INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH KOLKATA

End Semester Examination-May 2019

CH2201 (Fundamentals of Spectroscopy)

Time: $2_{1/2}$ hrs. **Answer *all 10* questions** Max. Marks: 40

1) At 330 nm, the ion $Fe(CN)_6^{3-}{}_{(aq)}$ has ε = 800 $dm^3\ mol^{-1}\ cm^{-1}$, and $Fe(CN)_6^{4-}{}_{(aq)}$ has ε = 320 $dm^3\ mol^{-1}\ cm^{-1}$. The reduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$ is being followed spectrophotometrically in 1.00 cm long cell. The solution has an initial $Fe(CN)_6^{3-}$ concentration of 1.00 x10^{-3} mol dm^{-3} and no $Fe(CN)_6^{4-}$. After 340 s, the absorbance is 0.701. Calculate the percent of $Fe(CN)_6^{3-}$ that has reacted. (4 Marks)

2) The J = 2 →3 pure-rotational transition for the ground vibrational state of $^{39}K^{37}Cl$ occurs at 22410 MHz. Neglecting centrifugal distortion, predict the frequency of the J = 0 → 1 pure-rotational transition of (*a*) $^{39}K^{37}Cl$; (*b*) $^{39}K^{35}Cl$. (4 Marks)

3) The fundamental vibrational frequencies for $^1H_2$ and $^2D_2$ are 4401 and 3115 cm^{-1}, respectively, and D_e for both molecules is 7.677 x 10^{-19} J. Calculate the bond energy of both molecules. (3 Marks)

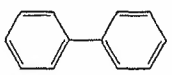
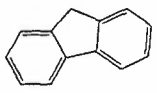
4) Obtain (in details) the ground state term symbol for Cr^{2+} & molecular term symbol for B_2. (2 + 3 Marks)

5) A few plausible electronic transitions are provided below. State (with proper justification) the probability, allowed/forbidden nature of the transitions. (4 Marks)

a. $^3\Pi_u \rightarrow {}^3\Sigma_g^-$ b. $^1\Sigma_g^+ \rightarrow {}^1\Pi_g$

c. $^3\Sigma_g^- \rightarrow {}^3\Pi_g$ d. $^1\Pi_g \rightarrow {}^1\Delta_u$

6) Explain the following observation ($\phi_{Fluorescence}$) with appropriate reason and diagrams: (4 Marks)

 biphenyl	$\lambda_{abs\ (maximum)}$= 300 nm $\phi_{Fluorescence}$ = 0.2
 Fluorene	$\lambda_{abs\ (maximum)}$= 310 nm $\phi_{Fluorescence}$ = 0.8

7) $Cu(H_2O)_6^{2+}$ has a strong blue colour & a single band in its electronic absorption spectrum. Provide a detailed discussion on this observation with appropriate term symbols of the electronic states. (4 Marks)

8) You are provided a solution of ML_4 complex in water. Assume that you have access to analytical facilities like IR & Raman spectroscopic instruments. How will you confirm the geometry of the ML_4 complex? (Hint: Possible geometry belongs to either T_d or D_{4h} point group). (4 Marks)

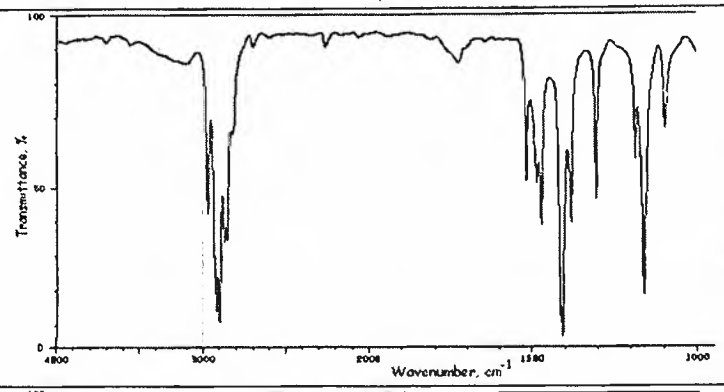
9) The fundamental and overtone frequencies of the C-H stretching vibrations of $CHCl_3$ are at 3019, 5900 and 8700 cm^{-1} respectively. Calculate the Anharmonicity constant, equilibrium vibration frequency (ω_e) and the force constant of C-H bond. (4 Marks)

Speed of light (*c*): 3 x 10^8 ms^{-1}	Boltzmann constant (k_b) : 1.38 x 10^{-23} JK^{-1}
Planck's constant (*h*): 6.626 x 10^{-34} Js	Atomic mass unit (a.m.u) : 1.66 x 10^{-27} kg
1 eV= 1.602 x 10^{-19} J	

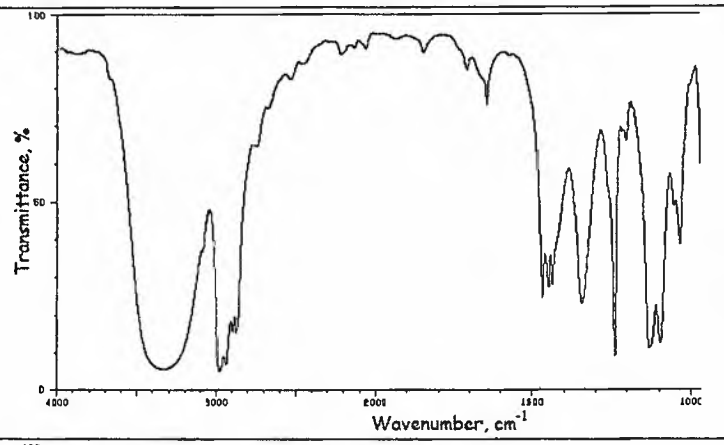
P.T.O

10) Each of the following IR spectra (shown below) corresponds to one of the five isomers of C_4H_8O. Match the spectrum to the correct structure with proper explanation. (4 Marks)

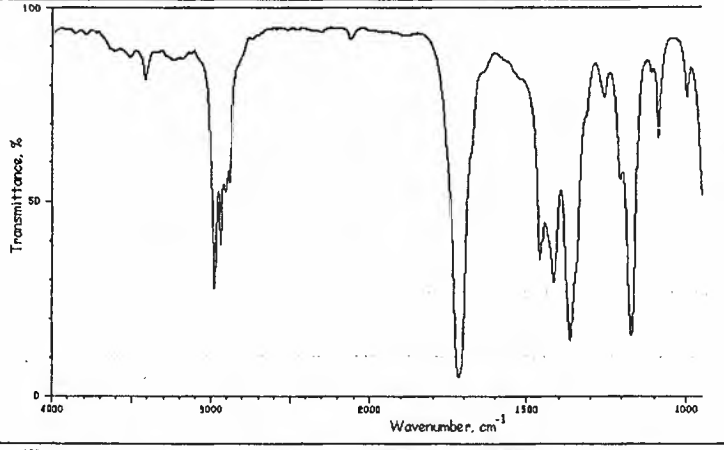
A



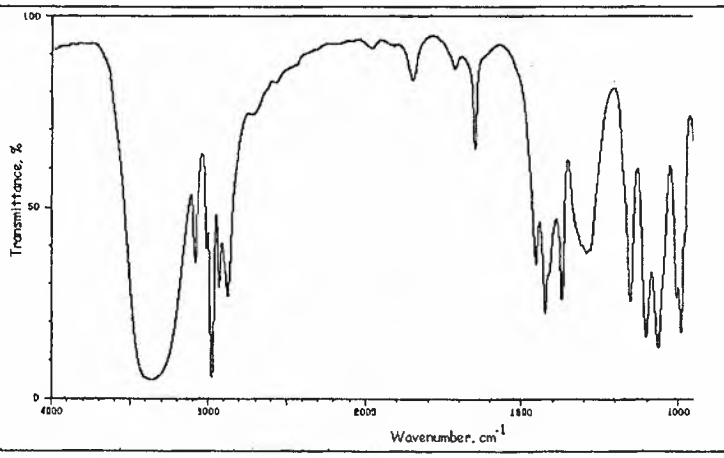
B



C



D



Possible Structures: