Electronic Supplementary Information for

Theoretical study on superalkali(Li_3) in ammonia: novel alkalides with considerably large first hyperpolarizabilities

Wei-Ming Sun, Di Wu, Ying Li*, Zhi-Ru Li

Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, Changchun 130023, People's Republic of China. E-mail: liyingedu@jlu.edu.cn

1. More computational details

As for the calculation of the static electric properties, the traditional B3LYP method has been recognized to overestimate the (hyper)polarizabilities for some large systems.[S1] In this regard, the MP2 method is more reliable but more time consuming. In recent years, some new hybrid DFT methods have been shown as suitable methods to calculate (hyper)polarizabilities for many different systems. For example, the Coulomb-attenuated hybrid exchange-correlation functional (CAM-B3LYP),[S2-S6] has been developed for charge transfer and long range interaction systems and the M06-2X functional recommended by Truhlar and co-workers[S7] has been employed to evaluate the static (hyper)polarizabilities for the long-range interaction[S8] and excess electron systems[S9]. Besides, Nakano and his co-workers pointed out that for a medium-sized system, the compromise BHandHLYP method can reproduce the (hyper)polarizabilities from the more sophisticated CCSD(T) method.[S10]

In order to choose an appropriate method to calculate the first hyperpolarizabilities (β_0) of the investigated complexes, we computed the β_0 value of a small analog Li(NH$_3$)Na by using the above mentioned methods with the 6-311++G(3df, 3pd) basis set. The results are given in Table S1. Comparing with the MP2 result, the M06-2X method obviously undervalues the hyperpolarizability of this system, while the B3LYP method yields an overestimated value and the BHandHLYP lessens this overestimate. As the β_0 value at the CAM-B3LYP level is quite close to that at the MP2 level, the CAM-B3LYP method in conjunction with 6-311++G(3df, 3pd) basis set was chosen to calculate the first hyperpolarizabilities of the investigated systems. The static mean polarizability (α_0) and mean first hyperpolarizability (β_0) are defined as follows:

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

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

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

The total static dipole moment (μ_0) is noted as:

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \tag{3}$$

2. Figures and tables

Fig. S1 The NBO charges on Li atoms of Li_3 and $Li_3(NH_3)_n$ (n = 1–4) at the B3LYP/6-311++G(3df, 3pd) level.

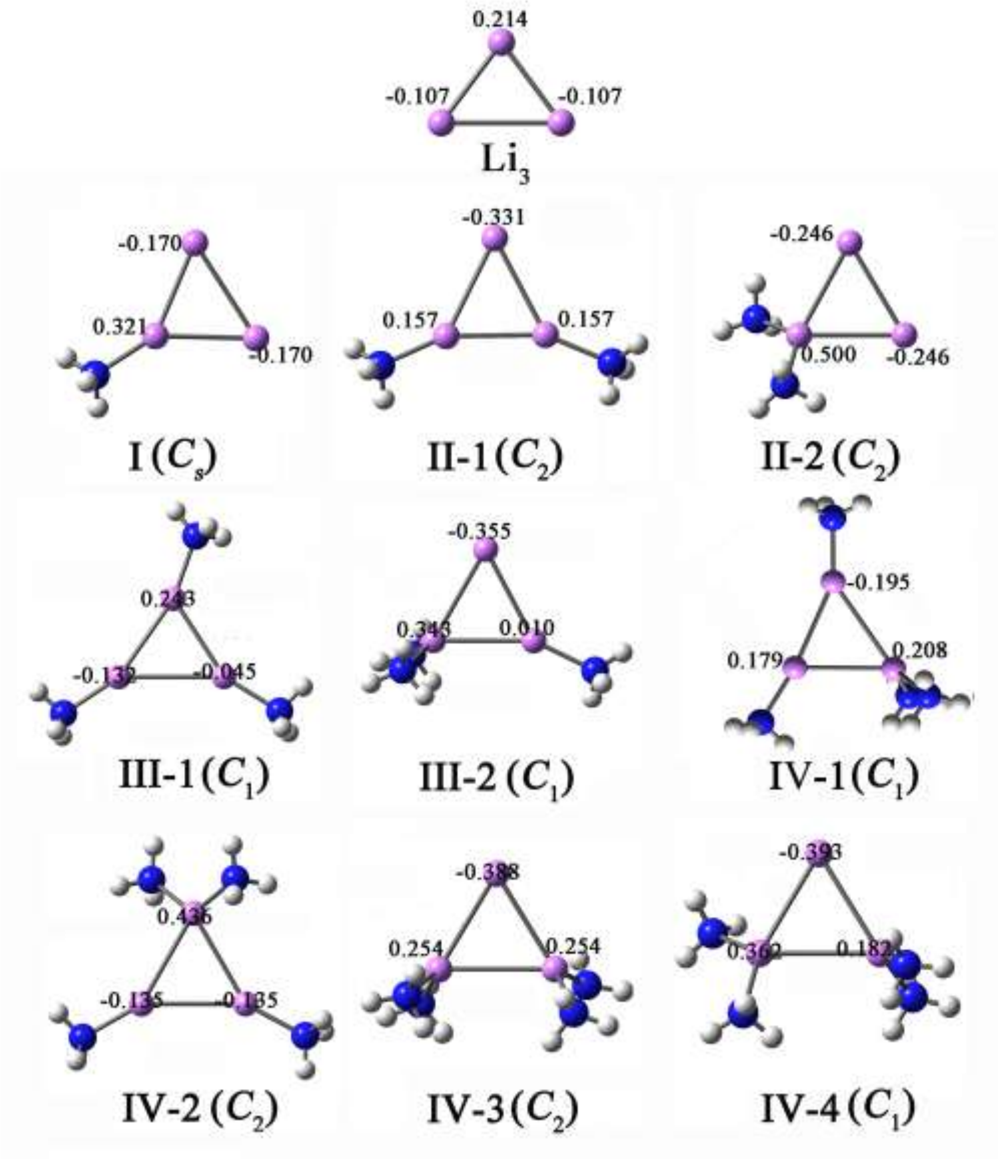

Fig. S2 The highest occupied molecular orbitals (HOMOs) of Li_3, $Li_3(NH_3)_n$, and $Li(NH_3)_n$ (n = 1–4).

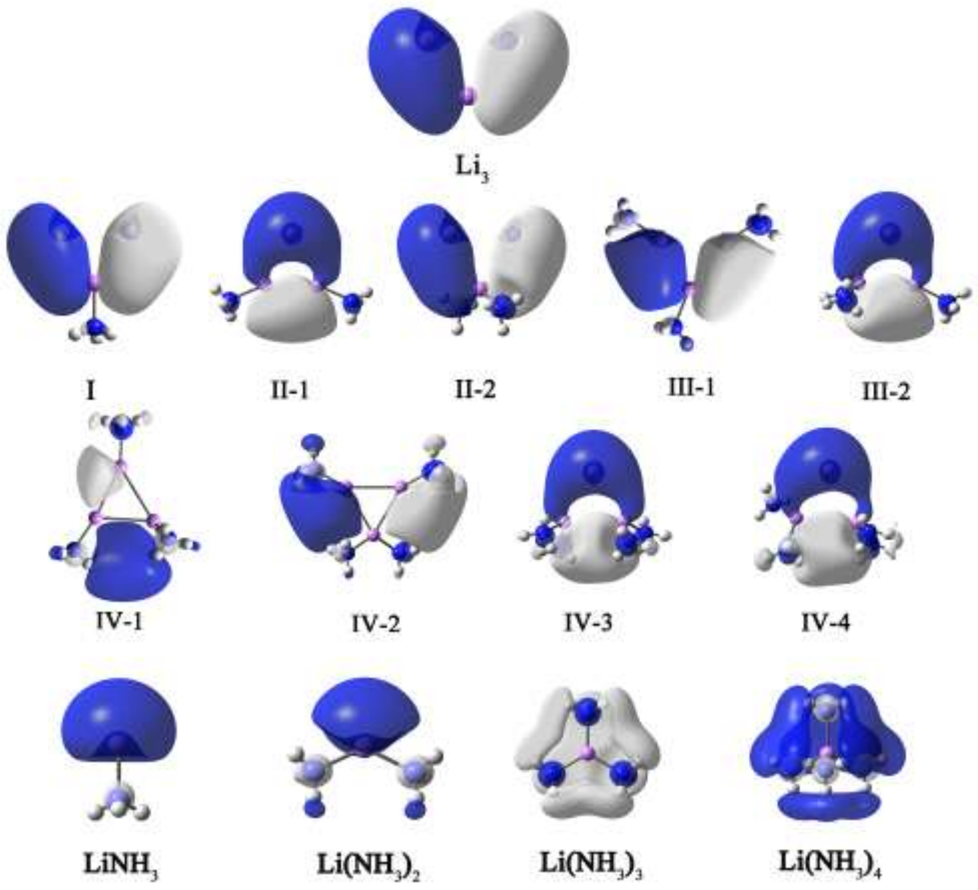

Fig. S3 The NBO charges on Li and Na atoms of $Li_3(NH_3)_nNa$ (n = 1–4) at the B3LYP/6-311++G(3df, 3pd) level.

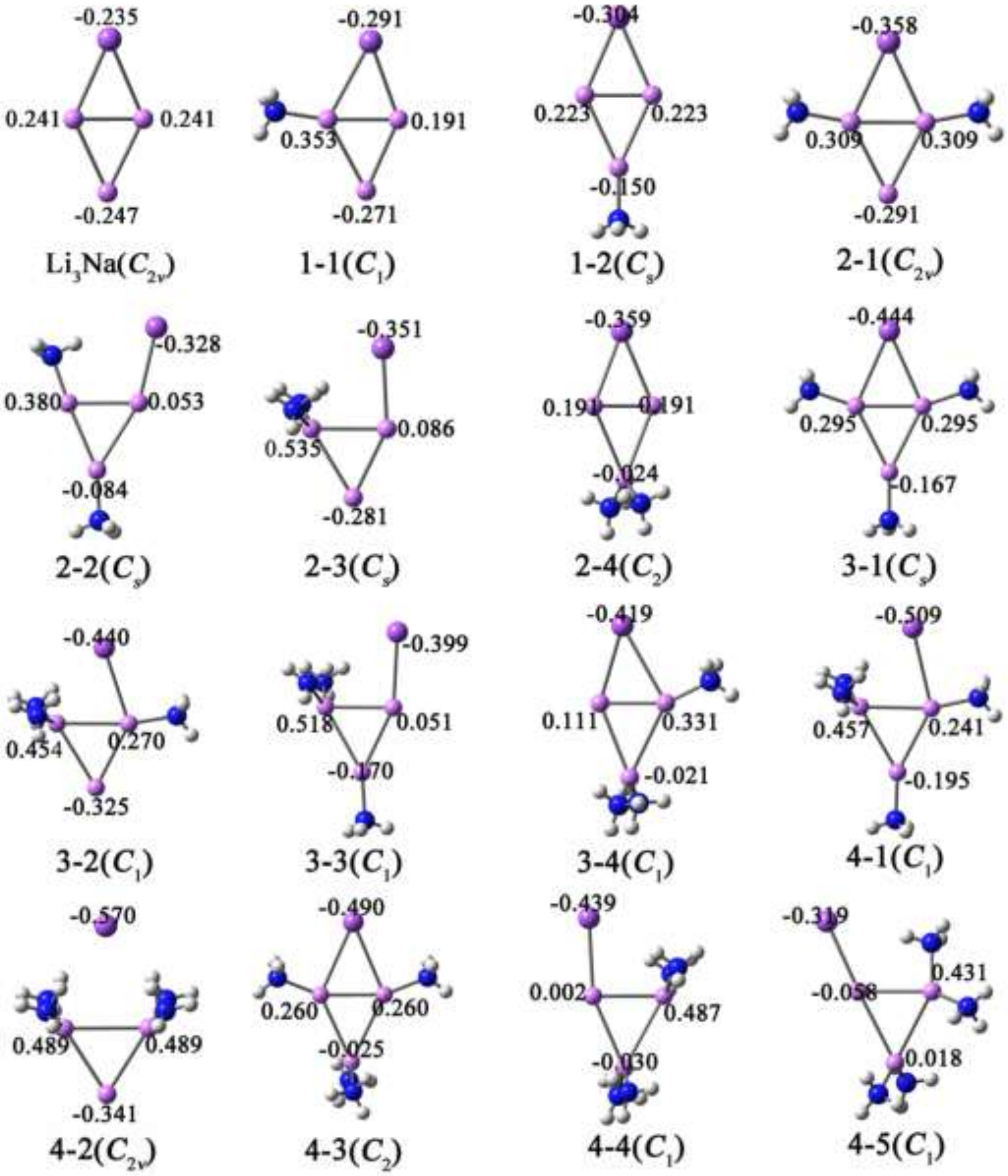

Fig. S4 The highest occupied molecular orbitals (HOMOs) of the lowest-energy structures of $Li_3(NH_3)_nNa$ (n = 1–4) and Li_3Na.

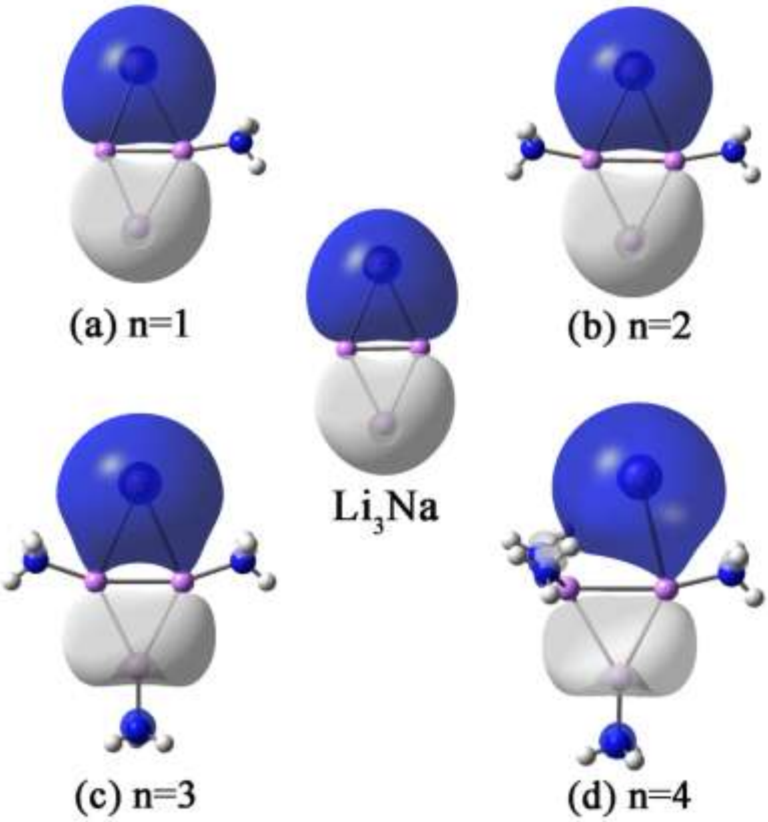

Table S1 Calculated β_0 values (in au) of Li(NH$_3$)Na by different methods with 6-311++G(3df, 3pd) basis set.

Methods	B3LYP	MP2	CAM-B3LYP	M06-2X	BHandHLYP
β_0	17641	12040	11761	6858	13173

Reference

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