



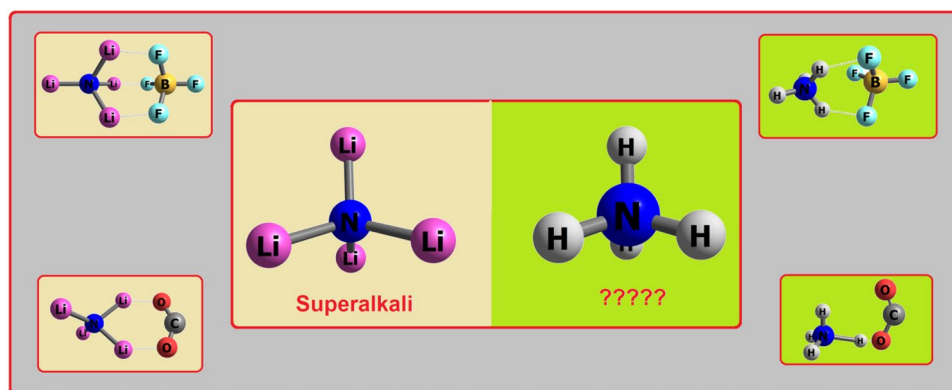
Superalkali behavior of ammonium (NH_4^+) and hydronium (OH_3^+) cations: a computational analysis

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Abstract

Superalkalis are unusual species having ionization energy (IE) lower than that of alkali atom. The examples of typical superalkali cations include FLi_2^+ , OLi_3^+ , NLi_4^+ , etc. Ammonium (NH_4^+) and hydronium (OH_3^+) cations form a variety of inorganic as well as organic compounds. Structurally, NH_4 and OH_3 appear a close analog of NLi_4 and OLi_3 , respectively. However, there is no study on the superalkali nature of OH_3 and NH_4 to the best of our knowledge and belief. This work highlights whether NH_4^+ and OH_3^+ are superalkali cations, like NLi_4^+ and OLi_3^+ for the first time. Our ab initio calculations suggest that NH_4 possesses lower IE than Li atom. However, the IE of OH_3 is found to be comparable to that of Li. Furthermore, NH_4 interacts with a superhalogen forming a supersalt and reduces CO_2 into CO_2^- . These two characteristics of NH_4 resemble to those of NLi_4 . These findings suffice to establish NH_4^+ as a superalkali cation. This may offer further opportunities to play with well-known NH_4^+ on a different ground.

Graphic abstract

**Keywords** Ammonium · Superalkali · Ammonium supersalt · CO_2 -reduction · Theoretical calculations

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1 Introduction

Ammonium ion (NH_4^+) is one of the most popular radicals, which is equally important in both inorganic as well as organic chemistry. It is also an important source of nitrogen for many plant species, particularly those growing on hypoxic soils. NH_4^+ forms a variety of salts, which are soluble in water. In some of these salts, ammonium is the reducing agent. Likewise, hydronium (OH_3^+) is an aqueous cation formed by protonation of water. It is an abundant molecular ion in the interstellar medium [1–3]. OH_3^+ also forms salts with many strong acids, which are typically known as acid monohydrates. OH_3 and NH_4 appear non-metallic analogues of typical superalkalis OLi_3 and NLi_4 [4]. These superalkalis belong to the general formula XM_{k+1} , where k is valence of electronegative atom X and M is alkali metal atom. The IE of these species has been theoretically analyzed by Gutsev and Boldyrev [4] and found to be lower than those of alkali atoms, hence the name ‘superalkalis’. The superalkali nature of FLi_2 , OLi_3 , etc. was experimentally confirmed by mass spectrometry and photoelectron spectroscopy [5, 6].

Superalkalis form some unusual compounds, known as supersalts with interesting properties [7, 8]. Superalkalis are also employed in the design of superbases [9, 10] and alkalides [11, 12]. It has been reported that the superalkalis are capable in the reduction of CO_2 [13–15] and NO_x [16]. The unusual structures and interesting applications lead to the exploration of a variety of superalkalis [17–23]. Our recent study [24] demonstrated that BH_6^+ possesses superalkali behaviour such that its vertical electron affinity is comparable to that of BLi_6^+ superalkali cation. In the continuation, herein we compare the structure and properties of OH_3 and NH_4 with OLi_3 and NLi_4 , respectively in their neutral as well as cationic forms. We aim to investigate that whether OH_3^+ and NH_4^+ can be regarded as superalkali cations. Nevertheless, this work also attempts to explain metallic properties of ammonium under certain conditions.

2 Materials and methodology

All calculations in this work are performed using ωB97xD density functional [25] with correlation consistent aug-cc-pVTZ basis set in Gaussian 09 program [26]. This functional incorporates dispersion corrected term, which is very appropriate for the system with long-range interactions. For NH_4 and NLi_4 (neutral and cations), additional calculations are performed at MP2/aug-cc-pVTZ and (single-point) CCSD(T)// ωB97xD /aug-cc-pVTZ levels.

The geometry optimization is carried out without any symmetry constraints and followed by vibrational frequency calculations. The vertical electron affinity (EA_v) of cations is obtained by the difference of total energies of optimized cations and corresponding neutral at cationic structure whereas adiabatic ionization energy (IE_a) of neutral structures are obtained by the difference of total energies of neutral and cations at their optimized structures. For BF_4 and CO_2 complexes of NLi_4 and NH_4 , we have considered only the lowest energy structures. The atomic charges are computed by natural bonding orbital (NBO) based population analysis as implemented in Gaussian 09.

3 Results and discussion

We first discuss the structure of OH_3^+ , NH_4^+ , OLi_3^+ and NLi_4^+ as displayed in Fig. 1. OLi_3^+ is trigonal planar with D_{3h} symmetry, unlike OH_3^+ , which is not planar with C_{3v} symmetry. On the contrary, NH_4^+ and NLi_4^+ structures assume tetrahedral (T_d) point group of symmetry. The structural parameters of OH_3^+ , NH_4^+ , OLi_3^+ and NLi_4^+ along with those of their neutral forms obtained at ωB97xD /aug-cc-pVTZ and MP2/aug-cc-pVTZ levels are listed in Table 1. One can note that our ωB97xD /aug-cc-pVTZ computed bond-lengths of OH_3^+ and NH_4^+ are close to those obtained by high-level ab initio MP2/aug-cc-pVQZ method [27]. Therefore, we have adopted ωB97xD /aug-cc-pVTZ level for further calculations. The bond angle is calculated 109.5° in NH_4^+ and NLi_4^+ at both ωB97xD and MP2 methods. However, the bond angle of OH_3^+ , smaller than that of OLi_3^+ , is only slightly different at different methods. The bond lengths of OH_3^+ and NH_4^+ are smaller than those of OH_3 and NH_4 , respectively. On the contrary, the bond lengths of OLi_3^+ and NLi_4^+ are larger than those of their

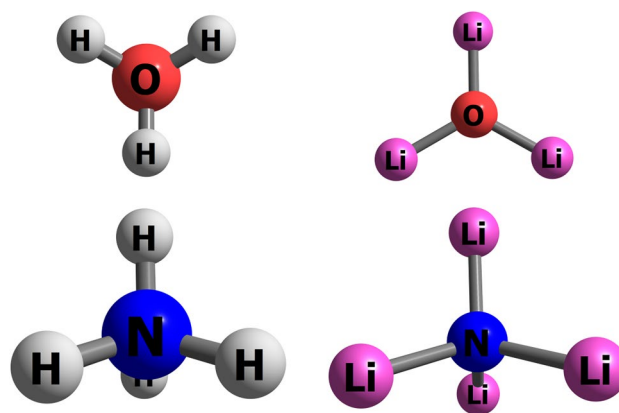


Fig. 1 The equilibrium structures of OH_3^+ , OLi_3^+ , NH_4^+ and NLi_4^+ . The structural parameters are listed in Table 1

Table 1 Calculated structural parameters, adiabatic ionization energy (IE_a) and vertical electron affinity (EA_v) of systems considered using different computational schemes

System	Method	Bond length (Å)		Bond angle (°)	EA _v or IE _a (eV)	
		This work	Previous work		This work	Previous work
OH ₃ ⁺	ωB97xD/aug-cc-pVTZ	0.975	0.977 ^a	112.7	5.17	–
	MP2/aug-cc-pVTZ	0.979		111.5	5.24	
	CCSD(T)//ωB97xD/aug-cc-pVTZ				5.25	
OH ₃	ωB97xD/aug-cc-pVTZ	1.018	1.018 ^a	108.0	5.28	5.27 ^b
	MP2/aug-cc-pVTZ	1.022		106.2	5.34	
	CCSD(T)//ωB97xD/aug-cc-pVTZ				5.38	
OLi ₃ ⁺	ωB97xD/aug-cc-pVTZ	1.690	–	120.0	3.40	–
	MP2/aug-cc-pVTZ	1.716		120.0	3.48	
	CCSD(T)//ωB97xD/aug-cc-pVTZ				3.57	
OLi ₃	ωB97xD/aug-cc-pVTZ	1.678	–	119.9	3.48	–
	MP2/aug-cc-pVTZ	1.702		119.9	3.49	
	CCSD(T)//ωB97xD/aug-cc-pVTZ				3.54	
NH ₄ ⁺	ωB97xD/aug-cc-pVTZ	1.021	1.020 ^a	109.5	4.36	–
	MP2/aug-cc-pVTZ	1.022		109.5	4.45	
	CCSD(T)//ωB97xD/aug-cc-pVTZ				4.50	
NH ₄	ωB97xD/aug-cc-pVTZ	1.040	1.037 ^a	109.5	4.38	4.62 ^c
	MP2/aug-cc-pVTZ	1.039		109.5	4.47	
	CCSD(T)//ωB97xD/aug-cc-pVTZ				4.53	
NLi ₄ ⁺	ωB97xD/aug-cc-pVTZ	1.775	–	109.5	3.36	–
	MP2/aug-cc-pVTZ	1.821		109.5	3.09	
	CCSD(T)//ωB97xD/aug-cc-pVTZ				3.53	
NLi ₄	ωB97xD/aug-cc-pVTZ	1.764	–	109.5	3.37	–
	MP2/aug-cc-pVTZ	1.753		109.5	3.21	
	CCSD(T)//ωB97xD/aug-cc-pVTZ				4.06	

^aCalculated value at MP2/aug-cc-pVQZ level from Ref. [27]

^bReported value in Ref. [28]

^cExperimental value from Ref. [29]

neutral counterparts. In Fig. 2, we have plotted the highest occupied molecular orbital (HOMO) surfaces of OH₃⁺, OLi₃⁺, NH₄⁺ and NLi₄⁺. One can note that the HOMOs of OLi₃⁺ and NLi₄⁺ are mainly contributed by central O and N atoms, excluding Li atoms. This is in contrast to OH₃⁺ and NH₄⁺ in which the HOMOs are composed of O, N atoms and significantly contributed by H atoms.

We have calculated adiabatic IE (IE_a) of NH₄ and NLi₄ as well as vertical EA (EA_v) of their cations using single-point energies at CCSD(T) method for ωB97xD/aug-cc-pVTZ optimized structures. Note that our ωB97xD/aug-cc-pVTZ computed IE_a of OH₃ is very close to previous report of Talbi and Saxon [28]. Furthermore, CCSD(T)//ωB97xD/aug-cc-pVTZ computed IE_a of NH₄ is in good agreement with the experimental IE of NH₄ [29] as compared to those calculated at ωB97xD/aug-cc-pVTZ and MP2/aug-cc-pVTZ levels (see, Table 1). Evidently, the IE_a of OLi₃ and NLi₄ as well as EA_v of OLi₃⁺ and NLi₄⁺, both are lower than the IE of alkali atom, for instance Na with 5.14 eV [30]. On the

contrary, IE_a of OH₃ and EA_v of OH₃⁺, both are larger than the IE of Na. More interestingly, the EA_v of NH₄⁺ and IE_a of NH₄, although larger than the corresponding values of NLi₄⁺ and NLi₄, are also smaller than the IE of Na atom. Therefore, NH₄⁺ should also be regarded as a superalkali cation. In order to verify whether NH₄⁺ is indeed a superalkali cation, we have considered two more characteristics. First, NH₄ should form a supersalt by interaction with superhalogen, like NLi₄ and other superalkalis. Next, NH₄ should be capable to reduce CO₂ into CO₂[−], like NLi₄ and other superalkalis.

It is reported [8] that the superalkalis such as FLi₂, OLi₃, NLi₄ interact with BF₄ superhalogen to form the supersalts. These supersalts are different from traditional salts such as alkali halides due to their preferred dissociation into ionic fragments. First, we study the interaction of NLi₄ superalkali with BF₄ superhalogen, which forms the NLi₄-BF₄ complex as shown in Fig. 3a. The dissociation energies of NLi₄-BF₄ complex against neutral (NLi₄ + BF₄) fragments

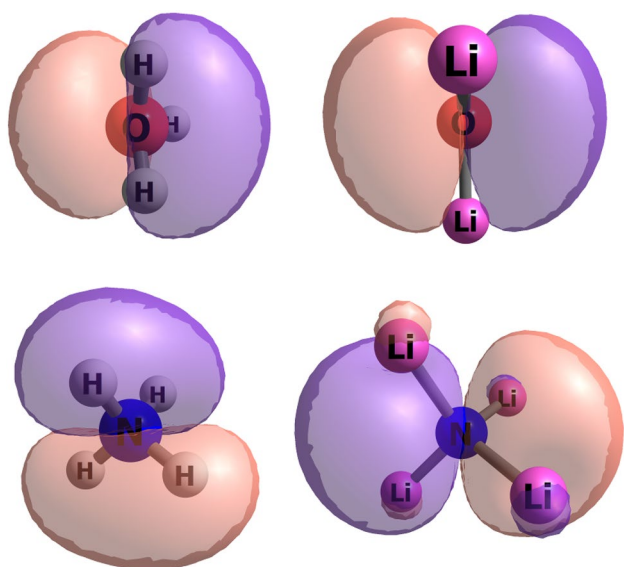


Fig. 2 The highest occupied molecular orbital (HOMO) surfaces of OH_3^+ , OLi_3^+ , NH_4^+ and NLi_4^+ with an isovalue of 0.02 a.u.

as well as ionic ($\text{NLi}_4^+ + \text{BF}_4^-$) fragments are calculated to be 9.21 eV and 5.11 eV, respectively. Clearly, $\text{NLi}_4\text{-BF}_4$ complex prefers to dissociate into $\text{NLi}_4^+ + \text{BF}_4^-$ fragments and therefore, it is a supersalt in which $-0.85e$ charge is transferred from NLi_4 to BF_4 . Similarly, we have also studied the interaction of NH_4 with BF_4 forming the $\text{NH}_4\text{-BF}_4$ complex, also displayed in Fig. 3a. In this complex, a charge-transfer of $0.92e$ takes place from NH_4 to BF_4 . The dissociation energy of $\text{NH}_4\text{-BF}_4$ against $\text{NH}_4^+ + \text{BF}_4^-$ fragments (4.94 eV) is smaller than that against $\text{NH}_4 + \text{BF}_4$ fragments (8.02 eV). Therefore, like NLi_4 , NH_4 also forms a supersalt by

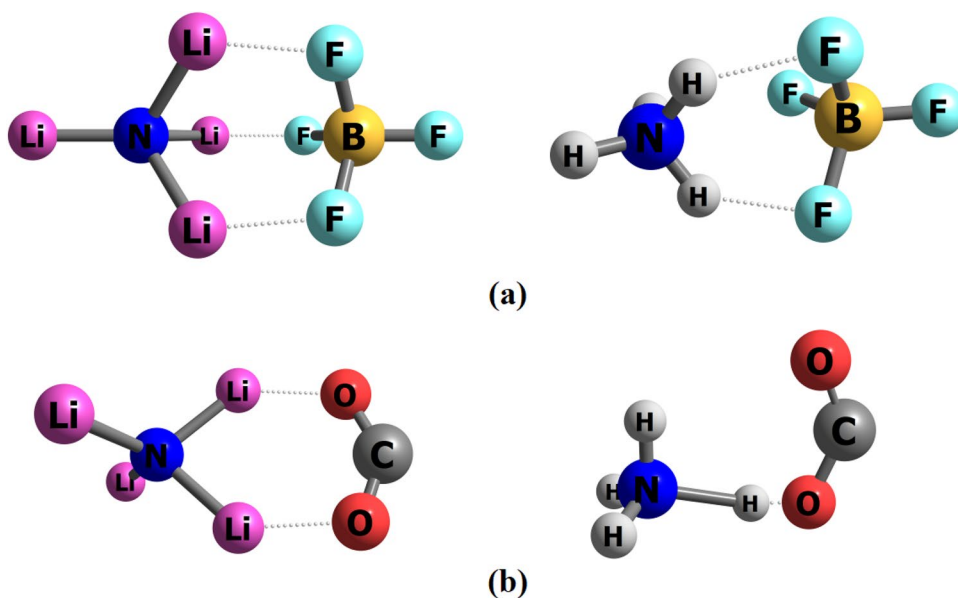
interacting with a superhalogen. However, the interaction takes place via three Li-F bonds in $\text{NLi}_4\text{-BF}_4$ supersalt but two H-F bonds in $\text{NH}_4\text{-BF}_4$ as depicted in Fig. 3.

We have already noticed [15] that superalkalis such as FLi_2^+ , OLi_3^+ , NLi_4^+ , are capable to reduce CO_2 into CO_2^- anion. CO_2 is a linear molecule, which is bent by single-electron reduction, i.e., in CO_2^- . We have studied the interaction of NLi_4 with CO_2 , which forms an $\text{NLi}_4\text{-CO}_2$ complex as displayed in Fig. 3 (b). The binding energy of $\text{NLi}_4\text{-CO}_2$ against dissociation to $\text{NLi}_4 + \text{CO}_2$ and $\text{NLi}_4^+ + \text{CO}_2^-$ is 1.33 eV and 5.31 eV, respectively. One can note that the structure of CO_2 in $\text{NLi}_4\text{-CO}_2$ complex is bent by 132.8° due to charge gained of $-0.82e$ by CO_2 . Similarly, the interaction of NH_4 with BF_4 leads to $\text{NH}_4\text{-CO}_2$ complex, also displayed in Fig. 3 (b). This complex is also stable with the binding energy of 0.83 eV for $\text{NH}_4 + \text{CO}_2$ fragments and 5.83 eV for $\text{NH}_4^+ + \text{CO}_2^-$. The charge contained by CO_2 moiety in the $\text{NH}_4\text{-CO}_2$ complex is $-0.59e$ such that the bond angle of CO_2 is reduced to 130.8° . Therefore, like NLi_4 , NH_4 can activate the CO_2 molecule. Albeit, the interaction in $\text{NLi}_4\text{-CO}_2$ takes place via two Li-O bonds but single H-O bond in $\text{NH}_4\text{-CO}_2$.

4 Conclusions and perspectives

For the first time, we attempted to explore whether NH_4^+ and OH_3^+ behave as superalkali cations. We have employed various methods such as ωB97xD , MP2 and single-point CCSD(T) along with aug-cc-pVTZ basis set. Our findings clearly suggest that the behaviour of NH_4 resembles that of a typical superalkali. Therefore, NH_4^+ might behave as superalkali cation. We strongly believe that NH_4^+ can be

Fig. 3 The lowest energy structures of $\text{NLi}_4\text{-BF}_4$ as well as $\text{NH}_4\text{-BF}_4$ complexes (a) and $\text{NLi}_4\text{-CO}_2$ as well as $\text{NH}_4\text{-CO}_2$ complexes (b). The interactions between two moieties are depicted by dotted lines



exploited further to design novel compounds with unusual properties, analogous to other superalkali cations. It should also be noticed that the radius of the NH_4^+ ion in a crystal (1.43 Å) is very close to the corresponding radii of potassium (1.33 Å) and rubidium (1.44 Å). Like alkalis and other superalkalis, therefore, this should also possess metallic properties. Our literature survey [31, 32] revealed that the metallic NH_4^+ indeed exists at least at high pressures. Thus, this work may also explain the metallic properties of NH_4^+ .

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest in the publication of this paper.

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