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ABSTRACT

Using a combination of Rydberg electron transfer and negative ion photoelectron spectroscopy, we revisited an earlier study which, based on several separate pieces of evidence, had concluded that *trans*- and *gauche*-succinonitrile can form quadrupole bound anions (QBAs) and dipole bound anions (DBAs), respectively. In the present work, succinonitrile anions were formed by Rydberg electron transfer and interrogated by negative ion photoelectron spectroscopy. The resulting anion photoelectron spectra exhibited distinctive spectral features for *both* QBA and DBA species in the *same* spectrum, thereby providing direct spectroscopic confirmation of previous indirect conclusions. Just as importantly, this work also introduces the integrated combination of Rydberg electron transfer and anion photoelectron spectroscopy as a powerful, tandem technique for studying diffuse excess electron states.

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INTRODUCTION

Negative ions can be formed not only through attachment of electrons to conventional, valence orbitals but also due to electron capture by long-range, electrostatic forces and/or dispersion effects. Negative ions formed by the latter route possess excess electrons that are very weakly bound and spatially diffuse. The component electrostatic potentials associated with these forces can be expressed through the multipole expansion for a given charge distribution as monopole, dipole, quadrupole, octupole, etc., moments, although this representation is strictly valid only at a distance. Nevertheless, in cases where there is no valence binding of the excess electron and where all but one of the electrostatic moments are null, it is customary to credit that nonzero moment as the primary interaction responsible for any excess electron binding that is observed. The best studied case among these are dipole-bound anions (DBAs), i.e., anions whose excess electrons are weakly bound due to the dipolar fields of the anions' neutral counterparts. The formation of dipole bound anions has been postulated as the first step in electron attachment to polar molecules, and for that reason, they are sometimes referred to as “doorway” states.^{1–16}

The next higher term in the multipole expansion is the quadrupole moment. Unlike dipole-bound anions, evidence for quadrupole-bound anions, where electrons are bound by long-range

charge-quadrupole attraction, has been scarce. Quadrupole-bound anions were first predicted theoretically in 1979.¹⁷ Early experimental searches for quadrupole-bound anions examined the negative ions of carbon disulfide,^{18,19} formamide,²⁰ *para*-dinitrobenzene,²¹ and small clusters of magnesium oxide.^{12,22} However, due either to a lack of theoretical confirmation and/or to strong indications that they were instead valence-bound, the excess electrons in none of these exhibited the weakly bound and/or spatially diffuse properties expected of quadrupole bound anions.

The first convincing evidence for the existence of quadrupole bound anions was presented by Schermann, Desfrancois, Bowen, and Compton in 2004.²³ Their conclusion that the *trans*-succinonitrile anion is a quadrupole bound anion was based on two different types of experimental measurements and on their theoretical calculations.

1. Rydberg electron transfer (RET) experiments were performed by crossing a beam of succinonitrile molecules with a beam of laser-excited Rydberg atoms and monitoring the formation of parent succinonitrile anions mass spectrometrically as a function of the Rydberg principle quantum number, n . The succinonitrile beam contained both *trans*- and *gauche*-conformers, with the former possessing a large quadrupole moment but a null dipole moment and with the latter exhibiting a large

dipole moment.²⁴ These experiments were conducted at both the University of Paris Nord using xenon Rydberg atoms and the University of Tennessee using rubidium Rydberg atoms. Both RET experiments gave fully consistent results, with each exhibiting a sharply peaked, anion intensity vs n feature at and around $n = 12$. Application of the semiempirical formula, electron affinity (EA) = $23 \text{ eV}/n^{2.8}$, implied an electron affinity (EA) of 22 meV for the molecules that formed anions at $n = 12$.²⁵ This was interpreted as the EA value of neutral *trans*-succinonitrile and as evidence for it having formed a ground state, quadrupole bound anion. Surprisingly, however, neither of the Rydberg electron transfer experiments showed discernible evidence for a sharply peaked feature, corresponding to the expected dipole bound anion of *gauche*-succinonitrile even though such peaks are characteristic of dipole bound anions formed in RET experiments.

2. The other type of experimental measurement performed on succinonitrile anions utilized negative ion photoelectron spectroscopy and was conducted at Johns Hopkins University. There, a beam of succinonitrile anions was formed by a nozzle-ion source, mass-selected, and photodetached, after which its photoelectrons were energy analyzed.²⁶ The resulting anion photoelectron spectrum exhibited a sharp peak at an electron binding energy (EBE) of 108 meV and with two weaker molecular vibrational features at higher electron binding energies. Its spectral profile was typical of dipole bound anion photoelectron spectra.³ Because of this distinctive signature and the EBE value of its principle peak, it was interpreted as being due to the dipole bound, *gauche*-succinonitrile anion with an EA value of 108 meV for neutral *gauche*-succinonitrile. Interestingly, however, there was no evidence for a photoelectron peak with an EBE value in the vicinity of 22 meV and thus no indication of a quadrupole bound anion. On the other hand, such weakly bound excess electrons could have easily been field-detached by the gauntlet of electric fields from multiple lenses along the ion path in that particular apparatus, if, in fact, quadrupole bound anions had been formed by the nozzle-ion source.

Thus, while the Rydberg electron transfer experiment gave evidence for a quadrupole bound, *trans*-succinonitrile anion but not for a dipole bound, *gauche*-succinonitrile anion, the anion photoelectron spectroscopic experiment gave evidence for a dipole bound, *gauche*-succinonitrile anion but not for a quadrupole bound, *trans*-succinonitrile anion. Nevertheless, DFT/B3LYP calculations conducted as part of that work found the anions of *trans*- and *gauche*-succinonitrile to be quadrupole bound and dipole bound, respectively. Thus, the conclusion that the *trans*-succinonitrile anion is a ground state, quadrupole bound anion was based on several separate pieces of evidence.

Subsequent high-level calculations on succinonitrile anions by Sommerfeld concluded that while the dipole moment of *gauche*-succinonitrile is sufficient to explain excess electron binding in its anion, excess electron binding in the *trans*-succinonitrile anion is more complex and is both due to the quadrupole moment of *trans*-succinonitrile and to electron correlation effects, with the latter playing the larger role.²⁴ Dispersion is an electron correlation effect. In diffuse excess electron states, such as dipole bound

and quadrupole bound anions, London dispersion forces, acting between the diffuse excess electron cloud and its home (neutral) molecule, can have attractive interactions that are comparable to or even exceed those of electron-multipole interactions.^{10,27} Dispersion appears to have made an important contribution to excess electron binding in the *trans*-succinonitrile anion and possibly in the *gauche*-succinonitrile anion as well. In anion photoelectron spectra, sharp peaks at low electron binding energies are characteristic of all types of *diffuse-electron anion states*, e.g., correlation-bound,^{9,28,29} polarizability-bound, dipole-bound,²⁻⁴ quadrupole-bound,²³ and double Rydberg anions.³⁰ This is because the weak interaction between the excess electron and its home molecule leads not only to low excess electron binding energies for the resulting anion, but it also leaves the anion and its corresponding neutral in nearly identical structures, leading to high Franck-Condon overlap and narrow peaks.

In the years since 2004, interest in quadrupole bound anions has continued to grow with the development of several new computational models,³¹⁻³⁴ the theoretical prediction of specific quadrupole-bound anions,^{24,35} and the observation of excited, quadrupole-bound states in a valence-bound, ground state anion.³⁶

In the present work, we revisit succinonitrile anions, using the unique combination of Rydberg electron transfer to efficiently prepare their ground state and diffuse-electron anion states and negative ion photoelectron spectroscopy to directly and spectroscopically measure their electron binding energies. This approach allows us to comprehensively tackle unfinished business from the earlier work and to present a more complete story.

EXPERIMENTAL METHOD

Figure 1 presents a schematic of our combined Rydberg electron transfer—anion photoelectron (photodetachment) spectroscopic apparatus. The RET region, where target molecules and optically prepared Rydberg atoms collide to form anions, is on the left, while the photoelectron region, where the resultant mass-selected anions are photodetached and their electrons energy-analyzed, is on the right. A beam of neutral succinonitrile molecules was generated by expanding succinonitrile vapor in helium (10 psig) through the nozzle of a pulsed valve into vacuum. This beam was then crossed with an effusive beam of potassium atoms, which had been excited to *nd* Rydberg states in two steps using two dye lasers. One dye laser pumped the potassium atoms to the $^2P_{3/2}$ state using 766.7 nm photons, while the other was tuned to reach specific Rydberg levels. Upon collisions between Rydberg excited potassium atoms and succinonitrile molecules inside the ion extraction region of the apparatus, charge transfer occurred, producing potassium cations and parent succinonitrile anions, which momentarily formed ion pairs before dissociating into their component ions. The nascent anions were then pulsed into the negative ion photoelectron spectrometer portion of the apparatus, where they were mass-selected using time-of-flight mass spectrometry before their electrons were photodetached using 1064 nm linearly polarized light from a Nd:YAG laser. The kinetic energies of these photoelectrons were then measured using a velocity-map imaging (VMI) spectrometer. (An available “magnetic bottle” type electron energy analyzer on this apparatus was not used in this work.) VMI analysis was achieved by accelerating the electrons along the axis of the ion beam toward a

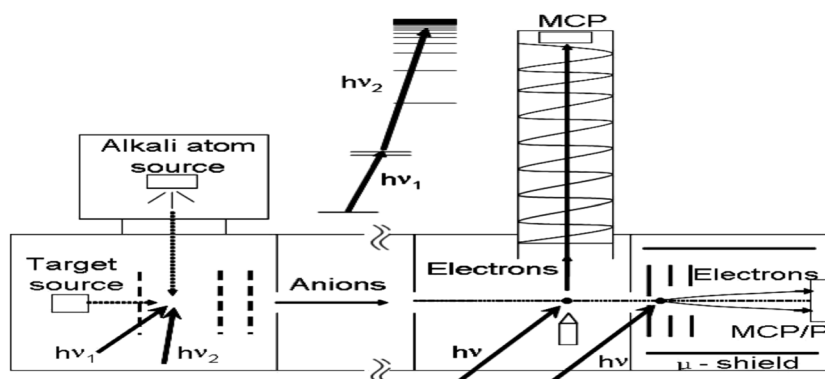


FIG. 1. Schematic of our combined Rydberg electron transfer anion source and its associated negative ion photoelectron spectrometer.

position-sensitive detector coupled to a CCD camera. The resulting two-dimensional image was then reconstructed via the BASEX method,³⁷ yielding the corresponding anion photoelectron spectrum. Since the photoelectron technique is governed by the energy-conserving relationship $h\nu = \text{EKE} + \text{EBE}$, where $h\nu$, EKE, and EBE are the photon energy, the electron kinetic energy, and the electron binding (transition) energy, respectively, knowing $h\nu$ and measuring EKE values provide corresponding EBE values. Photoelectron spectra in this work were calibrated against the well-known spectrum of NO^- .²⁶

RESULTS AND DISCUSSIONS

The study in 2004 was interpreted in terms of the *trans*-succinonitrile anion being a quadrupole bound anion, whose neutral counterpart had an electron affinity of 22 meV, and in terms of the *gauche*-succinonitrile anion being a dipole-bound anion state, whose corresponding neutral had an electron affinity of 108 meV. That work provides a reference point for the present combination RET—photoelectron study of succinonitrile anions.

Figure 2 presents the photoelectron spectra of succinonitrile anions made by charge transfer with Rydberg potassium atoms, $\text{K}^{**}(11d)$, presented alongside its corresponding velocity mapping image. In the anion photoelectron spectrum at the left, two sharp peaks at low electron binding energies are in evidence. For the reasons described above, both of these peaks are symptomatic of photoelectron spectroscopic signatures of diffuse excess electron states. The lower EBE peak is centered at 18 meV with a full width at half-maximum (fwhm) ~ 40 meV, while the higher EBE peak is centered at 135 meV with a fwhm of ~ 33 meV, where the peak widths are a consequence of the resolution of the instrument. These peak centers are vertical detachment energies (VDEs), i.e., the transition energy from the anion to its corresponding neutral at the geometry of the anion. Since the structures of diffuse excess electron states (anions) and their corresponding neutrals are essentially identical, their measured VDE values are also the adiabatic electron affinity (EA) values of their corresponding neutrals. Thus, the EA value of 22 meV estimated through RET in the earlier work and the EBE value of 11 meV calculated at about the same time²⁴ both compare reasonably well with the EA = VDE value of 18 meV determined in the present

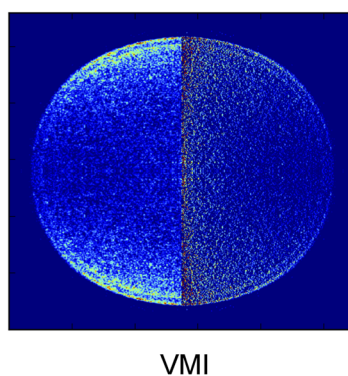
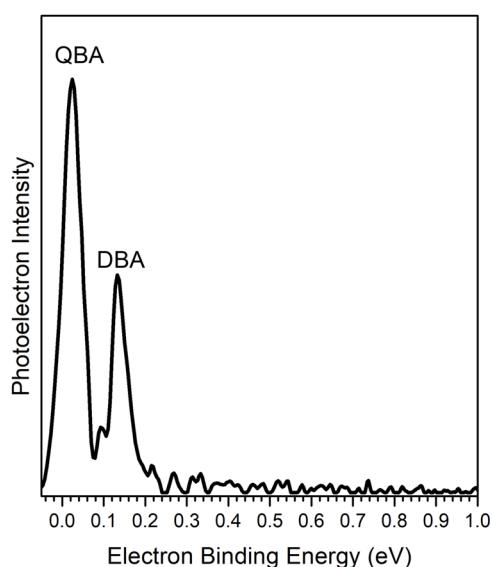


FIG. 2. At left: Anion photoelectron spectrum showing both quadrupole- and dipole-bound succinonitrile anions made by collisions of succinonitrile molecules with Rydberg potassium atoms, $\text{K}^{**}(11d)$. At right: The corresponding velocity mapping image (VMI), taken with linearly polarized light that was aligned perpendicular to the direction of the anion beam. The left side shows its raw image, while the right side shows its processed image. Note the two rings at the outer edge of the image.

photoelectron work. Furthermore, the EA = VDE value of 108 meV determined by photoelectron spectroscopy in the earlier work compares well with the EA = VDE value of 135 meV in the present combined RET-photoelectron work. It is clear that the VDE and EA values determined in the present work are in satisfactory accord with corresponding EA and VDE values measured in the earlier work albeit under different experimental circumstances. As a result, we interpret the lower EBE peak in Fig. 2 as arising from the ground state, quadrupole bound anion (QBA) of *trans*-succinonitrile and the slightly higher EBE peak there as arising from the ground state, dipole-bound anion (DBA) of *gauche*-succinonitrile. Figure 2 thus presents strong evidence for both QBA and DBA species in the same spectrum, i.e., measured by the same technique. Our sightings of both QBA and DBA species over our RET *n*-region of *n* = 11d–15d also raises the question of whether the sharp feature centered at *n* = 12 over the relatively narrow RET *n*-region of *n* = 10–15 in the earlier (2004) experiments might have also included both QBA and DBA species.

In addition to the foregoing, affirmation that the two peaks in Fig. 2 originate from different types of succinonitrile anions is also supported by the fact that we see slight yet definitive variations in their intensity ratios as a function of nearby *n* principal quantum numbers. This is because electron attachment to diffuse electron anion states in RET is a resonant process and maximal electron transfer efficiency can occur at different Rydberg *n* numbers, when electrons are attached via different multipole interactions.

The photoelectron VMI image in Fig. 2 reveals significant anisotropy in both the dipole- and quadrupole-bound states of the succinonitrile anion. The anisotropy parameters, β , for the photodetached quadrupole- and dipole-bound electrons were each calculated to be between 1.8 and 2.0, which is close to the theoretical upper limit. A large β value is consistent with an outgoing *p* wave, which means that photodetachment occurred from an *s*-orbital with nearly zero angular momentum.³⁸ Since both dipole- and quadrupole-bound succinonitrile anions are spatially diffuse excess electron states, their excess electrons can be viewed as possessing *s*-orbital character, consistent with the observed anisotropy.

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