Rydberg Bonding in $(NH_4)_2$

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Chemical binding of two monovalent Rydberg species to form a singlet-state Rydberg dimer molecule is predicted to be possible. Ab initio electronic structure methods that include electron correlation (at levels up through QCISD(T)/6-31++G**// MP2(full)/6-31++G** + ZPE) are shown to be essential to achieving a proper description of such bonding. The $(NH_4)_2$ molecule, selected as the prototype for this study, is shown to be bound with respect to its Rydberg-species fragments, $2NH_4$, by 7.5–9.7 kcal/mol, depending on the level of treatment of electron correlation, and to be electronically stable (by ca. 4.3 eV) with respect to $(NH_4)_2^+$ at the neutral's equilibrium geometry. The $(NH_4)_2$ Rydberg dimer is thermodynamically unstable with respect to $2NH_3 + H_2$ by 86–89 kcal/mol mol yet possesses all real vibrational frequencies; it is thus a metastable molecule held together by a weak Rydberg bond. The dissociation energy of the $(NH_4)_2^+$ cation to form $NH_4^+ + NH_4$ is found to be larger than that of the neutral $(NH_4)_2$.

I. Introduction

NH_4 is known[1] to exist as a Rydberg molecule in which a single electron occupies a diffuse orbital of a_1 symmetry and the remaining ten electrons occupy the nitrogen core 1s (a_1) orbital and four equivalent N–H σ-bonding orbitals (of a_1 and t symmetries). This species can be viewed as a tetrahedral (T_d) closed-shell NH_4^+ cation "core" with another electron attached to it in a Rydberg orbital. It turns out that although the T_d structure is a local minimum on the X^2A_1 ground-state energy surface, it is only metastable with respect to fragmentation to the energetically lower $H + NH_3$ products. The barrier to this dissociation is but a few kilocalories per mole, as a result of which the dissociation lifetime of isolated (even vibrationally cold) NH_4 is on the order of 10^{-6} s. The deuterated species ND_4 is significantly longer lived, but also undergoes dissociation to $D + ND_3$.

The corresponding anion NH_4^- has also been detected experimentally[2] and studied theoretically.[3,4] In this so-called double-Rydberg anion, *two* electrons occupy diffuse Rydberg orbitals and move around the underlying NH_4^+ cation core. Dissociation of NH_4^- to produce $H^- + NH_3$ is exothermic, but the barrier is larger than in the neutral NH_4 case for reasons described in ref 4. At its tetrahedral equilibrium geometry, the X^1A_1 ground state of NH_4^- lies ca. 0.5 eV below the neutral X^2A_1 NH_4, which, in turn, lies ca. 4.4 eV below the X^1A_1 NH_4^+ cation.

In this paper, we report results of our theoretical study of the two-electron *Rydberg bond* that is formed when the two $^2A_1$ Rydberg NH_4 fragments are brought close enough to permit their lowest-energy Rydberg a_1 orbitals to overlap and interact as illustrated in Figure 1. These data represent our first results in a project aimed at probing the strengths and nature of bonds formed by two or more Rydberg orbitals on two or more Rydberg-state fragments.

We find the *Rydberg cluster* species $(NH_4)_2$ to be stable with respect to fragmentation into two NH_4 radicals by 7.5–9.7 kcal/mol depending on the level at which electron correlation is treated, and to have a vertical ionization potential of ca. 4.2–4.3 eV. The $(NH_4)_2$ Rydberg dimer is not the global minimum on its ground-state potential surface; it is a local minimum with all positive vibrational force constants but its total energy is higher than that of $2NH_3 + H_2$ by 86–89 kcal/mol (again, depending on the treatment of electron correlation). After describing how we carried out our calculations in the following section, we provide further energetic and structural information about this new family of chemical bonds as embodied in $(NH_4)_2$ in section III.

II. Atomic Orbital Basis Sets and Treatment of Electron Correlation

The geometries of NH_4, $(NH_4)_2$, NH_3, NH_4^+, $(NH_4)_2^+$, and H_2 were optimized employing analytical energy gradient methods[5] with a polarized split-valence basis set augmented by diffuse s- and p-functions (this basis is denoted SCF/6-31++G**)[6,7] and

at correlated second-order Møller–Plesset perturbation theory MP2(full) levels using unrestricted Hartree–Fock (UHF) and unrestricted second-order MP theory (UMP2) for open-shell species. The fundamental vibrational frequencies, normal coordinates, and zero-point energies (ZPE) were calculated by standard FG matrix methods. The MP2 (full)/6-31++G** equilibrium geometries were used to evaluate electron correlation energies in the full fourth-order frozen-core approximation both by Møller–Plesset perturbation theory[8] and by the unrestricted quadratic configuration interaction including singles and doubles with approximate triples (U) QCISD(T)[9] method using 6-31++G** basis sets. The UHF wave functions for open-shell systems were spin projected to generate pure spectroscopic states for use in the subsequent energy calculations whose results are denoted PUHF, PMP2, PMP3 and PMP4.[10] The Gaussian 90 program suite[11] was used to perform all of the calculations whose results are discussed here.

III. Findings

A. Rydberg Bond Energy. As stated in the Introduction, we find the $(NH_4)_2$ dimer to be stable with respect to dissociation to two NH_4 Rydberg molecules by 7.5–9.7 kcal/mol, depending on the method used to treat electron correlation. At the Hartree–Fock self-consistent field (SCF) level, the dimer is not predicted to be stable. This lowest-energy structure for $(NH_4)_2$ is shown in Figure 2; perhaps surprisingly, it has the N–H bonds oriented in an *eclipsed* geometry; although the barrier to rotation connecting D_{3h} and D_{3d} (staggered) structures is a fraction of 1 kcal/mol.

Because the SCF wave function represents the starting point of our subsequent MP treatment of electron correlation, we also checked for Hartree–Fock instabilities. We found the UHF and RHF solutions to yield identical energies and geometries for the D_{3h} $(NH_4)_2$ species, but we found the SCF solution to be second-order unstable. This, in turn, brings into question the validity of our subsequent MP and QCI correlated results since both of these methods use the single SCF configuration as a starting point.

To further address this matter, we carried out small complete-active-space (CAS) SCF calculations in which the two Rydberg electrons were allowed to occupy two (the HOMO and LUMO) or four orbitals (the HOMO and the three lowest-energy unoccupied MOs which include the Rydberg bonding π-type orbitals). The resultant CAS-SCF wave functions (i) had dominant configurations with amplitudes of 0.9445 and 0.9473, respectively, and (ii) had no imaginary vibrational frequencies. These facts indicate that, even though the single-configuration SCF wave function displays second-order instability, there is indeed a single dominant configuration in the true ground-state wave function. Thus our higher order correlated (e.g., MP4 and QCISD(T)) results are likely to provide valid representations of the bonding in $(NH_4)_2$.

TABLE I: Energies (au), Geometries (Å and deg), and Vibrational Frequencies (cm⁻¹) of Minimum-Energy Structure D_{3h} (NH₄)₂

SCF/6-31++G**	MP2(full)/6-31++G**	MP2(full)/6-31++G**
$E_{SCF} = -113.381\,927$	$E_{MP2(full)} = -113.811\,496$	$E_{SCF} = -113.377\,88$
$R_{NN} = 4.0286$	$R_{NN} = 3.5766$	$E_{MP2} = -113.803\,66$
$R_{NH_f} = 1.0198^a$	$R_{NH_f} = 1.0398$	$E_{MP3} = -113.832\,28$
$R_{NH_t} = 1.0174^a$	$R_{NH_t} = 1.0361$	$E_{MP4} = -113.848\,46$
$\theta(H_tNH_f) = 111.26°$	$\theta(H_tNH_f) = 111.29°$	$E_{QCISD} = -113.837\,60$
ZPE = 64 kcal/mol	ZPE = 58 kcal/mol	$E_{QCISD(T)} = -113.850\,60$
$\nu_1(a'_1) = 3576.6$	$\nu(a'_1) = 3295.7$	
$\nu_2(a'_1) = 3392.8$	$\nu_2(a'_1) = 3097.0$	
$\nu_3(a'_1) = 1528.6$	$\nu_3(a'_1) = 1388.1$	
$\nu_4(a'_1) = 121.3$	$\nu_4(a'_1) = 129.1$	
$\nu_5(a''_1) = 28.5$	$\nu_5(a''_1) = 8.3$	
$\nu_6(a''_2) = 3580.7$	$\nu_6(a''_2) = 3309.5$	
$\nu_7(a''_2) = 3377.7$	$\nu_7(a''_2) = 3055.1$	
$\nu_8(a''_2) = 1572.9$	$\nu_8(a''_2) = 1388.1$	
$\nu_9(e') = 3480.5$	$\nu_9(e') = 3163.0$	
$\nu_{10}(e') = 1785.3$	$\nu_{10}(e') = 1622.4$	
$\nu_{11}(e') = 1511.4$	$\nu_{11}(e') = 1367.4$	
$\nu_{12}(e') = 101.2$	$\nu_{12}(e') = 76.2$	
$\nu_{13}(e'') = 3503.1$	$\nu_{13}(e'') = 3208.2$	
$\nu_{14}(e'') = 1799.7$	$\nu_{14}(e'') = 1639.8$	
$\nu_{15}(e'') = 1519.3$	$\nu_{15}(e'') = 1375.9$	
$\nu_{16}(e'') = 104.1$	$\nu_{16}(e'') = 109.6i$	

^{a} In this and all other tables, the index f is used to label the H atoms on one NH₄ moiety that are closest to the other NH₄ group. The H atom(s) that are further away are labeled t.
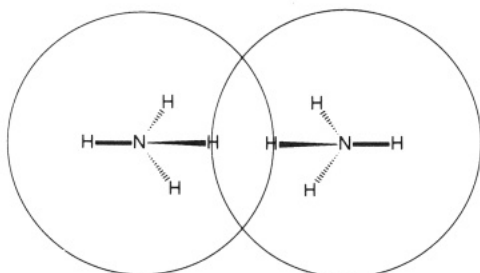

Figure 1. Bonding interaction between two s-type (a_1) Rydberg orbitals, each localized on a NH₄⁺ core.
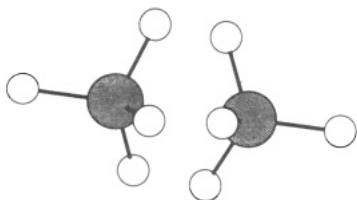

Figure 2. Minimum-energy (eclipsed) D_{3h} structure of (NH₄)₂ for $^1A'_1$ ground electronic state. The bond lengths and angles are given in Table I.

TABLE II: Energies (au), Geometries (Å and deg), and Vibrational Frequencies (cm⁻¹) of T_d (NH₄)

SCF/ 6-31++G**	MP2(full)/ 6-31++G**	MP2(full)/ 6-31++G**
$E_{SCF} = -56.693\,66$	$E_{MP2(full)} = -56.899\,70$	$E_{PUHF} = -56.692\,95$
$R_{NH} = 1.0201$	$R_{NH} = 1.0375$	$E_{PMP2} = -56.895\,86$
$\langle S^2 \rangle = 0.751$	$\langle S^2 \rangle = 0.751$	$E_{PMP3} = -56.909\,65$
ZPE = 31 kcal/mol	ZPE = 29 kcal/mol	$E_{PMP4} = -56.916\,47$
$\nu_1(a_1) = 3368.3$	$\nu_1(a_1) = 3115.0$	$E_{QCISD} = -56.912\,78$
$\nu_2(e) = 1786.5$	$\nu_2(e) = 1647.2$	$E_{QCISD(T)} = -56.917\,56$
$\nu_3(t_2) = 3456.1$	$\nu_3(t_2) = 3192.6$	
$\nu_4(t_2) = 1489.7$	$\nu_4(t_2) = 1370.8$	

**TABLE III: Energy Differences (kcal/mol) for Fragmentation of (NH₄)₂ at Various Levels of Correlation**

(NH₄)₂ → 2NH₄	(NH₄)₂ → 2NH₃ + H₂
$\Delta E(SCF) = -5.04$	$\Delta E(SCF) = -99.0$
$\Delta E(PMP2) = 7.45$	$\Delta E(PMP2) = -87.3$
$\Delta E(PMP3) = 8.14$	$\Delta E(PMP3) = -87.6$
$\Delta E(PMP4) = 9.74$	$\Delta E(PMP4) = -86.2$
$\Delta E(QCISD) = 7.55$	$\Delta E(QCISD) = -89.3$
$\Delta E(QCISD(T)) = 9.73$	$\Delta E(QCISD(T)) = -86.0$
$\Delta E(QCISD(T) + ZPE) = 9.12$	$\Delta E(QCISD(T) + ZPE) = -93.1$

B. Geometry and Vibrational Frequencies of (NH₄)₂. In Table I, we provide the equilibrium geometry and harmonic vibrational frequencies at the SCF and second-order Møller–Plesset levels, as well as total energies at various levels of electron correlation for (NH₄)₂ (at the MP2-optimized geometry). In Table II, similar data are presented for the Rydberg "monomer" NH₄; the deviation of the expectation value $\langle S^2 \rangle$ for the S^2 operator from the $(1/2)(1/2 + 1) = 3/4$ value expected for a pure doublet provides a sense of the spin contamination that remains in the NH₄ wave function.

It should be noted that, among the four low-frequency vibrations of (NH₄)₂, ν_4 (129 cm⁻¹) corresponds to the interfragment motion that evolves into the reaction coordinate for fragmentation into 2NH₄. It should also be noted that one imaginary vibrational frequency ($\nu_{16}(e'') = 109.6i$) occurs in the MP2(full) treatment. We believe the appearance of this imaginary frequency is an artifact that is caused by the second-order instability in the electronic wave function mentioned in the preceding paragraph as well as by using numerical finite-difference techniques for calculating second derivatives in the MP2(full) case. In support of this claim, we note (i) that no imaginary frequencies occur in the above SCF or CAS-SCF calculations and (ii) that all re-

maining frequencies of the SCF, CAS-SCF, and MP2 calculations agree well with one another.

C. Thermodynamic Energies for (NH₄)₂. Table III presents the zero-point corrected energy differences relating to the

$$(NH_4)_2 \rightarrow 2NH_4$$

and

$$(NH_4)_2 \rightarrow 2NH_3 + H_2$$
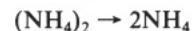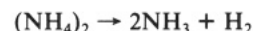
fragmentation processes obtained at various levels of electron correlation. Except for the SCF-level data, the correlated results provide consistent predictions of the stabilities of (NH₄)₂ with respect to dissociation.

D. Alternative Structures for (NH₄)₂. In addition to the stable structure shown in Figure 2, we examined the staggered D_{3d} structure of Figure 3a as well as the D_{2h}, D_{2d}, and head-on D_{3d} structures depicted in Figure 3b–d, but found them to possess one, two, three, and three negative Hessian eigenvalues, respectively. This means that none of these structures, even when energy optimized within these symmetry constraints, correspond to a stable isomer. The former, which lies only a fraction of a kilocalorie per mole above the minimum-energy structure of Figure 2, is

TABLE IV: Energies (au), Geometries (Å and deg), and Vibrational Frequencies (cm⁻¹) of D_{3d} $(NH_4)_2$

SCF/6-31++G**	SCF/6-31++G**	SCF/6-31++G**
$E_{SCF} = -113.381\,888$	$\nu_3(a_{1g}) = 1528.6$	$\nu_{11}(e_u) = 1515.5$
$R_{NN} = 4.0286$	$\nu_4(a_{1g}) = 121.1$	$\nu_{12}(e_u) = 99.2$
$R_{NH_f} = 1.0198$	$\nu_5(a_{1u}) = 29.9i$	$\nu_{13}(e_u) = 3489.5$
$R_{NH_t} = 1.0174$	$\nu_6(a_{2u}) = 3580.4$	$\nu_{14}(e_u) = 1785.6$
$\theta(H_tNH_f) = 111.26°$	$\nu_7(a_{2u}) = 3378.0$	$\nu_{15}(e_u) = 1514.7$
ZPE = 64 kcal/mol	$\nu_8(a_{2u}) = 1573.2$	$\nu_{16}(e_u) = 106.1$
$\nu_1(a_{1g}) = 3576.5$	$\nu_9(e_g) = 3497.5$	
$\nu_2(a_{1g}) = 3393.8$	$\nu_{10}(e_g) = 1798.5$	

TABLE V: Energies (au), Geometries (Å and deg), and Vibrational Frequencies[a] (cm⁻¹) of D_{2h} $(NH_4)_2$

SCF/6-31++G**		MP2(full)/6-31++G**
$E_{SCF} = -113.380\,926$ au		$E_{MP2(full)} = -113.811\,154$
$R_{NN} = 4.1809$		$R_{NN} = 3.7543$
$R_{NH_f} = 1.0226$		$R_{NH_f} = 1.0446$
$R_{NH_t} = 1.0158$		$R_{NH_t} = 1.0332$
$\theta(H_tNH_f) = 109.63°$		$\theta(H_tNH_f) = 109.76$
ZPE = 64 kcal/mol		
$\nu_1(a_g) = 3549$	$\nu_{13}(b_{2g}) = 113$	
$\nu_2(a_g) = 3364$	$\nu_{14}(b_{3g}) = 1798$	
$\nu_3(a_g) = 1782$	$\nu_{15}(b_{1u}) = 3375$	
$\nu_4(a_g) = 1520$	$\nu_{16}(b_{1u}) = 1501$	
$\nu_5(a_g) = 125$	$\nu_{17}(b_{1u}) = 84$	
$\nu_6(a_u) = 1802$	$\nu_{18}(b_{2u}) = 3619$	
$\nu_7(a_u) = 53$	$\nu_{19}(b_{2u}) = 1518$	
$\nu_8(b_{1g}) = 3620$	$\nu_{20}(b_{2u}) = 77i$	
$\nu_9(b_{1g}) = 1566$	$\nu_{21}(b_{3u}) = 3550$	
$\nu_{10}(b_{1g}) = 80i$	$\nu_{22}(b_{3u}) = 3359$	
$\nu_{11}(b_{2g}) = 3429$	$\nu_{23}(b_{3u}) = 1791$	
$\nu_{12}(b_{2g}) = 1503$	$\nu_{24}(b_{3u}) = 1544$	

[a] All frequencies listed $\nu_1-\nu_{24}$ were obtained at the SCF level.

TABLE VI: Energies (au), Geometries (Å and deg), and Vibrational Frequencies (cm⁻¹) of D_{2d} $(NH_4)_2$

SCF/6-31++G**	SCF/6-31++G**	SCF/6-31++G**
$E_{SCF} = -113.380\,70$	$\nu_3(a_1) = 1783$	$\nu_{12}(b_2) = 1542$
$R_{NN} = 4.1843$	$\nu_4(a_1) = 1523$	$\nu_{13}(e) = 3614$
$R_{NH_f} = 1.0219$	$\nu_5(a_1) = 124$	$\nu_{14}(e) = 3422$
$R_{NH_t} = 1.0161$	$\nu_6(a_2) = 1802$	$\nu_{15}(e) = 1540$
$\theta(H_fNH_f) = 106.30°$	$\nu_7(b_1) = 1799$	$\nu_{16}(e) = 1503$
$\theta(H_tNH_t) = 111.45°$	$\nu_8(b_1) = 45i$	$\nu_{17}(e) = 92$
ZPE = 64 kcal/mol	$\nu_9(b_2) = 3546$	$\nu_{18}(e) = 88i$
$\nu_1(a_1) = 3551$	$\nu_{10}(b_2) = 3365$	
$\nu_2(a_1) = 3380$	$\nu_{11}(b_2) = 1791$	

TABLE VII: Energies (au), Geometries (Å and deg), and Vibrational Frequencies[a] (cm⁻¹) of Head-On D_{3d} $(NH_4)_2$

SCF/6-31++G**		MP2(full)/6-31++G**
$E_{SCF} = -113.380\,28$		$E_{MP2(full)} = -113.809\,95$
$R_{NN} = 4.4247$		$R_{NN} = 4.1028$
$R_{H_fH_f} = 2.3541$		$R_{H_fH_f} = 1.9550$
$R_{NH_f} = 1.0353$		$R_{NH_f} = 1.0739$
$R_{NH_t} = 1.0147$		$R_{NH_t} = 1.0309$
$\theta(H_tNH_f) = 108.38°$		$\theta(H_fNH_t) = 108.89°$
ZPE = 63 kcal/mol		
$\nu_1(a_{1g}) = 3487.2$	$\nu_9(e_g) = 3630.4$	
$\nu_2(a_{1g}) = 3053.7$	$\nu_{10}(e_g) = 1798.6$	
$\nu_3(a_{1g}) = 1489.6$	$\nu_{11}(e_g) = 1556.6$	
$\nu_4(a_{1g}) = 145.9$	$\nu_{12}(e_g) = 75.8$	
$\nu_5(a_{1u}) = 16.6i$	$\nu_{13}(e_u) = 3629.9$	
$\nu_6(a_{2u}) = 3484.3$	$\nu_{14}(e_u) = 1787.7$	
$\nu_7(a_{2u}) = 3157.4$	$\nu_{15}(e_u) = 1509.4$	
$\nu_8(a_{2u}) = 1493.5$	$\nu_{16}(e_u) = 43.8i$	

[a] All frequencies listed $\nu_1-\nu_{16}$ were obtained at the SCF level.

certainly accessible within zero-point motions of the nuclei. The geometries, vibrational frequencies, and energies of each of these are given in Tables IV–VII.

E. Ionization Potential of $(NH_4)_2$ and Nature of the Rydberg Bond. At the equilibrium geometry of $(NH_4)_2$, we computed the
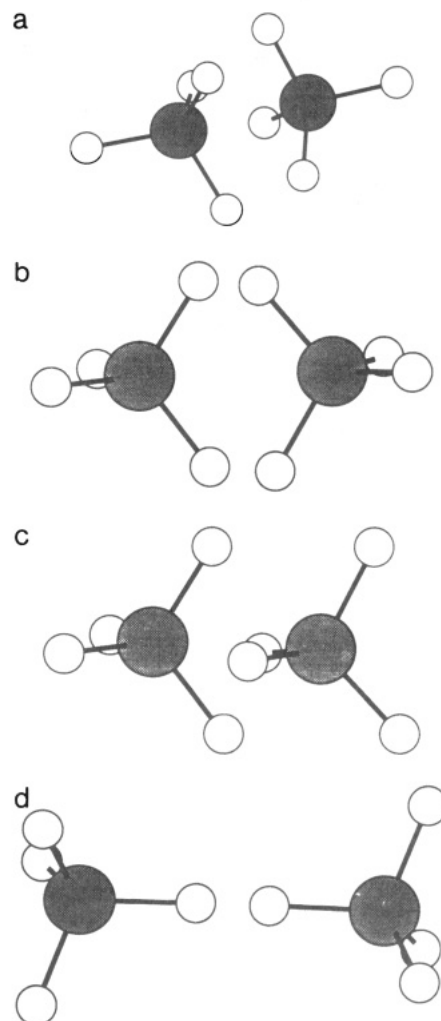

Figure 3. (a) Staggered D_{3d} structure of $(NH_4)_2$ for $^1A_{1g}$ ground state. The bond lengths and angles are given in Table IV. (b) D_{2h} structure of $(NH_4)_2$ for ^1A_g ground state. The bond lengths and angles are given in Table V. (c) D_{2d} structure of $(NH_4)_2$ for $^1A_1$ ground state. The bond lengths and angles are given in Table VI. (d) Head-on D_{3d} structure of $(NH_4)_2$ for $^1A'_{1g}$ ground state. The bond lengths and angles are given in Table VII.

TABLE VIII: ZPE-Corrected Adiabatic Ionization Energies (eV) and Dissociation Energies (kcal/mol) for[a] $(NH_4)_2^+$

$(NH_4)_2 \rightarrow (NH_4)_2^+$	$(NH_4)_2^+ \rightarrow NH_4 + NH_4^+$
$\Delta E(SCF) = 3.0$	$\Delta E(SCF) = 19.0$
$\Delta E(MP2) = 3.8$	$\Delta E(MP2) = 20.1$
$\Delta E(MP3) = 3.9$	$\Delta E(MP3) = 19.8$
$\Delta E(MP4) = 4.0$	$\Delta E(MP4) = 20.0$
$\Delta E(QCISD(T)) = 4.0$	$\Delta E(QCISD)(T)) = 19.8$
$\Delta E(QCISD(T) + ZPE) = 3.9$	$\Delta E(QCISD(T) + ZPE) = 19.4$

[a] All energies obtained with the 6-31++G** basis set.

vertical ionization potential IP of $(NH_4)_2$ and obtained 3.5 eV at the Koopmans' theorem level, and 3.5 eV (PUSCF), 4.2 eV (PMP2 and PMP3), and 4.3 eV (PMP4) at correlated levels. The adiabatic IP of $(NH_4)_2$ was also computed by carrying out a full geometry optimization of the $(NH_4)_2^+$ cation's geometry; IP values of 3.8–4.0 eV were obtained at levels of correlation as shown in Table VIII.

The IP of the NH₄ monomer calculated within this same atomic orbital basis (at its equilibrium geometry) ranges from 4.1 eV at the Koopmans' level to 4.5 eV at the ZPE-corrected MP2–MP4 and QCI levels. The fact that the IP of NH₄ exceeds that of $(NH_4)_2$ by ca. 0.5 eV implies that the dissociation energy of the $(NH_4)_2^+$ cation is ca. 0.5 eV *larger* than that of the neutral $(NH_4)_2$ even though the nominal bond orders of the cation and neutral are 1/2 and 1, respectively. This somewhat anomalous situation

TABLE IX: Energies (au), Geometries (Å and deg), and Vibrational Frequencies (cm^{-1}) of Minimum-Energy Head-On D_{3d} Structure of $(NH_4)_2^+$

| SCF/6-31++G**	MP2(full)/6-31++G**	MP2(full)/6-31++G**
E_{SCF} = -113.270 75	$E_{MP2(full)}$ = -113.670 24	E_{PUHF} = -113.268 92
R_{NN} = 4.7775	R_{NN} = 4.4581	E_{PMP2} = -113.662 43
R_{NH_f} = 1.0365	R_{NH_f} = 1.0653	E_{PMP3} = -113.690 30
R_{NH_t} = 1.0107	R_{NH_t} = 1.0225	E_{PMP4} = -113.702 59
$\theta(H_tNH_f)$ = 109.00°	$\theta(H_tNH_f)$ = 109.17°	E_{QCISD} = -113.696 04
ZPE = 65 kcal/mol	ZPE = 61 kcal/mol	$E_{QCISD(T)}$ = -113.704 46
$\nu_1(a_{1g})$ = 3586.0	$\nu_1(a_{1g})$ = 3413.4	
$\nu_2(a_{1g})$ = 3036.0	$\nu_2(a_{1g})$ = 2558.4	
$\nu_3(a_{1g})$ = 1542.3	$\nu_3(a_{1g})$ = 1431.8	
$\nu_4(a_{1g})$ = 108.7	$\nu_4(a_{1g})$ = 134.8	
$\nu_5(a_{1u})$ = 10.8	$\nu_5(a_{1u})$ = 15.2	
$\nu_6(a_{2u})$ = 3591.6	$\nu_6(a_{2u})$ = 3414.8	
$\nu_7(a_{2u})$ = 3100.5	$\nu_7(a_{2u})$ = 2666.4	
$\nu_8(a_{2u})$ = 1541.9	$\nu_8(a_{2u})$ = 1436.8	
$\nu_9(e_g)$ = 3720.5	$\nu_9(e_g)$ = 3573.9	
$\nu_{10}(e_g)$ = 1826.1	$\nu_{10}(e_g)$ = 1713.5	
$\nu_{11}(e_g)$ = 1594.2	$\nu_{11}(e_g)$ = 1488.3	
$\nu_{12}(e_g)$ = 235.9	$\nu_{12}(e_g)$ = 268.1	
$\nu_{13}(e_u)$ = 3720.7	$\nu_{13}(e_u)$ = 3574.1	
$\nu_{14}(e_u)$ = 1815.1	$\nu_{14}(e_u)$ = 1699.2	
$\nu_{15}(e_u)$ = 1538.5	$\nu_{15}(e_u)$ = 1406.0	
$\nu_{16}(e_u)$ = 186.6	$\nu_{16}(e_u)$ = 195.6	
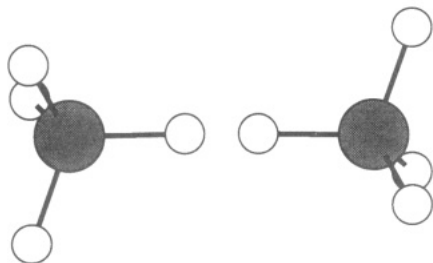
Figure 4. D_{3d} minimum-energy structure of $(NH_4)_2^+$ cation. The bond lengths and angles are given in Table IX.

occurs also in the Li_2, Li_2^+, and Li_2^- species, where the dissociation energies[12] are 1.0, 1.3, and 1.3 eV and the bond orders are 1, 1/2, and 1/2, respectively. The similarity between $(NH_4)_2$ and the isoelectronic alkali metal dimer Na_2 is also worth noting. The respective dissociation energies (0.72 eV for Na_2 and 0.4 eV for $(NH_4)_2$), IPs (4.9 vs 4.0 eV), and vibrational frequencies (159 vs 129 cm^{-1}) are quite similar.

F. Bonding in $(NH_4)_2^+$. The most stable geometry of the $(NH_4)_2^+$ cation is of the "head-on" variety; its geometry and vibrational frequencies are given in Table IX and it is depicted in Figure 4. This structure is very different from that of the neutral $(NH_4)_2$, although both are quite "floppy" species. The adiabatic $(NH_4)_2^+ \rightarrow NH_4 + (NH_4)^+$ energy data presented in Table VIII clearly indicate that a moderately strong bond exists in the $(NH_4)_2^+$ Rydberg dimer cation. In fact, as expected based on differences in the IPs of $(NH_4)_2$ and NH_4, the ca. 20 kcal/mol bond energy of the cation is 10-12 kcal/mol *stronger* than the bond energy in the neutral $(NH_4)_2$ dimer.

IV. Summary

The work described here represents our first efforts in the area of *Rydberg bonding* and the study of *Rydberg clusters*. In this study of the $(NH_4)_2$ Rydberg dimer, our primary observations are as follows:

1. $(NH_4)_2 \rightarrow 2NH_4$ is predicted to be endothermic by 7.5-9.7 kcal/mol, but an SCF-level treatment is not adequate to reach this conclusion. Treatment of electron correlation is essential to obtain even a qualitatively correct description of this Rydberg bond.

2. $(NH_4)_2 \rightarrow 2NH_3 + H_2$ is predicted to be exothermic by 86-89 kcal/mol depending upon the correlated treatment that is applied to the problem.

3. $(NH_4)_2$ possesses four very low frequency (i.e., 28-121 cm^{-1}) internal vibrational modes and is a very "loose" molecule that samples D_{3d} structures easily with zero-point motions.

4. The dissociation energy of the $(NH_4)_2^+$ cation into NH_4 + NH_4^+ (20 kcal/mol) is larger than that of the neutral $(NH_4)_2$ although the respective bond orders are 1/2 and 1.

5. It appears that Rydberg orbitals are indeed capable of forming weak chemical bonds between Rydberg fragment moieties.

It is hoped that the results and predictions discussed here will stimulate experimental chemists to explore routes through which Rydberg-bonded species might be synthesized (even if briefly and in the gas phase). It may be that attractive interactions, induced by electron density moving into regions between near-neighbor NH_4^+ moieties, may produce signatures in the phonon spectrum of ammonium halide crystals (i.e., by forming $(NH_4)_2^+$ bonding interactions). Of course, this remains speculation until experimental groups observe such effects of Rydberg bonding.

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