CSIR-NET (JRF)

DECEMBER-2019

PHYSICAL SPECTRA

ASSIGNMENT SHEET

GRAVITY ACADEMY OF
CHEMICAL SCIENCE

TAKE A CHANCE MAKE A CHANGE

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SECTION-A

[CSIR-JRF (NET) PREVIOUS PAPER QUESTIONS]

1. In IR spectrum of $[Co(CN)_5H]^{3-}$ the Co–H stretch is observed at 1840 cm^{-1}. The Co–D stretch in $[Co(CN)_5D]^{3-}$ will appear at nearly: **[JUNE-2011]**

   (A) 1300 cm^{-1} (B) 1400 cm^{-1} (C) 1500 cm^{-1} (D) 1600 cm^{-1}.

2. The rotational constant of $^{14}N_2$ is 2 cm^{-1}. The wave number of incident radiation in a Raman spectrometer is 20487 cm^{-1}. What is the wave number of first scattered Stokes line (in cm^{-1}) of $^{14}N_2$? **[JUNE-2011]**

   (A) 20479 (B) 20475 (C) 20499 (D) 20495

3. The Q band in the vibrational spectrum of acetylene is observed in the: **[JUNE-2011]**

   (A) C—C stretching mode (B) C—H symmetric stretching mode

   (C) Bending mode (D) C—H antisymmetric stretching mode

4. The vibrational energy levels, $v'' = 0$ and $v' = 1$ of a diatomic molecule are separated by 2143 cm^{-1}. Its anharmonicity constant ($\omega_e x_e$) is 14 cm^{-1}. The values of ω_e (in cm^{-1}) and first overtone (cm^{-1}) of this molecule are respectively. **[DEC.-2011]**

   (A) 2143 and 4286 (B) 2157 and 4286 (C) 2157 and 4314 (D) 2171 and 4258.

5. P_A and P_B denote the populations of two energy states E_A and E_B, and $E_A > E_B$. The correct statement when the temperature $T_1 > T_2$ is : **[DEC.-2011]**

   (A) $P_A(T_1) > P_B(T_1)$, $P_A(T_2) < P_B(T_2)$ and $(P_A/P_B)_{T_1} > (P_A/P_B)_{T_2}$

   (B) $P_A(T_1) < P_B(T_1)$, $P_A(T_2) > P_B(T_2)$ and $(P_A/P_B)_{T_1} < (P_A/P_B)_{T_2}$

   (C) $P_A(T_1) < P_B(T_1)$, $P_A(T_2) < P_B(T_2)$ and $(P_A/P_B)_{T_1} > (P_A/P_B)_{T_2}$

   (D) $P_A(T_1) < P_B(T_1)$, $P_A(T_2) < P_B(T_2)$ and $(P_A/P_B)_{T_1} > (P_A/P_B)_{T_2}$

6. For a diatomic molecule AB, the energy for the rotation transition from J = 0 to J = 1 state is 3.9 cm^{-1}. The energy for the rotational transition from J = 3 to J = 4 state would be : **[JUNE-2012]**

   (A) 3.9 cm^{-1} (B) 7.8 cm^{-1} (C) 11.7 cm^{-1} (D) 15.6 cm^{-1}.

7. For the vibrational Raman spectrum of a homonuclear diatomic molecule, the selection rule under harmonic approximation is : **[JUNE-2012]**

   (A) $\Delta v = 0$ only (B) $\Delta v = \pm 1$ only (C) $\Delta v = \pm 2$ only (D) $\Delta v = 0, \pm 1$

8. In the vibrational spectrum of CO_2, the number of fundamental vibrational modes common in both Infrared and Raman are: **[DEC-2012]**

   (A) Three (B) Two (C) One (D) Zero

9. The relative population in two states with energies E_1 and E_2 satisfying Boltzman distribution is given by $n_1/n_2 = (3/2)\exp[-(E_1 - E_2)/k_BT]$. The relative degeneracy g_2/g_1 is : **[DEC-2012]**

   (A) 2 (B) 2/3 (C) 3/2 (D) 3

10. The absorption spectrum of O_2 shows a vibrational structure that becomes continuum at 56875 cm^{-1}. At the continuum, it dissociates into one ground state atom (O_g) and one excited state atom (O_e). The energy difference between O_e and O_g is 15125 cm^{-1}. The dissociation energy (in cm^{-1}) of ground state of O_2 is : **[DEC-2012]**

    (A) $\frac{56875}{15125}$ (B) $\frac{15125}{56875}$ (C) 72000 (D) 41750.

11. The vibrational frequency and anharmonicity constant of an alkali halide are 300 cm^{-1} and 0.0025, respectively. The positions (in cm^{-1}) of its fundamental mode and first overtone are respectively : **[DEC-2012]**

    (A) 300,600 (B) 298.5, 595.5 (C) 301.5, 604.5 (D) 290, 580.

12. In the presence of an external magnetic field (normal Zeeman effect), the transition $^1D_2 \rightarrow {}^1P_1$ splits into **[JUNE-2013]**

(A) 9 lines (B) 8 lines (C) 7 lines (D) 6 lines

13. The equilibrium population ratio (n_i/n_i) of a doubly-degenerate energy level (E_3) lying at energy 2 units higher than a lower non-degenerate energy level (E_3), assuming $k_aT = 1$ unit, will be: **[JUNE-2013]**

(A) $2e^{-2}$ (B) $2e^{2}$ (C) e^{2} (D) e^{-2}

14. The atomic masses of fluorine and hydrogen are 19.0 and 1.0 amu, respectively (1 amu = 1.67×10^{-27} kg). The bond length of HF is 2.0 Å. The moment of inertia of HF is : **[DEC-2013]**

(A) 3.2×10^{-47} kg m^2 (B) 6.4×10^{-47} kg m^2 (C) 9.6×10^{-47} kg m^2 (D) 4.8×10^{-47} kg m^2.

15. The C = O bond length is 120 pm in CO_2. The moment of inertia of CO_2 would be close to (masses of C and O are 1.9×10^{-27} kg and 2.5×10^{-27} kg, respectively) **[JUNE-2014]**

(A) 1.8×10^{-45} kg m^2 (B) 3.6×10^{-45} kg m^2

(C) 5.4×10^{-45} kg m^2 (D) 7.2×10^{-45} kg m^2

16. Bond lengths of homonuclear diatomic molecules can be determined with the help of both

(A) Rotational and vibrational spectroscopy **[DEC-2014]**

(B) Rotational and rotational Raman spectroscopy

(C) Rotational Raman and electronic spectroscopy

(D) Vibrational and electronic spectroscopy

17. If the component of the orbital angular momentum along the molecular axis of a heteronuclear diatomic molecule is nonzero, the rotational-vibrational spectrum will show **[DEC-2014]**

(A) P and R branches only (B) P and Q branches only

(C) Q and R branches only (D) All the P, Q and R branches

18. If the bond length of a heternuclear diatomic molecule is greater in the upper vibrational state, the gap between the successive absorption line of P-branch **[DEC-2014]**

(A) Increases non-linearly (B) Decreases non-linearly

(C) Increases linearly (D) Decreases linearly

19. Intense band generally observed for a carbonyl group in the IR spectrum is due to

(A) The force constant of CO bond is large **[JUNE-2015]**

(B) The force constant of CO bond is small

(C) There is no change in dipole moment for CO bond stretching

(D) The dipole moment change due to CO bond stretching is large

20. The symmetric rotor among the following is: **[JUNE-2015]**

(A) CH_4 (B) CH_3Cl (C) CH_2Cl_2 (D) CCl_4

21. The spectroscopic technique, by which the ground state dissociation energies of diatomic molecules can be estimated, is: **[JUNE-2015]**

(A) Microwave spectroscopy (B) Infrared spectroscopy

(C) UV-visible absorption spectroscopy (D) X-ray spectroscopy

22. The molecule with the smallest rotational constant (in the microwave spectrum) among the following is : **[DEC-2015]**

(A) $N\equiv CH$ (B) $HC\equiv CCl$ (C) $ClC\equiv CF$ (D) $B\equiv CCl$

23. The spectroscopic technique that can distinguish unambiguously between *trans*-1,2- dichloroethylene and *cis*-1,2-dichloroethylene without any numerical calculation is **[DEC-2015]**

(A) Microwave spectroscopy (B) UV-Visible spectroscopy

(C) X-ray photoelectron spectroscopy (D) γ-ray spectroscopy

24. If the reduced mass of a diatomic molecule is doubled without changing its force constant, the vibrational frequency of the molecule will be **[DEC-2015]**

(A) $\sqrt{2}$ times the original frequency (B) $1/\sqrt{2}$ times the original frequency

(C) twice the original frequency (D) unchanged

25. Upon application of a weak magnetic field, a line in the microwave absorption spectrum of rigid rotor splits into 3 lines. The quantum number (J) of the rotational energy level from which the transition originates is : **[JUNE-2016]**

(A) 0 (B) 1 (C) 2 (D) 3

26. The rotational constant and the fundamental vibrational frequency of HBr are, respectively, 10 cm^{-1} and 2000 cm^{-1}. The corresponding values for DBr approximately are : **[DEC-2016]**

(A) 20 cm^{-1} and 2000 cm^{-1} (B) 10 cm^{-1} and 1410 cm^{-1}

(C) 5 cm^{-1} and 2000 cm^{-1} (D) 5 cm^{-1} and 1410 cm^{-1}

27. Among the following, both microwave and rotational Raman active molecule is : **[DEC-2016]**

(A) CH_4(B) N_2O (C) C_2H_4 (D) CO_2

28. Vibrations of diatomic molecules are usually modelled by a harmonic potential. If the.potential is given by x^2, the correct statement is : **[DEC-2016]**

(A) force is 2x and force constant is 2 (B) force is – 2x and force constant is 2

(C) force is 2x and force constant is –1 (D) force is – 2x and force constant is –1

29. The *v* = 0 to 1 vibration-rotation spectrum of a diatomic molecule exhibits transition for R(0), R(1), P(1) and P(2) lines at 2242, 2254, 2216 and 2203 cm^{-1}, respectively. From this data, we can conclude that the molecule : **[JUNE-2017]**

(A) has rigid rotation and harmonic vibration (B) has anharmonic vibration

(C) has rotational-vibrational interaction (D) is affected by nuclear spin-statistics

30. The pair that contains a spherical top and a symmetric top, among the following, is :

[DEC-2017]

(A) CH_4, CH_2Cl_2 (B) CH_2Cl_2, CH_3Cl (C) CH_3Cl, CH_4 (D) CH_4, $C(CH_3)_4$.

31. The spectrum of sodium atom has a closely separated doublet at 16956.2 and 16973.4 cm^{-1}. The higher energy transition is due to : **[DEC-2018]**

(A) $^2P_{3/2} \rightarrow {}^2S_{1/2}$ (B) $^2P_{1/2} \rightarrow {}^2S_{1/2}$ (C) $^2P_{3/2} \rightarrow {}^2P_{1/2}$ (D) $^2S_{1/2} \rightarrow {}^2P_{3/2}$

32. The third and fourth lines in the rotational Raman spectrum of CO are separated by 8 cm^{-1}. The CO bond length is given by : **[DEC-2018]**

(A) $\sqrt{\dfrac{h}{16\pi^2\mu c}}$ (B) $\sqrt{\dfrac{3h}{32\pi^2\mu c}}$ (C) $\sqrt{\dfrac{h}{32\pi^2\mu c}}$ (D) $\sqrt{\dfrac{5h}{32\pi^2\mu c}}$

33. For a linear molecule then mean energies for translation, rotation ($T>>\theta_R$) and vibration ($T>>\theta_V$) follow ratio : **[JUNE-2019]**

(A) 1 : 3/2 : 1 (B) 3/2 : 1 : 1 (C) 1 : 1/2 : 1 (D) 1/2 : 1 : 1

34. The populations of protron spins in the highest energy level of a sample in magnetic fields of 1.5 T and 7.0 T are N' and N, respectively. The value of ln N'/N is (γ, h, k, T are gyromagnetic ratio of the proton, Planck's constant, Boltzmann constant and temperature of the sample, respectively; assume that the partition functions for both systems can be approximated as 1) **[JUNE-2019]**

(A) $5.5\gamma\hbar$ / kT (B) $\dfrac{3}{14}\gamma\hbar$ / kT (C) $\dfrac{14}{3}\gamma\hbar$ / kT (D) $8.5\gamma\hbar$ / kT

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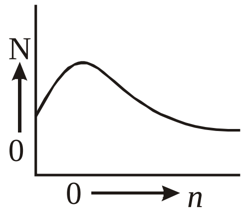
SECTION-B
[GRADUATE APTITUDE TEST IN ENGINEERING (GATE) PREVIOUS PAPER QUESTIONS]

1. The population (N) distribution over states (n) of a diatomic molecule corresponds to



[2000]

(A) translation (B) vibration (C) rotation (D) electronic

2. Radiation of 10^{14} Hz falls in the region of **[2002]**

(A) radiofrequency (B) microwave (C) visible (D) X-rays

3. The spacing between the rotational lines of HF is 40 cm^{-1}. The corresponding spacing between the rotational lines in DF is approximately **[2002]**

(A) 20 cm^{-1} (B) 30 cm^{-1} (C) 60 cm^{-1} (D) 7.5 cm^{-1}

4. Neglecting the mass of hydrogen (1.0 amu) and deuterium (2.0 amu) with respect to that of iodine (127 amu), the ratio between fundamental vibrational frequencies of HI and DI is : **[2004]**

(A) $\frac{1}{2}$ (B) 2 (C) $\frac{1}{\sqrt{2}}$ (D) $\sqrt{2}$

5. The population of Jth rotational lelvel N is given by $N_j = N_0(2J + 1)e^{-[j(j+1)B]/kT}$. The J value of rotational level with maximum population (J_{max}) is given by **[2004]**

(A) $\frac{(2kT/B)}{\sqrt{2}}$ (B) $\frac{\sqrt{2kT/B}-1}{2}$ (C) $\frac{kT}{B}$ (D) $\frac{B}{kT}$

6. Match the column. **[2005]**

Column-I (Spectral Technique)	**Column-II (Selection Rule)**
P. Rotational transition	I. $\Delta v = \pm 1$
Q. Vibrational transition	II. $\Delta J = 0$
R. Electronic transition in atoms	III. $\Delta J = \pm 1$
S. Molecular ensemble	IV. $\Delta l = \pm 1$
	V. $\Delta m_1 = \pm 1$
	VI. $\Delta v = 0$
	VII. $\Delta 1 = 0$

(A) P-I, Q-VI, R-VII, S-V (B) P-II, Q-I, R-IV, S-V

(C) P-III Q-I, R-IV, S-V (D) P-I, Q-VI, R-VII, S-V

7. The zero-point energy of the vibration of $^{35}Cl_2$ mimicking a harmonic oscillator with a force constant k = 2293.8 Nm^{-1} is : **[2006]**

(A) 10.5×10^{-21} J (B) 14.8×10^{-21} J (C) 20.9×10^{-21} J (D) 29.6×10^{-21} J

8. The selection rules for the appearance, of P branch in the rotational-vibrational absorption spectra of a diatomic molecule within rigid rotor-harmonic oscillator model are : **[2007]**

(A) $\Delta v = \pm 1$ and $\Delta J = \pm 1$ (B) $\Delta v = +1$ and $\Delta J = +1$

(C) $\Delta v = +1$ and $\Delta J = -1$ (D) $\Delta v = -1$ and $\Delta J = -1$

9. The J = 0 → 1 rotational transition for $^1H\,^{79}Br$ occurs at 500.72 GHz. Assuming the molecule to be a rigid rotor, the J = 3 → 4 transition occurs at : **[2007]**

(A) 50.1 cm^{-1} (B) 66.8 cm^{-1} (C) 16.7 cm^{-1} (D) 83.5 cm^{-1}

10. The rotational constants for CO in the ground and the first excited vibrational states are 1.9 and 1.6 cm^{-1}, respectively. The % change in the internuclear distance due to vibrational excitation is : **[2008]**

(A) 9 (B) 30 (C) 16 (D) 0

Linked Answer Questions 11 & 12

The infrared spectrum of a diatomic molecule exhibits transitions at 2144, 4262 and 6354 cm^{-1} correspoding to excitations from the ground state to the first, second and, third vibration states respectively. **[2008]**

11. The fundamental transition (cm^{-1}) of the diatomic molecule is at :

(A) 2157 (B) 2170 (C) 2183 (D) 2196

12. The anharmonicity constant (cm^{-1}) of the diatomic molecule is :

(A) 0.018 (B) 0.012 (C) 0.006 (D) 0.003

13. The fundamental vibrational wavenumbers of H_2 and I_2 are 4403.2 cm^{-1} and 214.5 cm^{-1}, respectively. The relative population of the first excited vibrational states of these two molecules compared to their respective ground states at 300 K are respectively : **[2009]**

(A) 6.75×10^{-1} and 3.57×10^{-1} (B) 6.75×10^{-10} and 3.57×10^{-1}

(C) 3.57×10^{-6} and 6.75×10^{-1} (D) 3.57×10^{-1} and 6.75×10^{-1}

14. The rotational Raman spectrum of $^{19}F_2$ shows a series of Stokes lines at 19230.769 cm^{-1}, 19227.238 cm^{-1} and 19223.707 cm^{-1}. The rotational constant for $^{19}F_2$ in GHz is : **[2009]**

(A) 26.484 (B) 52.968 (C) 105.936 (D) 3.531

15. The most populated rotational state for HCl (B = 8.5 cm^{-1}) at 300 K is **[2010]**

(A) 2 (B) 3 (C) 5 (D) 7

16. The ratio of life times of two states that gives rise to line widths of 1.0 cm^{-1} and 0.2 cm^{-1} respectively is **[2010]**

(A) 1 : 2 (B) 1 : 5 (C) 2 : 1 (D) 5 : 1

Common data for Qs. 17 and 18

A hypothetical molecule XY has the following properties

Reduced mass : 2×10^{-26} kg

X-Y bond length : 100 pm

Force constant of the bond : 8×10^2 N.m^{-1} **[2011]**

17. The frequency of radiation (in cm^{-1} units) required to vibrationally excite the molecule from $\upsilon = 0$ and $\upsilon = 1$ state is

(A) 3184.8 (B) 2123.2 (C) 1061.6 (D) 840.0

18. The frequency of radiation (in cm^{-1} units) required to rotationally excite the molecule form J = 0 to J = 1 state is

(A) 1.4 (B) 2.8 (C) 3.2 (D) 3.6

Statement for Linked Answer Qs. 19 and 20

A 20491 cm^{-1} laser line was used to excited oxygen molecules (made of ^{16}O only) to obtain the rotational Raman spectrum. The resulting rotational Raman spectrum of oxygen molecule has the first Stokes line at 20479 cm^{-1}. **[2012]**

19. The rotational constant (usually denoted as B) for the oxygen molecule is :

(A) 1.2 cm^{-1} (B) 2.0 cm^{-1} (C) 3.0 cm^{-1} (D) 6.0 cm^{-1}

20. The next rotational Stokes line is expected at :

(A) 20467 cm^{-1} (B) 20469 cm^{-1} (C) 20471 cm^{-1} (D) 20475 cm^{-1}

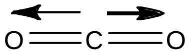
21. The infrared spectrum of HCl gas shows an absorption band centered at 2885 cm^{-1}. The zero point energy of HCl molecule under harmonic oscillator approximation is : **[2013]**

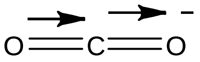
(A) 2.8665×10^{-22} J (B) 2.8665×10^{-20} J (C) 5.7330×10^{-22} J (D) 5.7330×10^{-20} J.

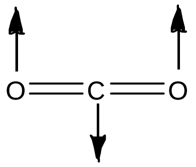
22. The ratio of molecules distributed between two states is 9.22×10^6 at 300 K. The frequencies in energy (in kJ mol^{-1}) of the two states is .... **[2014]**

23. Consider a two state system at thermal equilibrium with equal degeneracy where the excited state is higher in energy than the ground state for 0.1 eV. The ratio of the population of the excited state to that of the ground state, at a temperature for which $k_BT = 0.05$ eV, is .... **[2016]**

24. Of the vibrational modes given below, the IR active mode(s) is(are) :

(i) 

(ii) 

(iii) 

[2016]

(A) ii only (B) iii only (C) i and ii (D) ii and iii

25. For ortho-hydrogen, the nuclear wavefunction and the rotational quantum number, respectively, are : **[2017]**

(A) Antisymmetric and even (B) Symmetric and odd

(C) Symmetric and even (D) Antisymmetric and odd

26. The spacing between the two adjacent lines of the microwave spectrum of $H^{35}Cl$ is 6.35×10^{11} Hz. Given that the bond length of $D^{35}Cl$ is 5% greater than that of $H^{35}Cl$, the corresponding spacing for $D^{35}Cl$ is _______ 11 × 10^{11} Hz. (Up to two decimal places) **[2018]**

27. For a diatomic vibrating rotor, in vibrational level $\upsilon = 3$ and rotational level J, the sum of the rotational and vibrational energies is 11493.6 cm^{-1}. Its equilibrium oscillation frequency is 2998.3 cm^{-1}, anharmonicity constant is 0.0124 and rotational constant under rigid rotor approximation is 9.716 cm^{-1}. The value of J is ___________. (Up to nearest integer) **[2017]**

28. The energy of a hydrogen molecule in its ground state equilibrium configuration is –31.7 eV. Its dissociation energy is _________ eV. (Up to one decimal place) **[2018]**

29. At temperature T, the canonical partition function of a harmonic oscillator with fundamental frequency (v) is given by **[2018]**

$$q_{vib}(T) = \frac{e^{-hv/2k_BT}}{1-e^{-hv/k_BT}}$$

For $\frac{hv}{k_BT} = 3$, the probability of finding the harmonic oscillator in its ground vibrational state is _____. (Up to two decimal places)

30. For a diatomic vibrating rotor, in vibrational level $\upsilon = 3$ and rotational level J, the sum of the rotational and vibrational energies is 11493.6 cm^{-1}. Its equilibrium oscillation frequency is 2998.3 cm^{-1}, anharmonicity constant is 0.0124 and rotational constant under rigid rotor approximation is 9.716 cm^{-1}. The value of J is ___________. (Up to nearest integer) **[2018]**

31. Consider a two-state system at thermal equilibrium having energies 0 and 2 k_BT for which the degeneracies are 1 and 2, respectively. The value of the partition function at the same absolute temperature T is .... (Round off to two decimal places). (k_B is the Boltzmann constant) **[2019]**

32. Consider a system of three indential and distinguishable non-interacting particles and three available non-degenerate single particle energy levels having energies 0, ε and 2ε. The system is in contact with a heat bath of temperature T K. A total energy of 2ε is shared by these three particles. The number of ways the particles can be distributed is .... **[2019]**

33. Consider a two dimensional harmonic oscillator with angular frequency $\omega_x = 2\omega_y = 6.5 \times 10^{14}$ rad s^{-1}. The wavelength of x polarized light required for the excitation of a particle from its ground state to the next allowed excited state is .... × 10^{-6} m. (Round off to one decimal place). (Speed of light $c = 3.0 \times 10^8$ m s^{-1}) **[2019]**

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