First - principles investigation of geometry, charge and magnetic states for metal Phthalocyanine (MPc, M = Sn and Pb) molecules

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We have investigated the geometry, charge and magnetic states of the metal phthalocyanine (MPc, M = Sn and Pb) molecules using the first - principles method within the framework of density functional theory. We have shown that the inter - atomic bond distances of absorbed metals (M = Sn and Pb) on the Pc molecule are the different from each other due to the different atomic radii of absorbed metal atom. The absorbed metal atoms are affect to the charge state of system. The total magnetic moment generates to the metal Phthalocyanine molecules by absorbing metal atoms.

I. INTRODUCTION

The phthalocyanine ($Pc = C_{32}H_{16}N_8$) is a new class of stable metal phthalocyanine organic compound, which is structurally related to macrocyclic pigments such as the porphyrins [1]. The metal phthalocyanines have been intensively studied [2, 3] and their physical and chemical properties have been followed a broad application for optoelectronics and sensors.

The MPc (M = Sn and Pb) molecule has a non - planar 'shuttle - cock' structure with a C_{4v} molecular symmetry and forms a one - dimensional column in the crystal [4]. It is in - plane isotropic however, by reflectance anisotropy spectroscopy it has been revealed that molecules within PbPc layer arrange anisotropically ordered in the result of the tilting angle between molecular plane and the surface [5]. Greif *et. al.* have experimentally investigated the bonding geometry of SnPc molecule on the Ag(111) surface using the X - ray diffraction (XRD) and ultraviolet photoelectron diffraction (UPD) [6]. Their experimental diffraction patterns were compared to single - scattering - cluster calculations.

Our preliminary result shown that the binding energy between the metal (M = Sn amd Pb) atoms and phthalocyanine molecule was found 2.0 eV [7], which is a lower than that of Fe, Co, Ni, Cu, Zn and Mg atoms on the phthalocyanine molecule [8], moreover, a nanomechanical motion in molecular switches [9] that is followed their reversible conformational inversion on the surfaces [10].

Features of magnetism of nanoparticle molecules, such as C_{20} fullerene call interest in their charged magnetic states while there is a distortion of the starting symmetry caused by Coulomb distortion and Jahn - Teller effect [11, 12]. Recently, Poklonski *et. al.* have theoretically investigated the inversion of the SnPc molecule on graphene [13]. They have shown that it is necessary to overcome the energy barrier of 2.5 eV, when the inversion of SnPc molecule occurs and the abrupt inversion of this molecule occurs at a distance of 3.6 - 3.5 Å from the tin atom to the graphene plane by moving the tin atom to the graphene plane.

In this paper, we present the results of first - principles investigation of geometry, charge and magnetic states for metal phthalocyanine (MPc, M = Sn and Pb) molecules using the first - principles method within the framework of DFT [15–17].

II. CALCULATION DETAILS

Our calculations are based on the plane wave self - consistent field (PWscf) method using the generalized gradient approximation (GGA) by Perdew, Burke and Ernzerhof (PBE) [14] within the framework of DFT [15–17], as implemented in the QUANTUM ESPRESSO package [18]. Interaction between the ions and valence electrons is expressed as the ultrasoft pseudopotential [19]. The following electronic states are treated as valence states: $H(1s^1)$, $C(2s^2, 2p^2)$, $N(2s^2, 2p^3)$ $Sn(4d^{10}, 5s^2, 5p^2)$ and $Pb(5d^{10}, 6s^2, 6p^2)$ for atoms. The wave functions are expressed as plane waves up to a kinetic energy cutoff of 35 Ry. A tetrahedral method [20] is used when the electronic density of state (DOS) is evaluated. For the self - consistent cycle the total energy convergence is 10^{-8} eV. The occupation numbers of electrons are expressed Gaussian distribution function with an electronic temperature of kT = 0.001 Ry. The atomic ionic positions are relaxed until the residual forces are less than 0.05 eV/Å. In order to create an enough large vacuum space on the in - plane, we considered MPc (M = Sn and Pb) molecules (See Figure 1) within the large cube of 30 Å.
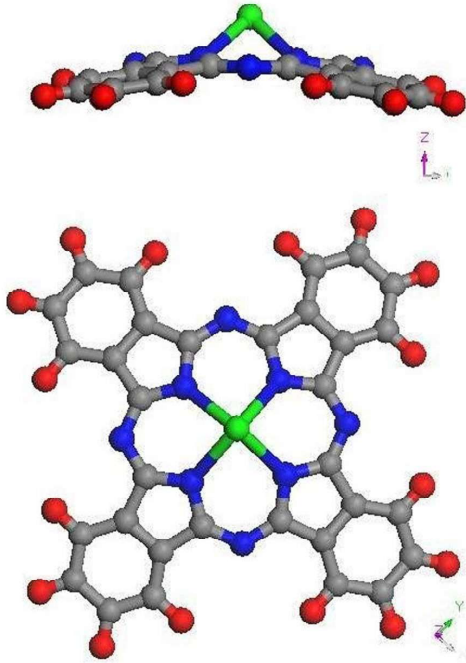
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FIG. 1: (Color online) The chemical structure for MPc (M = Sn and Pb) molecules. (top) the side view and (bottom) the top view of MPc molecules. Here the C, N and H atoms are denoted by the brown, blue and red balls respectively. The M atom is denoted by the green ball.

III.   RESULTS AND DISCUSSION

We have first performed the structure optimization of MPc (M = Sn and Pb) molecules. Our results are shown that the inter - atomic bond distances between the C - C and C - H bonds for the SnPc molecule are found to be 1.41 and 3.09 Å respectively (See table I). These predicted values for SnPc molecule are the same as that for the PbPc molecule. The inter - atomic bond distances between the C - N bonds for SnPc and PbPc molecules are similar and found to be 1.38 and 1.37 Å respectively. But the bond distances of metals (M = Sn and Pb) connected with the Pc molecule by the Nitrogen atoms are found to be 2.30 and 2.39 Å respectively. This value is related to the different atomic radii of Sn (1.45 Å) and Pb (1.54 Å) atoms and in good agreement with those of other researchers [9].

After the geometry prediction, in order to consider the charge and magnetic states of the MPc (M = Sn

TABLE I: For the MPc (M = Sn and Pb) molecules, the predicted inter - atomic bond distances, charge states (Q) and total magnetic moments (M_{tot}) . The results of other researchers are in the bracket [9].

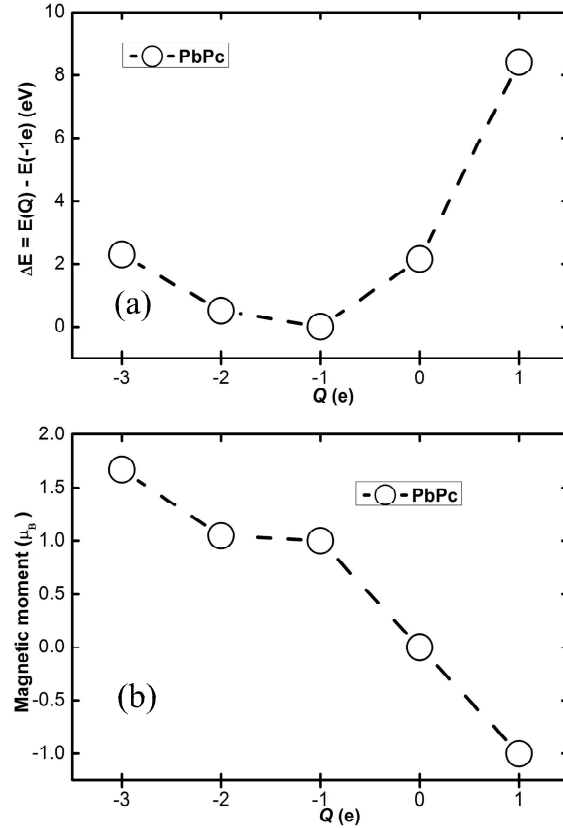|	SnPc	PbPc
Sn - N (Å)	2.30	-
Pb - N (Å)	-	2.39 (2.43)[9]
C - N (Å)	1.38	1.37 (1.37) [9]
C - C (Å)	1.41	1.41 (1.42) [9]
C - H (Å)	1.09	1.09
Q (e)	-1.0	-1.0
M_{tot} (μ_B)	1.0	1.0

FIG. 2: (a) The relative energy of the ground states as a function of charge states, (b) the total magnetic moment as a function of charge states in the the PbPc molecule.

and Pb) molecules, we have estimated the ground state energy of the MPc (M = Sn and Pb) molecules at the different charge states, such as (-3e), (-2e), (-1e), (0) and (+1e) (in units of elementary charge e) using the spin polarized calculation. The relative energy difference of the ground states with the respect to the charge states from (-3e) to (+1e) is shown in the Figure 2(a). The dependence of relative energy shows parabolic curve and the minimum

value of parabola is sited at the value of the charge of (-1e), as lowering by the energy of 2.15 eV from the neutral state of the PbPc molecule. It is shown that the ground state of the PbPc molecule belongs to the charge state (-1e) by absorbing the metallic Pb atom on the Pc molecule. In our previous study, we have observed that the charge transfer of 0.6e occurs from metal (M = Sn and Pb) atoms to the phthalocyanine molecule [7]. It is well in agreement with those of other researcher [21]. We note that the ground state of the SnPc molecule is similar to the that of the PbPc molecule.

From the spin polarized calculations, we predicted total magnetic moments of MPc (M = Sn and Pb) molecules on the each charge state. We have shown these results in the Figure 2 (b). At the ground state of molecules, the total magnetic moment is found to be +1.0 μ_B. Therefore, the MPc molecules are magnetic. The total magnetic moment M_{tot} of molecule is defined as $M_{tot} = (\chi - 1)\mu_B$, where μ_B is the Bohr magneton and χ is the multiplicity of molecule. It is found us that in the charge state (-1e) with multiplicity $\chi = 2$ and magnetic moment +1.0 μ_B, the MPc molecules have the lowest total ground energy. This result is the same as the carbododecahedron (C_{20}) fullerene [12]. Non stability of magnetic moments on the other charge states from the charge state (-1e) may be caused by the structural flexibility particularly, the molecular motion within the molecular film [5, 10].

IV. CONCLUSION

In conclusion, we have predicted the geometry, charge and magnetic states for metal phthalocyanine (MPc, M = Sn and Pb) molecules using the first - principles method within the framework of DFT. We have shown that the MPc molecules are magnetic and the ground state of molecules belongs to the charge state (-1e) with multiplicity $\chi = 2$ and magnetic moment +1.0 μ_B by absorbing metallic M (M = Sn and Pb) atoms on the Pc molecules.

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