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THEORETICAL RESEARCH ON STATIC FIRST HYPERPOLARIZABILITIES OF ALKALINE EARTH-BASED INORGANIC ALKALIDES $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Be, Mg And Ca)

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Abstract: For designing high-performance nonlinear optical (NLO) materials, two alkaline earth metal atoms were doped into the $(\text{NH}_2\text{CH}_3)_4$ cluster to form the inorganic alkaline earth-based alkalides $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Be, Mg, and Ca). Similar to the alkalide characteristics of the synthesized $\text{Li}^+(\text{NH}_2\text{CH}_3)_4\text{Na}^-$, the NBO charges of the outer alkaline earth metal atoms are negative, which indicates these $\text{Be}^+(\text{NH}_2\text{CH}_3)_4\text{M}^-$ present unusual alkaline earth-based alkalide's features. They also exhibit dramatically large static first hyperpolarizability (β_0) up to 657794(6.58×10^5) au ($\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Be}$). All the β_0 values of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ with alkaline earth-based alkalide features are much larger than that of the $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$) with alkalide features. These suggest that the alkaline earth metal atom doping is a well-performance method to enhance the NLO responses.

Key words: static first hyperpolarizability; inorganic alkalide; alkaline earth

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碱土金属类无机碱金属化合物的静态第一超极化率的理论研究

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摘要: 为设计品优的非线性光学材料, 我们把两个碱土金属原子掺杂于 $(\text{NH}_2\text{CH}_3)_4$ 形成了碱土金属类无机碱金属化合物 $\text{--Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Be, Mg 和 Ca), 和已被合成的 $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{Na}$ 类似, $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Be, Mg 和 Ca)的外侧碱土金属的 NBO 电荷是负值, 这说明它们展现出了良好的碱土金属类无机碱金属化合物特征。 $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Be, Mg 和 Ca)

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同时还具有相当大的静态第一超极化率(β_0), 其中最大值为 $657794 (6.58 \times 10^5)$ au ($\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Be}$)。所有的具有碱土金属类无机碱金属化合物特征的 $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($\text{M} = \text{Be}, \text{Mg},$ 和 Ca)比具有无机碱金属化合物特征的 $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}$ 和 K)有更大的 β_0 值。这些说明对于增加非线性光学响应来说, 碱土金属原子掺杂是一种品优的方式。

关键词: 第一超极化率; 碱金属化合物; 碱土金属

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Introduction

Recently, a novel kind of compounds, alkalide containing anionic alkali metal(s) (e.g., Na^- , K^- , Rb^- , or Cs^-) as electron-transfer reactions intermediary has attracted much attention because of their broad and potential applications in chemical synthesis, catalysis, and functional materials^[1]. The Dye's group synthesized the inorganic cage-like alkalide $\text{Li}^+(\text{NH}_2\text{CH}_3)_4\text{Na}^-$ ^[2].

For the nonlinear optics (NLO), much theoretical effort^[3-12] has been devoted to find the important influencing factors in order to result in a significant increase of the first hyperpolarizability (β_0). As an important strategy, doping is suggested to be a good method to enhance the NLO response^[6-12]. Recently, a series of alkali-doped amines with excess electrons, i.e., $\text{Li}^+(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na},$ and K)^[9], and $\text{Li}(\text{NH}_3)_n\text{Na}$ ($n = 1-3$)^[10] exhibit the alkalide feature as the valence electron of an alkali atom is polarized by a ligand to form an excess electron. Meanwhile, they are novel and potential high-performance NLO materials.

Can the two valence electrons of an alkaline earth metal atom also be pushed out to form excess electrons and an alkaline earth-doped molecule exhibit alkaline-earth-based alkalide feature similar to the alkali-based alkalide? As a logical consideration, can these alkaline earth-doped molecules are also novel candidates of high-performance NLO materials? On the basis of such a fundamental consideration, we have recently focused on some alkaline-earth-doped organic compounds, in which the Be-doped N-(2-(1H-imidazol-1-yl)ethyl)-N-(aminomethyl)-methanediamine (Be-IAD) and Be-doped 2-(2-(1H-imidazol-1-yl)ethyl)-2-(aminomethyl)-propane-1,3-diamine (Be-IPD) have alkaline earth-based alkalide features^[11]. However, it's much to be regretted that

the static first hyperpolarizabilities (β_0) of these reported alkaline-earth-doped organic compounds with alkaline earth-based alkalide features are smaller than that of the corresponding alkali-doped compounds with alkalide features.

To obtain more excellent NLO material model, in this work, we investigated the structures and electric properties of the inorganic alkaline earth-based alkalides $\text{Be}^+(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Be}, \text{Mg},$ and Ca) by comparing with the alkali-based alkalide $\text{Li}^+(\text{NH}_2\text{CH}_3)_4\text{M}''$ ($\text{M}'' = \text{Li}, \text{Na},$ and K).

1 Computational details

The geometries of the $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($\text{M} = \text{Be}, \text{Mg},$ and Ca) with all real frequencies were calculated at MP2/6-311++G (d, p) level. For the purpose of comparison, the structures of the $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na},$ and K) were also obtained at the same level, which is slightly different from Xu's MP2/6-311++G level. The natural bond orbital (NBO) charges, the static first hyperpolarizabilities (β_0), the interaction energies (E_{int}), and vertical ionization energies (VIEs) were all obtained at MP2/6-311++G (2d, p) level.

The dipole moment (μ_0), polarizability (α_0), and static first hyperpolarizability (β_0) are defined as follows:

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

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

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

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

Using the counterpoise (CP) procedure^[13], the E_{int} is the difference between the energy of the complex ($\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ or $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$) and the sum of the energies of the moieties (the two metal atoms and the $(\text{NH}_2\text{CH}_3)_4$, as illustrated by the following formula^[14]:

$$E_{\text{int}} = E_{\text{ABC}}(X_{\text{ABC}}) - E_{\text{A}}(X_{\text{ABC}}) - E_{\text{B}}(X_{\text{ABC}}) - E_{\text{C}}(X_{\text{ABC}}) \quad (4)$$

To eliminate the basis set superposition error (BSSE) effect, the same basis set, X_{ABC} , was used for both the moieties (A = Be (or Li), B = $(\text{NH}_2\text{CH}_3)_4$, and C = M (or M')) and the complex.

The VIEs were determined by using the following formulae:

$$\text{VIE (I)} = E[(\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M})^+] - E[\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}] \quad (5)$$

$$\text{VIE(II)} = E[(\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M})^{2+}] - E[(\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M})^+] \quad (6)$$

where $E[(\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M})^+]$ and $E[(\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M})^{2+}]$ are, respectively, the energies of the $(\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M})^+$ and $(\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M})^{2+}$ cations (calculated with the same geometry of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$).

The calculations were carried out with Gaussian 09 (A.02) program package.

2 Results and Discussion

2.1 Equilibrium geometries and stabilities

The optimized structures with all real frequencies of the $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Be, Mg, and Ca) as well as $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$) at MP2/6-311++G (d, p) level are shown in Figure 1, and their geometric parameters are depicted in Table 1.

Table 1 Optimized geometrical parameters of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Be, Mg, and Ca) as well as $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$) at MP2/6-311++G (d, p) level

	$\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$			$\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$			
	M = Be	M = Mg	M = Ca	$\text{M}' = \text{Li}$	$\text{M}' = \text{Na}$	$\text{M}' = \text{K}$	
Bond length (Å)	N-N	2.932	2.883	2.875	3.358	3.356	3.341
		2.808	2.789	2.779	3.318	3.340	3.360
		2.774	2.686	2.684	3.343	3.377	3.424
		2.868	2.922	2.925	3.364	3.360	3.356
		2.854	2.819	2.823	3.512	3.503	3.495
		2.860	2.916	2.919	3.481	3.455	3.428
		1.756	1.735	1.736	2.081	2.082	2.083
(inner) Be-N (Li-N)	1.726	1.741	1.739	2.075	2.076	2.077	
	1.756	1.743	1.743	2.072	2.071	2.071	
	1.746	1.736	1.732	2.097	2.099	2.100	
	3.402	5.056	5.301	4.372	4.559	4.926	
Be-M (Li-M')				(4.483) ^a	(4.689) ^a	(5.169) ^a	
Bond angle (°)							
N-Be-M (N-Li-M')	176.89	158.17	173.93	174.54	174.14	171.70	

^a The values in parentheses are calculated at MP2/6-311++G level, see ref 9

Comparing the equilibrium geometries of the $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Be, Mg, and Ca) with that of the alkali $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$), it

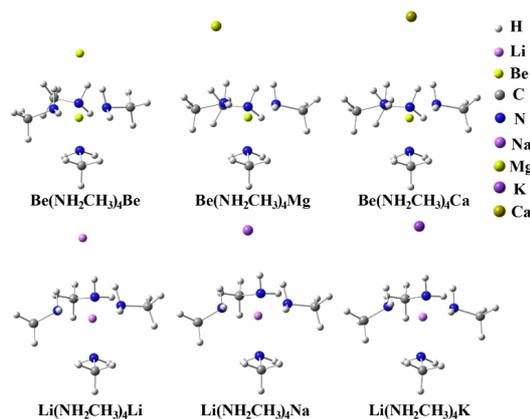


Fig.1 Optimized geometries of the $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Be, Mg, and Ca) and $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$) at MP2/6-311++G (d, p) level

Similar to the alkali metal doping complexes $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$), the first doping alkaline earth metal atom is enwrapped by NH_2CH_3 molecules and the second doping one is outside the $(\text{NH}_2\text{CH}_3)_4$ cluster. One thing to be noted is that, for the $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Mg}$, the second doping alkaline earth metal atom (Mg) considerably deviates from the N-Be line forming by the inner Be atom and the bottom N atom (see N-Be-Mg bond angle in Table 1), while the N-Be-M (M = Be and Ca) in $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ and N-Li-M' ($\text{M}' = \text{Li}, \text{Na}, \text{K}$) in $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ bond angles indicate that the second doping metal atoms (Be, Ca, Li, Na, and K) are, respectively, only slightly out of the N-Be or N-Li line.

is found that the N-N lengths in $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ are 0.426~0.740 Å shorter than the corresponding ones in $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$. As a result, the molecular framework

forming by NH_2CH_3 cluster are smaller for $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ than for $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ and the N-Be (inner) bond lengths of the $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ are $0.316 \sim 0.378 \text{ \AA}$ shorter than the corresponding N-Li (inner) bond lengths of the $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$.

The Be-M distances in $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Be, Mg, and Ca) and the Li-M' distances in $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ (M' = Li, Na, and K) complexes display the similar atomic number dependences. The Be-M distance in $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ increases with the increasing of the alkaline earth metal atomic number in the order of $3.402 \text{ (M = Be)} < 5.056 \text{ (M = Mg)} < 5.301 \text{ \AA}$ (M = Ca), and the Li-M' distance in $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ increases with increasing alkali metal atomic number in the order of $4.372 \text{ (M' = Li)} < 4.559 \text{ (M' = Na)} < 4.926 \text{ \AA}$ (M' = K). The Be-Be metal bond lengths in $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Be}$ are obviously shorter than the Li-M' metal bond lengths in $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ but both the Be-Mg and Be-Ca metal bond lengths in $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Mg and Ca) are clearly larger than the Li-M' metal bond lengths in $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$. For the $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ (M' = Li, Na, and K) complexes, the Li-M' lengths at our MP/6-311++G(d, p) level are slightly shorter than the corresponding values at the reported MP/6-311++G level^[9], which suggests that the additional polarization functions are necessary for the optimization of the geometries of the $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ and $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$.

Comparing with the other related alkaline-earth-based alkali systems, the N-Be distance of 1.756 , 1.736 and 1.735 \AA in $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Mg and Ca) are close to the values of 1.803 \AA in Be-IAD and 1.775 \AA in Be-IPD^[11].

Table 2 Interaction energies (E_{int} , kcal/mol), and vertical ionization energies (VIE(I&II), eV) of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Be, Mg, and Ca) as well as $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ (M' = Li, Na, and K) at MP2/6-311++G (2d, p) level

	$\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$			$\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$		
	M = Be	M = Mg	M = Ca	M' = Li	M' = Na	M' = K
E_{int}	-90.60	-93.59	-95.31	-83.69	-80.68	-78.19
VIE(I)	-2.957	-3.339	-3.423	-3.404	-3.270	-3.064
VIE(II)	-6.814	-6.169	-5.751	-8.538	-8.015	-7.190

For the stability of these molecules, we have obtained the interaction energies (E_{int}) and the vertical ionization energies (VIEs) of the $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Be, Mg, and Ca) as well as $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ (M' = Li, Na, and K) at MP2/6-311++G(2d, p) level. From Table 2, it is clear that both the $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ and the $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ have large E_{int} , which shows the stabilities of them. Interestingly, the E_{int} of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ and $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ complexes display opposite atomic number dependences. The E_{int} of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ increases with the increasing of the alkaline earth metal atomic number in the order of $-90.60 \text{ (M = Be)} < -93.59 \text{ (M = Mg)} < -95.31 \text{ kcal/mol}$ (M = Ca), while that of the $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ slightly decreases with increasing alkali metal atomic number in the order of $-83.69 \text{ (M' = Li)} > -80.68 \text{ (M' = Na)} > -78.19 \text{ kcal/mol}$ (M' = K). Even then, the smallest E_{int} of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (-90.60 kcal/mol) is still larger than the largest one of the $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ (-83.69 kcal/mol). Therefore, our new inorganic alkaline earth metal atom doped $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ are more stable than the reported alkali-doped $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ^[2,9].

From Table 2, the VIE(I)s of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (M = Be, Mg, and Ca) and $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ (M' = Li, Na, and K) complexes also display opposite atomic number dependences. The VIE(I) of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ slightly increases with the increasing of the alkaline earth metal atomic number in the order of $2.957 \text{ (M = Be)} < 3.339 \text{ (M = Mg)} < 3.423 \text{ eV}$ (M = Ca), while that of the $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ slightly decreases with increasing alkali metal atomic number in the order of $3.404 \text{ (M' = Li)} > 3.270 \text{ (M' = Na)} > 3.064 \text{ kcal/mol}$ (M' = K). Comparing the VIE(I)s of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ with that of $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$, alkaline earth metal atom doped $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Mg}$ and $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Ca}$ are more hardly oxidized than the reported alkali metal atom doped $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}$. Though $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Be}$ is more easily oxidized than the synthesized $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{Na}$, it's reducibility is very close to that of $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{K}$. For both $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ and $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ complexes, the VIE(II) of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ slightly decreases with the increasing of the alkaline earth metal atomic number in the order of $6.814 \text{ (M = Be)} > 6.169 \text{ (M = Mg)} >$

5.751 eV ($M = \text{Ca}$), and that of the $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ also slightly decreases with increasing alkali metal atomic number in the order of 8.538 ($\text{M}' = \text{Li}$) $>$ 8.015 ($\text{M}' = \text{Na}$) $>$ 7.190 kcal/mol ($\text{M}' = \text{K}$).

The ranges of the VIE(I)s and VIE(II)s of these $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$) are, respectively, $2.957\sim 3.423$ eV and $5.751\sim 6.814$ eV. Similar to the reported alkali-based and alkaline earth-based alkalides^[11], these $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$) also have small VIEs. These VIE(I)s are much smaller than the IP(I) of 9.32 eV of the isolated Be atom, 6.11 eV of the isolated Ca atom, and that of 5.39 eV of the isolated Li atom^[15]. For the

relative alkaline earth metal atom doped systems^[11-12], the VIE(I)s of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$) ($2.957 \sim 3.423$ eV) are very close that of 3.25 eV of Be-IPD^[11] and that of Li- $\text{H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ and K- $\text{H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ (3.70 and 3.50 eV)^[12]. These results also give the support for the stabilities of these alkaline earth metal atom doped molecules.

2.2 Alkaline-earth-based alkalide features

The NBO charges of the $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$) as well as $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$) at MP2/6-311++G (2d, p) level are listed in Table 3.

Table 3 NBO charges of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$) as well as $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$) at MP2/6-311++G (2d, p) level

	$\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$			$\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$		
	$M = \text{Be}$	$M = \text{Mg}$	$M = \text{Ca}$	$\text{M}' = \text{Li}$	$\text{M}' = \text{Na}$	$\text{M}' = \text{K}$
N	-0.950	-0.975	-0.972	-0.860	-0.861	-0.864
	-1.004	-1.225	-1.274	-0.933	-0.924	-0.922
	-1.063	-1.150	-1.147	-0.925	-0.918	-0.918
	-1.220	-1.088	-1.110	-0.930	-0.920	-0.913
Be (Li)	0.847	0.331	0.184	0.606	0.601	0.570
				(0.809) ^a	(0.795) ^a	(0.757) ^a
M (M') (N-Li-M')	-0.750	-0.187	-0.239	-0.772	-0.788	-0.755
				(-0.683) ^a	(-0.680) ^a	(-0.612) ^a

^a The values in parentheses are calculated at MP2 method with different basis sets for different atoms, see ref 9

From Table 3, it is clear that, similar to the alkalide $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$, the NBO charge of the outer alkaline earth metal atom (M , especially for $M = \text{Be}$) in each of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$) is negative. Being in accordance with the reported results^[16], our results also show the NBO charge of the M' atoms in $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$) are negative. Notice that, the absolute NBO charge of M considerably decreases firstly and then slightly increases with increasing of the alkaline earth metal atomic number for the $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ in order of 0.750 ($M = \text{Be}$) \gg 0.187 ($M = \text{Mg}$) $<$ 0.239 ($M = \text{Ca}$). This is mainly related to the dependence of Be- M lengths and the N-Be- M angles on the atomic number of alkali metal anion. The Be-Be lengths in $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Be}$ (3.402 Å) is much shorter than all the Li- M' lengths in $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$) (4.372 ~ 4.926 Å), which results in the large negative charge of outer Be atom. The Be- M lengths

in $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ (5.056 ($M = \text{Mg}$) and 5.301 Å ($M = \text{Ca}$)) are obviously longer than all the Li- M' lengths in $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$), which results in the smaller negative charge of the outer M atom than that of the corresponding M' . In addition, the largest angle of the N-Be- M in the three N-Be- M angles for $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ indicates that this doping alkaline earth metal atom (M) considerably deviates from the N-Be line forming by the inner Be atom and the bottom N atom. So, it has the smallest negative charge of the three. However, the charges of Mg (-0.187) in $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Mg}$ and Ca (-0.239) in $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Ca}$ are very close to that of Be atom in the reported alkaline earth-based alkalides Be-IAD, Be-PAD, and Be-IPD (-0.147~ -0.253)^[11]. The negative NBO charges of the outer alkaline earth metal atoms (M) in $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$) show that they act as anions which is just similar to the anions of the (outer) M' in $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li},$

Na, and K). The charges of M' in $\text{Li}(\text{NH}_2\text{CH}_3)_4M'$ ($M' = \text{Li}, \text{Na}, \text{and K}$) are $-0.755 \sim -0.788$. The NBO charges of the M' anions and the inner Li cations in $\text{Li}(\text{NH}_2\text{CH}_3)_4M'$ calculated at our MP/6-311++G(d, p) level are obviously smaller than the corresponding values calculated at the reported MP method with different basis sets for different atoms^[9], in which, the 6-311++G basis set is employed for the N and H atoms, and the 6-311++G(3df, 3pd) basis set employed for the Li and Na atoms. This indicates that the unbalanced utilization of the basis sets overestimates NBO charge of the alkali metal atoms.

The NBO charges of the inner alkaline earth metal atom (Be) in each of $\text{Be}(\text{NH}_2\text{CH}_3)_4M$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$) is positive ($0.331 \sim 0.847$), which is also similar to the cations of inner Li in $\text{Li}(\text{NH}_2\text{CH}_3)_4M'$ ($M' = \text{Li}, \text{Na}, \text{and K}$) ($0.773 \sim 0.847$). The NBO charge of the inner Be atom in $\text{Be}(\text{NH}_2\text{CH}_3)_4M$ also obviously decreases firstly and then increases with increasing of the alkaline earth metal atomic number for the $\text{Be}(\text{NH}_2\text{CH}_3)_4M$ in order of 0.862 ($M = \text{Be}$) > 0.339 ($M = \text{Mg}$) < 0.448 ($M = \text{Ca}$).

The inner alkaline earth metal atom Be of $\text{Be}(\text{NH}_2\text{CH}_3)_4M$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$) with a charge of about +1 is as a cation and the outer M with a charge of about -1 is as an anion; therefore, $\text{Be}(\text{NH}_2\text{CH}_3)_4M$ has alkalide characteristic and may be denoted as $\text{Be}^+(\text{NH}_2\text{CH}_3)_4M^-$, which is similar to that of $\text{Li}^+(\text{NH}_2\text{CH}_3)_4M'^-$.

The highest occupied molecular orbitals (HOMOs) are depicted in Figure 2. For the Be-Be and Be-Ca models, the p -style electron clouds of each HOMO are symmetric around the Be-M axis, while that are polarized by the coordination nitrogen atoms to form distended excess electron clouds (excess electron pair) for all of the $\text{Be}(\text{NH}_2\text{CH}_3)_4M$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$). For the purpose of comparison, the similar the electron clouds of Li-Na model and $\text{Li}(\text{NH}_2\text{CH}_3)_4M'$ are also shown in Figure 2 (or see ref 9). Similar to the reported alkali-based and alkaline earth-based alkalides, the distended excess electron clouds lead to the small VIEs of these $\text{Be}(\text{NH}_2\text{CH}_3)_4M$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$). The ranges of the VIE(I)s and VIE(II)s of these $\text{Be}(\text{NH}_2\text{CH}_3)_4M$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$) are, respectively, $2.957 \sim 3.423$ eV and $5.751 \sim 6.814$ eV.

Considering the negative charge of the outer alkaline earth metal atom (M), the distended excess electron clouds (excess electron pair in HOMO), and the lower VIEs than the above reviewed alkalides and the isolated alkaline earth metal atoms, these alkaline-earth-doped $\text{Be}^+(\text{NH}_2\text{CH}_3)_4M^-$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$) are isoelectronic analogues of the solide of $\text{Li}^+(\text{NH}_2\text{CH}_3)_4\text{Na}^-$ ^[9]. Therefore, these alkaline-earth-doped compounds are alkaline earth-based alkalides, which is similar to the alkaline earth-based alkalides of Be-IAD and Be-IPD^[11].

2.3 Static polarizability and the first hyperpolarizability

As novel candidates of high-performance NLO materials, the important electric properties of these alkaline earth-based alkalides ($\text{Be}(\text{NH}_2\text{CH}_3)_4M$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$)) should be considered. From Table 4, there is a plateau for the static first hyperpolarizabilities (β_0) of both $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Be}$ and $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{Li}$ in an applied electric field (AEF) range from 0.0003 to 0.0015 au. So, the AEF of 0.0010 au is suitable in the calculation of β_0 . The dipole moments (μ_0), static polarizabilities (α_0) and β_0 of the $\text{Be}(\text{NH}_2\text{CH}_3)_4M$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$) and $\text{Li}(\text{NH}_2\text{CH}_3)_4M'$ ($M' = \text{Li}, \text{Na}, \text{and K}$) were obtained at the MP2/6-311++G(2d, p) level and are listed in Table 5.

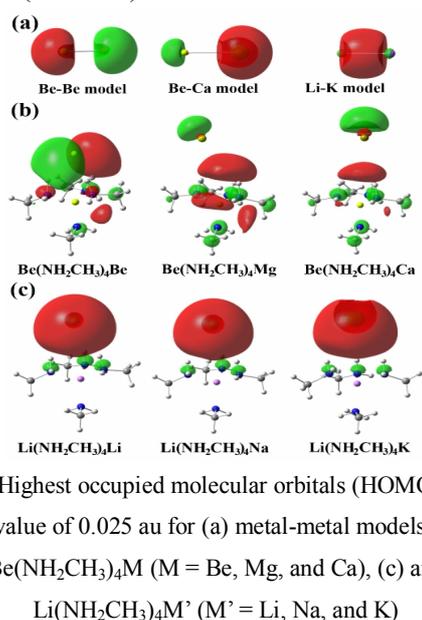


Fig.2 Highest occupied molecular orbitals (HOMOs) at the isovalue of 0.025 au for (a) metal-metal models, (b) $\text{Be}(\text{NH}_2\text{CH}_3)_4M$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$), (c) and $\text{Li}(\text{NH}_2\text{CH}_3)_4M'$ ($M' = \text{Li}, \text{Na}, \text{and K}$)

Table 4 Hyperpolarizabilities of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($\text{M} = \text{Be}, \text{Mg}, \text{and Ca}$) as well as $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$) at the MP2/6-311++G(2d,p) level in different applied electric fields

Field (au)	0.0003	0.0005	0.0007	0.0010	0.0012	0.0015
$\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$						
μ_0	2.594	2.594	2.594	2.594	2.594	2.594
α_0	693.4	697.0	702.2	712.9	721.6	735.7
β_{zzz}	1086369	1081649	1074433	1057933	1042396	1010651
β_0	678694	675215	669920	657794	646191	620935
$\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$						
μ_0	4.067	4.067	4.067	4.067	4.067	4.067
α_0	403.1	403.4	403.9	404.9	405.8	407.4
β_{zzz}	7043	7127	7246	7508	7742	8200
β_0	9167	9244	9365	9631	9885	10395

Table 5 Dipole moments (μ_0), static mean polarizabilities (α_0), hyperpolarizabilities (β_0), the oscillator strength f_0 , the difference of dipole moment between the ground state and the crucial excited state ($\Delta\mu$), and the transition energy (ΔE), for $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($\text{M} = \text{Be}, \text{Mg}, \text{and Ca}$) as well as $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$)

	μ_0 [au]	α_0 [au]	β_0 [au]	β_{zzz} [au]	ΔE [eV]	f_0	$\Delta\mu$ [au]	$(\Delta\mu f_0) / \Delta E^3$
$\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Be}$	2.594	712.9	657794	1057934	1.049	0.206	1.646	53407
$\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Mg}$	1.607	547.9	159979	121964	1.252	0.263	0.809	19680
$\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Ca}$	1.768	449.3	313791	249044	1.201	0.238	0.881	21981
$\text{Li}(\text{NH}_2\text{CH}_3)_4\text{Li}$	4.607	404.9	9631	8575	2.061	0.205	2.188	9277
			(18825) ^a					
$\text{Li}(\text{NH}_2\text{CH}_3)_4\text{Na}$	4.726	472.9	13689	10955	2.020	0.233	2.135	10949
			(27942) ^a					
$\text{Li}(\text{NH}_2\text{CH}_3)_4\text{K}$	4.443	593.6	28522	23975	1.731	0.231	1.896	15297
			(81094) ^a					

^a The values in parentheses are calculated at MP2 method with different basis sets for different atoms, see ref 9

Interestingly, both the μ_0 and α_0 of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($\text{M} = \text{Be}, \text{Mg}, \text{and Ca}$) complexes have reverse atomic number dependences from that of the $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$). From Table 5, the μ_0 of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ obviously decreases firstly and then slightly increases with increasing the alkaline earth metal atomic number, while that of $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ increases firstly and then slightly decreases with increasing the alkali metal atomic number. The orders of μ_0 are 2.594 ($\text{M} = \text{Be}$) > 1.607 ($\text{M} = \text{Mg}$) < 1.768 au ($\text{M} = \text{Ca}$) and 4.607 ($\text{M}' = \text{Li}$) < 4.726 ($\text{M}' = \text{Na}$) > 4.443 au ($\text{M}' = \text{K}$) for $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ and $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$, respectively. The α_0 of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($\text{M} = \text{Be}, \text{Mg}, \text{and Ca}$) decreases with increasing the alkaline earth metal atomic number in the order of 712.9 ($\text{M} = \text{Be}$) > 547.9 ($\text{M} = \text{Mg}$) > 449.3 au ($\text{M} = \text{Ca}$), while that of $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ decreases firstly and then increases with increasing the alkali metal atomic number in the

order of 449.3 ($\text{M}' = \text{Li}$) > 404.9 ($\text{M}' = \text{Na}$) < 472.9 au ($\text{M}' = \text{K}$).

Notice that, for the $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$), the values were calculated at MP2 method with different basis sets for different atoms in the previous work^[9], in which, the 6-311++G basis set is employed for the N and H atoms, and the 6-311++G(3df,3pd) basis set employed for the Li and Na atoms. Table 5 shows that each β_0 value of $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ at our MP2/6-311++G(2d, p) level (9631 ($\text{M}' = \text{Li}$), 13689 ($\text{M}' = \text{Na}$), and 28522 au ($\text{M}' = \text{K}$)) is considerably smaller than the corresponding reported one (18825 ($\text{M}' = \text{Li}$), 27942 ($\text{M}' = \text{Na}$), and 81094 au ($\text{M}' = \text{K}$)), which indicates that the unbalanced utilization of the basis sets significantly overestimates β_0 value.

The β_0 value obviously decreases firstly and then increases with increasing the alkaline earth metal atomic number for the $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($\text{M} = \text{Be}, \text{Mg}, \text{and Ca}$). The order of the β_0 values is 657794 ($\text{M} = \text{Be}$)

> 159979 ($M = \text{Mg}$) < 313791 au ($M = \text{Ca}$). This order is also remarkably different from that of $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$, for which the β_0 value increases with increasing the alkali metal atomic number (9631 ($M' = \text{Li}$) < 13689 ($M' = \text{Na}$) > 28522 au ($M' = \text{K}$)). For the $\text{Be}^+(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$), the β_0 value is related to the NBO charge of M' and thus to the diffuse extent of the excess electron (Figure 3). Among the three $\text{Be}^+(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$), the β_0 value of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Be}$ with the largest negative charge of outer Be is the largest one, while that of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Mg}$ with the smallest negative charge of outer Mg is the smallest one.

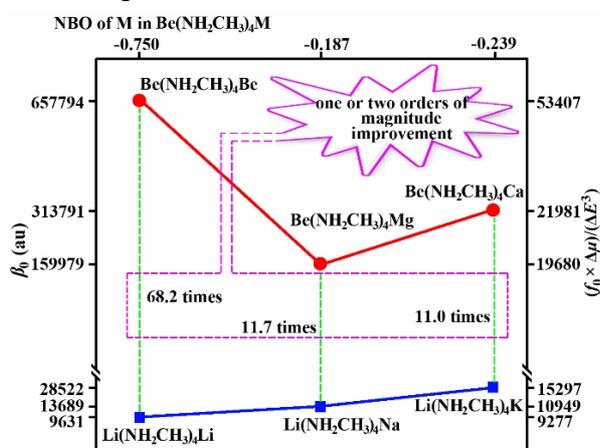


Fig.3 Two monotonic dependences of the β_0 value on NBO charge and the $(f_0 \times \Delta\mu)/(\Delta E^3)$ with atomic number of alkaline earth metal anion (M') in inorganic alkalides $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$)

It's worth noting that, from the alkali-doped $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ to the corresponding alkaline-earth-doped $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$, especially from $M' = \text{Li}$ to $M = \text{Be}$, every rise of the β_0 value constitutes one or two orders of magnitude improvement. It can be seen from Figure 3, the β_0 value is increased by approximately 68-fold from 9631 ($\text{Li}(\text{NH}_2\text{CH}_3)_4\text{Li}$) to 657794 au ($\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Be}$), 11-fold from 13689 ($\text{Li}(\text{NH}_2\text{CH}_3)_4\text{Na}$) to 159979 au ($\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Mg}$), and 68-fold from 28522 ($\text{Li}(\text{NH}_2\text{CH}_3)_4\text{K}$) to 313791 au ($\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Ca}$), respectively.

Comparing with the relative alkalides, the alkaline earth-based alkalides $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($M = \text{Be}, \text{Mg}$ and Ca) also have large β_0 values. The β_0 values of them ($1.60 \times 10^5 \sim 6.58 \times 10^5$ au) are much larger than that of the reported alkaline earth-based

alkalide of Be-IPD (2.76×10^4 au)^[11]. The β_0 values of these alkaline earth-based alkalides $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($M = \text{Be}, \text{Mg}$ and Ca) also close to that of the reported alkaline earth-based electrides of $\text{Li-H}_3\text{C}_4\text{N}_2 \cdots \text{Ca}$ (2.69×10^5 au), $\text{K-H}_3\text{C}_4\text{N}_2 \cdots \text{Ca}$ (2.45×10^5 au)^[12]. These results suggested that, besides the alkaline metal atom doping, the alkaline earth atom doping is also an important method to enhance the NLO responses.

To understand the order of the β_0 , one often considers the two-level model expression^[8-12]:

$$\beta_0 \propto (f_0 \times \Delta\mu)/(\Delta E^3) \quad (6)$$

where ΔE , f_0 , and $\Delta\mu$ are the transition energy, oscillator strength, and the difference of dipole moment between the ground state and the crucial excited state, respectively. According to the two-level expression, the static first hyperpolarizability is proportional to f_0 and $\Delta\mu$, and inversely proportional to the third power of the transition energy (ΔE). The corresponding f_0 , $\Delta\mu$, and ΔE values of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$) as well as $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($M' = \text{Li}, \text{Na}, \text{and K}$) at TD-CAM-B3LYP/6-311++G (d, p) level are listed in Table 5.

From Table 5 and Figure 3, it can be found that the β_0 value is well proportional to $(f_0 \times \Delta\mu)/(\Delta E^3)$ for the six structures. The β_0 values of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Be}$ and $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{Li}$ are, respectively, the largest and the smallest among the six, the $(f_0 \times \Delta\mu)/(\Delta E^3)$ values of them are, respectively, the largest and the smallest one.

Considering the β_0 value is inversely proportional to the third power of the transition energy (ΔE), thus, the transition energy is the decisive factor in the calculation of the β_0 value. Inversely to the order of the β_0 values, for the $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($M = \text{Be}, \text{Mg}, \text{and Ca}$), the ΔE value increases firstly and then decreases with increasing the alkaline earth metal atomic number in order of 1.049 ($M = \text{Be}$) < 1.252 ($M = \text{Mg}$) > 1.201 eV ($M = \text{Ca}$). This order is also remarkably different from that of $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$, for which the ΔE value decreases with the increasing of the alkali metal atomic number (2.061 ($M' = \text{Li}$) < 2.020 ($M' = \text{Na}$) > 1.731 eV ($M' = \text{K}$)). Comparing

$\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($\text{M} = \text{Be}, \text{Mg}, \text{and Ca}$) to $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$), the former show fairly smaller ΔE values of 1.049~1.252 eV, which may be the reason why they exhibit considerably larger β_0 values, while the later have larger ΔE values of 1.731~2.061 eV, which results in the smaller β_0 values of them.

To further understand the relative magnitude of those β_0 values, the changes of electron clouds in the crucial transitions is considered. These molecular orbital plots are depicted in Figure 4. From Figure 4, the charge transfers of both $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($\text{M} = \text{Be}, \text{Mg}, \text{and Ca}$) and $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$) are mainly from the doping metal atom to the bottom of the $(\text{NH}_2\text{CH}_3)_4$ cluster.

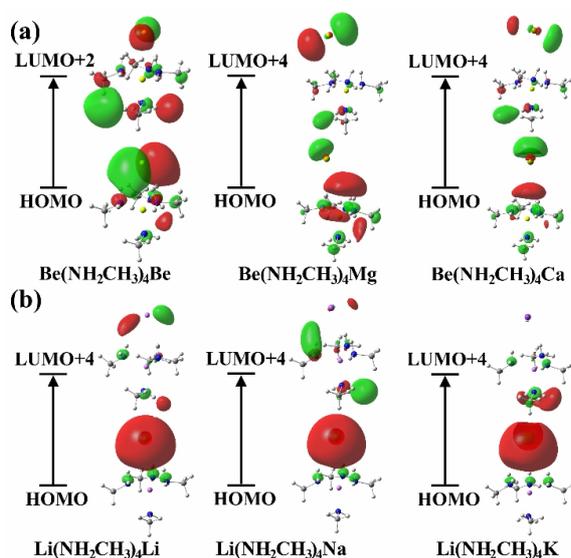


Fig.4 Crucial transitions of $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($\text{M} = \text{Be}, \text{Mg}, \text{and Ca}$), (c) and $\text{Li}(\text{NH}_2\text{CH}_3)_4\text{M}'$ ($\text{M}' = \text{Li}, \text{Na}, \text{and K}$) at the isovalue of 0.025 au

3 Conclusions

To explore new means for designing high-performance nonlinear optical materials, in the present study, two alkaline earth metal atoms were doped into the $(\text{NH}_2\text{CH}_3)_4$ cluster to form the inorganic alkaline earth-based alkalides $\text{Be}(\text{NH}_2\text{CH}_3)_4\text{M}$ ($\text{M} = \text{Be}, \text{Mg}, \text{and Ca}$).

These alkaline-earth-doped compounds not only present unusual alkaline-earth-based alkalide's features but also exhibit large static first hyperpolarizabilities

(β_0) up to 657794 au ($\text{Be}(\text{NH}_2\text{CH}_3)_4\text{Be}$). All the β_0 values of these alkaline-earth-doped compounds with alkaline earth-based alkalide's features are much larger than that of the corresponding alkali-doped compounds with alkalide's features. Therefore, besides the alkali metal atom doping, the alkaline earth metal atom doping is also an important and well-performance method to enhance the NLO responses.

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4.24、酶解时间 1.95 h、加酶量 1.5%，胶原蛋白的含量为 883.64 mg/g。为了方便实际操作，将鱼鳞胶原蛋白的最优工艺条件改为：酶解温度 31℃，pH 值 4.2，提取时间 2 h，加酶量 1.5%，得到实际胶原蛋白含量为 881.78mg/g，这与理论值基本相吻合，说明模型的可靠性较高。

3 小结

本研究采用响应面法优化酶解提取鳊鱼鱼鳞胶原蛋白的工艺，以对二甲氨基苯甲醛比色法测定胶原蛋白含量。在单因素实验的基础上，得出了酶解温度、pH 值、酶解时间对胶原蛋白含量的影响显著，因此根据 Box-Behnken 实验设计的原理，以胶原蛋白含量为响应值进行响应面优化分析，得出鱼鳞胶原蛋白的最佳工艺条件为：酶解温度 31.32℃、pH 值 4.24、酶解时间 1.95 h、加酶量 1.5%，胶原蛋白的含量为 883.64 mg/g。为了方便实际操作，将鱼鳞胶原蛋白的最优工艺条件改为：酶解温度 31℃，pH 值 4.2，提取时间 2 h，加酶量 1.5%，得到实际胶原蛋白含量为 881.78 mg/g，这与理论值基本相吻合，说明模型的可靠性较高。

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