

Theoretical search for large Rydberg molecules: NH_3CH_3 , $\text{NH}_2(\text{CH}_3)_2$, $\text{NH}(\text{CH}_3)_3$, and $\text{N}(\text{CH}_3)_4$

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On the basis of *ab initio* calculations, four new large metastable Rydberg molecules: NH_3CH_3 , $\text{NH}_2(\text{CH}_3)_2$, $\text{NH}(\text{CH}_3)_3$, and $\text{N}(\text{CH}_3)_4$ are predicted to exist. All of these neutral species possess high-symmetry local minima but are not thermodynamically stable with respect to loss of H or CH_3 . Because they have pronounced barriers on the dissociation pathways, they should be metastable. The dissociation barriers for $\text{NH}_n(\text{CH}_3)_{4-n}$ decomposing to $\text{NH}_{n-1}(\text{CH}_3)_{4-n} + \text{H}$ are smaller than for dissociation into $\text{NH}_n(\text{CH}_3)_{4-n-1} + \text{CH}_3$. Thus, the lifetime of $\text{N}(\text{CH}_3)_4$ should be much longer than that of NH_4 due to the larger dissociation barrier and the heavier mass of the departing CH_3 species.

I. INTRODUCTION

Small Rydberg molecules such as NH_4 have been observed experimentally¹⁻⁶ and studied theoretically.⁷⁻¹³ However, species larger than NH_4 have not been established. Rydberg species such as NH_4 can be viewed as consisting of a closed-shell cation "core" (e.g., NH_4^+) with another electron attached to it in a Rydberg orbital. For NH_4 , this orbital is referred to as a "3s" orbital because it has two radial nodes and thus is similar to the 3s orbital of the isoelectronic ten-electron Na^+ ion core.

Tetrahedral NH_4 is a local minimum on its potential energy surface and is separated from the dissociation products NH_3 and H by a small barrier. As a result, 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 $\text{ND}_3 + \text{D}$. In this article, we study the following molecules derived from NH_4 by replacing H by CH_3 : NH_3CH_3 , $\text{NH}_2(\text{CH}_3)_2$, $\text{NH}(\text{CH}_3)_3$, and $\text{N}(\text{CH}_3)_4$. We expect these molecules to be metastable Rydberg species, and we anticipate that the $\text{N}(\text{CH}_3)_4$ molecule may have a significantly longer lifetime than ND_4 due to the much larger mass of the tunneling group, CH_3 .

II. ATOMIC ORBITAL BASIS SETS AND TREATMENT OF ELECTRON CORRELATION

The geometries of NH_4^+ , NH_4 , NH_3CH_3^+ , NH_3CH_3 , $\text{NH}_2(\text{CH}_3)_2^+$, $\text{NH}_2(\text{CH}_3)_2$, $\text{NH}(\text{CH}_3)_3^+$, $\text{NH}(\text{CH}_3)_3$, $\text{N}(\text{CH}_3)_4^+$, and $\text{N}(\text{CH}_3)_4$ were optimized employing analytical energy gradient methods¹⁴ with polarized split-valence basis sets augmented by diffuse s and p functions [this basis is denoted self consistent field (SCF)/6-31++G**] (Refs. 15 and 16), and NH_4^+ , NH_4 , NH_3CH_3^+ , NH_3CH_3 , $\text{NH}_2(\text{CH}_3)_2^+$, and $\text{NH}_2(\text{CH}_3)_2$ were optimized at correlated second-order Møller-Plesset perturbation theory MP2(full) level using unrestricted Hartree-Fock (denoted USCF) and unrestricted second-order MP theory [denoted UMP2(full)] for the open-shell species. The fundamental vibrational frequencies, normal coordinates, and zero point energies (ZPE) were calculated by standard matrix methods. The MP2(full)/6-31++G** equilib-

rium geometries for the small and SCF/6-31++G** geometries for the larger systems were used to evaluate electron correlation energies at the full fourth-order frozen-core approximation both by Møller-Plesset perturbation theory¹⁷ and by unrestricted quadratic configuration interaction including singles and doubles with approximate triples (U)QCISD(T)¹⁸ using the 6-31++G** basis set. The USCF 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 PUSCF, PMP2, PMP3, and PMP4.¹⁹ Only modest spin contamination ($\langle S^2 \rangle = 0.7507$) was found for the doublet states of the neutral $\text{NH}_n(\text{CH}_3)_{4-n}$ species. The GAUSSIAN 90 program suite²⁰ was used to perform all of the calculations whose results are discussed here.

III. FINDINGS

A. NH_4^+ and NH_4

The calculated geometry of the tetrahedral NH_4^+ cation [$R(\text{N-H}) = 1.022$ Å] given in Table I agrees well with experimental data for NH_4^+ in the gas phase [$R(\text{N-H}) = 1.021 + 0.002$ Å (Ref. 21)] and with the best *ab initio* data [$R(\text{N-H}) = 1.025$ Å (Ref. 11)]. Our calculated harmonic frequency $\nu_3 = 3596$ cm^{-1} is also in reasonably good agreement with experimental data $\nu_3 = 3343.1$ cm^{-1} ,²² and $\nu_3 = 3342.54$ cm^{-1} ,²³ the difference being mainly due to anharmonicity. Our calculated proton affinity of NH_3 [206.3 kcal/mol at the QCISD(T)+ZPE level] agrees with the experimental value 204.0 kcal/mol,²⁴ and with the best *ab initio* data 205.4 kcal/mol.²⁵

The neutral NH_4 molecule was found to be a local minimum [its dissociation barrier is 9.0 kcal/mol at the QCISD(T) level] as was found earlier.¹⁰⁻¹² This radical lies higher than the dissociation products $\text{NH}_3 + \text{H}$ at our highest level treatment by 2.5 kcal/mol. It is important to note that in the absence of the ZPE correction we would predict NH_4 to be more stable than $\text{NH}_3 + \text{H}$. The other dissociation products, $\text{NH}_2 + \text{H}_2$ are also lower in energy than NH_4 , but by only 0.7 kcal/mol at the same level as quoted above for the $\text{NH}_3 + \text{H}$ path (see Table II). Our ionization

TABLE I. Calculated molecular properties of NH_4^+ and NH_4 .

$\text{NH}_4^+(T_d, ^1A_1)$	$\text{NH}_4(T_d, ^2A_1)$
$E_{\text{SCF}} = -56.546\ 044$	$E_{\text{USCF}} = -56.693\ 664$
$R(\text{N-H}) = 1.012\ \text{\AA}$	$R(\text{N-H}) = 1.020\ \text{\AA}$
$\nu_1(a_1) = 3574$	$\nu_1(a_1) = 3368$
$\nu_2(e) = 1853$	$\nu_2(e) = 1787$
$\nu_3(t_2) = 3716$	$\nu_3(t_2) = 3456$
$\nu_4(t_2) = 1611$	$\nu_4(t_2) = 1490$
ZPE = 33.3	ZPE = 31.1
	$\langle S^2 \rangle = 0.751$
MP2(full)/6-31++G**	MP2(full)/6-31++G**
$E_{\text{MP2}} = -56.738\ 665$	$E_{\text{UMP2}} = -56.899\ 695$
$R(\text{N-H}) = 1.022\ \text{\AA}$	$R(\text{N-H}) = 1.038\ \text{\AA}$
$\nu_1(a_1) = 3438$	$\nu_1(a_1) = 3115$
$\nu_2(e) = 1763$	$\nu_2(e) = 1648$
$\nu_3(t_2) = 3596$	$\nu_3(t_2) = 3193$
$\nu_4(t_2) = 1526$	$\nu_4(t_2) = 1371$
ZPE = 31.9	ZPE = 28.7
QCISD(T)/6-31++G**	QCISD(T)/6-31++G**
$E_{\text{SCF}} = -56.545\ 691$	$E_{\text{PUSCF}} = -56.692\ 954$
$E_{\text{MP2}} = -56.734\ 616$	$E_{\text{PMP2}} = -56.895\ 861$
$E_{\text{MP3}} = -56.749\ 124$	$E_{\text{MP3}} = -56.909\ 651$
$E_{\text{MP4}} = -56.754\ 479$	$E_{\text{MP4}} = -56.916\ 466$
$E_{\text{QCISD}} = -56.751\ 831$	$E_{\text{QCISD}} = -56.912\ 732$
$E_{\text{QCISD(T)}} = -56.755\ 341$	$E_{\text{QCISD(T)}} = -56.917\ 542$

potential (IP) for NH_4 is 4.6 eV (104.9 kcal/mol), which is even lower than the IPs of Li (5.39 eV) and Na (5.14 eV).

Although electron correlation is very important for the accurate estimation of the dissociation energies of NH_4^+ and NH_4 , ZPE corrections are found to contribute more to the dissociation barriers than does electron correlation (see Table III). Because we find good agreement between our data for NH_4^+ and NH_4 and the available experimental and the best theoretical data, we can anticipate that our results on the larger systems studied here will have similar accuracy.

B. NH_3CH_3

The NH_3CH_3^+ cation was found to have its global minimum at a staggered $C_{3v}(^1A_1)$ structure detailed in Table IV. The calculated proton affinity (Table II) of NH_2CH_3 is 216.7 kcal/mol which is 2.6 kcal/mol higher than that given in Ref. 24. As expected, the proton affinity increases when one CH_3 group replaces H in NH_3 . Our calculated CH_3^+ affinity of ammonia is 103.0 kcal/mol at the same level of theory (see Table II).

The neutral NH_3CH_3 molecule is a local minimum (i.e., has no imaginary vibrational frequencies) also at a staggered $C_{3v}(^2A_1)$ structure. The corresponding eclipsed $C_{3v}(^2A_1)$ structure is a saddle point for internal rotation (with a barrier of 2.1 kcal/mol). The optimized geometries for neutral CH_3NH_3 and the CH_3NH_3^+ cation are very similar which is much like the situation for NH_4 and NH_4^+ (see Tables I and IV), and correlation corrections to the

TABLE II. Calculated dissociation energies (kcal/mol) at MP2(full)/6-31++G** level.

Reaction	PUSCF/6	PMP2/6-31++G**	PMP3/6-31++G**	PMP4/6-31++G**	PMP4/6-31++G** + ZPE	QCISD(T)/6-31++G**	QCISD(T)/6-31++G** + ZPE	EXPT.
	-31++G**							
1. $\text{NH}_4 \rightarrow \text{NH}_3 + \text{H}$	-5.0	+2.1	+3.3	+3.7	-2.8	+4.0	-2.5	
2. $\text{NH}_4 \rightarrow \text{NH}_2 + \text{H}_2$	-7.7	+12.6	+8.6	+9.0	-0.8	+9.1	-0.7	
3. $\text{NH}_4 \rightarrow \text{NH}_4^+$	+92.6	+101.2	+100.8	+101.7	+104.9	+101.7	+104.9	
4. $\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$	+216.4	+214.7	+216.4	+215.8	+206.1	+216.0	+206.3	+204.0
5. $\text{NH}_3\text{CH}_3 \rightarrow \text{NH}_3 + \text{CH}_3$	-32.5	-17.1	-19.3	-17.8	-24.6			
6. $\text{NH}_3\text{CH}_3 \rightarrow \text{NH}_2\text{CH}_3 + \text{H}$	-4.6	+2.5	+3.7	+4.2	-3.8			
7. $\text{NH}_3\text{CH}_3 \rightarrow \text{NH}_2 + \text{CH}_4$	-34.3	-12.9	-17.8	-16.1	-23.0			
8. $\text{NH}_3\text{CH}_3 \rightarrow \text{NHCH}_3 + \text{H}_2$	-12.3	+6.2	+2.3	+2.6	-7.4			
9. $\text{NH}_3\text{CH}_3 \rightarrow \text{NH}_3\text{CH}_3^+$	+81.3	+91.1	+90.4	+91.6	+93.2			
10. $\text{NH}_3\text{CH}_3^+ \rightarrow \text{NH}_2\text{CH}_3 + \text{H}^+$	+227.8	+225.2	+227.1	+226.3	+216.7			+214.1
11. $\text{NH}_3\text{CH}_3^+ \rightarrow \text{NH}_3 + \text{CH}_3^+$	+94.9	+111.7	+109.6	+110.2	+103.0			
12. $\text{NH}_2(\text{CH}_3)_2 \rightarrow \text{NH}_2\text{CH}_3 + \text{CH}_3$	-31.8	-14.9	-17.5	-15.7	-22.6			
13. $\text{NH}_2(\text{CH}_3)_2 \rightarrow \text{NH}(\text{CH}_3)_2 + \text{H}$	-5.7	+1.0	+2.3	+2.8	-5.6			
14. $\text{NH}_2(\text{CH}_3)_2 \rightarrow \text{N}(\text{CH}_3)_2 + \text{H}_2$	-16.3	-0.9	-4.8	-4.4	-15.5			
15. $\text{NH}_2(\text{CH}_3)_2 \rightarrow \text{NHCH}_3 + \text{CH}_4$	-40.2	-17.5	-22.8	-20.9	-26.6			
16. $\text{NH}_2(\text{CH}_3)_2 \rightarrow \text{NH}_2(\text{CH}_3)_2^+$	+72.2	+82.1	+81.2	+82.6	+84.0			
16. $\text{NH}_2(\text{CH}_3)_2^+ \rightarrow \text{NH}(\text{CH}_3)_2 + \text{H}^+$	+235.9	+232.7	+234.9	+233.9	+224.0			+220.6
17. $\text{NH}_2(\text{CH}_3)_2^+ \rightarrow \text{NH}_2\text{CH}_3 + \text{CH}_3^+$	+105.0	+123.0	+120.6	+121.3	+110.0			
18. $\text{NH}(\text{CH}_3)_3 \rightarrow \text{NH}(\text{CH}_3)_2 + \text{CH}_3$	-32.9				(-39.7) ^a			
19. $\text{NH}(\text{CH}_3)_3 \rightarrow \text{N}(\text{CH}_3)_3 + \text{H}$	-9.0				(-17.5) ^a			
20. $\text{NH}(\text{CH}_3)_3 \rightarrow \text{N}(\text{CH}_3)_2 + \text{CH}_4$	-44.4				(-50.7) ^a			
21. $\text{NH}(\text{CH}_3)_3 \rightarrow \text{NH}(\text{CH}_3)_3^+$	+64.3				(+65.7) ^a			
22. $\text{NH}(\text{CH}_3)_3^+ \rightarrow \text{N}(\text{CH}_3)_3 + \text{H}^+$	+240.4				(+230.5) ^a			+225.1
23. $\text{NH}(\text{CH}_3)_3^+ \rightarrow \text{NH}(\text{CH}_3)_2 + \text{CH}_3^+$	+111.5				(+104.5) ^a			
24. $\text{N}(\text{CH}_3)_4 \rightarrow \text{N}(\text{CH}_3)_3 + \text{CH}_3$	-41.2				(-48.8) ^a			
25. $\text{N}(\text{CH}_3)_4^+ \rightarrow \text{N}(\text{CH}_3)_3 + \text{CH}_3^+$	+114.0				(+100.6) ^a			
25. $\text{N}(\text{CH}_3)_4 \rightarrow \text{N}(\text{CH}_3)_4^+$	+53.5				(+54.0) ^a			

^aSCF/6-31++G** + ZPE level.

TABLE III. Calculated dissociation barriers (kcal/mol).

Reaction	USCF/6-31++G**	PMP2/6-31++G**	PMP3/6-31++G**	PMP4/6-31++G**	PMP4/6-31++G**+ZPE	OCISD(T)/6-31++G**	OCISD(T)/6-31++G**+ZPE
1. $\text{NH}_4 \rightarrow \text{NH}_3 + \text{H}$	16.0	14.2	15.1	14.6	9.4	14.2	9.0
2. $\text{NH}_3\text{CH}_3 \rightarrow \text{NH}_3 + \text{CH}_3$	20.4	14.5	15.6	13.4	10.3		
3. $\text{NH}_3\text{CH}_3 \rightarrow \text{NH}_2\text{CH}_3 + \text{H}$	14.3	12.1	13.1	12.6	6.8		
4. $\text{NH}_2(\text{CH}_3)_2 \rightarrow \text{NH}_2\text{CH}_3 + \text{CH}_3$	22.5	16.8	18.0	17.1	13.5		
5. $\text{NH}_2(\text{CH}_3)_2 \rightarrow \text{NH}(\text{CH}_3)_2 + \text{H}$	11.5	8.6	9.6	9.2	3.2		
6. $\text{NH}(\text{CH}_3)_3 \rightarrow \text{N}(\text{CH}_3)_3 + \text{H}$	7.3						

geometries are not very large [$\Delta R(\text{C}-\text{N})=0.01 \text{ \AA}$, $\Delta R(\text{N}-\text{H})=0.02 \text{ \AA}$, $\Delta R(\text{C}-\text{H})=0.01 \text{ \AA}$, $\Delta \angle \text{CNH}=4^\circ$, $\Delta \angle \text{NCH}=0.5^\circ$].

For the neutral NH_3CH_3 molecule, four dissociation pathways are possible: (i) $\text{NH}_3 + \text{CH}_3$ ($D_0^0 = -24.6 \text{ kcal/mol}$); (ii) $\text{NH}_2\text{CH}_3 + \text{H}$ ($D_0^0 = -3.8 \text{ kcal/mol}$); (iii) NHCH_3 ($^2A'$) + H_2 ($D_0^0 = -7.4 \text{ kcal/mol}$); and (iv) NH_2 (2A_1) + CH_4 ($D_0^0 = -23.0 \text{ kcal/mol}$), with all of these data referring to the PMP4SDTQ+ZPE level. It follows that the neutral CH_3NH_3 molecule is unstable with respect to loss of H, H_2 , CH_3 , or CH_4 . We have located dissociation barriers on the $\text{CH}_3\text{NH}_3 \rightarrow \text{CH}_3\text{NH}_2 + \text{H}$ and the $\text{CH}_3\text{NH}_3 \rightarrow \text{CH}_3 + \text{NH}_3$ pathways (see Table III). However, the lifetime of CH_3NH_3 will be determined by its dissociation into $\text{NH}_2\text{CH}_3 + \text{H}$ because this dissociation barrier is lower and the tunneling mass of H is smaller. Because the barrier for loss of H is less than in NH_4 , the

lifetime of the NH_3CH_3 radical should be even shorter than that of NH_4 (10^{-6} s).

Finally, our calculated ionization potential for NH_3CH_3 is 3.9 eV (93.2 kcal/mol) which is lower than the IP of NH_4 and lower than the IPs of all alkali metal atoms (the lowest IP among these atoms is for Cs:IP=3.89 eV).

C. $\text{NH}_2(\text{CH}_3)_2$

The $\text{NH}_2(\text{CH}_3)_2^+$ cation has its minimum energy structure at a staggered $C_{2v}(^1A_1)$ geometry (see Table V). The calculated proton affinity (see Table II) of $\text{NH}(\text{CH}_3)_2$ is 224.0 kcal/mol (at the MP4SDTQ+ZPE level) which is within 3 kcal/mol with the recommended experimental value of 220.6 kcal/mol.²⁴ The second CH_3 group in $\text{NH}(\text{CH}_3)_2$ thus increases the proton affinity (compared to NH_2CH_3) which is in agreement with experimental obser-

TABLE IV. Calculated molecular properties of NH_3CH_3^+ and NH_3CH_3 .

NH_3CH_3^+	NH_3CH_3^+	NH_3CH_3	NH_3CH_3
$C_{3v} \ ^1A_1$	$C_{3v} \ ^1A_1$	$C_{3v} \ ^2A_1$	$C_{3v} \ ^2A_1$
$E_{\text{SCF}} = -95.589 \ 86$	$E_{\text{MP2}} = -95.927 \ 63$	$E_{\text{SCF}} = -95.719 \ 49$	$E_{\text{MP2}} = -96.072 \ 63$
$R(\text{N}-\text{C}) = 1.506 \ \text{\AA}$	$R(\text{N}-\text{C}) = 1.506 \ \text{\AA}$	$R(\text{N}-\text{C}) = 1.490 \ \text{\AA}$	$R(\text{N}-\text{C}) = 1.498 \ \text{\AA}$
$R(\text{N}-\text{H}) = 1.010 \ \text{\AA}$	$R(\text{N}-\text{H}) = 1.022 \ \text{\AA}$	$R(\text{N}-\text{H}) = 1.020 \ \text{\AA}$	$R(\text{N}-\text{H}) = 1.040 \ \text{\AA}$
$R(\text{C}-\text{H}) = 1.079 \ \text{\AA}$	$R(\text{C}-\text{H}) = 1.083 \ \text{\AA}$	$R(\text{C}-\text{H}) = 1.079 \ \text{\AA}$	$R(\text{C}-\text{H}) = 1.084 \ \text{\AA}$
$\angle \text{HNC} = 111.5$	$\angle \text{HNC} = 111.5$	$\angle \text{HNC} = 112.1$	$\angle \text{HNC} = 111.7$
$\angle \text{HCN} = 108.2$	$\angle \text{HCN} = 108.2$	$\angle \text{HCN} = 108.4$	$\angle \text{HCN} = 108.1$
$\angle \text{HNH} = 107.4$	$\angle \text{HNH} = 107.4$	$\angle \text{HNH} = 106.7$	$\angle \text{HNH} = 107.1$
$\angle \text{HCH} = 110.7$	$\angle \text{HCH} = 110.8$	$\angle \text{HCH} = 110.5$	$\angle \text{HCH} = 110.8$
		$\langle S^2 \rangle = 0.751$	
$\nu_1(a_1) = 3627$		$\nu_1(a_1) = 3409$	$\nu_1(a_1) = 3167$
$\nu_2(a_1) = 3249$		$\nu_2(a_1) = 3242$	$\nu_2(a_1) = 3108$
$\nu_3(a_1) = 1669$		$\nu_3(a_1) = 1582$	$\nu_3(a_1) = 1461$
$\nu_4(a_1) = 1588$		$\nu_4(a_1) = 1561$	$\nu_4(a_1) = 1429$
$\nu_5(a_1) = 988$		$\nu_5(a_1) = 1028$	$\nu_5(a_1) = 987$
$\nu_6(a_2) = 303$		$\nu_6(a_2) = 299$	$\nu_6(a_2) = 306$
$\nu_7(e) = 3727$		$\nu_7(e) = 3414$	$\nu_7(e) = 3289$
$\nu_8(e) = 3362$		$\nu_8(e) = 3344$	$\nu_8(e) = 3093$
$\nu_9(e) = 1803$		$\nu_9(e) = 1702$	$\nu_9(e) = 1559$
$\nu_{10}(e) = 1617$		$\nu_{10}(e) = 1618$	$\nu_{10}(e) = 1538$
$\nu_{11}(e) = 1383$		$\nu_{11}(e) = 1370$	$\nu_{11}(e) = 1278$
$\nu_{12}(e) = 976$		$\nu_{12}(e) = 966$	$\nu_{12}(e) = 906$
ZPE = 53.1		ZPE = 51.4	ZPE = 48.3
	MP4SDTQ/ 6-31++G**		MP4SDTQ/ 6-31++G**
	$E_{\text{MP2}} = -95.918 \ 36$		$E_{\text{PMP2}} = -96.063 \ 55$
	$E_{\text{MP3}} = -95.944 \ 52$		$E_{\text{PMP3}} = -96.088 \ 56$
	$E_{\text{MP4}} = -95.955 \ 96$		$E_{\text{PMP4}} = -96.101 \ 92$

TABLE V. Calculated molecular properties of $\text{NH}_2(\text{CH}_3)_2^+$ and $\text{NH}_2(\text{CH}_3)_2$.

$\text{NH}_2(\text{CH}_3)_2^+$	$\text{NH}_2(\text{CH}_3)_2^+$	$\text{NH}_2(\text{CH}_3)_2$	$\text{NH}_2(\text{CH}_3)_2$
SCF/6-31++G**	MP2(full)/6-31++G**	SCF/6-31++G**	MP2(full)/6-31++G**
$C_{2v} \ ^1A_1$	$C_{2v} \ ^1A_1$	$C_{2v} \ ^2A_1$	$C_{2v} \ ^2A_2$
$E_{\text{SCF}} = -134.630\ 77$	$E_{\text{MP2}} = -135.117\ 92$	$E_{\text{SCF}} = -134.745\ 84$	$E_{\text{MP2}} = -135.248\ 55$
$R(\text{C-N}) = 1.497\ \text{\AA}$	$R(\text{C-N}) = 1.500\ \text{\AA}$	$R(\text{C-N}) = 1.483\ \text{\AA}$	$R(\text{C-N}) = 1.489\ \text{\AA}$
$R(\text{N-H}) = 1.009\ \text{\AA}$	$R(\text{N-H}) = 1.023\ \text{\AA}$	$R(\text{N-H}) = 1.022\ \text{\AA}$	$R(\text{N-H}) = 1.047\ \text{\AA}$
$R(\text{C-H}') = 1.080\ \text{\AA}$	$R(\text{C-H}') = 1.084\ \text{\AA}$	$R(\text{C-H}') = 1.081\ \text{\AA}$	$R(\text{C-H}') = 1.087\ \text{\AA}$
$R(\text{C-H}'') = 1.079\ \text{\AA}$	$R(\text{C-H}'') = 1.084\ \text{\AA}$	$R(\text{C-H}'') = 1.080\ \text{\AA}$	$R(\text{C-H}'') = 1.085\ \text{\AA}$
$\angle\text{HNH} = 105.7$	$\angle\text{HNH} = 109.2$	$\angle\text{HNH} = 103.5$	$\angle\text{HNH} = 104.6$
$\angle\text{CNC} = 114.3$	$\angle\text{CNC} = 113.8$	$\angle\text{CNC} = 115.0$	$\angle\text{CNC} = 114.8$
$\angle\text{NCH}' = 108.7$	$\angle\text{NCH}' = 108.2$	$\angle\text{NCH}' = 108.1$	$\angle\text{NCH}' = 107.7$
$\angle\text{NCH}'' = 108.5$	$\angle\text{NCH}'' = 108.8$	$\angle\text{NCH}'' = 108.8$	$\angle\text{NCH}'' = 108.5$
$\angle\text{H}'\text{CH}'' = 110.4$	$\angle\text{H}'\text{CH}'' = 110.6$	$\angle\text{H}'\text{CH}'' = 110.2$	$\angle\text{H}'\text{CH}'' = 110.5$
$\angle\text{H}''\text{CH}'' = 110.4$	$\angle\text{H}''\text{CH}'' = 110.5$	$\angle\text{H}''\text{CH}'' = 110.7$	$\angle\text{H}''\text{CH}'' = 111.1$
		$\langle S^2 \rangle = 0.751$	
$\nu_1(a_1) = 3668$		$\nu_1(a_1) = 3382$	
$\nu_2(a_1) = 3349$		$\nu_2(a_1) = 3322$	
$\nu_3(a_1) = 3242$		$\nu_3(a_1) = 3228$	
$\nu_4(a_1) = 1802$		$\nu_4(a_1) = 1675$	
$\nu_5(a_1) = 1625$		$\nu_5(a_1) = 1617$	
$\nu_6(a_1) = 1607$		$\nu_6(a_1) = 1585$	
$\nu_7(a_1) = 1354$		$\nu_7(a_1) = 1354$	
$\nu_8(a_1) = 907$		$\nu_8(a_1) = 926$	
$\nu_9(a_1) = 406$		$\nu_9(a_1) = 405$	
$\nu_{10}(a_2) = 3350$		$\nu_{10}(a_2) = 3330$	
$\nu_{11}(a_2) = 1613$		$\nu_{11}(a_2) = 1608$	
$\nu_{12}(a_2) = 1502$		$\nu_{12}(a_2) = 1515$	
$\nu_{13}(a_2) = 1108$		$\nu_{13}(a_2) = 1111$	
$\nu_{14}(a_2) = 205$		$\nu_{14}(a_2) = 205$	
$\nu_{15}(b_1) = 3728$		$\nu_{15}(b_1) = 3333$	
$\nu_{16}(b_1) = 3352$		$\nu_{16}(b_1) = 3237$	
$\nu_{17}(b_1) = 1628$		$\nu_{17}(b_1) = 1621$	
$\nu_{18}(b_1) = 1383$		$\nu_{18}(b_1) = 1365$	
$\nu_{19}(b_1) = 869$		$\nu_{19}(b_1) = 849$	
$\nu_{20}(b_1) = 279$		$\nu_{20}(b_1) = 276$	
$\nu_{21}(b_2) = 3348$		$\nu_{21}(b_2) = 3327$	
$\nu_{22}(b_2) = 3240$		$\nu_{22}(b_2) = 3226$	
$\nu_{23}(b_2) = 1618$		$\nu_{23}(b_2) = 1613$	
$\nu_{24}(b_2) = 1575$		$\nu_{24}(b_2) = 1568$	
	MP4SDTQ/ 6-31++G**		MP4SDTQ/ 6-31++G**
$\nu_{25}(b_2) = 1561$	$E_{\text{SCF}} = -134.630\ 32$	$\nu_{25}(b_2) = 1546$	$E_{\text{PUSCF}} = -134.744\ 98$
$\nu_{26}(b_2) = 1157$	$E_{\text{MP2}} = -135.103\ 31$	$\nu_{26}(b_2) = 1163$	$E_{\text{PMP2}} = -135.234\ 09$
$\nu_{27}(b_2) = 1067$	$E_{\text{MP3}} = -135.140\ 32$	$\nu_{27}(b_2) = 1111$	$E_{\text{PMP3}} = -135.269\ 66$
ZPE = 72.3	$E_{\text{MP4}} = -135.158\ 37$	ZPE = 70.8	$E_{\text{PMP4}} = -135.289\ 99$

vation. The CH_3^+ affinity of NH_2CH_3 (110.0 kcal/mol) is increased as well compared to that of NH_3 .

The $\text{NH}_2(\text{CH}_3)_2$ radical is also the local minimum at a $C_{2v} (^2A_1)$ structure, which has nearly the same geometry as the $\text{NH}_2(\text{CH}_3)_2^+$ cation (see Table V). Correlation corrections to the SCF structures are not large. The $\text{NH}_2(\text{CH}_3)_2$ molecule is predicted (Table II) to be thermodynamically unstable to loss of H (-5.6 kcal/mol), H_2 (-15.5 kcal/mol), CH_3 (-22.6 kcal/mol), or CH_4 (-26.6 kcal/mol). The calculated barrier (Table III) on the $\text{NH}_2(\text{CH}_3)_2 \rightarrow \text{NH}(\text{CH}_3)_2 + \text{H}$ path is 14.3 kcal/mol (at the SCF/6-31++G** level) which is less than the corresponding values for NH_4 and NH_3CH_3 (at the same level). The barrier for $\text{NH}_2(\text{CH}_3)_2 \rightarrow \text{NH}_2\text{CH}_3 + \text{CH}_3$ dissociation (13.5 kcal/mol at PMP4/6-31++G**+ZPE level) is higher than for H atom loss and for $\text{NH}_3\text{CH}_3 \rightarrow \text{NH}_3 + \text{CH}_3$. Therefore the lifetime of $\text{NH}_2(\text{CH}_3)_2$ should be

determined by its loss of H and should be shorter than for NH_4 or NH_3CH_3 .

The ionization potential of $\text{NH}_2(\text{CH}_3)_2$ is predicted to be 3.6 eV (84.0 kcal/mol) which is lower than the IPs of NH_4 and NH_3CH_3 (see Table II).

D. $\text{NH}(\text{CH}_3)_3$

The largest species studied here, $\text{NH}(\text{CH}_3)_3$ and $\text{N}(\text{CH}_3)_4$, were studied only at the SCF/6-31++G** level, but, as we have shown above, correlation corrections contribute only weakly to the energies and geometries and are therefore unlikely to alter conclusions based on SCF level data.

The $\text{NH}(\text{CH}_3)_3^+$ cation has a global minimum at a staggered $C_{3v} (^1A_1)$ structure (see Table VI). The calculated proton affinity (240.4 kcal/mol) and CH_3^+ affinity

TABLE VI. Calculated molecular properties of $\text{NH}(\text{CH}_3)_3^+$ and $\text{NH}(\text{CH}_3)_3$.

$\text{NH}(\text{CH}_3)_3^+$	$\text{NH}(\text{CH}_3)_3$
SCF/6-31++G**	SCF/6-31++G**
$C_{3v} \ ^1A_1$	$C_{3v} \ ^2A_1$
$E_{\text{SCF}} = -173.669\ 51$	$E_{\text{SCF}} = -173.772\ 05$
$R(\text{N-H}) = 1.008\ \text{\AA}$	$R(\text{N-H}) = 1.039\ \text{\AA}$
$R(\text{C-N}) = 1.494\ \text{\AA}$	$R(\text{C-N}) = 1.481\ \text{\AA}$
$R(\text{C-H}') = 1.080\ \text{\AA}$	$R(\text{C-H}') = 1.082\ \text{\AA}$
$R(\text{C-H}'') = 1.080\ \text{\AA}$	$R(\text{C-H}'') = 1.081\ \text{\AA}$
$\angle\text{H'CN} = 108.5$	$\angle\text{H'CN} = 109.1$
$\angle\text{HNC} = 107.1$	$\angle\text{HNC} = 106.6$
$\angle\text{H''CN} = 109.0$	$\angle\text{H''CN} = 108.6$
$\angle\text{H'CH}'' = 110.1$	$\angle\text{H'CH}'' = 110.7$
$\angle\text{H''CH}'' = 110.1$	$\angle\text{H''CH}'' = 109.1$
	$\langle S^2 \rangle = 0.7504$
$\nu_1(a_1) = 3697$	$\nu_1(a_1) = 3320$
$\nu_2(a_1) = 3345$	$\nu_2(a_1) = 3226$
$\nu_3(a_1) = 3242$	$\nu_3(a_1) = 2972$
$\nu_4(a_1) = 1644$	$\nu_4(a_1) = 1644$
$\nu_5(a_1) = 1623$	$\nu_5(a_1) = 1607$
$\nu_6(a_1) = 1389$	$\nu_6(a_1) = 1379$
$\nu_7(a_1) = 848$	$\nu_7(a_1) = 858$
$\nu_8(a_1) = 484$	$\nu_8(a_1) = 479$
$\nu_9(a_2) = 3341$	$\nu_9(a_2) = 3325$
$\nu_{10}(a_2) = 1599$	$\nu_{10}(a_2) = 1595$
$\nu_{11}(a_2) = 1170$	$\nu_{11}(a_2) = 1171$
$\nu_{12}(a_2) = 197$	$\nu_{12}(a_2) = 188$
$\nu_{13}(e) = 3346$	$\nu_{13}(e) = 3322$
$\nu_{14}(e) = 3341$	$\nu_{14}(e) = 3314$
$\nu_{15}(e) = 3236$	$\nu_{15}(e) = 3216$
$\nu_{16}(e) = 1631$	$\nu_{16}(e) = 1627$
$\nu_{17}(e) = 1615$	$\nu_{17}(e) = 1606$
$\nu_{18}(e) = 1576$	$\nu_{18}(e) = 1569$
$\nu_{19}(e) = 1558$	$\nu_{19}(e) = 1532$
$\nu_{20}(e) = 1363$	$\nu_{20}(e) = 1374$
$\nu_{21}(e) = 1140$	$\nu_{21}(e) = 1140$
$\nu_{22}(e) = 1047$	$\nu_{22}(e) = 1083$
$\nu_{23}(e) = 421$	$\nu_{23}(e) = 432$
$\nu_{24}(e) = 272$	$\nu_{24}(e) = 255$
ZPE = 91.0	ZPE = 89.6

(111.5 kcal/mol) at the SCF/6-31++G** level for $\text{N}(\text{CH}_3)_3$ and $\text{NH}(\text{CH}_3)_2$, respectively, are larger than those of the molecules with one less CH_3 group (see Table II). The experimentally recommended proton affinity of $\text{N}(\text{CH}_3)_3$ is 225.1 kcal/mol.²⁴

The optimized geometrical parameters of the neutral $\text{NH}(\text{CH}_3)_3$ molecule are very close to the corresponding values of the $\text{NH}(\text{CH}_3)_3^+$ cation (see Table VI). This neutral is not thermodynamically stable with respect to loss of H, CH_3 , or CH_4 . Its dissociation barrier for decomposition into $\text{N}(\text{CH}_3)_3 + \text{H}$ is 7.3 kcal/mol which is the lowest H-atom-loss barrier in the $\text{NH}_n(\text{CH}_3)_{4-n}$ species. Finally, the calculated ionization potential of $\text{NH}(\text{CH}_3)_3$ is lower than that of $\text{NH}_2(\text{CH}_3)_2$, as expected.

E. $\text{N}(\text{CH}_3)_4$

The tetramethylammonium cation $\text{N}(\text{CH}_3)_4^+$ is also a minimum at a staggered $T_d(^1A_1)$ structure (see Table VII). The calculated CH_3^+ affinity of $\text{N}(\text{CH}_3)_3$ is 100.6 kcal/mol (at the SCF/6-31++G**+ZPE level), which

TABLE VII. Calculated molecular properties $\text{N}(\text{CH}_3)_4^+$ and $\text{N}(\text{CH}_3)_4$.

$\text{N}(\text{CH}_3)_4^+$	$\text{N}(\text{CH}_3)_4$
$T_d \ ^1A_1$	$T_d \ ^2A_1$
SCF/6-31++G**	SCF/6-31++G**
$E_{\text{SCF}} = -212.70499$	$E_{\text{SCF}} = -212.79028$
$R(\text{N-C}) = 1.496\ \text{\AA}$	$R(\text{N-C}) = 1.494\ \text{\AA}$
$R(\text{C-H}) = 1.080\ \text{\AA}$	$R(\text{C-H}) = 1.081\ \text{\AA}$
$\angle\text{HCN} = 109.0$	$\angle\text{HCN} = 108.9$
$\angle\text{HCH} = 109.9$	$\angle\text{HCH} = 110.0$
	$\langle S^2 \rangle = 0.7504$
$\nu_1(a_1) = 3247$	$\nu_1(a_1) = 3217$
$\nu_2(a_1) = 1644$	$\nu_2(a_1) = 1637$
$\nu_3(a_1) = 790$	$\nu_3(a_1) = 794$
$\nu_4(a_2) = 194$	$\nu_4(a_2) = 211$
$\nu_5(e) = 3339$	$\nu_5(e) = 3307$
$\nu_6(e) = 1616$	$\nu_6(e) = 1606$
$\nu_7(e) = 1288$	$\nu_7(e) = 1293$
$\nu_8(e) = 378$	$\nu_8(e) = 385$
$\nu_9(t_1) = 3338$	$\nu_9(t_1) = 3321$
$\nu_{10}(t_1) = 1602$	$\nu_{10}(t_1) = 1601$
$\nu_{11}(t_1) = 1173$	$\nu_{11}(t_1) = 1177$
$\nu_{12}(t_1) = 312$	$\nu_{12}(t_1) = 321$
$\nu_{13}(t_2) = 3346$	$\nu_{13}(t_2) = 3318$
$\nu_{14}(t_2) = 3235$	$\nu_{14}(t_2) = 3205$
$\nu_{15}(t_2) = 1647$	$\nu_{15}(t_2) = 1635$
$\nu_{16}(t_2) = 1578$	$\nu_{16}(t_2) = 1574$
$\nu_{17}(t_2) = 1436$	$\nu_{17}(t_2) = 1436$
$\nu_{18}(t_2) = 1027$	$\nu_{18}(t_2) = 1027$
$\nu_{19}(t_2) = 486$	$\nu_{19}(t_2) = 487$
ZPE = 109.6	ZPE = 109.1

is the largest CH_3^+ affinity in the NH_3 , NH_2CH_3 , $\text{NH}(\text{CH}_3)_2$, $\text{N}(\text{CH}_3)_3$ series.

The neutral tetramethylammonium $\text{N}(\text{CH}_3)_4$ molecule has a minimum-energy geometry with no imaginary frequencies (see Table VII) at a $T_d(^1A_1)$ structure that is similar to the cation's structure. This radical is not thermodynamically stable to loss of CH_3 (-48.8 kcal/mol). Although we were not able to locate the barrier on the $\text{N}(\text{CH}_3)_4 \rightarrow \text{N}(\text{CH}_3)_3 + \text{CH}_3$ pathway, we assume that it is not much less than that for $\text{NH}_2(\text{CH}_3)_2$ whose barrier was calculated to be 13.5 kcal/mol. If we use the latter barrier as an estimate for $\text{N}(\text{CH}_3)_4$, we should expect a much longer lifetime for $\text{N}(\text{CH}_3)_4$ than for NH_4 (because the CH_3 mass is larger than the mass of H).

IV. OVERVIEW

All of the Rydberg species studied here NH_4 , NH_3CH_3 , $\text{NH}_2(\text{CH}_3)_2$, $\text{NH}(\text{CH}_3)_3$, and $\text{N}(\text{CH}_3)_4$ possess stable local minima, and are stable to loss of an electron. The highest occupied molecular (HOMO) orbital energies of all these species are negative: -0.1506 a.u. (NH_4), -0.1335 a.u. (NH_3CH_3), -0.1204 a.u. [$\text{NH}_2(\text{CH}_3)_2$], -0.1105 a.u. [$\text{NH}(\text{CH}_3)_3$], and -0.0858 a.u. [$\text{N}(\text{CH}_3)_4$]. The geometries of the neutrals and the corresponding cations are quite similar, as is the case for the well known NH_4 Rydberg molecule and its NH_4^+ cation. These data support our claim that all of the neutral $\text{NH}_n(\text{CH}_3)_{4-n}$ species are Rydberg molecules. Further support for the Rydberg nature of these species is given in Table VIII,

TABLE VIII. LCAO-MO coefficients in the HOMO of the Rydberg $\text{NH}_n(\text{CH}_3)_{4-n}$ molecules.

Atom/AO	NH_4	NH_3CH_3	$\text{NH}_2(\text{CH}_2)_2$	$\text{NH}(\text{CH}_3)_3$	$\text{N}(\text{CH}_3)_4$
N 2S	0.165	0.137	0.105		
N 2S'	0.640	0.571	0.467	0.327	
3S	0.668	0.431	0.130	0.233	-1.314
3P _z		0.193	0.230	0.301	
H _N 1S'	-0.203	-0.198	-0.209	-0.314	
2S	-0.371	-0.554	-0.863	-1.643	
H _N 1S'	-0.203	-0.198	-0.209		
2S	-0.371	-0.554	-0.863		
H _N 1S'	-0.203	-0.198			
2S	-0.371	-0.554			
H _N 1S'	-0.203				
2S	-0.371				
C ₁ 2S'		0.121	0.157	0.195	0.302
3S		0.946	1.106	1.033	1.621
H _{C1} 2S		-0.198	-0.359	-0.090	-0.551
H _{C1} 2S		-0.198	-0.138	-0.302	-0.551
H _{C1} 2S		-0.198	-0.138	-0.302	-0.551
C ₂ 2S'			0.157	0.195	0.302
3S			1.016	1.033	1.621
H _{C2} 2S			-0.359	-0.090	-0.551
H _{C2} 2S			-0.138	-0.302	-0.551
H _{C2} 2S			-0.138	-0.302	-0.551
C ₃ 2S'				0.195	0.302
3S				1.033	1.621
H _{C3} 2S				-0.090	-0.551
H _{C3} 2S				-0.302	-0.551
H _{C3} 2S				-0.302	-0.551
C ₄ 2S'					0.302
3S					1.621
H _{C4} 2S					-0.551
H _{C4} 2S					-0.551
H _{C4} 2S					-0.551

where the linear combination of atomic orbitals-molecular orbitals (LCAO-MO) coefficients of the HOMOs of the $\text{NH}_n(\text{CH}_3)_{4-n}$ species are presented. It should be noticed that only the coefficients of the diffuse atomic orbitals (AOs) are significant, but not only the diffuse functions of the central nitrogen atom contribute to the Rydberg orbital. Diffuse functions on all atoms, including the hydrogen atoms, are strong contributors. We therefore conclude that the HOMOs in the $\text{NH}_n(\text{CH}_3)_{4-n}$ species are Rydberg orbitals that cover the entire molecule.

One of the most important questions in studying Rydberg molecules is the question of the height of the dissociation barriers. We repeated earlier calculations of the barrier for $\text{NH}_4 \rightarrow \text{NH}_3 + \text{H}$, and found it did not depend strongly on the *ab initio* method employed (e.g., the height of the barrier varies from 14.2-15.1 kcal/mol; see Table III), but we found ZPE corrections to be essential. Our final value for this barrier is 9.0 kcal/mol at the QCISD/6-31++G**/MP2(full)/6-31++G**+ZPE/MP2(full)/6-31++G** level.

The barriers for dissociation of $\text{NH}_n(\text{CH}_3)_{4-n}$ into $\text{NH}_{n-1}(\text{CH}_3)_{4-n} + \text{H}$ do not change substantially with the number of methyl groups. The barriers for fragmentation of these Rydberg radicals into $\text{NH}_n(\text{CH}_3)_{4-n-1} + \text{CH}_3$ are

larger than the barriers to loss of H, as a result of which the lifetimes will be determined by the rate of H loss. However, for $\text{N}(\text{CH}_3)_4$ the H-loss channel is absent and the lifetime will be determined by the loss of CH_3 . Because the CH_3 -loss barrier for $\text{N}(\text{CH}_3)_4$ is higher than the H-loss barriers of the other species, the lifetime of $\text{N}(\text{CH}_3)_4$ should be much longer than that of the other species.

The adiabatic ionization potentials of all the species studied here are very low: 4.5 eV (NH_4), 4.0 eV (NH_3CH_3), 3.6 eV [$\text{NH}_2(\text{CH}_3)_2$], 2.7 eV [$\text{NH}(\text{CH}_3)_3$], and 2.3 eV [$\text{N}(\text{CH}_3)_4$]. These IPs decrease with the number of methyl groups and are even lower than the IPs of alkali metal atoms (the lowest atomic IP = 3.89 eV is for the Cs atom²⁶) as a result of which these molecules may be called superalkali molecules (see Refs. 27-30). In fact, the $\text{N}(\text{CH}_3)_4$ Rydberg radical has the lowest IP of all known ground-state molecules.

V. CONCLUSIONS

1. All of the methyl substituted $\text{NH}_n(\text{CH}_3)_{4-n}$ neutral molecules are local minima on their ground-state potential energy surfaces and all of them are electronically stable to loss of an electron. However, all of these species are not thermodynamically stable to loss of an H atom or a CH_3 group.

2. All substituted $\text{NH}_n(\text{CH}_3)_{4-n}$ molecules are Rydberg molecules, and diffuse functions of all constituent atoms contribute to the highest occupied (Rydberg) molecular orbital.

3. All $\text{NH}_n(\text{CH}_3)_{4-n}$ species have very low ionization potentials, and for $n < 4$ are lower than the IPs of alkali metal atoms. These IPs decrease with the number of methyl groups. The $\text{N}(\text{CH}_3)_4$ molecule has the lowest IP of all known molecules.

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- G. Herzberg, Faraday Discuss. Chem. Soc. **71**, 165 (1981).
- F. Alberti, K. P. Huber, and J. K. G. Watson, J. Mol. Spec. **107**, 133 (1984).
- K. P. Huber and T. J. Sears, Chem. Phys. Lett. **113**, 129 (1985).
- J. K. G. Watson, J. Mol. Spectrosc. **107**, 124 (1984).
- G. Herzberg, J. Astrophys. Astron. **5**, 131 (1984).
- G. I. Gellene, D. A. Cleary, and R. F. Porter, J. Chem. Phys. **77**, 3471 (1982).
- S. Havriliak and H. F. King, J. Am. Chem. Soc. **105**, 4 (1983).
- S. Havriliak, T. R. Furlani, and H. F. King, Can. J. Phys. **62**, 1336 (1984).
- K. S. E. Niblaeus, B. O. Roos, and P. E. M. Siegbahn, Chem. Phys. **25**, 207 (1977).
- D. Talbi and R. P. Saxon, J. Chem. Phys. **91**, 2376 (1989).
- M. Gutowski and J. Simons, J. Chem. Phys. **93**, 2546, 3874 (1990).
- (a) H. Cardy, D. Liotard, A. Dargelos, and E. Poquet, Chem. Phys. **77**, 287 (1983); (b) H. Cardy, L. Larriue, and A. Dargelos, Chem. Phys. Lett. **131**, 3874 (1986).
- J. Simons and M. Gutowski, Chem. Rev. **91**, 669 (1991).
- H. B. Schlegel, J. Comput. Chem. **3**, 214 (1982).
- P. C. Hariharan and J. A. Pople, Theor. Chim. Acta. **28**, 213 (1973).
- M. J. Frisch, J. A. Pople, and J. S. Binkley, J. Chem. Phys. **80**, 3265 (1984).

- ¹⁷R. Krishnan and J. A. Pople, *Int. J. Quantum Chem.* **14**, 91 (1978).
- ¹⁸J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5968 (1987).
- ¹⁹H. B. Schlegel, *J. Chem. Phys.* **84**, 4530 (1986).
- ²⁰GAUSSIAN 90. M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzales, D. J. DeFrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, Gaussian Inc. Pittsburgh, Pennsylvania, 1990.
- ²¹M. W. Crofton and T. Oka, *J. Chem. Phys.* **86**, 5983 (1987).
- ²²M. W. Crofton and T. Oka, *J. Chem. Phys.* **79**, 3157 (1983).
- ²³E. Schafer, M. H. Begemann, C. S. Gudeman, and R. J. Saykally, *J. Chem. Phys.* **79**, 3159 (1983).
- ²⁴S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data* **13**, 695 (1984).
- ²⁵M. J. Frisch, J. E. Del Bene, K. Raghavachari, and J. A. Pople, *Chem. Phys. Lett.* **83**, 240 (1981).
- ²⁶S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, *Gas-Phase Ion and Neutral Thermochemistry* [*J. Phys. Chem. Ref. Data, Suppl.* **1**, 17 (1988)].
- ²⁷G. L. Gutsev and A. I. Boldyrev, *Chem. Phys. Lett.* **92**, 262 (1982).
- ²⁸G. L. Gutsev and A. I. Boldyrev, *Adv. Chem. Phys.* **61**, 169 (1985).
- ²⁹G. L. Gutsev and A. I. Boldyrev, *Usp. Khim. (Russ.)* **51**, 889 (1987).
- ³⁰E. Rehm, A. I. Boldyrev, and P. v. R. Schleyer, *Inorg. Chem.* (in press).