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Electronic, Structural, and Hyperfine Interaction Investigations on Rydberg Molecules: NH_4, OH_3, and FH_2

Feiwu Chen and Ernest R. Davidson*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405-7102

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The geometrical structures of NH_4 and OH_3 were optimized at the MP2 level with the aug-cc-pvdz, aug-cc-pvtz, and aug-cc-pvqz basis set plus s-type diffuse functions. The adiabatic ionization potential, barrier height, and dissociation energy of NH_4 and OH_3 were calculated with the above basis set series and were extrapolated to the infinite basis set limit. The theoretical ionization potential of NH_4 was in very good agreement with the experimental value. The N−H bond lengths of NH_4 and NH_4^+ at the infinite basis set limit were obtained by parabolic interpolation around the equilibrium point. FH_2 was optimized at the UHF, B3LYP, and MP2 levels. However, only a dissociated ground state was found. The potential energy curves for dissociation of the above molecules were calculated with MP2. The relative stabilities of these molecules and their isotopic counterparts are discussed. Theoretical hyperfine calculations were performed in the gas phase as well as in a neon matrix for NH_4 and OH_3 with a single-reference configuration interaction method (CI) and multireference single- and double-excitation methods (MRSD), respectively. For FH_2, only gas phase calculations are carried out. The contours of the singly occupied orbitals of NH_4 and OH_3 in the gas phase and in the neon matrix are plotted to show their s-type character.

I. Introduction

The radical NH_4 is a typical Rydberg molecule. The first experimental work on this radical was done by Herzberg.[1] NH_4 is not stable and has a very short lifetime because of its very shallow potential well. Most of the spectroscopic studies have been limited to the relatively stable ND_4.[2−7] The ionization potential was determined to be 5.90 eV by means of mass spectrometry.[8] This magnitude is larger than the later experimental value of 4.73 ± 0.06 eV determined by Porter et al. with neutralized ion-beam spectroscopy.[6] The photoionization potentials of ammoniated NH_4 clusters have been determined by Fuke and co-workers.[7] The theoretical investigation on NH_4 can be dated back to the early works by Mulliken.[9] In the 1960s and early 1970s, theoretical calculations showed the stability of the NH_4 radical using the one-center approximation.[8,10,11] An improved theoretical ionization potential value, 4.85 eV, was obtained by Broclawik et al. with the SCF-Xα-SW method.[12] The systematic studies on the dissociation potential energy surface of the NH_4 radical have been carried out by Cardy et al.[13] and McMaster et al.[14] Recently, the equilibrium structure of the NH_4 ground state was investigated by Sattelmeyer, Schaefer, and Stanton[44] with extensive coupled cluster calculations. The bond length was estimated to lie in the range of 1.0365 ± 0.0005 Å.

The Rydberg molecules OH_3 and FH_2 are isoelectronic with NH_4. Bernstein[15] first suggested that the radical OH_3 might exist on the basis of an analysis of thermodynamical relationships. Indirect kinetic evidence for the existence of OH_3 was presented by Sworski.[16] The same conclusion was also reached in the γ-radiolysis of water by Kongshaug et al.[17] The first direct experimental evidence for the stability of OH_3 in the gas phase was reported by Melton and Joy using mass spectrometric techniques.[8] An unbelievably high ionization potential, 10.9 eV, was determined as in the case of NH_4. Martin and Swift[18] claimed to have obtained the ESR spectrum of OH_3. However, the results could not be proved by others, and the spectrum was then suggested to be assigned to the methyl radical.[19−21] The experimental evidence for OD_3 metastable states was presented by Porter et al.[22] The ionization potential was estimated to be 4.3 ± 0.1 eV, and the electron affinity difference between OH_3^+ and OD_3^+ was determined to be 0.3 eV. On the other hand, single-center wave function calculations were also performed for the OH_3 radical by Bishop[23] and Melton and Joy.[8] Extensive ROHF investigations of the potential energy surface of OH_3 were carried out by Gangi and Bader.[24] A symmetrical geometry was found. A UHF-CI investigation of the potential energy surface of OH_3 was reported by Roos et al.[25] The potential barrier, 4.6 kcal/mol, calculated with UHF was lowered to 3.4 kcal/mol when the correlation effect was taken into account, and was further estimated to be 3.0 kcal/mol. However, the zero-point energy was above the barrier. Therefore, the metastable OH_3 in the gas phase was predicted not to exist. The electronic structures of Rydberg states of FH_2, OH_3, and NH_4 were investigated theoretically by Raynor and Herschbach with a floating spherical Slater orbital.[26] Higher-level studies such as quadratic single- and double-excited configuration interaction and coupled cluster double-excitation methods on NH_4, OH_3, and related molecules were carried out by Wang and Boyd with the 6-31++G(d, p) basis set.[27] Direct experimental evidence for a metastable state of FD_2 was reported by Porter et al. in 1986.[28] The ground and first few exited states of FH_2 were calculated by Petsalakis et al. with MRD-CI.[29] The ground state was dissociative. The first few excited states were all bound with a structure similar to FH_2^+ except the first exited state which was bound at a relatively larger bond length. Talbi and Saxon[45] studied the first two doublet and quartet states of OH_3 using the multiconfiguration self-consistent field/first-order

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* To whom correspondence should be addressed. E-mail: davidson@indiana.edu.

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configuration interaction method with the double-ζ plus polarization basis set augmented by diffuse s and p functions. The exponents of the most diffuse s and p functions are 0.03 and 0.02, respectively. The determined ionization potential is 5.27 eV. The calculated barrier heights for OH_3 and OD_3 are 0.4 and 1.3 kcal/mol, respectively, with the zero-point energy correction. McLoughlin and Gellene[46] reported an ab initio investigation on the same system at the MP3 level with 6-311G** augmented by diffuse functions. More attention was paid to the dynamic stability of the OH_3 radical.

It is well-known that electron spin resonance (ESR) spectroscopy is one of the techniques most widely used to study the distribution of unpaired electron density (spin density) within a molecule. ESR assesses the interaction of the intrinsic electronic spin with the magnetic nuclei. In recent years, there has been a number of ESR investigations (both theoretical and experimental) for gaining knowledge about electronic structures, spin density distributions, and hyperfine splittings for various radical/ion systems.[30−35] In this paper, we reexamine the electronic structures of NH_4, OH_3, and FH_2 at the MP2 level with a large basis set augmented with Rydberg-type diffuse orbitals. The potential energy surfaces are calculated, and the relative stabilities of NH_4, OH_3, FH_2, and their isotopic counterparts are discussed. The hyperfine splitting parameters of the above molecules are calculated with CI and MRSD in the gas phase and neon matrices.

II. Method of Calculation

We first briefly describe how to calculate the hyperfine splitting parameters. More detailed information can be found in refs 30, 31, and 35. The interaction of the electron spin with a magnetic nucleus can be written as

$$H_{\text{macro}} = \mathbf{I}\cdot\mathbf{A}\cdot\mathbf{S} \tag{1}$$

where **I** is the nuclear magnetic moment, **S** is the total electronic spin, and **A** is the hyperfine splitting tensor. The microscopic form of eq 1 is

$$H_{\text{micro}} = (g_e g_n \beta_e \beta_n) \sum_{i=1}^{N} \left[\frac{8\pi}{3} (S_i \cdot I)\delta(r_i) - \frac{S_i \cdot I}{r_i^3} + \frac{3(S_i \cdot r_i)(r_i \cdot I)}{r_i^5} \right] \tag{2}$$

Via comparison of eqs 1 and 2, the matrix elements of **A** can written as follows

$$A_{ij} = \delta_{ij} A_{\text{iso}} + A_{\text{aniso}}(i,j),\ i, j = x, y, z \tag{3}$$

where

$$A_{\text{iso}} = \frac{8\pi}{3} g_e g_n \beta_e \beta_n \langle \delta(r) \rangle_{\text{spin}} \tag{4}$$

and examples of diagonal and off-diagonal elements are

$$A_{\text{aniso}}(x,y) = g_e g_n \beta_e \beta_n \left\langle \frac{3xy}{r^5} \right\rangle_{\text{spin}} \tag{5}$$

$$A_{\text{aniso}}(z,z) = g_e g_n \beta_e \beta_n \left\langle \frac{3z^2 - r^2}{r^5} \right\rangle_{\text{spin}}$$

In the above equation, the parameters g_e and g_n are the g value of the free electron and nucleus, respectively. The constants β_e and β_n are the Bohr magneton and nuclear magneton, respectively. The subscript spin indicates that the average is performed using the electron spin density normalized to one unpaired electron.

TABLE 1: 7s3p1d Basis Set for the Hydrogen Atom

	exponent	coefficient
1s	1803.494000	$0.4286062816186 \times 10^{-3}$
	270.155600	$0.3330748578243 \times 10^{-2}$
	61.481580	$0.1747528958450 \times 10^{-1}$
	17.411220	$0.7317970199351 \times 10^{-1}$
	5.677801	0.2596911295059
2s	2.048055	1.000
3s	0.797488	1.000
4s	0.329563	1.000
5s	0.142256	1.000
6s	0.062126	1.000
7s	0.018644	1.000
1p	3.92857	1.000
2p	0.93041	1.000
3p	0.28770	1.000
1d	2.26566	0.139
	0.55794	0.231

All calculations in this paper are performed using the MELD[39] and Gaussian 98[40] programs. The isotropic and anisotropic hyperfine parameters, A_{iso} and A_{aniso}, were evaluated with ROHF, CIS, CISD, and MRSD using the geometry described below in the gas phase. The same calculations were also carried out in a neon matrix for NH_4 and OH_3. The geometrical structures of NH_4 and OH_3 are the same as in the gas phase. All neon orbitals were frozen. In the neon matrix, neon has the close-packed, face-centered cubic-type structure at low temperatures. Each neon atom is surrounded by 12 neon atoms. The distance between two neon atoms is 3.16 Å.[34] In our calculations, only one shell was employed and the center neon atom was replaced with NH_4 and OH_3 molecules.

The quality of the basis set is very important for an ESR calculation. The basis set used for the hydrogen atom in this work is unpublished and is listed in Table 1. This basis set generated a spin density of 0.3141 with UHF very close to the theoretical value ($1/\pi$) of 0.3183 at the hydrogen nuclei. The basis set for the nitrogen atom was Dunning's correlation consistent basis set with diffuse functions,[37] aug-cc-pVTZ, including all six of the d components and 10 of the f components. Two additional d diffuse orbitals with the exponents 0.052 and 0.018644 were used to describe the behavior of the nearly free electron. This basis set will hereafter be termed basis I. The original purpose of using six-component d-type diffuse orbitals was to find out whether the ground state of NH_4 was in A_1 symmetry or not by including an $l = 0$ basis function without introduction of an s-type diffuse Gaussian. After extensive ab initio calculations, we found A_1 was indeed the ground state of NH_4 in the gas phase as well as in the neon matrix. The basis sets for oxygen and fluorine (hereafter basis II) were cc-pVTZ, Dunning's correlation consistent basis set,[38] augmented with two s orbitals, two p orbitals, and one d orbital with exponents of 0.03, 0.007, 0.03, 0.0067, and 0.0133.[29] The 18s13p basis set for Neon[36] was contracted to 2s1p using the SCF orbital coefficients. The geometrical structures of NH_4 and OH_3 were optimized at the MP2 level. FH_2 and FH_2^+ were optimized at three levels, B3LYP,[41,42] UHF, and MP2. The potential energy surfaces of NH_4 and OH_3 were calculated with MP2.

The basis set impacts on the geometrical structure, adiabatic ionization potential (IP), dissociated energy (ΔE), and barrier height (BH) were further examined with the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis set series plus one s-type diffuse function with an exponent of 0.018644 (hereafter basis

TABLE 2: Geometry Parameters of NH_4^+, NH_4, OH_3^+, OH_3, FH_2^+, and FH_2[a]

	NH_4^+	NH_4	IP (eV)[b]	
	N−H	N−H	NH_4	ND_4
aug-cc-pvdz + s	1.0274	1.0450	4.618	4.578
aug-cc-pvtz + s	1.0220	1.0392	4.624	4.583
aug-cc-pvqz + s	1.0203	1.0373	4.625	4.583
infinite[c]	1.0196	1.0366	4.625	4.584
expt[7]			4.62	

	OH_3^+		OH_3		IP (eV)[b]	
	O−H	∠H−O−H	O−H	∠H−O−H	OH_3	OD_3
aug-cc-pvdz + s	0.9831	111.0	1.0252	105.9	5.585	5.520
aug-cc-pvtz + s	0.9795	111.4	1.0218	106.2	5.597	5.532
aug-cc-pvqz + s	0.9770	111.7	1.0188	106.3	5.591	5.526
infinite[c]					5.583	5.517
expt		111.3[d]				4.30[e]

	FH_2^+		FH_2			IP (eV)	
	F−H	∠H−F−H	$F-H_1$	$F-H_2$	∠H−F−H	FH_2	FD_2
HF	0.9410	115.0	0.8972	4.0572	105.6	8.544	8.467
B3LYP	0.9673	113.3	0.9221	3.0080	104.6	8.650	8.652
MP2	0.9615	111.9	0.9169	3.5072	105.3	8.553	8.480

[a] NH_4^+, NH_4, OH_3^+, and OH_3 were optimized with MP2. FH_2^+ and FH_2 were optimized with basis II. The bond lengths are in angstroms. The angles are in degrees. [b] IP was calculated at the MP2 level. [c] Infinite basis set limit. MP2 energies and zero-point energies at this limit were extrapolated with eq 7. [d] Reference 47. [e] Reference 22.

III). The infinite basis set results are obtained according to the following equation[43]

$$E_n = E_\infty + ae^{-cn},\ n = 1, 2, \text{ or } 3 \text{ for VDZ, VTZ, or VQZ} \tag{6}$$

where E_∞ corresponds to the infinite basis set limit. The expression for E_∞ can be easily obtained from eq 6 as

$$E_\infty = E_3 - \frac{(E_3 - E_2)^2}{E_1 + E_3 - 2E_2} \tag{7}$$

The MP2 energies and zero-point corrections have been extrapolated separately with this equation and then added. The MP2 frequencies have not been scaled. To the extent that the usual 0.900 scaling is a correction of the harmonic vibrational excitation energy for anharmonicity, the corresponding correction for the zero-point energy would be 0.975.

III. Results and Discussion

In Table 2 are optimized geometrical parameters of NH_4, OH_3, and their cation counterparts with the basis set series basis III. The bond lengths of NH_4, NH_4^+, OH_3, and OH_3^+ with MP2 are in good agreement with the latest reports by Wang and Boyd[27] with QCISD/6-31++(d, p) and CCD/6-31++G(d, p). The basis set effect was further examined for the bond lengths of NH_4 and NH_4^+ at the MP2 level. Three points around the equilibrium ground state were calculated with the basis set series basis III. Then the energies were extrapolated to the infinite basis set limit with eq 7. With these data, a parabolic interpolation procedure was applied to obtain the equilibrium bond length. A bond length of 1.0366 Å for NH_4 is very close to the latest estimate of 1.0365 ± 0.0005 Å by an extrapolation procedure of large [up to CCSD(T)/aug-cc-pv5z] coupled cluster calculations and analysis of experimental rotational constants.[44] The computed bond length of NH_4^+ is 1.0196 Å. However, the bond length and bond angle of OH_3 and OH_3^+ at the infinite basis set limit were not computed since it would require a two-dimensional potential energy surface. The ionization potential energy (IP) of NH_4 at the MP2 level in Table 2 is in excellent agreement with the experimental value.[7] However, the difference between our theoretical IP and the experimental magnitude of OD_3[22] is ∼1.2 eV unexpectedly larger. Our result for OH_3 (5.583 eV) is close to the value of 5.27 eV reported by Talbi and Saxon.[45] On the basis of our series of calculations on NH_4 and the result by Talbi and Saxon, we think that the experimental estimate may be somewhat too small for OD_3. In the series of calculations listed in Table 3, the geometrical structures of NH_4, NH_4^+, NH_3, OH_3, OH_3^+, and OH_2 are those optimized with MP2 and aug-cc-pvqz plus s-type diffuse functions for both the minimum equilibrium point and maximum saddle point. The infinite basis set MP2 energies and zero-point energies are computed with eq 7 and are then used for calculations of the ionization potential, dissociation energy, and barrier height. The only ground state minimum of FH_2 is the HF•H van der Waals complex as reported by Petsalakis et al.[29] The ionization potentials calculated with UHF, B3LYP, and MP2 agree with each other reasonably.

In Figure 1 is the potential curve for dissociation of NH_4 optimized at the MP2 level with basis I. In Figure 2 is the potential curve of OH_3 optimized at the same level with basis II. The barrier height labels shown in the two figures correspond to the infinite basis limit listed in Table 4. In comparison with NH_4, OH_3 has a shallower potential well that lies well above

TABLE 3: MP2 Energies of NH_4 and OH_3[a]

	NH_4(min)	NH_4(max)	NH_4^+(min)	NH_3(min)
aug-cc-pvdz + s	−56.9039150	−56.8850442	−56.7396721	−56.4047682
aug-cc-pvtz + s	−56.9606294	−56.9421852	−56.7961600	−56.4605622
aug-cc-pvqz + s	−56.9778741	−56.9597070	−56.8133748	−56.4777803
infinite[b]	−56.9854085	−56.9674561	−56.8209207	−56.4854655
infinite(H)[c]	0.044553	0.036394	0.050025	0.034699
infinite(D)[d]	0.032558	0.026585	0.036544	0.025344
	OH_3(min)	OH_3(max)	OH_3^+(min)	OH_2(min)
aug-cc-pvdz + s	−76.7264485	−76.7228351	−76.5300569	−76.2608893
aug-cc-pvtz + s	−76.7969875	−76.7934313	−76.6002187	−76.3290049
aug-cc-pvqz + s	−76.8197986	−76.8163633	−76.6232082	−76.3519239
infinite[b]	−76.8307010	−76.8273962	−76.6344122	−76.3635460
infinite(H)[c]	0.025898	0.022755	0.034738	0.020691
infinite(D)[d]	0.018862	0.016562	0.025316	0.015103

[a] Calculations were carried out at the minimum and maximum stationary points optimized with the aug-cc-pvqz basis set plus s-type diffuse functions. The energies of the hydrogen atom calculated with basis set series basis III are −0.4993343, −0.4998212, and −0.4999483. The corresponding infinite basis set limit is −0.4999932 atomic units. [b] MP2 energy at the infinite basis set limit. [c] Zero-point energy at the infinite basis set limit for the hydrogen compounds. [d] Zero-point energy at the infinite basis set limit for the associated deuterium compounds.

TABLE 4: Barrier Height and Dissociation Energy of NH_4 and OH_3 at the MP2 Level[a]

	dissociation energy					barrier height				
	ΔE_0	ΔZP_H	ΔZP_D	ΔE_H	ΔE_D	ΔBH_0	ΔZP_H	ΔZP_D	ΔBH_H	ΔBH_D
					NH_4					
aug-cc-pvdz + s	−0.008	−0.265	−0.194	−0.273	−0.202	0.508	−0.222	−0.162	0.286	0.346
aug-cc-pvtz + s	0.007	−0.270	−0.198	−0.263	−0.191	0.501	−0.222	−0.163	0.279	0.338
aug-cc-pvqz + s	0.004	−0.269	−0.197	−0.265	−0.193	0.494	−0.222	−0.163	0.274	0.331
infinite[b]	−0.001	−0.268	−0.196	−0.269	−0.197	0.489	−0.222	−0.163	0.267	0.326
					OH_3					
aug-cc-pvdz + s	−0.919	−0.117	−0.085	−1.036	−1.004	0.096	−0.086	−0.063	0.010	0.033
aug-cc-pvtz + s	−0.866	−0.119	−0.087	−0.985	−0.953	0.096	−0.084	−0.062	0.012	0.034
aug-cc-pvqz + s	−0.872	−0.118	−0.087	−0.990	−0.959	0.093	−0.084	−0.062	0.009	0.031
Infinite[b]	−0.894	−0.142	−0.102	−1.036	−0.996	0.090	−0.086	−0.063	0.004	0.027

[a] Units of electron volts. $\Delta E_0 = E(NH_3) + E(H) - E(NH_4)$, $\Delta BH_0 = E[NH_4(max)] - E[NH_4(min)]$, and so forth. ΔZP_H is the difference of the zero-point energies, while ΔZP_D is the corresponding zero-point energy difference when hydrogen is replaced with deuterium. $\Delta E_H = \Delta E_0 + \Delta ZP_H$. $\Delta E_D = \Delta E_0 + \Delta ZP_D$. $\Delta BH_H = \Delta BH_0 + \Delta ZP_H$. $\Delta BH_D = \Delta BH_0 + \Delta ZP_D$. [b] Infinite basis set energies are taken from Table 3.

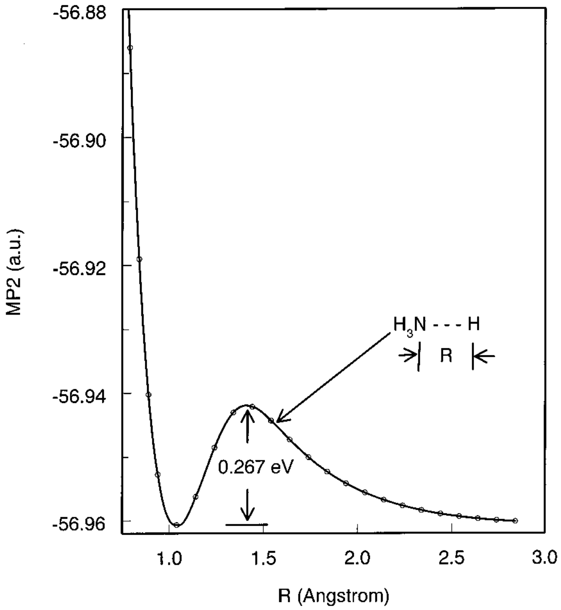

Figure 1. Potential curve of NH_4 dissociated along the N−H bond calculated with MP2.

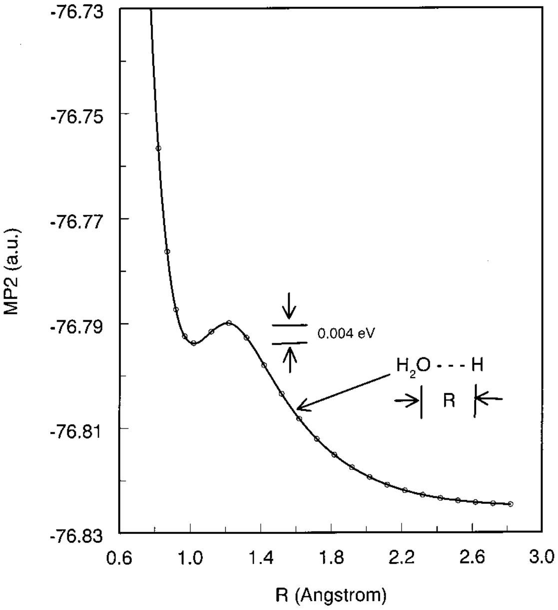

Figure 2. Potential curve of OH_3 dissociated along the O−H bond calculated with MP2.

its dissociation limit. Further refined calculations were performed at the equilibrium point and the saddle point optimized with basis set series basis III. The MP2 energies at the infinite basis set limit were taken from Table 3. With these data, the dissociation energy and barrier height of NH_4, ND_4, OH_3, and OD_3 were evaluated and presented in Table 4. All zero-point energies were taken into account. The dissociation energy of NH_4 is −0.269 eV at the infinite basis set limit, meaning the ground state minimum is slightly above the dissociation limit. The barrier height at the infinite basis set limit is 0.267 eV. When all hydrogens are replaced with deuterium nuclei, the barrier height is increased to 0.326 eV and the absolute value of the dissociation energy decreases. Therefore, ND_4 is more nearly stable and should have a longer lifetime. When the zero-point energy correction is considered, the barrier heights of 0.004 and 0.027 eV for OH_3 and OD_3, respectively, at the infinite basis set limit are all smaller than those values of 0.017 and 0.056 eV reported by Talbi and Saxon.[45] On the other hand, our barrier heights (0.010 and 0.033 eV) with aug-cc-pvdz plus the diffuse s function are close to their values. It may be partially due to the fact that these two basis sets are almost at the same level. In comparison with that of NH_4, the barrier height of OH_3 is very much smaller. The dissociation energy is also more negative. The same isotopic effect is also observed for OD_3. Thus, OH_3 and OD_3 are more unstable than NH_4 and ND_4, respectively.

In hyperfine parameter calculations for NH_4, OH_3, and FH_2, basis sets basis I and basis II were the same as those used for their geometry optimization. The N−H bond length of 1.03726 Å is very close to the value of 1.03734 Å optimized with the aug-cc-pvqz basis set plus s-type diffuse functions shown in Table 2. The OH_3 geometry was optimized with basis II. The O−H bond length of 1.0178 Å and the bond angle of 105.4° are also close to the values of 1.0188 Å and 106.3°, respectively, at the aug-cc-pvqz level in Table 2. These comparisons show that the aug-cc-pvqz level basis set might be a needlessly expensive choice in our geometry optimization step considering its large number of basis functions and the time-consuming frequency job. However, these basis set series provide a systematic way of studying the basis set effects on the electronic energy as well as other molecular properties, as demonstrated in Tables 2−4.

The energies of NH_4 and OH_3 in the neon matrix are calculated with SCF, CIS, CISD, and MRSD. The energies listed in the third column of Tables 5 and 6 are those with the 12 Ne SCF energies subtracted from their total energies. They are all slightly higher than the corresponding energies of NH_4 and OH_3 in the gas phase, indicating a small repulsion between the inorganic molecules and the neon cage. The hyperfine calcula-

TABLE 5: Hyperfine Parameters of NH_4 and NH_4 plus 12 Neon Atoms Calculated with SCF, CIS, CISD, and MRSD

	size	energy[a]		isotropic[b]		anisotropic[b]	
			NH_4				
SCF	1	−56.71283	N	141.427	0.0000	0.0000	0.0000
			H	6.560	−3.9877	7.9753	−3.9876
SCI	35104	−56.71845	N	198.329	0.0000	0.0000	0.0000
			H	−0.597	−4.2707	8.5411	−4.2704
MRCI	94360	−56.98425	N	203.182	−0.0005	−0.0005	0.0011
			H	4.830	−4.3481	8.6922	−4.3441
SDCI	207754	−56.98526	N	203.346	0.0000	0.0000	0.0000
			H	4.813	−4.3575	8.7149	−4.3574
MRSD	252883	−56.99469	N	211.834	−0.0006	−0.0006	0.0013
			H	6.073	−4.3021	8.6105	−4.3084
			$NH_4 + 12Ne$				
SCF	1	−56.64263	N	133.366	0.0000	0.0000	0.0000
			H	7.983	−3.5622	7.1244	−3.5622
SCI	35104	−56.64731	N	186.238	0.0000	0.0000	0.0000
			H	2.253	−4.0784	8.1566	−4.0782
MRCI	100262	−56.89800	N	200.619	−0.0003	−0.0003	0.0005
			H	7.802	−4.2443	8.4866	−4.2423
SDCI	207754	−56.89943	N	201.130	0.0000	0.0000	0.0000
			H	7.849	−4.2678	8.5356	−4.2678
MRSD	234148	−56.90649	N	215.836	0.0052	0.0052	−0.0103
			H	9.628	−4.3896	8.7803	−4.3907

[a] In atomic units. [b] In megahertz.

tions on NH_4 and NH_4 plus 12 neon atoms are shown in Table 5. As expected, the anisotropic term of the nitrogen atom is almost zero because of space symmetry. The SCF hyperfine parameters of NH_4 in the neon solid state are smaller than in the gas phase. However, the differences become smaller when the correlation effect is taken into account. It seems that the neon cage does not have as much influence on NH_4 in comparison with OH_3 as discussed below. The two contours of the singly occupied orbital of NH_4 and $NH_4{\cdot}Ne_{12}$ are shown in Figures 3 and 4. They are all 3s orbitals. The contour plane in Figure 3 is cut through the nitrogen and two hydrogen nuclei, while in Figure 4, there are two additional neon atoms in the contour plane.

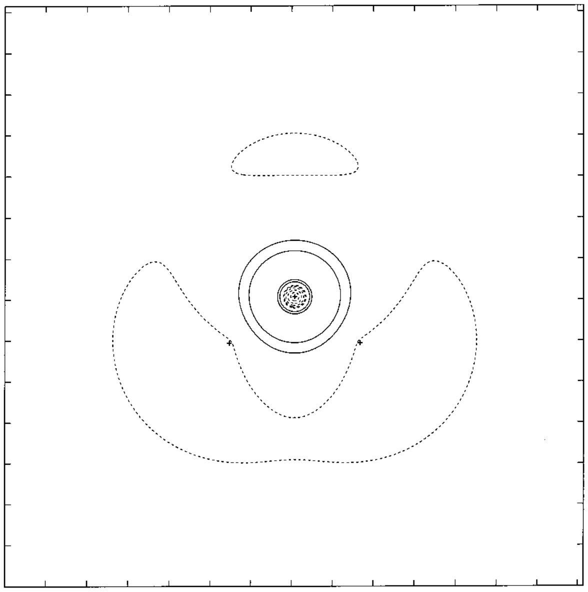

Figure 3. Contour of the singly occupied orbital of NH_4 in the gas phase. The + symbols show the positions of nuclei. The nitrogen nucleus is at the center with two hydrogen atoms around it.

The hyperfine parameters of OH_3 in the gas phase and in the neon matrix are listed in Table 6. There are two nonequivalent hydrogen atoms in the present coordinate system. The difference between SCF and the higher-level MRSD calculations is much larger. The correlation effect plays an important role in obtaining better hyperfine isotropic and anisotropic constants. The hyperfine parameters in the neon matrix are quite different from values in the gas phase. Analysis indicates that the single electron is diffusely distributed among oxygen and hydrogen atoms in the gas phase and is somewhat shrunk into the inner shells in the neon matrix due to the repulsion from the surrounding neon atoms. Therefore, it is very possible that the redistribution of the singly occupied electron density will lead

TABLE 6: Hyperfine Parameters of OH_3 and OH_3 plus 12 Neon Atoms Calculated with SCF, CIS, CISD, and MRSD

	size	energy[a]		isotropic[b]		anisotropic[b]	
			OH_3				
SCF	1	−76.51147	O	−383.619	5.2309	−10.4617	5.2308
			H_1	33.386	13.0917	−7.5145	−5.5773
CIS	63463	−76.52193	O	−490.141	11.0527	−22.1044	11.0517
			H_1	28.966	15.6341	−8.9412	−6.6929
MRSD	98424	−76.80286	O	−505.065	9.0157	−18.0387	9.0230
			H_1	39.412	13.9481	−8.1793	−5.7688
CISD	214512	−76.80415	O	−505.081	9.0064	−18.0160	9.0096
			H_1	39.433	13.9422	−8.1751	−5.7671
MRSD	242959	−76.81522	O	−521.241	10.0516	−20.0953	10.0436
			H_1	44.145	13.8650	−8.2514	−5.6136
			$OH_3 + 12Ne$				
SCF	1	−76.45388	O	−593.876	7.6598	−15.3278	7.6680
			H_1	59.854	18.4726	−11.2166	−7.2559
			H_2	61.762	19.0973	−11.5559	−7.5414
CIS	63463	−76.46884	O	−746.397	14.8340	−29.4648	14.6307
			H_1	58.148	21.0323	−12.6849	8.3474
			H_2	59.497	21.9138	−13.1899	−8.7239
MRSD	112564	−76.73420	O	−748.878	12.4746	−24.7822	12.3076
			H_1	69.445	19.2354	−11.8619	−7.3735
			H_2	71.209	19.9564	−12.2769	−7.6796
CISD	214512	−76.73545	O	−748.976	12.4741	−24.7887	12.3147
			H_1	69.487	19.2309	−11.8567	−7.3741
			H_2	71.326	19.9722	−12.2827	−7.6895
MRSD	222984	−76.74424	O	−761.967	13.4544	−26.7449	13.2905
			H_1	74.790	18.8935	−11.7899	−7.1036
			H_2	76.880	19.6139	−12.2020	−7.4119

[a] In atomic units. [b] In megahertz.

TABLE 7: Hyperfine Parameters of FH_2 Calculated with SCF, CIS, CISD, and MRSD

	size	energy[a]		isotropic[b]		anisotropic[b]	
SCF	1	−100.56018	F	8.481	8.6639	−4.3154	−4.3486
			H_1	0.015	4.1103	−1.9790	−2.1313
			H_2	1406.339	−0.7635	0.4797	0.2837
CIS	68267	−100.56163	F	17.638	15.1081	−7.4323	−7.6758
			H_1	−0.132	4.1239	−1.8530	−2.2709
			H_2	1405.660	−0.7773	0.4853	0.2920
MRSD	27958	−100.84363	F	13.388	10.8622	−5.3609	−5.5013
			H_1	−0.089	4.1184	−1.9418	−2.1766
			H_2	1406.020	−0.7132	0.4552	0.2580
CISD	143966	−100.84439	F	13.572	11.0161	−5.4164	−5.5997
			H_1	−0.107	4.1165	−1.9365	−2.1801
			H_2	1406.252	−0.7192	0.4569	0.2623
MRSD	136104	−100.85472	F	14.253	11.1648	−5.4991	−5.6657
			H_1	−0.108	4.1180	−1.9355	−2.1824
			H_2	1406.104	−0.7050	0.4496	0.2555

[a] In atomic units. [b] In megahertz.

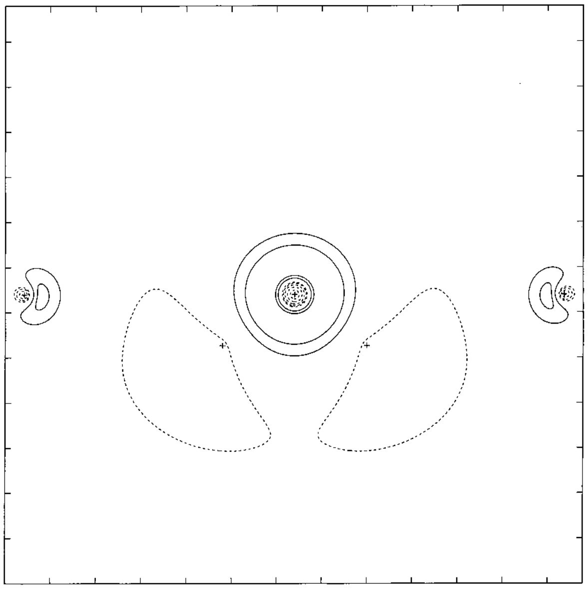

Figure 4. Contour of the singly occupied orbital of NH_4 in the neon matrix. The + symbols show the positions of nuclei. The nitrogen nucleus is at the center with two hydrogen atoms around it. The two neon atoms are at the two sides of the figure.

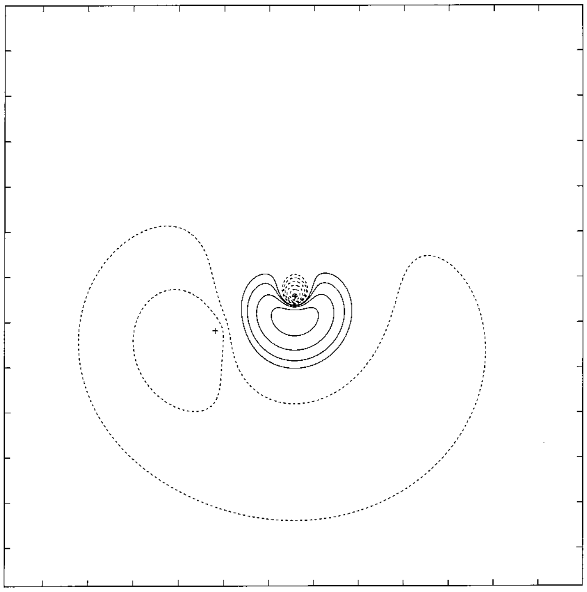

Figure 5. Contour of the singly occupied orbital of OH_3 in the gas phase. The + symbols show the positions of nuclei. The oxygen nucleus is at the center with one hydrogen atom around it.

to a difference in the hyperfine parameters in the two phases. The contours of the singly occupied orbitals of OH_3 and OH_3 plus 12 Ne were shown in Figures 3 and 4, respectively. They are s-type orbitals. The shapes of these two contours show the expected effect.

In Table 7 are given the results of hyperfine parameters of FH_2. No calculation was performed in the neon matrix. Since FH_2 is actually a van der Waals molecule close to the dissociation limit, the free electron is almost located on a hydrogen atom. In Table 7, as expected, the Fermi contact term of 1406.339 MHz for H_2 in the gas phase is comparable to the value of 1403.840 MHz for the free hydrogen. For the same reason, the changes in the hyperfine parameters in Table 7 are very much smaller with all correlation calculations.

IV. Conclusion

In this paper, the electronic structures of three isoelectronic Rydberg molecules (NH_4, OH_3, and FH_2) are investigated with extensive ab initio calculations. Calculations on geometrical structure, adiabatic ionization potential, dissociated energy, and barrier height are carried out for of NH_4, NH_4^+, NH_3, OH_3, OH_3^+, and OH_2 at the MP2 level with an aug-cc-pvxz series basis set (x = d, t, or q). The results are stable and converged. The IP of NH_4 is in excellent agreement with the experimental data. However, the difference between our theoretical IP and the experimental one for OH_3 is unexpectedly larger. We think that the experimental estimate may be somewhat too small. The equilibrium bond lengths of NH_4 and NH_4^+ at the infinite basis set limit are obtained by a parabolic interpolation around the minimum energy point. The bond length of NH_4 is very close to the value determined by Sattelmeyer, Schaefer, and Stanton by an extrapolation procedure of large [up to CCSD(T)/aug-cc-pv5z] coupled cluster calculations and analysis of experimental rotational constants.[44] The difference is ~10^{-3} Å. NH_4 and OH_3 are s-type Rydberg molecules. NH_4 is more nearly stable than OH_3. On the other hand, the isotopic counterparts are relatively more stable because of the reduction of their zero-point energies.

The hyperfine interaction calculations are carried out for these molecules in the gas phase as well as in the neon matrix at SCF, CIS, CISD, and MRSD levels. The geometrical parameters of the neutral molecules are close to their cation counterparts, which means that the excess electron is somewhat loosely bound to their corresponding cation cores. Thus, CIS could be regarded as a good starting point for these Rydberg molecules. The

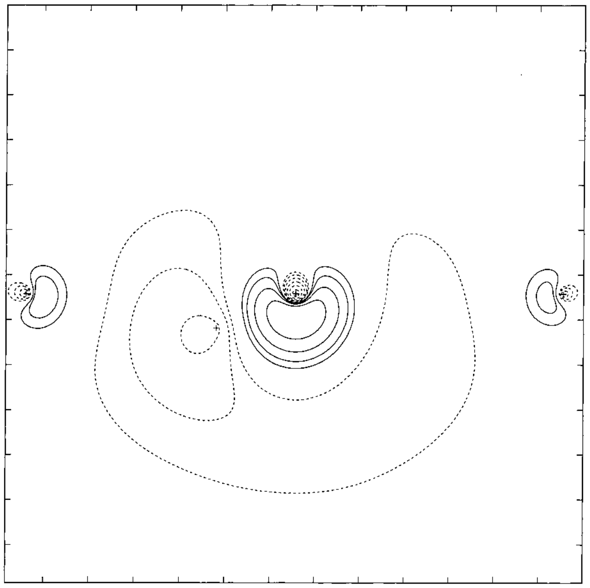

Figure 6. Contour of the singly occupied orbital of OH_3 in the neon matrix. The + symbols show the positions of nuclei. The oxygen nucleus is at the center with one hydrogen atom around it. The two neon atoms are at the two sides of the figure.

hyperfine parameters calculated with CIS in Tables 5−7 are all reasonable, though higher-level correlation methods such as MRSD are essential for obtaining highly accurate results.

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