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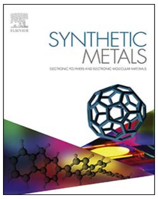

Research paper

The important role of superalkalis on the static first hyperpolarizabilities of new electrides: Theoretical investigation on superalkali-doped hexamethylenetetramine (HMT)

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ABSTRACT

On the basis of Hexamethylenetetramine (HMT), a new class of (super)alkali-doped electrides $HMT-X$, $HMT-FX_2$, and $HMT-OX_3$ (X = Li, Na, and K) were designed in theory. The results reveal that superalkali FX_2 and OX_3 can keep their structural integrity in these studied compounds. These electrides possess significantly large first hyperpolarizabilities (β_0) in the range of 0.65×10^3–4.72×10^5 au due to diffuse excess electrons from chemical doping. It is found that the superalkali effect on the β_0 value is more significant than that of simple alkali doping. Furthermore, employing the heavier superalkali (FK_2 and OK_3) can dramatically enhance the β_0 values of the $HMT-FK_2$ and $HMT-OK_3$. The further investigations show that small transition energies is the decisive factor for the large β_0 values of (super)alkali-doped electrides. The ratios between the vibrational and electronic contributions on (hyper)polarizability demonstrate that the vibrational contributions play an important role in determining the static (hyper)polarizabilities. This paper not only designs novel electrides with large NLO response but also expands the application range of superalkali cluster.

1. Introduction

Over the last several decades, the designs and synthesis of novel nonlinear optical (NLO) materials have attracted widespread attention for their potential applications in photonic and electro-optical devices. Up to now, a great many effective strategies have been developed to increase the first hyperpolarizability (β_0) of NLO materials [1–6]. An increasing amount of research has shown that the introduction of diffuse excess electrons into a molecule is a useful method to considerably enhance its β_0 value. Alkalides and electrides are representative compounds with diffuse excess electron. The specific structures and the NLO properties of different kinds of compounds with excess electron were studied, such as solvated electron cluster [7], alkali doped organic electrides/alkalides [8–10], alkaline earth-based alkalides [11,12], boron nitride nanotubes with excess electrons [13], all-metal electride molecules [14,15]. The alkali metal doped effect is one of the most commonly used methods to design electride/alkalide compounds [16–21]. When an alkali atom with low ionization energy (IE) interacts with the complexant, the *s* valence electron of alkali atom can be pushed/pulled by complexant to form the diffuse excess electron. Thus, these compounds exhibit dramatically large first hyperpolarizabilities.

Recently, the efforts to replace alkali atoms with superalkalis have afforded a variety of new NLO materials [22,23]. Superalkali clusters are extraordinary compounds exhibiting lower IE values than those of alkali metal atoms [24–28]. As a result, they can serve as a better source of excess electrons, which is loosely bound and responsible for their very high hyperpolarizabilities. In addition, superalkali structures can maintain their structural and electronic integrities when combined with other species [26]. This means that they can be used as building blocks to construct new materials. According to reports in the literature, the β_0 value of superalkali-based electride $(K_3O)^+(e@C_{20}F_{20})^-$ is 1.00×10^4 au, which is obviously larger than that 6.00×10^2 au of $K^+(e@C_{20}F_{20})^-$ [22]. Recently, Mai et al. reported a novel class of superalkalides $M^+(en)_3M_3'O^-$ (M, M′ = Li, Na, K) [29]. Based on the calculations, it can be seen that both superalkalides $M^+(en)_3M_3'O^-$ and alkalides $M^+(en)_3M_3'^-$ have significantly large β_0 values. However, the $M^+(en)_3M_3'O^-$ are more promising candidates than $M^+(en)_3M_3'^-$ for NLO materials because of they have higher stabilities. Finally, Sun et al. have recently predicted a series of superalkali-doped nanocages and

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have identified $Li_3O@Al_{12}N_{12}$ as inorganic electrides [30]. The largest reported β_0 value computed at the MP2/6–31 + G(d) level computations was of 1.86×10^7 au. Clearly, compared with alkali atom, superalkali metal doping may be a more effective way to improve NLO properties of materials.

Hexamethylenetetramine (HMT, $C_6H_{12}N_4$), known as urotropine or tetraazaadamantane, is one simple carbon-nitride heterocyclic compound with a cage-like structure. It was first discovered by Butlerow [31,32] and its crystal structure was first determined by Dickinson and Raymond [33]. HMT has been extensively used in organic synthesis as solvent due to its high solubility in water and polar organic solvents [34] as well as in organometallic coordination chemistry as a versatile ligand [35–37]. In addition, act as a good hydrogen bonds acceptor, HMT can form a variety of molecular adducts and supramolecular architectures [38–42]. In 2012, a new second-order NLO compound $[Cu(C_4H_5NO_4)\text{-}(C_6H_{12}N_4)(H_2O)]$ was synthesized, in which intramolecular charge transfer is a key factor for the existence of NLO properties [43]. The main contribution of this study is to investigate the influence of the (super)alkali metals interaction with the HMT on the NLO properties. Dye et al. proposed that the traditional organic alkalides with C − O bond are thermally unstable at room temperature, whereas the complexants with the C − N bond are considered to form stable alkalide compounds [44–48]. Subsequently, different metal atoms were introduced into the compounds with C − N bonds to construct new electrides/alkalides, which had very good NLO properties [9,49]. Thus, we attempt to design a novel class of (super)alkali-doped electrides HMT − X, HMT − FX_2, and HMT − OX_3 (X = Li, Na, and K).

This work main aims at exploring the structures and the stabilities of (super)alkali-doped compounds, exhibiting the electride characteristics of these doped compounds, predicting the NLO properties of such electrides, exploring the relationships between the first hyperpolarizability and the atomic number of the X, and revealing the influencing factors for the large first hyperpolarizability. We expect that more and more people are concerned about the design of the electride NLO molecules using superalkali clusters as building blocks.

2. Computational methods

The geometric structures with all real frequencies were obtained by employing the second-order Møller-Plesset perturbation (MP2) combined with the 6–31 + G(d) basis set. The calculations of static electronic first hyperpolarizability (β_0) for related structures were evaluated using the finite field (FF) approach at the MP2 level. It is known that the MP2 method is proper in calculating NLO properties. This is because the computed results from MP2 are very close to those obtained from the more sophisticated correlation methods (such as, QCISD) [50]. To select a suitable basis set to calculate β_0, the basis set effect in calculations of β_0 was considered. Taking HMT − Li as an example, the β_0 values at the MP2 level with the 6–311 + + G(d,p), 6–311 + + G(d), 6–311 + G(2d), 6–31 + + G(d), 6–311 + G(d), 6–31 + G(d), and 6–31 + G basis sets were 4974, 3873, 4038, 4880, 4154, 4244, and 4541 au, respectively. Obviously, the medium-sized 6–31 + G(d) result was very close to the corresponding ones from the other basis sets. Therefore, the 6–31 + G(d) basis set was chosen to calculate the electronic and vibrational contributions to the first hyperpolarizabilities of all the investigated systems in this study.

The energy of a molecular system in the weak and homogeneous electric field can be expressed as:

$$E = E(0) - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - \cdots \tag{1}$$

where $E(0)$ is the molecular total energy without the electric field, and F_α is the electric field component along the α direction; μ_α, $\alpha_{\alpha\beta}$, and $\beta_{\alpha\beta}\gamma$ are the components of dipole moment, polarizability, and first hyperpolarizability tensor, respectively. The mean polarizability (α_0), first hyperpolarizability (β_0), and the hyperpolarizability along the molecular dipole moment (β_{vec}) are defined as follows:

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{2}$$

$$\beta_0 = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2} \tag{3}$$

$$\beta_{vec} = \frac{\beta_x\mu_x + \beta_y\mu_y + \beta_z\mu_z}{\sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2}} \tag{4}$$

where$\beta_i = \frac{3}{5}(\beta_{iii} + \beta_{ijj} + \beta_{ikk})$, $(i, j, k = x, y, z)$

In addition, the natural bond orbital (NBO) charges of these compounds were calculated at the MP2/6 − 311 + G(2d) level. The time-dependent density functional theory (TD-DFT) calculations were performed at the B3LYP/6 − 31 + G(d) level to obtain the crucial excited states and absorption spectra of the investigated structures. The vertical ionization energies (VIE) and interaction energies (E_{int}) were calculated at the MP2/6 − 31 + G(d) level. The counterpoise procedure was used to calculate the E_{int} according to the following equation [51]:

$$E_{\text{int}} = E_{\text{AB}}(X_{\text{AB}}) - E_{\text{A}}(X_{\text{AB}}) - E_{\text{B}}(X_{\text{AB}}) \tag{5}$$

where the same basis set, X_{AB}, was used for the subunit calculation as for the compound calculation.

The corresponding $< S^2 >$ values are very close to the value of 0.750 for the pure doublet state. Thus, the spin contamination is negligible and the computational results are reliable. All calculations reported in this work were carried out by using the Gaussian 09 program package [52]. The density of states (DOS) spectra were plotted with the help of the Multiwfn software[53] based on the data from MP2/6 − 31 + G(d) calculations.

3. Results and discussion

3.1. Structure characteristics and stability

The optimized geometrical structures with all real frequencies of HMT, HMT − X, HMT − FX_2, and HMT − OX_3 (X = Li, Na, and K) at the MP2/6 − 31 + G(d) level are presented in Fig. 1. The corresponding geometrical parameters and symmetries of these species are summarized in Table 1. The structure of HMT possesses T_d symmetry, where the calculated C − N and C − H bond lengths are 1.473 and 1.097 Å, respectively, which are in good agreement with the results of previous experimental and theoretical studies [54–57]. Based on the optimized HMT structure, we designed several possible structural candidates for the interaction between HMT and (super)alkali atoms (X, FX_2, and OX_3). After geometry optimization, the ground energy structures for the HMT − X/FX_2 indicated the X and FX_2 subunits only occupied the on-top N atom site of the HMT moiety. As shown in Fig. 1, the interaction between the X/FX_2 and HMT has a slight effect on the structure of the HMT, namely, the structural integrity of the HMT remains very well in each of compounds. As can be seen from Fig. 1 and Table 1, the equilibrium geometries of HMT − X have C_{3v} symmetry and the alkali atoms are link to the N atom of HMT moiety, in which the X1 − N1 bond lengths are equal to 2.111, 2.594, and 2.975 Å, respectively.

The stable structures of superalkali-doped HMT − FX_2 are found to possess the same C_s symmetry, which the FX_2 subunits bind with the HMT cage *via* one Li − N bond. Comparing with the HMT − X, the X1 − N1 bond lengths of HMT − FLi_2, HMT − FNa_2, and HMT − FK_2 systems are 2.051, 2.478, and 2.868 Å, respectively, which are shorter than those of corresponding HMT − X systems, namely, FX_2 doped systems have larger chemical stability. It is important to note that the interaction between FX_2 and HMT has no large impact on the structural integrity of the former since the average bond length F − X and θ angle of FX_2 subunits are close to those values for isolated FX_2 clusters (see Table 1 and Fig. S1 in the Supporting information).