PHOTOELECTRON SPECTROSCOPY OF ORGANIC MAGNETS

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Introduction

The Photoelectron spectroscopy is a analytical tool which gives Quantitative as well as Qualitative data of surface of a compound. It measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within material. In this presentation we are going to discus about the photoelectron spectra of some molecules (organic magnets) which exhibit ferromagnetism. We divide this presentation into three topics.1.what are organic magnets 2.brief introduction of about photoelectron spectra 3.photoelectron spectra of some magnetically active molecules.

organic magnets

organic magnet is a material exhibiting bulk magnetic ordering and possessing un paired electron spin residing in p- orbital's that contributing magnetic ordering.In general magnetism was observed in Inorganic elements such as Fe,Co,Ni,…etc, alloys (perm alloy)and some simple compounds(Transition metal oxides).All these atoms contains unpaired spin densities in their "d" and "f" orbitals. These un paired spin densities results net magnetism. So building blocks of these magnets are atoms. But in this new class of compounds not atoms but molecules. These new classes of compounds open new doors in chemistry, physics and material sciences. Molecular magnets are two types based on either the organic molecule contain metal or not. Those two are 1.organic magnets 2. Organic based magnets.

1. Organic magnets: These compounds contains only carbon based molecular species which bear an unpaired spin.
2. Organic based magnets: These are molecular magnets in which magnetic transitions metal ions are introduced but Organic molecules are used either to simply mediate the interactions or to also a role in the magnetism themselves.

Example of organic magnets

According to the definition the molecules which contain unpaired spin density act as an organic magnet, such as

1. Stable free radicals

2.Radical cations and radical anions

3.Di radicals

| verdazyl | TEMPO | galvinoxyl |

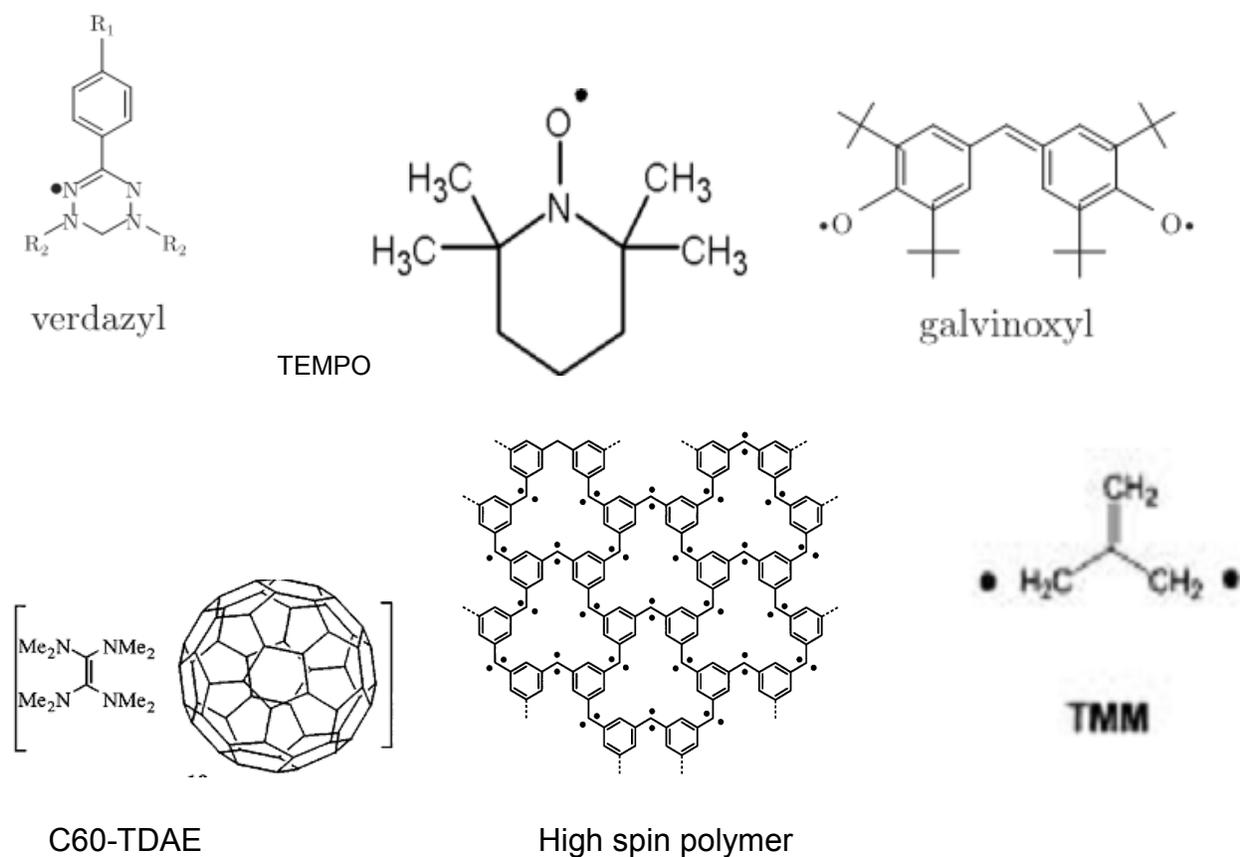| C60-TDAE | High spin polymer | TMM |

Fig-1 Organic molecules exhibiting magnetism(either alone or by complex formation)

From the definition one can understand that the organic molecule which has un paired spin density in p- orbital can act as organic magnet .The magnetic interactions between this un paired spin densities ,located on the singly occupied molecular orbital(somo) of free radicals, di radicals and poly radicals or adjacent open shell molecule in crystals gives net

magnetic momentum of particular substances. These magnetic interactions alone determine the magnetic behavior of organic compounds.

According to Aufbau type principle of Kitaigorodskii's , when molecular building blocks pack to form molecular crystals the total energy of crystal is at minimum. Initially these Building forms crystalline motifs (discrete clusters, chains, ribbons, stacks, plans, etc) by strong intermolecular interactions (coordination, ionic, or hydrogen bonds). These crystalline structures are called "Primary structure". These crystalline structures motifs use remaining weaker intermolecular forces (pi staking Van der Waals interactions) to complete the 3D crystal packing. The primary structure of any molecular solid propagates in 3D way by spontaneous action of self organization. The interactions responsible for self-organization are less specific, less directional and are called secondary and tertiary structure or quaternary according to their level of complexity. Many organic radicals exist which have unpaired spins, but few are stable enough to be assembled into crystalline structure. More over even that is possible aliening these spin Ferro magnetically is impossible .hence few number of compounds are successfully attempted.
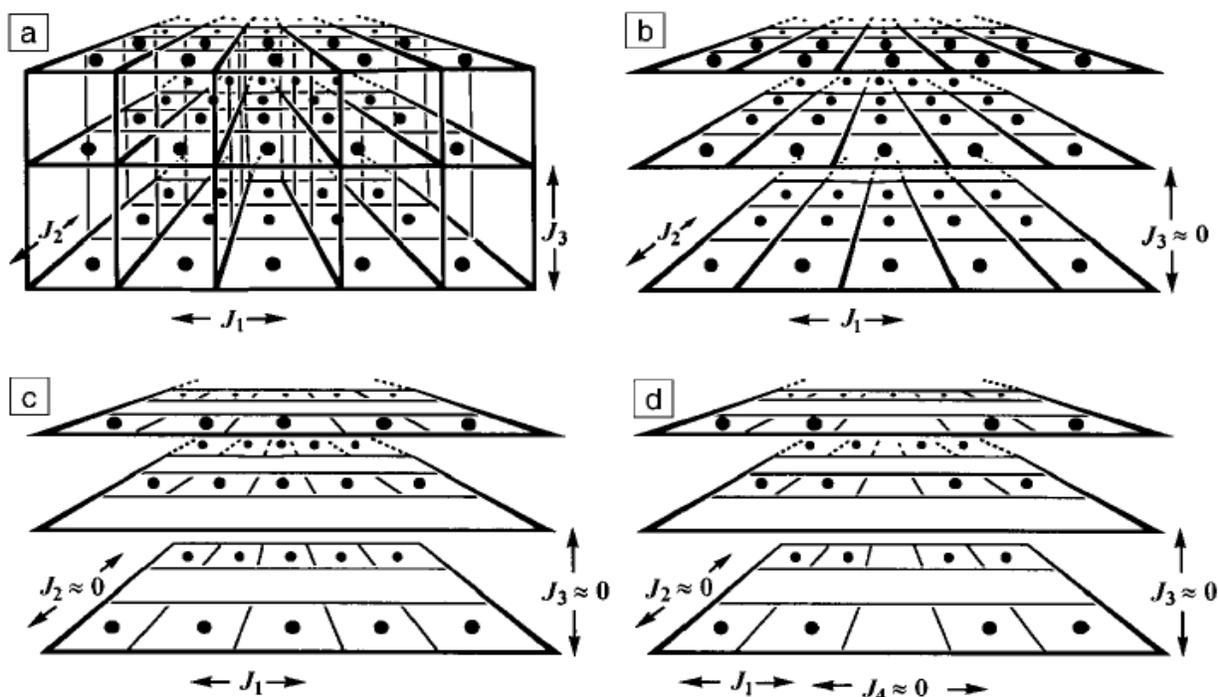

Fig-2   Scematic representation of four solids with different magnetic dimentionalities. (a)-(c) solids with 3D(j_1 ,j_2 ,j_3),2D(j_1 ,j_2>>j_3), and 1D(j_1>>j_2 ,j_3) magnetic exchange interactions, respectively.(d) Another molecular solid that has a distinct structural dimensionality(dimers) and exhibit a zero magnetic dimentionality(j_1>>j_2 ,j_3 ,j_4

History of organic magnets

1.1956- several Hexacyanomettaliates reported to magnetically ordering (Tc <_50k).

2.1967-First molecular based magnet reported $Fe_{III}(S_2CNEt_2)_2Cl$

3.1967-Galvinoxyl reported to exhibiting relatively strongly ferromagnetic coupling.

4.1968-High spin organic molecules reported.

5.1973-Tanol substrate reported to be Ferro magnet & however recharacterized as organic magnet in 1980.

6.1989-Nitroxide based ferrimagnet reported.

7.1989-Nitroxide based ferrimagnet reported.

8.1991-First room temperature organic based magnet V(TCNE)x (Tc 400K) reported.

9.1991.Ferromagnatic (TDAE-C60) (Tc 16K) reported.

10. Hybrid material exhibiting metallic conductivity and ferromagnetic behavior reported

Introduction of Photoelectron spectroscopy

Photoelectron spectroscopy works on a principle known as the "photoelectric effect", discovered by Albert Einstein. The photoelectric effect states that if a photon, or particle of light, has more energy than an electron it is interacting with, it will ionize that electron and separate it from the molecule it is attached to. Furthermore, if the photon has more than the amount of energy it needs to ionize the electron, it will transfer the additional energy to the electron in the form of kinetic energy. Important starting point for quantification, the fundamental energy conservation equation in photoemission is the following,

$$E_{\text{binding}} = E_{\text{photon}} - \left(E_{\text{kinetic}} + \phi \right)$$

where E_{binding} is the binding energy (BE) of the electron, E_{photon} is the energy of the X-ray photons being used, E_{kinetic} is the kinetic energy of the electron as measured by the

instrument and φ is the Work function of the spectrometer (not the material).

When a beam of light or some other electromagnetic radiation, such as x-rays or ultraviolet light, is purposely intensified and directed onto an object, it will force the object to emit some of its electrons. Because atoms have varying weights and properties, they will emit electrons in different proportions. This means that one can use photoelectron spectroscopy to distinguish one time of atom from another, resulting in a relatively conclusive analysis of an object's physical and chemical properties. However, photoelectron spectroscopy almost always requires high-vacuum conditions and can only measure electrons that are emitted up to ten nanometers away from the object's surface.

The XPS (X-Ray Photoelectron Spectroscopy) it is also known as ESCA (Electron Spectroscopy for Chemical Analysis). This technique is based on the theory of the photoelectric effect that was developed by Einstein; The XPS is very useful because it is a sensitive surface technique. It gives information about the elements that compose the surface by the irradiation of X-Rays into the sample. The electrons ejected from the sample will travel through the Cylindrical Mirror Analyzer and finally, through the detector. The data will be given by a spectrum with the Binding Energies (BE) which are characteristic of each element. There are many applications for the XPS such as the analysis of polymer surface, catalyst, thin film coating and others.
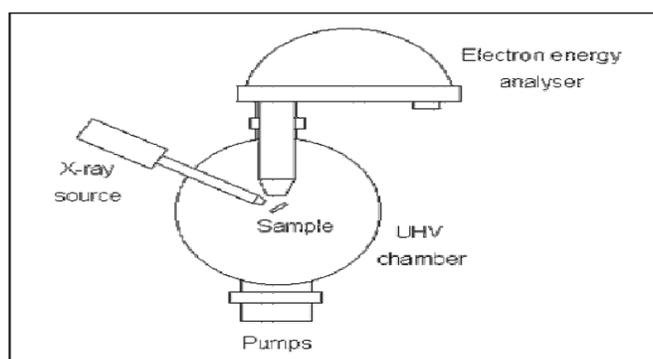

Schematic representation of Photoelectron spectroscopy

In the this presentation we are going to discuses about some organic molecule which exhibits at particular temperature, those are 1.Sulfonyl substituted TEMPO, 2.TDAE-C_{60} complex 3.Galvonoxyl radical.

1-Photoelectron spectra of 4-Methyl-Sulfonyloxy-TEMPO free radical

       HeI and HeII photoelectron spectra of persistent free radical: 2,2,6,6-tetramethyl-4-(methylsulfonyloxy)piperidinyl-1-oxide $(CH_3SO_3$-TEMPO$)^1$ have been measured. The analysis of the electronic structure is based on comparison with the spectra of related radicals and with DFT calculations. The molecular structure of this radical: 2,2,6,6-tetramethyl-4-(methylsulfonyloxy)piperidinyl-1-oxide $(CH_3SO_3$-TEMPO$)$ has been characterized by single crystal X-ray diffraction and it was shown that the N—O bond length 1.283 Å is the same as in the parent TEMPO . This observation suggests that the influence of substituent at 4-position on the nitroxide functional group is likely to be small.

| Neutral radical | Cation state X | Cation state A | Cation state B |
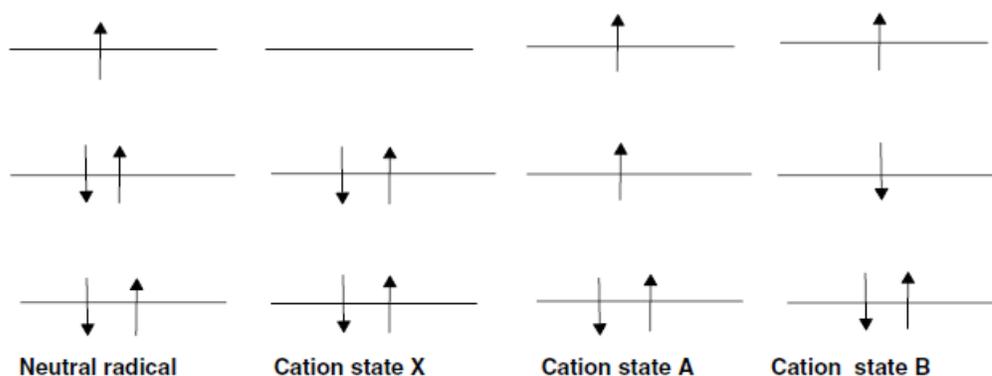
Scheme-1   M O Energy level of CH_3SO_3- TEMPO

Table 1
Vertical ionization energies E_i, calculated ionization energies (ΔDFT and TDDFT) and band assignments for 5

Band	E_i (eV)	ΔDFT (eV)	Assignment
X	7.30	7.70	π_{NO}^*
A	9.05	9.28	$n_{NO}(T)$
B	9.60	9.44	$n_{NO}(S)$
C	10.8		π_O^+

    The spectra of CH_3SO_3-TEMPO IS shown in and the assignments are summarized in the table. The band at 7.30 eV can be attributed to the antibonding π_{NO}^* orbital located at NO moiety[4]. This assignment is supported by DFT calculations. The next two bands at

9.05 eV and 9.60 eV correspond to ionization from oxygen lone pair of NO group (n_{NO}). Two cationic states with the same electronic configuration are created by photo ionization from n_{NO} orbital: singlet (*B*) and triplet (*A*). The triplet state has spin degeneracy of 3 while the singlet has degeneracy of 1. The degeneracy of these two states is consistent with the 3:1 intensity ratio for 9.05 eV and 9.60 eV bands. The band observed at 10.8 eV can be attributed to the ionization from π_O^+ orbital localized on SO_3 group. No significant variation in relative band intensity was observed on going from HeI to HeII radiation because of the small difference in HeII/HeI atomic photo ionization cross-section[5] ratios for O2p and N2p orbitals. The molecular orbitals which correspond to the bands discussed above, have largely O2p and N2p character.
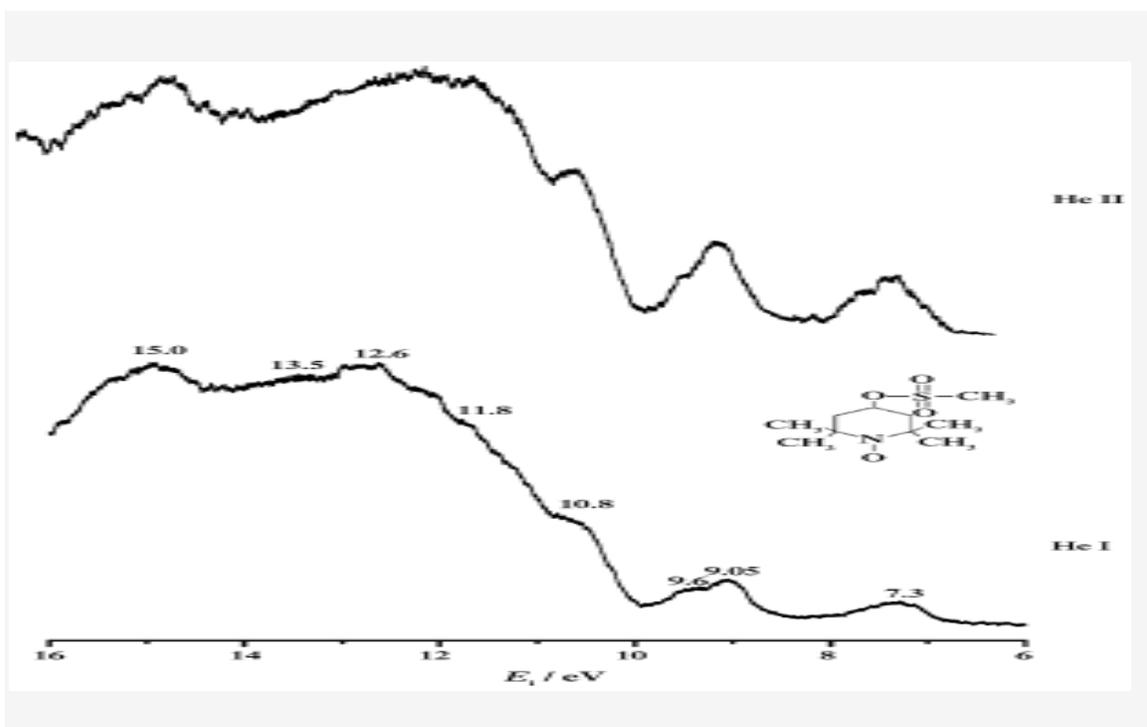

Fig-3 HeI and HeII photoelectron spectra of MeSO$_3$-TEMPO

2.Electronic structure of TDAE-C$_{60}$ Complex

The TDAE-C60 complex is a ferromagnetic because of its permanent magnetic momentum, where TDAE is tetrakis(dimethylamino)ethylene. The ferromagnetic behavior of TDAE-C60 has been ascribed to an electron spin localized on C60- and the effective exchange interaction between the spins has been estimated $5.03*10^{-4}$eV by using electron spin resonance spectroscopy (ESR). The X band of ESR shows, only C60- signal appears without TDAE signal. The Raman spectroscopy of TDAE-C$_{60}$ and TDAE-C$_{70}$ ha shown presence of TDAE mono cation. This TDAE radical cation should play a certain important role in magnetism of TDAE-C$_{60}$ complex. We have studied the XPS photoelectron spectra of TDAE- C$_{60}$ complex to determine electronic structure.

The UPS of C60 are also shown for comparison. Five structures labeled **A**-**E** are observed in the spectrum of TDAE-C60, and the corresponding structures are also observed in the spectra of C60. There are, however, several different points among these spectra. In the spectrum of TDAE-C60, the deeper the binding energy (lower kinetic energy), the stronger the intensity, which is not observed in the spectrum of the C60 due to the electron scattering in the sample film (a typical phenomenon when the
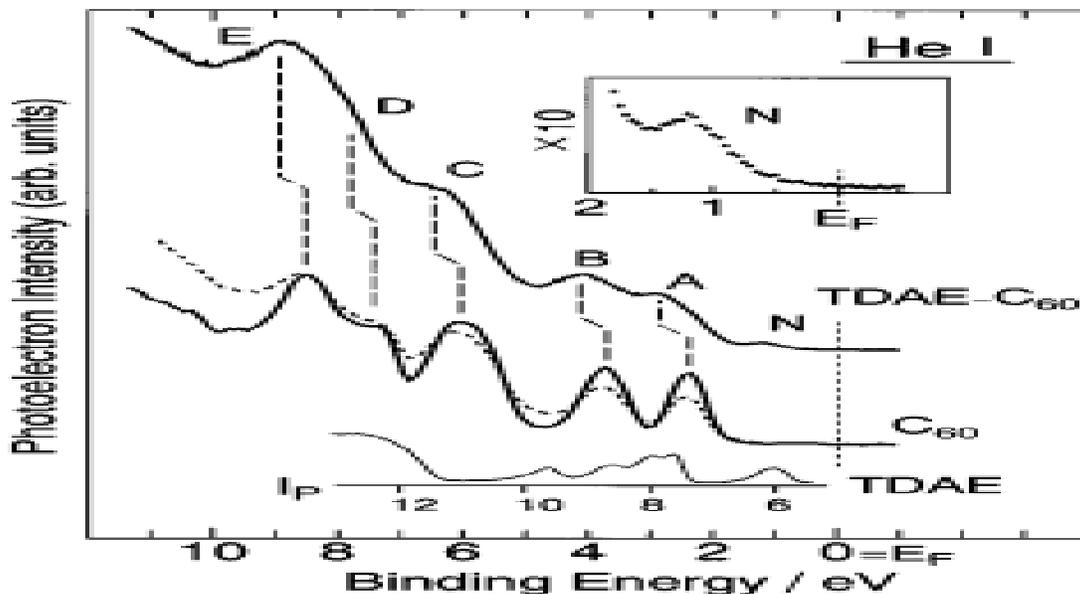

Fig-4 UPS Spectra of TDAE-C$_{60}$ Complex

An additional structure **N arises in** the spectrum ofTDAE-C60 just (1.2eV only) below the Fermi level. Clearly, gap between the Fermi level and the structure N indicates that TDAE-C60 solid is not metallic but semiconductive. Since TDAE is a strong electron donor, the new peak N is due to the electron transfer from the highest occupied molecular orbital (HOMO) of TDAE to the lowest unoccupied molecular orbital (LUMO) of C60. The appearance of a new peak near to the Fermi level has also been observed in the course of successive alkali metal dosing to C60 and fullerenes (34). All the spectral structures of TDAE-C60 are shifted by 0.5 eV uniformly toward the higher binding energy side than those of C60 spectra. The width of each structure in the TDAE-C60 spectrum is much broader than that in the C60 spectrum (typically structures A and B) due to superposition of the spectrum of TDAE to that of C60 or to the result of an interaction between C60 and TDAE, besides the electron scattering induced by the contaminants. The first bands of the TDAE and C60 spectra consisted of 2 and 10 electrons, respectively, causing the contribution from TDAE itself to the spectrum of TDAE-C60 small in the low binding energy region. Therefore the broadening derives mainly from the interaction between C60 and TDAE. Upon complex formation, C60 MO levels are spread to form wide bands due to charge transfer from TDAE to C60.

Here we have studied the XPS photoelectron spectra of TDAE- C_{60} complex to determine electronic structure. The C1s core electron spectra of complex measured using Mg k alpha radiation (1253.6eV) as shown in fig1, where dotted line represents powder sample of C_{60} and thick line corresponds to TDAE- C_{60} complex. The C1s peak appeared at 285.1eV with 1.9eV full width at half maximum. As shown the peak position shifts towards the high binding energy side and also peak profile is asymmetric with C_{60}. There may be two possibilities

for this peak profile. One I related to superposition of the photoelectron from TDAE, due to this the binding energy of 10 carbon atoms in TDAE molecules might be larger than C_{60}, since TDAE is electron deficient due to electron transfer from TDAE to C_{60}. Another one is due to shakeup effect. The N1s core spectra of

the complex also shown in fig2. It contains both main and satellite peak (S). This main peak can be deconvoluted into two peaks, labeled as A and B located at 399.8 and 401.3eV respectively

Fig-5 XPS Spectra (C1s & N1s) of TDAE-C_{60} Complex   .
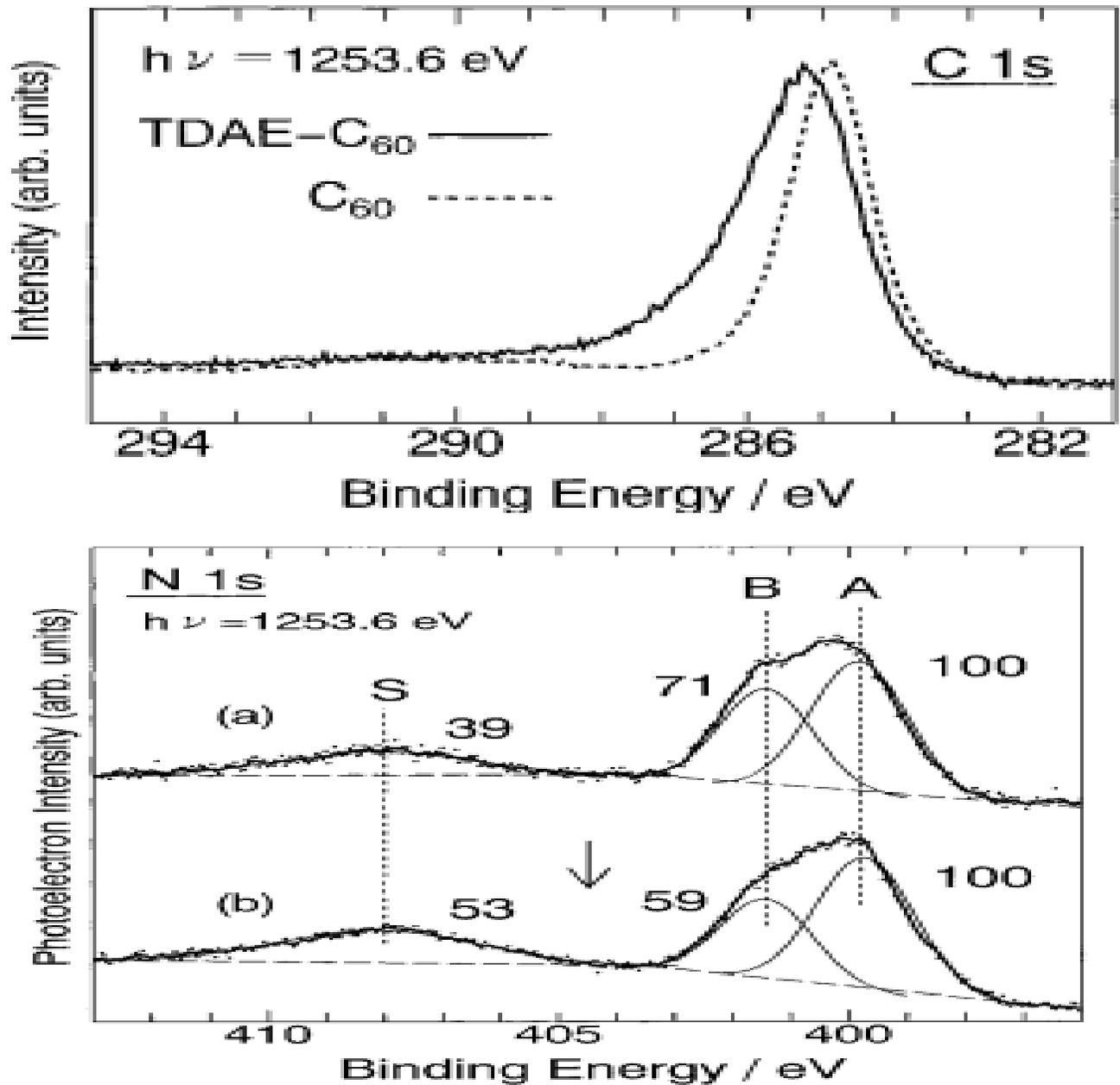
ELECTRONIC STRUCTURE OF GALVINOXYL RADICAL

Generally radicals are more reactive which contain open shall electronic configurations and odd number of valency electrons. The stabilization of this radical using bulk substituent's like TEMPO, Galvinoxyl radical. Here we have studied the galvinoxyl radical which is ferromagnetic because of its permanent magnetic momentum using UPS photoelectron spectroscopy. The bulky t-butyl groups stabilize the galvinoxyl radical by preventing recombination of molecular species in solid state and formation of covalent bonds. The molecular structure of this radical has been studied by x ray Diffraction and its electronic structure studied by using ESR Spectroscopy The C-O bond length in Galvinoxyl radical with equal length (1.271A). It contains C2 symmetry which unpaired electron is delocalized throughout the conjugated system and thus the molecule can be represented as a resonance hybrid of two structures.

2,5-dimethyl-1,4-benzoquenone

DBMQ   BPQ
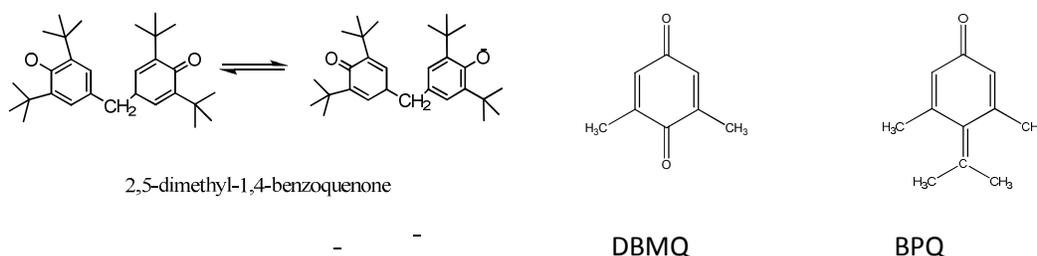
The He I photoelectron spectrum calibrated with small amount of Xe gas. The spectral resolution measured with FWFM of 2P3/2 3p-1 Ar+ line, 25 meV.The He I photoelectron spectroscopy of Galvinoxyl radical shown in spectra which contains broad band width range below 10eV with maximum at 7.5, 8.2 and 8.7eV respectively. The assigning of this bands based on quantum chemical calculations and compare the spectra with related molecules 2,5 dimethyl 1,4-bezoquinone (DMPBQ) and 2,5 dimethyl 1,4-bezoquinonedimethene(BQP). molecular orbital energy configuration shown in above diagram.

Photoelectron bands in the spectra of mentholated PBQ which correspond to nO ionizations have narrow Franck–Condon contours with prominent 0–0 transition. The narrowest band in the galvinoxyl spectrum is at 8.2 eV which is consistent with it is assignment to oxygen lone pair (nO) ionization. The comparison of vertical ionization

energies in galvinoxyl radical with DMPBQ and BQD shows that the unpaired electron is strongly delocalized along the whole length of the p-conjugated system even though the radical molecule is not planar. This can be rationalized as follows. HOMO ionization energies in DMPBQ (9.60 eV) and BQD (7.58 eV) correspond to n and p ionizations, respectively Comparison of the SOMO vertical ionization energy in galvinoxyl (7.5 eV) with DMPBQ and BQD vertical energies suggests that the SOMO is essentially of p-character [The strong delocalization of the unpaired electron in galvinoxyl can also be inferred from the comparison of the SOMO vertical ionization energies in galvinoxyl (7.5 eV) and phenoxy radicals (8.84 eV)The difference between ionization energies suggests that SOMO characters in the two radical species are different. The second ionization (in order of increasing ionization energy) corresponds to ionization from the p-orbital which has significant electron density at the methane bridge (pb). The 3rd and 4th ionizations are associated with in-plane oxygen lone pairs (n_ and n+). The 5th and 6th ionization correspond to p-orbital's localized on the benzoquinone moieties (π_ and π+). The measured ratio of relative intensities of the band manifolds centered at 7.5, 8.2 and 8.6 eV, respectively, is approximately 2:1:3. The removal of electron from every orbital (except the first) creates two ionic states (triplet and singlet) and gives rise to two closely spaced bands whose relative intensity ratio is 3:1. The removal of electron from SOMO creates a singlet ionic state which gives rise to a single band.

The first ionization energy of galvinoxyl radical is 7.5eV with compared to phenoxyl radical with 8.84eV which mean strong delocalization of the free radical happens. The second ionization corresponds to ionization from the pi orbital which has significant electron density at the methane bridge. The third and forth ionization energies belongs to the in plane of oxygen lone pairs (n- and n+). The 5th and 6th ionization belongs to pin orbital's localized on benzoquinone (pi- and pi+).

The measured ratio of relative intensity of the band centered and 8.6eV respectively with intensity 2:1:3. The removal of electron from every orbital (except the first) creates two ionic states (triplet and singlet) and gives rise to two closely space bands whose relative intensity ratio is 3:1. The removal of electron from SOMO creates a singlet ionic state which gives single band.
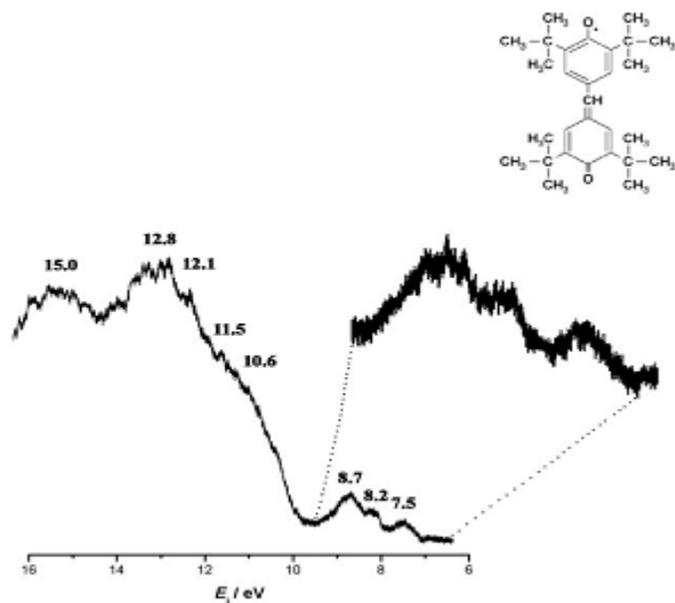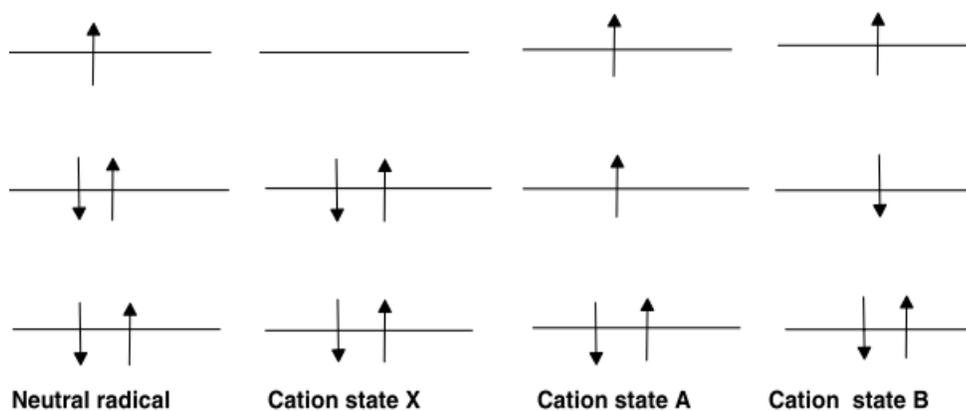
Fig 6 : UPS of Galvinoxyl radical at room temperature

| Neutral radical | Cation state X | Cation state A | Cation state B |

Scheme-2 The electronic state of radical & its cation

Conclusion

With the help of theoretical calculation (DFT & TDFT), comparison with other related molecule & Experimental method like XPS, UPS we can able to determine the orbital energy of organic molecules which shows ferromagnetic behavior at very low temperature. Here we have taken to consideration three molecules i.e TDAE-C_{60}, GALVINOXIL, & CH_3SO_3-TEMPO.

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