The dipole bound-to-covalent anion transformation in uracil

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Nucleic acid base anions play an important role in radiation-induced mutagenesis. Recently, it has been shown that isolated (gas-phase) nucleobases form an exotic form of negative ions, namely, dipole bound anions. These are species in which the excess electrons are bound by the dipole fields of the neutral molecules. In the condensed phase, on the other hand, nucleobase anions are known to be conventional (covalent) anions, implying the transformation from one form into the other due to environmental (solvation) effects. Here, in a series of negative ion photoelectron spectroscopic experiments on gas-phase, solvated uracil cluster anions, we report the observation of this transformation. © 1998 American Institute of Physics. [S0021-9606(98)01901-1]

Nucleic acid bases govern the storage and processing of genetic information. When ionizing radiation interacts with a living cell, electrons and hydroxyl radicals are among the most abundant reactive species formed. Here, we focus on the fate of the electrons. Numerous studies have shown that nucleobases provide trapping sites for these electrons. The resultant radical anions then participate in chemical reactions that can lead to the permanent alteration of the original bases and to genetic damage. Nucleic acid base anions thus play a central role in the electron-driven aspects of radiation-induced mutagenesis.

As a result of their relevance to this important biological problem, nucleic acid bases anions have been the subject of many experimental studies in the condensed phase. The nature and extent of electron binding in isolated (gas-phase) nucleic acid base anions, on the other hand, has been explored primarily by theoretical studies, and until relatively recently, such calculations were the main source of information regarding the inherent properties of naked nucleic acid base anions. Computational studies on nucleic acid base anions were conducted as early as the 1960’s and have continued to be performed to the present day. Among the objectives of such work has often been the determination of adiabatic electron affinities (EA’s) of nucleic acid bases, since EA’s defines the thermodynamic stability of a neutral molecule relative to its corresponding anion, with a positive sign indicating that the anion is lower in energy than its corresponding neutral and thus stable. Interestingly, however, despite voluminous evidence that nucleobase anions exist in both solutions and the solid state, none of these calculations found stable anions of naked nucleic acid bases in isolation, i.e., the EA’s of their neutrals had negative values.

This situation persisted until just a few years ago, when Adamowicz and co-workers, noting the large dipole moments (~5 D) of nucleic acid bases, conducted calculations which found stable, albeit fragile, anions of uracil and other nucleobases in which their excess electrons were bound by the dipolar fields of these molecules. It is now well established that excess electrons can be bound by the dipole fields of neutral molecular or cluster systems to form anions (often loosely referred to as “dipole-bound anions”) if the dipole moment of the system is larger than ~2.5 D. The nucleic acid base anions found in the Adamowicz group’s calculations exhibited the properties expected of negative ions having dipole bound excess electrons. Their excess electron binding energies were very small (with a predicted EA of 86 meV for uracil); and their structures were virtually the same as those of their corresponding neutrals.

On the heels of these theoretical predictions, two complementary experiments were conducted on isolated, gas-phase nucleic acid base molecular anions. One was performed by Desfrancçois and co-workers and the other by us, and both studies were published as companion papers. In the experiment of Desfrancçois and co-workers, nucleic acid base molecular anions were generated through electron transfer collisions between the bases and laser-excited Rydberg atoms and characterized via the dependence of anion formation rates on Rydberg electron quantum numbers. In our experiment, the molecular anions of nucleic acid bases were generated using a supersonic expansion nozzle ion source and characterized via negative ion photoelectron spectroscopy. Both experiments found that isolated nucleic acid base monomer anions do indeed form dipole-bound anions, confirming the theoretical predictions of Adamowicz.

While the realization that nucleic acid bases form dipole-bound anions answered some questions, it also raised new intriguing ones, and some of these are addressed in this communication. Consider the following. Electron spin resonance studies of nucleic acid base anions in condensed phase conclusively show them to be conventional (covalent) anions. If nucleic acid base anions are dipole bound anions in isolation and yet covalent anions in biologically relevant condensed phase environments, then a transformation must have occurred when the bare anions experienced the solvation and multi-body interactions of the condensed phase. Here, we present our experimental results pertaining to this problem; results which were obtained by studying gas-phase, solvated...
nucleic base anions by means of negative ion photoelectron spectroscopy.

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon (laser) beam and energy analyzing the resultant photodetached electrons. This is a straightforward approach to the determination of electron binding energies (EBE’s), relying as it does on the relationship, $h\nu = \text{EBE} + \text{EKE}$, in which $h\nu$ is the photon energy and EKE is the measured electron kinetic energy. Our apparatus has been described in detail previously. The spectra presented here were calibrated against the well-known photoelectron spectra of O$^-$ and NO$^-$, the resolution (FWHM) of our electron analyzer was $\sim$25 meV, and photodetachment typically was accomplished with $\sim$200 circulating watts of 2.540 eV photons. In the supersonic expansion nozzle ion source which we used to generate the anions, relatively low energy electrons were injected directly into the high density portion of the expanding jet (nucleic acid base vapor diluted in argon at several atm) in the presence of weak axial magnetic fields, and negative ions were extracted from the resulting microplasma. The negative ion formation environment most probably involves the attachment of even lower energy secondary electrons to target species in the presence of many cooling collisions.

Dipole bound anions exhibit a distinctive photoelectron spectral signature, characterized by a single, strong, narrow feature at very low electron binding energies and by several much lower intensity features at slightly higher electron binding energies. We have seen this spectral fingerprint in all of the many ground state, dipole bound anions which we have studied thus far. These spectra are unique, i.e., they are unlike those of any other anionic species we have encountered. The photoelectron spectra of dipole bound anions are exemplified by our previously reported$^7$ spectrum of the uracil anion, an important reference species in the present study [see Fig. 1(a)]. Essentially, the dominant peak in this spectrum is due to the origin transition between the ground state of the uracil anion and its corresponding neutral. The fact that its electron binding energy is so small indicates that the excess electron is bound very weakly, while the relative strength and especially the unusual narrowness of this peak (almost instrumentally limited) imply that the structure of the anion and its corresponding neutral are very similar. The much weaker intensity features lying to slightly higher EBE are assignable to vibrations of molecular uracil. The vertical detachment energy (VDE) is the electron binding energy corresponding to the maximum in the dominant peak in this spectrum. The VDE of the uracil anion was measured to be $93 \pm 7$ meV. As mentioned above, the spectrum of the uracil anion strongly implies that the uracil anion has essentially the same structure as does it neutral. Under such circumstances, the VDE is either equal to or just slightly larger than the EA$_a$ in value, and thus the EA$_a$ of uracil is near 93 meV, in good agreement with the calculations of Adamowicz and co-workers. In addition to explaining the photoelectron spectrum of the uracil anion, this description also sets the stage for recognizing and interpreting the spectra of the other dipole bound anions that will be presented below.

With this background material in place, we return to the issue of the transformation that occurs when nucleic acid base anions experience condensed phase interactions. Naturally, the condensed phase environment with the most relevance to biological problems is that provided by water. Rydberg electron transfer data had earlier provided a hint that small hydrated uracil anions have covalent character, even though contemporary calculations indicated otherwise. To investigate this question further, we mimicked the essential interactions of the aqueous environment by solvating uracil anions with various numbers of water molecules form-
ing uracil–water cluster anions, $U^-(\text{H}_2\text{O})_n$, and then looked, as a function of cluster size, for evidence of a dipole bound-to-covalent state transformation by using negative ion photoelectron spectroscopy. Intuitively, we expected this to take several, if not many, water solvents per uracil anion to definitively accomplish such a transformation. Thus, we were initially surprised when we recorded the photoelectron spectrum of uracil anion solvated by one water molecule, i.e., $U^-(\text{H}_2\text{O})_1$, shown in Fig. 1(e). The dipole bound signature of the unsolvated uracil anion was completely gone from this spectrum, and instead there had appeared a broad, relatively high EBE feature, indicative of a substantial structural difference between this anion and its corresponding neutral and typical of many valence (covalent) anions. Evidently, the dipole bound-to-covalent state transformation for the uracil anion requires only one water molecule to achieve. Our interpretation of this is that the covalent form of the uracil anion is pulled down in energy (stabilized) by its interaction with a water molecule, below the energy of the dipole bound form of the uracil solvated by water. The reason that the covalent form is stabilized more than the dipole bound form is that the excess electron density on the covalent uracil anion is much higher than that on the dipole bound uracil anion, and the water molecule’s interaction energy is greater with the denser excess electron distribution.

We also measured the photoelectron spectra\(^9\) of $U^-(\text{H}_2\text{O})_n$, with $n$ ranging from 1 to 12. All of these exhibited similar shaped covalentlike spectral features, which shifted to higher EBE’s with increasing $n$, in accord with typical valence anion–neutral solvent interaction energies. In addition, to rule out the possibility of our uracil/water results being due to a tautomORIZATION reaction, we conducted a parallel set of control experiments\(^9\) using $N,N$-dimethyluracil, which can not undergo tautomORIZATION with water. Again, just as in the case of uracil, its monomer anion was dipole bound and all of its hydrated anions were covalent, eliminating tautomORIZATION as an explanation for our observations.

Struck by the fact that the interaction of a single water molecule with the uracil anion is enough to bring about the sought-after dipole bound-to-covalent conversion, we next turned to weaker solvents in hopes of seeing the actual transition take place. First, we tried argon, making the uracil anion–argon complex, $U^-(\text{Ar})_1$, and recording its photoelectron spectrum. As seen in Fig. 1(b), it retained its dipole bound spectral signature. We then used krypton, generating $U^-(\text{Kr})_1$ and recording its spectrum [see Fig. 1(c)]. While $U^-(\text{Kr})_1$ showed some stabilization relative to $U^-$, (e.g., $\text{VDE}[U^-(\text{Kr})_1]=101 \pm 7$ meV), it too retained its dipole bound signature and character. Neither argon nor krypton are strong enough solvents, it seems to affect the transformation of interest.

Next, we turned to xenon, an atom which, because of its high polarizability, has substantial solvating power. Here, in the case of $U^-(\text{Xe})_1$, we saw a dramatic effect. As shown in Fig. 1(d), both a dipole bound and a covalentlike feature exhibit themselves together simultaneously in the spectrum of $U^-(\text{Xe})_1$. This appears to be a system in which the crossover from dipole bound to covalent behavior is well illustrated. Probably, this is because the EA’s (the stabilities) of both forms are essentially the same. For the dipole bound feature, the VDE~$\text{EA}_a$ as previously discussed, and $\text{VDE}[U^-(\text{Xe})_1]=111 \pm 7$ meV. For the covalent form, there is clearly a substantial structural difference between the anion and its neutral (as evidenced by the broad width of its partially resolved vibrational progression), and thus, $\text{VDE}>\text{EA}_a$. In the absence of hot bands, the EA’s of the covalent form will lie at the low EBE edge of this feature, i.e., essentially at the same EBE as the VDE of the dipole bound form. Figures 1(a)–1(e) can now be seen as illustrating the gradual evolution, with increasing solvation power, of the dipole bound state of the uracil anion into its covalent manifestations in xenon and water.

At this point, the nature of the covalent form of the uracil anion and its relationship to its dipole bound forms are interesting to consider. In regard to the covalent state, electron transmission spectroscopy along with calculations seem to indicate that the uracil molecule has a slightly negative EA’s, i.e., that the covalent form of the uracil anion is a low-lying temporary anion state, but it is also possible that it has a slightly positive EA’s, i.e., between 0 and 90 meV. Whichever is the case, it is clear that the covalent form of the uracil anion is very close in energy to that of neutral uracil. Whether the covalent form of the uracil anion is slightly stable or slightly unstable, the systems which we have studied and reported upon here can be viewed as involving the competitive stabilization of both the covalent and the dipole bound isomers of the uracil anion. When the dipole bound form is the most stable, as in the cases of $U^-$, $U^-(\text{Ar})_1$, and $U^-(\text{Kr})_1$, then we observe the dipole bound form of these anions, since our source tends to discriminate in favor of the more stable form of a given anionic species. When the dipole bound and the covalent forms are essentially of the same stability, as in $U^-(\text{Xe})_1$, we see both forms, and when the covalent form has overtaken the dipole bound form (in terms of stability), as in $U^-(\text{H}_2\text{O})_1$, then we observe only the covalent form. Of course, both forms continue to exist, just with the higher energy state unoccupied.

More generally, we see here, in the cases of uracil anion’s solvation by water and xenon, examples of phenomena which one knows must occur relatively often in the condensed phase; that of an unstable or marginally stable anion being stabilized and made observable by virtue of solvation. There are many other examples of this important and general phenomenon, many of them having nothing to do with dipole bound species, where a given anion has a stable existence in the condensed phase, but is not stable and thus is not seen in the gas phase as an isolated ion. Solvated anions of this type exist as stable species only in solution and have no stable molecular counterpart, owing their very existence to solvation and multi-body condensed phase interactions.

The first order view of dipole bound and covalent forms as being separate isomers may require some further refinement, however, especially when the two are close in energy. Emerging evidence for this comes from the fact that when we solvate $U^-(\text{Xe})_1$ with additional xenon atoms,\(^9\) (i) both the dipole bound and the covalent features of the $U^-(\text{Xe})_{1-3}$
spectra move together, i.e., they shift by the same amount of energy, and (ii) the slope of a plot of the ion–solvent total interaction energy versus solvent polarizability, is somewhat steeper for $U^-(\text{Xe})_{1-3}$ than that for uncomplicated dipole bound species, such as $U^-(\text{Ar})_{1-2}$ or $U^-(\text{Kr})_1$. If the dipole bound and the covalent forms were simply unconnected isomers, they should shift by different amounts of energy with increasing solvation. Also, the steep slope of the ‘dipole bound’ feature in the $U^-(\text{Xe})_{1-3}$ spectra is more like a valence anion’s solvation behavior than that of a pure dipole bound species, such as $U^-(\text{Ar})_{1-2}$ or $U^-(\text{Kr})_1$. Thus, in the case of $U^-(\text{Xe})_{1-3}$ than that for uncomplicated dipole bound and the covalent states were simply unconnected isomers, they should shift by different amounts of energy with increasing solvation. Also, the steep slope of the ‘dipole bound’ feature in the $U^-(\text{Xe})_{1-3}$ spectra is more like a valence anion’s solvation behavior than that of a pure dipole bound anion. Thus, in the case of $U^-(\text{Xe})_n$ species at least, there is some reason to believe that the dipole bound and the covalent states may be coupled. There is a precedent for this in the nitromethane anion,\(^{10}\) where the dipole bound and the covalent states are not nearly as close in energy as they are in $U^-(\text{Xe})_n$. Additional experiments are planned to further elucidate the degree of coupling between the dipole bound and the covalent forms of these species.

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