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## AFFILIATIONS

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## ABSTRACT

Close-lying dipole-bound and valence-bound states in the nitromethane anion make this molecule an ideal system for studying the coupling between these two electronically different states. In this work, dipole-bound and valence-bound nitromethane anions were generated by Rydberg electron transfer and characterized by anion photoelectron spectroscopy. The presence of the dipole-bound state was demonstrated through its photoelectron spectral signature, i.e., a single narrow peak at very low electron binding energy, its strong Rydberg quantum number,  $n^*$ , dependence, and its relatively large anisotropy parameter,  $\beta$ . This work goes the furthest yet in supporting the doorway model of electron attachment to polar molecules.

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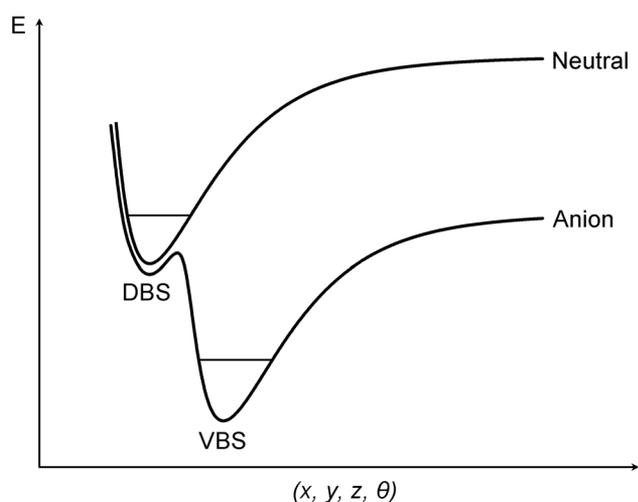
## INTRODUCTION

Dipole-bound electron states can form when electrons interact with polar neutral molecules or clusters, the main requirement being that their dipole moments be  $\geq 2.5 D$ .<sup>1–4</sup> The resulting dipole-bound anions exhibit very weakly bound and highly delocalized excess electrons as well as geometric structures that, in most cases, are quite close to those of their neutral counterparts. The excess electrons in dipole-bound vs valence-bound anions are bound by fundamentally different interactions. In dipole-bound anions, a combination of excess electron-electrostatic and correlation interactions are responsible for binding, whereas in valence-bound anions, their excess electrons reside in specific molecular orbitals. The resulting valence-bound anions tend to have strongly bound excess electrons and geometric structures that can and often do differ significantly from those of their neutral counterparts. In most cases, molecules that form dipole-bound anions do not also form valence-bound anions, and vice versa, but there are exceptions. In cases where both occur in the same molecule, forming electronically distinct, anionic isomers, they share a potential energy surface and, thus, have a pathway between them. [Figure 1](#) schematically illustrates the energetic, structural, and

connectivity relationship between a dipole-bound anion (DBS) and its valence-bound anion (VBS) counterpart along their common ground state surface. Since the formation of dipole-bound states is suspected of being the first step in electron attachment to polar molecules and thus the formation of their valence-bound anions, dipole-bound anions are sometimes referred to as the “doorway” or “stepping stone” states.<sup>5–12</sup> In this context, the solvent-induced transformations of dipole-bound to valence-bound anions have also been studied.<sup>13,14</sup>

Nitromethane is an example of a molecule that can form both dipole-bound and valence-bound anionic isomers. The coupling and thus the transition between its two anionic isomers have been widely investigated both experimentally and theoretically.<sup>15–25</sup> In the 1970s, the nitromethane anion,  $\text{CH}_3\text{NO}_2^-$ , was formed in experiments that utilized fast atom charge transfer, Rydberg charge exchange, and free electron attachment, where in the last case, stabilization was facilitated by three body collisions.<sup>26,27</sup>

In the mid-1990s, a set of experiments was conducted that employed a combination of Rydberg charge exchange, field detachment, and negative ion photoelectron spectroscopy.<sup>15</sup> The



**FIG. 1.** Schematic showing the energetic, structural, and connectivity relationship between a dipole-bound anion (DBS) and its valence-bound anion (VBS) counterpart along their common ground state surface.

Rydberg charge exchange experiments involved crossing beams of nitromethane molecules with Cs (ns, nd) and Xe (nf) optically excited Rydberg atoms on two different apparatuses. Mass spectrometry detected and identified the resulting  $\text{CH}_3\text{NO}_2^-$  products. The data were presented as plots of relative anion formation yields vs effective Rydberg quantum numbers,  $n^*$ , with both apparatuses producing essentially identical data. Since the formation of dipole-bound anions by Rydberg electron transfer is a resonant process, one expects those anions to be formed at almost a single Rydberg quantum number,  $n^*$ ; experience with several chemical systems supports that expectation. Thus, the observation of a narrow “peak” in Rydberg charge transfer patterns, i.e., plots of relative anion formation yields vs effective Rydberg quantum numbers,  $n^*$ , is generally taken to be a characteristic signature for dipole-bound anion formation. With a dipole moment of 3.46 D, nitromethane would be expected to form a dipole-bound anion, and indeed a prominent maximum was observed at  $n^* = 13 \pm 1$ . Additionally, however, the observed Rydberg charge transfer anion formation pattern had a breadth of  $\Delta n \sim 5$  (FWHM). Anion production over a broad range of  $n^*$  quantum numbers is typical of valence-anion formation. Thus, while the data supported the conclusion that dipole-bound nitromethane anions had been made, it also implied that valence-bound nitromethane anions had been formed. These observations provided the first evidence for valence-bound anion formation through a “doorway” dipole-bound state mechanism as described above.

Field detachment of resultant nitromethane anions at various  $n^*$  quantum numbers resulted in complex plots of fast neutral production vs electric field, providing evidence not only for the formation of dipole-bound anions but also for the production of valence-bound anions. Those results bolstered support to the “doorway” mechanism. Furthermore, analysis of the field ionization data implied a dipole-bound electron affinity of  $12 \pm 3$  meV.<sup>15</sup> While

early calculations had predicted the dipole-bound electron affinity of  $\sim 3$  meV,<sup>28</sup> calculations that were contemporary with these experiments<sup>15</sup> predicted it to be 13 meV.<sup>16</sup>

In addition to forming nitromethane anions by Rydberg charge transfer, nitromethane anions were also formed in a supersonic expansion nozzle-ion source, where low energy electrons were injected into an expanding jet in the presence of a weak magnetic field. Anion photoelectron spectra of the resulting  $\text{CH}_3\text{NO}_2^-$  and  $\text{CD}_3\text{NO}_2^-$  species exhibited rich vibrational progressions over a significant range of electron binding energies, implying substantial structural differences between the anions and their neutral counterparts. These were valence-bound nitromethane anions.<sup>15</sup> A revised assignment of the low electron binding energy peaks in the photoelectron spectra established the adiabatic electron affinity of nitromethane to be  $172 \pm 6$  meV.<sup>22</sup> While there was no evidence of a dipole-bound anion peak in the original photoelectron spectrum<sup>15</sup> described above, a latter nitromethane anion photoelectron spectrum, which had utilized argon tagging, found a very weak feature at an electron binding energy of  $8 \pm 8$  meV, which was attributed to the dipole-bound anion.<sup>22</sup>

Other relevant studies include time-resolved photoelectron imaging of iodide-nitromethane anionic complexes,  $\text{I}^- \cdot \text{CH}_3\text{NO}_2$ , that confirmed the ultra-fast conversion of the dipole-bound state of  $\text{CH}_3\text{NO}_2^-$  to the valence-bound state, thereby supporting the dipole-bound to valence-bound “doorway” mechanism for electron attachment to polar molecules;<sup>23</sup> Rydberg electron transfer investigations of transient ion-pair formation in  $\text{K}(\text{np}) + \text{CH}_3\text{NO}_2$  collisions;<sup>19,25</sup> vibrational autodetachment spectroscopic studies of nitromethane anions;<sup>29–31</sup> as well as experiments colliding fast alkali atoms with oriented nitromethane molecules to form nitromethane anions.<sup>20</sup> Additionally, several non-dipole-bound, diffuse electron states, e.g., correlation-bound and quadrupole-bound anions, have also been studied.<sup>32–36</sup>

Recently, we introduced an apparatus that utilized the combination of Rydberg electron/charge transfer (RET) to form the anions of interest and anion photoelectron spectroscopy (aPES) to measure their electron binding energies. Our RET-aPES apparatus has demonstrated that it is an ideal tool for preparing diffuse excess electron states, such as dipole-bound anions, and for acquiring a comprehensive picture of their energetics.<sup>33–35,37–40</sup> In this work, we present a photoelectron spectroscopic study of nitromethane anions made by Rydberg electron transfer over a wide range of Rydberg quantum energy states,  $n^*$ . Owing to the properties of dipole-bound states enumerated above, the signature of dipole-bound anions in photoelectron spectra is usually a single, sharp peak at very low electron binding energy. The presence of the nitromethane dipole-bound state in this photoelectron study is confirmed by a narrow peak at very low electron binding energy, the strong Rydberg quantum number dependence of its formation, and the anisotropy in its photoelectron imaging pattern. The spectral pattern seen in the rest of its photoelectron spectrum persists over all Rydberg quantum numbers explored and is consistent with both of the previously measured photoelectron spectral patterns of nitromethane valence-bound anions. By measuring photoelectron spectra that clearly show the simultaneous presence of dipole-bound and valence-bound anions of nitromethane, this work brings together various, not always conclusive studies from the past into a single consistent picture.

## EXPERIMENTAL METHODS

The details of our RET-aPES apparatus are described elsewhere.<sup>33,34,37,38</sup> Briefly, anion photoelectron spectroscopy is conducted by crossing a mass-selected 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,  $h\nu = EKE + EBE$ , where  $h\nu$ ,  $EKE$ , and  $EBE$  are the photon energy, the electron kinetic energy, and the electron binding (photodetachment transition) energy, respectively. Electron kinetic energies were measured using a velocity-map imaging (VMI) spectrometer. Mass-selected anions were crossed with 1064 nm, linearly polarized photons in an electric field. The resultant photodetached electrons were accelerated along the axis of the ion beam toward a position-sensitive detector coupled to a CCD camera. The two-dimensional image formed from the sum of the electrons was reconstructed into a portion of the three-dimensional distribution via the BASEX<sup>41</sup> method. Photoelectron spectra were thus extracted from the velocity map images and were calibrated against the well-known spectrum of  $\text{NO}^-$ .<sup>42</sup>

Nitromethane anions were generated by a Rydberg electron/charge transfer (RET) source. Neutral nitromethane molecules were expanded in helium using a pulsed valve backed with 10 psi helium. Anions were formed when the neutral nitromethane molecules collided with a thermal beam of potassium atoms, which had been excited to specific  $nd$  Rydberg states in two steps using two dye lasers. One dye laser pumped the potassium atoms to the  $^2P_{3/2}$  state with 766.7 nm light, while the other was tuned to reach specific Rydberg levels between  $12d$  and  $19d$ . The resultant anions were then extracted, mass-selected using a time-of-flight mass spectrometer, and their excess electrons photodetached before being energy-analyzed via VMI spectrometry.

## RESULTS AND DISCUSSION

Figure 2 presents a representative photoelectron image and spectrum of nitromethane anions formed by charge transfer between nitromethane molecules and excited potassium atoms in the  $n^* = 16d$  Rydberg level. The prominent sharp peak located on the

low electron binding energy (EBE) side of the spectrum is due to the photodetachment transition between dipole-bound anion of nitromethane and its neutral counterpart, and it is labeled as DB. Instrumentally narrow single peaks at very low EBE values are distinctive signatures of dipole-bound and other diffuse excess electron states. The fitted intensity maximum of this peak, i.e., its vertical detachment energy (VDE), occurs at an EBE of 14 meV. Due to the close similarity between the structures of dipole-bound anions and their neutral counterparts, a dipole-bound anion's VDE value is essentially identical to the value of its corresponding neutral's electron affinity. Thus, we find the dipole-bound electron affinity of nitromethane to be  $14 \pm 10$  meV. This value is consistent with the most previous experimental and theoretical values of the dipole-bound electron affinity of nitromethane, i.e.,  $12 \pm 3$  meV,<sup>15</sup>  $8 \pm 8$  meV,<sup>22</sup> 13 meV,<sup>16</sup> and 3 meV.<sup>28</sup>

The velocity map image of  $\text{CH}_3\text{NO}_2^-$  shown in Fig. 2, from which its companion photoelectron spectra were extracted, also corroborates the observation of the dipole-bound state. In that photoelectron image, the outermost ring, labeled as DB, possesses an anisotropy that differs significantly from the inner rings, i.e., those of the photodetached valence-bound electrons. While the anisotropy parameters,  $\beta$ , of the inner, photodetached valence electron rings were found to be around zero, the  $\beta$  value of the outermost photoelectron ring was  $1.41 \pm 0.17$ . This drastic difference suggests that this outermost ring originates from a different electronic state than that responsible for the inner rings. A large  $\beta$  value is consistent with an outgoing  $p$  wave, which results from photodetachment of electrons out of an  $s$ -character orbital. The dipole-bound state can be regarded as a spatially diffuse, somewhat spherical,  $s$ -character orbital. The weak feature, observed in the photoelectron study that used argon tagging,<sup>22</sup> also exhibited a large  $\beta$  value, consistent with detachment from an  $s$ -character orbital and thus with a dipole-bound state.

The majority of the nitromethane anion photoelectron spectra shown in Fig. 2, i.e., all of the peaks on the high EBE side of the dipole-bound anion peak (DB), are due to photodetachment of valence-bound nitromethane anions. The vibrational progressions evident in all of the photoelectron spectra of the nitromethane anion measured to date are consistent with a substantial difference in

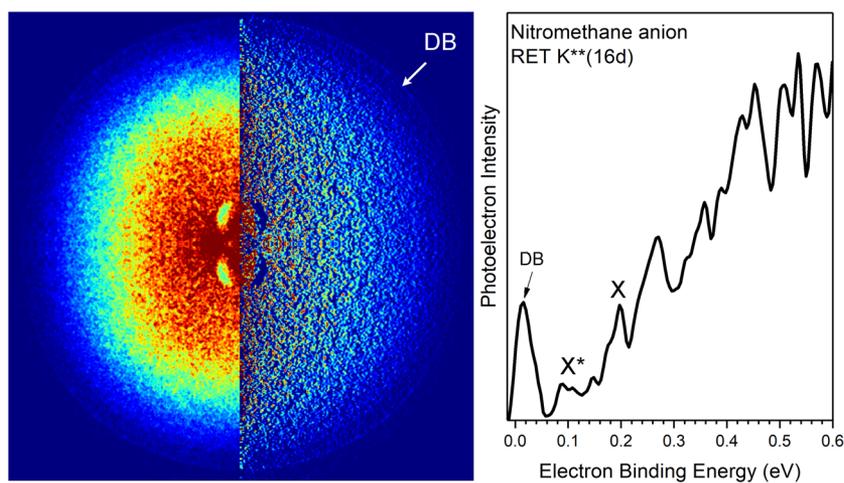
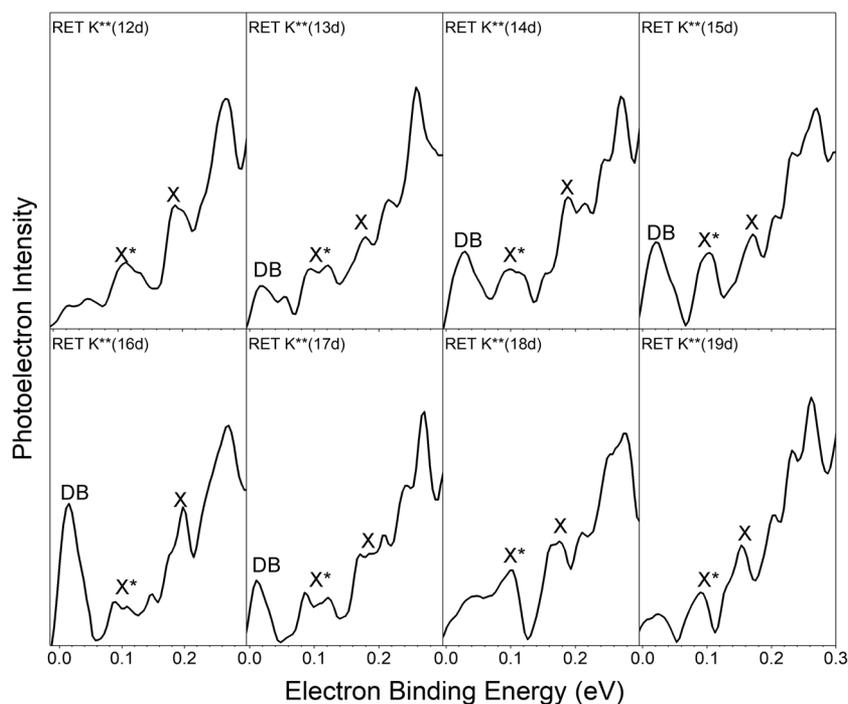


FIG. 2. Photoelectron image and anion photoelectron spectrum of  $\text{CH}_3\text{NO}_2^-$  made by Rydberg electron transfer at the  $K^{**}(16d)$  Rydberg level. The hot band is marked as  $X^*$ , and the electron affinity-determining, origin peak is marked as  $X$ . DB denotes the dipole-bound feature.



**FIG. 3.** Photoelectron spectra of nitromethane anions formed by Rydberg electron transfer over  $12d$ – $19d$  Rydberg levels. The hot bands are marked as  $X^*$ , and the electron affinity peaks are marked as  $X$ . DB denotes the dipole-bound features.

the equilibrium structure of the valence-bound anion and its corresponding neutral.<sup>15,21–24</sup> We and others<sup>22</sup> both assign the peak around  $\text{EBE} = 0.10$  eV (labeled as  $X^*$  in Fig. 2) as a vibrational hot band. While in our original photoelectron spectrum of the valence-bound nitromethane anion (formed by a non-RET source), we had assigned the origin, i.e., electron affinity-determining, transition to the peak located at  $240 \pm 80$  meV,<sup>15</sup> a convincing re-assignment by Adams *et al.*<sup>22</sup> shifted the assignment of the (0, 0) transition to the adjacent peak at  $172 \pm 6$  meV. Accepting this re-assigned peak as the origin transition and utilizing our photoelectron spectrum of  $\text{CH}_3\text{NO}_2^-$  in Fig. 2, we determined the (0, 0) transition energy (labeled as  $X$  in Fig. 2) and thus the adiabatic electron affinity of nitromethane to be  $184 \pm 10$  meV.

The photoelectron spectral dependence of the dipole-bound feature on Rydberg quantum numbers,  $n^*$ , was also investigated. Figure 3 presents photoelectron spectra of nitromethane anions formed at Rydberg levels from  $K^{**}(nd) = 12d$  to  $19d$ , this range having been chosen because it had previously been found to facilitate the formation of dipole-bound nitromethane anions.<sup>15,19</sup> While the valence-bound anion features in all of the spectra are quite similar, the dipole-bound anion peak (labeled as DB in Fig. 3) found at low EBE values varies in strength with the Rydberg quantum number,  $K^{**}(nd)$ , as do all characteristic dipole-bound states. The dipole-bound signal is most apparent at Rydberg levels between  $14d$  and  $17d$ , reaching its maximum intensity at  $n = 16d$ . This signal distribution is consistent with the original study, where the Rydberg charge transfer anion formation pattern had a breadth of  $\Delta n \sim 5$  (FWHM).<sup>15</sup> Since electron attachment into dipole-bound states is expected to occur via resonant electron transfer over a relatively narrow range of Rydberg quantum numbers, the

$\Delta n$  dependence observed in the present experiments further supports the assignment of the lower EBE feature as the dipole-bound signature. The narrow Rydberg number range also implies the dipole-bound/valence-bound anion coupling and a doorway mechanism for electron attachment into the valence-bound, nitromethane anion.<sup>15</sup>

## SUMMARY

This study utilizes the RET-aPES technique, which combines Rydberg electron transfer (RET) and anion photoelectron spectroscopy (aPES), to study the dipole-bound and valence-bound anions of nitromethane. By measuring photoelectron spectra that show the simultaneous presence of dipole-bound and valence-bound anions of nitromethane, this work brings together a variety of studies from the past into a single consistent picture and goes the furthest yet in supporting the doorway model of electron attachment to polar molecules.

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## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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