

# What Is the Role of the Complexant in the Large First Hyperpolarizability of Sodide Systems $\text{Li}(\text{NH}_3)_n\text{Na}$ ( $n = 1-4$ )?

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Received: January 27, 2006; In Final Form: April 4, 2006

To explore the coordination number (around the cation) dependence of the nonlinear optical (NLO) properties in alkaliides, this paper studies the structures and large NLO responses of model alkaliides,  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ). At the MP2/aug-cc-pVDZ level, the structural characteristic is determined to be that the Li–Na distance increases (from 3.030 to 4.646 Å) with the increasing of the number of  $\text{NH}_3$  ( $n$  from 1 to 4). Results show that  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) have considerably large first hyperpolarizabilities ( $\beta_0$ ). Especially, a prominent coordination number dependence of the  $\beta_0$  value is found as follows:  $\beta_0 = 13\,669$  ( $n = 1$ ) <  $26\,840$  ( $n = 2$ ) <  $39\,764$  ( $n = 3$ ) <  $77\,921$  au ( $n = 4$ ) at the MP2 level. With the same coordination number (four N atoms) of  $\text{Li}^+$  cations, the  $\beta_0$  value (77 921 au) of this “small” inorganic molecule  $\text{Li}(\text{NH}_3)_n\text{Na}$  is over five times larger than that of the “big” organic molecule  $\text{Li}@\text{Calix}[4]\text{pyrrole-Na}$  (14 772 au). This indicates that the  $\beta_0$  value is strongly related to the flexibility of the complexant. Obviously, the flexibility of  $(\text{NH}_3)_4$  is much greater than that of the cuplike shaped  $\text{Calix}[4]\text{pyrrole}$ . This work suggests that two important factors should be taken into account to enhance the first hyperpolarizability of alkaliide, i.e., the coordination number around the cation and the flexibility of the complexant.

## Introduction

During the past twenty years, a great deal of work has been carried out to study the nonlinear optical (NLO) properties for many different types of NLO materials.<sup>1</sup>

In our previous works,<sup>2</sup> it has been found that systems (without center symmetry) with excess electrons have large NLO responses. For example, the solvated electron,  $(\text{FH})_2\{\text{e}\}(\text{HF})$ , has the extraordinary first hyperpolarizability of  $\beta_0 = 8.1 \times 10^7$  au,<sup>2a</sup> and the dipole-bound electron,  $(\text{H}_2\text{O})_3\{\text{e}\}$ , has the  $\beta_0$  value of  $1.7 \times 10^7$  au.<sup>2b</sup> It is demonstrated that the loosely bound excess electron plays a crucial role in the large first hyperpolarizability.

Recently, two kinds of novel compounds with the excess electrons have been experimentally synthesized. They are “alkaliide” and “electride”, which contain loosely bound excess electrons.

Electrides are a novel kind of ionic salts in which anionic sites are occupied solely by electrons.<sup>3</sup> In contrast to electrides, alkaliides are other ionic salts where anionic sites are occupied by alkali anions (e.g.,  $\text{Na}^-$ ,  $\text{K}^-$ ,  $\text{Rb}^-$ , or  $\text{Cs}^-$ ).<sup>4</sup> But the excess electron in the alkali anion is loosely bound in space because of the small electron affinity (<0.62 eV for Li)<sup>5</sup> for alkali atoms. This is similar to the sole electrons in the electrides.

From the previous works,<sup>2f</sup> alkaliides have not only a small transition energy but also a larger oscillator strength in the

crucial excited transition than the corresponding electrides. Therefore, alkaliides have larger first hyperpolarizability than electrides with the same cation and complexant. In alkaliides, the sodide with a  $\text{Na}^-$  anion as a sole anion is one of the important alkaliides because the sodide anion is much more stable than other alkali anions.<sup>6</sup> In the theoretical study on the alkaliide compounds  $\text{Li}^+(\text{Calix}[4]\text{pyrrole})\text{M}^-$  ( $\text{M} = \text{Li}, \text{Na}, \text{and K}$ ),<sup>2f</sup> it is revealed that the  $\beta_0$  value of alkaliide compounds depends on the atomic number of the alkali anion and it can be enhanced by choosing the alkali anion with the larger atomic number. Meanwhile, the investigation on the complexant effects on the first hyperpolarizability for alkaliides has not been carried out yet.

We can imagine that the complexant of the alkaliides with more flexibility should have larger NLO responses because such a complexant easily yields excess electron.

The Dye group proposed a simple sodide  $\text{Li}^+(\text{CH}_3\text{NH}_2)_n\text{Na}^-$  and suggested that the electron is delocalized in an expanded lithium orbital and most of the “excess” electron density is located on the sodium atom to yield a  $\text{Na}^-$  anion.<sup>7</sup> They also found that the properties (EPR, NMR, and so on) are as a function of  $n$ , and when  $n = 4$ ,  $\text{Li}^+(\text{CH}_3\text{NH}_2)_4\text{Na}^-$  has a conductivity comparable to that of metal.<sup>7a</sup> This indicates that physical properties are dependent upon the number of coordinations around the cation.

Therefore, we design the simplest relevant sodide compounds  $\text{Li}^+(\text{NH}_3)_n\text{Na}^-$  ( $n = 1-4$ ) to investigate the effect of the coordination number around the cation and the complexant

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flexibility on the enhancement of the first hyperpolarizability in alkali compounds.

### Computational Details

The stable structures of  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) complexes with all real frequencies are obtained at the MP2/aug-cc-pVDZ level. The (hyper)polarizabilities are evaluated by a finite-field approach at the MP2 level. The 6-311++G basis set is employed for the N and H atoms, and the 6-311++G(3df,3pd) basis set, for the alkali atoms Li and Na, which have been already adopted in our previous work<sup>2f</sup> and proven to be sufficient to well reproduce hyperpolarizabilities as the effects of basis sets on NLO have been systematically investigated by Maroulis et al.<sup>8</sup>

The average dipole moment ( $\mu_0$ ) and polarizability ( $\alpha_0$ ) are defined as follows:

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

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

The first hyperpolarizability is noted as

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

where

$$\beta_x = \frac{3}{5}(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}) \quad (4)$$

$$\beta_y = \frac{3}{5}(\beta_{yyy} + \beta_{yxx} + \beta_{yzz}) \quad (5)$$

$$\beta_z = \frac{3}{5}(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}) \quad (6)$$

The calculation of the natural bond orbital (NBO) charge is also performed at the MP2/aug-cc-pVDZ level.

Using the CP procedure,<sup>9</sup> intermolecular interaction energies of  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) complexes were calculated at the CCSD(T)/6-311G\* level. The interaction energy ( $E_{\text{int}}$ ) is calculated as the difference between the energy of the complex and the sum of the energies of the monomers by the following formula:<sup>10</sup>

$$E_{\text{int}} = E_{\text{ABC}}(X_{\text{ABC}}) - E_{\text{A}}(X_{\text{ABC}}) - E_{\text{B}}(X_{\text{ABC}}) - E_{\text{C}}(X_{\text{ABC}}) \quad (7)$$

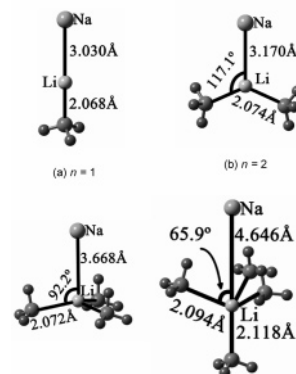
To eliminate the basis set superposition error (BSSE) effect in the interaction energy given by eq 7 above, the same basis set,  $X_{\text{ABC}}$ , is also used for the monomers' ( $\text{A} = \text{Na}$ ,  $\text{B} = \text{Li}$ ,  $\text{C} = (\text{NH}_3)_n$ ) calculation as for the complex's calculation.

The vertical ionization energies (VIE) are obtained at the CCSD(T)/6-311G\* level. The VIE is calculated as

$$\text{VIE} = E[(\text{Li}(\text{NH}_3)_n\text{Na})^+] - E[(\text{Li}(\text{NH}_3)_n\text{Na})] \quad (8)$$

where  $E[(\text{Li}(\text{NH}_3)_n\text{Na})^+]$  is the energy of the cationic complex  $(\text{Li}(\text{NH}_3)_n\text{Na})^+$ , which maintains the same structure as  $\text{Li}(\text{NH}_3)_n\text{Na}$ .

All of the calculations were performed with the GAUSSIAN 03 program package.<sup>11</sup> The dimensional plots of molecular



**Figure 1.** Optimized structures of  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ).

orbitals were generated with the GaussView program (Gaussian, Inc. Pittsburgh, PA).

### Results and Discussions

**A. Equilibrium Geometries.** The optimized structures of  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) complexes and the geometrical parameters are shown in Figure 1.

The structures of  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) complexes display an interesting coordination number (around the cation) dependence. The Li–Na distance increases with the number of complexant  $\text{NH}_3$  molecules. From Figure 1, the Li–Na distances are found to be 3.030 ( $n = 1$ ) < 3.170 ( $n = 2$ ) < 3.668 ( $n = 3$ ) < 4.646 Å ( $n = 4$ ). However, the changes of Li–N distance (2.068–2.118 Å) are very small and did not exceed 0.05 Å.

With the increasing of the  $\text{NH}_3$  coordination number, the Li atom runs toward the center of the  $\text{NH}_3$  molecules. Gradually, the Li atom is enwrapped by  $\text{NH}_3$  molecules. Ultimately, for  $n = 4$ , the Li atom locates at the center of the four  $\text{NH}_3$  molecules to form a “cage” with almost the  $T_d$  symmetry (see Figure 1d). This shows that the  $(\text{NH}_3)_n$  complexant has great flexibility.

Comparing with the other related systems,<sup>12</sup> for  $n = 1$  and 2, the Li–Na distances (3.030 and 3.170 Å) in  $\text{Li}(\text{NH}_3)_n\text{Na}$  are shorter by about 0.4 Å than the corresponding Na–Na distances (3.431 and 3.546 Å) in  $[\text{Na}_2(\text{NH}_3)_n]^-$  ( $n = 1, 2$ ).<sup>12a</sup> The Li–N distances in  $\text{Li}(\text{NH}_3)_n\text{Na}$  are shorter by about 0.36 Å than the corresponding Na–N distances in  $[\text{Na}_2(\text{NH}_3)_n]^-$  ( $n = 1, 2$ ).<sup>12a</sup> and  $[\text{Na}(\text{NH}_3)_n]^-$  ( $n = 1, 2$ ).<sup>12b</sup> (see Table 1). The reason for this is that the atomic radius of Na (1.80 Å) is 0.35 Å larger than that of Li (1.45 Å).<sup>5</sup> For  $n = 4$ , the Li–N distance in  $\text{Li}(\text{NH}_3)_n\text{Na}$  is about 2.1 Å and slightly longer than that (2.05 Å) in  $\text{Li}(\text{NH}_3)_4$ .<sup>13</sup>

**B. NBO Charges of Li and Na.** Table 2 lists the NBO charges of the Li, Na, N, and H atoms. We find an interesting relationship between the coordination number and the NBO charges. The absolute NBO charge of Li or Na increases with the increasing of number of  $\text{NH}_3$  ( $n$  from 1 to 4). From Table 2 and also Figure 2, the charges of Li are the following: 0.116 ( $n = 1$ ) < 0.300 ( $n = 2$ ) < 0.553 ( $n = 3$ ) < 0.762 ( $n = 4$ ). The charges of Na are the following:  $-0.132$  ( $n = 1$ ) <  $-0.322$  ( $n = 2$ ) <  $-0.525$  ( $n = 3$ ) <  $-0.562$  ( $n = 4$ ). Because the charges of Na are negative and Na acts as an anion, the four structures of  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) complexes show characteristics of sodide.

The Na atom has smaller electron affinity (0.54 eV),<sup>5</sup> and thus, the excess electron in the Na anion ought to be loosely bound in space. From the highest occupied molecular orbitals (HOMOs) in Figure 3, the excess electron from the Li atom is pushed away by lone pairs of  $\text{NH}_3$  molecules toward the Na atom in  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) complexes. Furthermore, the

**TABLE 1: Comparing  $\text{Li}^+(\text{NH}_3)_n\text{Na}^-$  ( $n = 1, 2$ ) with Other Related Systems<sup>a</sup>**

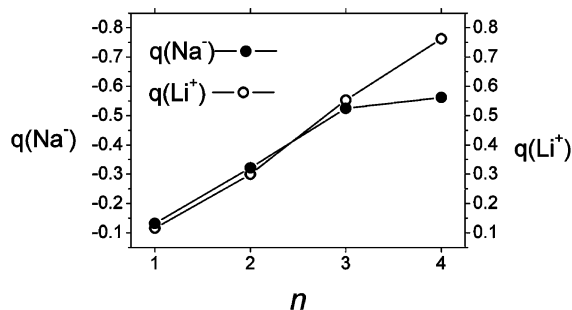
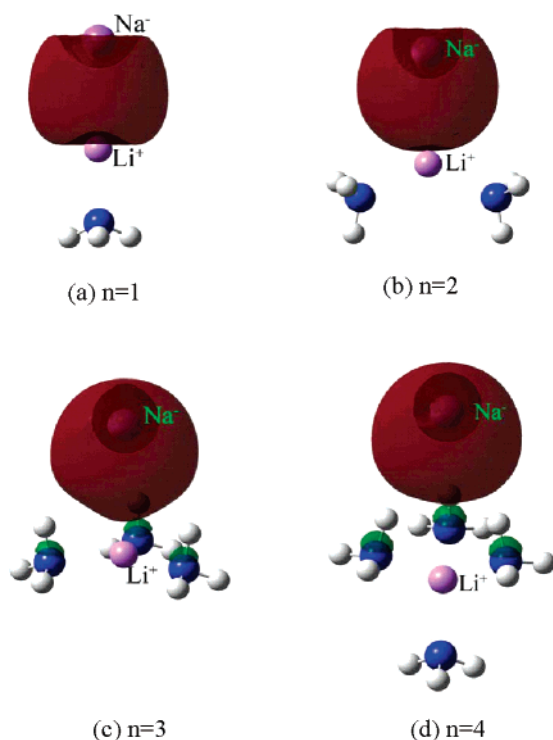
structure	$\text{Li}^+(\text{NH}_3)\text{Na}^-$	$\text{Li}^+(\text{NH}_3)_2\text{Na}^-$	$[\text{Na}_2(\text{NH}_3)]^-$	$[\text{Na}_2(\text{NH}_3)_2]^-$	$[\text{Na}(\text{NH}_3)]^-$	$[\text{Na}(\text{NH}_3)_2]^-$
$R(\text{M}-\text{Na})^b$	3.030	3.170	3.431	3.546		
$R(\text{M}-\text{N})$	2.068	2.074	2.424	2.460	2.422	2.410
ref	this work	this work	12a	12a	12b	12b

<sup>a</sup> Distances are in angstroms. <sup>b</sup> M = Li in  $\text{Li}^+(\text{NH}_3)_n\text{Na}^-$  ( $n = 1, 2$ ) and M = Na in the other related systems.

**TABLE 2: NBO Charges in  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) at the MP2/aug-cc-pVDZ Level**

$n$	1	2	3	4
Na	-0.132	-0.322	-0.525	-0.562
Li	0.116	0.300	0.553	0.762
N	-1.188	-1.190	-1.205	-1.232
				-1.139
H	0.401	0.403	0.393	0.388
	0.402	0.404	0.410	0.379
	0.401	0.393	0.393	0.388
				0.391

greater the coordination number of the  $\text{NH}_3$  molecules, the greater the repulsion effect of complexant  $(\text{NH}_3)_n$  to the 2s electron of the Li atom. Consequently, the NBO charge of the Li or Na atom increases with the coordination number. As a

**Figure 2.** NBO charges of  $\text{Na}^-$  anion and  $\text{Li}^+$  cation against the number of coordination.**Figure 3.** 0.035 isosurface of  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ). Upon increasing  $n$ , the excess electron cloud from the Li atom gradually approaches and enwraps the Na atom to yield a  $\text{Na}^-$  anion.**TABLE 3:  $E_{\text{int}}$  and VIE (in eV) for  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) at the MP2 Level**

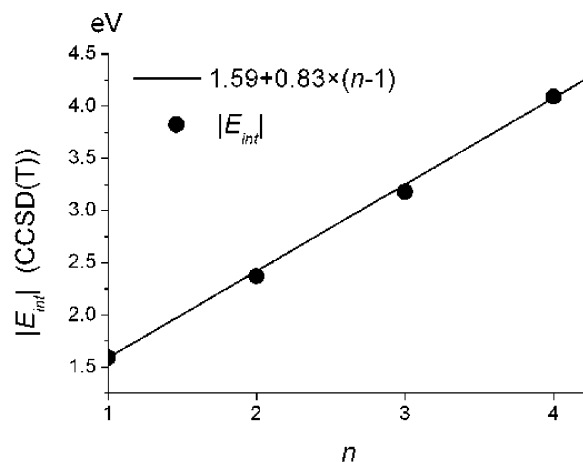
$n$	$E_{\text{int}}$				VIE			
	1	2	3	4	1	2	3	4
HF	-0.82	-1.55	-2.29	-3.21	3.55	3.16	2.92	2.66
MP2	-1.32	-2.12	-2.97	-3.91	4.05	3.70	3.51	3.27
CCSD(T)	-1.59	-2.37	-3.18	-4.09	4.31	3.95	3.75	3.49
CCSD(T)-HF	-0.76	-0.82	-0.88	-0.88	0.77	0.78	0.82	0.83
(CCSD(T)-HF)/CCSD(T) (%)	48.2	34.7	27.7	21.4	17.8	20.0	21.9	23.8

result, using the coordination number dependence of the NBO charge, the charge of the  $\text{Na}^-$  anion with the excess electron can be controlled by adjusting the coordination number. This is helpful for designing and studying materials with properties depending on the charge of the anion for alkali systems.

**C. Interaction Energies ( $E_{\text{int}}$ ) and Vertical Ionization Energies (VIEs).** The interaction energies for  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) complexes are presented in Table 3 using eq 7 at the HF, MP2, and CCSD(T)/6-311G\* levels. From Table 3, the order of the interaction energies at the CCSD(T)/6-311G\* level of  $\text{Li}(\text{NH}_3)_n\text{Na}$  is  $-1.59$  ( $n = 1$ )  $< -2.37$  ( $n = 2$ )  $< -3.18$  ( $n = 3$ )  $< -4.09$  eV ( $n = 4$ ). It is clear that the interaction energy depends on the coordination number. As one  $\text{NH}_3$  molecule increases, on average, the interaction energy about 0.83 eV, an approximate formula can be obtained as follows:  $|E_{\text{int}}| = 1.59 + 0.83(n - 1)$  eV for the  $\text{Li}(\text{NH}_3)_n\text{Na}$  complexes (see Figure 4).

The (CCSD(T)-HF) part represents the electron correlation contribution to the interaction energy. From Table 3, the change of the contribution ( $-0.76$  to  $-0.88$  eV) is not so large with the increasing  $n$ , while the change of relative electron correlation contribution of the interaction energy is large (48.2–21.4%).

The VIE values for the  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) complexes are also presented in Table 3. The VIE values are smaller than the IP (5.138 eV)<sup>5</sup> of the Na atom. Interestingly, the VIE decreases with the increase of the coordination number. The VIE order is  $4.31$  ( $n = 1$ )  $> 3.95$  ( $n = 2$ )  $> 3.75$  ( $n = 3$ )  $> 3.49$  eV ( $n = 4$ ). Also, from Table 3, one can see that the

**Figure 4.** Interaction energy function (in eV):  $|E_{\text{int}}| = 1.59 + 0.83(n - 1)$ .

**TABLE 4: Dipole Moment ( $\mu_0$ ), Polarizability ( $\alpha_0$ ), First Hyperpolarizability ( $\beta_0$ ), and Transition Energy ( $\Delta E$ ) at the MP2 Level for  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ )**

	$(\text{NH}_3)\text{Li}^+\text{Na}^-$	$(\text{NH}_3)_2\text{Li}^+\text{Na}^-$	$(\text{NH}_3)_3\text{Li}^+\text{Na}^-$	$(\text{NH}_3)_4\text{Li}^+\text{Na}^-$
$\mu_0$ (au)	2.127	2.881	3.389	4.916
$\alpha_0$ (au)	302.2	373.3	453.3	524.8
$\beta_0$ (au)	13669	26840	39764	77921
$\Delta E$ (eV)	2.175	1.896	1.662	1.534

electron correlation contribution to the VIE is large (17.8–23.8%) and is important for the calculation of the VIE.

**D. First Hyperpolarizabilities.** The electric properties of four structures of  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) are given in Table 4. It is shown that  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) have considerably large (hyper)polarizability. Especially, a coordination number dependence of the  $\beta_0$  value is found. The  $\beta_0$  value increases with the coordination number (number of  $\text{NH}_3$  molecules). The order of  $\beta_0$  values is 13 669 ( $n = 1$ ) < 26 840 ( $n = 2$ ) < 39 764 ( $n = 3$ ) < 77 921 au ( $n = 4$ ) (see Table 4). This shows that increasing the coordination number around the  $\text{Li}^+$  cation can greatly enhance the first hyperpolarizabilities of  $\text{Li}(\text{NH}_3)_n\text{Na}$  complexes.

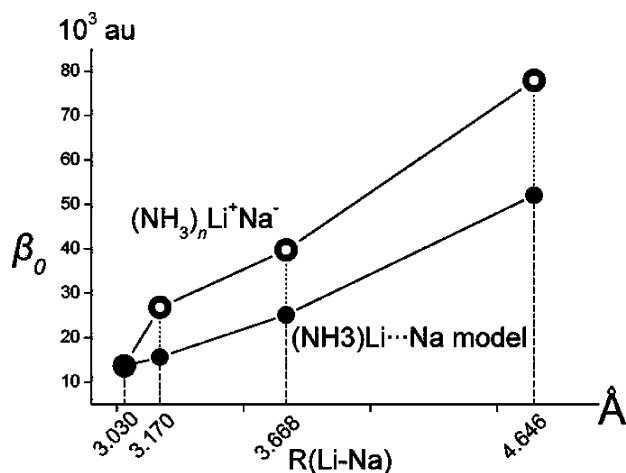
To further understand the coordination number dependence of the  $\beta_0$  value, we consider the two-level model:<sup>14</sup>

$$\beta_0 = (3/2)\Delta\mu f_0/\Delta E^3 \quad (9)$$

where  $\Delta E$ ,  $f_0$ , and  $\Delta\mu$  are respectively the transition energy, oscillator strength, and the difference of dipole moment between the ground state and the crucial excited state. In the two-level expression, the third power of the transition energy is inversely proportional to the  $\beta_0$  value. So, the transition energy is the decisive factor in the calculation of the  $\beta_0$  value.

The transition energies ( $\Delta E$ ) of  $\text{Li}(\text{NH}_3)_n\text{Na}$  ( $n = 1-4$ ) are estimated by the CIS method with the 6-311+G basis set and listed in Table 4. Table 4 shows that the order of the transition energy of  $\text{Li}(\text{NH}_3)_n\text{Na}$  is 2.175 ( $n = 1$ ) > 1.896 ( $n = 2$ ) > 1.662 ( $n = 3$ ) > 1.534 eV ( $n = 4$ ). Because the transition energy decreases with the increasing of the coordination number, the  $\beta_0$  value increases with the increasing of number of  $\text{NH}_3$  molecules.

From Figure 5, one can see that the ratio of  $\beta_0$  for the  $\text{Li}(\text{NH}_3)_n\text{Na}$  complexes is approximately 1:2:3:6 for  $n = 1, 2, 3$ , and 4, respectively. Obviously, a great enhancement of  $\beta_0$  occurs at  $n = 4$ . Figure 1 shows that the distance  $R(\text{Li}-\text{Na})$  for  $n = 4$  is much larger than that for  $n = 3$ . This indicates that the great enhancement of  $\beta_0$  may come from the difference in  $R(\text{Li}-$

**Figure 5.**  $\beta_0$  against  $n$  for  $(\text{NH}_3)_n\text{Li}^+\text{Na}^-$  systems (open circles with solid line) and  $\beta_0$  at different Li–Na distances for  $(\text{NH}_3)\text{Li}\cdots\text{Na}$  (circles with solid line).**TABLE 5: First Hyperpolarizability (in au) and NBO Charges of  $(\text{NH}_3)\text{Li}\cdots\text{Na}$  Model Systems at Different Li–Na Distances (in angstroms)**

$R(\text{Li}-\text{Na})$	3.030	3.170	3.668	4.646
$\beta_0$	13669	15657	25173	52044
$q(\text{Li})$	0.116	0.119	0.128	0.134
$q(\text{Na})$	−0.132	−0.135	−0.144	−0.149

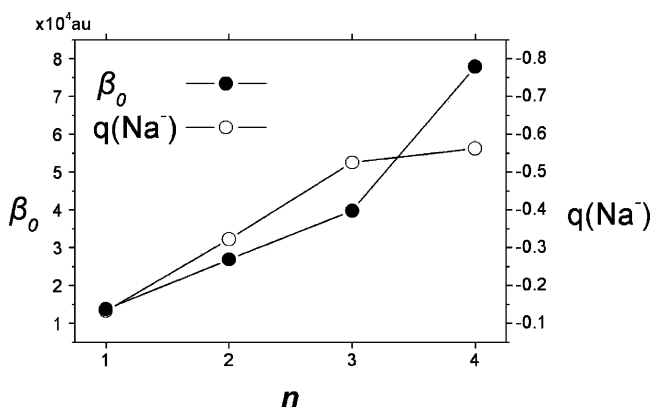
$\text{Na}$ ). Thus, we design a simple model  $(\text{NH}_3)\text{Li}\cdots\text{Na}$ , where the  $R(\text{Li}-\text{Na})$  values are taken from the equilibrium geometries of  $(\text{NH}_3)_n\text{Li}^+\text{Na}^-$  ( $n = 1, 2, 3$ , and 4). The Li–Na distances of 3.030, 3.170, 3.668, and 4.646 Å are used while the  $(\text{NH}_3)\text{Li}$  part is kept the same as that in the equilibrium geometry of  $(\text{NH}_3)\text{Li}^+\text{Na}^-$ . Obviously, the structure of  $(\text{NH}_3)\text{Li}\cdots\text{Na}$  at  $R(\text{Li}-\text{Na}) = 3.030$  Å is the structure of  $(\text{NH}_3)\text{Li}^+\text{Na}^-$ .

The  $\beta_0$  values and the NBO charges of the model system  $(\text{NH}_3)\text{Li}\cdots\text{Na}$  at the different  $R(\text{Li}-\text{Na})$  values are given in Table 5. The ratio of  $\beta_0$  for the  $(\text{NH}_3)\text{Li}\cdots\text{Na}$  models is approximately 1:1.2:4 for  $R(\text{Li}-\text{Na}) = 3.030, 3.170, 3.668$ , and 4.646 Å, respectively. A great enhancement in  $\beta_0$  is found for the very long Li–Na distance at 4.646 Å (from  $n = 4$ ). This shows that the main reason for the enhancement in  $\beta_0$  for  $n = 4$  is due to the very long Li–Na distance.

Figure 6 is a plot of the  $\beta_0$  value and the NBO charge of Na against the coordination number. It can be seen that the  $\beta_0$  value is dependent on the charge of  $\text{Na}^-$  and the number of coordination. Thus, for systems containing the sodium anion, an effective method for enhancing the first hyperpolarizability is to increase the coordination number to form more charged  $\text{Na}^-$  anions.

Comparing to  $\text{Li@Calix[4]pyrrole-Na}$ ,<sup>2f</sup> the  $\beta_0$  value (77 921 au) of small inorganic alkali  $\text{Li}(\text{NH}_3)_4\text{Na}$  with  $T_d$  coordination is 5.3 times larger than that of big organic alkali  $\text{Li@Calix[4]pyrrole-Na}$  with  $C_{4v}$  coordination (14 772 au). Comparing the two complexants, Calix[4]pyrrole and  $(\text{NH}_3)_4$ , they both contain four coordination N atoms but the  $(\text{NH}_3)_4$  complexant has more flexibility than Calix[4]pyrrole. The  $(\text{NH}_3)_4$  complexant with flexibility can form the  $T_d$  cage with a large coordination effect, whereas the Calix[4]pyrrole complexant cannot form this kind of cage. Therefore, the small inorganic  $(\text{NH}_3)_4$  complexant can lead to the larger first hyperpolarizability than the big organic Calix[4]pyrrole complexant. Hence, the complexant flexibility is also a principle factor for the first hyperpolarizability.

We also carried out MP2 finite-field calculations to obtain the second-order hyperpolarizability ( $\gamma$ ) by using the GAMESS program.<sup>15</sup> The diagonal elements  $\gamma_{xxxx}$  of  $\text{Li}(\text{NH}_3)_n\text{Na}$  are found to be 1.0, 1.7, 2.2, and 6.6 (in  $10^7$  au) for  $n = 1, 2, 3$ , and 4, respectively. The  $\gamma_{xxxx}$  ratio among different  $n$  values is

**Figure 6.** Changes of  $\beta_0$  and  $q(\text{Na}^-)$  against  $n$ .



consistent with that of  $\beta_0$ , where the ratio of  $\beta_0$  is given as 1:2:3:6. The other two diagonal elements are determined to be 1.7, 4.3, 8.3, and 12 (in  $10^6$  au) for  $n = 1, 2, 3$ , and 4, respectively. This gives similar ratios as those of  $\beta_0$  and  $\gamma_{xxxx}$ . This clearly shows that a great enhancement is found in  $\text{Li}(\text{NH}_3)_n\text{Na}$  when  $n = 4$  for both  $\beta$  and  $\gamma$ .

This work suggests that to enhance first hyperpolarizability for alkalides, two important factors should be considered, i.e., coordination number around the cation and flexibility of the complexant.

**Acknowledgment.** This work was supported by the National Natural Science Foundation of China (No. 20573043 and No. 20503010) and also by Research and Development Applying Advanced Computational Science and Technology of the Japan Science and Technology Agency (ACT-JST).

**Supporting Information Available:** Complete ref 11. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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