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The structures and nonlinear optical responses of Li/Na doped adamantane: A density functional study

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ABSTRACT

On the basis of adamantane, adamantane-Li_n (Ad-Li, n = 1–4) and adamantane-Na_n (Ad-Na, n = 1–4) were theoretically constructed, for the first time, by Li/Na atom substituting the H atom of adamantane. Eight stable structures of adamantane-Li_n (Ad-Li, n = 1–4) and adamantane-Na_n (Ad-Na, n = 1–4) are obtained at B3LYP/6-31G(d) level. As Li atoms substituting the edge H atoms of adamantane, first hyperpolarizability of adamantane-Li_n decrease with increasing number Li atoms. However, as Na atoms substituting the edge H atoms of adamantane, first hyperpolarizability of adamantane-Na_n show an opposite trend and change in the order of Ad-Na_{1a} < Ad-Na_{2b} < Ad-Na_{3b} < Ad-Na_4. Among these structure, Ad-Na_4 possessed the largest first hyperpolarizability up to 243980 au, which can be attributed to low excitation energies. Furthermore, Ad-Na_4 exhibit deep-ultraviolet transparency, which is of great importance in practical applications. We hope that this study could provide an effective method for designing novel nonlinear optical materials.

1. Introduction

In the past twenty years, many scientists have paid attention to design novel materials with considerable nonlinear optical response because of their potential application in many fields, for example, optical computing and optical signal processing [1–4]. So far, many methods of enhancing first hyperpolarizability, which is the microscopic parameter of the macroscopic second nonlinear optical (NLO) materials, have been found. For example, prolonged π-electron molecules [5,6], distorted π-electron molecules [7], increasing push-pull effect [8,9], etc.

A series of molecules with large first hyperpolarizability have been designed in theory using quantum chemistry method [10–19]. For example, zhang et al. investigated the natural bond orbital and nonlinear optical properties of Li@n-acenessalt(n = 1–4) [11]. The natural bond orbital charges of Li^+ is close to 1, which show Li@n-acenes are Li salt. The result indicates that the first hyperpolarizabilities of α-Li@n-acenes are decreasing with increasing the number of conjugated benzenoid rings; however, the first hyperpolarizabilities of β-Li@n-acenes are increasing with increasing the number of conjugated benzenoid rings. Xu et al. investigated [5]cyclacene complexed with Li and found the first hyperpolarizability is greatly enhanced about 1200 times from 7 au ([5]cyclacene) to 7938 au (Li_5-[5]cyclacene) au [12]. The natural bond orbital

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charges of Li^+ show Li_5-[5]cyclacene are multilithium salt. The studies mention above indicate that the novel kind of ionic salts exhibit large first hyperpolarizability, in which excess electron plays an important role.

The relationship between different structure and nonlinear optical properties have also been investigated using quantum chemistry method. For example, Wu et al. investigated the effect of dehydrogenation/hydrogenation on nonlinear optical properties. The result shows that the first hyperpolarizability increase from 0 to 2465 au [13]. Different complexant of molecular system have also greatly influences nonlinear optical properties. Such as, the first hyperpolarizabilities of $Li(NH_3)_nNa$ were explored by Jing et al. [14]. The result shows that the first hyperpolarizability of $Li(NH_3)_nNa$ increase when n increase from 1 to 4. Xu et al. invested nonlinear optical properties of $Li(NH_2CH_3)_4M$ (M = Li, Na, K) by using a more flexible complexant [15].

Adamantane is allotropes of carbon and symmetric cage structure. People made great efforts to synthesize this molecule [20–23] and found a conventional method until 1957 [24]. Adamantane and adamantane derivatives have been synthesized in experiment, which have aroused great interest in many fields, including application of medicine [25–31]. Such as, scientists used adamantane and adamantane derivatives to treat Parkinson's disease [30]. The H of adamantane possess high activity, which had been demonstrated in previous research work [32–36]. Complexes (adamantane with Li atom) had been obtained in experiment soon afterwards [37]. The related research about Li atom substituting the H atom of adamantane had been made. For example, the hydrogen storage capacity of Li functionalized adamantine had been studied using first-principle density functional theory [38]. The result show that adamantine.Li is an ideal candidate for hydrogen storage with a gravimetric weight percent of more than 7%. The first hyperpolarizability of adamantane substituted alkali metals had been invested using quantum chemical calculations. The result show that alkali metals lead to large first hyperpolarizability [19]. The largest first hyperpolarizability of adamantine-k is 76626 au. Adamantane substituted alkali metals may be potential candidates for high performance nonlinear optical materials.

Some work have reported the effect of multiple lithium atoms on the nonlinear optical property of materials. For example, five Li atoms-substituted effect on the first hyperpolarizability of BN edge-doped graphene had been invested in our previous study [39]. Compare with one Li-substituted, five Li atoms-substituted is a kind of effective method. However, how the number and location of alkali metals affect the nonlinear optical property of adamantane.

In this work, we will discuss the following questions: (1) How does the H atoms of adamantane substituted by multiple alkali metals affect the electronic property of adamantane? (2) How does the H atoms of adamantane substituted by multiple alkali metals affect the absorption spectrum? (3) When multiple alkali metals substitute H atom of adamantane, will they have large β_0 values for adamantane-Li_n (Ad-Li_n, n = 1–4) compound and adamantane-Na_n (Ad-Na_n, n = 1–4) compound. In order to clarify the above mentioned questions, we studied the equilibrium geometries, electronic property, absorption spectrum and nonlinear optical responses of the studied system and expect that such a theoretical study may provide helpful information for further experimental studies about nonlinear optical materials of adamantane derivatives.

2. Computational details

When a system is in the weak and homogeneous electric field, its energy can be written as [40–42]:

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

Here, E^0 is the molecular total energy without the electric field, and F_α is the electric field component along α direction; μ_α, $\alpha_{\alpha\beta}$, and $\beta\alpha\beta_\gamma$ are the dipole, the polarizability, and the first hyperpolarizability, respectively. The dipole moment (μ_0) and polarizability (α_0) are defined as follows:

$$\mu_0 = (\mu_x{}^2 + \mu_y{}^2 + \mu_z{}^2)^{1/2}$$

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

The first hyperpolarizability is obtained as

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

In which

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

The optimized geometric structures of the studied molecules with real frequencies in the ground state were obtained by the density functional theory B3LYP/6-31G(d) level. In order to prove the structure of the studied molecules is reasonable, we compared adamantine's experimental and theoretical infrared spectra. Pirali et al. measured the infrared spectra of adamantine and observed a peak at about 3.4 μm [43]. We also computed the infrared spectra of adamantane. The result show that there is peak at 3.288 μm, which is close to the experimental result. Thus, the B3LYP method is suitable for optimizing these structures. The HOMO-LUMO gaps were computed at the B3LYP/6-31G(d) level. When we compute the (hyper)polarizability of molecule, choosing an appropriate method is very important. The static (hyper)polarizabilities were