# Valence and Dipole Binding of Electrons to Uracil

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Rydberg electron attachment to gas-phase isolated uracil molecules and mixed uracil−argon clusters is examined in a crossing beam experiment. By means of reproducible uracil beam conditions, it is possible to control the electron-binding process, which is strongly influenced by solvation. Attachment followed by evaporation of a single argon atom is already sufficient to switch from dipole-bound to valence monomer uracil anions, as demonstrated by field-detachment measurements. The existence of both types of anions is in good agreement with two separate previous theoretical predictions. A DFT calculation of the valence adiabatic electron affinity of uracil provides a small but positive value of 70 meV, close to the measured value of the dipole-bound electron affinity.

## 1. Introduction

Molecular beams provide means to determine experimental gas-phase ionization potentials[1] and electron affinities[2−4] of small molecules of biological interest, such as DNA and RNA bases, which can be directly compared to elaborate quantum chemistry calculations.[5−8] While the situation today is rather satisfactory for ionization energies,[1] theoretical predictions and measurements of the valence electron affinities $EA_{val}$ of those molecules still represent difficult tasks. One problem, for the determination of electron affinities of DNA and RNA bases, comes from the large polarity of these molecules, which allows for the existence of two very different types of anions. According to the used quantum chemistry methodologies[9,10] or experimental techniques,[3,4] valence or dipole binding of electrons can be favored and thus lead to results that are only apparently different and represent two complementary aspects of reality. Polar molecular systems can indeed trap electrons in their long-range dipole field provided their dipole moment[11−13] is larger than a critical value of about 2.5 D. Dipole-bound anions are then observed where the excess electron resides in a very diffuse orbital, nearly entirely located outside the neutral parent molecular frame. It is the unique mechanism responsible for the observation of long-lived anions created from electron attachment to a large number of closed-shell molecules.[14] However, such polar molecules with $\pi$ molecular orbitals can also give birth to valence (conventional) anions[15] where the excess electron is attached to the valence molecular orbitals. This possibility had been predicted[16] long before the appearance of experimental techniques enabling the creation of ground-state dipole-bound anions.[14,17,18] Following electron attachment to the same parent molecule, valence or dipole-bound anions can be observed[19] according to the design and operation conditions of the anion sources. In parallel, whether very diffuse orbitals are included in the anion basis sets or not, ab initio calculations predict the existence of dipole-bound or valence anions.[10]

We here consider the biologically relevant problem[20] of electron attachment to the uracil molecule, which has a very large dipole of about 4.3 D. Several quantum calculations of the uracil electron affinity have already been performed, suggesting the possible existence of valence[5,8] as well as dipole-bound anions[7] and raised some interesting questions.[21] Long-lived uracil anions have since been experimentally observed and studied by means of photoelectron spectroscopy (PES)[3,22] and Rydberg electron transfer (RET) spectroscopy.[4] PES measurements have provided a very accurate determination of the vertical detachment energy (VDE) of uracil equal to 93 ± 7 meV.[3] RET measurements have also demonstrated the existence of a dipole-bound state and provided a value of the adiabatic electron affinity $EA_{DB}$ equal to 54 ± 35 meV. The aim of the present work is to investigate the simultaneous existence of both valence and dipole-bound states of the uracil anion, in the light of new experimental and theoretical studies.

## 2. Apparatus and Experimental Conditions

In a preliminary RET experimental study of very low energy electron attachment to uracil,[4] we observed a definite peak in the Rydberg atom principal quantum number *n*-dependence of the uracil anion creation rate constant. The presence of this peak was a clear signature of the existence of a dipole-bound state.[13] However, we also found, superimposed to this peak, a significant background of anions over the whole range of *n*-values, which could be suspected to be valence anions produced by free electron dissociative attachment.[14] In the previous work, we had only used helium as a carrier gas to produce the uracil beam. Here, we use both helium or argon as carrier gases with an improved absolute mass calibration and an important reduction of free electron scattering. The neutral uracil beam is created by means of a heated pulsed valve (General Valve, 0.15-mm conical nozzle) followed by a 1-mm heated skimmer. This beam crosses downstream a beam of laser-excited xenon atoms. Anions are created by charge-exchange between the molecular beam and the excited beam, and they are further mass-analyzed in a Wiley-McLaren time-of-flight tube.[23] A very careful mass-calibration allows us to be sure that the observed anions always correspond to the same mass of the intact uracil molecules. Electric field detachment measurements can be performed by means of a set of three planar grids perpendicular to the anion path.[13] These grids with 80% transparencies are equally spaced by 2 mm. A fourth grid in front of the microchannel detector can be biased at a negative

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voltage to repel anions. The detected particles are then fast neutrals corresponding to field-detached dipole-bound anions.

By varying the time delay between the pulsed valve opening and the firing of the pulsed laser creating the Rydberg atoms, we can sample different beam pressures and we thus can vary the neutral molecular beam composition. At the very early beginning of the valve opening corresponding to weak beam densities, we observe only uracil monomer $U^-$ or dimer $U_2^-$ anions, whether the carrier gas is helium or argon. When increasing the time delay, the beam density and the probability of clustering increase.[19] Monomers, homogeneous clusters, and mixed cluster anions $U^-(Ar)_N$ are then observed. Under these high-density beam conditions, the detected monomer anions are thus created either by direct Rydberg electron attachment to isolated uracil molecules or by attachment to mixed clusters eventually followed by evaporation of one or several argon atoms. We will further label these anions respectively $U^-$ or $U^-(Ar)_0$. The notation $(Ar)_0$ is only an image to recall the souvenir of the creation conditions. As pointed out below, it is very unlikely that uracil anions can originate from homogeneous clusters.

## 3. Rydberg Electron Energy Dependence of Anion Formation Rates

Anion creation rates for $U^-$, $U^-(Ar)_0$, and $U^-(Ar)_1$, obtained with the different beam conditions, are displayed in Figure 1 as a function of the Rydberg principal quantum number $n$ involved in the RET collisions. The RET $n$-dependencies of the $U^-$ anion creation rates at low beam density, either with helium or argon as carrier gas, are characteristic of dipole-bound anions (Figure 1a). In contrast with our preliminary results,[4] the here measured anion creation rates at low beam densities fall down to zero for $n$-values larger than 20, demonstrating the absence of any covalent anion production. We can now interpret our previously observed backgrounds outside the peaked regions for uracil as dehydrogenated valence $(U-H)^-$ anions produced by spurious free electron scattering. Those anions are no longer observed in the present measurements. Our present results are thus in total agreement with those of Bowen and co-workers[3] since only dipole-bound $U^-$ anions are observed with both experimental techniques when electron attachment to isolated uracil molecules is concerned.

The detailed explanation of the peaked behavior is given in ref 24 and derived from an ionic−covalent curve-crossing model. RET anion creation rates are maximum at $n_{max} = 9$ in helium, corresponding to a dipole-bound electron affinity of about 50 meV,[4] and only at $n_{max} = 10-11$ in argon, due to the lowest collision energy in this last case.[14] Both peaks are however wider than what could be expected for pure dipole-bound anions.[4] This could indicate that the dipole-bound anion geometry could be slightly distorted with respect to the neutral geometry. This has been previously reported in theoretical studies of rather strongly dipole-bound anions of uracil[7] and thymine,[25] in which part of the excess electron wave function is localized around the molecular frame. Structural distortions have also been seen in experimental studies on dipole-bound anions of hydrogen-bonded dimers,[26] in which the geometry changes can favor dipole binding by the increase of the total dipole moment. It has then been shown[24] that the true adiabatic dipole-bound electron affinity ($EA_{DB}$) is larger than the above value deduced from the position $n_{max}$ of the maximum anion formation rates. In the present case this would lead to a better estimate of $EA_{DB} = 85 \pm 15$ meV, the slight distortion explaining the difference between this estimate and the measured value of VDE = 93 ± 7 meV. The RET $n$-dependencies of the $U^-(Ar)_0$ or $U^-(Ar)_1$ anion creation rates, obtained at high beam density, are indeed both smooth and more or less maximum and constant for large Rydberg quantum number $n$ (see Figure 1b). The shape of these curves is similar to the RET $n$-dependencies of the creation rates observed for a large number of well-known conventional anions such as $SF_6^-$, and it is characteristic of the creation of a valence anion. The excess electron orbital is no longer diffuse and the electron−molecule interaction range is very short as compared to that of the interactions between the Rydberg positive core $Xe^+$ and the excess electron or the neutral molecule. As shown by Hotop and co-workers,[27] a quasi-free electron model, such as Matsuzawa's model,[28] is then relevant, and it predicts constant anion creation rates for high Rydberg levels (high $n$) corresponding to low energy attaching electrons (s-wave attachment). These results thus suggest that stable (long-lived) valence uracil anions can be formed and that they originate from electron attachment only to mixed $U(Ar)_N$ clusters, with subsequent evaporation of one or a few argon atoms, but not from isolated molecules or even homogeneous $U_2$ dimers.

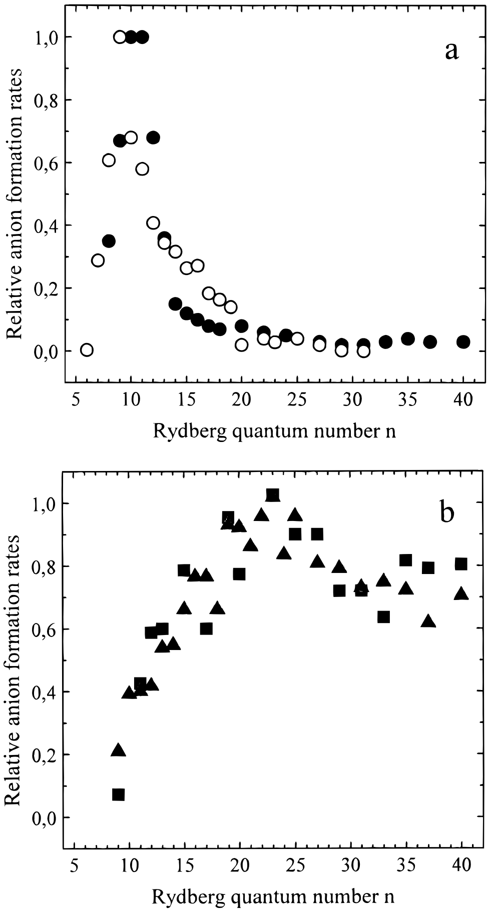

**Figure 1.** (a) Rydberg $n$-dependencies for the formation of uracil ($U^-$) anions in collisions between laser-excited Xe(nf) atoms and uracil seeded in helium (open circles) and argon (solid circles), at low beam densities. (b) Rydberg $n$-dependencies for the formation of $U^-(Ar)_0$ (solid squares) and $U^-(Ar)_1$ (solid triangles) anions in collisions between laser-excited Xe(nf) atoms and uracil seeded in argon, at high beam densities (see text).

## 4. Field-Detachment Measurements

Figure 2 displays the corresponding field-detachment curves for $U^-$ anions, created from isolated uracil molecules seeded in helium or argon at low beam densities, and for $U^-(Ar)_0$ and

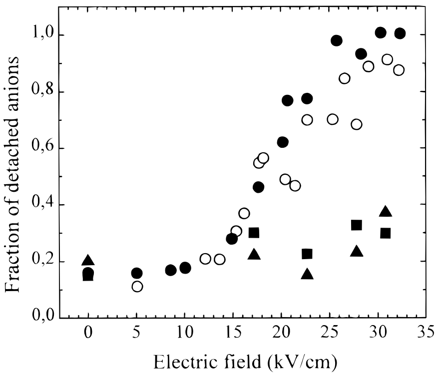

**Figure 2.** Experimental field-detachment curves for uracil ($U^-$) anions created in collisions between laser-excited Xe(10f) atoms and uracil seeded in helium (open circles) and argon (solid circles) at low beam densities and $U^-(Ar)_0$ (solid squares) and $U^-(Ar)_1$ (solid triangles) anions created in collisions between laser-excited Xe(20f) atoms and uracil seeded in argon (see text).

$U^-(Ar)_1$, at high argon beam density. These field-detachment measurements have been performed for negative ions created from Rydberg atoms with respective principal numbers *n* equal to 10 for $U^-$ and 20 for $U^-(Ar)_0$ and $U^-(Ar)_1$. In the first case, the long-distance and weakly bound dipolar character of the electron excess orbital of the $U^-$ anions is confirmed. As expected, these field-detachment curves are independent from the carrier gas since these anions are not the results of any evaporation process. However, on the basis of a simple field-detachment model for pure dipole-bound anions[24] and in view of the reported $EA_{DB}$ and VDE, the critical detaching field of about 20 kV/cm is too low and the two curves do not increase steeply enough in the vicinity of this electric field value. This is again an indication that uracil dipole-bound anions possess a slightly different geometry as compared to neutral molecules.

The existence of a valence state of the uracil anion is also confirmed by the field-detachment curve of the $U^-(Ar)_0$ and $U^-(Ar)_1$ anions in which electric fields up to 35 kV/cm are unable to induced the complete detachment of the excess electron. This is in clear contrast with the behavior of dipole-bound anions, and this corresponds to a common feature observed for valence negative ions such as $SF_6^-$ or $U_2^-$.

## 5. Discussion and DFT Calculations

The existence of two different types of anions created from electron attachment to the same molecule is the central point of the present work. Before discussing the uracil case, we here recall that this coexistence has been recently experimentally demonstrated for the nitromethane molecule, which possesses both an adiabatic valence electron affinity of 0.26 ± 0.08 eV and a dipole-bound electron affinity of only 12 meV. The two anion sources that were employed to measure the electron affinities of nitromethane[19] are the same as those employed for uracil in refs 3 and 4 and in the present work. The photodetachment experiment of Bowen and co-workers[3] which demonstrated the existence of the valence state of nitromethane employs a source of cold anions created by free electrons injected in the high-pressure region of a supersonic expansion. Following electron attachment, the resulting nascent anions are collisionally relaxed and further observed in their lowest energetic state, i.e. the valence state for nitromethane. The RET anion source uses Rydberg electrons in very diffuse orbitals, and in direct Rydberg electron attachment to nitromethane monomers only dipole-bound anions were observed. However, by tuning the pulsed supersonic expansion to higher beam density conditions, it was possible to produce nitromethane clusters as well as nitromethane monomers due to dimer evaporation, which then turned out to be in their valence state, as demonstrated by a field-detachment measurement. Internal conversion through vibronic coupling between the two states, which seems unlikely or very difficult in the isolated monomer,[10] becomes allowed if the electron-accepting molecule is bound in a complex.

The theoretical interpretation of these results concerning nitromethane requires rather elaborate calculations. The first attempt using MPBT (many-body perturbation theory) suggested the existence of a valence state[29,30] but failed to obtain a positive value of the valence electron affinity. For the dipole-bound state,[30] a small value of 3 meV was predicted, but there was no evidence of a valence state. The first quantitative calculation of both states was only achieved recently,[10] requiring the HFDFT (Hartree−Fock density functional theory) method for the valence state and the EA-EOMCC (electron attached equation of motion coupled cluster) method for the dipole-bound state.

The situation is here somewhat similar for uracil. Employing ROHF (spin-restricted open-shell Hartree−Fock) and ROMP2 (spin-restricted open-shell followed by the many-body perturbation theory calculation of the second-order electron correlation correction) methods, Sevilla and co-workers[8] computed the energy of the LUMO (lowest unoccupied molecular orbital) and the valence vertical electron affinity, which were both negative. By proper scaling to experimental determinations of vertical electron affinities of similar molecules, they then predicted a positive value $EA_{val} = 0.4$ eV for the adiabatic electron affinity corresponding to a valence state of the uracil anion. On the other hand, by adding a set of very diffuse orbitals localized in a point located away from the molecular frame in the direction of the molecular dipole, Oyler and Adamowicz[7] predicted a positive value for the dipole-bound electron affinity. This value has since proved to be in very good agreement with the experimental measurements[3,4] performed with both the photodetachment anion source and the RET anion source. The RET method has demonstrated its ability to determine dipole-bound electron affinities in a broad energy range (0.3−80 meV) but fails to directly provide values of valence affinities, except for the sign. We thus here must rely on a calculation to estimate the valence electron affinity of uracil. We use the density functional theory (DFT),[31] which has already been employed to predict accurate electron affinities,[32] either for covalent binding of the extra electron corresponding to large affinity values in the eV range[33] or low values where the role of diffuse orbitals can become crucial.[10,26] For example, the calculated values[26] of the adiabatic electron affinity $EA_{ad}$ of the water dimer and of the vertical detachment energy VDE of its anion are rather small (respectively 30 and 45 meV) but nevertheless in very good agreement with the experimemtal values. The Becke's three-parameters functional[34] with the nonlocal transformed correlation functional of Lee−Yang−Parr has been used. As the uracil molecule and its anion are not planar, optimization of the geometries has been performed in $C_1$ symmetry. The starting point for the basis set [6-31++G(2d)] used for the uracil molecule and the corresponding anion is that of refs 35. We have added two sp and two d functions for oxygen, carbon, and nitrogen atoms, one s and two p functions for hydrogen atoms. The exponents of the last three sp functions are [0.69, 0.33, 0.091], [0.168, 0.04, 0.028], and [1, 0.21, 0.06] for oxygen, carbon, and nitrogen atoms, respectively. For hydrogen atoms,

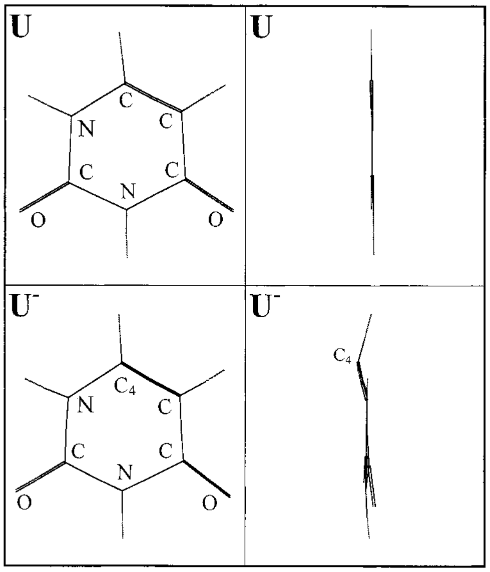

**Figure 3.** Optimized geometries of the uracil molecule (U) and its anion ($U^-$), deduced from a DFT calculation (see text). Figures on the left represent face views and on the right represent side views.

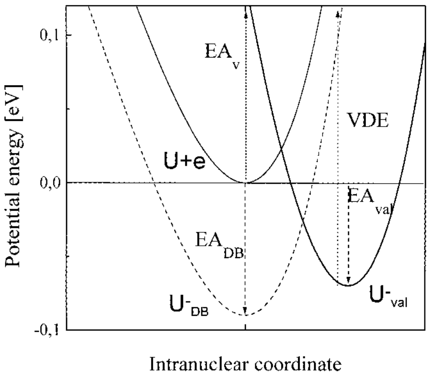

**Figure 4.** Schematic potential energy diagram of the uracil (neutral) plus electron system and uracil anion in its dipole-bound state (dashed curve) and valence state (solid curve).

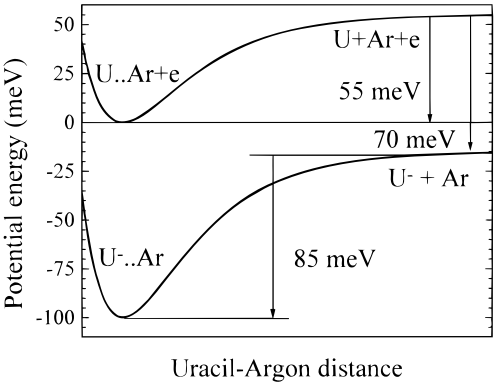

**Figure 5.** Schematic potential energy diagrams of the mixed uracil (neutral)−argon dimer plus electron at infinity and of the mixed uracil−argon anion dimer in its valence state.

the exponents of the two last s functions are 0.4 and 0.2, while those of the p functions are 1.58 and 0.43.

The calculated geometrical structures of uracil and its covalent anion are displayed in Figure 3. The neutral structure is almost planar[36] but covalent electron attachment induces a rather large departure from planarity for the anion. The predicted values for the potential energies of the valence states are the following. The calculated difference between the energies of the neutral uracil and the anion with the same nuclear configuration is negative and equal to $-40$ meV, much less than the experimental value of the negative vertical electron affinity $\mathrm{EA_v}$ equal to $-190$ meV.[37] This calculation is not able to provide the correct $\mathrm{EA_v}$ since the vertical valence anion state is not bound but nevertheless confirms our experimental observation that valence binding of very low energy electrons to isolated uracil cannot take place. On the other hand, the valence adiabatic electron affinity $\mathrm{EA_{val}} = +70$ meV is positive. The calculation of the neutral molecule energy in the geometry of the anion provides the valence vertical detachment energy VDE, which is equal to 700 meV. This last value must be compared to the photodetachment value of Bowen and co-workers[3] for the uracil dipole-bound anion, which is only 93 meV, corresponding to a vertical transition between the anion and its neutral parent with nearly the same nuclear configurations. This large valence VDE of 700 meV is also an indication of the large nuclear reorganization induced by valence binding.

Figure 4 summarizes our results concerning the existence of the two uracil anion states. Our observation of two very different types of anions according to the uracil source conditions can be understood if we consider the potential energy curves of the neutral and negatively charged mixed uracil−argon dimers, as displayed in Figure 5. These curves have been calculated by means of a simple empirical model with atom−atom interactions[38] and partial charges which respect the values of dipole and quadrupole moments of the isolated molecules.[39] The excess negative charge of the anion is here equally distributed over the different uracil atoms, but we also performed a more realistic calculation using our actual DFT distribution of charges in the anion without any significant modification of the result. A genetic algorithm[40] provides us the potential energy minima. The above-calculated valence electron affinity of about 70 meV is larger than the obtained value of the intermolecular binding energy of $\mathrm{U(Ar)_1}$ of 55 meV, while that for $\mathrm{U^-(Ar)_1}$ is 85 meV. Following electron attachment to $\mathrm{U(Ar)_1}$ neutral dimers, the nascent valence $\mathrm{U^-(Ar)_1}$ anions thus have an excess internal energy larger than their dissociation energy and can thus rapidly evaporate argon atoms, leading to the observation of $\mathrm{U^-(Ar)_0}$ valence anions.

The remaining question we finally try to address is why direct attachment of Rydberg electrons to isolated gas-phase uracil does not lead to the observation of valence anions, and attachment to mixed uracil−argon clusters followed by evaporation does. The negative value of the valence vertical electron affinity of the isolated molecule precludes direct attachment of Rydberg electrons at large *n*-values since their quantum distributions in momentum space fall off very rapidly. At low *n*-values (higher electron energies) the electron attachment process is dominated by dipole binding. On the contrary, in the mixed uracil−argon clusters, because of solvation, the valence vertical electron affinity is lowered and becomes closer to zero, allowing for a curve crossing at very low electron energies. Electron attachment in the valence state then becomes energetically allowed even at larger Rydberg *n*-values. The excess energy of the nascent anions is further removed by evaporation of one or several argon atoms (for a discussion of the influence of electron binding energy upon evaporation of anion clusters, see ref 41), leaving monomer uracil anions in their valence state. The absence of covalent uracil anions in the photoelectron spectroscopy (PES) experiment of Bowen and co-workers can thus be explained by the smaller value of the covalent electron affinity $\mathrm{EA_{val}}$ than for the dipole-binding electron affinity $\mathrm{EA_{DB}}$ since the PES anion source favors the most stable anion production, as demonstrated in the nitromethane case.[19] The values of 70 meV given here for the covalent electron affinity and 55 meV for the binding energy of the U···Ar dimer are compatible with the evaporation of an argon atom from an excited $(U\cdots Ar)^-$ anion (Figure 5). However, the neutral uracil−argon clusters are not totally cold and possess some internal energy, typically 10 meV, which must be taken into account to evaluate a lower bound of $EA_{val}$.

## 6. Conclusion

The apparent discrepancy[21] between the theoretical predictions[6,7] concerning the nature of the uracil anion seems to be solved since the predictions of positive values of the dipole-bound and valence electron affinities are both verified in the present experimental work. The experimental observation of dipole-bound uracil anions demonstrates that the valence electron affinity is smaller than 93 meV. Our observation of valence $U^-$ anions following evaporation of argon atoms leads us to the conclusion that the valence electron affinity must be larger than the binding energies of neutral uracil−argon clusters, typically between 30 and 60 meV. Our calculated DFT value falls between these lower and upper limits, but the study of electron attachment to the isolated uracil molecule however still represents a difficult test of quantitative predictions of the valence electron affinity since its value is very close to zero. A more accurate calculation of the uracil valence electron affinity would thus be desirable. The rather large width of the RET $n$-dependence of the dipole-bound $U^-(Ar)_0$ anions (Figure 1a), as compared to "pure" dipole-bound anion states, suggests a coupling between dipole-bound and valence states. This problem, which is complicated and has been studied in ref 10 for the nitromethane anion, remains an open question for the uracil anion.

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