

# Double-Rydberg anions: ground-state electronic and geometric stabilities

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Each member of the class of Double-Rydberg (DR) molecular anions consists of an underlying closed-shell cation core around which a pair of highly correlated electrons move in diffuse orbitals. We have examined the geometric and electronic stabilities of the ground states of candidate DR anions resulting from the following cation cores:  $\text{H}_3^+$ ,  $\text{NeH}^+$ ,  $\text{FH}_2^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{NH}_4^+$ , and  $\text{CH}_5^+$ . Near the equilibrium geometry of the cation, all of the DR anions, except  $\text{H}_3^-$ , are electronically stable with respect to the corresponding Rydberg radicals. Results of our geometry optimizations indicate, however, that only  $\text{NH}_4^-$  and  $\text{H}_3\text{O}^-$  are locally geometrically stable; the other DR anions undergo fragmentation. Vertical ionization potentials for the  $T_d$  isomer of  $\text{NH}_4^-$  and the  $C_{3v}$  isomer of  $\text{H}_3\text{O}^-$  are found to be 0.45 and 0.46 eV, respectively.

## I. INTRODUCTION

A member of the class of anions that we have termed double-Rydberg (DR) anions<sup>1</sup> consists of a geometrically and energetically stable cation core around which two "extra" electrons move in diffuse orbitals. The corresponding cation cores do not have unfilled valence orbitals; as a result, the DR states are the lowest states of these species at these geometries. We are primarily interested in highly symmetric molecular cores such as  $\text{H}_3^+$ ,  $\text{CH}_5^+$ ,  $\text{NH}_4^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{FH}_2^+$ , and  $\text{NeH}^+$ . A common feature of these cation cores, except for  $\text{H}_3^+$ , is that the lowest unoccupied molecular orbital transforms according to the totally symmetric irreducible representation of the relevant point group. Neutral or anion states that are formed with the nuclear framework not far from the cation equilibrium geometry are termed Rydberg (neutral) or double-Rydberg (anion) states, respectively.

### A. Rydberg neutrals

The earliest examples of neutral Rydberg (R) molecules are the diatomic noble gas dimers and hydrides.<sup>2</sup> Discrete spectra for rare gas hydrides  $\text{XH}$  were observed in discharges through mixtures of  $\text{X}$  and  $\text{H}_2$ ,<sup>3-5</sup> in neutralized ion beam experiments<sup>6-9</sup>, in mixtures of  $\text{X}$  and  $\text{H}_2$  irradiated with synchrotron radiation<sup>10</sup> and in translational spectroscopy measurements.<sup>11,12</sup> That the ground  $^2\Sigma$  states of these species are probably repulsive was deduced from broadening of the  $^2\Pi-^2\Sigma$  spectral lines for many  $\text{XH}$  systems<sup>2</sup> and was found in theoretical studies.<sup>13-17</sup>

The first polyatomic Rydberg molecule was discovered only in 1979. The existence of metastable Rydberg states of  $\text{H}_3$  was deduced by Herzberg from emission spectra in hollow-cathode discharges through  $\text{H}_2$  (Ref. 18) and by Vogler in the translational energy spectrum of  $\text{H}-\text{H}_2$  fragment pairs arising from predissociation of  $\text{H}_3$ .<sup>19</sup> Herzberg also predicted the geometry of the underlying cation core  $\text{H}_3^+$  ( $D_{3h}$  symmetry).

This pioneering work inspired many theoretical<sup>20-22</sup> and other experimental studies.<sup>23-28</sup> Simultaneous calculations on  $\text{H}_3$  by King and Morokuma,<sup>20</sup> Jungen<sup>21</sup> and Martin<sup>22</sup> confirmed the pattern of energy levels proposed by Herzberg. King and Morokuma also predicted the main Jahn-Teller constants which agreed remarkably well with the experimental data. Later, highly excited metastable states were calculated,<sup>29</sup> geometrical stabilities of various Rydberg states have been studied,<sup>30</sup> and, recently, in highly correlated calculations, Petsalakis *et al.* examined electronic transition moments among several low lying Rydberg states at various geometries.<sup>31</sup> Finally, the existence of Rydberg states of  $\text{H}_3$  has been confirmed in neutralized ion beam experiments.<sup>23-28</sup>

The  $\text{NH}_4$  Rydberg molecule was observed in 1981 (Ref. 32) using hollow-cathode discharges through  $\text{NH}_3$ . For  $\text{ND}_4$  the emission spectrum was more intense and sharper than for  $\text{NH}_4$ . Also, results from the neutralized ion beam experiments are more definitive for  $\text{ND}_4$  than for  $\text{NH}_4$ .<sup>33</sup> These observations are thought to be consequences of the 20  $\mu\text{s}$  lifetime for the ground state of  $\text{ND}_4$  and the 1  $\mu\text{s}$  lifetime for  $\text{NH}_4$ . They suggest that there is a small barrier on the ground-state surface which separates the  $T_d$  symmetry minimum from the dissociative channel (i.e.  $\text{H} + \text{NH}_3$ ). The fragmentation rate is slower for  $\text{ND}_4$  than for  $\text{NH}_4$  because the barrier tunneling rate is slower. Conclusions of many theoretical studies on  $\text{NH}_4$  (Refs. 34-39) are consistent with this picture: the  $^2A_1(3s)$  ground state is thermodynamically unstable at the  $T_d$  geometry, although there is a substantial barrier along the dissociation path. Among the excited states, the  $^2T_2(3p)$ ,  $^2A_1(4s)$  and  $^2T_2(3d)$  states are spectroscopically important.

The lifetime of the Rydberg  $\text{D}_3\text{O}$  radical was found in neutralization-reionization experiments to exceed 6  $\mu\text{s}$  whereas that of  $\text{H}_3\text{O}$  was estimated to be less than 70 ns.<sup>40</sup> However, the results of Griffiths *et al.* indicate that the lifetime of  $\text{H}_3\text{O}$  is larger than 0.4  $\mu\text{s}$ .<sup>26</sup> Theoretical studies by Raynor and Herschbach<sup>33</sup> and by Ortiz<sup>41</sup> indicate that the ground state is of  $^2A_1(3s)$  symmetry and has a minimum near the cation  $C_{3v}$  geometry.

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Other polyatomic Rydberg molecules, such as  $\text{FH}_2$  or  $\text{CH}_5$  have so far not been observed,<sup>2</sup> although preliminary results of Raksit *et al.* suggested existence of metastable states of  $\text{FD}_2$ .<sup>42</sup>

## B. Double-Rydberg anions

In 1987, the only experimentally verified example of a molecular DR anion was observed in photoelectron spectroscopy experiments in the Bowen group.<sup>43</sup> Photoelectron spectra of  $\text{NH}_4^-$  revealed, in addition to peaks ascribed to the removal of an electron from the  $\text{H}^- \cdots \text{NH}_3$  complex, another small but sharp feature, the position of which was not significantly affected by D isotopic substitution. This small peak was ascribed to detachment of an electron from a tetrahedral isomer of  $\text{NH}_4^-$ . Even before the experimental breakthrough, the  $\text{NH}_4^-$  tetrahedral structure had been studied theoretically by Kalcher *et al.*,<sup>44</sup> Cremer and Kraka<sup>45</sup> and Cardy *et al.*<sup>46</sup> Cardy *et al.* found that the ground state  $^1A_1(3s^2)$  is thermodynamically unstable by about 6 kcal mol<sup>-1</sup> relative to the  $\text{H}^- + \text{NH}_3$ , but that a relatively high barrier along the dissociative pathway (about 19 kcal mol<sup>-1</sup>) could make  $\text{NH}_4^-$  lived long enough to be observed experimentally.<sup>46</sup>

The result from the Bowen group inspired further theoretical studies. Ortiz carried out detailed geometry optimization and energy calculations of the different isomers of  $\text{NH}_4^-$  (Ref. 47) and  $\text{H}_3\text{O}^-$  (Ref. 41); Ortiz recently extended these studies to  $\text{FH}_2^-$ ,  $\text{ClH}_2^-$ ,  $\text{PH}_4^-$ ,  $\text{SH}_3^-$ .<sup>48</sup> The present authors, together with Hernandez and Taylor, performed a configuration interaction energy study on the ground and excited states of several atomic ( $\text{H}^-$ ,  $\text{Li}^-$ ,  $\text{Na}^-$ ) and molecular ( $\text{NeH}^-$ ,  $\text{FH}_2^-$ ,  $\text{H}_3\text{O}^-$ ,  $\text{NH}_4^-$ ,  $\text{CH}_5^-$ ,  $\text{H}_3^-$ ) DR anions.<sup>1</sup>

## C. This study

In the present paper we analyze the geometric and electronic stabilities of the ground states of several DR anions and their corresponding R radicals. The electronic stability of DR species is examined within the configuration interaction method in which the electrons that occupy diffuse orbitals are highly correlated. Geometry optimization is performed at the complete active space (CAS) multiconfigurational self-consistent field (MCSCF) level of theory. Harmonic vibrational frequencies are calculated using analytical second derivatives. All of the DR species considered here are found to be electronically stable, (i.e., their energies are lower than those of neutral counterparts) except for  $\text{H}_3^-$ . However, only two of the DR anions ( $\text{NH}_4^-$ ,  $\text{H}_3\text{O}^-$ ) are found to be geometrically stable near the geometry of the corresponding cation.

In Sec. II, our computational approach is discussed; our numerical results are presented in Sec. III, and our study is summarized in Sec. IV.

## II. METHOD OF CALCULATION

### A. Electronic stability

Accurate calculations of electron affinities are usually very demanding in terms of the one-electron basis sets and

the electronic configuration spaces that must be employed.<sup>49</sup> For R radicals and DR anions, however, the physical nature of the systems inevitably suggests a methodological simplification. Computational effort should be focused on correlating the outermost one or two electrons, whereas the closed-shell cation core can probably be considered more approximately. In a sense, the core can be thought of as providing an electrostatic potential for the outer two electrons. A similar model has been successfully used in theoretical studies of several electronic states for neutral R molecules<sup>20,21,29,30,34</sup>; this model must, of course, be verified (as it is later in this paper) before it can be used with any confidence.

In our approach, an initial SCF-level calculation for the underlying cation core is followed by an anion calculation that includes *all* electronic configurations that can be formed by distributing the two extra electrons among all available orbitals, with the cation core orbitals kept doubly occupied in all configurations. This we call the frozen cation core (FCC) full CI approach. The energy of the counterpart neutral Rydberg species is then calculated by distributing its single electron among all available orbitals keeping the cation core orbitals doubly occupied. This is equivalent to the Koopmans' theorem treatment of the Rydberg species.

The FCC approach completely neglects polarization of the underlying closed-shell core by two extra electrons. One could include static polarization effects by using the SCF orbitals of the anion to describe the core. In such an approach, the orbitals of the closed-shell core are then doubly occupied and the two-electron full-CI calculation is performed for the two active electrons. This alternative is denoted the frozen relaxed core (FRC) approach.

### B. Geometry optimization

All molecular geometries have been optimized for the cation, neutral, and anion species. The SCF-level geometry optimizations for the closed-shell cation cores have been performed using analytic first and second derivatives method. The R radical and DR anion geometry optimizations were performed at the CAS MCSCF level of theory with analytic first and second derivatives<sup>50</sup> starting from the cation equilibrium geometry and using our potential surface walking algorithm.<sup>51</sup> Symmetry breaking problems,<sup>52</sup> which may occur during optimization of the MCSCF wave function, have been avoided by using a computational strategy proposed by Earl.<sup>53</sup> After this geometry optimization, full-CI level calculations were carried out on the two active electrons of the DR species.

For our ten-electron cation cores, there are five doubly occupied orbitals at the SCF level. The symmetries of these orbitals depend upon the particular point group. In an atomic-limit notation, these orbitals correspond to 1s, 2s, and 2p orbitals. Using this shorthand notation, the orbital occupancies employed in all our CAS MCSCF calculations can be described compactly. In all MCSCF wave functions the 1s and 2s orbitals were kept doubly occupied. The remaining seven (R) or eight (DR) electrons were distributed in all possible ways among the 2p, 3s, 3p, and 4s orbitals. This

generated 1764 configuration state functions in the anion calculations.

The choice of the active space for use in our CAS MCSCF geometry optimizations (recall that a full valence electron CI calculation is used to obtain our final energies) was arrived at by performing several numerical tests. We carried out a series of MCSCF calculations for  $\text{Na}^-$  with the  $1s$ ,  $2s$ , and  $2p$  orbitals doubly occupied in all configuration state functions and the remaining two electrons in valence orbital spaces of different sizes. For example, the anion energy was only 0.002 eV lower when the  $3s$ ,  $3p$ ,  $4s$ ,  $4p$  orbitals were used as a valence space than when the  $3s$ ,  $3p$ ,  $4s$  orbitals were employed. Moreover, the latter result differed by less than 0.003 eV from the FRC result (full CI for the two outermost electrons in the field of the relaxed core). After examining such valence space possibilities, we decided to restrict the valence space in all DR anion geometry optimizations to the  $2p$ ,  $3s$ ,  $3p$ , and  $4s$  orbitals.

Whenever stable minima were found for the R radical and DR anion, the cation geometry optimization was repeated at the CAS MCSCF level of theory, with six electrons in the  $2p$ ,  $3s$ ,  $3p$ ,  $4s$  valence orbital space. The purpose of this calculation was to obtain geometries and vibrational frequencies that are consistent among the cation, neutral and anion.

### C. Basis sets and tests on atomic systems

The atomic orbital basis sets used for the geometry optimizations contain triple-zeta plus polarization contracted Gaussian basis sets (to represent the underlying closed-shell cores) plus seven sets of uncontracted diffuse  $s$ - and  $p$ -type Gaussian functions to improve the treatment of the one or two extra electrons which arise in the neutral and anion species. The exponents of these diffuse  $s$  and  $p$  functions are given in Table I. In Table I we also list exponents of diffuse  $d$ -type functions that were used in the atomic calculations ( $\text{H}^-$ ,  $\text{Li}^-$ ,  $\text{Na}^-$ ) and in selected molecular CI calculations as discussed later. These diffuse basis functions were located on the heavy atom except for the  $\text{H}_3$  case where they were located at the molecular center. The contracted Gaussian basis functions which are most important for the closed-shell cores were extracted from the correlation consistent Dunning basis sets by removing all but one of their polarization parts.<sup>54</sup> Copies of our combined basis sets for all nine systems considered in this study are available upon request (to reproduce them here in tabular form would be unwieldy).

The ability of the particular diffuse basis functions to

TABLE I. Exponents ( $a_0^{-2}$ ) of the Diffuse  $s$ -,  $p$ - and  $d$ -type Gaussian basis functions.

$s$ -type	$p$ -type	$d$ -type
1.000 0	1.000 0	0.900 0
0.244 74	0.282 54	0.272 28
5.989 9E-2	7.983 0E-2	8.419 2E-2
1.466 0E-2	2.468 4E-2	2.603 3E-2
5.710 7E-3	7.632 5E-3	8.049 7E-3
2.224 5E-3	2.360 0E-3	2.489 1E-3
8.665 5E-4	7.297 3E-4	7.696 7E-4

TABLE II. Electron affinities (eV) of H, Li and Na calculated within the FCC and FRC approaches. Results in parentheses were obtained with diffuse  $s$ ,  $p$  and  $d$  basis functions.

System	FCC	FRC	Ref. 71
H	0.72 (0.74)	0.72 (0.74)	0.75
Li	0.62 (0.62)	0.62 (0.62)	0.62
Na	0.54 (0.55)	0.54 (0.55)	0.55

reproduce Rydberg states was tested in calculations on excited states of the hydrogen, lithium, and sodium atoms. It was found that the  $s$ ,  $p$ , and  $d$ , energy levels of the hydrogen atom were reproduced with errors not exceeding 0.1, 0.4, 2.0, and 9.0 % for principal quantum numbers 2,3,4, and 5, respectively. Also, the experimentally observed spacings of the lowest four  $^2S$ ,  $^2P$ , and  $^2D$  states of Li and Na, (Ref. 55) were reproduced, using Koopmans' theorem, within 0.1 eV.

As a further test of our basis sets and computational approach, electron affinities of the H, Li and Na atoms were calculated within the FCC and FRC methods and are presented in Table II. The very good agreement with experimental data strongly supports the validity of the approximation of keeping the closed-shell core orbitals frozen in the R and DR calculations. Moreover, the close agreement between the FCC and FRC results shows that the relaxation of the closed-shell core in the presence of one or two extra  $s$ -type electrons is essentially the same. In addition, the full relaxation energy is quite small; for the sodium atom, it does not exceed 0.005 eV. Finally, the fact that the electron affinities calculated with and without diffuse  $d$ -type basis functions are different by no more than 0.02 eV suggests that diffuse  $d$ -type functions may not be crucial for determining the properties of DR anions in their ground states.

## III. RESULTS AND DISCUSSION

All of our *ab initio* calculations were performed using our in-house Utah MESS KIT (molecular electronic structure kit) software modules,<sup>56</sup> which treat SCF, MCSCF, and CI wave functions, as well as analytical energy derivatives (forces and force constants) and nonadiabatic couplings (wave function derivatives) among various electronic states.

### A. Geometric stability and vibrational frequencies of the molecular Rydberg and double-Rydberg systems

#### 1. The cation core geometries

Experimental geometry information about the closed-shell cation cores treated here is collected in Table III and compared with the results obtained in our SCF geometry optimizations. These systems have been carefully studied in recent years using direct absorption in a discharge with tunable infrared difference frequency lasers<sup>57-59</sup> and by velocity modulation absorption spectroscopy.<sup>60-64</sup> As was expected, our SCF internuclear distances are too short by a few hun-

TABLE III. Experimental and theoretical (SCF) values of interatomic distances (a.u.) and angles (deg) in cation cores.

Core	Experiment	Geometry
		This work (SCF)
$(\text{H}_3^+)^a D_{3h}$ (Ref. 57)	$r = 1.650$	1.650
$\text{NeH}^+ C_{\infty v}$ (Ref. 58)	$r = 1.827$	$r = 1.851$
$\text{FH}_2^+ C_{2v}$ (Ref. 60)	$r(\text{H-F}) = 1.827$	$r(\text{H-F}) = 1.788$
$\text{H}_3\text{O}^+ C_{3v}$ (Refs. 63,64)	$\angle_{\text{HFH}} = 113.21^\circ$	$\angle_{\text{HFH}} = 115.7^\circ$
	$r(\text{O-H}) = 1.859$	$r(\text{O-H}) = 1.818$
	$\angle_{\text{HOH}} = 115.3^\circ$	$\angle_{\text{HOH}} = 114.1^\circ$
$\text{NH}_4^+ T_d$ (Refs. 61, 62)	$r(\text{N-H}) = 1.931$	$r(\text{N-H}) = 1.912$
$(\text{CH}_5^+)^b C_s$	$r(\text{C-H}_2) = 2.039$	$r(\text{C-H}_4) = 2.061$
	$r(\text{C-H}_5) = 2.327$	$r(\text{C-H}_6) = 2.325$
	$r(\text{H}_5\text{-H}_6) = 1.643$	$\alpha(\text{H}_2\text{-C-H}_3) = 117.92^\circ$
	$\alpha(\text{H}_2\text{-C-H}_4) = 111.23^\circ$	$\alpha(\text{H}_2\text{-C-H}_5) = 96.69^\circ$
	$\alpha(\text{H}_4\text{-C-H}_6) = 80.97^\circ$	$\beta(\text{H}_2\text{-C-H}_6) = 114.80^\circ$
	$\beta(\text{H}_4\text{-C-H}_5) = 122.34^\circ$	

<sup>a</sup>Full CI calculation.

<sup>b</sup>There are no experimental results for  $\text{CH}_5^+$ ; we use the same notation for geometrical parameters as in Ref. 65.

dredths of an  $a_0$ , and our stretching frequencies (discussed later) are too high by 10–13 %. It should be mentioned that the  $\text{CH}_5^+$  ion is not a typical closed-shell protonated molecule. In a recent SCF-CI study by Komornicki and Dixon,<sup>65</sup> its equilibrium structure was shown to resemble a distorted hydrogen molecule bonded to a methyl cation, in which rotation of the methyl group relative to the hydrogen molecule is essentially free. These SCF optimized cation structures were used as starting points for the CAS MCSCF geometry optimizations on the R and DR systems.

## 2. Trends in potential energy surfaces

Before examining our CAS MCSCF results for R and DR species, it is useful to examine a general pattern that appears in our computational data. It appears that the geometrical force field operative in the cation provides stronger restoring forces than that of the DR anion which, in turn, is stronger than that of the R neutral. This is reflected in vibrational frequencies that are highest for the cation and smallest for the R neutral.

These trends can be rationalized by considering the electronic configurations that dominate the neutral and anion

species near the cation geometry and near dissociation. For example, consider the R and DR species arising from  $\text{NeH}^+$ . The cation  $\text{NeH}^+$  contains two electrons in its  $\sigma$  bond, and none in its  $\sigma^*$  antibonding orbital or in its R Rydberg orbital(s). As shown in Figs. 1 and 2, the Rydberg neutral has a  $\sigma^2 R^1$  configuration near the cation geometry and a  $\sigma^2 \sigma^{*1}$  configuration at dissociation. These two configurations differ by a single-spin orbital occupancy and therefore undergo a strongly avoided crossing. In contrast, the anion has a  $\sigma^2 R^2$  configuration near the cation geometry and a  $\sigma^2 \sigma^{*2}$  configuration at dissociation. These two configurations undergo a weakly avoided crossing because they differ by two-spin orbitals.

The weakly avoided crossing on the anion surface and the more strongly avoided crossing on the neutral surface are postulated to be the source of the stronger restoring force (along the dissociative coordinate) for the anion than for the neutral. The above qualitative analysis is in agreement with the Cardy *et al.* numerical results who found a higher barrier along a  $C_{3v}$  dissociation pathway for dissociation of  $\text{NH}_4^-$  than for  $\text{NH}_4^+$ .<sup>46</sup>

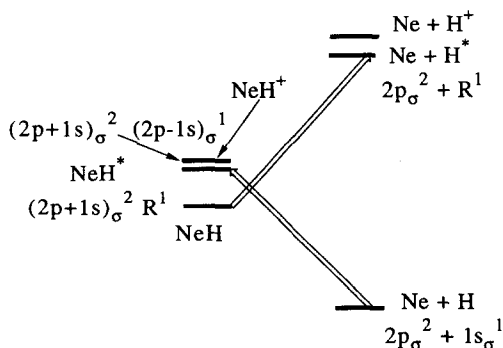


FIG. 1. Configuration correlation diagram for NeH and Ne + H.

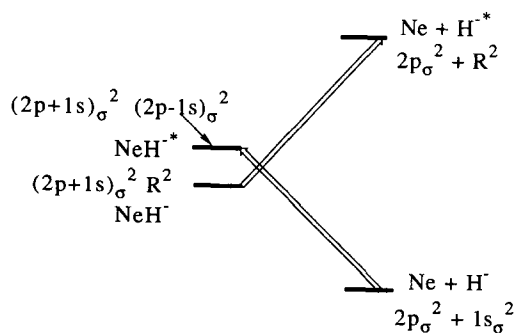


FIG. 2. Configuration correlation diagram for DR  $\text{NeH}^-$  and  $\text{Ne} + \text{H}^-$ .

### 3. Findings: geometrically unstable species

For  $\text{H}_3^-$ ,  $\text{NeH}^-$ ,  $\text{FH}_2^-$ , and  $\text{CH}_5^-$  we did not find minima on the ground-state potential surfaces in the vicinity of the respective parent cation equilibrium geometry. There may, of course, be minima corresponding to the hydride-molecule complexes which are bound due to their electrostatic and induction interactions. These structures, however, are not the topics of the present work. We also found the neutral Rydberg forms of  $\text{NeH}$ ,  $\text{FH}_2$ ,  $\text{CH}_5$ , and  $\text{H}_3$  species to be geometrically unstable.

### 4. $\text{FH}_2^+$ and the lowest stable Rydberg states of $\text{FH}_2$

Despite the geometrical instability of the corresponding ground-state R radical and DR anion, we studied these systems for two reasons. First, our calculations on  $\text{FH}_2^+$  allow us to evaluate the errors in our calculations by comparison with experimental data on this species.<sup>60</sup> Second, in view of the unresolved existence of metastable excited states of  $\text{FH}_2$ ,<sup>42</sup> we felt that theoretical studies on such states would be appropriate.

Our geometries and harmonic vibrational frequencies for  $\text{FH}_2^+$  and for the two lowest geometrically stable states of  $\text{FH}_2$  are presented in Table IV. For  $\text{FH}_2^+$ , our geometrical parameters compare better to the experimental results of Schafer and Saykally<sup>60</sup> than to results of Petsalakis *et al.*<sup>66</sup> In any case, the discrepancy does not exceed 0.02  $a_0$  for the bond lengths and 0.5 deg for the HFH angle. Our stretching frequencies are too high by about 200  $\text{cm}^{-1}$  when compared with the experimental results.<sup>60</sup> Perusal of Botschwina's review article<sup>67</sup> and Petsalakis *et al.* work<sup>66</sup> suggests that the bulk of the errors in our frequencies are caused by anharmonicity of the potential energy surface.

As already mentioned, the ground  $^2A_1(4a_1)$  state of the neutral  $\text{FH}_2$  was found to be geometrically unstable in the asymmetric stretching mode and to lie nearly 6 eV below cation's energy. Since Raksit *et al.* found the vertical electron affinity of  $\text{FH}_2^+$  to be about 6.6 eV, our result supports their speculation that the ground state of  $\text{FH}_2$  was accessed in their experiment.<sup>42</sup> Our results, however, do not show a dissociative barrier on the potential energy surface as was deduced from the enhanced metastability of  $\text{FD}_2$  relative to  $\text{FHD}$ .

The first two excited states  $^2B_2(2b_2)$  and  $^2B_1(2b_1)$  of  $\text{FH}_2$  are found to be geometrically stable, as shown in Table IV. The geometries of the  $^2B_2$  state and the cation are very different, as are the vibrational frequencies; those of the  $^2B_2$

TABLE IV. CAS MCSCF geometries (a.u. and deg) and local harmonic frequencies ( $\text{cm}^{-1}$ ) of  $\text{H}_2\text{F}^+$  and two lowest geometrically stable<sup>a</sup> Rydberg states of  $\text{FH}_2$ .

	Cation	$^2B_2$ neutral	$^2B_1$ neutral
$r(\text{F-H})$	1.827	2.316	1.818
Angle	112.7	97.0	112.5
$A_1$ vib.	1482	1473	1496
$B_2$ vib.	3563	4150	3633
$A_1$ vib.	3542	1025	3601

<sup>a</sup>The  $^2A_1$  ground state of the neutral is geometrically unstable.

state are rather unusual: 1025 and 4150  $\text{cm}^{-1}$  for the symmetric and asymmetric stretching, respectively. The reason for this unusual behavior is that the neutral's  $2b_2$  orbital is dominated by an antibonding combination of hydrogens'  $s$ -type orbitals rather than by a nonbonding fluorine  $np$ , symmetry orbital. This antibonding interaction is responsible for a dramatic elongation of the FH bonds (by 0.5  $a_0$ ) and a reduction of the symmetric stretching frequency (by 2500  $\text{cm}^{-1}$ ). Therefore, we see that the lowest geometrically stable state of  $\text{FH}_2$  is not a typical Rydberg state. However, the next excited state, the  $^2B_1(2b_1)$  state, is the first representative of the Rydberg family for  $\text{FH}_2$ . It has a geometry and vibrational frequencies quite like those of its parent cation (see Table IV). These qualitative features of the low lying states of  $\text{FH}_2$  are in agreement with the results of Petsalakis *et al.*<sup>68</sup>

### 5. $\text{H}_3\text{O}^-$

The ground states of the cation, neutral, and anion are found to be locally geometrically stable at the  $C_{3v}$  geometries shown in Table V. In comparison with the cation, we find the R and DR species to have elongation of the OH bonds by 0.06 and 0.05  $a_0$ , respectively, and slightly larger pyramidization of the nuclear framework. The cation has the "stiffest" vibrational modes. Addition of one or two extra electrons leads to a significant decrease of the stretching vibrational frequencies, with the neutral having softer vibrations than the anion. In particular, the frequency of the dissociative asymmetric stretching mode is reduced by 584 and 903  $\text{cm}^{-1}$  in the anion and neutral, respectively.

Comparison of our cation vibrational frequencies with experimental data is hindered not only by our use of the harmonic approximation but also by the presence of inversion splitting in the vibrational levels.<sup>59</sup> Our anion and neutral results compare well to those of Ortiz<sup>41</sup> who found, at the MP2 level of theory,  $r(\text{O-H})$  distances of 1.946  $a_0$  and 1.920  $a_0$  and bond angles of 107.2° and 107.0° for  $\text{H}_3\text{O}^-$  and  $\text{H}_3\text{O}$ , respectively. Ortiz's vibrational frequencies for the DR anion are always lower than ours; the largest discrepancy amounts to 17% (asymmetric stretching). Unfortunately, his frequencies for the neutral and cation are not available for further comparison.

### 6. $\text{NH}_4^-$

The ground states of the cation, neutral, and anion were all found to be locally stable at the tetrahedral geometries

TABLE V. Bond lengths (a.u.), angles (deg) and local harmonic frequencies ( $\text{cm}^{-1}$ ) for the  $\text{H}_3\text{O}$  cation, neutral and DR anion obtained in  $C_{3v}$  CAS MCSCF calculations

	$\text{H}_3\text{O}^+$	$\text{H}_3\text{O}$	$\text{H}_3\text{O}^-$
$r(\text{O-H})$	1.862	1.919	1.908
$\angle_{\text{HOH}}$	110.59	105.93	107.80
$A_1$ vib.	1042	1035	980
$A_1$ vib.	3527	3004	3106
$E$ vib.	1632	1629	1566
$E$ vib.	3630	2727	3046

TABLE VI. Bond lengths (a.u.) and local harmonic vibrational frequencies ( $\text{cm}^{-1}$ ) for tetrahedral structures of  $\text{NH}_4^+$ ,  $\text{NH}_4$ , and  $\text{NH}_4^-$  resulting from CAS MCSCF calculations.

	$\text{NH}_4^+$	$\text{NH}_4$	$\text{NH}_4^-$
$r(\text{N-H})$	1.937	1.960	1.964
$T_2$ vib	1543	1439	1434
$E$ vib	1776	1700	1717
$A_1$ vib	3384	3108	3140
$T_2$ vib	3629	3328	3276

described in Table VI. In comparison with the cation, we observed a slight elongation of the bond lengths in neutral and anion ( $0.02\text{--}0.03 a_0$ ). The cation has the “stiffest” vibrational modes. Not surprisingly, the  $T_2$  dissociative stretching mode is affected most strongly by the presence of the one or two extra electrons, but there is little difference between the corresponding neutral and anion frequencies. Because of the relatively low height of the barrier on the  $C_{3v}$  dissociative pathway,<sup>46</sup> anharmonic corrections are expected to be the largest for the  $T_2$  dissociative mode. Comparison of the experimental data for  $\text{NH}_4^+$  indicates a discrepancy in the cation’s  $T_2$  stretching frequency of  $285 \text{ cm}^{-1}$ ,<sup>61,62</sup> the bulk of which we ascribe to anharmonicity effects. Our CAS MCSCF geometries of the R and DR species compare favorably with the Ortiz results obtained at the MP2 level of correlation<sup>47</sup>; discrepancies in bond lengths do not exceed  $0.007 a_0$ .

## B. Electronic stability of the molecular DR systems

The electronic stabilities of the ground states of the molecular DR anions were examined at the SCF cation geometries given in Table III, except for  $\text{NH}_4^-$  and  $\text{H}_3\text{O}^-$ , for which the calculations were performed at the geometries given in Tables V and VI. The energies of the R and DR ground states were calculated within the FCC and FRC approaches and are given in Table VII, relative to the respective SCF cation core energies. For  $\text{NH}_4^-$  and  $\text{H}_3\text{O}^-$  the diffuse  $d$ -symmetry basis functions listed in Table I were also used.

All of the DR molecular systems, except  $\text{H}_3^-$ , are electronically stable with respect to the corresponding neutral R radical. For the two geometrically stable DR anions ( $\text{NH}_4^-$ ,  $\text{H}_3\text{O}^-$ ) the neutral–anion energy gaps are nearly independent of the computational approach, (FCC or FRC), which suggests that the polarization of the closed-shell cores is nearly the same in the presence of one or two extra  $a_1$ -type electrons. For  $\text{CH}_5^-$ , and especially for  $\text{NeH}^-$ , the neutral-

TABLE VII. Electronic stabilities (eV; calculated relative to the closed-shell cation cores) of the ground states of Rydberg (R) and double-Rydberg (DR) molecules in the FCC and FRC approximations.

	NeH		$\text{FH}_2$		$\text{H}_3\text{O}$		$\text{NH}_4$		$\text{CH}_5$	
	R	DR	R	DR	R	DR	R	DR	R	DR
FCC	6.99	7.07	5.51	5.92	4.81	5.27	4.03	4.48	3.89	4.23
FRC	7.25	7.29	5.60	6.01	4.88	5.34	4.06	4.51	4.01	4.29

anion energy differences calculated in the FCC and FRC approaches differ more significantly. This might be related to the geometrically unstable nature of these species.

The cation–neutral energy gaps are found to decrease in the series:  $\text{CH}_5^- < \text{NH}_4^- < \text{H}_3\text{O}^- < \text{FH}_2^- < \text{NeH}^-$ . The 4.94 eV cation–neutral gap for the sodium atom is the closest to the  $\text{H}_3\text{O}^-$  system. The neutral–anion energy differences form a more complicated pattern:  $\text{H}_3\text{O}^- \approx \text{NH}_4^- < \text{FH}_2^- < \text{CH}_5^- < \text{NeH}^-$ . The  $\text{H}_3\text{O}^-$  system, which is the closest to Na in the cation–neutral sense, is also closest in the anion–neutral sense (0.46 eV for  $\text{H}_3\text{O}^-$  versus 0.55 eV for Na).

The computed electron binding energy for  $\text{NH}_4^-$ , 0.45 eV, is in good agreement with the experimental value of 0.47 eV<sup>43</sup> and with the value of 0.42 eV obtained by Ortiz within electron propagator theory.<sup>47</sup> The electron binding energy for  $\text{H}_3\text{O}^-$ , 0.46 eV, compares favorably with the recent Ortiz result of 0.43 eV.<sup>41</sup> There is no experimental evidence about the DR  $\text{H}_3\text{O}^-$ ; only the conventional  $\text{H}^- \cdots \text{H}_2\text{O}$  structure has been found in the photoelectron spectroscopy experiments<sup>69</sup> although recent charge-inversion experiments<sup>70</sup> suggest the existence of other isomers whose structures have not yet been resolved.

For  $\text{H}_3^-$  we did not find any state with energy below the  $D_{3h} \ ^2E'(2p)$  ground state of the neutral. This neutral state is unstable with respect to fragmentation to  $\text{H} + \text{H}_2$ . On the other hand, certain excited states of neutral  $\text{H}_3$  must be geometrically stable<sup>2</sup> and we have found the anionic  $^1A_1(2s^2)$  state to lie 0.49 eV below the first excited neutral state  $^1A_1(2s)$  of  $\text{H}_3$ . The  $^1A_1(2s^2)$  state may be electronically metastable because its dominant  $2s^2$  electronic configuration differs by two orbitals from that of the underlying neutral  $^2E'(2p)$  plus an ejected  $p$ -wave electron.

## IV. SUMMARY

We have found, using correlated CI calculations, that the ground states of the molecular double-Rydberg anions  $\text{CH}_5^-$ ,  $\text{NH}_4^-$ ,  $\text{H}_3\text{O}^-$ ,  $\text{FH}_2^-$ , and  $\text{NeH}^-$  are *electronically stable* relative to the ground states of the corresponding Rydberg radicals;  $\text{H}_3^-$  is *electronically unstable*. Our CAS MCSCF geometry optimization shows that  $\text{NH}_4^-$ ,  $\text{H}_3\text{O}^-$  are also locally *geometrically stable* in the vicinity of the parent cation equilibrium geometry, while  $\text{FH}_2^-$ ,  $\text{CH}_5^-$  and  $\text{NeH}^-$  are *geometrically unstable*. We find the lowest R states of  $\text{FH}_2$ ,  $\text{CH}_5$ ,  $\text{H}_3$ , and  $\text{NeH}$  to be geometrically unstable, while those of  $\text{H}_3\text{O}$  and  $\text{NH}_4$  are locally stable.  $\text{FH}_2$  is found to have interesting geometrically stable excited states. All of these anions and neutrals are thermodynamically unstable with respect to fragmentation.

Our calculations, although demonstrating the local stability of certain ground-state DR anions, say nothing about their lifetimes with respect to dissociation. The rates of fragmentation, which depend on the “height” and “thickness” of the barrier, separating the local minimum from the fragments, will be the subject of a future study.

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