Important Questions On Inorganic Spectroscopy

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1.Which of the following molecules is EPR inactive?

A. B_2

B. O_2

C. O_2^{-2}

D. H_2^+

2. No. of signals in ^{31}P NMR of P_4S_3 is:

A. 2

B. 3

C. 4

D. 5

3. No. of lines in Benzoquinone in EPR spectrum is:

A. 5

B. 6

C. 8

D. 4

4.In Mossbauer spectroscopy, we study ....transitions using .... radiation.

A. valence electrons, X- rays respectively.

B. Core electrons, X- rays respectively.

C. Nuclear spin, cosmic rays respectively.

D. Nuclear, gamma rays respectively.

5. Which of the following molecules shows isomeric shift?

a) $[PtCl_4]^{-2}$

b) NH_4^+

c) BF_4^-

d) All of the above

6. For a complex of V^{+2} in zero field splitting, no. of Kramers doublet will be?

A. 4

B. 2

C. 1

D. 6

7. Choose the correct statement:

A. For a tetragonally elongated geometry, order of g is $g_x,g_y > g_z$.

B. For an achiral molecule, $g_x = g_y \neq g_z$.

C. For an amorphous solid, $g_x = g_y = g_z$, but the same is not true for gaseous .

D. For tetragonally compressed geometry, $g_x,g_y > g_z$.

8. Trans – $[Ti(H_2O)_4(NH_3)_2]^{+2}$ has ......no. of lines .

A. 180

B. 36

C. 72

D. 360

9. What will be the sum of no. of signals observed for Fe in Mossbauer spectroscopy of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$.

A. 2

B. 4

C. 5

D. 3

10. Which of the following statements is incorrect about Mossbauer spectroscopy?

A. It is also known as NGR.

B. It is used to estimate oxidation state of metal.

C. This does not give any information about the symmetry of molecules.

D. This spectroscopy is applicable to Au, Sn, Fe .

Answer Key:

1. C	6. B
2. A	7. D
3. A	8. D
4. D	9. D
5. C	10. C

Solutions:

Solution1. For EPR inactive, molecules should have all paired electrons.

B_2: No. of electrons =10

Electronic configuration will be: $\sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \pi_{2px}^{1} = \pi_{2py}^{1}$.

So, this configuration has unpaired electrons which means it will be an EPR active molecule.

O_2: No. of electrons =16

Electronic configuration will be : $\sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2pz}^2 < \pi_{2px}^{2} = \pi_{2py}^{2} < \pi_{2px}^{*1} = \pi_{2py}^{*1}$.

So, this configuration has unpaired electrons which means it will be an EPR active molecule.

O_2^{-2}: No. of electrons =18

Electronic configuration will be: $\sigma_{1s}^2 < \sigma_{1s}^{*2} < \sigma_{2s}^2 < \sigma_{2s}^{*2} < \sigma_{2pz}^{*2} < \pi_{2px}^{2} = \pi_{2py}^{2} < \pi_{2px}^{*2} = \pi_{2py}^{*2}$.

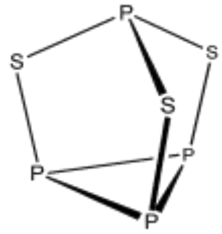
So, this configuration has all paired electrons which means it will be an EPR inactive molecule.

H_2^+ : No. of electrons = 3

Electronic configuration will be: $\sigma_{1s}^2 < \sigma_{1s}^{*1}$

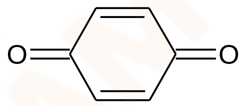
So, this configuration has unpaired electrons, which means it will be an EPR active molecule.

Solution 2. The structure of P_4S_3 is:



In this structure, there are two types of P atoms present, one type of P has only P-S-P bonds while the second type has P-S-P bonds along with P-P bonds. So, no. of signals will be 2. One has q and second has d because there are 3 P of one type and one P of second type.

Solution 3. The structure of benzoquinone is:



It has 4 H's and the chemical environment of all the hydrogens is the same. So, all H's are chemically equivalent.

No of lines = (2nI +1)

Where n= no. of Hydrogens

I = spin of proton (here)

No. of lines = (2× 4× 0.5) + 1 = 5

Solution 4. In Mossbauer spectroscopy, we study nuclear transitions using gamma radiations. In this, we observe very broad signals because the energy difference between the levels is very high. Gamma radiations are the second most energetic radiations.

Solution 5. In the given molecules, only BF_4^- shows isomer shift because both isomers have different chemical shift values. Boron has two isotopes :^{10}B ,^{11}B. Due to the existence of isotopic shift, BF_4^- has two signals in ^{19}F NMR with different chemical shift values.

Solution 6. For V^{+2}, electronic configuration will be: $[Ar]3d^3\ 4s^0$

Here, 3 unpaired electrons are present, and for each unpaired electron, I = ½ .

So, for 3 unpaired electrons, I= 3 /2

Its splitting pattern will be 3/2, 1/2, -1/2, -3/2.

So, we have 2 Kramers doublet here and these are:

(1/2, -1/2), (3/2, -3/2)

Solution 7. For a tetragonally elongated geometry, one extra electron is present in d_z^2 orbital than $d_x^2\text{-}_y^2$, so more electron density is present in the z axis. So, order of g will be:

$g_z > g_x, g_y$

While in tetragonally compressed geometry, one extra electron is present in $d_x^2\text{-}_y^2$ orbital than d_z^2.So, more electron density is in xy axes, The order of g value will be:

$g_x, g_y > g_z$.

For achiral molecule,

$g_x \neq g_y \neq g_z$.

For an amorphous solid,

$g_x = g_y = g_z$, also the same is true for gaseous.

Solution 8. According to Drago's rule: Only the proton attached to nonmagnetic nuclei will participate in splitting. Here in the given complex, O has the nonmagnetic nuclei whereas N has a magnetic nucleus. Also, only the 8 protons attached to O will participate in splitting. Ti has a magnetic active nucleus with I =3/2.

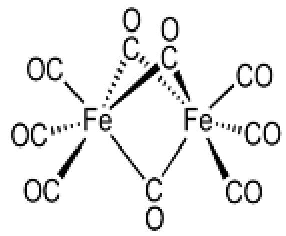
So, no. of lines = $(2n_1I_1+1) \times (2n_2I_2+1) \times (2n_3I_3+1)$

$= [\ (2\times3/2\times1)\ +1] \times [(2\times1\times2)\ +1] \times [(2\times1/2\times8)\ +1]$

$= 4\times9\times5 = 180$

Since, Ti has two unpaired electrons, so, total no. of lines = 2×180 = 360

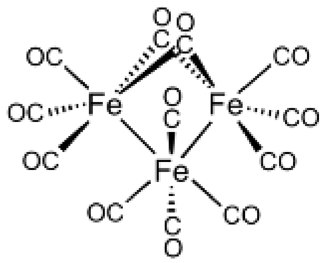
Solution 9. The structure of $Fe_2(CO)_9$ is:



In this, only 1 type of Fe is present, so,

No. of signal = 1

The structure of $Fe_3(CO)_{12}$ is:



In this, two types of Fe are present, one which is connected to 5CO and 1Fe and second one is connected to 4CO and 2 Fe, So, no. of signals for different Fe = 2.

Sum of signals of Fe = 1+2 =3

Solution 10. Mossbauer spectroscopy is also known as NGR (nuclear gamma resonance) since this spectroscopy uses gamma radiations. It also helps to determine the oxidation state, as more the oxidation state, less will be electron density then this will affect the isomer shift (can have inverse or direct relation, depending on molecule). This gives information about the symmetry of molecules. If the symmetry (electronic and ligand both) of molecule is spherical, then electric field gradient is zero and quadrupole splitting will be absent, whereas if symmetry is non spherical, then electric field gradient is nonzero and quadrupole splitting will be present. This spectroscopy is applicable to Au, Sn, Fe.