Characterization of the Rydberg Bonding in $(NH_4)_2^-$

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The Rydberg bonding in $(NH_4)_2^-$ and in its neutral and cationic counterparts have been examined using ab initio electronic structure theory. Analogous calculations on Li_2^-, Na_2^-, and K_2^- and on their neutral molecules and cations have also been performed for comparison with the Rydberg bonding cases. The dissociation energy D_e for $(NH_4)_2^- \rightarrow NH_4 + NH_4^-$ is found to be 4 kcal mol^{-1} at the highest level of theory used, while the corresponding D_e's for the cation and the neutral molecule are 20 and 9 kcal mol^{-1}, respectively. The vertical electron detachment energy of $(NH_4)_2^-$ is predicted to be 0.46 eV, which is nearly the same as that of NH_4^-. The trends in the interfragment equilibrium distances R_e, the harmonic vibrational frequencies ω, and the dissociation energies within alkali dimers, NH_4 dimers, and their respective anions and cations have been examined and are discussed.

I. Introduction

The ammonium cation NH_4^+ is a closed-shell species which is known[1] to produce, upon electron attachment, a neutral NH_4 that is thermodynamically unstable with respect to $NH_3 + H$ and has its outermost electron in a Rydberg orbital, as shown in Figure 1. The attachment of another electron to NH_4 produces the so-called double-Rydberg anion[2] NH_4^-, which has its two outermost electrons occupying Rydberg orbitals. This anion is electronically stable by ca. 0.4 eV relative to $NH_4 + e^-$ but thermodynamically unstable with respect to $NH_3 + H^-$.

In earlier efforts, the geometries, vibrational frequencies, and chemical bonding properties of NH_4, NH_4^-, and other species containing electrons in Rydberg orbitals have been characterized using ab initio electronic structure theory. We also examined the possibility that chemical bonds can be formed[3] when Rydberg orbitals on neighboring fragments overlap. For example, we studied the bonding that arises when two NH_4 neutral molecules combine to form $(NH_4)_2$, with two electrons occupying a bonding Rydberg molecular orbital (mo), as shown in Figures 1 and 2. We also considered the bonding in the corresponding cation $(NH_4)_2^+$ with only one electron in the bonding Rydberg mo and found that the dissociation energy (D_e) of $(NH_4)_2^+ \rightarrow NH_4 + NH_4^+$ is considerably larger than the dissociation energy of the neutral $(NH_4)_2 \rightarrow NH_4 + NH_4$ even though the neutral molecule nominally has two electrons in the bonding Rydberg mo whereas the cation has only one such electron.[4]

None of the species we investigated has its antibonding Rydberg orbital occupied. Therefore, we decided to delve deeper into the nature of Rydberg bonding by probing how D_e and the interfragment vibrational frequency and geometry depend on the number of Rydberg electrons. In the present study, we consider the anion $(NH_4)_2^-$, in which two electrons occupy the bonding Rydberg mo and one electron occupies the antibonding Rydberg mo (shown in Figure 2). We also examine the bonding (characterized via bond lengths, harmonic vibrational frequencies or force constants, and dissociation energies) in several alkali dimer cations, neutral molecules, and anions, which we view as analogues to our Rydberg-bound $(NH_4)_2$ species because they contain one, two, or three electrons in bonding or antibonding mos formed from their outermost valence s orbitals. By comparing the trends seen in the neutral and charged alkali species to what we find in $(NH_4)_2^+$, $(NH_4)_2$, and $(NH_4)_2^-$, we shed further light on the nature of the Rydberg bond.

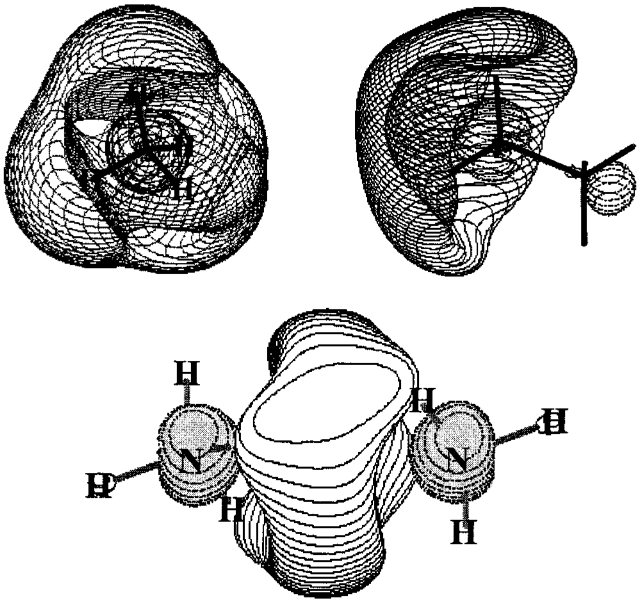

Figure 1. Rydberg orbital of NH_4 (left) and H_3C-NH_3 (right) and the Rydberg bonding orbital of $(NH_4)^+_2$ (bottom).

II. Methods

The equilibrium geometries of the cationic, neutral molecule, and anionic species were optimized and their harmonic vibrational frequencies calculated at the second-order Møller−Plesset (MP2) perturbation level of theory[5]. In all calculations, the values of $\langle S^2 \rangle$ never exceeded 0.7508 (after annihilation) for

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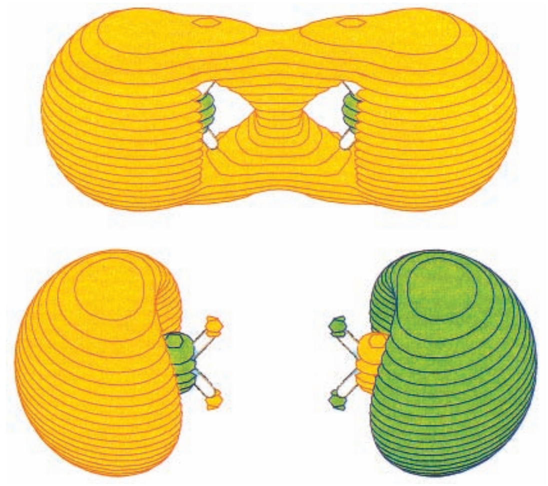

Figure 2. Rydberg bonding (top) and antibonding (bottom) orbitals in $(NH_4)_2^-$.

doublet states, so we are confident that spin-contamination effects are negligible. The electron binding energies were studied at the Koopmans' theorem (KT),[6] SCF, MP*n* ($n = 2-4$), and coupled-cluster (CCSD(T)) levels. The dissociation energies for the charged and neutral NH_4 dimers were also studied at the SCF, MPn, and CCSD(T) levels, and the basis set superposition errors (BSSE) were removed as described in ref 7. All calculations were performed with the GAUSSIAN 98 program[8] on 500 MHz dual processor Intel Pentium III computers on an SGI Origin2000 numerical server. The three-dimensional plots of molecular orbitals were generated with the MOLDEN program.[9]

The choice of the atomic orbital basis sets describing the cationic molecules and additional bound electrons is very important for producing reliable geometries, frequencies, and dissociation energies. They must be flexible enough to describe the static charge distribution of the cationic molecular host, allow for the polarization and dispersion stabilization of the neutral molecule and anion upon electron attachment, and properly describe the Rydberg bonds. To describe the fundamental valence orbitals, we carried out calculations with the 6-311++G** basis set.[10] This constitutes the fundamental valence bases for our calculations both on $(NH_4)_2$ and its ions and on alkali dimers and their ions. We employed the 6-311++G** basis because it has been proven reliable in previous studies on $(NH_4)_2$.

Following the procedure we used had in an earlier study on Rydberg and dipole-bound species, we supplemented the valence basis sets with extra diffuse functions having very low exponents, which are necessary to properly describe the Rydberg orbitals and resulting Rydberg bonding and antibonding mos. In particular, we supplemented the valence basis sets with extra even-tempered[11] three-term *s* and *p* sets of diffuse functions centered on both the N atoms. We started to build up the exponents of these diffuse functions from the lowest *s* and *p* exponents included in the nitrogen valence basis set, and we used a geometric progression ratio of 3.2 based on our earlier experience in designing bases for Rydberg species.[12] As a result, the extra diffuse *s* and *p* functions share exponent values and have the lowest exponent of 1.950070×10^{-3} au for *s* and *p* symmetries.

We verified that the MP2 electron binding energy of the parent NH_4^- anion, which has been studied both theoretically and experimentally,[13] changes by <0.0005 eV if one more set of *s* and *p* diffuse functions is added to the basis. Also, when a set of diffuse functions possessing *d* symmetry is added to our basis, the electron binding energy remains approximately the same. Moreover, we verified that the electron binding energy of the anionic dimer changes by only ca. 0.019 eV upon the addition of two s, two p, and three d diffuse basis functions when calculated at the CCSD(T) level. As a result, we feel confident that the extra diffuse s and p basis functions are adequate for describing the neutral NH_4 and $(NH_4)_2$ and their anions.

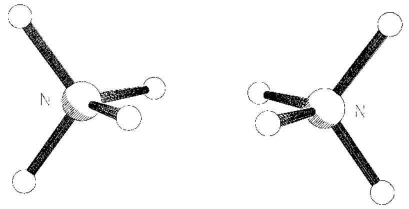

Figure 3. Equilibrium structure of $(NH_4)_2^-$.

TABLE 1: Bond Energies (kcal mol^{-1}) and N−N Distances (Å, MP2 Level) for Cationic, Neutral, and Anionic NH_4 Dimers

	6-311++G**+3(sp)		
	$(NH_4)_2^+$	$(NH_4)_2$	$(NH_4)_2^-$
SCF	19.2	−5.2	7.0
MP2	20.7	8.6	9.4
MP3	20.4	9.1	8.6
MP4	20.5	10.9	7.0
CCSD(T)	20.4	10.7	9.8
CCSD(T) + ΔZPE[a]	20.3	9.2	4.2
CCSD(T)[b] + ΔZPE	20.1	8.6	3.8
R_e	4.48	3.65	4.22

[a] ΔZPE denotes zero-point energy correction. [b] Denotes basis set superposition correction (all BSSE corrections were <1 kcal mol^{-1}).

Our calculations on the alkali dimers and their ions were performed using the same methods (i.e., basis sets and methods for treating electron correlation) we had used on the Rydberg species. These data on the alkalis are not meant to represent more accurate data than are currently available from experimental or theoretical sources. Instead, they represent the D_e, ω_e, and R_e values that are most comparable to those we achieved for the Rydberg molecules because they were obtained using the same tools used on the Rydberg systems. In tabulating our findings on the alkali dimers and their ions, we compare our calculated D_e, ω_e, and R_e values to the data obtained through other (experimental and theoretical) means, and we find our data to be in line with the earlier observations.

III. Results

A. Equilibrium Geometries. Figure 3 shows the equilibrium structure of $(NH_4)_2^-$, and Table 1 gives the N−N distances (R_e) calculated at the MP2 level of the cation, anion, and neutral molecule.[14] We note that R_e decreases from the cation to the neutral molecule and then increases from the neutral molecule to the anion, which is in line with the Rydberg-bond orders of the cation, neutral molecule, and anionic species (these bond orders are $^1/_2$, 1, and $^1/_2$, respectively).

B. Vibrational Frequencies of NH_4 Dimer Species. All 24 harmonic frequencies for the cation, neutral molecule, and anion are given in Table 2. Because the internal geometries (i.e., N−H bond lengths and angles) do not vary substantially among these three species, most of the variation in the $(NH_4)...(NH_4)$ interfragment vibrational frequency (shown in bold in Table 2) should be due to variations in the corresponding force constants.

TABLE 2: Harmonic Frequencies for Cationic, Neutral, and Anionic NH_4 Dimers (cm^{-1})

6-311++G**+3(sp)		
$(NH_4)_2^+$	$(NH_4)_2$	$(NH_4)_2^-$
16 a_{1u}	70 a_u	25 a_g
127 a_{1g}	79 b_u	41 a_u
128 e_g	**110 a_g**	69 b_u
128 e_g	140 a_u	**85 a_g**
190 e_u	164 a_g	115 b_g
190 e_u	218 b_g	352 a_u
1368 e_u	1343 b_g	1342 b_g
1368 e_u	1346 a_u	1353 a_g
1400 a_{1g}	1351 a_g	1376 b_u
1406 a_{2u}	1351 b_u	1376 a_g
1432 e_g	1367 a_g	1491 b_u
1432 e_g	1416 b_u	1587 b_u
1652 e_u	1591 a_u	1594 a_g
1652 e_u	1603 b_u	1605 b_g
1659 e_g	1608 b_g	1607 a_u
1659 e_g	1625 a_g	1998 a_u
2485 a_{1g}	3014 b_u	3019 b_u
2579 a_{2u}	3042 a_u	3063 ag
3392 a_{1g}	3044 a_g	3186 ag
3398 a_{2u}	3091 b_g	3192 ag
3537 e_g	3211 b_u	3203 b_g
3537 e_g	3212 a_g	3206 b_u
3538 e_u	3287 a_g	3206 b_u
3538 e_u	3295 b_u	5484 a_u

We computed these force constants (k) and found them to have the ratio of 2.2:1.7:1.0 for the cation, neutral molecule, and anion, which is indeed close to the ratio of the squares of the harmonic frequencies in Table 2 (shown in bold). These trends in k (or ω) do not follow the nominal Rydberg bond orders, in contrast to the trends in R_e, which, for the cation, neutral molecule, and anion are 4.5, 3.6, and 4.2 Å, respectively.

C. Rydberg Bond Dissociation Energies of NH_4 Dimers. The energies (D_e) needed to break the Rydberg bonding in the cation, neutral molecule, and anion are shown in Table 1, and they are 20, 9, and 4 kcal mol^{-1}, respectively, computed at the highest level (CCSD(T)) and including the zero-point energies and the basis set superposition corrections (<1 kcal mol^{-1} in all cases). When comparing the trends in D_e to those in R_e, k, and ω, we noted significant differences. The trends in R_e (4.5, 3.6, and 4.2 Å) do follow the progression in Rydberg bond orders, but the trends in k, ω (127, 110, 85 cm^{-1}), and D_e (20, 9, 4 kcal mol^{-1}) do not.

D. Comparison of NH_4 Dimers with Selected Alkali Dimers. Our NH_4 dimer and its ions are isoelectronic with the sodium dimer and its cation and anion, which contain a total of 22, 21, and 23 electrons, respectively. Of course, the sodium dimers employ valence 3s orbitals to form their bonding and antibonding mos, whereas the NH_4 dimers use Rydberg orbitals. The NH_4 Rydberg orbital is more diffuse than the Na 3s orbital (reflected by its lower ionization potential and electron affinity), so it is to be expected that overlap-induced bonding will be weaker in the NH_4 dimer than in Na_2. Nevertheless, to better understand the trends of D_e, k, ω, and R_e in our Rydberg-bound dimers, we carried out a series of calculations on several alkali dimers and their ions, aimed in particular at probing analogous trends in these species. We used the 6-311++G**+3(sp) basis set again for Na_2^+, Na_2, Na_2^-, and the Li and K counterparts, and we optimized the geometries for all species at the MP2 level. The resulting R_e, ω, and D_e values are shown in Table 3 along with data from Huber and Herzberg.[15]

In Figure 4, the trends in D_e, R_e, and ω are summarized graphically, and the bond lengths (R_e) among the alkali dimers show trends (Figure 4b) consistent with expectations based on bond order, similar to the trend in NH_4 dimers. In contrast, the variation in ω among the alkali dimers again follows the nominal bond orders, but the ω values of the NH_4 dimers deviate (see Figure 4c). The trends in the D_e of alkali and NH_4 dimers are shown in Figure 4a. In all cases, the values of D_e are largest for the cation, smaller for the neutral molecule, and smallest (except for K_2^-) for the anion.

TABLE 3: Bond Lengths (Å), Frequencies (cm^{-1}), and Energies (kcal mol^{-1}) of Selected Alkali[a] and NH_4 Dimers

dimer	R_e	ω_e	D_e (6-311++G**+3(sp))
Li_2^+	3.13	260	29.2 (33.2)
Li_2	2.74 (2.67)	342 (351)	22.8 (24.1)
Li_2^-	3.18 [3.1]	212 [230]	18.3 (20.3) [18]
Na_2^+	3.66 (3.54)	117 (126)	22.0 (22.1)
Na_2	3.12 (3.08)	161 (159)	15.9 (16.6)
Na_2^-	3.61 [3.6]	93 [99]	13.5 (10.1) [14]
K_2^+	4.58 (4.11)	71 (67)	17.4 (19.6)
K_2	3.91 (3.91)	92 (92)	9.7 (11.85)
K_2^-	4.54	53	10.2
NH_4^+	4.5	127	20
NH_4	3.6	110	9
NH_4^-	4.2	85	4

[a] Values in parentheses are from ref 16. Values in square brackets are from ref 15C.

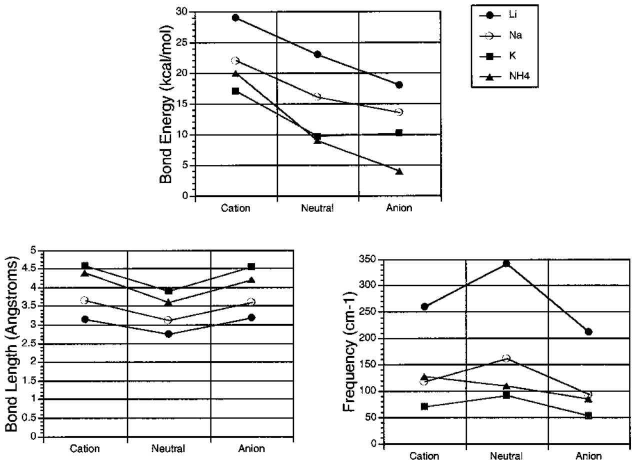

Figure 4. (a) Dissociation energies (kcal mol^{-1}), (b) bond lengths (Å), (c) and harmonic vibrational frequencies (cm^{-1}) for the alkali and NH_4 dimers.

IV. Summary of Findings and Possible Interpretation of Trends

The primary findings of this research are that (a) $(NH_4)_2^-$ is bound relative to $NH_4^- + NH_4$ by 4 kcal mol^{-1} at the highest level of theory employed, (b) $(NH_4)_2^-$ is predicted to have a vertical electron detachment energy of 0.46 eV, (c) the geometry of $(NH_4)_2^-$ is as described in Figure 3 and Table 1, and (d) the trends in D_e, R_e, and ω within the NH_4 dimers are very similar to what is seen in the alkali dimers.

However, the data summarized in Figure 4 show that these trends do not track the nominal bond orders. We suggest that deviations from bond order trends in the alkalis and NH_4 arise primarily from two sources: (a) electron repulsion among the two and three valence electrons of the neutral molecule and anion, respectively, and (b) additional attractive long-range charge−polarization interaction energies $-\alpha e^2/R^4$, which are absent for the neutral molecule but active for the cations and anions.

Let us elaborate on how we believe these two effects cause the bonding in the alkali and NH_4 cases to deviate from the pattern of nominal bond orders.

Because the valence orbitals of the alkalis and the Rydberg orbitals of NH_4 are quite diffuse, their overlaps are small at the respective dimer equilibrium geometries. As a result, the overlap-induced contribution to the bonding arising from the attraction of the valence electron(s) to the two valence centers (i.e., the alkali cations or the NH_4^+) is not as large as that from conventional covalent bonds involving more electronegative elements. Indeed, it is well-known for the alkalis[15] that there is very little buildup of electron density in the internuclear region when a bond is formed, which relates to the metallic behavior of these elements.

The weak overlap-induced bonding causes the effects of electron−electron repulsion to be relatively more important in such systems. Especially in the NH_4 dimers considered here, electron repulsion gives rise to significant changes in the form of the Rydberg bonding and antibonding orbitals, depending on how many electrons occupy these orbitals. For example, the bonding orbital of the $(NH_4)_2^+$ cation in Figure 1 differs substantially from the bonding orbital of the $(NH_4)_2^-$ anion in Figure 2. In the cation, there is no (valence) electron repulsion, but in the anion, there are three electrons that repel; these differences cause the σ and σ^* orbitals of the cation and anion to be quite different.

We therefore suggest that these electron−electron (e−e) repulsion effects contribute to the trends in D_e values as follows:
(a) For the alkali and Rydberg cations, where there is no valence e−e repulsion, the bonding is dominated by overlap effects but is further enhanced by the additional $-\alpha e^2/R^4$ energy that must be overcome to effect dissociation.
(b) For the corresponding neutral molecules, there is e−e repulsion between two σ electrons in the σ^2 dimer, but the repulsion vanishes in the separated fragments (e.g., Li or NH_4) where these two electrons are infinitely distant. As a result, the bond strength of the neutral molecule is diminished (relative to that of the cation) by this repulsion to more than offset the overlap-induced bonding of the neutral molecule's two (σ^2) electrons. Moreover, there is no additional $-\alpha e^2/R^4$ energy required in this case. Hence, D_e is smaller in the neutral molecules than in the cations (see Figure 4a).
(c) For the anions, there is a e−e repulsion among three electrons (two σ's and one σ^*) in the dimer that evolves into e−e repulsion between two electrons (σ^2) in the anion fragment (e.g., Li^- or NH_4^-). In addition, the $-\alpha e^2/R^4$ must be overcome to effect dissociation. However, the fact that e−e repulsion is larger in the anion dimers than in their fragments combines with the antibonding character of the σ^* orbital, which is now occupied, to reduce D_e beyond that of the neutral molecule (Figure 4a).

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(4) It should be noted, as Wright et al. showed,[3] that the neutral $(NH_4)_2$ is metastable against fragmenting to $H_2 + 2\ NH_3$ and has a low dissociation barrier in this channel. On the other hand, the cation $(NH_4)_2^+$ is stable with respect to $H_2 + NH_3 + NH_3^+$. In the present investigation, our goal is to characterize and understand the strength and nature of the Rydberg bond, so we restrict our attention to the dissociation of $(NH_4)_2$ into 2 NH_4, $(NH_4)_2^+$ into $NH_4 + NH_4^+$, and $(NH_4)_2^-$ into $NH_4 + NH_4^-$ because these dissociation energies, although not necessarily the lowest in each case, reflect the Rydberg bond strength.

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(13) Our computed vertical detachment energy for NH_4^- is 0.463 eV, which compares to the experimental value[2] of 0.4 eV. For $(NH_4)_2^-$, our computed vertical detachment energy is 0.461 eV.

(14) Complete information for the anion, in the form of the Cartesian coordinates of all atoms, is available by contacting the author. The geometries of the cation and neutral molecule can be found in the article by Boldyrev et al. in ref 3.

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