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Dipole-bound anions: formed by Rydberg electron transfer (RET) and studied by velocity map imaging–anion photoelectron spectroscopy (VMI–aPES)^{*}

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Abstract. Here, we demonstrate the capabilities of the unique combination of Rydberg electron transfer (RET) and velocity map imaging–anion photoelectron spectroscopy (VMI–aPES) to form dipole bound anions and to measure their photoelectron spectra. For these purposes, we have chosen the dipole bound anions of acetonitrile, ammonia–water dimer, water dimer, dimethyl sulfoxide and thymine as examples. All of these had been previously formed and/or studied but by other methodologies.

1 Introduction

The interactions between electrons and atoms, molecules, or clusters govern many processes in chemistry and physics. When stable negative ions are formed as a result of these interactions, they may exist either as valence anions or as diffuse electron states [1–39]. As negative ions, they can be mass-analyzed in mass spectrometers and, once mass-selected, their anion photoelectron spectra can be measured. While we can utilize a variety of ion sources to create negative ions, we focus here on the Rydberg electron transfer (RET) anion source as a means of forming them and on velocity map imaging as a technique for measuring their anion photoelectron spectra.

Rydberg electron transfer (RET) is a gentle process that transfers an electron from a highly-excited atom to a neutral molecule, forming a negative ion. In RET, a pulsed, helium-seeded beam of neutral molecules is crossed with a continuous, thermal beam of potassium atoms, which have been excited to one of their Rydberg levels by two dye laser pulses: one set at a fixed frequency to pump the potassium atoms to their $2P_{3/2}$ state and the other tuned to the appropriate nd Rydberg level. Upon collision of the neutral molecule and the highly excited Rydberg atom, charge transfer occurs, forming an ion pair. Once it separates into ions, the anions produced by RET are pulsed through a time-of-flight mass spectrometer, mass-selected, photodetached by another laser pulse, and their resultant

electrons energy-analyzed by anion photoelectron spectroscopy (aPES). Negative ion photoelectron spectroscopy (aPES) is a powerful tool for probing electronic structure information about neutral molecules and/or clusters. Anion PES is governed by the energy-conserving relationship, $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the energy of the photon beam, EBE is the binding energy of the electron, and EKE is the kinetic energy of the electron. Our time-of-flight mass spectrometric and photoelectron spectroscopic apparatus has previously been described [11,40]. The apparatus includes both a magnetic bottle energy analyzer, which has a resolution of about 35 meV at EKE of 1 eV, as well as a velocity-map imaging (VMI) energy analyzer, with $\Delta E/E \sim 0.03$. The most common information provided by anion photoelectron spectra is the vertical detachment energy (VDE) of the anion being studied. The VDE is the photodetachment transition energy from the anion's ground state to its neutral counterpart at the structure of the anion. (Photodetachment is an ultra-fast and therefore vertical process.) The adiabatic electron affinity (EA) is the energy difference between the ground states of the anion and its neutral counterpart. Its appearance in a photoelectron spectrum is dependent on the structural similarity between the anion and its neutral, i.e., on Franck–Condon overlap. In most of the anions presented here, the structures of the anion and its neutral are almost identical, making the VDE and the EA values essentially the same values. The VDE value in a given photoelectron spectrum is the electron binding energy (EBE) corresponding to the intensity maximum of the lowest EBE peak in the spectrum. When the VDE value is small, the electron binding energy for that anion is also small and in all likelihood the geometries of the anion and its corresponding neutral molecule are quite

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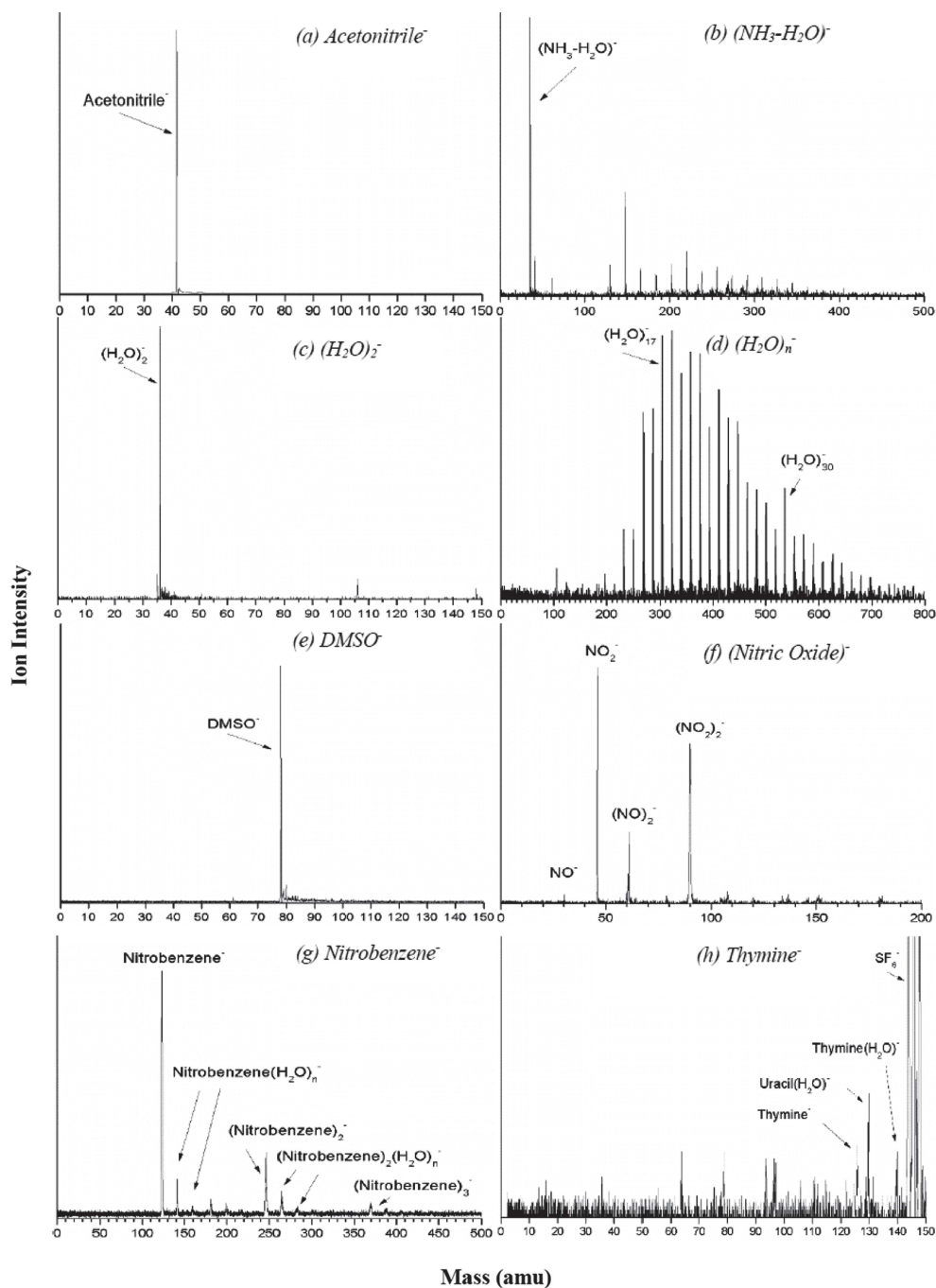


Fig. 1. Mass spectra of the anions: (a) acetonitrile anion, (b) ammonia–water dimer anion, $(\text{NH}_3\text{-H}_2\text{O})^-$, (c) water dimer anion, $(\text{H}_2\text{O})_2^-$, (d) water cluster anions, $(\text{H}_2\text{O})_n^-$, (e) dimethyl sulfoxide anion, DMSO^- , (f) nitric oxide anions, NO^- , (g) nitrobenzene anions, and (h) thymine anions, made with the Rydberg electron transfer (RET) source and analyzed by our TOF mass spectrometer.

similar. The RET technique allows us to create unusually fragile anions. Here, we demonstrate some of the capabilities of this one-of-a-kind combination of a Rydberg electron transfer anion source and velocity map imaging-anion photoelectron spectroscopy. Velocity map imaging is the electron energy analysis technique of choice for measuring the anion photoelectron spectra of low VDE anions.

2 Results

In Figure 1, we present mass spectra of eight anions made with our RET ion source, whereas in Figures 2–7, we present the corresponding anion photoelectron spectra of six of those same systems. Five of the six anions presented in Figure 2 are dipole bound anions. For molecules

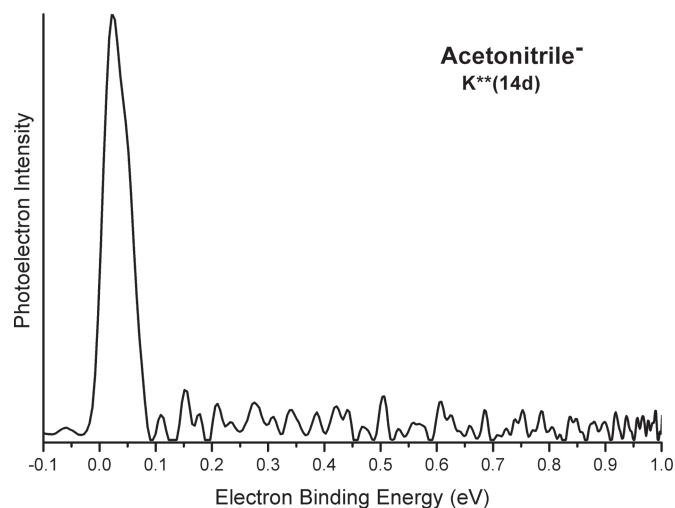


Fig. 2. Photoelectron spectrum of the acetonitrile anion taken with the first harmonic (1064 nm) of a Nd:YAG laser.

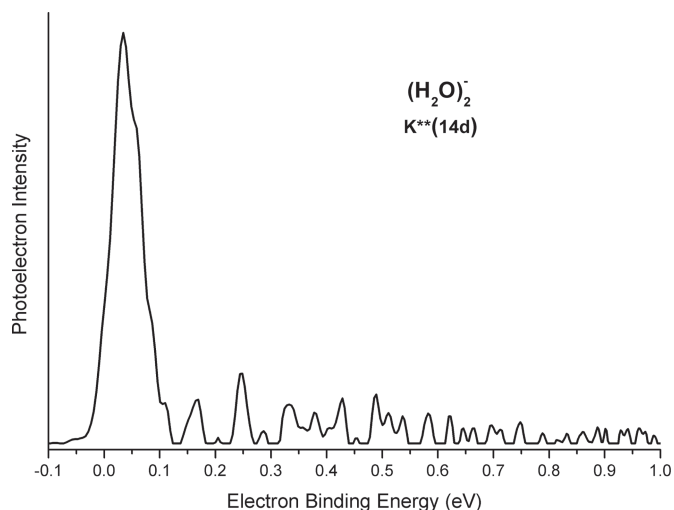


Fig. 4. Photoelectron spectrum of the water dimer anion taken with the first harmonic (1064 nm) of a Nd:YAG laser.

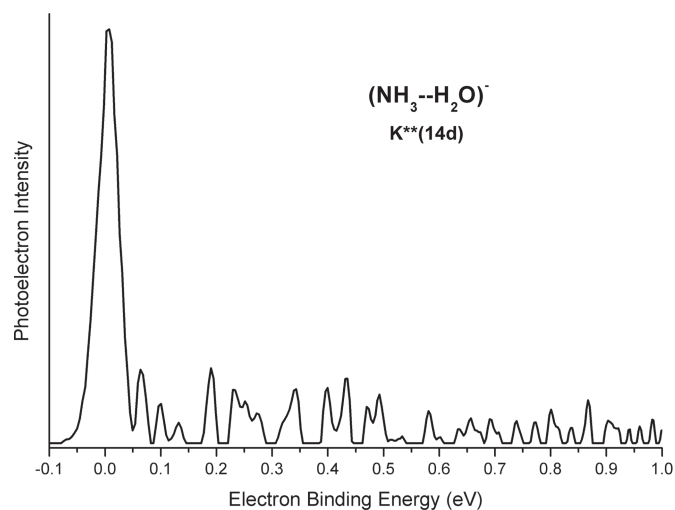


Fig. 3. Photoelectron spectrum of the ammonia–water dimer anion taken with the first harmonic (1064 nm) of a Nd:YAG laser.

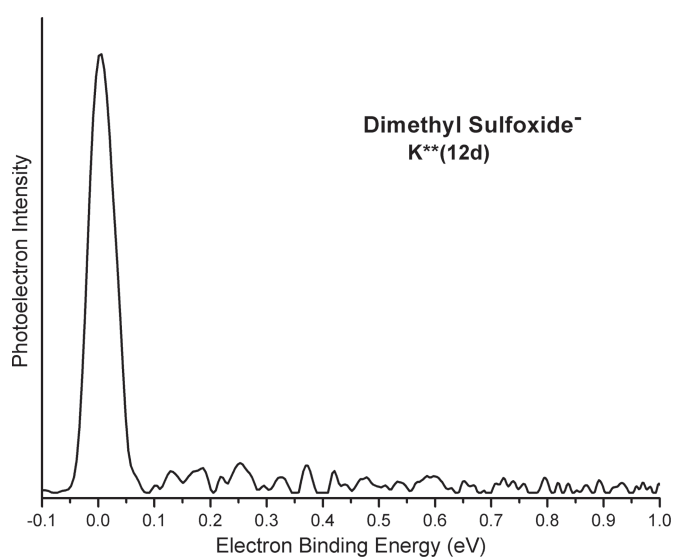


Fig. 5. Photoelectron spectrum of the dimethyl sulfoxide anion, DMSO[−], taken with the first harmonic (1064 nm) of a Nd:YAG laser.

(or small clusters) that do not form valence anions, they can often form dipole bound anions when their dipole moments are large enough to capture an excess electron. The critical dipole moment required is equal or greater than ~ 2.5 Debye. The RET and VMI–aPES combination is especially well-suited for studying dipole bound anion states.

Figures 2–7 present anion photoelectron spectra of the species we formed by RET. Since RET is a resonant process, the K^{**} Rydberg level used to make a given anion is indicated on the spectrum by nd , where n is the principal quantum number. For the five dipole bound anions discussed here, Table 1 compares VDE values from previous experiments, from the present RET–aPES experiments, and from theory, along with listing the dipole moments of their neutral counterparts.

Acetonitrile was found to form a dipole bound anion in both stand-alone RET experiments [14–16], in

conventional anion photoelectron experiments using a non-RET anion source [17,20,30,36], and through theoretical calculations [19,30]. Our photoelectron spectrum of the acetonitrile anion, generated and measured by the combined RET–VMI–aPES technique, is shown in Figure 2. The single, narrow peak at very low electron binding energy (EBE) is characteristic of diffuse electron states, such as dipole bound anions. The peak's narrowness is due to the structures of the anion and the neutral being nearly identical. The low EBE value of its peak center (low VDE) is due to its excess electron being weakly bound. While there is some variation in the acetonitrile anion's VDE values listed in Table 1, they are also broadly consistent.

While ammonia alone has a relatively low dipole moment of $\sim 1.4D$, its hetero-dimer with water, i.e., (NH_3-H_2O) , has a dipole moment of $2.9D$. This led us to

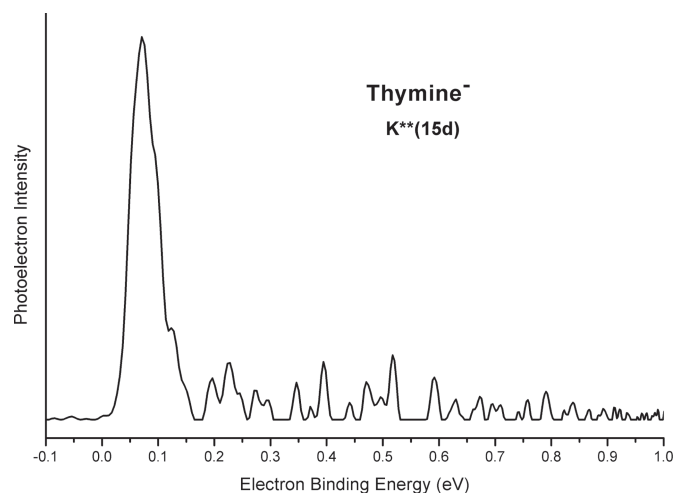


Fig. 6. Photoelectron spectrum of the thymine anion taken with the first harmonic (1064 nm) of a Nd:YAG laser.

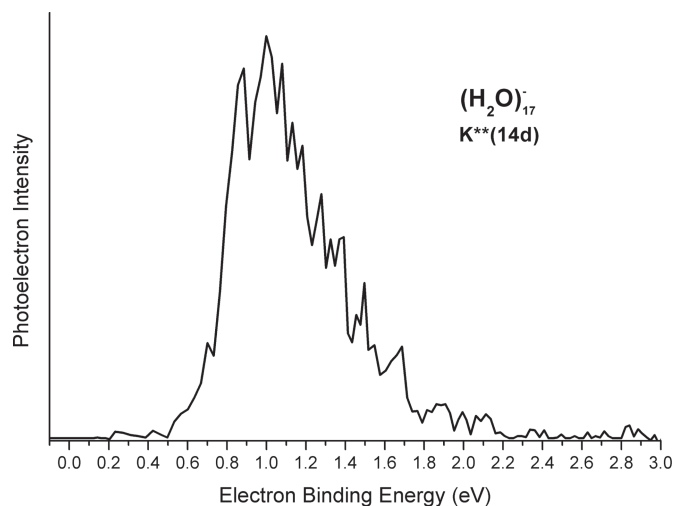


Fig. 7. Photoelectron spectrum of the water cluster anion, $(\text{H}_2\text{O})_{17}^-$, taken with the third harmonic (355 nm) of a Nd:YAG laser.

Table 1. Comparison of the vertical detachment energy (VDE) values from this work, previous experiments, and theoretical calculations for the studied anionic species.

Anionic species	Dipole moment (μ , D)	VDE (meV)		
		Current exp.	Previous exp.	Theory
Acetonitrile	3.92 ^{a,b}	22	3, ^c 11, ^d 12, ^e 18.0, ^f 18.2 ^g	13.4, ^h 15.5 ^g
$(\text{NH}_3\text{-H}_2\text{O})^-$	2.9 ⁱ	7	9 ⁱ	13.5 ^j
$(\text{H}_2\text{O})_2^-$	2.6 ^{i,k}	35	42 ^{i,l} 45, ^{k,m} 48 ⁿ	41.9 ^o
DMSO	3.96 ^{a,b}	5	7.4, ^a 13.9 ^b	13.9 ^b
Thymine	4.13 ^p	71	69 ^q	51, ^r 69 ^g

^a See reference [16]; ^b See reference [26]; ^c See reference [20]; ^d See references [15,16,36]; ^e See reference [14]; ^f See reference [17]; ^g See reference [30]; ^h See reference [19]; ⁱ See reference [21]; ^j See reference [22]; ^k See reference [23]; ^l See reference [33]; ^m See reference [13]; ⁿ See reference [24]; ^o See reference [25]; ^p See reference [28]; ^q See reference [27]; ^r See reference [38].

predict that it would form a dipole bound dimer anion. Stand-alone RET experiments and calculations showed that it does [21,22]. Our anion photoelectron spectrum of $(\text{NH}_3\text{-H}_2\text{O})^-$, generated and measured by the combined RET-VMI-aPES technique, is shown in Figure 3. VDE comparisons in Table 1 are again broadly consistent with one another.

While the water molecule also has a modest dipole moment of ~ 1.85 D, its dimer, i.e., $(\text{H}_2\text{O})_2$, has a dipole moment of ~ 2.6 D [21,23] and, since it is greater than 2.5 D, it forms a dipole bound anion. The water dimer anion, $(\text{H}_2\text{O})_2^-$, was the first dipole bound anion to be seen by anion photoelectron spectroscopy [13,21,23,24,33]. Our anion photoelectron spectrum of $(\text{H}_2\text{O})_2^-$, generated and measured by the combined RET-VMI-aPES technique, is shown in Figure 4. VDE comparisons in Table 1 are consistent with one another.

Dimethyl sulfoxide ($(\text{CH}_3)_2\text{SO}$) has a dipole moment of 3.96 D and was shown by through stand-alone RET experiments to form a dipole bound anion [16,26]. Our anion photoelectron spectrum of DMSO⁻, generated and measured by the combined RET-VMI-aPES technique, is shown in Figure 5, again in broad agreement with other measurements.

Thymine has a dipole moment of 4.13 D and, thus, is also able to bind an excess electron via its dipolar field. A combination of experimental and theoretical assessments agrees [27,28,30,38]. Our anion photoelectron spectrum of the thymine dipole bound anion, generated and measured by the combined RET-VMI-aPES technique, is shown in Figure 6, and is again in broad agreement with other measurements.

The last spectrum to be presented is that of $(\text{H}_2\text{O})_{17}^-$. While not a dipole bound anion, it is nevertheless a diffuse electron state and is usually considered to be an embryonic hydrated electron state. It was originally measured by both stand-alone RET and conventional anion photoelectron spectroscopy [24,33]. Our anion photoelectron spectrum of $(\text{H}_2\text{O})_{17}^-$, generated and measured by the combined RET-VMI-aPES technique, is shown in Figure 7 and matches previous anion photoelectron spectra of it quite well.

3 Summary

Here, we have presented a collection of mostly dipole-bound, anion photoelectron spectra, generated and

measured by our combined RET–VMI–aPES technique, for the purpose of demonstrating the capabilities of this unique methodology.

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Author contribution statement

S.M.C., G.L., and K.H.B. contributed to writing this manuscript. S.M.C., G.L., J.D.G., and A.M.B. conducted the RET–VMI–aPES experiments.

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