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Dipole polarizabilities of trimetallic nitride endohedral fullerenes $M_3N@C_{2n}$ (M = Sc and Y; $2n$ = 68–98)

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ABSTRACT

The electronic structures and static dipole polarizabilities of $M_3N@C_{2n}$ fullerenes (M = Sc and Y; $2n$ = 68–98) were studied by using density functional theory. Unlike nonmetal endohedral fullerenes, $M_3N@C_{2n}$ show smaller static dipole polarizabilities than the corresponding C_{2n} ones do. It is because the induced electric field of carbon cages is reduced by inserting M_3N cluster. The mean dipole polarizabilities of $M_3N@C_{2n}$ fullerenes were found to correlate closely to their chemical hardness and electron delocalization volume. The refractive indexes of the face-centered-cubic crystals assembled by $M_3N@C_{2n}$ fullerenes were also estimated.

1. Introduction

The endohedral metallofullerenes have attracted special attention for their potential applications in electronics [1], optics [2], and bio-medicine [3]. Trimetallic nitride endohedral fullerene is one of most important endohedral metallofullerenes for their plentiful species, higher yields relative to empty cage fullerenes and mono(di)-metallofullerenes, and high thermal stabilities [4]. The character that the physical and chemical properties can be easily controlled by altering encaged species without changing the structures of the outer cages enables them as promising functional material [5]. Many trimetallic nitride endohedral fullerenes including the families of $Gd_3N@C_{2n}$ ($2n$ = 80–88) [6], $Dy_3N@C_{2n}$ ($2n$ = 76–98) [5], $Nd_3N@C_{2n}$ ($2n$ = 80–98) [7], and $Tm_3N@C_{2n}$ ($2n$ = 78–88) [8] have been synthesized and characterized up to now. Meanwhile, some theoretical works have been performed to predict the most stable structures and explore the stabilization mechanisms of $M_3N@C_{2n}$ fullerenes. Popov and Dunsch [9] reported the most stable configurations of $M_3N@C_{2n}$ fullerenes (M = Sc and Y; $2n$ = 68–98) by using extensive semiempirical and DFT methods and they further confirmed the reliability of the ionic model $M_3N^{6+}@C_{2n}^{6-}$ proposed by Campanera et al. [10].

The dipole polarizability of a molecule closely connects to its electronic structure and other intrinsic properties, such as chemical hardness, ionization potential, acidity or basicity, and electron delocalization volume [11]. The (hyper)polarizabilities of fullerenes and their derivants have attracted much interest because the delocalized π-electron systems have potential nonlinear optical applications [12]. The polarizabilities of C_{60} and C_{70} have been extensively investigated both in experiment and theory [12–21]. To best of our knowledge, however, there is no work focusing on the polarizabilities of $M_3N@C_{2n}$ fullerenes. The understanding of the effects of M_3N cluster on the polarizability of carbon fullerene, the electron transfer between carbon cage and M_3N cluster under electric field, and the relationship between the polarizability and the electronic structure is strongly expected. In this Letter, we systematically studied the electronic structures and dipole polarizabilities of $M_3N@C_{2n}$ fullerenes (M = Sc and Y; $2n$ = 68–98) based on density functional theory (DFT) method.

2. Computational details

In our study, the most stable isomers of $Sc_3N@C_{2n}$ fullerenes in Ref. [9] were re-optimized by using Vosko–Wilk–Nusair (VWN) [22] and Becke–Perdew (BP86) [23,24] exchange and correlation (XC) functionals. All-electron basis set of triple ζ plus double polarization quality (TZ2P) was employed for all atoms and the combined scalar approach zeroth order regular approximation (ZORA) [25] was taken into account for relativistic calculation. At the same time, the C_{2n} and $Y_3N@C_{2n}$ fullerenes with the similar carbon cages to $Sc_3N@C_{2n}$ were also re-optimized at the same computational level for comparison.

The computational polarizabilities of C_{60}, C_{70}, and C_{80} were tested with various XC functionals (VWN, BLYP [23,26], PBE [27], PW91 [28], LB94 [29], and SAOP [30]). The basis set effect was evaluated with even tempered (ET-DZP-polar) and TZ2P basis sets. The results are summarized in Table 1, comparing with experimental and other theoretical results. The polarizabilities calculated by LB94 XC potential, which consider coulombic asymptotic (long range) correction in linear response calculation [29], are closer to experimental values than other functionals. The polarizabilities

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Table 1
The theoretical and experimental values of mean polarizabilities (Å^3) for C_{60}, C_{70}, and C_{80} (1 a.u. of dipole polarizability = 0.14818 Å^3).

Method	C_{60}-I_h^{a}	C_{70}-D_{5h}^{a}	C_{80}-D_3
Theory			
LB94-TZ2P/LB94-ET	79.25/80.35	98.52/99.94	120.58/122.13
SAOP-TZ2P/SAOP-ET	81.09/81.93	100.68/101.84	123.03/124.24
PW91-TZ2P/PW91-ET	81.46/82.38	101.09/102.03	123.45/124.38
PBE-TZ2P/PBE-ET	81.51/82.09	101.17/101.87	123.53/124.14
BLYP-TZ2P/BLYP-ET	82.68/83.07	102.58/103.10	125.17/125.46
VWN-TZ2P/VWN-ET	82.05/82.20	101.86/102.06	124.37/124.44
Ab initio SCF 6-31++G [14]	75.1	89.8	
Point dipole interaction model [13]	77.5	91.5	106.0
B3LYP/6-311G(d) [20]	73.8	91.8	119.6
LB94/TZP [12]	80.6		
LDA/TZP [12]	82.5		
LR-LCAO [12]	81.1		
RPA-PBE/NRLMOL [17]	79.0		
PBE/NRLMOL [21]	82.9	102.8	
Experiment			
Molecular beam deviation [15]	76.5 ± 8	102 ± 14	
C_{60} and C_{70} films optical measurements: ellipsometry and reflection/transmission [18]	79.0	97.0	
Electron energy-loss spectroscopy [19]	83.0	103.5	
Matter-wave interferometer [16]	88.9 ± 0.9 ± 5.1	108.5 ± 2.0 ± 6.2	

[a] Before and after the diagonal are the values of polarizabilities in this work with two different basis set: TZ2P and ET-DZP-polar, respectively.

based on ET-DZP-polar basis set are systematically slightly larger (1.5%) than those with TZ2P basis set, indicating the small influence of the diffused function on the polarizabilities of these fullerenes. Consequently, LB94 XC potential along with TZ2P basis set was adopted in the calculations of the polarizabilities of C_{2n} and $M_3N@C_{2n}$ fullerenes (M = Sc and Y; $2n = 68–98$). All calculations were performed with ADF package [31]. The mean polarizability and the polarizability anisotropy are defined following Buckingham's conventions [32],

$$\langle\alpha\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \tag{1}$$

$$\Delta\alpha = \sqrt{\frac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{yy})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{zy}^2)]}. \tag{2}$$

3. Results and discussions

3.1. Dipole polarizabilities

Based on the optimized geometries, which agree very well with Ref. [9], the dipole moments (μ) and dipole polarizabilities (α) of C_{2n} and $M_3N@C_{2n}$ fullerenes (M = Sc and Y; $2n = 68–98$) were calculated at LB94/TZ2P level. The μ of $Sc_3N@C_{2n}$ and $Y_3N@C_{2n}$ fullerenes are almost equal to each other in small size, but when $2n$ larger than 84 the μ of $Sc_3N@C_{2n}$ fullerenes are much larger than those of the C_{2n} (even $Y_3N@C_{2n}$) fullerenes due to the deviation of Sc_3N cluster far from the central site of C_{2n} fullerene for larger-sized cages. The mean dipole polarizabilities ($\langle\alpha\rangle$) and polarizability anisotropies ($\Delta\alpha$) of $M_3N@C_{2n}$ fullerenes are slightly smaller than those of the corresponding empty cage carbon fullerenes with the same size in general, indicating that the doping M_3N cluster into the carbon fullerenes makes a negative contribution to the dipole polarizabilities. This is quite different from the cases of carbon buckyonions $C_{60}@C_{240}$ and noble gas endohedral fullerenes [33,34], where the endohedral species enlarge the polarizabilities of whole systems. On the other hand, the mean polarizability of $Y_3N@C_{2n}$ fullerene is slightly larger than that of $Sc_3N@C_{2n}$ fullerene of same size, showing the evidence that the dipole polarizabilities of $M_3N@C_{2n}$ fullerenes can be tuned by altering M. And the more effective tuning is expected to be achieved by replacing Sc or Y with other metal such as rare earth.

To shed light on the origin of the reduced dipole polarizabilities, we further studied the charge distributions on the M atoms of $M_3N@C_{2n}$ fullerenes when applying a homogeneous external electric field with magnitude of 0.01 a.u. along coordinate axis direction by means of the multipole derived charge analysis method [35], which can provide an accurate representation of the charge distribution on the atom of a molecule. Take the $Y_3N@C_{80}$ fullerene for example, if the external field is applied along x direction then the electric field induced by carbon cage will be along the opposite ($-x$) direction (see Fig. 1), the amount of positive charge on the Y atoms at A and C are reduced while at B site increased simultaneously as compared to the field free case (see Table 2). It behaves as an equifinal electric field which is anti-parallel to the induced field of carbon shell and thus reduces the later one. When a homogeneous field along y direction is applied, the charge on Y atom at A site is reduced while those at sites B and C are increased. Consequently, an extra electric field along the y direction (opposite to the induced field of carbon cage) is created. The similar phenomena can be observed in the cases of the external electric fields are applied along $-x$ and $-y$ directions (see Table 2). It is noteworthy that the redistributions of charge on Y atoms are not evident when the external field is applied along $+z$ or $-z$ directions because the Y_3N cluster is nearly in the plane that vertical to z axis. The similar results are clearly shown in other $M_3N@C_{2n}$ fullerenes, whereas we only listed the cases of $2n = 70$ and 80 in Table 2 for simplification and clarification. In a word, applying a week electric field to $M_3N@C_{2n}$ fullerene, the induced electric filed by carbon cage is slightly balanced by the M_3N cluster induced field with the opposite direction and therefore results in smaller dipole polarizability.

3.2. The relationships between dipole polarizabilities and electronic structures

The ionization potential (IP) and electron affinity (EA) are the important parameters to characterize the reactivity of a molecule. In this Letter, the vertical ionization potential (VIP) and the vertical electron affinity (VEA) were calculated, which are defined as the energy differences between the neutral molecule and its cation or anion with the same geometries as the neutral one, respectively. The results show that the $Sc_3N@C_{2n}$ and $Y_3N@C_{2n}$ fullerenes have

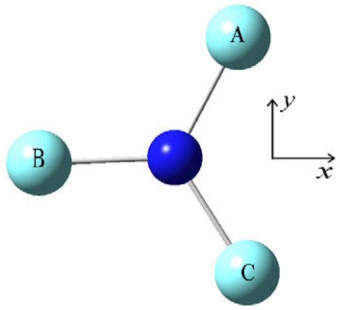

Fig. 1. The coordinate orientation of $Y_3N@C_{80}$ fullerene. The carbon cage C_{80} is neglected in order to clearly view. The blue one is N and the cyan ones are Y atom, respectively. (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)