# Intramolecular Electron Transfer from Dipole-Bound to Valence Orbitals: Uracil and 5-Chlorouracil

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The electronic interaction between dipole-bound and valence anions of uracil and chlorouracil is investigated. In general, dipole-bound and valence states of an anion show very different electronic structures and the extra electron occupies completely different regions of space. Here, the coupling strength between the different attachment states is computed by fitting a simple diabatic model potential to a cut through the two adiabatic surfaces of the anions obtained from ab initio calculations. During these calculations, electron affinities of uracil and chlorouracil as well as resonance energies associated with vertical attachment into the valence orbitals of these molecules are obtained, and our results are compared with the available experimental and theoretical data. The estimated electronic coupling governs the intramolecular electron transfer from dipole-bound to valence orbitals, and the associated transfer rate has implications for the mechanism of electron attachment and electron-induced bond cleavage of uracil and 5-chlorouracil with “zero-energy” electrons.

## 1. Introduction

Both the RNA base uracil (U) and the substituted 5-chlorouracil (UCl) belong to the class of polar molecules that can bind electrons in two fundamentally different ways. On one hand, U and UCl form so-called conventional or valence anions where the extra electron occupies a compact valence orbital. Since the unoccupied valence orbitals of a neutral are—as a rule—antibonding in character, valence anions typically exhibit equilibrium structures markedly different from their corresponding neutrals. For example, $U^-$ and $UCl^-$ have puckered rings.[1−3] On the other hand, U and UCl possess large permanent dipole moments sufficient for binding an extra electron by purely electrostatic forces.[1,4−8] In these dipole-bound states, the extra electron occupies a very diffuse Rydberg-like orbital (Figure 1), and therefore the geometry of the dipole-bound anions is virtually identical with those of the neutral molecules (for reviews on dipole-bound anions see refs 9-13).

In this communication, we investigate the interaction between valence and dipole-bound states of $U^-$ and $UCl^-$. This interaction or electronic coupling is closely related to the intramolecular electron transfer from the dipole-bound to the valence orbital and to the question whether the diffuse dipole-bound states can act as “doorways” to the formation of valence anions. The wider contexts of this study are, on one hand, electron-attachment properties of polar molecules and, on the other hand, electron-induced reactions of $U^-$ and $UCl^-$. So far, these two fields have had limited overlap, and in the following we briefly consider both viewpoints.

The notion of dipole-bound states providing doorways into valence states originates from Rydberg electron-transfer experiments where it has been convincingly demonstrated that initially formed dipole-bound states act as precursors for valence anions,[14−19] or, in cases where the valence state is dissociative, as doorways for dissociative attachment processes (see, e.g., refs 20,21). Yet, it is an open question whether this mechanism—initial electron attachment into a dipole-bound orbital followed by intramolecular electron transfer into a valence orbital—can operate efficiently in free-electron attachment. The crucial difference is of course that in Rydberg electron transfer the

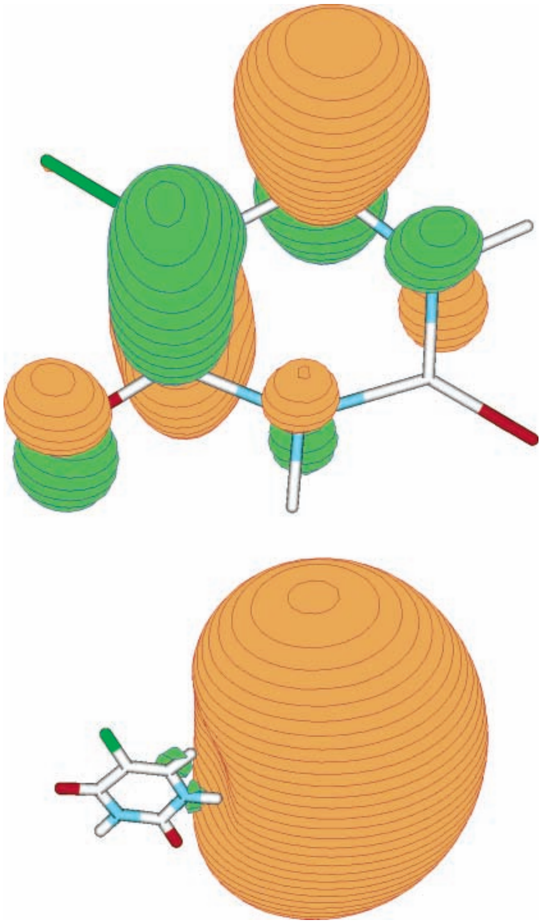

**Figure 1.** Singly occupied orbitals of the valence (upper panel) and dipole-bound (lower panel) states of the UCl anion. Note the different length scales and the different values employed to compute the isosurfaces: 0.05 and 0.005, respectively.

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electron is truly bound to the target molecule and can therefore not escape, whereas in free-electron attachment the autodetachment channel is open, and thus the intramolecular transfer needs to be very fast to compete successfully with electron re-ejection.

While the participation of dipole-bound states is an open question, for both molecules U and UCl there is ample evidence for electron-induced processes at threshold, that is, processes induced by essentially zero-energy electrons.[22−26] These and other electron-induced reactions of U and UCl did gain considerable attention in the contexts of radiation damage of genetic material[22] and charge-transfer phenomena of DNA.[27] The two issues are in fact closely related, since radiation damage is thought to be largely caused by reactions initiated by secondary low-energy electrons rather than by direct impact of the high-energy photon. When RNA or DNA are exposed to ionizing radiation, the pyrimidine bases uracil or thymine, respectively, and cytosine represent the major anionic centers, and since replacement of U or thymine by 5-halouracils enhances the damage substantially, these compounds have been suggested as sensitizer in radiation therapy (see ref 23 and references therein and ref 28 for references to early work).

Considering electron-induced reactions in general, one typically finds resonances, that is, specific energies where the reaction is most efficient. These resonances are usually rationalized in terms of temporary anion intermediates; energy transfer to the nuclei takes some time, and only at those energies where temporary anion states with noticeable autodetachment lifetimes $\tau$ are formed can processes such as vibrational excitation, rearrangement, formation of long-lived anions, or dissociation proceed efficiently. In the energy range of a few eV, temporary anion intermediates are typically associated with the occupation of antibonding valence orbitals, and for UCl this process has been examined in ref 29. In contrast, in thinking about zero-energy attachment, what comes to mind are dipole-bound or dipole-bound-like states. While it is possible that a specific molecule does possess an empty orbital at zero energy, it is well established that dipole-bound states do in general strongly influence the threshold region in electron-scattering experiments.[30]

In the following, we focus on obtaining a reasonable estimate for the electronic coupling between the dipole-bound and valence states of U and UCl. These coupling elements are the key properties characterizing the intramolecular electron transfer and its competition with autodetachment. In the next section, we discuss the coupling between dipole-bound and valence states from a general point of view and describe our approach to compute the coupling strength as well as details of the needed ab initio calculations. Section 3 is an overview about the electron-attachment properties of U and UCl, computational results are presented in section 4, and our conclusions are discussed in section 5.

## 2. Electronic Structure Considerations

In this section, we briefly describe the diabatization procedure we use to extract the coupling from a series of electronic structure calculations, and then the computational details of these calculations are outlined.

In general, there are two ways to think about a molecule possessing both a dipole-bound and a valence anion. In the *adiabatic* picture, the two anions correspond to different minima on the lowest adiabatic potential energy surface (PES). In going from one minimum to the other, the character of the electronic wave function changes dramatically; there is an avoided crossing between the ground and the first excited state, and in this region the two states are strongly coupled by the nuclear kinetic energy operator. On the other hand, one can think in terms of *diabatic* states[31,32] that retain their character while the nuclei move. In the diabatic picture, the two diabatic PES will cross on a path connecting the two respective minima, and the dominant part of the coupling has been moved to the electronic Hamiltonian.[31,32] Both pictures represent equally valid descriptions, and only in a specific context one may be more adequate or practical than the other.

Thinking in terms of an interaction between dipole-bound and valence states does actually imply a diabatic viewpoint, and here we estimate the electronic coupling between the two diabatic states by fitting a simple avoided crossing model potential to a cut through the two adiabatic ab initio surfaces that connects the equilibrium structures of the neutral and the valence anion (cf. ref 33). The cut chosen here is a linear transit between the equilibrium geometries obtained at the Møller−Plesset second-order perturbation theory (MP2) level (see below for basis set). The barrier height along this path is an upper limit for the barrier height associated with the minimal energy pathway, and we assume the crossing structure to be largely independent of the particular pathway. The avoided crossing model potential is defined as follows:

$$\mathbf{V} = \begin{pmatrix} V_1 & W \\ W & V_2 \end{pmatrix}$$

The diagonal terms $V_1$ and $V_2$ are harmonic potentials in the coordinate $s$ defining the cut

$$V_i = \frac{1}{2}\omega_i(s - s_i^0)^2 + \upsilon_i^0$$

and the off diagonal coupling element $W$ is either assumed to be constant or depends linearly on $s$: $W = \lambda s$ (for more elaborate diabatization schemes see ref 32 and references therein; a good starting point for more recent work is ref 34). For U and UCl, the coupling vanishes for planar geometries, and therefore, in principle, a linear coupling term should be used. Yet, both ansätze lead to virtually identical fit qualities ($\chi^2$ values). Clearly, for U and UCl only the value of $W$ close to the intersection is relevant within the model, and this value will be given.

The computation of the *two* adiabatic surfaces is somewhat more involved than typical quantum chemistry applications that focus on only *one* electronic (ground) state. In the first place, the two anionic states have very different electronic structures, and a balanced description of both states (within a single calculation) is vital. In the second place, close to the avoided crossing in question the upper adiabatic state crosses the PES of the neutral molecule and is transferred into a resonance or temporary anion state that requires a nonstandard treatment by itself. Thus, computing the avoided crossing structure we cannot aim for the same level accuracy that can typically be achieved in a calculation for the ground state of a comparable size anion.

As discussed in ref 33, a reasonably balanced description of the two anionic states can be achieved employing electron propagator based approaches. For U and UCl, we employed the second-order perturbation expansion of the Green's function, and we will refer to this method as ADC(2).[35] The quality of the ADC(2) results is roughly comparable with MP2 calculations for the closed-shell ground states, but owing to the strong orbital relaxation of the valence states, a slight imbalance in favor of the dipole-bound states is expected.

Let us now address the region close to the equilibrium geometry of the neutral where the upper adiabatic state is a

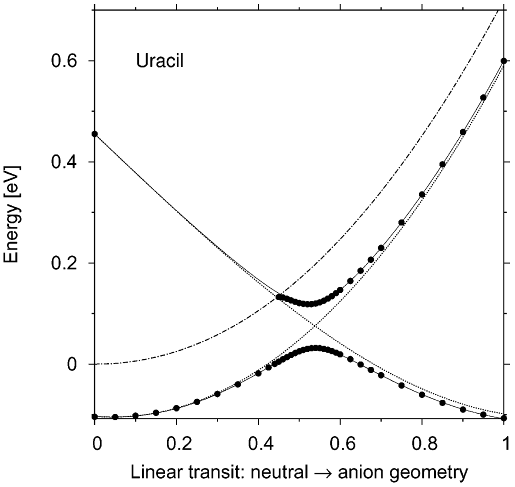

**Figure 2.** Cut through the potential energy surface of U and its two anionic states. The dashed−dotted curve is the MP2 surface of neutral U, and the full circles represent the ab initio results for the two anionic states obtained at the ADC(2) level of theory. The adiabatic and diabatic curves obtained from fitting our model potential are indicated as continuous and dotted lines, respectively.

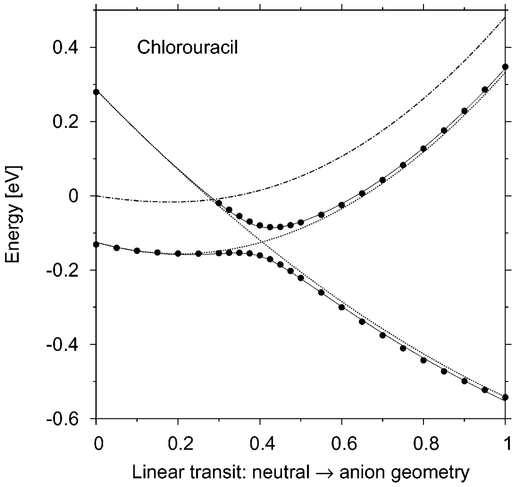

**Figure 3.** Cut through the potential energy surface of UCl and its two anionic states. The dashed−dotted curve is the MP2 surface of neutral U, and the full circles represent the ab initio results for the two anionic states obtained at the ADC(2) level of theory. The adiabatic and diabatic curves obtained from fitting our model potential are indicated as continuous and dotted lines, respectively.

resonance or temporary anion state. A resonance can be characterized by a complex Siegert energy $E = E_r - i\Gamma/2$, where $E_r$ is the energy above the neutral ($-E_r$ is the negative electron affinity) and $\Gamma$ is the resonance width, that is, related to its autodetachment lifetime $\tau = \hbar/\Gamma$. Neither $E_r$ nor $\Gamma$ can be computed using standard bound-state quantum chemistry techniques. Instead, either full-blown electron-scattering calculations are necessary, or $\mathcal{L}^2$-approaches such as the stabilization,[36,37] the complex-scaling,[38,39] or the complex absorbing potential (CAP)[40,41] methods can be used. To compute Siegert energies consistent with the ADC(2) results, we employed the recently developed complex absorbing potential ADC combination CAP/ADC(2).[42,43] In brief, an absorbing (negative imaginary) potential is added to the molecular Hamiltonian, and by this means resonance wave functions become square integrable, and the associated Siegert energies can be obtained as an eigenvalue of a complex symmetric effective Hamiltonian.[41] These calculations are expensive, and only the geometry of the neutrals was considered. The real parts of the computed Siegert energies provide a consistent anchor point for the diabatization procedure (Figure 3), and the autodetachment lifetimes are of course relevant by themselves, since the associated temporary anions are the intermediates for electron-induced reactions at higher energies.[29,44,52]

In the electronic structure calculations, Dunning's double-$\zeta$ (DZ) basis set[45] was used for UCl, and for U the standard set of d-type polarization functions was included. In the computations for the electronically bound states, these basis sets were augmented with a [1s1p] set of diffuse functions (dividing the smallest s-type and p-type exponents of the DZ set by 3) on the heavy atoms and a floating [8s6p] set (even-tempered exponents between 1.0 and 0.00016 for s-type and between 0.14 and 0.00027 for the p-type functions) located 4 Å from the ring in the direction of the dipole vector.[46] In the calculations of the Siegert energy, the DZ basis sets were augmented with a (1s6p)/[1s5p] set of diffuse functions on the heavy atoms, where the exponents have even-tempered exponents starting from the single set of diffuse exponents mentioned above and using a scaling factor of 1.6. For the computation of the equilibrium geometries of the neutrals and the valence anions of both U and UCl, the DZ sets were augmented with polarization and diffuse functions (DZPD). Geometries were optimized employing the Gaussian98 package;[47] all other calculations are based on self-consistent field computations with the MOLCAS5 package of programs,[48] and our own codes were employed to compute the MP2 energy of the neutrals and the ADC(2) electron-attachment energies.

## 3. Anionic States of Uracil and Chlorouracil

In this section, we briefly summarize—and slightly complement—what is known about the electron-binding energies of the different anionic states of $U^-$ and $UCl^-$. These values set the stage for discussing the coupling between the different anionic states. However, only the electron affinity (EA) associated with the dipole-bound state of U is well characterized, whereas there is considerable controversy regarding the electron affinities associated with the valence states. Here and in the following sections, we need to distinguish between the EA associated with dipole-bound and valence states, and in the latter case between vertical and adiabatic values (owing to their almost unchanged geometry, for dipole-bound states the vertical and adiabatic EAs are almost identical). We will refer to the vertical and adiabatic EA of a valence state as VEA and AEA and to the EA of the dipole-bound states as $EA_{DB}$.

For the U molecule, the dipole-bound $EA_{DB} \approx 90$ meV[5−8] and the negative vertical attachment energy VEA $= -0.22$ eV[49] are well known from experiment, and the adiabatic value has been bracketed $0 < AEA < EA_{DB}$.[7,8] For UCl, on the other hand, to the best of our knowledge there are no experimental values.

Regarding computed values, first some words of caution are in order. Computing EAs for both dipole-bound and valence state is a notoriously challenging task, and even for obtaining reasonable accurate results high level ab initio calculations and large basis sets are needed.[12,13,50] This is especially true for U and UCl, since their AEA values are very small. Yet, so far the few available ab initio calculations have been restricted to small basis sets,[1,4] and most theoretical studies rely on density functional theory based approaches (see, e.g., refs 2, 3, 8, 44, 51, 52). The currently available density functionals, however, are for principle reasons unsuitable for anions, in particular, for diffuse anions or weakly bound anions.[53,54] It has been observed that density functionals can yield on average quite satisfactory AEAs for certain classes of anions,[55] provided not "too diffuse" basis sets are used. Yet, this attractive low-cost technique has great difficulties when electrons are added to closed shells (see section IV.A and IV.C of ref 55), and, thus, the predictive power of these methods rests entirely on the reproduction of known AEA of similar systems.

Thus, to arrive at a reasonable estimate for the AEA of UCl one can, on one hand, "calibrate" one of the popular functionals, say B3LYP. Comparison of the available experimental[7,8] and theoretical data[2,3,8,44,51] for U suggests that the B3LYP functional overestimates the EA by 0.1−0.2 eV, and a similar conclusion has been reached by others[56] and by us on the basis of ab initio calculations. Thus, from the B3LYP results for UCl[3,44] one would infer an AEA in the range of 0.4−0.5 eV. On the other hand, one can employ empirical approaches such as G3(MP2)[57] which combine results from several relatively inexpensive ab initio calculations in an empirical formula that typically yields very accurate values. For U and UCl, we find at the G3(MP2) level AEA values of 1 meV and 0.39 eV, respectively. The value for U is in fair agreement with what is known from experiment, and since high-level ab initio methods have so far been restricted to relatively small basis sets and in the absence of any experimental value, our G3(MP2) result is arguably the most reliable AEA value presently available for UCl.

## 4. Coupling between Dipole-Bound and Valence States

The computed cuts through the adiabatic PES as well as the associated diabatic curves derived from our model potential are displayed in Figures 2 and 3. Regarding the overall accuracy of the computed curves, we reemphasize that in view of the correlated, but not highly correlated, ADC(2) level and our relatively small basis sets, we do not expect particularly accurate results. As detailed above, we are primarily aiming for the avoided crossing structure, and our EA values can certainly not compete with calculations that focus on a single state. Nevertheless, both AEA values (Figures 2 and 3) are in fair agreement with the available experimental data and other theoretical results, and the same is true for the $\mathrm{EA}_{\mathrm{DB}}$ value for U (cf. section 3). Thus, we expect that our $\mathrm{EA}_{\mathrm{DB}}$ value for UCl and, in particular, the trends between U and UCl are also sound. At the ADC(2) level we find for UCl $\mathrm{EA}_{\mathrm{DB}} = 130$ meV which is somewhat higher than the $\mathrm{EA}_{\mathrm{DB}}$ of U at the same level (104 meV) in accordance with the computed dipole moment of UCl that is about 10% larger than that of U.

Applying our simple diabatization scheme, we find diabatic potential curves that only close to the intersection deviate notably from the adiabatic curves indicative of a relatively sharp avoided crossing (Figures 2 and 3). As discussed above (section 2), from a fit quality viewpoint, there is no difference between a constant ($W$ = const) or a linear ($W = \lambda s$) coupling term. The $W$ values we present in the following originate from using a constant $W$ during the fitting procedure and are virtually identical to using a linear coupling term and evaluate it at the crossing point ($\lambda s_{\mathrm{cross}}$). In this way, we find for both molecules $\mathrm{U}^-$ and $\mathrm{UCl}^-$ almost identical electronic coupling elements of $W = 43$ meV.

These very similar values suggest that the electronic coupling is essentially independent of halogen substitution in 5 position. In view of the substantially different EAs and crossing locations of U and UCl, this is at first surprising, but since neither the dipole-bound nor the relevant valence orbital (Figure 1) shows significant contributions at the substituent, a weak dependence on the substitution in this position is plausible. The computed coupling strength should thus be transferable to UF and UBr.

Similar to the findings in ref 33, the computed coupling elements are astonishingly robust with respect to the basis set. While the particular potential energy curves, the different EA values, and the location of the crossing depend quite strongly on the employed basis set, the coupling term is virtually unchanged when, for example, the basis set is extended with polarization function (DZ vs DZP). Thus, in contrast to the great challenge of computing accurate EAs of both dipole-bound and valence states, it seems to be far easier to compute reasonable estimates of the electronic coupling between these states.

## 5. Discussion and Conclusions

We have investigated the electronic coupling of dipole-bound and valence states of U and UCl, and fitting the computed adiabatic ab initio results to a diabatic model potential we find an electronic interaction of $W = 43$ meV for both anion pairs. This value is about 1 order of magnitude smaller than the vertical energy differences of the diabatic states at their respective equilibrium structures, and thus both U and UCl are still in the weak coupling regime, though at the threshold of a valid adiabatic description. A somewhat smaller but comparable coupling strength of 30 meV had been found for the dipole-bound and valence states of nitromethane ($\mathrm{H_3C{-}NO_2}$).[33] For the time being, it is a very long leap, and more species need to be investigated, but it may turn out that this order of magnitude is typical for dipole-bound/valence state interactions.

For both U and UCl (as well as for nitromethane), the dipole-bound states are clearly very efficient doorways to the valence states. In first-order perturbation theory, the transition rate is essentially $W^2$ times a Franck−Condon factor, and since the main difference between the geometries of neutral and valence anion of U and UCl, respectively, is a slight ring puckering, the Franck−Condon factors can hardly be small. Yet, for U the formation of the valence state is nevertheless improbable, since it is somewhat higher in energy than the dipole-bound state (cf. section 3). Thus, on the contrary, the strong coupling does provide a doorway for the decay of the valence anion via (vibrationally excited) dipole-bound states. In contrast, the valence state of UCl is expected to lie at least 300 meV below its dipole-bound state (section 3), and thus there is a sufficient amount of energy that can be "dissipated" by intramolecular vibrational relaxation and that can stabilize the valence state creating a long-lived anion (300 meV $\approx$ 2400 $\mathrm{cm}^{-1}$ corresponding to several quanta of the different ring-pucking modes that show harmonic frequencies between 80 and 800 $\mathrm{cm}^{-1}$).

In conclusion, the UCl example shows that zero- and near zero-energy electrons with thermal energies may be trapped or induce reactions in the following way: As a first step, the electron is captured into the dipole-bound orbital. As long as the system is in this state, energy transfer to the nuclei is unlikely, owing to the essentially parallel PES of neutral and dipole-bound state. Yet, since the dipole-bound state exhibits a strong electronic interaction with the lowest valence state, intramolecular electron transfer from the dipole-bound orbital onto the nuclear framework will be fast and can compete with electron reejection. Then, depending on the valence EA, the EA of possible dissociation products, and on the details of the intramolecular redistribution of vibrational energy, long-lived radical anions can be formed or dissociations can proceed. While this doorway scheme has been demonstrated to be valid in the Rydberg electron-transfer context, the importance of its role in free-electron attachment remains an open question. Our calculations suggest that this indirect mechanism may well turn out to govern attachment of thermal electrons to a great variety of polar species. More experimental and theoretical work is needed to test the proposed scheme and to put it on a firm basis.

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**Note Added in Proof.** In a recent letter (Scheer, A. M.; Aflatooni, K.; Gallup, G. A.; Burrow, P. D. *Phys. Rev. Lett.* **2004**, *92*, 068102) a dipole-bound state of uracil was invoked as an intermediate to explain electron-induced cleavage of an N−H bond.

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