

Photoelectron spectrum of valence anions of uracil and first-principles calculations of excess electron binding energies

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(Received 17 March 2008; accepted 3 July 2008; published online 5 August 2008)

The photoelectron spectrum (PES) of the uracil anion is reported and discussed from the perspective of quantum chemical calculations of the vertical detachment energies (VDEs) of the anions of various tautomers of uracil. The PES peak maximum is found at an electron binding energy of 2.4 eV, and the width of the main feature suggests that the parent anions are in a valence rather than a dipole-bound state. The canonical tautomer as well as four tautomers that result from proton transfer from an NH group to a C atom were investigated computationally. At the Hartree–Fock and second-order Møller-Plesset perturbation theory levels, the adiabatic electron affinity (AEA) and the VDE have been converged to the limit of a complete basis set to within ± 1 meV. Post-MP2 electron-correlation effects have been determined at the coupled-cluster level of theory including single, double, and noniterative triple excitations. The quantum chemical calculations suggest that the most stable valence anion of uracil is the anion of a tautomer that results from a proton transfer from N1H to C5. It is characterized by an AEA of 135 meV and a VDE of 1.38 eV. The peak maximum is as much as 1 eV larger, however, and the photoelectron intensity is only very weak at 1.38 eV. The PES does not lend support either to the valence anion of the canonical tautomer, which is the second most stable anion, and whose VDE is computed at about 0.60 eV. Agreement between the peak maximum and the computed VDE is only found for the third most stable tautomer, which shows an AEA of ≈ -0.1 eV and a VDE of 2.58 eV. This tautomer results from a proton transfer from N3H to C5. The results illustrate that the characteristics of biomolecular anions are highly dependent on their tautomeric form. If indeed the third most stable anion is observed in the experiment, then it remains an open question why and how this species is formed under the given conditions. © 2008 American Institute of Physics. [DOI: 10.1063/1.2965128]

I. INTRODUCTION

There is growing evidence that anions of nucleic acid bases (NBs) can be formed due to the trapping of low-energy electrons, which are produced in living cells by high-energy radiation. Recent experiments suggest that single and double strand breaks develop in DNA that is exposed to low-energy electrons.¹ Furthermore, charged nucleobases play a critical role in electron and hole transfer in DNA.^{2,3} Pyrimidine bases, that is, uracil (U), thymine (T) and cytosine (C), are believed to have higher electron affinities than purine bases (guanine and adenine) as deduced from both experimental^{4–6} and computational studies.^{7–10} As a consequence, pyrimidine rather than purine bases have been considered as trapping sites for excess electrons in DNA.^{11–13}

Our recent results have provided new insights into the stability of the valence anions of NBs. We have recognized that the most stable tautomers of neutral NBs, which were routinely probed in computational^{7–10} and some experimental

studies,^{5,6} are typically not the most stable structures for anionic NBs.^{14–20} The most stable tautomers of anionic NBs appeared to be the ones with a proton transferred from an NH group of the canonical tautomer to a C atom (but not to an O or N atom, which had been assumed before). At first, the stability of the new anionic tautomers was counterintuitive, and their discovery had been facilitated by a series of studies on intermolecular proton transfer reactions involving anions of NBs.^{21–23}

Ab initio results, obtained at the coupled-cluster level of theory with single, double, and perturbative triple excitations [CCSD(T)] (Refs. 24–28) with an augmented correlation-consistent polarized valence double-zeta basis set (aug-cc-pVDZ, in the following abbreviated as AVDZ)^{29,30} indicated that some of the new tautomers of uracil,¹⁵ thymine,¹⁶ guanine,^{17,18} and adenine¹⁹ support valence anions that are adiabatically bound with respect to the corresponding canonical neutral. The theoretical predictions for guanine and adenine were in good agreement with the photoelectron spectra of their anionic species.^{18,19} In the case of uracil,¹⁵ the computational results indicated that such a rare-tautomer

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anion was adiabatically *bound* by only 171 meV. For comparison, at the same CCSD(T)/AVDZ level of theory, the valence anion of the canonical uracil tautomer was *unbound* by 51 meV. However, the most recent and more accurate computational results indicate that the canonical tautomer is bound by 40 ± 5 meV.³¹ The significantly improved accuracy of the adiabatic electron affinity (AEA) and the electron vertical detachment energy (VDE) was accomplished by obtaining basis-set saturated contributions at the Hartree–Fock and second-order Møller–Plesset (MP2) levels of theory and including high-order electron-correlation effects at the CCSD(T) level.

The purpose of the present work is twofold: (i) to apply the same computational methods, as used in Ref. 31 for the canonical tautomer, to four other tautomers in order to obtain accurate AEA and VDE data for uracil, and (ii) to measure the photoelectron spectrum of valence anions of uracil.

II. METHODS

A. Negative ion photoelectron spectroscopy

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed frequency photon source and energy analyzing the resultant photodetached electrons. This technique is governed by the energy-conserving relationship $h\nu = EKE + EBE$, where $h\nu$ is the photon energy, EKE is the measured electron kinetic energy, and EBE is the electron binding energy. Briefly, both mass spectra and photoelectron spectra were collected on an apparatus consisting of a laser vaporization source employing a Nd:YAG (yttrium aluminum garnet) laser, a linear time-of-flight mass spectrometer for mass analysis and selection, a second Nd:YAG laser used for photodetachment, and a magnetic bottle used for electron energy analysis. The details of our apparatus have been described elsewhere.³² The ion source consisted of a rotating, translating uracil-coated metal rod (Cu or Ag), a laser beam entrance port, a pulsed gas valve to feed pulses of helium into the laser-sample interaction region, and a gas expansion exit nozzle. Typically, helium gas at 4 bars was expanded in synchronization with laser ablation pulses. The uracil-coated rods were prepared by pressing uracil powder directly onto the metal rod to form a thin layer on its surface. The uracil coating was then ablated at very low laser power with the second harmonic (532 nm) of a Nd:YAG laser. We speculate that the role of the metal rod was to supply photoemitted electrons. No mixed metal/uracil cluster anions were observed.

This ion source arrangement produces anion states that differ dramatically from those generated in our previous studies. In our earlier work, NBs were thermally evaporated in an argon filled stagnation chamber before being expanded out a small nozzle. At that point, low-energy electrons from a filament were injected into the jet in the presence of a weak axial magnetic field, and the resultant NB anions were then extracted into the photoelectron spectrometer. Photoelectron spectra of parent NB anions formed in this way revealed them to be dipole-bound states,^{33–35} whereas the photoelectron spectra of U^- generated by the laser irradiation method

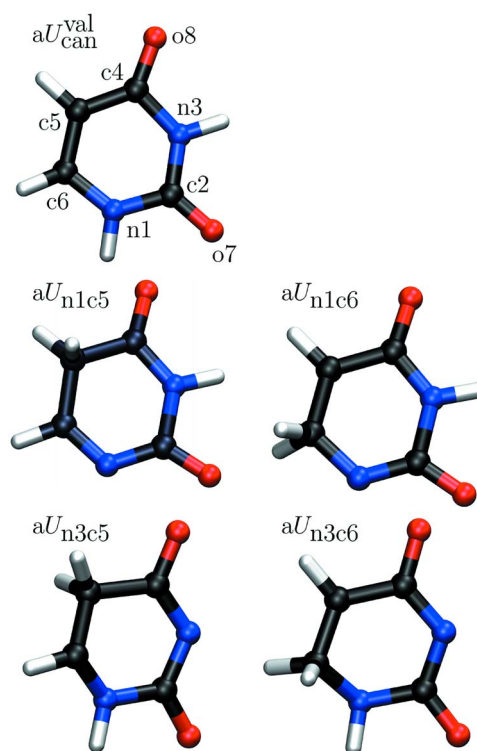


FIG. 1. (Color online) The tautomers of uracil anion considered in this study.

described above showed them to be valence anion states with no evidence for the presence of dipole-bound anions.

B. The RI-MP2-R12 method for open-shell systems

In the present work, we are interested in the electronic structure of uracil anions that are open-shell doublet systems. For the explicitly correlated calculations, therefore, the open-shell extension of the RI-MP2-R12 method (RI-MP2: resolution-of-the-identity second-order Møller–Plesset) as implemented in TURBOMOLE (Refs. 36–38) and described in Ref. 31 was applied, which computes the second-order energy in a spin-unrestricted manner using an unrestricted Hartree–Fock (UHF) or restricted open-shell Hartree–Fock (ROHF) reference wave function. In the present work, we exclusively use the augmented correlation-consistent polarized valence X -tuple zeta basis sets AVXZ^{29,30} with $X = D, T, Q,$ and 5 .

C. Geometries and harmonic vibrational frequencies

Our *ab initio* calculations were performed for the five tautomers that had been identified in previous studies.^{15,16} They are presented in Fig. 1. Besides the canonical form there are four other tautomers obtained via proton transfer from the N1H or N3H nitrogens to the C5 or C6 carbon atoms (see Fig. 1 for atom labels). These species differ from the conventional “rare tautomers” of uracil, where the NH proton acceptors are the O7 and O8 oxygens.

The equilibrium geometries of the negative ion tautomers were optimized, and harmonic frequencies were computed. The neutral species were optimized starting from the equilibrium structure of the corresponding anion. For some

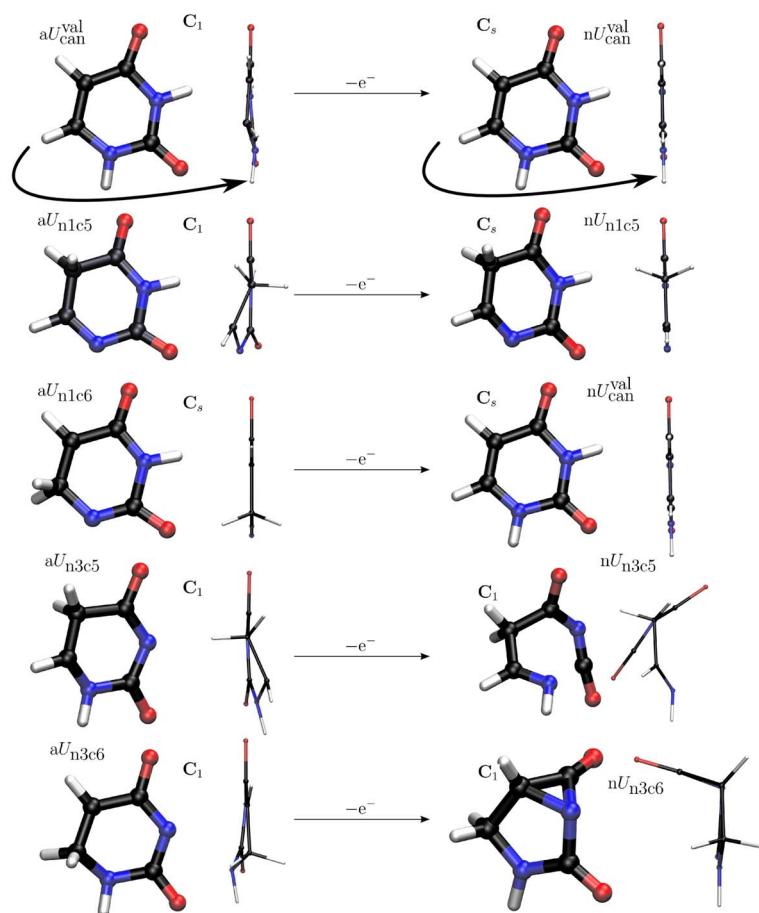


FIG. 2. (Color online) Some of the new tautomers of uracil anion are unstable upon the electron detachment. They might evolve along barrier-free pathways to chainlike (aU_{n3c5}) or bicycliclike (aU_{n3c6}) forms.

neutral tautomers, the ring structure was unstable after electron detachment, and geometry optimizations converged to a bicyclo- or chainlike structure (see Fig. 2). The geometry optimizations were performed at the RI-MP2(FC) level^{39,40} of theory with the AVTZ basis set^{29,30} using the TURBOMOLE program.³⁸ All of the electron-correlation calculations of the present work were carried out in the frozen-core (FC) approximation, and the label “FC” will be omitted in the following. A UHF reference wave function was used for the geometry optimization of the anions. The final geometries are shown in Figs. 1 and 2.

The UHF calculations of the doublet states of the anions were spin contaminated with $\langle \hat{S}^2 \rangle$ values in the range of 0.76–0.79 \hbar^2 . In order to estimate the geometry and energy change of the anion at the MP2 level when changing from a UHF to a ROHF reference wave function, we have performed geometry optimizations at the ROHF-MP2/AVDZ level of theory (a small basis was used since the RI approximation could not be exploited in this calculation). The MOLPRO program^{41–45} was employed, computing the ROHF-MP2 gradients by numerical differentiation. Geometry relaxation corrections to the AEAs were obtained by comparing the ROHF-MP2 energies at the equilibrium UHF-MP2 and ROHF-MP2 geometries. These corrections are relatively small (the energy differences were 12 meV for the anion of the canonical tautomer and only 4, 1, 1, and 2 meV for the tautomers U_{n1c5} , U_{n1c6} , U_{n3c5} , and U_{n3c6} , respectively), and we believe that the UHF-MP2/AVTZ geometries are appro-

appropriate for further investigations. Zero-point vibrational energies (ZPVEs) were calculated in the harmonic approximation at the UHF-RI-MP2/AVTZ level.

As the interpretation of the PES spectrum proved to be difficult, we briefly considered open-ring anionic structures. They were investigated at the density-functional theory (DFT) level using the B3LYP exchange-correlation functional⁴⁶ in the def2-TZVP basis.⁴⁷ The geometry optimizations of the open-ring anionic structures were started from the equilibrium geometry of the canonical neutral by elongating the bonds between pairs of neighboring atoms in the ring. Also the dihedral angles were distorted to prevent the geometry optimization to collapse to the canonical structure.

D. Extrapolated Hartree–Fock energies

We have performed Hartree–Fock calculations with the family of AVXZ basis sets^{29,30} with $X=D, T, Q,$ and 5. The corresponding basis sets comprise 220, 460, 824, and 1336 basis functions on uracil, respectively. We have extrapolated the Hartree–Fock energy to the limit of a complete basis by fitting the calculated energies to the functional form proposed by Halkier *et al.*,⁴⁸

$$E_X^{\text{HF}} = E_\infty^{\text{HF}} + a \exp(-bX), \quad (1)$$

where X is the cardinal number of the basis set. In the present study, we have investigated three-point fits for closed-shell restricted Hartree–Fock (RHF) as well as for UHF and ROHF energies.

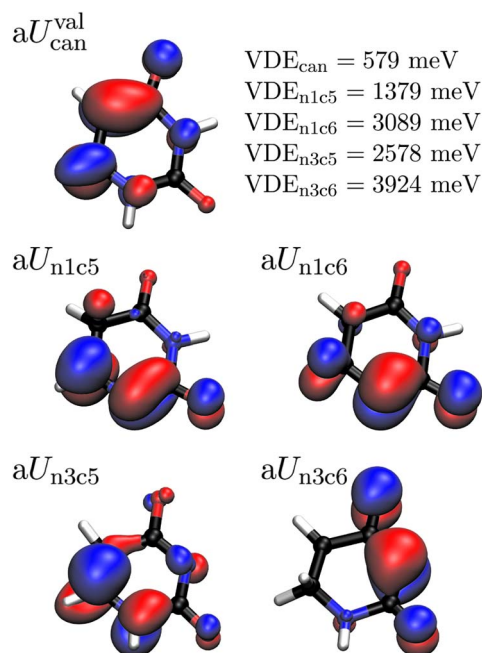


FIG. 3. (Color online) Singly occupied molecular orbitals (SOMOs) of various tautomers of the uracil anion.

E. Extrapolated correlation energies

Electron-correlation effects have been taken into account at several levels of theory. At the RI-MP2 level, we have performed calculations with the AVDZ, AVTZ, AVQZ, and AV5Z basis sets. Explicitly correlated RI-MP2-R12 calculations were performed with the same family of augmented correlation-consistent basis sets. Finally, CCSD calculations were performed with the AVDZ and AVTZ basis sets including the perturbative contribution from triple excitations with the AVDZ basis set. All coupled-cluster calculations were performed using the MOLPRO (Refs. 41–45) program. For all electron-correlation energies, we have applied the two-point extrapolation scheme of Helgaker *et al.*,⁴⁹

$$E_X^{\text{corr}} = E_\infty + cX^{-3}, \quad (2)$$

where X is the cardinal number of the basis set.

F. Best estimates of AEA and VDE

The excess electron in valence anionic states of uracil occupies a π antibonding molecular orbital (see Fig. 3). Our main computational goal was to determine accurate AEA and VDE values for the considered tautomers. We therefore decided to apply a scheme, in which the final quantities are computed by adding incremental contributions from various levels of theory. This approach was used in our previous study,³¹ where the obtained AEA of nU_{can} was in good agree-

TABLE I. Experimental and theoretical values of AEA (in meV) for various tautomers of uracil. The AEA values are defined with respect to the canonical neutral, and only valence anions are considered.

Method	AEA	Ref.
aU_{can}		
B3LYP/6-311++G**	215	50
B3LYP/6-311+G(2df,p)	180	9
B3LYP/TZ2P++	190	8
B3LYP/6-31+G*	180	51
MP2/6-31+G(d)	-250	52
CCSD(T)/AVDZ	-51	15
Additivity scheme	40 ± 5	31
Additivity scheme	21	This study
Expt.	150 ± 120	35
Expt.	62 ± 32	53
aU_{n1c5}		
CCSD(T)/AVDZ	171	15
Additivity scheme	135	This study
aU_{n1c6}		
CCSD(T)/AVDZ	-275	15
Additivity scheme	-311	This study
aU_{n3c5}		
CCSD(T)/AVDZ	-60	15
Additivity scheme	-101	This study
aU_{n3c6}		
CCSD(T)/AVDZ	-308	16
Additivity scheme	-370	This study

ment with the experimental values (see Table I for comparison with Refs. 50–53 and others). Our final values for the AEA and VDE are computed as follows:

$$\text{AEA}^{\text{tot}} = \sum_{L \in A} \Delta \text{AEA}_L + \Delta \text{AEA}_{\text{ZPVE}}, \quad (3)$$

$$\text{VDE}^{\text{tot}} = \sum_{L \in A} \Delta \text{VDE}_L,$$

$$A = \{\text{Hartree-Fock, MP2, CCSD, (T)}\}. \quad (4)$$

The sums on the right-hand side of Eqs. (3) and (4) include incremental contributions to the AEA or VDE calculated at the L level of theory, where L can be Hartree-Fock, MP2, CCSD or (T). The incremental contribution calculated at the L level of theory is defined as

$$\Delta \text{AEA}_L = E_{N@N,L}^{\text{inc}} - E_{A@A,L}^{\text{inc}}, \quad (5)$$

$$\Delta \text{VDE}_L = E_{N@A,L}^{\text{inc}} - E_{A@A,L}^{\text{inc}}, \quad (6)$$

where $E_{N@N,L}^{\text{inc}}$ and $E_{A@A,L}^{\text{inc}}$ are increments of the electronic energy of the neutral molecule and its anion calculated at their optimal geometries. $E_{N@A,L}^{\text{inc}}$ is an increment of the electronic energy of the neutral molecule calculated at the equilibrium geometry of the anion. It is convenient to associate the series of labels {Hartree-Fock, MP2, CCSD, (T)} with the numbers {1, 2, 3, 4}. The increments can be calculated as

$$E_{Y,1}^{\text{inc}} = E_{Y,1}^{\text{ele}}, \quad (7)$$

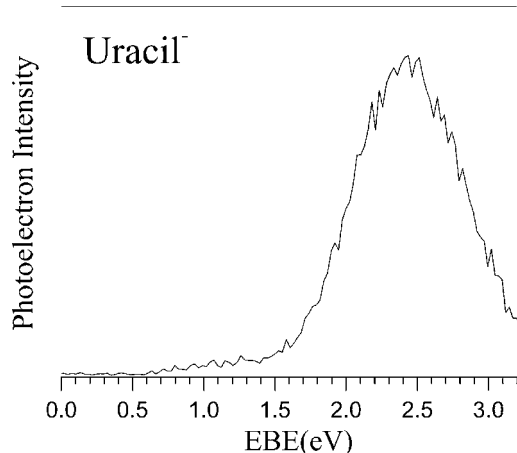


FIG. 4. Photoelectron spectrum of the uracil anion.

$$E_{Y,L}^{\text{inc}} = E_{Y,L}^{\text{ele}} - E_{Y,L-1}^{\text{ele}} \quad \text{for } 1 < L \leq 4, \quad (8)$$

where Y can be N@N, A@A, or N@A. The electronic energies at the two levels L and $L-1$ must of course be computed in a consistent way, that is, using the same basis set or extrapolation scheme. Equation (3) contains a difference in ZPVEs ($\Delta\text{AEA}_{\text{ZPVE}}$) of the neutral and anionic systems, as obtained at the UHF-RI-MP2/AVTZ level.

III. RESULTS

A. Photoelectron spectrum

The photoelectron spectrum of the uracil anion was measured with 3.493 eV photons, and the result is presented in

Fig. 4. Nonzero photoelectron intensity begins at EBE ≈ 0.6 eV and remains low until 1.5 eV. There, a broad peak with a maximum at EBE ≈ 2.4 eV develops. Because a dipole-bound anion state has a distinctive photoelectron signature, characterized by a single narrow peak at very low EBE,^{33–35} the spectrum presented here is clearly not that of a dipole-bound state but is, in fact, due to a valence bound state (or states) of the uracil anion.

B. Hartree–Fock and MP2 increments

The incremental contributions to the AEA and VDE for each tautomer but the canonical are shown in Tables II–V. Details for the canonical tautomer can be found in Ref. 31. The anions of all tautomers are vertically bound but adiabatically unbound at the Hartree–Fock level. The Hartree–Fock contributions converge quickly, and already the AVQZ basis set provides values that are accurate to within 1–2 meV with respect to the basis-set limit, which has been estimated from the AV(TQ5)Z extrapolation.

The MP2 contributions to the AEA stabilize the anion relative to the neutral, and they are of the same order of magnitude as the Hartree–Fock contributions. The MP2 basis-set limits were obtained using two independent approaches, that is, using the extrapolation procedure as well as the explicitly correlated MP2 method. These two approaches give essentially the same results. The RI-MP2-R12 contributions obtained with the AV5Z basis and the AV(Q5)Z extrapolated conventional MP2 values mutually agree to within 1 meV. Apparently, the basis-set limit has been reached at the Hartree–Fock and MP2 levels.

TABLE II. Contributions to the AEA and VDE of the aU_{n1c5} tautomer of uracil (in meV). AV(DTQ)Z and AV(DT)Z denote the extrapolated Hartree–Fock and electron-correlation contributions, respectively.

Contribution	AVDZ	AVTZ	AVQZ	AV5Z	AV(DT)Z	AV(DTQ)Z and AV(TQ)Z	AV(TQ5)Z and AV(Q5)Z
AEA with respect to the canonical form							
HF	–673	–769	–778	–780	...	–773	–780
MP2 _{conv}	597	688	701	709	726	710	717
MP2 _{R12}	24	9	13	9
MP2 _{conv+R12}	621	697	714	718
SD	90	55	40
(T)	39	48	52
ZPVE(MP2 _{conv})	...	114
AEA with respect to the corresponding neutral							
HF	–51	–83	–88	–89	...	–89	–89
MP2 _{conv}	680	779	810	822	821	833	834
MP2 _{R12}	75	31	19	12
MP2 _{conv+R12}	755	810	829	834
SD	–24	–47	–57
(T)	46	58	63
ZPVE(MP2 _{conv})	...	69
VDE							
HF	852	864	867	868	...	868	868
MP2 _{conv}	314	438	478	493	490	507	509
MP2 _{R12}	164	51	26	16
MP2 _{conv+R12}	477	488	504	508
SD	54	45	41
(T)	–38

TABLE III. Contributions to the AEA and VDE of the aU_{n1c6} tautomer of uracil (in meV). AV(DTQ)Z and AV(DT)Z denote the extrapolated Hartree-Fock and electron-correlation contributions, respectively.

Contribution	AVDZ	AVTZ	AVQZ	AV5Z	AV(DT)Z	AV(DTQ)Z and AV(TQ)Z	AV(TQ5)Z and AV(Q5)Z
AEA with respect to the canonical form							
HF	-970	-1070	-1082	-1083	...	-1078	-1083
MP2 _{conv}	389	480	492	500	518	500	508
MP2 _{R12}	48	15	15	10
MP2 _{conv+R12}	437	494	507	509
SD	150	122	110
(T)	16
ZPVE(MP2 _{conv})	...	136
VDE							
HF	4079	4099	4102	4103	...	4102	4103
MP2 _{conv}	-225	-110	-73	-59	-62	-46	-45
MP2 _{R12}	189	56	26	15
MP2 _{conv+R12}	-35	-55	-47	-45
SD	-54	-38	-31
(T)	-938

C. Post-MP2 correlation effects

Correlation effects beyond the MP2 level of theory must be included to obtain accurate results, for instance, by performing CCSD and CCSD(T) calculations. CCSD calculations were performed in the AVDZ and AVTZ basis sets. These energies were AV(DT)Z extrapolated, and the differences between the AVTZ and AV(DT)Z values were adopted as error bars on the CCSD contributions. They do not exceed 15 meV and are the largest for the aU_{can} and the aU_{n1c5} tautomers. A further source of error is due to using a small basis for the (T) contribution, which was computed in the AVDZ basis. In previous work, the difference between the (T)/AVDZ and (T)/AVTZ contributions was 19 meV for the canonical tautomer,³¹ and we therefore conclude that the final AEA and VDE values may be in error by at least ± 25 meV due to the approximate treatment of post-MP2 electron-correlation effects.

Another source of error is due to the complicated electronic structure of the systems, which cannot be described easily by a single-reference determinant (*vide infra*). The AEA is obtained from calculations of the neutral and the anion at their respective equilibrium geometries, but the VDE is obtained from calculations of the neutral and the anion at the equilibrium geometry of the anion. For the neutral, this geometry may be somewhat away from the equilibrium structure, which is reflected in the comparably large SD and (T) contributions.

Table VI presents the final estimates of the AEA and VDE for all five tautomers. The main result of the present study is that the most stable valence anion of uracil is aU_{n1c5} . It is more stable by 135 and 114 meV than the canonical form of the neutral and the anion, respectively. Surprisingly, the VDE of this tautomer, estimated at 1379 meV, is not reflected in the photoelectron spectrum (Fig. 4). The VDE of

TABLE IV. Contributions to the AEA and VDE of the aU_{n3c5} tautomer of uracil (in meV). AV(DTQ)Z and AV(DT)Z denote the extrapolated Hartree-Fock and electron-correlation contributions, respectively.

Contribution	AVDZ	AVTZ	AVQZ	AV5Z	AV(DT)Z	AV(DTQ)Z and AV(TQ)Z	AV(TQ5)Z and AV(Q5)Z
AEA with respect to the canonical form							
HF	-731	-830	-839	-840	...	-833	-841
MP2 _{conv}	403	488	498	507	524	506	515
MP2 _{R12}	21	9	13	9
MP2 _{conv+R12}	423	497	512	516
SD	128	98	85
(T)	23
ZPVE(MP2 _{conv})	...	115
VDE							
HF	2441	2460	2463	2464	...	2464	2465
MP2 _{conv}	-76	41	78	92	90	105	107
MP2 _{R12}	177	55	27	16
MP2 _{conv+R12}	102	96	105	108
SD	138	139	139
(T)	-134

TABLE V. Contributions to the AEA and VDE of the aU_{n3c6} tautomer of uracil (in meV). AV(DTQ)Z and AV(DT)Z denote the extrapolated Hartree-Fock and electron-correlation contributions, respectively.

Contribution	AVDZ	AVTZ	AVQZ	AVSZ	AV(DT)Z	AV(DTQ)Z and AV(TQ)Z	AV(TQ5)Z and AV(Q5)Z
AEA with respect to the canonical form							
HF	-889	-1007	-1019	-1021	...	-1013	-1021
MP2 _{conv}	297	391	399	407	430	405	415
MP2 _{R12}	28	9	14	8
MP2 _{conv+R12}	325	399	413	415
SD	162	132	120
(T)	9
ZPVE(MP2 _{conv})	...	105
VDE							
HF	3946	3960	3963	3964	...	3964	3964
MP2 _{conv}	30	132	167	180	175	192	194
MP2 _{R12}	156	48	24	14
MP2 _{conv+R12}	185	180	191	194
SD	53	60	62
(T)	-296

the aU_{n3c5} tautomer, estimated at 2578 meV, agrees well with the peak maximum at ≈ 2.4 eV, but this anion is 101 meV less stable than the canonical neutral and as much as 236 meV less stable than aU_{n1c5} . Our calculations suggest that the aU_{n3c5} tautomer is observed in the photoelectron spectrum, but it remains unclear how this anion is formed if this interpretation of the spectrum is correct.

Because the most stable anionic tautomer does not dominate the PES spectrum, we have carried out DFT calculations on open-ring structures of the uracil anion (see Sec. II C for technical details). In one case, the geometry optimization led to an open-ring structure that is 1.6 eV less stable than the canonical anion. In some other cases, the structures partially dissociated and were 2.6–3.8 eV less stable than the canonical anionic form. We have also observed that such an alternative geometry optimization can lead to a three-membered-ring form that is 6.5 eV less stable than the canonical anion. In other cases, we obtained the canonical anionic form. The DFT results for the open-ring anionic structures demonstrated that they are high in energy and that it is unlikely that they had been produced in the PES experiment.

D. T1 diagnostics

The values of the T1 diagnostics⁵⁴ for the anionic and neutral tautomers in many cases exceed the commonly accepted threshold value of 0.02 (see Table VII). The diagnostics are particularly large for the neutral tautomers that have been identified as biradicals in Fig. 5: 0.08 for nU_{n1c6} and 0.04 for nU_{n3c6} (but, very surprisingly, only 0.02 for nU_{n3c5}). The diagnostics are about 0.02 for the tautomers with closed-shell resonance Lewis-type structures (Fig. 5), that is, for nU_{can} and nU_{n1c5} . We suspect that the large value of T1 for nU_{n1c6} is the reason for the unusual convergence of the VDE for the corresponding anion (see Table III). The Hartree-Fock contribution exceeds 4 eV, and the MP2 and CCSD contributions are opposite in sign to the HF contribution and smaller by two orders of magnitude. Finally, the (T) contribution is large (-938 meV) and due to the (T) triples correction to the energy of the neutral.

E. Triplet instabilities

As already mentioned, the VDEs are computed from calculations on the neutral and anionic species at the geometries

TABLE VI. Final estimations of the AEA and VDE (in meV) for the tautomers of uracil obtained using various additivity schemes. The values of AEA contain the ZPVE and geometry relaxation contributions (see Sec. II C). The electronic contributions are from Tables II–V.

Contribution HF/MP2/SD/(T)	aU_{can}^{val}	aU_{n1c5}	aU_{n1c6}	aU_{n3c5}	aU_{n3c6}
AEA with respect to the canonical form					
AVTZ/AVTZ/AVTZ/AVDZ	-13	131	-315	-105	-368
AVQZ/AVQZ/AVTZ/AVDZ	10	135	-315	-104	-372
AV(TQ5)Z/AV(Q5)Z/AV(DT)Z/AVDZ	22	134	-312	-102	-370
AV(TQ5)Z/AV5Z _{R12} /AV(DT)Z/AVDZ	21	135	-311	-101	-370
VDE					
AVTZ/AVTZ/AVTZ/AVDZ	506	1309	3013	2506	3856
AVQZ/AVQZ/AVTZ/AVDZ	550	1352	3053	2546	3894
AV(TQ5)Z/AV(Q5)Z/AV(DT)Z/AVDZ	579	1380	3089	2577	3924
AV(TQ5)Z/AV5Z _{R12} /AV(DT)Z/AVDZ	579	1379	3089	2578	3924

TABLE VII. T1 diagnostics of the CCSD solutions for the tautomers of uracil.

System	$U_{\text{can}}^{\text{val}}$	U_{n1c5}	U_{n1c6}	U_{n3c5}	U_{n3c6}
A@A/AVDZ	0.023	0.023	0.022	0.022	0.021
A@A/AVTZ	0.022	0.022	0.021	0.020	0.020
N@A/AVDZ	0.019	0.021	0.086	0.025	0.044
N@A/AVTZ	0.018	0.020	0.083	0.024	0.042
N@N/AVDZ	0.018	0.018
N@N/AVTZ	0.017	0.017

of the anions. A relatively large source of error is due to the calculations on the neutral species at the anionic geometries. All Hartree–Fock calculations except the calculation on nU_{n3c5} showed triplet instabilities, and UHF solutions with $\langle \hat{S}^2 \rangle$ values of about $0.4 \hbar^2$ and $1.2 \hbar^2$ (see Table VIII) were found below the RHF solutions. With the RHF reference, the electron-correlation energies were larger in magnitude than with the UHF reference, and the overall UHF-CCSD(T) energies of the neutrals were found slightly above the RHF-CCSD(T) energies. Therefore, UHF-CCSD(T) calculations yield somewhat larger VDEs than RHF-CCSD(T) calculations, and the corresponding shifts in the VDE values are presented in Table VIII. For the most relevant species U_{can} , U_{n1c5} , and U_{n3c5} , the shifts are of the order of 50 meV and not significant. The UHF-CCSD(T) calculations⁵⁵ were performed with the Mainz-Austin-Budapest version of ACES II.⁵⁶

IV. SUMMARY

In the present work, we have reported the PES of U^- and compared it with *ab initio* calculations of various tautomer anions. The calculations have been carried out at a level of accuracy similar to that of Ref. 31. We have confirmed earlier predictions^{15,16} that the most stable tautomer of the valence anion results from a proton transfer from N1H to C5 (for atomic labels, see Fig. 1). It is adiabatically bound with

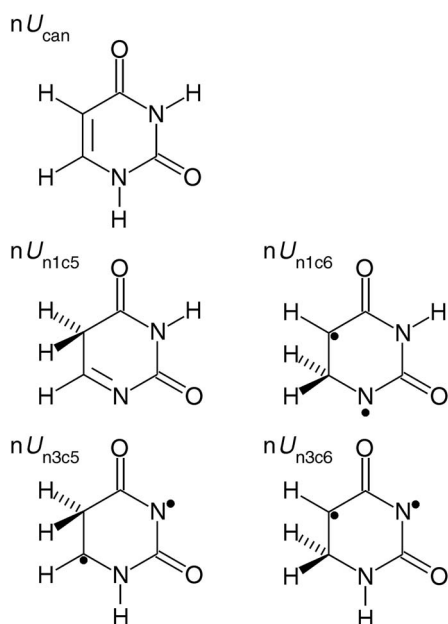


FIG. 5. Lewis structures of various tautomers of uracil.

respect to the canonical neutral by only 135 meV, but its VDE is as large as 1.4 eV. The second most stable valence anion is that of the canonical tautomer (AEA=21 meV and VDE=0.58 eV), and the third most stable valence anion is that of the tautomer resulting from a proton transfer from N3H to C5 (AEA=-101 meV and VDE=2.6 eV). All AEA values are with respect to the canonical neutral. The valence anions of the five tautomers analyzed here differ in stability by less than 0.6 eV, but their VDEs span a broad range of 3.3 eV. The tautomer anions with the largest VDEs detach the electron to form neutrals that have some biradical character, leading to significant geometry relaxation. The valence anions are usually strongly buckled, whereas common neutral tautomers display C_s symmetry.

The AEA values for the five tautomers span a relatively narrow range from -370 to +135 meV. Their VDE values, however, span a much wider range from 579 to 3924 meV (Table VI). The energies of the neutral species primarily determine the broad range of the VDE values. This is depicted in Fig. 6, which shows the total CCSD(T)/AVDZ energies for all neutral and anionic tautomers at the anion geometries. The largest VDE values are obtained for the least stable neutral tautomers with significant T1 diagnostics⁵⁴ (Table VII) and some biradical character (Fig. 5).

The PES suggests the existence of valence anionic states. However, the spectral intensity is surprisingly low at the EBE of about 1.4 eV, where the VDE of the most stable anion is expected. Furthermore, the spectrum has essentially no intensity up to 0.6 eV, where the VDE of the canonical valence anion is expected. Instead, the spectrum is dominated by a broad peak with a maximum at an EBE of 2.4 eV, near the VDE of the third most stable valence anion. The most stable open-ring uracil anion is 1.6 eV less stable than the canonical form, and it is rather unlikely that this species is observed in the experiment.

From a computational point of view, the AEAs are con-

TABLE VIII. Shift of the VDE (in meV) due to a triplet instability, obtained from the difference between the RHF-CCSD(T)/AVDZ and UHF-CCSD(T)/AVDZ energies of the neutral molecule at the geometry of its anion. The expectation value $\langle \hat{S}^2 \rangle$ (in \hbar^2) of the UHF solution is also given.

System	Shift	$\langle \hat{S}^2 \rangle$
$U_{\text{can}}^{\text{val}}$	48	0.39
U_{n1c5}	55	0.40
U_{n1c6}	489	1.26
U_{n3c5}	0	0.0
U_{n3c6}	58	1.21

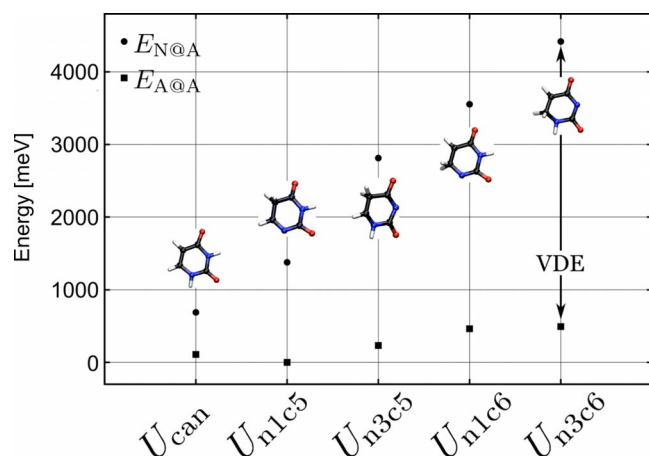


FIG. 6. (Color online) The electronic energies of neutral and anionic tautomers of uracil computed at the optimal geometry of the anion. The electronic energy of aU_{n1c5} is assumed as zero.

sidered to be more accurate and reliable than the VDEs because the latter have involved calculations of the neutral species at the geometries of their negative ions. In view of the AEA, aU_{n1c5} is the most stable anion and a good candidate for the source of the PES. In contrast to this, aU_{n3c5} is the anion whose VDE agrees with the peak maximum of the PES.

In an earlier work on anions of NBs, we had found only dipole-bound states. Theory had confirmed that for most of the bases, the canonical forms would not form stable valence anions. Under the harsh laser vaporization conditions used in the present work, however, we indeed did see valence anions. They hence must be due to other (uncommon) tautomers. Structures other than the ones studied here (such as open-ring structures) may also seem possible but DFT searches for such alternative structures were unsuccessful.

Other photon energies were not used in the present work, and thus, we cannot rule out anion resonances. Note, however, that several wavelengths had been used in the case of the uridine anion, where we had observed no change.

We feel that the structure of the uracil anion is influenced by the harshness of the source conditions. In the present work, the sample powder was pressed directly onto a metal rod and was not sticky enough to form thick layers. Although the laser power was weak, it was still strong enough to shoot through the layer and remove the sample. More importantly, the same uracil anion rare tautomer was also formed via an alternative source, where the uracil powder was desorbed by infrared laser radiation. Thus, the wavelength was not a factor for producing the rare tautomer. Moreover, both source conditions were different from those used to make dipole-bound uracil anions.

Further research is required to unravel the mechanism by which the U_{n3c5} tautomer may have been formed under the conditions of the present experiment or which other anionic species may explain the observed PES. We therefore hope that the present work may stimulate further experimental as well as computational work.

ACKNOWLEDGMENTS

This research was supported by the Deutsche Forschungsgemeinschaft (DFG) (Project No. FZT 47 C3.3) in conjunction with a grant from the Ministry of Science, Research and the Arts of Baden-Württemberg (Grant No. Az: 7713.14–300) (W.K.), and by the Polish State Committee for Scientific Research (KBN) (Grant No. DS/8000–4–0026–8) (M.G.). This material is based in part on work supported by the U.S. National Science Foundation under Grant No. CHE-0517337 (K.H.B. and X.L.).

The calculations were performed on the Xeon cluster of the Lehrstuhl für Theoretische Chemie of the Universität Karlsruhe (TH) and at the Molecular Science Computing Facility (MSCF) in the William R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. DOE OBER and located at PNNL, which is operated by Battelle for the U.S. DOE. The MSCF resources were available through a Computational Grand Challenge Application grant. The VMD (Ref. 57) program was used to prepare the figures.

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