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CO_2 binding in the (quinoline-CO_2)$^-$ anionic complex

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We have studied the (quinoline-CO_2)$^-$ anionic complex by a combination of mass spectrometry, anion photoelectron spectroscopy, and density functional theory calculations. The (quinoline-CO_2)$^-$ anionic complex has much in common with previously studied (N-heterocycle-CO_2)$^-$ anionic complexes both in terms of geometric structure and covalent bonding character. Unlike the previously studied N-heterocycles, however, quinoline has a positive electron affinity, and this provided a pathway for determining the binding energy of CO_2 in the (quinoline-CO_2)$^-$ anionic complex. From the theoretical calculations, we found CO_2 to be bound within the (quinoline-CO_2)$^-$ anionic complex by 0.6 eV. We also showed that the excess electron is delocalized over the entire molecular framework. It is likely that the CO_2 binding energies and excess electron delocalization profiles of the previously studied (N-heterocycle-CO_2)$^-$ anionic complexes are quite similar to that of the (quinoline-CO_2)$^-$ anionic complex. This class of complexes may have a role to play in CO_2 activation and/or sequestration. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4922652]

INTRODUCTION

Carbon dioxide has long been known to bind weakly to certain amines,[1] and more recently, it has been found to bind to some metal organic frameworks (MOFs).[2] Carbon dioxide also forms gas-phase, anionic complexes with several atoms and molecules.[3–27] In the $[CO_2(H_2O)]^-$ anionic complex, for example, an intact CO_2^- sub-anion is stabilized by its interaction with water.[3,4] In seminal work, using a combination of mass spectrometry, photoelectron spectroscopy, and *ab initio* calculations, Kim and coworkers[5] found significant covalent character in the intermolecular bond between CO_2 and pyridine in the gas phase (pyridine-CO_2)$^-$ anionic complex. Vibrational predissociation studies by Johnson and coworkers[6] confirmed its structure and the covalent bonding character inferred by Kim. In further studies with CO_2 and the heterocyclic nitrogen molecules, pyrazine, pyridazine, pyrimidine, triazine, and 2-aminopyridine, analogously bonded binary anionic complexes were also found.[7,8]

In all these cases, bonding took place between the carbon atom in CO_2 and a nitrogen atom in its heterocyclic molecular partner. From a Lewis acid-base perspective, the heterocycle's nitrogen atom, i.e., its lone electron pair, was the electron donor and CO_2 was the electron acceptor, both well-known properties of these constituents. As neutral adducts, some degree of binding would have been expected, but with the addition of excess electrons, robust binary anionic complexes were formed. Kim referred to the process by which this occurs as "associative electron attachment", i.e., where a chemical bond was formed due to electron attachment, even though there was no such bond in the corresponding neutral.[7] In each of the cases considered here, bond formation was likely due to delocalization of the excess electron over both the heterocycle's ring and the CO_2 moiety, i.e., over the entire molecular framework. This helps to rationalize why even though neither CO_2 nor any of its above-mentioned partners possess positive adiabatic electron affinities, together, they formed stable anionic complexes.

While covalent bonding character has been demonstrated for (N-heterocycle-CO_2)$^-$ anionic complexes, carbon dioxide's binding energy there has not. Neither of the experimental techniques used to study them could have provided that information, and theoretical calculations were stymied by the necessity of dealing with molecules having negative adiabatic electron affinities. Quinoline, on the other hand, is different from the other N-heterocyclic molecules listed above because it has a positive adiabatic electron affinity (EA) (0.16 eV).[28] This affords an opportunity to determine carbon dioxide's binding energy in the (quinoline-CO_2)$^-$ anionic complex and by implication to estimate it in other (N-heterocycle-CO_2)$^-$ anionic complexes as well. In the work presented here, we used a combination of mass spectrometry, anion photoelectron spectroscopy, and density functional calculations to study the (quinoline-CO_2)$^-$ anionic complex and to identify a value for carbon dioxide's binding energy there.

EXPERIMENTAL AND COMPUTATIONAL METHODS

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. The photodetachment process is governed by the relationship $h\nu = \mathrm{EBE} + \mathrm{EKE}$, where $h\nu$ is the photon energy, EBE is the electron binding energy, i.e., the transition energy between the anion and a particular vibronic state of its neutral counterpart, and EKE is the electron kinetic energy.

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Negative ions of quinoline were formed in a biased (−500 V) supersonic expansion nozzle-ion source, where the quinoline sample was placed in the source's stagnation chamber, heated to 70 °C, and co-expanded with ∼2 atm of argon gas through a 23 μm orifice into a vacuum maintained at 10^{-4} Torr. Simultaneously, CO_2 was admitted very near the nozzle on its vacuum side and allowed to mix with the jet. Negative ions were formed by injecting low energy electrons from an even more negatively biased, thoriated-iridium filament into the expanding jet, where a micro-plasma was formed in the presence of a weak axial magnetic field. The resulting anions were then extracted, collimated, and transferred into the flight tube of a 90° magnetic sector mass spectrometer with a mass resolution of 400. Mass-selected anions of (quinoline-CO_2)$^-$ were then crossed with the intracavity laser beam of an argon ion laser (∼100 W), while photodetached electrons were energy-analyzed in a hemispherical electron energy analyzer having a resolution of 20 meV.[29] The photoelectron spectrum reported here was recorded with 2.540 eV photons (488 nm), and it was calibrated against the photoelectron spectrum of the O^- anion. An identical photoelectron spectrum of (quinoline-CO_2)$^-$ was also observed in our lab using a pulsed anion photoelectron spectrometer that employed time-of-flight mass selection, a Nd:YAG laser, and a magnetic bottle electron energy analyzer.[30]

Density functional theory (DFT) calculations were conducted using the Gaussian 09 software package.[31] All calculations were performed using the wb97xd functional[32] and aug-cc-pVTZ basis set.[33,34] The wb97xd functional was used because it provided reasonable results in our previous quinoline anion work.[28] Geometry optimizations were performed without symmetry constraints and were followed by vibrational frequency calculations to verify the identification of stationary points and to obtain zero point energies.

RESULTS

The photoelectron spectrum of the (quinoline-CO_2)$^-$ anionic complex is presented in Figure 1. This spectrum consists of a single broad band with an onset at EBE ∼1.3 eV and an intensity maximum at EBE = 1.8 eV ± 0.05, the latter being its vertical detachment energy (VDE). Unlike the vibrationally structured photoelectron spectrum of the quinoline molecular anion,[28] no vibrational features were resolved in the photoelectron spectrum of the (quinoline-CO_2)$^-$ anionic complex.

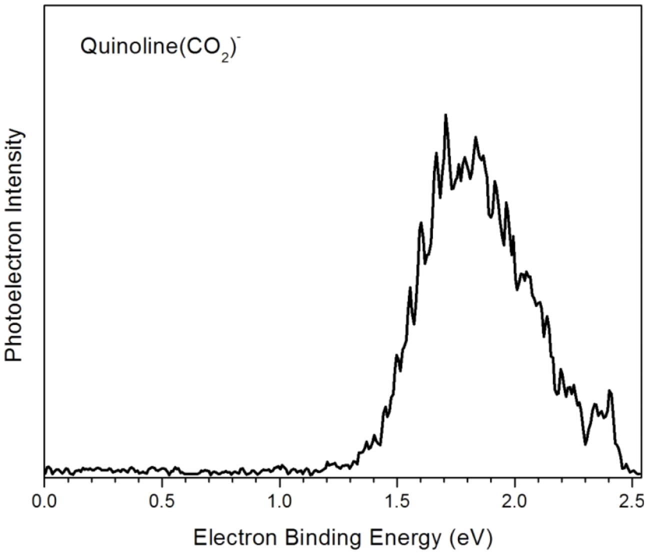

FIG. 1. The anion photoelectron spectrum of the (quinoline-CO_2)$^-$ anionic complex recorded with 488 nm photons.

Figure 2 presents the optimized geometries that we calculated for both the (quinoline-CO_2)$^-$ anionic complex (Fig. 2(a)) and the quinoline-CO_2 neutral complex (Fig. 2(a)). As can be seen in Fig. 2(a), the C–N bond length in the (quinoline-CO_2)$^-$ anionic complex is 1.55 Å and its CO_2 moiety is bent by 132°. By comparison, the C–N bond distance in the quinoline-CO_2 neutral complex is 2.83 Å. These structural parameters are quite similar to those of (pyridine-CO_2)$^-$ and (pryridine-CO_2). Kim[5] and Johnson[6] calculated the C–N bond length in the (pyridine-CO_2)$^-$ anionic complex to be 1.46 Å and 1.52 Å, respectively, while Leopold[35] measured the C–N bond distance in the pyridine-CO_2 neutral complex to be 2.798 Å. Furthermore, based on a Natural Population Analysis (NPA), we found the negative charge on the quinoline moiety to be 0.41e, while that on the CO_2 moiety is 0.59e. Even though the excess negative charge is delocalized over the entire anionic complex, it is somewhat more localized on the CO_2 moiety

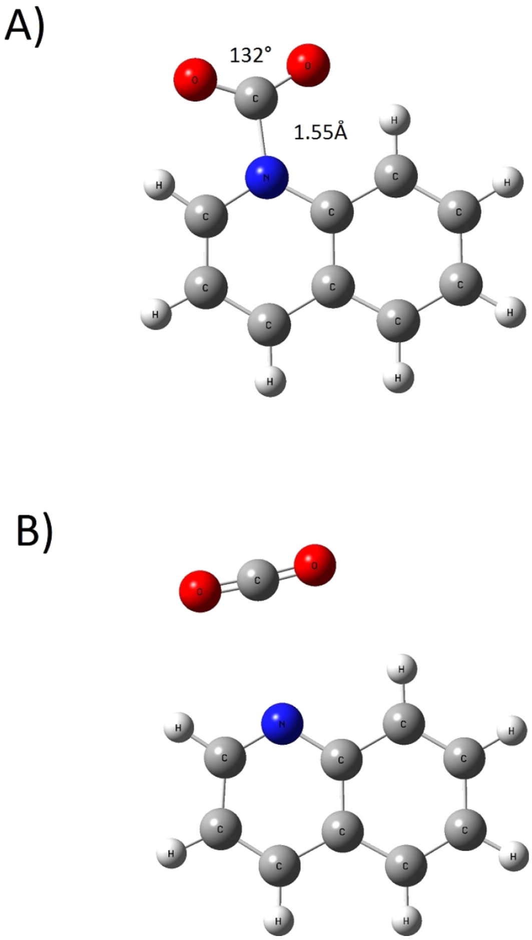

FIG. 2. Relaxed geometries of (a) the (quinoline-CO_2)$^-$ anionic complex and (b) the quinoline-CO_2 neutral complex.

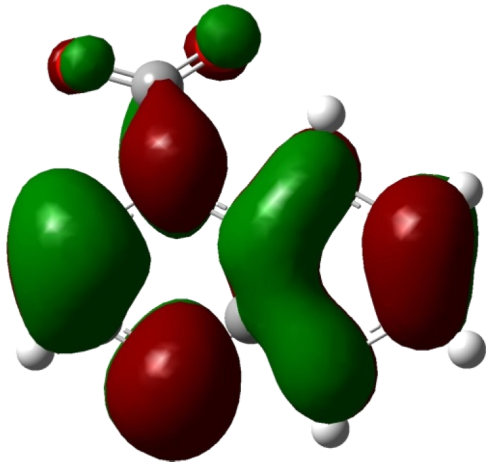

FIG. 3. The HOMO of the (quinoline-CO_2)$^-$ anionic complex.

than on the quinoline moiety. Figure 3 presents the highest occupied molecular orbital (HOMO) of the (quinoline-CO_2)$^-$ anionic complex. While both the HOMO and NPA approaches indicate electron delocalization over the whole complex, they are mapping different aspects of excess electron density.

The energy difference between the (quinoline-CO_2)$^-$ anionic complex in its relaxed geometry and the quinoline-CO_2 neutral complex in that same geometry is the VDE value. Our calculated VDE of 1.8 eV is in very good agreement with the experimentally observed value of 1.8 eV. We also calculated the zero-point corrected adiabatic EA of quinoline-CO_2 and found it to be 0.7 eV. However, due to the geometry difference between the relaxed structure of the anionic complex (Fig. 2(a)) and that of its neutral counterpart (Fig. 2(b)), it would not be surprising if Franck-Condon overlap between the two was to be insufficient for the origin transition to be observed in the experimental spectrum. That appears to be the case, since no significant features were seen in the spectrum in the vicinity of EBE = 0.7 eV. Thus, the EA value of the quinoline-CO_2 complex could not be determined from the photoelectron spectrum alone.

Additionally, the zero-point corrected adiabatic electron affinity of quinoline itself was calculated to be 0.19 eV, compared with our experimental value of 0.16 eV.[28] Since the latter value derives from a straightforward assignment of our vibrationally structured photoelectron spectrum of the quinoline molecular anion and is thus probably quite accurate, the 0.03 eV discrepancy between theory and experiment is probably a measure of the accuracy of our calculations. Relevant values are summarized in Table I.

TABLE I. Experimental and calculated electron affinities and vertical detachment energies for quinoline and quinoline-CO_2 complexes.

	Expt. EA	Calc. EA	Calc. EA with ZPE	Expt. VDE	Calc. VDE
Quinoline	0.16[a]	0.05[a]	0.19[a]	…	…
Quinoline-CO_2	<1.3	0.64	0.67	1.8	1.77

[a] Reference 28.

DISCUSSION

How strongly is CO_2 bound in the (quinoline-CO_2)$^-$ anionic complex? Initially, we had hoped to determine this from the thermochemical relationship,

$$D_0(\text{quinoline-}CO_2)^- = EA(\text{quinoline-}CO_2) - EA(\text{quinoline}) + D_0(\text{quinoline-}CO_2), \quad (1)$$

using our experimental values for EA (quinoline-CO_2) and EA (quinoline) and a calculated value for D_0 (quinoline-CO_2), which was in any case expected to be relatively small. This approach, however, could not be used when the origin transition failed to appear in the photoelectron spectrum of the (quinoline-CO_2)$^-$ anionic complex, due to a lack of Franck-Condon overlap.

We then turned to a computational approach. Theoretical attempts to calculate the binding energy of CO_2 in the earlier mentioned (N-heterocycle-CO_2)$^-$ anionic complexes would have been stymied by the difficulty of dealing with molecules having negative adiabatic electron affinities, i.e., both CO_2 and the N-heterocyclic molecules mentioned above. Quinoline, on the other hand, possesses a positive adiabatic electron affinity, and that made it possible for us to calculate the absolute energy of its anion. The dissociation energy of the (quinoline-CO_2)$^-$ anionic complex, D_0 (quinoline-CO_2)$^-$, breaking into the quinoline molecular anion, (quinoline)$^-$, and CO_2, is given by

$$D_0[(\text{quinoline-}CO_2)^-] = E[(\text{quinoline})^-] + E[CO_2] - E[(\text{quinoline-}CO_2)^-], \quad (2)$$

where E [M] refers to the calculated absolute energy of species, M, in its relaxed geometry and with its zero point energy included. By this approach, D_0 [(quinoline-CO_2)$^-$] was found to be 0.6 eV.

Likewise, the dissociation energy of the (quinoline-CO_2) neutral complex, D_0 (quinoline-CO_2), breaking into the neutral quinoline molecule and CO_2, is given by

$$D_0[(\text{quinoline-}CO_2)] = E[\text{quinoline}] + E[CO_2] - E[(\text{quinoline-}CO_2)], \quad (3)$$

where again E [M] refers to the calculated absolute energy of species, M, in its relaxed geometry and with its zero point energy included. In this way, D_0 [(quinoline-CO_2)] was found to be 0.16 eV. By comparison, the binding energy of the pyridine-CO_2 neutral complex has been calculated to be 0.10–0.20 eV.[36]

Our results indicate that carbon dioxide is bound by 0.64 eV in the (quinoline-CO_2)$^-$ anionic complex. This suggests that the earlier discussed (N-heterocycle-CO_2)$^-$ anionic complexes also have comparable CO_2 binding energies. Following the conclusions of Kim and Johnson that the (pyridine-CO_2)$^-$ anionic complex exhibits significant covalent bonding character, it seems likely that the (quinoline-CO_2)$^-$ anionic complex does too. Still, 0.64 eV is well below the bond strength of most covalent bonds. On the other hand, it is much stronger than a van der Waals bond and also stronger than most hydrogen bonds. A binding energy of 0.64 eV lies in an intermediate range, i.e., along a continuum of bond strengths between those of van der Waals and chemical interactions. It fits best among the interaction strengths of Lewis acid-base pairs (adducts). Interestingly, the cationic cluster pyridine$^+$(H_2O)

was found to be similarly bound by 0.66 eV; however, the ionic hydrogen bonding in this complex is unlikely to be the bonding type occurring in the (quinoline-CO_2)$^-$ anion.[40] The binding energy of binary neutral complexes span from ~0.2 eV to significantly over an electron volt.[37,38] For binary complexes with net negative charges, however, there are few signposts to guide us within the context of Lewis acid-base pairs. Perhaps, the best we have are $O_2^-(CO_2)$ and $NO^-(CO_2)$, which could be thought of as Lewis acid-base pairs and whose binding energies have been measured[16] or calculated[39] to be 0.82 eV and 0.9 eV, respectively. Like (quinoline-CO_2)$^-$, their non-CO_2 moieties form stable negative ions, but unlike (quinoline-CO_2)$^-$, neither $O_2^-(CO_2)$ nor $NO^-(CO_2)$ can significantly delocalize their excess charges. In fact, both $O_2^-(CO_2)$ and $NO^-(CO_2)$ might better be considered to be ion-molecule complexes. By contrast, because all the (N-heterocycle-CO_2)$^-$ anionic complexes discussed here owe their stabilities to their ability to delocalize their excess charges, they belong to a distinct class of negatively charged complexes.

For CO_2, taking on partial negative charge means that it must bend to a corresponding degree, and correspondingly, bending presumes the acquisition of negative charge density. They are two sides of the same coin; for CO_2, bending and accepting negative charge are synonymous. This relationship lies at the heart of CO_2 activation, and it is much in evidence in the binding of CO_2 within (N-heterocycle-CO_2)$^-$ anionic complexes.

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