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: H$_3^+$, NeH$_2^+$, FH$_2^+$, H$_2$O$^+$, NH$_2^+$, and CH$_2^+$. Near the equilibrium geometry of the cation, all of the DR anions, except H$_3^+$, are electronically stable with respect to the corresponding Rydberg radicals. Results of our geometry optimizations indicate, however, that only NH$_2^+$ and H$_2$O$^-$ are locally geometrically stable; the other DR anions undergo fragmentation. Vertical ionization potentials for the $T_d$ isomer of NH$_2^+$ and the $C_{2v}$ isomer of H$_2$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 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 H$_3^+$, CH$_2^+$, NH$_2^+$, H$_2$O$^+$, FH$_2^+$, and NeH$_2^+$. A common feature of these cation cores, except for 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. Discrete spectra for rare gas hydrides XH$_2$ were observed in discharges through mixtures of X and H$_2$ in neutralized ion beam experiments in mixtures of X and H$_2$ irradiated with synchrotron radiation and in translational spectroscopy measurements. 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 XH systems and was found in theoretical studies.

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

This pioneering work inspired many theoretical and other experimental studies. Simultaneous calculations on H$_3$ by King and Morokuma, Jungen and Martin 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, geometrical stabilities of various Rydberg states have been studied, and, recently, in highly correlated calculations, Petralakis et al. examined electronic transition moments among several low lying Rydberg states at various geometries. Finally, the existence of Rydberg states of H$_3$ has been confirmed in neutralized ion beam experiments.

The NH$_2$ Rydberg molecule was observed in 1981 (Ref. 32) using hollow cathode discharges through NH$_3$. For ND$_4$ the emission spectrum was more intense and sharper than for NH$_4$. Also, results from the neutralized ion beam experiments are more definitive for ND$_4$ than for NH$_4$. These observations are thought to be consequences of the 20 $\mu$s lifetime for the ground state of ND$_4$ and the 1 $\mu$s lifetime for 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. H + NH$_3$). The fragmentation rate is slower for ND$_4$ than for NH$_4$ because the barrier tunneling rate is slower. Conclusions of many theoretical studies on NH$_4$ (Refs. 34–39) are consistent with this picture: the $2^1A_1(3s)$ 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 $2^2A_1(3p)$, $2^2A_1(4s)$ and $2^2A_2(3d)$ states are spectroscopically important.

The lifetime of the Rydberg D$_2$O radical was found in neutralization-reionization experiments to exceed 6 $\mu$s whereas that of H$_2$O was estimated to be less than 70 ns. However, the results of Griffiths et al. indicate that the lifetime of H$_2$O is larger than 0.4 $\mu$s. Theoretical studies by Raynor and Herschbach and by Ortiz indicate that the ground state is of $4^1A_1(3s)$ symmetry and has a minimum near the cation $C_{3v}$ geometry.

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Other polyatomic Rydberg molecules, such as FH₂ or CH₃, have so far not been observed, although preliminary results of Rakit et al. suggested existence of metastable states of FD₂. 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. Photoelectron spectra of NH₄⁺ revealed, in addition to peaks ascribed to the removal of an electron from the H⁻····NH₃ 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 NH₄⁺. Even before the experimental breakthrough, the NH₄⁺ tetrahedral structure had been studied theoretically by Kalcher et al., Cremer and Krakà and Cardy et al. Cardy et al. found that the ground state \( ^4A_1 (3\Sigma^c) \) is thermodynamically unstable by about 6 kcal mol⁻¹ relative to the H⁻ + NH₃, but that a relatively high barrier along the dissociative pathway (about 19 kcal mol⁻¹) could make NH₄⁺ lived long enough to be observed experimentally.

The result from the Bowen group inspired further theoretical studies. Ortiz carried out detailed geometry optimization and energy calculations of the different isomers of NH₂⁻ (Ref. 47) and H₂O⁺ (Ref. 41); Ortiz recently extended these studies to FH₂⁻, ClH₂⁻, PH₄⁻, SH₂⁻. The present authors, together with Hernandez and Taylor, performed a configuration interaction energy study on the ground and excited states of several atomic (H⁻, Li⁻, Na⁻) and molecular (NeH⁻, FH₂⁻, H₂O⁺, NH₄⁻, CH₃⁻, H₃⁻) DR anions.

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 H₃⁻. However, only two of the DR anions (NH₄⁻, H₃O⁺) 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. 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; 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 starting from the cation equilibrium geometry and using our potential surface walking algorithm. Symmetry breaking problems, which may occur during optimization of the MCSCF wave function, have been avoided by using a computational strategy proposed by Earl. 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 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 outer-
most electrons in the field of the relaxed core). After exam-
ining 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 fre-
quencies 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 opti-
mizations 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 spe-
cies. 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
(H\(^+\), Li\(^+\), Na\(^+\)) and in selected molecular CI calculations
as discussed later. These diffuse basis functions were located
on the heavy atom except for the 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.\(^{54}\) Copies of our combined basis sets for all nine systems
considered in this study are available upon request (to repro-
duce them here in tabular form would be unwieldy).

The ability of the particular diffuse basis functions to
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, respec-
tively. Also, the experimentally observed spacings of the
lowest four S, P, and D 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 pre-
sented in Table II. The very good agreement with experi-
mental data strongly supports the validity of the approxima-
tion 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 affini-
ties calculated with and without diffuse d-type basis func-
tions 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 \textit{ab initio} calculations were performed using
our in-house Utah MESS KIT (molecular electronic structure
kit) software modules,\(^{56}\) 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 tun-
able infrared difference frequency lasers\(^{57-59}\) and by velocity
modulation absorption spectroscopy.\(^{50-64}\) As was expected,
our SCF internuclear distances are too short by a few hun-

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

<table>
<thead>
<tr>
<th>(s)-type</th>
<th>(p)-type</th>
<th>(d)-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000 0</td>
<td>1.000 0</td>
<td>0.900 0</td>
</tr>
<tr>
<td>0.244 74</td>
<td>0.282 54</td>
<td>0.272 28</td>
</tr>
<tr>
<td>5.989 9E-2</td>
<td>7.983 0E-2</td>
<td>8.419 2E-2</td>
</tr>
<tr>
<td>1.466 0E-2</td>
<td>2.468 4E-2</td>
<td>2.603 3E-2</td>
</tr>
<tr>
<td>5.710 7E-3</td>
<td>7.632 0E-3</td>
<td>8.097 7E-3</td>
</tr>
<tr>
<td>2.224 0E-3</td>
<td>2.360 0E-3</td>
<td>2.489 0E-3</td>
</tr>
<tr>
<td>8.665 5E-4</td>
<td>7.297 3E-4</td>
<td>7.696 7E-4</td>
</tr>
</tbody>
</table>

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**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.**

<table>
<thead>
<tr>
<th>System</th>
<th>FCC</th>
<th>FRC</th>
<th>Ref. 71</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.72 (0.74)</td>
<td>0.72 (0.74)</td>
<td>0.75</td>
</tr>
<tr>
<td>Li</td>
<td>0.62 (0.62)</td>
<td>0.62 (0.62)</td>
<td>0.62</td>
</tr>
<tr>
<td>Na</td>
<td>0.54 (0.55)</td>
<td>0.54 (0.55)</td>
<td>0.55</td>
</tr>
<tr>
<td>Core</td>
<td>Experiment</td>
<td>Geometry This work (SCF)</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>------------</td>
<td>-------------------------</td>
<td></td>
</tr>
<tr>
<td>(H⁺)⁺ D₃h (Ref. 57)</td>
<td>( r = 1.650 )</td>
<td>1.650</td>
<td></td>
</tr>
<tr>
<td>NeH⁺ C₃v (Ref. 58)</td>
<td>( r = 1.827 )</td>
<td>1.851</td>
<td></td>
</tr>
<tr>
<td>FH₂⁺ C₃v (Ref. 60)</td>
<td>( \angle_{\text{H-F-H}} = 113.21^\circ )</td>
<td>( \angle_{\text{H-F-H}} = 115.7^\circ )</td>
<td></td>
</tr>
<tr>
<td>H₂O⁺ C₂v (Refs. 63, 64)</td>
<td>( r = 1.859 )</td>
<td>( r = 1.818 )</td>
<td></td>
</tr>
<tr>
<td>( \angle_{\text{H-O-H}} = 115.3^\circ )</td>
<td>( \angle_{\text{H-O-H}} = 114.1^\circ )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄⁺ Tₐ (Refs. 61, 62)</td>
<td>( r = 1.931 )</td>
<td>( r = 1.912 )</td>
<td></td>
</tr>
<tr>
<td>(CH₃⁺)⁺ C₁</td>
<td>( r = 2.039 )</td>
<td>( r = 2.061 )</td>
<td></td>
</tr>
<tr>
<td>( r = 2.327 )</td>
<td>( r = 2.325 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( r(H₃-H₄) = 1.643 )</td>
<td>( r(H₃-H₄) = 1.643 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha(H₃-C₃H₄) = 111.23^\circ )</td>
<td>( \alpha(H₃-C₃H₄) = 111.23^\circ )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \beta(H₃-C₃H₄) = 80.97^\circ )</td>
<td>( \beta(H₃-C₃H₄) = 80.97^\circ )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha(H₃-C₃H₄) = 117.92^\circ )</td>
<td>( \alpha(H₃-C₃H₄) = 117.92^\circ )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \beta(H₃-C₃H₄) = 114.8^\circ )</td>
<td>( \beta(H₃-C₃H₄) = 114.8^\circ )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Full CI calculation.
*There are no experimental results for CH₃⁺; 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 CH₃⁺ ion is not a typical closed-shell protonated molecule. In a recent SCF-CI study by Komornicki and Dixon,[65] 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 NeH⁺. The cation NeH⁺ contains two electrons in its σ bond, and none in its σ* antibonding orbital or in its R Rydberg orbital(s). As shown in Figs. 1 and 2, the Rydberg neutral has a \( \sigma^2 \) R¹ configuration near the cation geometry and a \( \sigma^2 \sigma^* \) 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 \( \sigma^2 \) R¹ configuration near the cation geometry and a \( \sigma^2 \sigma^* \) 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 which found a higher barrier along a C₃v dissociation pathway for dissociation of NH₄⁻ than for NH₄⁺.[46]

![FIG. 1. Configuration correlation diagram for NeH and Ne + H.](http://ojps.aip.org/jcpo/jcpcr.jsp)

![FIG. 2. Configuration correlation diagram for DR NeH⁺ and Ne + H⁻.](http://ojps.aip.org/jcpo/jcpcr.jsp)
3. Findings: geometrically unstable species

For H₃⁺, NeH⁺, FH₂⁺, and CH₃⁺, 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 NeH, FH₂, CH₅⁺, and H₃⁺ species to be geometrically unstable.

4. FH₃⁺ and the lowest stable Rydberg states of FH₂

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 FH₃⁺ allow us to evaluate the errors in our calculations by comparison with experimental data on this species.⁶⁶ Second, in view of the unresolved existence of metastable excited states of FH₂⁺,⁷² we felt that theoretical studies on such states would be appropriate.

Our geometries and harmonic vibrational frequencies for FH₃⁺ and for the two lowest geometrically stable states of FH₂ are presented in Table IV. For FH₃⁺, our geometrical parameters compare better to the experimental results of Schafer and Saykally⁶⁶ than to results of Petsalakis et al.⁷⁶ In any case, the discrepancy does not exceed 0.02 a₀ for the bond lengths and 0.5 deg for the HFH angle. Our stretching frequencies are too high by about 200 cm⁻¹ when compared with the experimental results.⁶⁰ Perusal of Bottswina’s review article⁶⁷ and Petsalakis et al. work⁶⁸ suggests that the bulk of the errors in our frequencies are caused by the harmonic approximation of the potential energy surface.

As already mentioned, the ground ¹A₁ (4A₁) state of the neutral FH₂ was found to be geometrically unstable in the asymmetric stretching mode and to lie nearly 6 eV below cation’s energy. Since Rakst et al. found the vertical electron affinity of FH₂⁺ to be about 6.6 eV, our result supports their speculation that the ground state of FH₂ was accessed in their experiment.⁴² Our results, however, do not show a dissociative barrier on the potential energy surface as was deduced from the enhanced metastability of FD₂ relative to FHD.

The first two excited states ²B₁(2B₁) and ²B₁(2B₁) of FH₂ are found to be geometrically stable, as shown in Table IV. The geometries of the ²B₁ state and the cation are very different, as are the vibrational frequencies; those of the ²B₂ state are rather unusual: 1025 and 4150 cm⁻¹ for the symmetric and asymmetric stretching, respectively. The reason for this unusual behavior is that the neutral’s 2b₂ orbital is dominated by an antibonding combination of hydrogens’ s-type orbitals rather than by a nonbonding fluorine np₄ symmetry orbital. This antibonding interaction is responsible for a dramatic elongation of the FH bonds (by 0.5 a₀) and a reduction of the symmetric stretching frequency (by 2500 cm⁻¹). Therefore, we see that the lowest geometrically stable state of FH₂ is not a typical Rydberg state. However, the next excited state, the ²B₁(2B₁) state, is the first representative of the Rydberg family for FH₂. 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 FH₂ are in agreement with the results of Petsalakis et al.⁶⁸

5. H₂O⁻

The ground states of the cation, neutral, and anion are found to be locally geometrically stable at the C₃ᵥ 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 a₀, 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 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.⁹⁶ Our anion and neutral results compare well to those of Ortiz⁴¹ who found, at the MP2 level of theory, r(O-H) distances of 1.946 a₀ and 1.920 a₀ and bond angles of 107.2° and 107.0° for H₂O⁻ and H₂O, 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. NH₄⁺

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

### Table IV. CAS MCSCF geometries (a.u. and deg) and local harmonic frequencies (cm⁻¹) of H₂F⁺ and two lowest geometrically stable Rydberg states of FH₂.

<table>
<thead>
<tr>
<th>Cation</th>
<th>²B₁ neutral</th>
<th>²B₁ neutral</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(F-H)</td>
<td>1.827</td>
<td>2.316</td>
</tr>
<tr>
<td>Angle</td>
<td>112.7</td>
<td>97.0</td>
</tr>
<tr>
<td>A₁ vib.</td>
<td>1482</td>
<td>1473</td>
</tr>
<tr>
<td>B₁ vib.</td>
<td>3563</td>
<td>4150</td>
</tr>
<tr>
<td>A₁ vib.</td>
<td>3542</td>
<td>1025</td>
</tr>
</tbody>
</table>

*The ⁷A₁ ground state of the neutral is geometrically unstable.

### Table V. Bond lengths (a.u.), angles (deg) and local harmonic frequencies (cm⁻¹) for the H₂O cation, neutral and DR anion obtained in C₃ᵥ, CAS MCSCF calculations

<table>
<thead>
<tr>
<th>H₂O⁺</th>
<th>H₂O</th>
<th>H₂O⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(O-H)</td>
<td>1.862</td>
<td>1.919</td>
</tr>
<tr>
<td>A₁ vib.</td>
<td>1042</td>
<td>1035</td>
</tr>
<tr>
<td>A₁ vib.</td>
<td>3527</td>
<td>3004</td>
</tr>
<tr>
<td>A₁ vib.</td>
<td>3630</td>
<td>2727</td>
</tr>
<tr>
<td>E vib.</td>
<td>1632</td>
<td>1629</td>
</tr>
<tr>
<td>E vib.</td>
<td>3630</td>
<td>2727</td>
</tr>
</tbody>
</table>
TABLE VI. Bond lengths (a.u.) and local harmonic vibrational frequencies (cm$^{-1}$) for tetrahedral structures of NH$_4^+$, NH$_6^-$ and NH$_7^-$ resulting from CAS MCSCF calculations.

<table>
<thead>
<tr>
<th></th>
<th>NH$_4^+$</th>
<th>NH$_6^-$</th>
<th>NH$_7^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(N-H)</td>
<td>1.937</td>
<td>1.960</td>
<td>1.964</td>
</tr>
<tr>
<td>T$_1$ vib</td>
<td>1543</td>
<td>1439</td>
<td>1434</td>
</tr>
<tr>
<td>E vib</td>
<td>1776</td>
<td>1700</td>
<td>1717</td>
</tr>
<tr>
<td>A$_1$ vib</td>
<td>3384</td>
<td>3108</td>
<td>3140</td>
</tr>
<tr>
<td>T$_2$ vib</td>
<td>3629</td>
<td>3328</td>
<td>3276</td>
</tr>
</tbody>
</table>

described in Table VI. In comparison with the cation, we observed a slight elongation of the bond lengths in neutral and anion (0.02–0.03 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, anharmonic corrections are expected to be the largest for the T$_2$ dissociative mode. Comparison of the experimental data for NH$_6^-$ indicates a discrepancy in the cation’s T$_2$ stretching frequency of 285 cm$^{-1}$, which is a 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; 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 NH$_4^+$ and H$_2$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 NH$_6^-$ and H$_2$O$^-$ the diffuse d-symmetry basis functions listed in Table I were also used.

All of the DR molecular systems, except H$_2$O, are electronically stable with respect to the corresponding neutral R radical. For the two geometrically stable DR anions (NH$_4^+$, H$_2$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 CH$_3^-$, and especially for NeH$^-$, the neutral-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: CH$_3$ < NH$_4$ < H$_2$O < FH$_2$ < NeH. The 4.94 eV cation–neutral gap for the sodium atom is the closest to the H$_2$O system. The neutral–anion energy differences form a more complicated pattern: H$_2$O ≈ NH$_4$ < FH$_2$ < CH$_3$ < NeH. The H$_2$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 H$_2$O versus 0.55 eV for Na).

The computed electron binding energy for NH$_6^-$, 0.45 eV, is in good agreement with the experimental value of 0.47 eV and with the value of 0.42 eV obtained by Ortiz within electron propagator theory. The electron binding energy for H$_2$O$^-$, 0.46 eV, compares favorably with the recent Ortiz result of 0.43 eV. There is no experimental evidence about the DR H$_2$O$^-$; only the conventional H$^-$ ⋯ H$_2$O structure has been found in the photoelectron spectroscopy experiments although recent charge-inversion experiments suggest the existence of other isomers whose structures have not yet been resolved.

For H$_3^-$ we did not find any state with energy below the D$_3h$ $^1E$ (2p) ground state of the neutral. This neutral state is unstable with respect to fragmentation to H + H$_2$. On the other hand, certain excited states of neutral H$_3$ must be geometrically stable and we have found the anionic $^1A_1^-$ (2p$^2$) state to lie 0.49 eV below the first excited neutral state $^1A_1^+$ (2s) of H$_3$. The $^1A_1^-$ (2p$^2$) state may be electronically metastable because its dominant 2p$^2$ electronic configuration differs by two orbitals from that of the underlying neutral $^3E$ (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 CH$_3^-$, NH$_4^+$, H$_2$O$^-$, FH$_2^-$, and NeH$^-$ are electronically stable relative to the ground states of the corresponding Rydberg radicals; H$_3^-$ is electronically unstable. Our CAS MCSCF geometry optimization shows that NH$_4^+$, H$_2$O$^-$ are also locally geometrically stable in the vicinity of the parent cation equilibrium geometry, while FH$_2^-$, CH$_3^-$ and NeH$^-$ are geometrically unstable. We find the lowest R states of FH$_2$, CH$_3$, H$_2$, and NeH to be geometrically unstable, while those of H$_2$O and NH$_4$ are locally stable. 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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