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ABSTRACT

The *p*-chloroaniline anion was generated by Rydberg electron transfer and studied via velocity-map imaging anion photoelectron spectroscopy. The vertical detachment energy (VDE) of the *p*-chloroaniline anion was measured to be 6.6 meV. This value is in accord with the VDE of 10 meV calculated by Skurski and co-workers. They found the binding of the excess electron in the *p*-chloroaniline anion to be due almost entirely to electron correlation effects, with only a small contribution from the long-range dipole potential. As such, the *p*-chloroaniline anion is the first essentially correlation-bound anion to be observed experimentally.

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INTRODUCTION

Very weak attractions between electrons and neutral molecules exert subtle influences on many phenomena in chemistry. When these attractions result in the formation of bound anions, their weakly bound excess electrons occupy extremely diffuse orbitals. In principle, there exist several types of diffuse excess electron anion states, their binding deriving from electron-correlation, electron-polarizability, electron-dipole, or electron-quadrupole interactions, or, as often is the case, from some combination thereof. Anions formed by these particular interactions may be expected to possess excess electron binding strengths that increase roughly in the following order: correlation-bound, quadrupole-bound, polarizability-bound, and dipole-bound anions. In order to study these anion categories separately, it is desirable to select examples whose excess electron binding interactions, other than the one of interest, are either absent or negligible.

Contributions to excess electron binding and anion stability due to the aforementioned excess electron binding interactions have been examined in several theoretical studies.^{1–10} Among these interactions, electron correlation effects are perhaps the most elusive, in part because they contribute to excess electron binding to some degree in most weakly bound anions. Excess electron binding due to correlation has been the focus of several landmark computational investigations.^{5–10}

Calculations by Skurski and co-workers¹⁰ found the excess electron in the *p*-chloroaniline anion to be highly spatially diffuse and its binding to be overwhelmingly due to electron correlation effects. While *p*-chloroaniline has a significant dipole moment (3.28 D), leading to competition between dipole-binding and correlation, it is electron correlation that was found to dominate excess electron binding in the *p*-chloroaniline anion. Even so, it is the anion's residual dipole-bound character that is likely responsible for the excess electron density preferring to reside toward the positive end of the molecular dipole. Upon finding the structures of the anion and its neutral counterpart to be essentially identical, Skurski *et al.* chose to calculate the excess electron binding energy (EBE) at the equilibrium geometry of the *p*-chloroaniline anion. Their calculated value of 10 meV is therefore the vertical detachment energy (VDE) of the *p*-chloroaniline anion. Because of the close structural similarity between the *p*-chloroaniline anion and its neutral counterpart, this anion's VDE value can be assumed to be only incrementally greater than neutral *p*-chloroaniline's electron affinity (EA) value.

We have examined excess electron binding to *p*-chloroaniline by measuring the photoelectron spectrum of its parent anion. Neutral *p*-chloroaniline is an aromatic amine, also known as 4-chloroaniline. It has many agricultural, pharmaceutical, and industrial uses and has been characterized by a wide variety of physical and chemical means.^{11–42} In addition to studies of neutral *p*-chloroaniline, its positive ion has also been characterized by both

mass spectrometric and spectroscopic methods. While theory predicted its parent anion to be stable, the *p*-chloroaniline anion had not been observed experimentally prior to the current study.

In this work, we present the negative ion mass spectrum of the *p*-chloroaniline anion, which was made by Rydberg electron transfer (RET), along with its anion photoelectron spectrum, which was measured via velocity-map imaging (VMI) anion photoelectron spectroscopy. Using the latter, we determine the VDE value of the *p*-chloroaniline anion and compare it to its theoretically predicted value.

EXPERIMENTAL METHODS

Rydberg electron transfer (RET) provides a fragile-anion-friendly environment in which to form previously inaccessible diffuse and otherwise weakly bound electron states. In RET, an electronically excited Rydberg atom transfers its outer electron to a target neutral molecule during their collision, resulting in an ion pair which separates into atomic cation and molecular anion products.^{43,44} RET is a slow electron attachment process in which the receding positive ion plays a uniquely stabilizing role. As a result, Rydberg electron transfer provides an unusually gentle, highly quantum state-specific, laser-tunable, anion formation environment. In a typical RET experiment, atoms are optically pumped to specific Rydberg states (n^*) at the point where they collide with a beam of neutral target molecules. In the present case, the target is a beam of *p*-chloroaniline molecules, these having been vaporized in a heated pulsed valve and expanded with 10 psig of helium gas. To

generate high intensities of product anions, we use alkali (K) atoms and two pulsed dye lasers. One laser optically pumps to the $^2P_{3/2}$ level of the potassium atoms, while the second laser selectively excites that population to the ns and nd Rydberg levels of interest. Beams of Rydberg-excited K atoms and neutral target molecules cross between the ion extraction grids of our time-of-flight mass analyzer/selector. There, parent anions of *p*-chloroaniline are formed by RET and accelerated (after a short delay) into a flight tube, along which they are mass-selected, prior to being photodetached. See Fig. 1 for a schematic of our apparatus.

Anion photoelectron (photodetachment) spectroscopy is conducted by crossing a beam of negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. This technique is governed by the energy-conserving relationship: $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EBE is the electron binding (photodetachment transition) energy, and EKE is the electron kinetic energy. The electron energies of the photodetached electrons are measured using a velocity-map imaging (VMI) anion photoelectron spectrometer, which has been described previously.⁴⁴ There, mass-selected anions are crossed with 1064 nm linearly polarized photons from a Nd:YAG laser. The resultant photodetached electrons are then accelerated along the axis of the ion beam toward a position-sensitive detector, which is coupled to a CCD camera. The basis set expansion (BASEX) Abel transform method is used to reconstruct the two-dimensional image, formed by the sum of these electrons, into a portion of the three-dimensional distribution. Our resulting anion photoelectron spectrum is calibrated relative to the well-known photoelectron spectrum of NO^- .⁴⁵

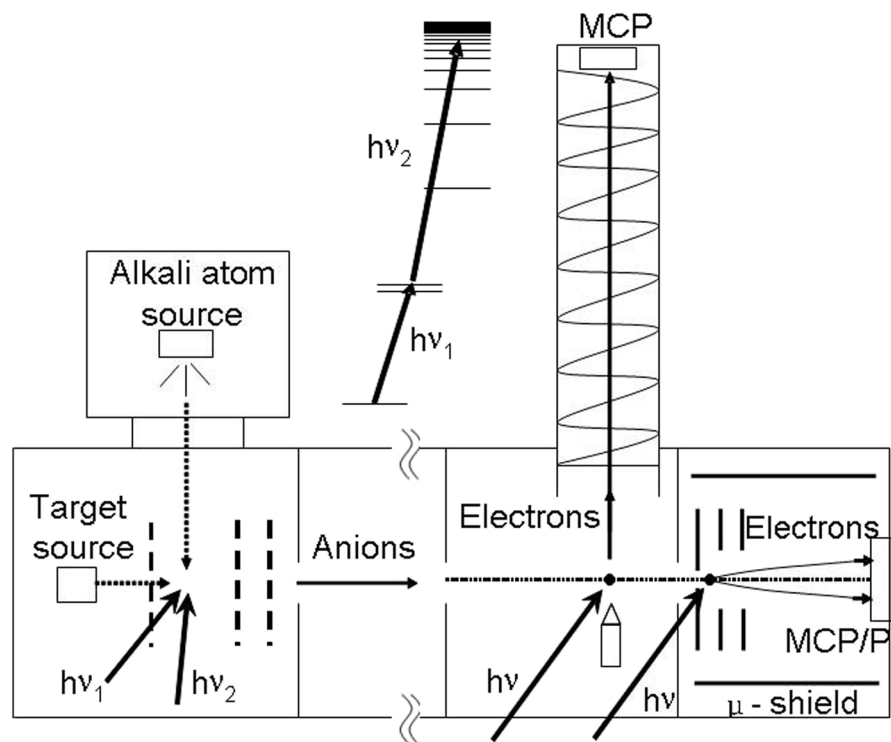


FIG. 1. Schematic of our combined Rydberg electron transfer (RET)—velocity-map imaging (VMI) anion photoelectron spectrometer.

RESULTS AND DISCUSSION

The mass spectrum of *p*-chloroaniline anions is presented in Fig. 2. All four nested mass peaks are due to the natural abundance isotope pattern of the *p*-chloroaniline parent anion. Since RET is a resonant process, we surveyed several Rydberg levels, i.e.,

$n^* = 12d-15d$, to find the most intense ion signal. It occurred at the $n^* = 14d$ Rydberg level. The photoelectron spectrum for the *p*-chloroaniline anion is presented in Fig. 3. It consists of a single broad, symmetric peak located near an EBE of zero. The width of this peak is entirely due to instrumental resolution limitations. To precisely locate the EBE value of the peak's maximum,

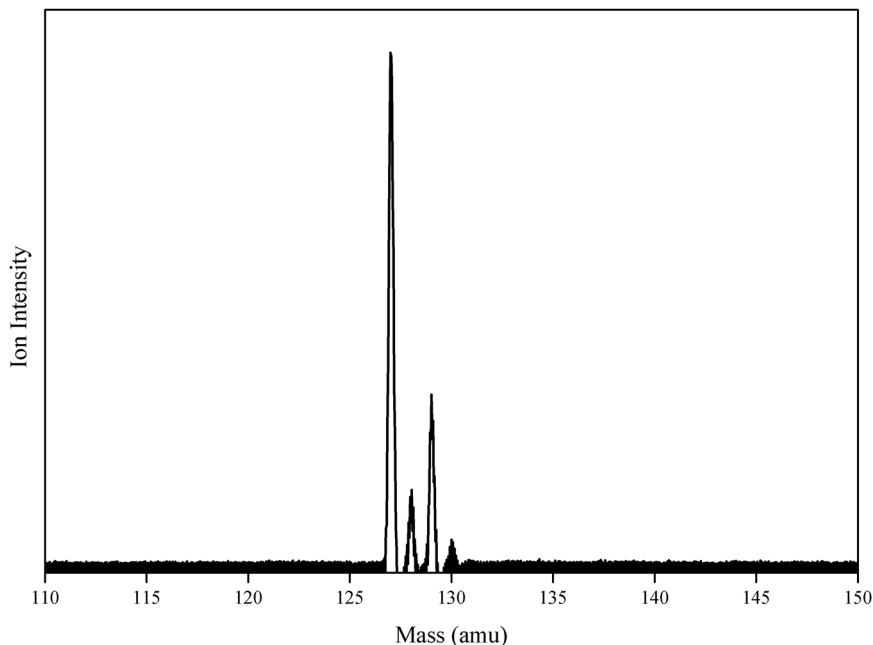


FIG. 2. Mass spectrum of *p*-chloroaniline anions made by Rydberg electron transfer ($n^* = 14d$).

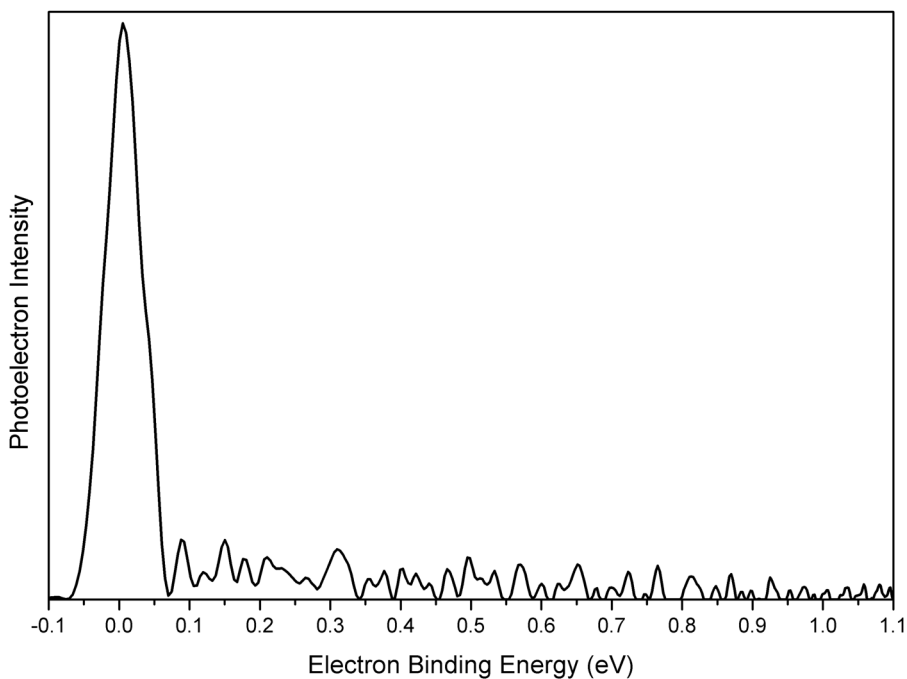


FIG. 3. Anion photoelectron spectrum of *p*-chloroaniline anions measured by velocity-map imaging (VMI) photoelectron spectroscopy using 1.165 eV (1064 nm) photons.

we applied a Gaussian fit, finding it to be 6.6 meV. This is the VDE value of the *p*-chloroaniline anion, and as mentioned above, this value is only slightly greater than the EA value of neutral *p*-chloroaniline. Thus, our measured VDE value is in good agreement with the predicted VDE value of 81 cm⁻¹ or 10 meV, calculated by Skurski and co-workers, using *ab initio* coupled-cluster single double (triple) [CCSD(T)]/aug-cc-pVDZ+5s4p3d methodology.¹⁰ The agreement between our measurement and their computations supports Skurski and co-workers' finding that the *p*-chloroaniline anion is primarily a correlation-bound anion with minor excess electron binding contributions from dipole binding. Thus, the *p*-chloroaniline anion, whose excess electron is incredibly weakly bound, sits near the base of a hierarchy of increasing excess electron binding interaction strengths. In addition, the *p*-chloroaniline anion is the first essentially correlation-bound anion to be observed experimentally.

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