
E''	2	-1	0	-2	1	0		

6. Why are octahedral Mn^{2+} complexes (weak field) much less intensely colored than those of Cr^{3+} ? (8 %)
7. The d^2 ions CrO_4^{4-} , MnO_4^{3-} , FeO_4^{2-} , and RuO_4^{2-} have been reported.
- Which of these has the largest value of Δ_t ? Explain briefly. (4 %)
 - The charge-transfer transitions for the first three complexes occur at 43,000, 33,000, and 21,000 cm^{-1} , respectively. Are these more likely ligand to metal or metal to ligand charge-transfer transitions? Explain briefly. (6 %)
8. The ion $\text{Re}_2\text{Cl}_8^{2-}$ is made up of two square planar ReCl_4 units joined by a $\text{Re}-\text{Re}$ bond. The two planes are parallel and the chlorines are eclipsed.
- Determine the point group for the ion. (2 %)
 - In $\text{Re}_2\text{Cl}_8^{2-}$, the transition of an electron from the b_{2g} orbital to the b_{1u} orbital is a $d-d$ transition in a molecule with a center of inversion. Is it allowed? Explain. (8 %)
9. Of the compounds $\text{Cr}(\text{CO})_5(\text{PF}_3)$ and $\text{Cr}(\text{CO})_5(\text{PCl}_3)$, which would you expect to have:
- the shorter $\text{C}-\text{O}$ bonds?
 - the higher energy $\text{Cr}-\text{C}$ stretching bands in the infrared spectrum?
- Explain your results. (8 %)
10. Give structural formulas for A through D:



B has strong IR bands at 1880 and 1830 cm^{-1} ; D has a ^1H NMR spectrum consisting of two singlets of relative intensity 1:5 at approximately δ -12 ppm and δ 5 ppm, respectively. (12 %)