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# Double-Rydberg Molecular Anions

JACK SIMONS\* and MACIEJ GUTOWSKI

Chemistry Department, University of Utah, Salt Lake City, Utah 84112

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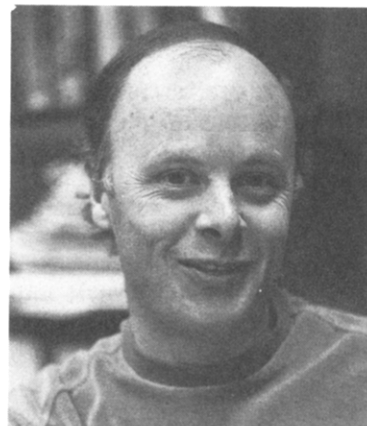
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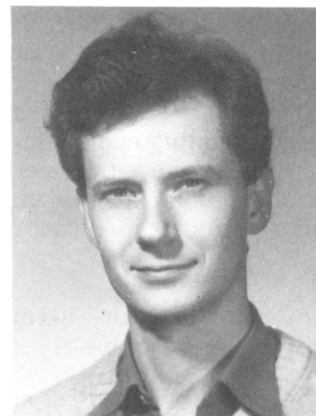
## I. Introduction

### A. The Nature of Double-Rydberg Electronic States

Studies of families of unusual species such as the double-Rydberg (DR) anions discussed in this review are of fundamental importance. These investigations expand our knowledge base and understanding of electronic structure and electronic dynamics. As science enters the 1990's, the search for new materials, new reaction pathways, and the design of materials with specified physical and chemical properties will require chemists to extend their conceptual understanding of chemical bonding and electronic structure and their relation to macroscopic behavior. It is the belief of the authors that any and all experience in which novel bonding situations or unusual electronic structures are encountered can contribute to the broadening of chemists' conceptual base. The class of anions treated here are unusual because (i) they are *local minima* on respective ground-state potential energy hypersurfaces where much more stable global minima exist, so rearrangement of the DR species via barrier tunneling is possible, (ii) they are electronically stable *only* because the motions of the outermost pair of electrons (i.e., those that occupy the diffuse Rydberg-like orbitals) involve highly radially and angularly correlated motions (i.e., their electronic structures can *not* be viewed in the conventional "electron pair occupying an orbital" picture), (iii) they possess a multitude of *excited electronic*



Jack Simons was born in Youngstown, OH on April 2, 1945. He attended Case Institute of Technology in Cleveland, OH, where he earned a B.S. degree in chemistry in 1967. He then attended the University of Wisconsin, where he earned a Ph.D. in theoretical chemistry in 1970. After a year as an NSF Postdoctoral Fellow at MIT, he joined the Utah faculty in 1971, where he was recently appointed to the Henry Eyring Chair in Chemistry. Professor Simons has been recognized by a University of Utah Distinguished Research Award, Alfred P. Sloan, Camille and Henry Dreyfus, and J. S. Guggenheim Fellowships. In 1983, he was given the Medal of The International Academy of Quantum Molecular Sciences. He and his co-workers have focused their efforts on theoretical modeling of negative molecular ions.



Maciej Gutowski was born in Warsaw, Poland, in 1955. He received his M.S. degree in theoretical chemistry from the University of Warsaw in 1978. In 1979 he joined Włodzimierz Kolos' group at the Chemistry Department, University of Warsaw. He spent a short period as a research associate with Frans van Duijneveldt at the University of Utrecht. In 1987 he received his Ph.D. in theoretical chemistry working with Lucjan Piela and Grzegorz Chalasinski on intermolecular interactions and ionic crystals. He is currently a postdoctoral associate with Jack Simons at the University of Utah. His research interests focus on ab initio investigations of intermolecular interactions, Rydberg molecules, and double-Rydberg anions.

*states* that are metastable with respect to electron autodetachment but which may be long lived and hence experimentally accessible.

Each member of the so-called family of double-Rydberg anions<sup>1</sup> consists of an underlying geometrically and electronically stable cation core (referred to as the *parent cation*) around which a pair of electrons move in diffuse orbitals. Examples of parents that have been studied experimentally or theoretically include the closed-shell 10-electron species  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{CH}_5^+$ ,  $\text{Na}^+$ ,  $\text{H}_2\text{F}^+$ , and  $\text{NeH}^+$ , as well as two-electron cations such as  $\text{H}_3^+$  and  $\text{Li}^+$ . The  $\text{H}^-$  species, whose parent is the "zero-electron"  $\text{H}^+$  has also been characterized. In such studies, it has been of interest to compare the pattern of electronic energy levels observed for iso-electronic systems to determine, for example, if one can analyze these patterns in terms of "crystal field" like splittings of the spherically symmetric case (i.e., can the levels for  $\text{NH}_4^-$  be determined as  $T_d$  derivatives of those for  $\text{Na}^-$ ). As discussed later in this review, such a model has indeed been successful for the 10-electron DR species.

When might one expect to encounter such DR species? If the cation parent of a DR anion is, *at its equilibrium geometry*, a closed-shell species such as those mentioned above, the lowest energy states of both the *neutral species* formed when a single electron moves in a diffuse orbital around the underlying cation core and of the corresponding DR anion involve, in the neighborhood of the parent cation's equilibrium geometry, Rydberg-like rather than valence-like electronic structures. That is, if the parent has no unfilled valence orbitals at its equilibrium geometry, both the neutral and anion must utilize Rydberg orbitals at this geometry.

In contrast, if the parent cation is valence "unsaturated" at its most stable geometry, its neutral daughter and anion may have both stable valence-type electronic states as well as Rydberg-like states. For example,  $\text{Cl}^+$  certainly forms stable valence  $\text{Cl}$  and  $\text{Cl}^-$  states. In addition, both the neutral ( $1s^2 2s^2 2p^6 3s^2 3p^4 4s^1$ )  $\text{Cl}$  and anion ( $1s^2 2s^2 2p^6 3s^2 3p^4 4p^2$ )  $\text{Cl}^-$  states exist and consist, respectively, of a  $1s^2 2s^2 2p^6 3s^2 3p^4$  cation core with one  $4s$  or a pair of  $4p$  Rydberg-like orbitals (i.e., orbitals one or more quantum number higher than that of the outer valence orbitals). Of course, in these cases for which the parent cation possesses unfilled valence orbitals, the DR anion states will not be the lowest energy states.

## B. The Global Geometrical or Thermodynamic Stability of Rydberg and Double-Rydberg States

The Rydberg states of the neutral and of the DR species may or may not be stable with respect to distortion or fragmentation of the underlying nuclear framework. Global stability depends on the strengths of the bonds in the cation and the products of fragmentation as well as the ionization potentials (IPs) and electron affinities (EAs) of these products. For example, the stability of neutral  $\text{NeH}$  is, as shown in Figure 1, determined by the IP of the Rydberg  $\text{NeH}$ , the  $\text{Ne-H}$  bond strength in  $\text{NeH}^+$ , and the IP of  $\text{H}$ . Likewise, the stability of  $\text{NeH}^-$ , as shown in Figure 2, is governed by the IP of the DR  $\text{NeH}^-$ , the  $D_e$  of  $\text{NeH}$ , and the EA of  $\text{H}$ .

It should therefore be clear that the Rydberg states of the neutral are unlikely to be thermodynamically stable<sup>2</sup> unless the bond strength in the parent cation

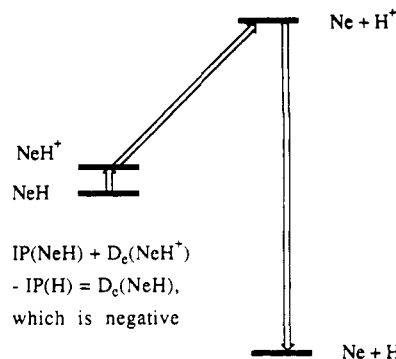


Figure 1. Relative energies of  $\text{NeH}$ ,  $\text{NeH}^+$ ,  $\text{Ne} + \text{H}$ , and  $\text{Ne} + \text{H}^+$ .

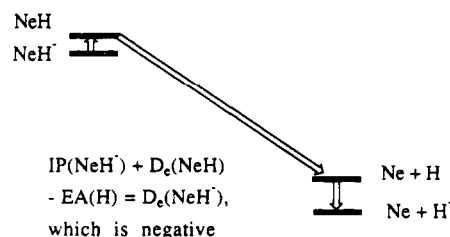


Figure 2. Relative energies of  $\text{NeH}$ , DR  $\text{NeH}^-$ ,  $\text{Ne} + \text{H}$ , and  $\text{Ne} + \text{H}^-$ .

( $\text{NeH}^+$  here) is larger than the lowest IP of the fragment species ( $\text{H}$  atom here). Moreover, the DR anion will probably not be thermodynamically stable unless the neutral Rydberg is, because the IP of the DR state is not likely to exceed that of the fragment ( $\text{H}$  here).

In addition to the (probable) thermodynamic instability of the Rydberg and DR states, it is important to emphasize that there exist geometries of even lower energy than the fragment species. For example, the lowest energy geometry of  $\text{NeH}^-$  corresponds to an  $\text{H}^-$  ion bound to a  $\text{Ne}$  atom through van der Waals attraction; this complex has lower total energy than the separated  $\text{Ne} + \text{H}^-$ . Likewise, the neutral  $\text{NeH}$  may exist as a van der Waals  $\text{Ne} \cdots \text{H}$  complex if the zero-point vibrational energy of the complex does not exceed the depth of the attractive van der Waals potential.

## C. Local Geometrical Stability of Rydberg and Double-Rydberg States

In contrast, local geometrical stability for the neutral or the anion (i.e., the shape of the electronic energy surface in the neighborhood of the parent cation's geometry) depends on the forces that the outer electron(s) exert on the underlying core. These forces are partially governed by the symmetry of the occupied Rydberg orbitals of the neutral or anion. State degeneracies arising from Rydberg orbital degeneracies give rise to local Jahn-Teller instability. Crossings of electronic configurations, as shown in Figures 3 and 4, strongly affect the local curvatures and barrier heights and thicknesses on the neutral and anion energy surfaces. Rydberg and DR species can be stable or metastable with respect to tunneling through the barrier if such a barrier exists and is sufficiently "high" and "thick".

In Figure 3, the dominant electronic configuration of the  $\text{NeH}$  contains two electrons in a bonding ( $2p_\sigma + 1s_\sigma$ ) orbital connecting the  $\text{Ne}$  and  $\text{H}$  atoms and thus forming  $\text{NeH}^+$  plus a single electron in a Rydberg orbital

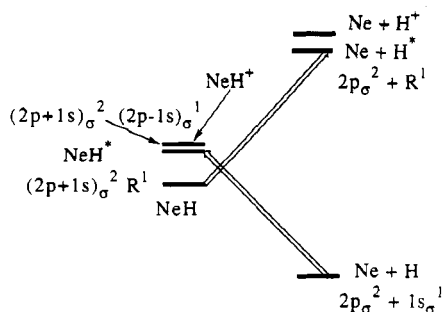


Figure 3. Configuration correlation diagram for NeH and Ne + H.

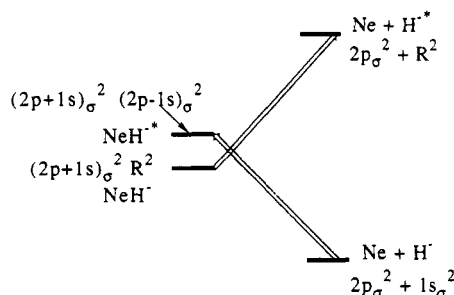


Figure 4. Configuration correlation diagram for DR NeH<sup>-</sup> and Ne + H<sup>-</sup>.

denoted R. In contrast, the lowest electronic state of the fragmentation products Ne + H has all three of these electrons in valence orbitals (two in the  $2p_\sigma$  on Ne and one in the  $1s_\sigma$  on H). The  $(2p_\sigma + 1s_\sigma)^2 R^1$  configuration that dominates the Rydberg NeH correlates with an excited Rydberg state of the products  $\text{Ne}(2p_\sigma^2) + \text{H}^*(R)$ . The  $2p_\sigma^2 1s_\sigma^1$  configuration that dominates Ne + H correlates with a  $\sigma^2 \sigma^*$  configuration  $(2p_\sigma + 1s_\sigma)^2 (2p_\sigma - 1s_\sigma)$  of NeH.

The avoided crossing between the two configurations depicted in Figure 3 may, depending on the extent to which the two configurations are coupled, produce a barrier on the  $\text{NeH} \rightarrow \text{Ne} + \text{H}$  energy surface. Because the two configurations differ by a single spin-orbital occupancy (i.e., the R orbital in one configuration occurs where the  $\sigma^*$  orbital appears in the second configuration), it would be expected<sup>3</sup> that this configuration crossing would be "strongly avoided", and thus that the barrier on the surface would either be low or nonexistent.

In Figure 4, the dominant electronic configuration of the DR NeH<sup>-</sup> contains two electrons in a bonding  $(2p_\sigma + 1s_\sigma)$  orbital between the Ne and H atoms plus two Rydberg electrons, denoted  $R^2$  (these two electrons need not be in the same Rydberg orbital; the notation  $R^2$  is used simply to indicate that there are two electrons that occupy nonvalence orbitals). In contrast, the lowest electronic state of the fragmentation products Ne + H<sup>-</sup> has all of these electrons in valence orbitals (two in the  $2p_\sigma$  on Ne and two in the valence orbitals on H). The  $(2p_\sigma + 1s_\sigma)^2 R^2$  configuration that dominates NeH<sup>-</sup> correlates with an excited Rydberg state of the products  $\text{Ne}(2p_\sigma^2) + \text{H}^-(R^2)$ . The  $2p_\sigma^2 1s_\sigma^2$  configuration that dominates Ne + H<sup>-</sup> correlates with a  $\sigma^2 \sigma^{*2}$  configuration  $(2p_\sigma + 1s_\sigma)^2 (2p_\sigma - 1s_\sigma)^2$  of NeH<sup>-</sup>.

The avoided crossing between these configurations depicted in Figure 4 may, depending on the extent to which the two configurations are coupled, produce a barrier on the  $\text{NeH}^- \rightarrow \text{Ne} + \text{H}^-$  energy surface. In the

anion case, unlike that of the neutral, the two configurations that cross differ by two spin-orbital occupancies. In this case, only the two-electron part of the electronic hamiltonian can couple these configurations, and such crossings can be expected<sup>3</sup> to be "weakly avoided". As a result, the barrier on the anion surface is more likely to be substantial.

The difference in the dominant electronic configurations of the Rydberg neutral species and its fragmentation products as well as the DR anion and its fragments gives rise to the possibility that barriers may exist on the respective electronic energy surfaces. The possibilities are better for the DR anion than for the neutral. If such a barrier exists, the corresponding species may be sufficiently long-lived to be experimentally observed.

## D. Electronic Stability and Metastability of Double-Rydberg States

In addition to the possibility of geometrical instability, some states of the DR species may be stable with respect to electron autodetachment and others may be unstable (but perhaps long lived). This depends on the relative energies of the anion and neutral states as functions of geometry. Even if the anion's lowest-energy state lies below the ground state of the neutral at the parent cation geometry (and is therefore locally electronically bound), the ground-state anion surface may "penetrate" the neutral surface at some other geometry, upon which facile electron ejection may occur.

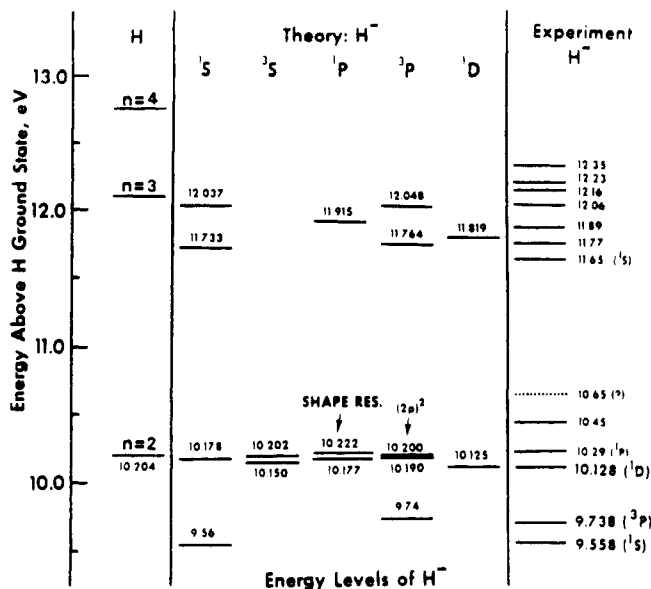
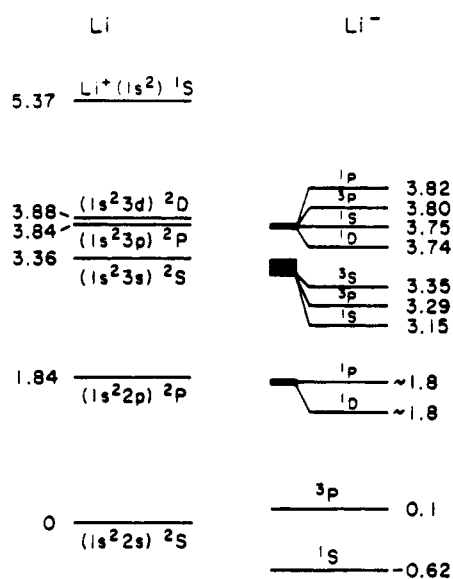
The possibility of electronically metastable DR states has to do with the electronic structure of the specific anion state relative to the electronic structure(s) of neutral-species states that lie energetically below it. For example, the  $4s^2 \ ^1S$  DR state of Na<sup>-</sup> lies above the  $3s^1 \ ^2S$  and  $3p^1 \ ^2P$  states of neutral Na, so this DR state is not stable<sup>4</sup> with respect to electron loss. However, because the  $4s^2$  configuration differs from the "detachment-channel"  $^1S$  configurations to which the hamiltonian can couple it (i.e.,  $3s^1 k s^1$  and  $3p^1 k p^1$ , where ks and kp denote outgoing continuum orbitals of s- and p-wave symmetry) by two spin-orbital occupancies, the coupling to these detachment channels can be expected to be weak. As a result, the  $4s^2$  state may be rather long-lived and may appear as a "resonance" in spectroscopic or electron-scattering experiments.

## E. Summary

DR atomic and molecular anions clearly show potential for displaying novel electronic and geometrical structure characteristics. For each such species, one expects a progression of neutral Rydberg electronic states with energies converging to the energy of the parent cation; some of these Rydberg states may be locally geometrically stable, and others may not.

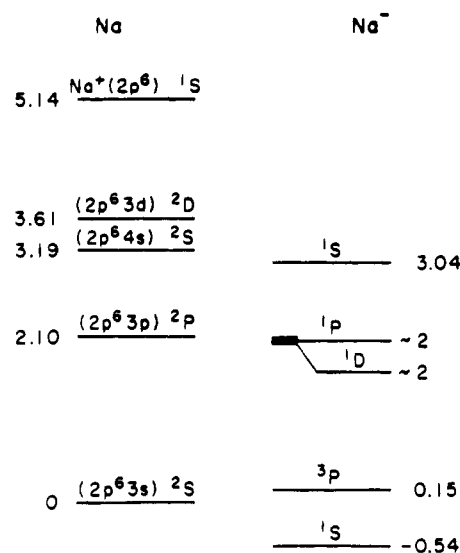
In the neighborhood of each Rydberg state of the neutral, the possibility of DR states arises. If the neutral Rydberg state has a single electron in an orbital of quantum number  $n$ , the DR states that are most likely to arise involve either  $n^2$  or  $n^1 n'^2$  orbital occupancy, with  $n' > n$ . For example, see in Figures 5-7 the rich pattern of neutral and anion states that Schulz reports<sup>4</sup> for H<sup>-</sup>, Li<sup>-</sup>, and Na<sup>-</sup>.

If the lowest energy DR state lies below the lowest neutral Rydberg state, it is termed "electronically

Figure 5. Energy level patterns for H and H<sup>-</sup> (from ref 4).Figure 6. Energy level patterns for Li and Li<sup>-</sup> (from ref 4).

stable". Excited DR states that lie above neutral Rydberg states whose electronic configurations require a "two-electron" process for electron ejection are termed "Feshbach resonances" (e.g., the  $4s^2$  state of Na<sup>-</sup> discussed above lies below the  $4s$  state of Na but above the  $3s$  and  $3p$  states of Na). Such states may be rather long lived because of the weak coupling that occurs between these two configurations. The higher energy configuration contains two orbitals of principal quantum number  $n$  greater than that of the other configuration, which contains one orbital with  $n' < n$  and one oscillatory continuum orbital.

DR states that lie above neutral Rydberg states to which they can autoionize via a "one-electron" process can be metastable if the orbital that is involved in the electron ejection possesses angular momentum (i.e., is a  $p$ ,  $d$ , etc. orbital). For example, the  $2s^1 2p^1 \ ^3P$  state of Li<sup>-</sup> is metastable<sup>4</sup> although it can autoionize to the  $2s^1$  state of Li by ejecting the  $2p$  electron (but it can not eject the  $2s$  electron to produce the  $2p^1$  state because its energy is not high enough). Also, the  $3s^1 3p^1 \ ^3P$  state

Figure 7. Energy level patterns for Na and Na<sup>-</sup> (from ref 4).

of Li<sup>-</sup> is metastable although it lies above the  $3s$  state (but not the  $3p$  state) of Li.

These states are metastable because the electron ejection process requires tunneling of the electron through the centrifugal barrier provided by the  $l(l+1) \hbar^2/2m_e r^2$  factor in the radial kinetic energy operator. Such metastable states are termed "shape resonances". In the former example, where decay can occur to the ground  $2s^1$  state of the neutral species, one says that the  $2s^1 2p^1 \ ^3P$  state is a *simple* shape resonance. In the latter case, where decay can occur to the nearby excited  $3s^1$  state of the neutral, one says that the  $3s^1 3p^1 \ ^3P$  state is a "core-excited" shape resonance because the neutral is produced in an excited state when the  $3p$  electron is ejected.

In addition to these electronic-state intricacies, the Rydberg and DR species present interesting local and global geometrical-stability issues. Both molecular species are probably not, even in their ground states, thermodynamically stable. However, depending on the nature of the Rydberg and valence orbitals that appear in their electronic configurations, they may be locally stable; the DR anions have better chances for achieving local stability than do the Rydberg neutrals. Local stability, of course, only means that a barrier exists and that this barrier can slow fragmentation, whose rate is determined by the masses of the atoms involved and the height and thickness of the barrier.

## II. What Is Known about Double-Rydberg Anions?

### A. H<sub>3</sub><sup>-</sup>

The low-energy Rydberg states of neutral H<sub>3</sub> were observed by Herzberg in 1979 in emission spectra<sup>5</sup> and by Vogler in translation spectra.<sup>6</sup> This work and subsequent efforts by Garvey and Kuppermann,<sup>7</sup> Griffiths, Harris, and Benyon,<sup>8</sup> and by Gellene and Porter<sup>9</sup> established the lowest electronic state of H<sub>3</sub> at the  $D_{3h}$  geometry of the parent cation to be the  $^2E'(2p)$  Rydberg state. This state was seen to be Jahn-Teller unstable locally, and, in fact, globally unstable with respect to fragmentation to H + H<sub>2</sub>. Excited Rydberg states of

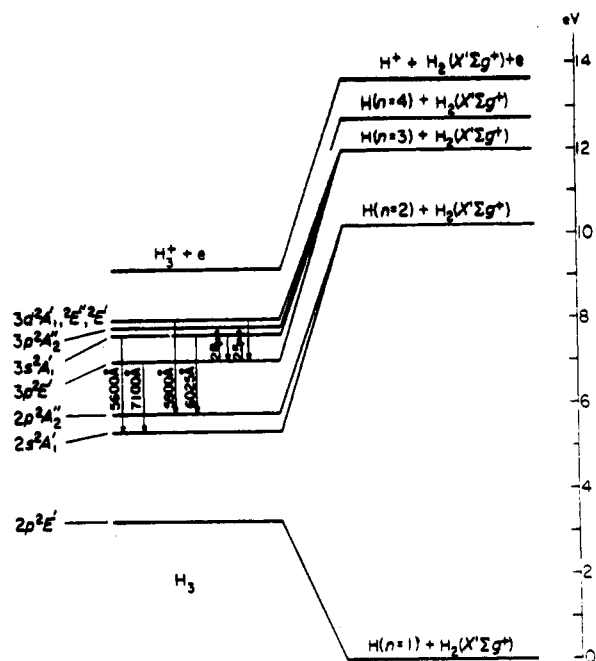


Figure 8.  $H_3$  Rydberg state energy level pattern (from ref 18).

$H_3$  having  $2A'_1(2s)$ ,  $2A''_2(2p)$ ,  $2E'(3p)$ ,  $2A'_1(3s)$ ,  $2A''_2(3p)$ ,  $2A'_1(3d)$ ,  $2E''(3d)$ , and  $2E'(3d)$  symmetries have also been characterized spectroscopically<sup>10-12</sup> (see Figure 8).

Theoretical calculations using explicit Rydberg-like basis functions were carried out in 1979 by King and Morokuma,<sup>13</sup> by Jungen,<sup>14</sup> and by Martin.<sup>15</sup> The results of these calculations were essentially in agreement with what Herzberg<sup>5</sup> found that same year. Subsequently, Nager and Jungen<sup>16</sup> examined many more excited states (most of which were not yet observed), Raynor and Herschbach<sup>2</sup> studied the geometrical stabilities of various Rydberg states of  $H_3$  and of other species, and Petsalakis, Theodorakopoulos, and Wright<sup>17</sup> examined electronic transition moments among several low-energy Rydberg states at various geometries.

To the best of our knowledge, DR  $H_3^-$  has not been seen experimentally. Its lowest energy state, at the parent cation geometry, might be expected to doubly occupy the  $e'$  ( $2p$ ) orbitals. However, our calculations<sup>1</sup> indicate that the lowest electronic state of DR  $H_3^-$  has a dominant  $a_1'$  ( $2s^2$ ) Rydberg orbital occupancy. We find this  $1A'_1$  state to be electronically unstable with respect to the dissociative  $2E'$  state of the neutral; it may be metastable because its  $2s^2$  occupancy differs by two orbitals from that of the  $2E'$  ( $2p$ ) neutral with an ejected p-wave electron. We also identified<sup>1</sup> excited states of  $H_3^-$  of  $3A''_2(2s2p)$ ,  $1A'_1(3s^2)$ , and  $3A''_2(3s3p)$  symmetry, each of which lies below the states of the neutral to which it can decay via one-electron processes.

## B. $NH_4^-$

The Rydberg neutral species  $NH_4$  has been the subject of several experimental and theoretical studies. In 1981, Herzberg<sup>18</sup> obtained the first experimental evidence for Rydberg states of this species. Gallene, Cleary, and Porter<sup>19</sup> in 1982 used their neutralized ion-beam experimental method to determine that  $NH_4$  has a lifetime, presumably with respect to fragmentation, of less than 1  $\mu s$ , while  $ND_4$  has a lifetime in excess of 20  $\mu s$ . These data indicate that there is a small

barrier on the  $NH_4$  surface and that the slower tunneling of the D isotope leads to a longer lifetime.

In 1982, Havriliak and King<sup>20</sup> studied several Rydberg states of  $NH_4$  using Rayleigh-Schrödinger perturbation theory, focusing on transition moments, force constants, energies, and Jahn-Teller parameters. Raynor and Herschbach,<sup>2</sup> as part of their systematic study of several Rydberg species, examined several low-lying electronic states of  $NH_4$  in 1982. Havriliak, Furlani, and King<sup>21</sup> improved on their earlier calculations in 1984, and Cardy, Liotard, Dargelos, Marinelli, and Roche<sup>22</sup> examined vibronic coupling effects in the  $2T_2(3p)$  state in 1988. The thermodynamic and kinetic stabilities of  $NH_4$  and its deuterated forms have been studied by McMaster et al.,<sup>23</sup> Cardy et al.,<sup>24</sup> Kaspar et al.,<sup>25</sup> and by Kassab and Evleth.<sup>26</sup> The conclusions of these papers concerning the relative energies and stabilities of the Rydberg states are qualitatively similar. The  $2A_1(3s)$  ground state is thermodynamically unstable although there is a substantial barrier along the dissociation path. There are excited  $2T_2(3p)$ ,  $2A_1(4s)$ , and  $2T_2(3d)$  states all of which are spectroscopically important.

The  $NH_4^-$  DR structure was studied in 1984 by Kalcher, Rosmus, and Quack<sup>27</sup> and in 1986 by Cardy, Larrieu, and Dargelos<sup>28</sup> as well as Cremer and Kraka.<sup>29</sup> These workers did not, to the best of our knowledge, recognize the DR nature of the ground state they examined, and they did not search for excited DR states. They concluded that the  $1A_1(3s^2)$  ground state is thermodynamically unstable (but not by more than a few kcal/mol) and that there is a barrier that makes this state locally stable. The potential energy barrier for the dissociation of  $NH_4^-$  was found to be higher than that for dissociation of the neutral (18.6 versus 13.8 kcal mol<sup>-1</sup>)<sup>28</sup> in agreement with the avoided configuration crossing arguments discussed earlier in this review (Figures 3 and 4).

In 1987, after the announcement by Bowen and Eaton<sup>30</sup> that DR  $NH_4^-$  had probably been seen in photoelectron spectroscopy experiments, Ortiz<sup>31</sup> carried out detailed geometry optimization and energy studies of the  $NH_3 + H^-$ ,  $NH_3 \cdots H^-$  and DR  $NH_4^-$  species. The electron-binding energy of 0.42 eV obtained by Ortiz for DR  $NH_4^-$  is in excellent agreement with the experimental value<sup>30,32,33</sup> of 0.50 eV.

It was rather surprising to have seen any appreciable amount of the DR structure of  $NH_4^-$  in the ion sources used by the Bowen group. These workers were interested in studying  $H^- \cdots (H_3N)_k$  complexes by using laser photoelectron spectroscopic methods. Their source conditions were designed to produce large amounts of these "solvated"  $H^-$  species, after which mass spectroscopic tools were used to extract anions of the proper charge-to-mass ratio. At this time, it is not known how any significant amount of the DR structure, which is very thermodynamically unfavored, was formed under these source conditions. In the future, it may be possible, with  $NH_4^+$  used as a precursor and passing this cation through, for example, Cs vapor, to use double charge exchange methods to produce even larger currents of the DR  $NH_4^-$  species. This method may also be of great use in the search for other DR anions.

In 1988, the authors, together with Hernandez and Taylor, performed ab initio configuration interaction

**TABLE I. Bond Lengths (au) and Local Harmonic Vibrational Frequencies (cm<sup>-1</sup>) for Tetrahedral Structures of NH<sub>4</sub><sup>+</sup>, NH<sub>4</sub>, and NH<sub>4</sub><sup>-</sup> Resulting from CAS MCSCF Calculations**

	NH <sub>4</sub> <sup>+</sup>	NH <sub>4</sub>	NH <sub>4</sub> <sup>-</sup>
<i>r</i> (N-H)	1.937	1.960	1.964
T <sub>2</sub> vib	1543	1439	1434
E vib	1776	1700	1717
A <sub>1</sub> vib	3384	3108	3140
T <sub>2</sub> vib	3629	3328	3276

calculations<sup>1</sup> on several DR states of NH<sub>4</sub><sup>-</sup> (as well as H<sub>3</sub><sup>-</sup>, H<sub>3</sub>O<sup>-</sup>, H<sub>2</sub>F<sup>-</sup>, CH<sub>5</sub><sup>-</sup>, and NeH<sup>-</sup>). The electron-binding energy obtained there (0.45 eV) is in excellent agreement with that of Ortiz.<sup>31</sup> Excited <sup>3</sup>T<sub>1</sub>(3p<sup>2</sup>), <sup>1</sup>A<sub>1</sub>-(4s<sup>2</sup>), <sup>3</sup>T<sub>1</sub>(4p<sup>2</sup>), and <sup>1</sup>A<sub>1</sub>(5s<sup>2</sup>) DR states were identified, each of which lies below neutral NH<sub>4</sub> states to which it might detach via one-electron processes. Thus, these states may be metastable Feshbach resonances.

The ground states of the cation, neutral, and anion have all been found by Gutowski and Simons<sup>34</sup> to be locally stable at tetrahedral geometries with NH bond lengths (in atomic units; 1 au = 0.529 Å) of 1.937, 1.960, and 1.964, respectively. The corresponding vibrational frequencies of these species are given in Table I. Clearly, the frequencies do not differ much among the three; there are four easily identified NH stretch frequencies near 3500 cm<sup>-1</sup> and four internal bending vibrations near 1600 cm<sup>-1</sup> in all cases.

### C. H<sub>3</sub>O<sup>-</sup>

Experimental evidence for metastable states of D<sub>3</sub>O, but not of H<sub>3</sub>O, has been reported by Gellene and Porter from analysis of fast neutral beam scattering profiles and collisional reionization mass spectra.<sup>35</sup> Raskit and Porter,<sup>36</sup> however, found no evidence of metastable D<sub>3</sub><sup>18</sup>O. Griffiths, Harris, and Beynon<sup>8</sup> in 1987 reported experimental evidence by neutralization-reionization spectroscopy of H<sub>3</sub>O radicals with a lifetime of 0.41 μs. However, from an independent neutralization-reionization experiment, March and Young<sup>37</sup> have concluded that there is insufficient evidence to support the claim the H<sub>3</sub>O radical survives for a transit time of 0.41 μs.

Raynor and Herschbach<sup>2</sup> predicted the <sup>2</sup>A<sub>1</sub>(3s) state to be the ground state at the parent cation (C<sub>3v</sub>) geometry, and they speculate that this state may be locally geometrically stable. This conjecture has been recently confirmed in highly correlated calculations by Ortiz<sup>38</sup> and by Talbi and Saxon.<sup>39</sup>

In 1982, Paulson and Henchman<sup>40</sup> reported seeing H<sub>3</sub>O<sup>-</sup> in a reaction of OH<sup>-</sup> with H<sub>2</sub>O. Griffiths and Harris<sup>41</sup> also studied H<sub>3</sub>O<sup>-</sup> in 1987, but it is not clear whether their experimental source contained any of the DR species. Theoretical investigations of the DR states of this anion include those of Cremer and Kraka<sup>29</sup> in 1986, of Gutowski, Simons, Hernandez, and Taylor<sup>1</sup> in 1988, of Ortiz<sup>38</sup> in 1989, and of Gutowski and Simons in 1990.<sup>34</sup> The Ortiz work<sup>38</sup> yields an electron binding energy for the <sup>1</sup>A<sub>1</sub>(3s<sup>2</sup>) DR structure of 0.43 eV, which compares well with that of Gutowski and Simons<sup>34</sup> (0.46 eV). Candidates for metastable Feshbach excited states of <sup>3</sup>A<sub>2</sub>(3p<sup>2</sup>), <sup>1</sup>A<sub>1</sub>(4s<sup>2</sup>), and <sup>3</sup>A<sub>2</sub>(4p<sup>2</sup>) symmetry were also identified.<sup>1</sup>

The ground states of the cation, neutral, and DR anion have been found by Gutowski and Simons<sup>34</sup> to

**TABLE II. Bond Lengths (au), Angles (deg), and Local Harmonic Frequencies (cm<sup>-1</sup>) for the H<sub>3</sub>O Cation, Neutral, and DR Anion Obtained in C<sub>3v</sub> CAS MCSCF Calculations**

	H <sub>3</sub> O <sup>+</sup>	H <sub>3</sub> O	H <sub>3</sub> O <sup>-</sup>
<i>r</i> (O-H)	1.862	1.919	1.908
∠HOH	110.59	105.93	107.80
A <sub>1</sub> vib	1042	1035	980
A <sub>1</sub> vib	3527	3004	3106
E vib	1632	1629	566
E vib	3630	2727	3046

be locally geometrically stable and to possess the geometries and local harmonic vibrational frequencies detailed in Table II.

As in the NH<sub>4</sub><sup>-</sup> case discussed above, no major structural changes occur when one or two electrons are added to the H<sub>3</sub>O<sup>+</sup> core. The largest change takes place in the E symmetry OH stretching vibration which changes by 900 cm<sup>-1</sup> moving from the cation to the neutral. This trend is not surprising, however, because it is precisely along this asymmetric distortion that the neutral and anion experience barriers due to avoided configuration crossings. In line with this point, it is also not surprising that this vibration occurs at lower frequency in the neutral than in the anion.

### D. NeH<sup>-</sup>

In Herzberg's 1987 review of Rydberg molecules,<sup>10</sup> experimental evidence is summarized that indicates that the lowest Rydberg state of NeH, which consists of a NeH<sup>+</sup> cation surrounded by a single Rydberg electron, is geometrically unstable. Emissions from higher Rydberg states are seen, but they are broadened in a way that is interpreted to indicate dissociative instability of the ground state. Also, recent speculations<sup>42</sup> on the existence of a shallow potential well and a dissociation barrier for NeH were proven to be wrong.<sup>43,44</sup>

The 1982 calculations of Raynor and Herschbach,<sup>2</sup> those of Theodorakopoulos, Petsalakis and Buenker<sup>45</sup> in 1987, and those of Gutowski, Simons, Hernandez, and Taylor<sup>1</sup> and Gutowski and Simons<sup>34</sup> indicate that the lowest Rydberg state of NeH is of <sup>2</sup>Σ character and that this state does not possess a barrier of sufficient strength to prohibit dissociation. Thus, the ground Rydberg state of NeH is most probably unstable geometrically. All three of these theoretical studies found excited states of <sup>2</sup>Π and <sup>2</sup>Σ symmetry; Raynor and Herschbach<sup>2</sup> examined electric dipole transition moments among several such states.

A DR state of the NeH<sup>-</sup> anion has not been seen experimentally. The 1988 calculations of Gutowski, Simons, Hernandez, and Taylor<sup>1</sup> predict that a DR NeH<sup>-</sup> state of <sup>1</sup>Σ symmetry should be electronically stable with respect to <sup>2</sup>Σ NeH at the NeH<sup>+</sup> geometry. However, the recent work of Gutowski and Simons<sup>34</sup> finds that this anion state is geometrically unstable with respect to Ne + H<sup>-</sup>. Thus it appears that both NeH and NeH<sup>-</sup> are geometrically unstable as Rydberg or DR species.

### E. CH<sub>5</sub><sup>-</sup>

Neither the Rydberg species CH<sub>5</sub> nor its DR CH<sub>5</sub><sup>-</sup> have been seen experimentally.<sup>10</sup> Raynor and Herschbach<sup>2</sup> computed electric dipole transition moments



TABLE III. CAS MCSCF Geometries (Bond Length, au, and Bond Angle, 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	$^2\text{B}_2$ neutral	$^2\text{B}_1$ neutral
$r$ (F-H)	1.827	2.316	1.818
angle	112.7	97.0	112.5
$\text{A}_1$ vib	1482	1473	1496
$\text{B}_2$ vib	3563	4150	3633
$\text{A}_1$ vib	3542	1025	3601

<sup>a</sup>The  $^2\text{A}_1$  ground state of the neutral is geometrically unstable.

among several Rydberg states at the geometry of the  $\text{CH}_5^+$  cation, but they did not examine the geometrical stability of any of the  $\text{CH}_5$  Rydberg states. Gutowski, Simons, Hernandez, and Taylor<sup>1</sup> and subsequently Gutowski and Simons<sup>34</sup> studied both  $\text{CH}_5$  and  $\text{CH}_5^-$  and found several DR states that are candidates for Feshbach resonances. However, the latter workers find both the ground state of Rydberg  $\text{CH}_5$  and the DR state of  $\text{CH}_5^-$  to be geometrically unstable with respect to fragmentation. Cremer and Kraka<sup>29</sup> studied  $\text{CH}_5^-$ , but did not examine its local geometrical stability or lack thereof; they did consider the overall thermodynamic stability of this species and predicted it to be unstable by 54.5 kcal/mol with respect to  $\text{H}^- + \text{CH}_4$ .

## F. $\text{H}_2\text{F}^-$

The only evidence for metastable states of  $\text{D}_2\text{F}^-$  comes from the Raksit, Jeon, and Porter neutralized ion beam experiments.<sup>46</sup> Petsalakis, Theodorakopoulos, Wright, and Hamilton,<sup>47</sup> in 1988, and Gutowski and Simons,<sup>34</sup> in 1989, examined the ground and low-lying excited states of this species and found the ground state to be geometrically unstable, while some bound excited states were predicted to exist. Geometries and harmonic vibrational frequencies for  $\text{H}_2\text{F}^+$  and for the two lowest geometrically stable states of  $\text{H}_2\text{F}$  ( $^2\text{B}_2(2b_2)$  and  $^2\text{B}_1(2b_1)$ ) are presented in Table III. The geometries of the  $^2\text{B}_2$  state and the cation are very different, as are the vibrational frequencies. The reason 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  $np_y$  symmetry orbital. This antibonding interaction is responsible for a dramatic elongation of the FH bonds (by 0.5 au) 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  $^2\text{B}_1(2b_1)$  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 III). Electric dipole transition moments among certain states of  $\text{H}_2\text{F}$  were calculated by Raynor and Herschbach<sup>2</sup> and by Petsalakis et al.<sup>47</sup>

In 1986, Cremer and Kraka<sup>29</sup> looked at the  $\text{H}_2\text{F}^-$  DR species near the geometry of its parent cation. They found DR  $\text{H}_2\text{F}^-$  to be thermodynamically unstable with respect to  $\text{HF} + \text{H}^-$  by 37.9 kcal/mol. Gutowski, Simons, Hernandez, and Taylor<sup>1</sup> studied the ground and excited states of DR  $\text{H}_2\text{F}^-$  and identified several excited states as candidates for Feshbach resonances. Subsequently, Gutowski and Simons<sup>34</sup> as well as Ortiz<sup>48</sup> found the ground state of  $\text{H}_2\text{F}^-$  to be geometrically unstable

in the vicinity of the parent cation equilibrium geometry.

## G. Other DR Systems

The DR systems involving a third-row heavy atom were studied by Ortiz.<sup>48</sup> The  $\text{SH}_3^-$  ( $\text{C}_{3v}$ ) and  $\text{ClH}_2^-$  ( $\text{C}_{2v}$ ) structures were found to be geometrically unstable in their ground states. For  $\text{PH}_4^-$  a stable tetrahedral structure was found with a PH distance of 2.72 au and detachment energy of 0.38 eV. Another structure, with  $\text{C}_{2v}$  geometry and detachment energy of 0.95 eV was also found.<sup>48</sup> After including zero-point energy corrections, the  $\text{C}_{2v}$  structure was predicted to be 1.45 eV more stable than the DR isomer.

## III. Autodetachment Lifetimes of Metastable DR States

In addition to these energetic and structural studies on  $\text{NeH}^-$ ,  $\text{H}_2\text{F}^-$ ,  $\text{H}_3\text{O}^-$ ,  $\text{H}_4\text{N}^-$ , and  $\text{H}_5\text{C}^-$ , the authors have undertaken an investigation<sup>49</sup> of the lifetimes with respect to electron detachment of various excited DR states of  $\text{H}_2\text{F}^-$  and are extending this study to the other DR anions covered in this review.

In using the stabilization method<sup>50</sup> to compute the energies and lifetimes of metastable Feshbach, shape, and core-excited shape (CES) resonances, one must find a large number of eigenvalues of the hamiltonian matrix  $H$  belonging to the DR anion's electronic configuration space. The lowest root of this  $H$  matrix corresponds to the electronically bound  $\text{H}_2\text{F}^-$  state for the example at hand. Many of the next eigenvalues correspond to "scattering states" which describe a Rydberg neutral  $\text{H}_2\text{F}$  coupled to a continuum orbital containing an unbound electron. Among this multitude of such scattering states are the desired metastable states. The stabilization method provides a tool for finding the metastable states that are buried in the continuum.

To effect the stabilization technique, one finds all of the eigenvalues of  $H$  within some specified energy range of interest. This calculation is carried out over and over as the exponents ( $\alpha_i$ ) of all of the diffuse Rydberg-type basis functions used in the calculation are varied by a uniform "scale factor". This orbital exponent scaling corresponds to varying the radius of the orbitals and hence of the region of space within which the electrons are constrained. Constraining the electrons of a bound state should have no effect on such a state as long as the region to which they are constrained is large enough to contain the vast majority of their (square integrable) charge density.

In contrast, constraining a continuum state to any finite region of space amounts to placing it in a "box" and thus forcing its oscillatory function to match boundary conditions imposed by the box. This amounts to forming discrete states in place of the continuum. As the "box radius" is increased (i.e., as the orbital exponents are uniformly decreased), the energies of all such continuum states decrease.

As the orbital exponents of the diffuse basis functions are scaled, one finds a pattern in the eigenvalues of the  $H$  matrix such as shown in Figure 9. This data depict a situation in which the energy of an electronic configuration of symmetry  $^1\text{A}_1(6a_1^2)$  remains rather constant as the  $\alpha_i$  are scaled until a continuum configura-



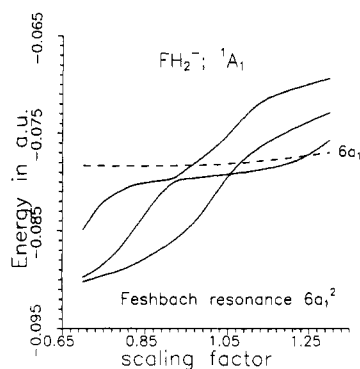


Figure 9. Stabilization plot for the longest-lived Feshbach  $^1A_1(6a_1^2)$  resonance. The energy of the nearby neutral state is depicted by dashed line.

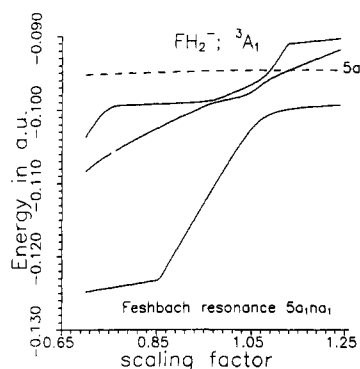


Figure 10. Stabilization graph for the two-open-channel Feshbach  $^3A_1(5a_1na_1)$  resonance. The energy of the nearby neutral state is depicted by dashed line.

tion of the same symmetry approaches from "below" as the box size is made smaller (i.e., as the  $\alpha_i$  are increased). As the two configurations approach, they are coupled via the electronic hamiltonian (i.e., they are both used in forming the  $H$  matrix) and they undergo an avoided crossing.

These avoided crossings characterize the nature of the metastable states; these states consist of a superposition of continuum and bound electronic configurations. The strength of the coupling between the configurations influences the lifetime of the metastable state. Building on Simons' original treatment<sup>51</sup> of this problem, Frey and Simons demonstrated<sup>52</sup> in 1986 how such lifetimes could be extracted from the "avoided crossings" that occur in stabilization plots.

The present authors used this technique to compute the lifetimes of several singlet and triplet Feshbach and core-excited shape resonances of the  $A_1$ ,  $B_1$ ,  $B_2$ , and  $A_2$  states of  $H_2F^-$ .<sup>49</sup> Shape resonances that lie just above the (geometrically unstable)  $^2A_1$  ground state of the neutral were not observed. Several of the pertinent stabilization graphs are shown in Figures 9–13 (where the energies relative to those of the parent cations are displayed in Hartree units (27.21 eV)), and the resulting state symmetries, energies, and lifetimes are given in Table IV.

The longest lived Feshbach resonance is of  $^1A_1(6a_1^2)$  symmetry (Figure 9) and its lifetime is  $34 \times 10^{-14}$  s. Among the five Feshbach resonances that we found, three have been classified as two-open-channel species, (see Figures 10 and 11 and Table IV). The  $^3A_1(5a_1na_1)$  resonance (Figure 10) can decay via ejection of an

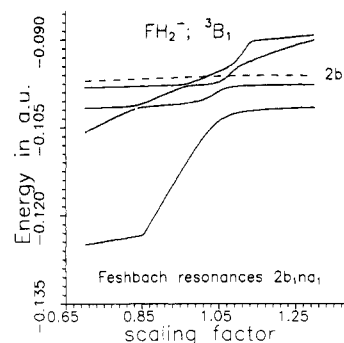


Figure 11. Stabilization graphs for two two-open-channel Feshbach  $^3B_1(2b_1na_1)$  resonances. The energy of the nearby neutral state is depicted by dashed line.

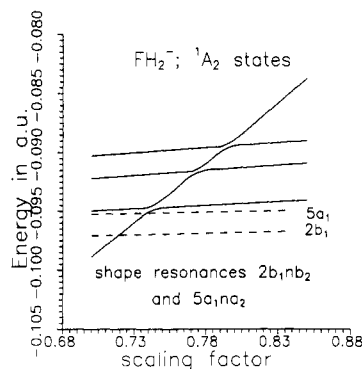
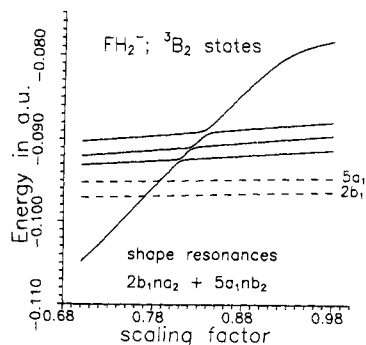


Figure 12. Three-term cluster of CES  $^1A_2$  resonances. The two lower resonances are dominated by  $2b_1nb_2$  electron configurations. The highest one has  $5a_1na_2$  character. The middle one is the longest lived CES resonance. The energies of nearby neutral states  $2b_1$  and  $5a_1$  are depicted by dashed lines.

TABLE IV. Metastable State Symmetries, Types,<sup>a</sup> Energies, and Lifetimes for Double Rydberg  $H_2F^-$

symmetry	type <sup>a</sup>	configuration <sup>b</sup>	energy <sup>c</sup>	lifetime <sup>d</sup>
$^1A_1$	CES	$2b_2nb_2$	-0.123 69	3
$^1A_1$	CES	$2b_2nb_2$	-0.119 33	7
$^1A_1$	F	$6a_1^2$	-0.079 17	34
$^3A_1$	CES	$2b_2nb_2$	-0.125 13	14
$^3A_1$	CES	$2b_2nb_2$	-0.123 26	32
$^3A_1$	F	$5a_1na_1$		
		( $4a_1ka_1$ channel)	-0.098 86	1
		( $2b_2kb_2$ channel)	-0.098 81	5
$^1A_2$	CES	$2b_1nb_2$	-0.094 71	14
$^1A_2$	CES	$2b_1nb_2$	-0.091 57	80
$^1A_2$	CES	$5a_1na_2$	-0.089 46	26
$^3A_2$	CES	$2b_1nb_2$	-0.094 26	18
$^3A_2$	CES	$2b_1nb_2$	-0.091 59	19
$^3A_2$	CES	$5a_1na_2$	-0.089 59	24
$^1B_1$	F	$2b_1na_1$	-0.100 69	4
$^3B_1$	CES	$2b_2na_2$	-0.123 39	17
$^3B_1$	F	$2b_1na_1$		
		( $2b_2ka_2$ channel)	-0.101 45	8
		( $4a_1kb_1$ channel)	-0.102 55	1
$^3B_1$	F	$2b_1na_1$		
		( $2b_2ka_2$ channel)	-0.097 82	10
		( $4a_1kb_1$ channel)	-0.097 96	6
$^3B_1$	CES	$2b_1na_1+5a_1nb_1$	-0.090 25	17
$^3B_2$	CES	$2b_2na_1$	-0.125 80	11
$^3B_2$	CES	$2b_2na_1$	-0.122 97	2
$^3B_2$	CES	$2b_1na_2+5a_1nb_2$	-0.092 41	14
$^3B_2$	CES	$2b_1na_2+5a_1nb_2$	-0.090 92	46
$^3B_2$	CES	$2b_1na_2+5a_1nb_2$	-0.089 10	7

<sup>a</sup> Feshbach (F) and core-excited shape (CES). <sup>b</sup> The notation  $n\lambda$  ( $\lambda = a_1, a_2, b_1$ , or  $b_2$ ) is used to indicate that one Rydberg-type electron is distributed among many  $\lambda$ -symmetry orbitals. <sup>c</sup> The energies are given relative to the parent cation species (in hartrees) in all cases. <sup>d</sup> The lifetimes are given in units of  $10^{-14}$  s. A lifetime of  $10^{-14}$  s corresponds to an energy width of 0.066 eV in the resonance.



**Figure 13.** Three-term cluster of CES  ${}^3B_2$   $2b_1na_2 + 5a_1nb_2$  resonances. The energies of nearby neutral states  $2b_1$  and  $5a_1$  are depicted by dashed lines.

electron either to the ground  ${}^2A_1(4a_1)$  state of the neutral, or to the first excited  ${}^2B_2(2b_2)$  state. The former and the latter channels are reflected in Figure 10 in the steeply and less steeply rising branches of the stabilization graph, respectively. The slopes of these branches reflect the different kinetic energies of the ejected electron. In Figure 11, two other two-open-channel resonances of  ${}^3B_1(2b_1na_1)$  symmetry are displayed. For such two-open-channel cases, the total decay rate depends on the coupling of the resonant wavefunction with both open channels.

The CES resonances reported in Table IV frequently appear in clusters of two or three states, (see Figures 12 and 13). These clusters correspond to states of the same spatial and spin symmetry and are different solutions of the Schrödinger equation for the same neutral target states and with the same centrifugal barrier. The longest lived CES resonance is the  ${}^1A_2(2b_1nb_2)$  state (Figure 12), with a lifetime of  $80 \times 10^{-14}$  s.

On the basis of the range of lifetimes found here, it is expected that electronically metastable states of  $FH_2^+$  can display vibrational and may even show some rotational structure. Since the ground states of the  $FH_2^+$  anion and  $FH_2$  neutral are geometrically unstable near the cation equilibrium geometry, the observation of the CES and Feshbach resonances studied here could probably not be realized by using standard photoelectron or photodetachment techniques. However, experiments in which ground-state  $FH_2^+$  is used to produce, via double charge exchange, metastable states of  $FH_2^+$  may be a fruitful avenue of approach. Alternatively, an approach using electron attachment to excited Rydberg states of neutral  $FH_2$ , which were predicted to be geometrically stable, may be successful.

As such, the experimental studies of DR states present significant challenges. The novelty of their electronic structures will hopefully provide sufficient incentive for experimentalists to examine the multitude of stable and metastable states that are predicted to occur.

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