Two new double Rydberg anions plus access to excited states of neutral Rydberg radicals via anion photoelectron spectroscopy

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We have observed and characterized two new double Rydberg anions $N_6H_{19}^-$ and $N_7H_{22}^-$ through their anion photoelectron spectra. The vertical detachment energies of these anions were found to be 0.443 and 0.438 eV, respectively. In addition, for three of the seven double Rydberg anions now known, we measured photodetachment transitions not only to the ground electronic states of their corresponding neutral Rydberg radicals but also to their first electronically excited states. In each spectrum, the energy spacing between the resulting peaks provided the ground-to-first electronically excited-state transition energy for the double Rydberg anion's corresponding neutral Rydberg radical. For the radicals, N_4H_{13}, N_5H_{16}, and N_6H_{19}, the spacings were found to be 0.83, 0.70, and 0.67 eV, respectively. These values are in excellent agreement with ground-to-first excited-state transition energies measured in absorption for the same neutral Rydberg radicals by Fuke and co-workers [Eur. Phys. J. D **9**, 309 (1999); J. Phys. Chem. A **106**, 5242 (2002).] The duplication of this neutral Rydberg property by photodetachment of double Rydberg anions further confirms that double Rydberg anions are indeed the negative ions of their corresponding neutral Rydberg molecules and cluster-like systems. © *2005 American Institute of Physics.*
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The term Rydberg radical refers to neutral molecular or cluster-like systems which are composed of a closed-shell cation and a hydrogenic (Rydberg) electron.[1] The closed-shell cation at the core of a Rydberg radical is itself a protonated molecule. For instance, the simplest ammonia-based Rydberg radical is NH_4, and it could have been denoted as $(NH_4^+)^-$. There is growing evidence for the role of Rydberg-like moieties in chemical phenomena. The Rydberg radicals, $NH_4(NH_3)_{n-1}$, have been postulated as the crucial intermediates in hydrogen atom transfer reactions[2] occurring in the excited states of clusters such as phenol–$(NH_3)_n$. The presence of hydronium cations and diffuse electrons $[H_3O^+ \cdots e^-]$ are central to an alternative model of the hydrated electron.[3] The positively charged arms of α-amino acid zwitterions $[-R\text{-}N^+H_3]$ are cationic precursors to Rydberg radicals, and excess electrons attaching to zwitterions might associate themselves with these cationic moieties to form Rydberg radical-like centers.[4,5] In addition, there has been speculation for many years that ammoniated NH_4 radicals are involved in reactions of ammoniated electrons and in their electrochemistry.[6–9]

The term, double Rydberg anion refers to the negative ions of (neutral) Rydberg radicals. Double Rydberg anions are composed of a closed-shell cationic core and two Rydberg-like electrons. The simplest ammonia-based, double Rydberg anion is NH_4^-, and it could have been denoted as $(NH_4^+)^=$. Some time ago,[10] we discovered NH_4^- through its anion photoelectron spectrum, and we interpreted it as described above. Theoretical studies by Ortiz,[11] Gutowski *et al.*,[12] and Matsunaga and Gordon[13] all supported that in-terpretation. In the meantime, we discovered four more double Rydberg anion analogs, having the stoichiometry, $(N_nH_{3n+1})^-$, $n=2$–5. In each case, we measured the photodetachment transitions between their ground electronic states and the ground electronic states of their corresponding neutral Rydberg radical.[14] All of these spectra were dominated by narrow peaks at low electron binding energies (0.4–0.5 eV) with one or more weaker intensity features, lying at slightly higher electron binding-energy values and due to vibrations of the neutral. This distinctive spectral signature is typical of highly diffuse, excess electron states. In addition, we observed three examples of double Rydberg anions solvated by ammonia, i.e., the anion-molecule complexes, $NH_4^-(NH_3)_1$, $NH_4^-(NH_3)_2$, and $N_2H_7^-(NH_3)_1$. These are true *solvated* double Rydberg anions with their own spectral features, and as such, they are distinct from other $(N_nH_{3n+1})^-$, species, in which all of the ammonia molecules in a given species appear to be part of its hydrogen-bonded cationic core. As examples, compare $NH_4^-(NH_3)_1$ versus $N_2H_7^-$ in our experimental study[14] and in Ortiz's theoretical study.[15]

Here, we report finding two more double Rydberg anion systems, $N_6H_{19}^-$ and $N_7H_{22}^-$. In both cases, we measured the photoelectron transitions between their ground electronic states and the ground electronic states of their corresponding neutral Rydberg radicals. In addition, for three of the seven double Rydberg anions now known, we have also measured photoelectron transitions between their ground electronic states and the first, electronically excited states of their corresponding neutral Rydberg radicals.

Negative-ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of anions with the fixed-
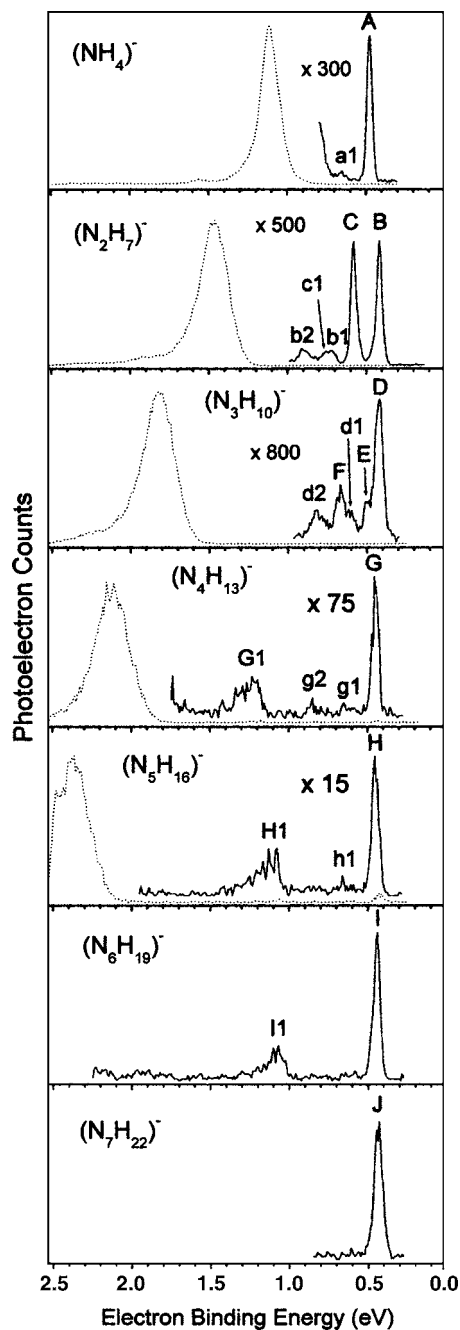
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FIG. 1. Anion photoelectron spectra of $(N_nH_{3n+1})^-$, $n=1-7$, measured with 2.54 eV photons. The solid traces are the spectra of double Rydberg anions, while the faint, dotted traces are the spectra of the much more abundant anion-molecule complexes, $H^-(NH_3)_n$.

frequency photon beam and energy analyzing the resultant photodetached electrons. This technique is governed by energy-conserving relationship, $h\nu=EKE+EBE$, where $h\nu$ is the photon energy, EKE is measured electron kinetic energy, and EBE is electron binding energy. Knowing the photon energy and measuring the electron kinetic energy yields the electron binding energy for each observed transition directly. Our anion photoelectron spectrometer consists of a nozzle ion source, ion transport optics, a 90° magnetic sector mass selector (resolution ~ 400), an argon-ion laser operated intracavity (~ 150 circulating W at 4880 Å), and a hemispherical electron energy analyzer (resolution ~ 25 meV). Photo-

electron spectra in this study were recorded with 2.54 eV photons and were calibrated against the well-known[16] photoelectron spectrum of NO^-. The entire apparatus has been described previously in detail.[17]

Double Rydberg anions were generated in a supersonic expansion, nozzle ion source in which $1-3$ atm of pure ammonia was expanded through a 23-μm-diameter nozzle into high vacuum. A negatively biased, thoriated iridium filament near the expansion provided electrons, and a magnetic field confined the resulting microplasma just outside the nozzle. The filament bias voltage was maintained between -40 and -70 V relative to the nozzle stagnation chamber which itself was biased at -500 V. The filament emission current was typically ~ 2 mA. Electrons, neutral molecules and clusters, anions, and cations all had the opportunity to interact in this environment. Only the negatively charged species would have been extracted into the spectrometer.

One can imagine that NH_4^+ cations picked up electrons to become NH_4 Rydberg molecules, which in turn picked up additional electrons to become NH_4^- double Rydberg anions. After all, NH_4 is more stable than NH_4^+, and NH_4^- is more stable than NH_4. Nevertheless, while this is an appealing mechanism, it has a flaw. While neutral ND_4 has been seen in beam experiments, as have its larger deuterated analogs and the larger analogs of NH_4, neutral NH_4 has an extremely short lifetime and has not been observed on the time scale of beam experiments.[18–20] How then does NH_4^- form, if for practical purposes, NH_4 is not present?[20] This is an interesting dilemma which we felt should be brought to the attention of the community. Perhaps, NH_4^- is formed due to the fragmentation of its larger analogs, but at this stage, the formation mechanism remains an open question.

Two new double Rydberg anion systems were found during this study, $N_6H_{19}^-$ and $N_7H_{22}^-$. For comparison, Fig. 1 shows all the double Rydberg anion photoelectron spectra
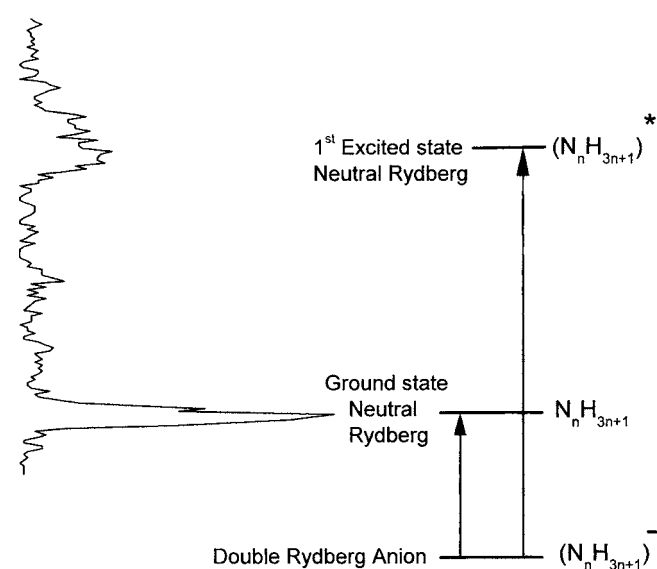

FIG. 2. Schematic showing photodetachment transitions from the ground state of a double Rydberg anion to the ground and first electronically excited states of its corresponding neutral Rydberg radical along with the resulting photoelectron spectrum. The energy spacing between the two peaks in the spectrum corresponds to the ground state to first excited-state energy difference in the *neutral* Rydberg radical.

that we have measured, including those of $N_6H_{19}^-$ and $N_7H_{22}^-$. The spectrum of $N_6H_{19}^-$ exhibits two transitions, labeled I and I1. Peak I is due to the transition between the ground electronic state of $N_6H_{19}^-$ and the ground electronic state of its corresponding neutral Rydberg radical, N_6H_{19}, and from it, we determined the vertical detachment energy of $N_6H_{19}^-$ to be 0.443 eV. Peak I1 will be discussed below. The spectrum of $N_7H_{22}^-$ exhibits a single transition in the range of our data, and it is labeled J. Peak J is due to the transition between the ground electronic state of $N_7H_{22}^-$ and the ground electronic state of its corresponding neutral Rydberg radical, N_7H_{22}, and from it, we found the vertical detachment energy of $N_7H_{22}^-$ to be 0.438 eV.

For three double Rydberg anions, we measured photoelectron transitions not only between their ground electronic states and the ground electronic states of their corresponding neutral Rydberg radicals but also between their (anion) ground electronic states and the first electronically excited states of their corresponding neutral Rydberg radicals. We made these measurements on only three cases largely because of photoelectron signal interference from same-mass

$H^-(NH_3)_n$ anion-molecule complexes in three of the other cases.[21] These three new measurements were conducted on $N_6H_{19}^-$ and on two double Rydberg anions whose anion ground state to neutral ground state transitions we had recorded previously, i.e., on $N_4H_{13}^-$ and $N_5H_{16}^-$. Each of these three systems exhibited two electronic transitions (peaks), with the energy spacing between them being a measurement of the ground-to-first excited electronic transition in the *neutral* Rydberg radical. Figure 2 shows a schematic for such transitions. These two transitions in $N_4H_{13}^-$ are labeled G and G1, and the G1-G spacing is 0.83 eV. (Peaks g1 and g2 are due to vibrational excitations.) These two transitions in $N_5H_{16}^-$ are labeled H and H1 and the H1-H spacing is 0.70 eV. (Peak h1 is due to a vibrational excitation.) These two transitions in $N_6H_{19}^-$ are labeled I and I1, and the I1-I spacing is 0.67 eV. In each case, the higher EBE peak is broader than the lower EBE peak, suggesting a structural difference between the ground and first excited neutral states. While Table I includes these new values, it also brings all measured values relating to experimentally observed double Rydberg anions and their larger analogs up to date.

TABLE I. Electron binding energies (EBEs) of peak positions, assignments, spacings, and solvation shifts. Energies are in eV. (VDE=vertical detachment energy.)

Anion composition	Solvated hydride anions				Double Rydberg anions			
	EBE[a]	Assignment	Spacing	Shift	EBE[b]	Assignment[c]	Spacing[d]	Solvent shift
NH_4^-	1.110	VDE of $H^-(NH_3)$	...	...	0.472 (**A**)	VDE of $(NH_4^+)^=$	...	...
	1.546	NH_3 stretch	0.436		0.651 (**a1**)	ν_4 of NH_4	0.179 (**a1-A**)	
$N_2H_7^-$	1.460	VDE of $H^-(NH_3)_2$	...	0.350	0.415 (**B**)	VDE of $(N_2H_7^+)^=$	...	...
	1.896	NH_3 stretch	0.436		0.578 (**C**)	VDE of $(NH_4^+)^=(NH_3)$	...	0.106 (**C-A**)
					0.723 (**b1**)	Proton motion	0.308 (**b1-B**)	
					0.757 (**c1**)	ν_4 of NH_4	0.179 (**c1-C**)	
					0.894 (**b2**)	N_2H_7 stretch	0.479 (**b2-B**)	
$N_3H_{10}^-$	1.820	VDE of $H^-(NH_3)_3$	...	0.360	0.424 (**D**)	VDE of $(N_3H_{10}^+)^=$	...	...
	2.256	NH_3 stretch	0.436		0.495 (**E**)	VDE of $(N_2H_7^+)^=(NH_3)$	...	0.080 (**E-B**)
					0.660 (**F**)	VDE of $(NH_4^+)^=(NH_3)_2$	...	0.082 (**F-C**)
					0.605 (**d1**)	N_3H_{10} umbrella	0.181 (**d1-D**)	
					0.824 (**d2**)	N_3H_{10} stretch	0.400 (**d2-D**)	
$N_4H_{13}^-$	2.111	VDE of $H^-(NH_3)_4$	...	0.291	0.427 (**G**)	VDE of $(N_4H_{13}^+)^=$	...	...
					0.632 (**g1**)	N_4H_{13} umbrella	0.205 (**g1-G**)	
					0.803 (**g2**)	N_4H_{13} stretch	0.376 (**g2-G**)	
					1.26 (**G1**)	First excited state	0.83 (**G1-G**)	
$N_5H_{16}^-$	2.360	VDE of $H^-(NH_3)_5$	...	0.249	0.434 (**H**)	VDE of $(N_5H_{16}^+)^=$	...	...
					0.610 (**h1**)	N_5H_{16} umbrella	0.176 (**h1-H**)	
					1.13 (**H1**)	First excited state	0.70 (**H1-H**)	
$N_6H_{19}^-$	...	...	...	...	0.443 (**I**)	VDE of $(N_6H_{19}^+)^=$		
					1.11 (**I1**)	First excited state	0.67 (**I1-I**)	
$N_7H_{22}^-$	...	...	...	...	0.438 (**J**)	VDE of $(N_7H_{22}^+)^=$	...	...

[a]Errors for the main peaks in the solvated hydride anion spectra are ±0.010 eV, while those for the NH_3 stretch peaks are ±0.060 eV.
[b]Errors for peaks labeled with capital letters are ±0.005 eV (except for peak E which is 0.015 eV and peaks G1, H1, and I1 which are ±0.060 eV each). Errors for vibrations labeled with lower case letters are ±0.060 eV.
[c]VDE's listed here for double Rydberg anions are also equivalent to adiabatic electron affinities, EA_a.
[d]Errors for the spacings, G1-G, H1-H, and I1-I are ±0.060 eV.

The electronic absorption spectra of several neutral Rydberg radicals, N_nH_{3n+1}, $n=2-7$, have been measured by Fuke and co-workers[22,23] using a photodissociation, pump-probe technique coupled with time-of-flight mass spectrometry. Since their experiment provided ground-to-first excited-state electronic transition energies for neutral Rydberg systems directly, it afforded the opportunity to check whether our measured peak spacings (the ground-to-first electronically excited-state energy differences in the neutral Rydberg radical) are the same. Making this comparison is valid, even though the values were obtained by two different experimental techniques. Since the lowest EBE peak in each spectrum is relatively narrow, the structures of the ground states of the double Rydberg anions and their corresponding neutral Rydberg radicals can be presumed to be very similar. Thus, any energy effects due to structural differences between the two neutral Rydberg states will be similarly reflected in the peak maxima of both the absorption and the photoelectron spectra.

For the spectrum of $N_4H_{13}^-$, our peak spacing is 0.83 eV, while the ground-to-first excited-state transition energy of neutral N_4H_{13}, measured by absorption, is 0.81 eV. For $N_5H_{16}^-$, our peak spacing is 0.70 eV, while the transition energy of neutral N_5H_{16}, again measured by absorption, is 0.71 eV. For $N_6H_{19}^-$, our peak spacing is 0.67 eV, while the transition energy of neutral N_6H_{19}, measured by absorption, is 0.69 eV. Given that the uncertainty in each of these six values is about ±0.06 eV, the agreement is quite good.

Since we were able to duplicate the known, ground-to-first excited-state electronic transition energies in neutral Rydberg systems by photodetaching electrons from their stoichiometrically corresponding double Rydberg anions, the implication is that double Rydberg anions are indeed the negative ions of neutral Rydberg systems. This quantitative connection between double Rydberg anions and their corresponding neutral Rydberg systems further confirms their relationship.

[1] G. Herzberg and J. T. Hougen, J. Mol. Spectrosc. **97**, 430 (1983).
[2] G. Gregoire, C. Dedonder-Lardeux, C. Jouvet, S. Martrenchard, and D. Solgadi, J. Phys. Chem. A **105**, 5971 (2001).
[3] A. L. Sobolewski and W. Domcke, Phys. Chem. Chem. Phys. **5**, 1130 (2003).
[4] J. V. Ortiz (private communication).
[5] M. S. Gutowski (private communication).
[6] J. K. S. Wan, J. Chem. Educ. **45**, 40 (1968).
[7] J. M. Brooks and R. R. Dewald, J. Phys. Chem. **75**, 986 (1971).
[8] E. Kariv-Miller, C. Nanjundiah, J. Eaton, and K. E. Swenson, J. Electroanal. Chem. Interfacial Electrochem. **167**, 141 (1984).
[9] E. M. Evleth and E. Kassab, Pure Appl. Chem. **60**, 209 (1988).
[10] J. T. Snodgrass, J. V. Coe, C. B. Freidhoff, K. M. McHugh, and K. H. Bowen, Faraday Discuss. Chem. Soc. **86**, 241 (1988).
[11] J. V. Ortiz, J. Chem. Phys. **87**, 3557 (1987).
[12] M. Gutowski, J. Simons, R. Hernandez, and H. L. Taylor, J. Phys. Chem. **92**, 6179 (1988).
[13] N. Matsunaga and M. S. Gordon, J. Phys. Chem. **99**, 12773 (1995).
[14] S.-J. Xu, J. M. Nilles, J. H. Hendricks, S. A. Lyapustina, and K. H. Bowen, J. Chem. Phys. **117**, 5742 (2002).
[15] J. V. Ortiz, J. Chem. Phys. **117**, 5748 (2002).
[16] M. J. Travers, D. C. Cowles, and G. B. Ellison, Chem. Phys. Lett. **164**, 449 (1989).
[17] J. V. Coe, J. T. Snodgrass, C. B. Friedhoff, K. M. McHugh, and K. H. Bowen, J. Chem. Phys. **84**, 618 (1986).
[18] G. I. Gellene, D. A. Cleary, and R. F. Porter, J. Chem. Phys. **77**, 3471 (1982).
[19] K. Fuke, R. Takasu, and F. Misaizu, Chem. Phys. Lett. **229**, 597 (1994).
[20] F. Merkt (private communication).
[21] In the case of N_7H_{22}, the signal was too weak to make this measurement.
[22] S. Nonose, T. Taguchi, K. Mizuma, and K. Fuke, Eur. Phys. J. D **9**, 309 (1999).
[23] S. Nonose, T. Taguchi, F. Chen, S. Iwata, and K. Fuke, J. Phys. Chem. A **106**, 5242 (2002).