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Nonconventional Hydrogen Bonds: A Theoretical Study of [uracil-L]$^-$ (L = F, Cl, Br, I, Al, Ga, In) Complexes

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The interaction of L$^-$ (L = F, Cl, Br, I, Al, Ga and In) with a uracil molecule has been studied with B3LYP density-functional geometry optimizations and electron-propagator calculations of vertical electron detachment energies. Because the extra electron of the anion is localized on L, nonconventional hydrogen bonds are formed. The interactions of halide anions with uracil are similar to the interactions of uracil with Cu$^-$, Ag$^-$ and Au$^-$ that were reported previously. Whereas halide and transition metal anion complexes with uracils are singlets, the anions formed with Al, Ga and In are triplets. Vertical electron detachment energies (VEDEs) are higher for (uracil-L)$^-$ than the analogous values for isolated L$^-$ anions. Predicted VEDEs are assigned to Dyson orbitals that may be localized on L$^-$ or uracil.

Introduction

It is well-known that DNA is a very important molecule, with fundamental relevance in biological systems and possible applications in the development of miniature electronic devices.[1−4] In biological processes involving DNA, the interaction of metal ions with nitrogen bases can stabilize different tautomers, modifying the orientation of hydrogen bonds that are crucial for the formation of the double helix structure.[5−17] Some authors suggested that metal atoms and ions interacting with DNA provide extra electrons that can induce structural modifications,[18,19] with great consequences for the biological function of this molecule. For the development of miniature electronic devices, it is very important to obtain a detailed understanding of the charge transfer processes that take place within the DNA strand. With this in mind, interactions of metal atoms and ions with the DNA molecule have been the subject of several investigations in recent years. Their main conclusion is that metal cations and anions attached to conjugated molecular systems such as the nitrogen bases of DNA are associated with substantial charge-transfer effects. These ions may function as electron donors or acceptors and therefore modulate the properties of the system.

Several studies of the interaction of metal atoms and ions with DNA and RNA nitrogen bases have been reported previously.[12,20−38] Toxicity, reactivity and conductivity of various metal atoms and ions attached to nitrogen bases are some of the main subjects of these investigations. Some experiments are focused on the detachment of an extra electron[39,40] using photoelectron spectroscopy (PES), a very effective tool in the study of small anionic systems in gas phase. In these experiments, the anion spectroscopically accesses the ground electronic states of the neutral, when an extra electron is photodetached from the system. This is important because many electronic states of the neutral species may be difficult to detect with other spectroscopic techniques. Theoretical studies are useful for the interpretation of these spectra, because the electron vertical detachment energies can be calculated with several methods. With these values, it is possible to define the structures that are present in the experiment and to understand the charge transfer that is at hand.

To study the interaction of DNA bases with metal atoms, an analysis of the interaction between copper atoms and ions with guanine and uracil was performed.[20] For the anionic systems, the vertical detachment energies are similar to the dissociation energies of a hydrogen atom. We also analyzed the interaction of cytosine with metal atoms which have closed shell electronic configurations such as Ca, Zn and Cd and with metal atoms that have open shell electronic configurations such as Al, Cu and Ag.[32,37] Neutral, cationic and anionic systems were studied to assess the influence of atomic charge on bond formation. In these systems, the most stable isomer is derived from the canonical isomer of cytosine. The interaction between metals and cytosine is predominantly electrostatic, and becomes stronger as the global charge of the metal increases. In general, metal cations bind more strongly than metal atoms to cytosine molecules. For the anions, the results are more interesting. Al, Ca, Zn and Cd atoms in the corresponding [M-cytosine]$^-$ complexes are almost neutral, for the metal atoms have a closed shell electronic configuration. An extra electron on the metal atoms produces less stable systems. In the case of Cu and Ag, the extra electron produces a closed shell metal electron configuration, which stabilizes the systems. Metal atoms (Cu and Ag) in [M-cytosine]$^-$ are negatively charged and represent proton acceptors containing lone-pair electrons. Whereas interaction in the case of the neutrals and the cations is electrostatic, for the anions it is similar to a hydrogen bond. The bond is formed between a proton donor group (N−H) and a proton acceptor (Cu$^-$ and Ag$^-$) containing lone-pair electrons. In both cases, the anions show nonconventional hydrogen bonds, similar to those previously reported for gold atoms and clusters.[41] To

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TABLE 1: Additional Functions for Stuttgart Pseudopotential Basis Sets and Calculated Electron Affinities

	exponents of additional functions				VEDE (eV)	
atom	s	p	d	f	P3	exp
Ag	0.005	0.008	0.022 0.007 0.002	0.199 0.050 0.001	1.00	1.30[67]
Au	0.005	0.008	0.006	0.45 0.15 0.05 0.01	2.00	2.30[67]
I			1.00 0.30 0.10	0.50 0.125	2.90	3.06[68]
In	**0.020**	**0.010**	**0.50** **0.13** **0.04** **0.01**	**0.38** **0.10** **0.02**	**0.34**	**0.30**[69]

continue the study of the formation of these nonconventional hydrogen bonds, interactions of Cu, Ag and Au anions with uracil were examined.[38] As can be expected, these closed shell, anionic metal atoms form stable complexes with DNA bases. In these systems, metal atoms could serve as nonconventional proton acceptors, and nonconventional hydrogen bonds could be formed, playing a significant role in stabilizing as well as destabilizing DNA base pairs.

An important question addressed in the present work is if nonconventional hydrogen bonds are also present when other anions (with stable, closed shell electronic configurations) interact with DNA bases. Here we continue with the analysis of (uracil-L)$^-$ (L = F, Cl, Br, I, Al, Ga and In) and we compare with previous reported results (anions of uracil-Cu, uracil-Ag and uracil-Au). We would like to know if the interaction of uracil with halogens is similar to the interaction of metal atoms with the same nitrogen base. To establish the influence of the metal and nonmetal atomic charge on the bond formation, and to examine the presence of nonconventional hydrogen bonds, optimized geometries, Mulliken atomic charges and dissociation energies are used to provide insights on the binding mechanism of these complexes. To analyze if it is possible to produce the detachment of an electron from the anion and also the dissociation of the compounds, dissociation energies are also reported. This information could be useful for further experimental studies.

Computational Methods

Density functional theory[42−44] as implemented in *Gaussian 03*[45] was used for all the calculations. Complete optimizations without symmetry constrains were done with the hybrid three parameter B3LYP[46−48] functional. Two basis sets were employed: LANL2DZ[49−51] for Cu, Ag, Au, I, In, and 6-311G**[52] for F, Cl, Br, Al, C, H, O, and N. Harmonic frequency analyses allowed us to verify optimized minima.

Previous studies show that DFT reproduces equilibrium geometries and relative stabilities with hybrid functionals, which partially include the Hartree−Fock exchange energy. These results are largely consistent with those obtained using Møller−Plesset perturbational theory at second order and basis sets of medium quality, such as 6-31G(d,p), and cc-pVDZ.[53−55]

An adequate number of isomers used during the initial stage of the study allowed us to extensively explore the potential surface energy, in search of the global minimum. The number of initial geometries examined here is large enough to reliably identify the global minima. To compute the vertical electron detachment energies (VEDEs) of anionic species, further single-point calculations were required. The most stable structures with X = F, Cl, Br and I are in singlet states. Optimized triplets for (uracil-M)$^-$ with M = Al, In and Ga are more stable than singlets by more than 10 kcal/mol.

Global minima found in the above calculations were reoptimized with second-order Møller−Plesset (MP2) theory. Augmented, correlation−consistent triple-ζ bases (aug-cc-pVTZ) were used for H, C, N, O, F,[56] Al,[57] Cl,[57] Cu,[58] Ga,[59] and Br.[59] Stuttgart pseudopotential bases[60] augmented with extra functions were used for I, Ag, Au, and In. Basis augmentations produced close agreement between electron propagator calculations[61−66] and experimental[67−69] electron detachment energies of atomic anions. Exponents of the additional functions and VEDEs of atomic anions are presented in Table 1. VEDEs were calculated with the Partial Third Order[66] (P3) approximation of electron propagator theory. Newly optimized structures differed little from DFT-optimized ones except for L = F and Ga. In the case of F, almost complete detachment of a proton from uracil occurred. The (Ga-Uracil)$^-$ system became nonplanar. VEDEs of (U-L)$^-$ structures were then calculated with the P3 method and the basis sets described above. Semidirect algorithms[70,71] were involved in electron propagator calculations. Resulting VEDE values are compiled in Tables 3–5.

In P3 and OVGF electron propagator calculations, an electron binding energy, E_p, may be expressed as

$$E_p = \varepsilon_p + \sum\nolimits_{pp} (E_p)$$

where ε_p is the Hartree−Fock orbital energy and $\Sigma_{pp}(E_p)$ is a diagonal element of the self-energy matrix.[62,66] For each VEDE calculated with electron propagator methods, there corresponds a Dyson orbital defined by

$$\varphi^{\text{Dyson}}(x_1) = N^{-1/2} \int \Psi^*_{N-1}(x_2,x_3,x_4,\ldots x_N)\, \Psi_N(x_1,x_2,x_3,x_4,\ldots x_N) \times \mathrm{d}x_2\, \mathrm{d}x_3,\ \mathrm{d}x_4, \ldots, \mathrm{d}x_N$$

where N is the number of electrons in the initial state and x_i is the space-spin coordinate of electron i. Pole strengths, p, are defined by

$$p = \int \left|\varphi^{\text{Dyson}}(x_1)\right|^2 \mathrm{d}x_1$$

and are proportional to photoionization intensities. When pole strength values are greater than 0.85, the Dyson orbitals are very close to canonical Hartree−Fock orbitals. For the systems under current investigation, all pole strengths were greater than 0.86.

Although there is no universally accepted method for assigning electrostatic charges to atoms, and no clearly pertinent experimental technique is currently available, in a previous study, de Oliveira et al.[72] reported a comparison of the charges obtained using the Mulliken and Bader population analysis methods. With both methods, the qualitative description of the atomic charges is the same. For this reason, in this paper, Mulliken atomic charges are used in the discussion of the qualitative behavior involved in the charge-transfer process. Results were analyzed, using the MOLEKEL[73] and the BALL&STICK[74] packages.

Results and Discussion

To form nonconventional hydrogen bonds, at least four prerequisites must be satisfied,[35,41] namely, (i) there should be

TABLE 2: Results with B3LYP/6-311G for [uracil-L]$^-$ [a]**

anion	atomic charge of L	VEDE	I_{ad}	ΔE_{dh}	ΔE_{dis}	bond distance		bond angle
						N1−H1	H1−L	(N1−H1−L)
uracil-F	−0.5	5.6	4.7	5.7	3.7	1.6	1.0	165
uracil-Cl	−0.9	4.7	4.6	5.0	1.2	1.1	2.1	152
uracil-Br	−0.9	4.4	4.4	4.8	1.2	1.0	2.3	148
uracil-I	−0.9	4.2	4.0	4.6	1.2	1.0	2.6	145
uracil-Cu	*−0.9*	*2.1*	1.6	*2.1*	1.2	1.0	*2.3*	*144*
uracil-Ag	*−0.9*	*2.1*	2.0	*2.7*	1.1	1.0	*2.5*	*144*
uracil-Au	*−0.9*	*3.8*	3.3	*3.6*	1.2	1.0	*2.3*	*148*
uracil-Al	**−0.8**	**1.0**	**0.5**	**0.9**	**0.8**	**1.0**	**3.0**	**144**
uracil-Ga	**−0.8**	**1.1**	**0.5**	**1.2**	**0.8**	**1.0**	**2.9**	**145**
uracil-In	**−0.8**	**1.0**	**0.6**	**1.2**	**0.9**	**1.0**	**3.3**	**136**

[a] For [uracil-I]$^-$ results were obtained with B3LYP and LANL2DZ. For each complex, the L Mulliken atomic charge, the vertical electron detachment energy (VEDE in eV), the adiabatic ionization energy (I_{ad} in eV), the dehydrogenation energy (ΔE_{dh} in eV), the dissociation energy (ΔE_{dis} in eV), bond distances (Å) and angles (deg) are reported. Geometric parameters correspond to the optimized anions. Some of the results with transition metal atoms (*in italics*) are from refs 20 and 38.

TABLE 3: MP2 Optimized Structural Parameters and Vertical Electron Detachment Energies of Anionic Halouracils

ligand (L)	bond length		bond angle	VEDE (eV)	
	N1−H1	H1−L	N1−H1−L	P3	MO
F	1.52	1.00	170.8	4.68	6a″ π_1 U
				6.07	28a′ n_1 U
				6.40	5a″ π_2 U
				6.70	27a′ n_2 U
Cl	1.05	1.98	151.0	5.11	7a″ p Cl
				5.14	31a′ p Cl
				5.28	30a′ p Cl + N−H
				6.08	6a″ π_1 U
Br	1.04	2.18	147.6	4.74	10a″ p Br
				4.78	37a′ p Br
				4.93	36a′ p Br + N−H
				6.21	9a″ π_1 U
I	1.04	2.44	146.3	4.16	6a″ p I
				4.18	27a′ p I
				4.36	26a′ p I + N−H
				6.37	5a″ π_1 U

TABLE 4: MP2 Optimized Parameters and Vertical Electron Detachment Energies of Anionic Metallouracils (Cu, Ag, and Au)

ligand (L)	bond length		bond angle	VEDE (eV)	
	N1−H1	H1−L	N1−H1−L	P3	MO
Cu	1.04	2.29	145.8	1.94	35a′ s Cu
				6.34	9a″ π_1 U
Ag	1.04	2.32	141.5	1.96	31a′ s Ag
				6.32	8a″ π_1 U
				6.33	7a″ d Ag
				6.33	30a′ d Ag
				6.42	6a″ d Ag
				6.42	29a′ d Ag
Au	1.08	2.00	149.9	3.45	31a′ s Au
				5.50	30a′ d Au
				5.50	7a″ d Au
				5.68	29a′ d Au
				5.68	28a′ d Au
				5.96	8a″ π_1 U

TABLE 5: MP2 Optimized Parameters and Vertical Electron Detachment Energies of Anionic Triplet Metallouracils (Al, Ga, In)

ligand (L)	bond length		bond angle	VEDE (eV)	
	N1−H1	H1−L	N1−H1−L	P3	MO
Al	1.03	2.80	148.2	1.03	7a″ π_1, p Al
				1.32	30a′ α_2, sp Al
				4.42	29a′ β_1, s Al
				6.57	5a″ β_2, π_1 U
Ga[a]	1.03	3.00	140.9	1.08	40a α_1, p Ga
				1.24	39a α_2, sp Ga
				5.09	38a β_1, s Ga
				6.61	37a β_2, π_1 U
In	1.03	3.03	143.1	0.98	27a′ α_1, p In
				1.21	26a′ α_2, sp In
				4.78	25a′ β_1, s In
				6.63	5a″ β_2, π_1 U

[a] Ga complex is nonplanar.

evidence of bond formation (one X−H stretching mode around 80 cm^{-1}), (ii) the bond has to involve one hydrogen atom which is bonded to L along the N−H bond direction, (iii) the N−H bond must be elongated in the compound, relative to the isolated uracil, and (iv) the sum of the van der Waals radii is required to be larger than the hydrogen bond distances.

(uracil-L)$^-$ (L = F, Cl, Br, I). Despite the importance of the effects that halogens can have on the stability of nitrogen bases, little is known concerning the interaction of DNA nitrogen bases with halogen atoms. Structures and properties of halouracils (halogen replaces the H atoms at five sites of uracil) were reported previously,[75] but there is little knowledge concerning the interaction of halogen atoms with nitrogen bases, specifically in the anionic state. For halouracils, the compounds adopt a nonplanar structure that is not suitable for stacking, and halogen substitution has a smaller effect on the ionization energy than the electron affinity of uracil. These results are consistent with previous suggestions that establish that halouracils enhance the sensitivity of DNA and RNA to ionizing radiation. On the other hand, the interaction of metal atoms with nitrogen bases may stabilize different tautomers of the nitrogen bases, but until now, the effect of the halogens in the stabilization of diverse tautomers has been unknown. For this reason, in the analysis of halogens with uracil, initial geometries include several tautomers and bonding schemes to different hydrogen atoms. The general picture of optimized ground-state structures of (halogen -uracil)$^-$ complexes is shown in Figure 1A. Structures are planar and for Cl, Br and I, the optimized geometries are more or less the same. Table 2 reports the atomic charge on the L atom, selected bond distances, bond angles, vertical electron detachment energies (VEDEs) and dissociation energies (ΔE_{dh} and ΔE_{dis}) according to the following schemes:

$$[\text{uracil-L}]^- \rightarrow \text{uracil} + \text{L}^-$$

$$\Delta E_{dis}[\text{uracil-L}]^- \rightarrow (\text{uracilL-H})^- + \text{H} \qquad \Delta E_{dh}$$

(The notation (uracilL-H)$^-$ signifies a dehydrogenated uracil coordinated to L$^-$.) Positive values of the dissociation energies

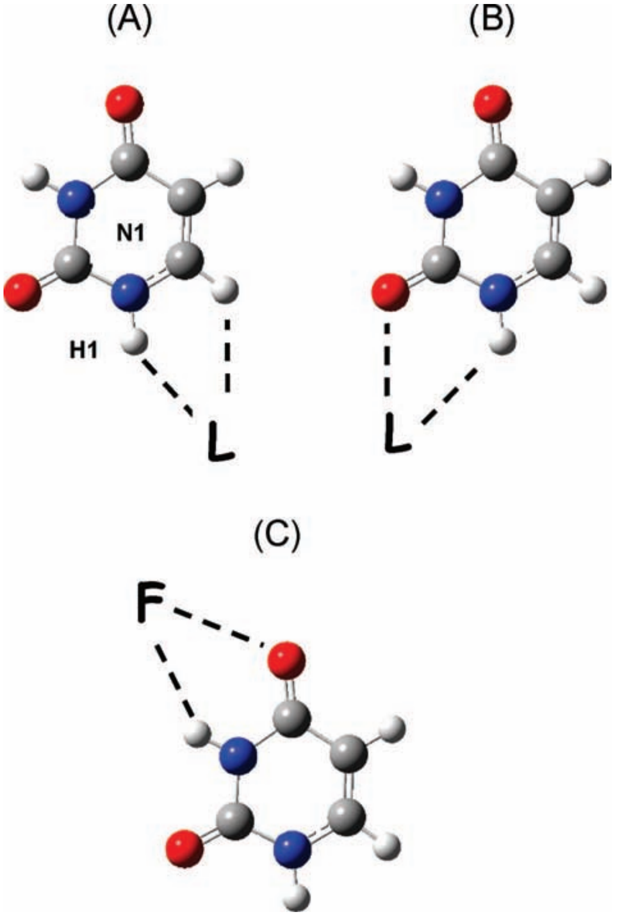

Figure 1. (A) Schematic representation of the optimized structures of [uracil-L]$^-$. Selected bond distances and angles are reported in Table 2. (B) Schematic representation of the optimized structures of [uracil-L]. (L = Al, Ga, In). For Cl, Br and I, the optimized neutral structure is equal to the optimized anion (structure A). Structure C is a schematic representation of [uracil-F] (neutral).

indicate that the compound is more stable than uracil plus L$^-$ or (uracilL-H)$^-$ plus H atom.

The results for Cl, Br and I are similar. The halogen atom is negatively charged and it is bonded to one hydrogen atom of the uracil molecule that is partially positive. For F$^-$, the results are different. The atomic negative charge of F is smaller, the dissociation energy is higher, the N−H bond distance is longer, the H-L distance is shorter, the bond angle is larger and the VEDE is higher. These results can be explained with the optimized structures. For (uracil-F)$^-$, the hydrogen atom is almost dissociated from the uracil molecule. The system is more like HF and a dehydrogenated uracil anion, and for this reason, the results for the dissociation energy and VEDEs are different.

In our systems with halogens, all the prerequisites for the nonconventional hydrogen bonds are satisfied as can be seen in Table 2. Also, there is one stretching X-L mode that is equal to 230, 158, 107 and 90 cm^{-1}, for F, Cl, Br and I, respectively. The stretching modes also indicate that the F−H bond is stronger than the Cl−H bond. The weakest bond according to the L-H stretching modes is with I.

Nonconventional hydrogen bonds are geometrically described in terms of bond lengths and angles. In the case of (uracil-L)$^-$ (L = Cl, Br and I), N−H−L bond angles fall within a range of 145−152°. When we compare this bond angle with those previously reported[76] (N−H−O hydrogen bond angles were 177° and 127° for strong and weak hydrogen bonds, respectively) these can be classified as intermediate. However, dissociation energies (ΔE_{dis}) are equal to 1.2 eV; therefore these can be classified as strong hydrogen bonds. In these hydrogen bonds, the negative atom (Cl, Br and I) represents a proton acceptor. In the case of uracil, the bond is formed between a proton donor group (N−H) and a proton acceptor (Cl$^-$, Br$^-$ and I$^-$). To explain the high value for the dissociation energy, we must consider the possibility that another hydrogen bond is formed by the C−H group which is close to the halogen atom. With Cl, Br and I, the C−H−L bond length is approximately 3.0 Å and the bond angle is equal to 110−20°. These hydrogen bonds are weak but may have an influence on the stabilization of the system. The individual hydrogen bond is intermediate, if one refers to the bond angle, but the second hydrogen bond strengthens the interaction between uracil and the halogen anion and thus the binding energy is raised. We reported previously[20,38] similar results for (uracil-Cu)$^-$, (uracil-Ag)$^-$ and (uracil-Au)$^-$. These values are included in Table 1 for comparison. The N−H−L (L = Cu, Ag and Au) bond angles fall within a range of 144−148° and hence, the interaction may also be considered as representing an intermediate hydrogen bond. That the binding energies are between 1.1 and 1.2 eV points to the same conclusions. It can also be possible that the halide ions act as conventional proton acceptors. In this case, the dissociation energies agree with the corresponding values for ionic conventional hydrogen bonds, specifically negative-ion hydrogen bonds.[77] In summary, in the case of halogens, the anions show hydrogen bonds, similar to those previously reported for other systems[32,35−38,41] with transition metal atoms interacting with uracil or other molecules, but these hydrogen bonds are stronger than for other molecules and we can conclude that, for these systems, there are ionic conventional hydrogen bonds.

(uracil-L)$^-$ (L = Al, Ga and In). Optimized structures of these systems are reported in Figure 1A. In these cases, the ground states are triplets. The compounds adopt a planar structure with the metal atom interacting with one hydrogen atom. For Al, Ga and In, the optimized structures are more or less the same. Results are summarized in Table 2 and, as can be seen, they are similar. Metal atoms are negatively charged and the bond is toward one hydrogen atom that is positive. The atomic negative charges are almost equal and the dissociation energies also are alike. N−H bond distances are identical in the three cases, but the H−Ga distance is shorter than the H−Al and H−In distances. VEDEs are smaller than for (uracil-L)$^-$ (L = halogen) and uracil interacting with transition metals. In our systems with Al, Ga and In, all the requirements for nonconventional hydrogen bonds are satisfied, as can be seen in Table 2. Also, there is one stretching L-H mode that is equal to 77, 57, 53 cm^{-1}, for Al, Ga, and In, respectively. The stretching modes also indicate that the Al−H bond is stronger than the Ga−H bond. The weakest bond, according to the L-H stretching modes, is with In. Comparing these values with those reported above for halogen atoms, it can be seen that the L-H bond strength with these metal atoms is smaller than with halogens. The dissociation energies with Al, Ga and In are also smaller than the corresponding ones for the halogen atoms. In the case of (uracil-L)$^-$ (L = Al, Ga and In), N−H−L bond angles fall within a range of 136−145° and can be classified as intermediate. According to the calculated dissociation energies (0.8 and 0.9 eV), the interactions can be classified as strong hydrogen bonds. Metal ions also represent proton acceptors, and also in these cases, other hydrogen bonds are formed. With Al, Ga and In, the C−H − L bond length is approximately 3.4 Å and the bond angle is equal to 110−125°. These hydrogen bonds are weak but may have an influence on the stabilization of the system. In summary, in the case of these metal atoms, the anions show nonconventional hydrogen bonds, similar to those previously reported for other systems[32,35−38,41] with metal atoms interacting with uracil or other molecules, and comparable also to those formed with the halogen ions. To this point, the interactions between anionic halogens and metal atoms with uracil are alike.

Ionization, Dissociation and Dehydrogenation. One important question concerning these systems is if it is possible to carry out photoelectron experiments. For this purpose, it is important to have the vertical ionization energies of the anions and some dissociation energies. The comparisons between these values allow us to predict some results that could occur in a photoelectron experiment. In Table 2 these values are reported. As can be seen, VEDEs for (uracil-L)$^-$, when L = Al, Ga and In are considerably smaller than the corresponding values for F, Cl, Br and I. For transition metal atoms interacting with uracil in the anionic state, VEDEs are intermediate. It is possible to explain these differences in terms of electronic configurations. Anionic halogens present the configurations of noble gas atoms, which are very stable. Anions of the transition metal atoms Cu, Ag and Au show closed shell electronic configurations that are isoelectronic with Zn, Cd and Hg. On the other hand, for Al, Ga and In the anions are triplets that have open shell, less stable electronic configurations. This comparison explains the low value for the vertical electron detachment energies. In any case, the hydrogen bond increases the VEDEs of the anions.

Such transitions place the resulting neutral complexes energetically above dissociation thresholds for the halogen and transition metal systems. For the triplet cases, the VEDEs are close to the dissociation energies. The predicted VEDEs are within the energetic range of typical anion photoelectron experiments. Discrete transitions may be observable provided that neutral minima with structures that are similar to the anions exist (see Figure 1). For uracil-F, the N−H bond distance is shorter for the neutral (1.02 Å) than for the anion (1.6 Å) whereas the F−H bond length is longer for the neutral (1.8 Å) than for the anion (1.0 Å). These results indicate that the proton is transferred from uracil to the fluoride in the anionic structure. For the other systems, the N−H bond distance is similar and the L−H bond length is different. For the neutrals, it becomes longer for Cl, Br and I and shorter for Al, Ga and In. In the neutral systems, Al, Ga and In also present an interaction with one oxygen atom of the uracil molecule. The L−O bond distances are (in Å) 2.13, 2.40 and 2.47 for Al, Ga and In, respectively. With the optimized neutral, the adiabatic ionization energy (I_{ad} in Table 2) of the anion was obtained. As can be seen in Table 2, for uracil-halogen the VEDE and I_{ad} values are similar, except for uracil-F because in this case, the anion is a dissociated system (the anion uracil-H plus HF). For Al, Ga and In, metal atoms are closer to the uracil molecule and the I_{ad} is smaller than the VEDE. For these systems we can say that there is an influence of the L−O anchor on the stabilization of the neutral systems, which is reflected in the I_{ad} values for these molecules.

Vertical Electron Detachment Energies. Electron propagator results for VEDEs of the halide-uracil complexes are displayed in Table 3 along with structural information on the anionic ground state. The character of the Dyson orbitals is summarized in the MO column. The lowest VEDEs for the fluoride complex correspond to π or lone pair functions on the base. However, Dyson orbitals for the three lowest VEDEs in the other three complexes are localized on the halide. Stronger anion−molecule interactions in the F case cause greater stabilization of the anion-centered Dyson orbitals. The fourth VEDEs for these three systems have Dyson orbitals that resemble the base HOMOs. Whereas the halide VEDEs are increased by the presence of intermolecular interactions, the base VEDEs are decreased by the presence of an anion's electrostatic potential.

Transition metal systems are considered in Table 4. Here the lowest VEDE of each complex corresponds to a Dyson orbital that resembles a valence s orbital on the metal atom. For all of these complexes, there is a large gap between the first and second VEDEs. The latter transitions may be associated chiefly with a base π orbital or with a metal d orbital.

For the triplet complexes with group 13 metals, the first two VEDEs that are listed in each case correspond to final state doublets (Table 5). Dyson orbitals for these transitions consist chiefly of p functions on the metal atoms. For all three complexes, there is a large gap between the second and third VEDEs. The latter transitions correspond to quartet final states where an electron has been removed from a valence s orbital on the metal atom. The last entries belong to higher quartet states with π holes on uracil.

Conclusions

In all the complexes under study, the most stable structures include the most stable tautomer of the uracil molecule. As a consequence of the electronic configuration of the atoms bonded to uracil, halogens and metal atoms are negatively charged in (uracil-L)$^-$. These results are similar to those previously reported for Cu, Ag and Au. As a consequence, nonconventional hydrogen bonds are formed with the negatively charged halogen or metal atoms. Stable anion−molecule complexes are formed when L$^-$ has a closed-shell electron configuration. In such cases, L may be a halide or a coinage metal atom. Both kinds of atoms are capable of being proton acceptors. However, L$^-$ need not have a closed-shell configuration for stable [uracil-L]$^-$ complexes to form. For complexes with Al, Ga and In, the extra electron also localizes on the metal atom. Formation of anion−molecule complexes increases the anion's electron detachment energy and reduces the electron binding energies of the base. In other words, the electron affinity of uracil-L is higher than the corresponding value of the halogen or metal atoms and the uracil molecule. This may be important for future applications, where the movement of the electrons is important.

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