

Role of Rydberg radicals in electrochemistry

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Abstract - A review is given of a relatively unknown area of the electronic structures of Rydberg radicals. The primary examples of such structures are H_3 , NH_4 and H_3O . The condensed phase existence of the latter two has long been proposed. Mercury amalgams of organic ammonium radicals, R_4N , have been reported. Theoretical studies are reported on some of these species. An estimate is made of the relative stability of NH_4 in liquid ammonia vis-à-vis $NH_4^+ + e^-$.

INTRODUCTION

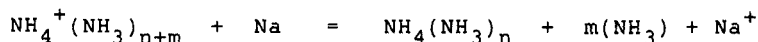
The role of Rydberg states in atomic and molecular photophysics and photochemistry is a specialized experimental and theoretical area (refs. 1-4). Ground-to-excited state Rydberg transitions are usually thought to occur in the region above 5-6 eV. Because of their extravalent characters and high energies, computations in this area are thought to be difficult. This is shown by the extreme upper state surface complexities found in even as simple a diatomic molecule as Cl_2 (ref. 5). However, we have demonstrated that small basis sets and a modest treatment of the correlation energy yield significant qualitative information on the photochemistry of small organic systems (CH_3 , CH_4 , CH_3OH , CH_3NH_2 , $CH_2=CH_2$, e.g. refs. 6-9).

The idea that Rydberg chemistry (refs. 1, 10) occurred only in high energy species created a conceptual mental block with regard to low energy Rydberg species until very recently. However, Herzberg pointed out in 1966 that species like NH_4 , H_3O and CH_5 (ref. 11) might have Rydberg ground states since the 3s orbital would be available for bonding. He certainly knew that these species would have low lying Rydberg excited states. The basic idea is that Rydberg radicals will have low lying Rydberg excited states described by the binding interaction of an electron in a Rydberg orbital with the valence closed shell cationic core. Herzberg discovered emission from excited H_3 radicals in 1979 and from NH_4 shortly thereafter (for a discussion see Ref. 12).

Herzberg's discovery of Rydberg radicals was a surprise to most theoretical chemists. Ground and excited state surface calculations of Rydberg radicals generated no extensive theoretical interest until after Herzberg's discovery (refs. 13, 14). The case of H_3 is generally misleading since there is 2-fold degenerate D_{3h} Jahn-Teller ground-excited state intersection and no significant local minima on the ground state surface. At the Jahn-Teller intersection the ground state is only partially Rydbergized ($2p, ^2E'$). The fully Rydbergized first excited state has 2s character and lies less than 2 eV above the Jahn-Teller ground state intersection (ref. 13). However, in the much studied case of NH_4 (ref. 14) the ground state is fully 3s Rydbergized at the T_d minimum. What was even more surprising was that it was found that the ground state energy of NH_4 was about the same as the products of its decomposition, $NH_3 + H$. An earlier theoretical study (ref. 15) on H_3O found the 3s structure of the ground state of this species. However, the species was found to have such a small barrier for OH bond rupture to exoenergetically (ca. 30 kcal/mol) yield $H_2O + H$ that it was concluded that it would be difficult to ever observe such a species. Historically, theoretical computations in this area had led to some wrong conclusions with regard to the stabilities of these kinds of species. Some work had wrongly predicted that NH_4 would be unstable (ref. 16). These wrong predictions were due to the lack of inclusion of Rydberg (i.e. diffuse) components in the basis set actually used in early work (ref. 17).

It is now recognized that Rydberg radicals are qualitatively easy to compute. In any case, the idea that Rydberg states are only high energy excited species with respect to the ground state was completely destroyed with the discovery and theoretical characterization of the NH_4 radical. However, theoretical studies on Rydberg radicals indicate that they will not be very stable but may serve as intermediates in chemical reactions. These studies also indicate that in certain kinds of transition states, diffuse components should be used in the basis sets.

The next part of the Rydberg radical story occurred with the preparation of molecular beams of Rydberg radicals by Porter, Gellene and coworkers (ref. 18). The method of preparations of such species in cluster forms was experimentally simple. For example, molecular beams of $\text{NH}_4^+(\text{NH}_3)_n$ can be easily prepared and accelerated through dilute clouds of metal atoms. Direct collisions do not occur readily at very low pressures but long distance electron transfers can. Therefore the reaction,



can occur. Neither uncomplexed NH_4 nor H_3O have been detected but their deuterated counterparts have. It has been concluded (ref. 14,18) that the ND and OD bond rupture activation energies are only several kcal/mole. Therefore, both zero point energy effects and reduced tunneling play a role in stabilizing ND_4 and D_3O . However, NH_3 complexed forms of NH_4 have long beam lifetimes. Attempts to prepare organic Rydberg radicals (e.g. CH_5) have not yet been successful nor as equally well explored. Our discussion below will allow one to estimate stability of Rydberg radicals and rationalize the kinetic barrier for bond rupture.

Rydberg radicals have some relevance to interstellar chemistry since electron-cation dissociative recombination,



is an important process in ion-molecule chemistry. Our goal here is to theoretically speculate on the possible role of Rydberg radicals as metastable intermediates in condensed phase chemistry formed by a similar process, either by the capture of a solvated electron or at an electrode surface. It turns out that organic ammonium radicals, R_4N , have been known much longer than the above discussion would indicate. Poorly characterized mercury amalgams, formed by the electron reduction of tertiary ammonium salts at mercury surfaces, have been known since the beginning of this century (refs. 19,20). The possible existence of NH_4 and H_3O radicals in electrochemistry and in the reactions of the solvated electron has been speculated on for a number of years (ref. 21). The major questions are: what are the structures of these amalgams? Do isolated organic ammonium radicals have any stability? What is the role of these kinds of radicals in electrochemistry, in the reaction of the solvated electron? We will address some of these points with a theoretical description of the properties of NH_4 and related structures.

SOME COMMENTS ON COMPUTING RYDBERG RADICALS

The ground and lowest excited states of Rydberg radicals can be computed using a standard valence basis set supplemented by the diffuse components necessary to describe the Rydberg character of the structures under investigation. Although spectroscopic accuracy will require large basis sets, significant chemical information can be obtained at the DZ+3s,p level in the case of NH_4 . Since the NH_4 radical ground state has a simple electronic structure, qualitatively described as $(\text{NH}_4^+)(e^-)_{3s}$, it can be treated at single configuration RHF or UHF open shell level. Subsequent correlation corrections can be done using Moller-Plesset (MP) perturbation or CI methods. A single parent configuration will dominate the MP or CI expansion for the ground state minima. The treatment of the reaction surfaces is more complicated. The ground state surface for the reaction: $\text{NH}_4 = \text{NH}_3 + \text{H}$, is monconfigurational in character using a MO method. In this case, the highest half-filled MO will have $3s\sigma^*$ character, the approximate functional form being: $c_1(3s) + c_2(1s\text{H})$. At the T_d geometry, the 3s part of the function dominates. At large NH distances the function is dominated by the 1sH component. At intermediate NH distances some NH_3 antibonding components will also be mixed in. The $3s\sigma^*$ designation implies bonding in Rydberg space and antibonding in valence space. This behavior can be reformulated in at the state level using a VB-type structural

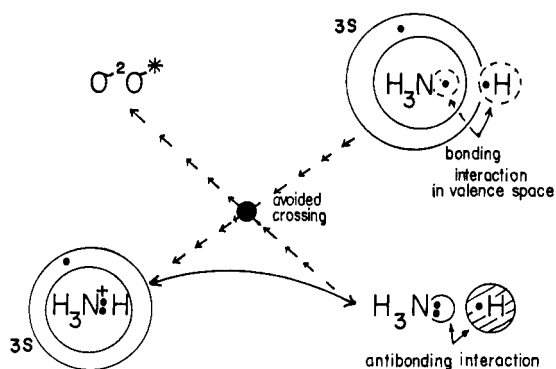


Figure 1. Structural correlation diagram explaining the behavior of the ground and first excited state surface for NH bond rupture in the NH_4 Radical (see ref. 14e for the correlations of the excited states).

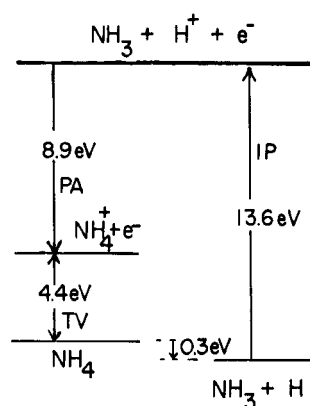


Figure 2. A thermospectroscopic estimation of the stability of NH_4 vis-à-vis $\text{NH}_3 + \text{H}$.

correlation diagram (Fig. 1). The theoretical origins of the stability and electronic structure of NH_4 are due to its structural correlation with the first excited (Rydberg) state of $\text{NH}_3 + \text{H}$. The first excited state of NH_3 is described by the excitation of one of the non-bonding electrons from an n-orbital to a 3s Rydberg orbital as structurally shown in Fig. 1. In n,3s excited NH_3 , the half-filled n-orbital is available for $\sigma(\text{NH})$ -bond formation with the H atom. Therefore, the excited state interaction of $\text{NH}_3 + \text{H}$ is bonding. However, in the ground state of $\text{NH}_3 + \text{H}$, there is an antibonding interaction due to three electrons occupying the same symmetry σ space. In MO terms this 3-electron configuration is described as a $\sigma^2\sigma^*$ interaction. If one were to perform a calculation without Rydberg components (i.e. ref. 16) only a repulsive NH surface would be obtained for an H atom approaching the filled n-orbital of NH_3 . However, with a 3s-Rydberg component, the ground state surface VB-like wavefunction can be expressed in a simple two configurational form: $c_1(\sigma^2\sigma^*) + c_2(\text{NH}_3^+, 1s\text{H})(3s)$. The latter term becomes a NH bond in valence space as the 1sH orbital couples to the NH_3 component. As shown in Fig. 1, the ground state behavior results from an avoided crossing of VB-type frozen configurations. However, in MO-CI terms, this surface form can also be expressed in single configurational terms as an evolution of only the σ^* MO. The advantage of the structural correlation diagram is that one anticipates a surface barrier in passing from NH_4 to $\text{NH}_3 + \text{H}$. At the maximum of this barrier one expects about 50-50 mixed Rydberg³-valence character as the wavefunction evolves from being fully Rydberg at NH_4 to fully valence at $\text{NH}_3 + \text{H}$. The calculations show this behavior.

The reasons for the near isoenergicity of NH_4 and $\text{NH}_3 + \text{H}$ on the ground states surface can be rationalized using the thermospectroscopic cycle shown in Fig. 2. Of the three energies necessary to construct this cycle, the ionization potential (IP) of the H-atom and the proton affinity of NH_3 (PA) are known experimentally. The IP for the NH_4 radical can be assumed to be close to the term value (TV) for the lowest excited state of NH_3 (ref. 4). Using these numbers, the reaction $\text{NH}_4 = \text{NH}_3 + \text{H}$ is 0.3 eV exoergic. Ab initio calculations show a value near zero. The work of Porter et al. (ref. 18) is in accord with these estimates as are the direct calculations (ref. 14). Fig. 2 demonstrates that one can make reasonable estimates of the thermodynamic stabilities of Rydberg radicals without direct computations. Experimental information on the IP, PA, and TV will be sufficient to make a reasonable first order guess.

COMPLEXATION OF NH_4 RADICAL WITH NH_3 IN CLUSTERS AND LIQUID NH_3

Since the NH_4 radical ground state is descriptively an electron in a 3s orbital bound to an NH_4^+ core, the complexation of the NH_4 with NH_3 will be partially ionic in character. Figure 3 shows the variation of the scaled ab initio complexation energies with cluster size (ref. 14e) for both the neutral and cationic species. For $n = 1$, the complexation energy of NH_4 with NH_3 is 1.08 eV, for the Rydberg radical, 0.42 eV. For neutral NH_3 with itself, the experimental value is about 0.25 eV. As the size of the

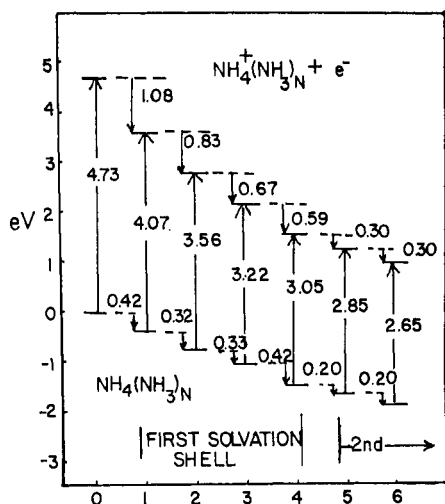


Figure 3. Scaled ab initio complexation energies of both NH_4^+ and NH_4 with NH_3 (from ref. 14e).

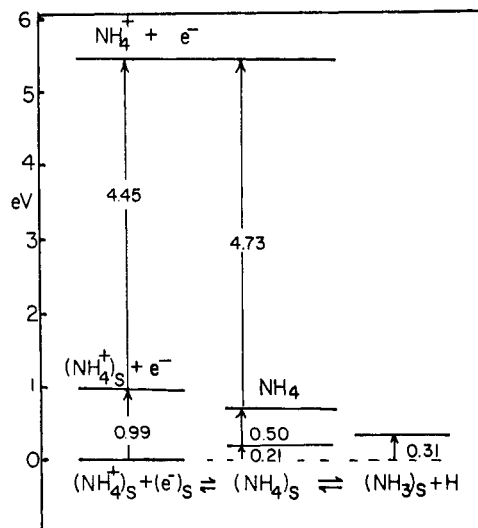


FIGURE 4. Estimate relative energies of NH_4^+ , NH_4 and the electron in the gas phase and liquid NH_3 .

$\text{NH}_4(\text{NH}_3)_n$ cluster increases beyond the first solvation shell ($n > 4$), the extrabonding of NH_3 units onto an existing Rydberg cluster does not exceed the bonding of NH_3 with itself. As seen from Figure 3, the IP of NH_4 in NH_3 clusters gradually decreases. Since the solvation energy of (e^-) in liquid NH_3 (ref. 22) is 0.99 eV, one can predict that the IP of NH_4 in liquid NH_3 would not be more than 2 eV. However, using the estimated solvation energy of NH_4^+ in liq. NH_3 (ref. 22), 4.45 eV, as well as the gas phase IP of NH_4 (ref. 18), 4.73 eV, one can estimate that NH_4 in the gas phase is only 0.71 eV higher in energy than $(\text{NH}_4^+)_s + (e^-)_s$ in liq. NH_3 (Fig. 4). In order to estimate the energy of NH_4 in liq. NH_3 one needs to estimate the solvation energy of NH_4 . Figure 4 indicates that this solvation energy is much greater (several eV) than NH_3 with itself (0.25 eV). The total computed energy for forming the first solvation shell complex ($n=4$) is -1.50 eV. However, in forming this species, one has to remove 4 NH_3 from liq. NH_3 ($4 \times 0.25 \text{ eV} = 1.00 \text{ eV}$). Therefore, if $\text{NH}_4(\text{NH}_3)_4$ has no additional solvation energy in liq. NH_3 , the solvation energy of NH_4 would be 0.50 eV (i.e. $-1.50 + 1.00$). Figure 4 shows this solvation energy and places $(\text{NH}_4)_s$ intermediate in energy between $(\text{NH}_4^+)_s + (e^-)_s$ and $(\text{NH}_3)_s + \text{H}$ (refs. 14e, 22). Figure 3 shows that the solvation energy of NH_4 might even be higher than this value. However, we have argued (ref. 14e) that due to the bubble structure that Rydberg states must have in condensed media, the solvation energy of NH_4 in liq. NH_3 can not exceed 0.5 eV. It is the requirement for a bubble structure which differentiates the solvation of Rydberg species from ordinary valence species.

BUBBLE STATE STRUCTURES OF RYDBERG STATES IN CONDENSED MEDIA

For Rydberg species, an electron in a Rydberg orbital is moving in a spatial region where, in general, the valence electrons are not. The average electron densities of a 3s Rydberg orbital are in the order of 100 times less than in valence space. The maximum of the Rydberg electron density lies outside the valence Van der Waals radii of the molecule. If another molecule should enter into the Rydberg space, the Rydberg electron will also avoid this intruder's valence space. This simple model also suggests that the intruder will also be repulsed. However, this is not always the case if sufficient non-intruder space exists for the Rydberg electron to move in and there is an overpowering interaction in valence space between the intruder and parent's cationic core. In fact, as we have seen in Fig. 1 the interaction between an excited Rydberg species and an atom may be large. In addition, Rydberg bimolecular reactions sometimes strongly mimic ion-molecule reactions (for additional discussion see refs. 1, 14e). One sees here exoergic stepwise complexation energies for the $\text{NH}_4(\text{NH}_3)_n$ clusters up to $n=6$. However, calculations placing either 6 H_2 or 6 He atoms symmetrically around n, 3s excited NH show strongly repulsive interactions

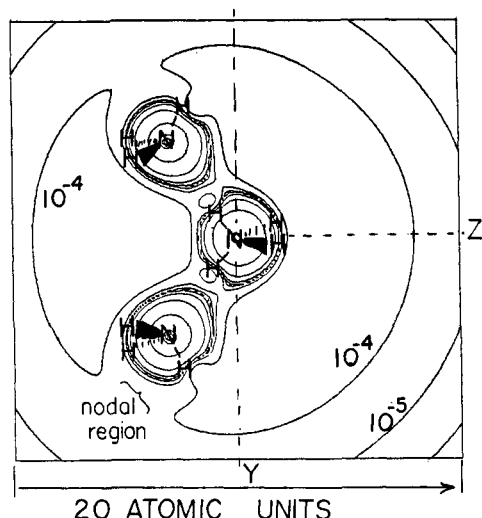


Figure 5. Electron density map of the 3s orbital in the complex $\text{NH}_4(\text{NH}_3)_2$ in the xz C_{2v} symmetry plane. Density units in electrons per cubic atomic unit. Note the nodal valence region avoided by the Rydberg electron.

(ca. 1 eV) at the ground state vertical excitation geometry. In this case the intruders are repulsed to beyond 5 Å. Therefore, intruders which can not interact in some bonding manner with a Rydberg species will be repulsed. In condensed media, in order to maintain a Rydberg species, a bubble will have to be constructed to house the Rydberg electron.

In Figure 5 is shown, for the $\text{NH}_4(\text{NH}_3)_2$ cluster, the 3s orbital electron density. The maximum of Rydberg³ electron density lies within the 10^{-4} electrons/au³ region. This is outside the valence space of the cluster.

The shown nodal region is the valence space of the molecule, which although containing some electron density is low on an integrated scale. The $\text{NH}_4(\text{NH}_3)_4$ cluster also shows 3s electron density lying between the complexing NH_3 units. For the $\text{NH}_4(\text{NH}_3)_6$ cluster, in which two NH_3 units themselves are themselves complexed, the 3s density is pushed out around the uncomplexed NH_3 units. Technically, calculations at larger clusters were yet not possible. Our assumption is that endoergic stepwise complexation energies would be encountered at the $n=7,8$ and larger clusters. Our suggested optimum model for NH_4 in liq. NH_3 is the $\text{NH}_4(\text{NH}_3)_4$ cluster in which additional NH_3 units are repulsed beyond the size of the Rydberg orbital. This structure would allow taking advantage of its -1.50 eV complexation energy. In this case the bubble would be created around the $\text{NH}_4(\text{NH}_3)_4$ structure in which no additional NH_3 solvent molecules could approach for additional binding.

COMMENTS ON THE STABILITY OF ORGANIC AMMONIUM RADICALS AND RELATED STRUCTURES

The instability of NH_4 radical under isolated conditions is in contrast with the stability of alkyl ammonium radicals, R_4N , in amalgam forms. The composition of these amalgams, ca. $\text{R}_4\text{N}(\text{Hg})_{1,2}$, is not really known. But the amalgams are stable at 0°C. We have performed (ref. 14e) calculations on the C-N rupture surfaces for: $(\text{CH}_3)_4\text{N} = (\text{CH}_3)_3\text{N} + \text{CH}_3$. We concluded that the activation energy for this reaction would lie below 10 kcal/mol. If so, isolated $(\text{CH}_3)_4\text{N}$ species would have kinetic lifetimes much shorter than observed in the amalgams. Our conclusion is that the stabilities of the ammonium radical amalgams are due to delocalization or deRydbergization of the organic species on complexation with $(\text{Hg})_n$. One can generally envisage metallic-like bonding between Rydberg radicals and other electron sharing species. The complicating feature is that other reaction channels may exist. In the case of NH_4 dimer (Na_2 -like), we found a low MCSCF activation energy to yielding $2\text{NH}_3 + \text{H}_2$ (ref. 23).

Finally we should mention that the electron affinities of $-\text{NR}_3^+$ units will be in the 4 eV region as found for NH_4 . Therefore, one should not automatically assume that the zwitterionic forms should be the ground states in structures containing, for example, both $-\text{NR}_3^+$ and negatively charged moieties. Diradical ground state structures may be encountered in special structural situations. Computational verification of which is the most stable structure will require either an MCSCF technique or CI determination of the relative ground and lower excited state energies.

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