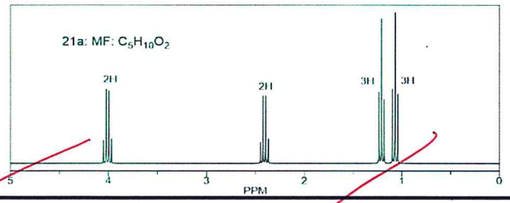
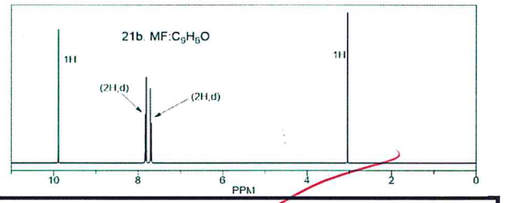
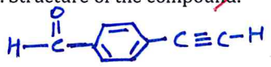
20. In the following statements mark the True statement as (T) and False (F). **(0.5 + 0.5) Mark**

(i) A triene will have lower λ_{max} than a diene (F)	(i) λ_{max} for β-carotene will observed in the UV region (T)
(ii) Carbonyl group is auxochrome of cyclohexanone (F)	(ii) Styrene (vinyl benzene) will have higher λ_{max} than Toluene (T)
(iii) A fair skin person requires high SPF factor sun cream (T)	(iii) Nitrile absorption is stronger than internal Acetylenes (F)
(iv) Molar absorptivity is constant for compound at a particular wavelength (T)	(iv) pK_a of aniline can be determined using UV Spectroscopy (T)
(v) A glass cell can be used both in the UV and Visible region (F)	(v) An optical brightener absorbs and emits in the same wavelength (T)

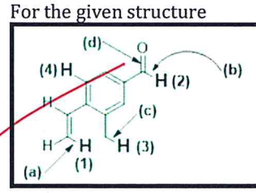
21. Derive the structure of the compound from the given ^{1}H-NMR **(0.5 + 0.5) Mark**





21a. Structure of the compound:	21b. Structure of the compound:
$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3$	$H-\overset{O}{\overset{\|}{C}}-$  $-C\equiv C-H$

22. For the given structure **(0.5 + 0.5) Mark**



Arrange the marked protons (1, 2, 3 and 4) in order of their increasing chemical shift

(3) < (1) < (4) < (2)

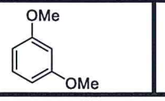
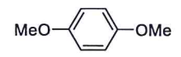
Arrange the marked bonds (a, b, c & d) in increasing order of their stretching frequency (cm^{-1}).

(d) < (b) < (c) < (a)

23. In the following statements mark the True statement as (T) and False (F). **0.5 Mark**

(i) Protons in electron-poor environment have large δ value	(T)
(ii) Protons in electron-dense environments are more shielded	(T)
(iii) Chemical shift depends on the operating frequency of the NMR spectrometer	(F)
(iv) 1,3-di-Nitrobenzene have four chemically equivalents protons	(F)
(v) Flipping of proton from α to β state requires less energy than an electronic transition	(F)

24. Number of signals obtained in ^{1}H NMR spectra of compounds below **0.5 Mark**

	3		4		2

25. 25a. If two signals differ by 100 Hz in a 400 MHz spectrometer by how much do they differ in a 200 MHz spectrometer

50 Hz

25b. If two signals differ by 1.85 ppm in a 300MHz spectrometer, by how much will they differ in a 600 MHz spectrometer.

1.85 ppm

25a+25b = **0.5 Mark**

27/30 = 27/30

Indian Institute of Technology, Guwahati
Guwahati, INDIA 781 039

Department of Chemistry

Date: 20 September 2018; 2:00-4.00 p.m.

CH-101 **Mid Semester Exam** **Maximum Marks = 30**

Name: Tukit Changoiwala Division: I Signature of Invigilator

Roll No.: 180104065 Tutorial Group: T8

Answer only in this sheet. Only fully correct answers will be accepted. All questions are compulsory. Rough work is mandatory.

1. For a particle-in-a-box of length L, the wavefunction is written as, $\Psi(x)=\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$. If for the first excited state, the value of energy is 5.5×10^{-19} J, then the length of the box (in Å) would be about, **2.0 Marks**

(Z) 3.32	(Y) 4.42	(X) 6.63	(W) 8.84	*Use ($h = 6.630\times10^{-34}$ Js, $m = 9.11\times10^{-31}$ kg)*

2. With the length of the box, L, the probability of finding electron in the ground state to be 0.41 is between, **2.0 Marks**

(V) x=0.25L and x=0.75L	(U) x=0 and x=0.75L	(T) x=0.5L and x=L	(S) x=0.5L and x=0.75L

3. The hydrogenic Hamiltonian for the electron with mass m_e and nucleus with mass m_N can be rewritten using reduced mass (μ) and total mass (m) as, **2.0 Marks**

(R) $H=-\frac{\hbar^2}{2\mu}\nabla^2_{c.m.}-\frac{\hbar^2}{2m}\nabla^2-\frac{Ze^2}{4\pi\varepsilon_0 r}$	(Q) $H=-\frac{\hbar^2}{2m}\nabla^2_{c.m.}-\frac{\hbar^2}{2\mu}\nabla^2+\frac{Ze^2}{4\pi\varepsilon_0 r}$
(P) $H=-\frac{\hbar^2}{2\mu}\nabla^2_{c.m.}-\frac{\hbar^2}{2m}\nabla^2+\frac{Ze^2}{4\pi\varepsilon_0 r}$	(S) $H=-\frac{\hbar^2}{2m}\nabla^2_{c.m.}-\frac{\hbar^2}{2\mu}\nabla^2-\frac{Ze^2}{4\pi\varepsilon_0 r}$

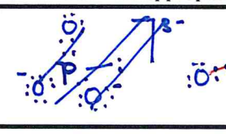
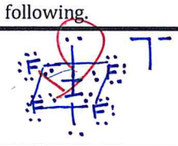
4. Two copper nanowires are insulated by a copper oxide nano-layer that provides a 10.0-eV potential barrier. The tunneling probability between the nanowires by electron, with energy 9.00-eV, through a 1.00-nm thick oxide layer would be, **2.0 Marks**

(L) 0.86 %	(M) 0.68 %	(N) 0.43 %	(O) 0.34 %	*Use* $T=16\varepsilon(1-\varepsilon)e^{-2\kappa L}$ *Also,* $\varepsilon=E/V$ *and* $\kappa=\{2m(V-E)\}^{1/2}/\hbar$.

5. Considering harmonic oscillator model, when average potential energy is equal to average kinetic energy, the expression for the vibrational energy of a chemical bond can be written as, $E_v=(v+1/2)\hbar\omega$, where $\omega=\sqrt{k/\mu}$ and v is vibrational quantum number. The uncertainly in the displacement of the bond i.e., Δx in the ground state can be written as, **2.0 Marks**

(J) $\sqrt{\hbar/\mu\omega}$	(I) $\sqrt{\hbar/2\mu\omega}$	(H) $\sqrt{2\mu\omega/\hbar}$	(G) $\sqrt{\mu\omega/\hbar}$

6. Draw the Lewis structure with appropriate molecular geometry for the following. **1 Mark**

$[PO_3]^{3-}$ 	$[IF_4]^-$ 

7. Using Slater's rules, calculate the effective nuclear charge for a 3*d* and a 4*s* electron in nickel **1.0 Mark**

(i) 3*d* = 7.55	(ii) 4*s* = 4.05

8. Indicate if the following exhibit Strong (S), Weak (W) or No (N) Jahn-Teller distortion **1 Mark**

	$[CoF_6]^{3-}$	$[Ru(ox)_3]^{3-}$	$[Cr(CN)_6]^{3-}$	$[Co(NH_3)_6]^{2+}$	$[Cr(H_2O)_6]^{2+}$
Strength of Jahn-Teller distortion	W	N	N	S	S

9. Which of the following statements are true (T) and which are false (F). (Suppose the answer for the statements (i), (ii), (iii) and (iv) follows the order; True, True, False and True respectively, then the option is "TTFT") **1+ 1 Mark**

9a

(i) In a tetragonally elongated (*z*-out) octahedral complex, d_{z2} orbitals are destabilized

(ii) In d^4 octahedral complexes with π-acceptor ligands, the LUMO is e_g^* molecular orbital

(iii) In octahedral complex with I^- ligand, the first d electron is filled in t_{2g}^* molecular orbital

(iv) Asymmetry in t_{2g} orbital occupancy results in strong Jahn-Teller distortion

8a Tick right option	
(V) FTFT	
(U) FTTF	✓
(A) TTFT	
(S) TFTT	

9b

(i) Using VBT, one can infer that $[CoF_6]^{3-}$ involves d^2sp^3 hybrid orbitals

(ii) Br^- has a larger ionic radius than Rb^+

(iii) There is an large increase in atomic radii as one moves from Si to Ge

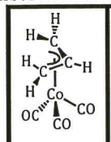
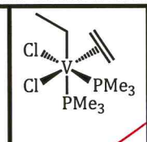
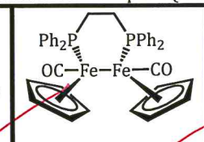
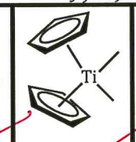
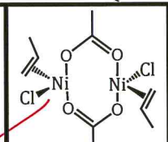
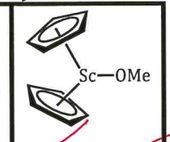
(iv) For EH_3 (E = As, N & P), the increasing order of their H-E-H angle is $AsH_3 < PH_3 < NH_3$

8b Tick right option	
(H) FTFT	✓
(K) TTFT	
(G) FTTF	
(E) TFTT	

10. Which of the following are true when, one compares bond angles and bond lengths that are highlighted **1.5 Marks**

Angle Ir–O–CH_2	≫	>	< ✓	=
Length Ir–O	=	> ✓	≤	<

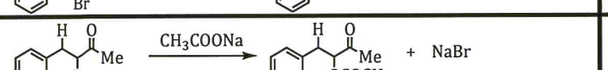
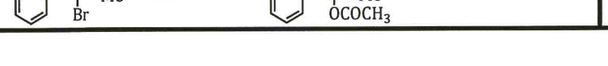
11. Indicate the number of valence electron on each metal complex. (*Answer any five*) **(0.5 × 5) = 2.5 Marks**

						
Electron Count		14	18	16	16	14

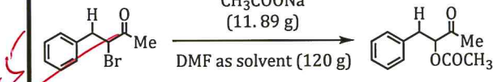
12. For given set of elements or complexes, arrange them in the increasing order of the indicated property **1.0 Mark**

Elements / Complexes	*Property*	*Arrange in the increasing order*
Mg, Al, P, S	Ionization Potential (First)	Al < Mg < S < P
Si, Rb, Na, Cl	Metallic Character	Cl < Si < Na < Rb
$Fe(H_2O)_6^{2+}$, $Ru(H_2O)_6^{3+}$, $Fe(H_2O)_6^{3+}$	CFSE	$Fe(H_2O)_6^{2+} < Fe(H_2O)_6^{3+} < Ru(H_2O)_6^{3+}$
$[Co(H_2O)_6]^{3+}$, $[CoF_6]^{3-}$, $[Co(CN)_6]^{3-}$	Wavelength of Absorption	$[Co(CN)_6]^{3-} < [CoF_6]^{3-} < [Co(H_2O)_6]^{3+}$

13. Calculate the % atom economy of the following reactions: (MW: Br = 80, Na = 23) **0.5 Mark**

(i) 	% atom economy =	57.24 %
(ii) 	% atom economy =	66.67 %

14. Calculate the % yield and E-factor of the following reaction **0.5 Mark**



For chromatographic separation, 200 g of solvent and for crystallization, 50 g of solvent is needed

% yield = 80.26

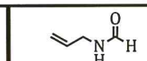
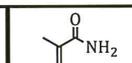
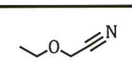
E-factor = 16.36

15. Identify the correct statement (*Please Tick in the space provided*) **(0.5 + 0.5) Mark**

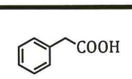
15a. A CASCADE reaction is one where:		15b. The GREENEST solvent is:	
(i) Several components react together to give a single product.		(i) Diethylether	
(ii) Reaction generating no waste.		(ii) Ethylacetate	✓
(iii) Multiple chemical transformations take place within a single reactant.	✓	(iii) Benzene	
(iv) Where atom economy is 100 %.		(iv) Chloroform	

16. Identify the structure of the compound from their IR absorption bands(*Please Tick in space provided*) **(0.5 + 0.5) Mark**

16a. MF:C_4H_7NO, IR (KBr): 3375, 3165, 2986, 2823, 2728, 1685, 1660 cm^{-1}.

 (P)		 (R) ✓		 (S)		 (T)	

16b. MF:$C_8H_8O_2$, IR (KBr) cm^{-1}: 2967, 3155, 1745, 1250.

 (L) ✓		 (O)		 (N)		 (M)	

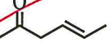
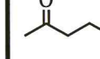
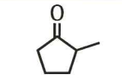
17. In the following statements mark the True statement as (T) and False (F). **(0.5 + 0.5) Mark**

(i) Vibrational frequency is independent on the mass of the atoms	(F)
(ii) In a standard IR spectrum Y-axis represents absorption	(F)
(iii) IR spectra of two compounds can be identical in their finger print region	(F)
(iv) In IR, the energy absorbed will increase the amplitude of vibration of the bond but not the frequency	(T)
(v) In IR, a C-D stretching will require more energy than a C-H stretching	(F)
(i) According to Hooks' law C-Cl (str) will require less energy than C-O (str).	(T)
(ii) Region between 600-1400 cm^{-1} is called functional group region	(F)
(iii)The carbonyl group of acetone absorb at highest cm^{-1} than the carbonyl group of acetamide	(T)
(iv)A nitrile absorption peak is stronger than a terminal acetylene peak	(T)
(v) Diphenyl acetylene will show weak or no absorption ~2156 cm^{-1}	(T)

18. The absorbance (at 228 nm) of a solution of benzonitrile in ethanol (1×10^{-4} molar) is determined to be 1.30. The cell length is 2 cm. What is the molar absorptivity? **0.5 Mark**

Molar absorptivity = 6.5×10^3 $l\,mol^{-1}\,cm^{-1}$

19. For an aliphatic carbonyl compound, typical electronic transitions observed are n→π* λ_{max} = 277 (ε =14.2) and π→π* λ_{max} = 198 (ε =9660). Which one of the listed (X, W, Y, Z) compound will show the given transition, n→π* λ_{max} = 337 (ε =28) and π → π* λ_{max} = 208 (ε = 9887) (*Please Tick in the space provided*) **0.5 Mark**

 (X)		 (W)	✓	 (Y)		 (Z)	