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Electron propagator and coupled-cluster calculations on the photoelectron spectra of thiouracil and dithiouracil anions

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Electron affinities, vertical electron detachment energies, and isomerization energies of 4-thiouracil, 2-thiouracil, and 2,4-dithiouracil and their valence anions have been calculated with *ab initio* electron propagator and other many-body methods. Anions in which protons have been transferred to the C5 from the N1 or N3 ring positions have been considered, but the canonical forms are most stable for the 4-thiouracil and 2,4-dithiouracil anions. Electron affinities of 0.61, 0.26, and 0.87 eV have been determined for 4-thiouracil, 2-thiouracil, and 2,4-dithiouracil, respectively. Electron propagator calculations on the canonical anions yield vertical electron detachment energies that are in close agreement with experimental peaks at 1.05, 3.21, and 3.32 eV for 4-thiouracil and at 1.4 eV for 2,4-dithiouracil. © 2011 American Institute of Physics. [doi:10.1063/1.3555179]

I. INTRODUCTION

Electrons with low kinetic energy, including those produced as secondary products of ionizing radiation, may induce single and double strand breaks in the double-helix of DNA.^{1–3} Among the chemically important initial events in such processes are attachments of electrons to nucleobases.⁴ In the gas phase, electrostatic potentials of polar purine and pyrimidine molecules suffice to bind diffuse electrons that barely disturb the nuclear framework.^{5–8} However, such anionic states have limited relevance to processes that occur in condensed phases and that have biological implications. When electrons enter unoccupied molecular orbitals composed chiefly of valence atomic functions, chemical bonding is altered, with consequent changes in bond lengths and angles. Recent calculations have established that the most stable isomers of anionic nucleobases may exhibit tautomeric forms that are relatively unstable in uncharged species.^{9,10}

Chemical modifications of nucleobases may alter this energetic connection between electron attachment and tautomerism. The simplest nucleobase, uracil, may be modified by substitution of oxygen by sulfur in one or two positions to produce 4-thiouracil, 2-thiouracil, or 2,4-dithiouracil (Fig. 1). Whereas the anion photoelectron spectra of uracil^{7,11} exhibit sharp, low-energy peaks that are characteristic of diffusely bound electrons, their counterparts for 4-thiouracil and 2,4-dithiouracil do not.¹² Instead, broad features with widths of 0.8–0.9 eV exhibit maxima that lie within 0.4 eV of the ionization threshold. Peaks at higher energies may be evidence of excited final states of the nucleobases.

To interpret these anion photoelectron spectra, the structural and energetic consequences of electron attachment to thiouracil and dithiouracil molecules will be explored with *ab initio* electron propagator, many-body perturbation theory,

and coupled-cluster methods. Vertical and adiabatic electron affinities of sulfur-substituted uracil molecules will be determined. Isomerization energies, including tautomerization energies, will disclose whether a given structure is likely to be represented in the spectra. Vertical electron detachment energies (VEDEs) of various anions will be calculated to provide a direct comparison with experiment.

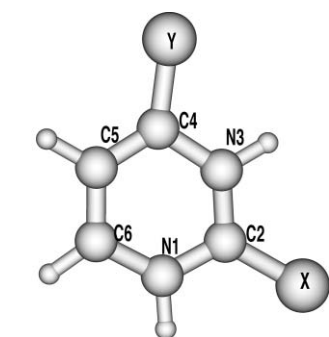
II. METHODS

All calculations were performed with the GAUSSIAN 03 (Ref. 13) program package.

Geometry optimizations were performed at the second-order level of theory (MP2) with closed-shell Hartree–Fock reference configurations for uncharged singlets and unrestricted Hartree–Fock reference configurations for anionic doublets. To remove the effects of spin contamination in the latter class of calculations, projected MP2 (PMP2) (Ref. 14) total energies were also evaluated. At the geometries optimized with MP2, harmonic frequencies were obtained to verify minima in potential energy surfaces. These results also yielded zero-point energies. At the same geometries, total energies were determined at two higher levels of theory: coupled-cluster singles and doubles (CCSD) (Ref. 15) and CCSD with perturbative triples corrections,¹⁶ or CCSD(T).

Electron propagator calculations in various quasiparticle approximations^{17,18} were executed to determine vertical electron binding energies. Relaxation and correlation corrections to the results of Koopmans's theorem (KT) were included by employing the Outer Valence Green's Function (OVGF) A, B, and C renormalization schemes (listed in this order in the tables below)^{19,20} and the P3 (Refs. 21 and 22) and P3+ (Ref. 23) methods. All pole strengths exceeded 0.85 and confirmed the qualitative validity of the quasiparticle approximations and their perturbative corrections to KT results.

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2-Thiouracil: X=S, Y=O
 4-Thiouracil: X=O, Y=S
 2,4-Dithiouracil: X=S, Y=S

FIG. 1. Schematic representation of thioracils.

The 6-311++G(2df,2p) basis set²⁴ was employed in all calculations.

III. RESULTS AND DISCUSSION

Total energies obtained at various levels of theory are displayed in Tables I–III. For the uncharged molecules, geometry optimizations yield structures (designated by the abbreviation opt.) that have C_s symmetry and that therefore have $^1A'$ term symbols. At the highest level of theory, CCSD(T), 4-thiouracil is only 2 kcal/mol more stable than 2-thiouracil. Consideration of zero-point-energy corrections calculated at the MP2 level has a negligible effect on the latter prediction. In each of these cases, only the canonical tautomeric structure is considered.

At these geometries, the corresponding anions may be classified as $^2A'$, for the reference configuration has an extra electron assigned to a π orbital. The anionic total energies are lower than their uncharged counterparts except in the case of 2-thiouracil. Vertical electron affinities (see below) of the molecules may be inferred from the first two lines of data in Tables I–III.

Geometry optimizations on anions initiated at the neutral geometries lead to structures with C_1 symmetry and to the third line of data in each table. These canonical anions (designated by C in the tables) have the same arrangement of protons as their neutral precursors. Optimized, anionic

TABLE I. Total energies +736. a.u. of 4-thiouracil and related anions.

State	E_{MP2}	$E_{MP2+ZPE}$	E_{PMP2}	E_{CCSD}	$E_{CCSD(T)}$
$^1A'$ opt.	-0.64926	-0.56400		-0.67526	-0.74507
$^2A'$ at $^1A'$	-0.64735		-0.65812	-0.68181	-0.75381
2A C opt.	-0.65627	-0.57461	-0.66678	-0.69139	-0.76371
1A at 2A C	-0.63763			-0.65800	-0.73437
2A R15 opt.	-0.65068	-0.55694	-0.65686	-0.66994	-0.74770
1A at 2A R15	-0.54138			-0.56331	-0.64356
2A R35 opt.	-0.63984	-0.55867	-0.64210	-0.66781	-0.74200
1A at 2A R35	-0.54138			-0.56331	-0.64356

TABLE II. Total energies +736. a.u. of 2-thiouracil and related anions.

State	E_{MP2}	$E_{MP2+ZPE}$	E_{PMP2}	E_{CCSD}	$E_{CCSD(T)}$
$^1A'$ opt.	-0.64650	-0.56130		-0.66805	-0.74237
$^2A''$ at $^1A'$	-0.63823		-0.64479	-0.66075	-0.73600
2A C opt.	-0.64763	-0.56572	-0.65163	-0.67418	-0.74875
1A at 2A C	-0.62610			-0.64593	-0.72278
2A R15 opt.	-0.65063	-0.56888	-0.65904	-0.68421	-0.75801
1A at 2A R15	-0.59574			-0.61926	-0.69678
2A R35 opt.	-0.64058	-0.55945	-0.64285	-0.66870	-0.74315
1A at 2A R35	-0.55088			-0.57198	-0.65307

total energies are lower than those of the molecules and imply positive, adiabatic electron affinities in all three cases. At the anionic geometries, total energies of uncharged species may be evaluated. The fourth line of data in each table therefore implies VEDEs for the canonical anions.

Rare tautomeric forms of each anion that involve proton transfer to the C5 from the N1 or N3 ring positions are designated, respectively, by R15 and R35 in Tables I–III. The resulting anions are less stable than the canonical forms except for the 2-thiouracil case. (See the fifth and seventh lines of data in each Table.) At each optimized anionic structure, the total energy of the uncharged molecule is recalculated. From these data (in the sixth and eighth lines), VEDEs may be inferred.

A summary of VEDEs calculated indirectly through total energies is given in Table IV. The CCSD(T) results for 4-thiouracil and 2,4-dithiouracil (0.80 and 1.06 eV, respectively) are in fair agreement with the observed peaks¹² at 1.05 and 1.4 eV. CCSD(T) predictions for the VEDEs of the R15 tautomers (1.30 and 1.77 eV) are at higher energies, but still lie within the observed envelopes that span 0.7–1.5 for 4-thiouracil and 1.0–1.9 for 2,4-dithiouracil. VEDEs for the canonical and R15 tautomers of 2-thiouracil are within a few tenths of an eV of their 4-thiouracil counterparts. (It is unlikely that such species are represented in the experimental spectrum because of high barriers to isomerization from the precursor molecules described therein.)

Vertical and adiabatic electron affinities of the three molecules are displayed in Table V. At the CCSD and CCSD(T) levels, vertical and adiabatic values differ by approximately 0.3 eV. These results and those of the geometry optimizations imply that considerable nuclear relaxation occurs after attachment of an electron to each molecule. The

TABLE III. Total energies +1059. a.u. of 2,4-dithiouracil and related anions.

State	E_{MP2}	$E_{MP2+ZPE}$	E_{PMP2}	E_{CCSD}	$E_{CCSD(T)}$
$^1A'$ opt.	-0.22281	-0.13992		-0.25529	-0.33196
$^2A''$ at $^1A'$	-0.22900		-0.24002	-0.27528	-0.34945
2A C opt.	-0.23888	-0.15943	-0.24934	-0.28656	-0.36065
1A at 2A C	-0.21126			-0.24360	-0.32176
2A R15 opt.	-0.23320	-0.15054	-0.24188	-0.26786	-0.34660
1A at 2A R15	-0.16885			-0.20236	-0.28160
2A R35 opt.	-0.22222	-0.14350	-0.22500	-0.26207	-0.33905
1A at 2A R35	-0.13099			-0.16327	-0.24674

TABLE IV. VEDEs of 4-thiouracil, 2-thiouracil, and 2,4-dithiouracil anions, in eV.

4-thiouracil				
Anion	ΔE_{MP2}	ΔE_{PMP2}	ΔE_{CCSD}	$\Delta E_{\text{CCSD(T)}}$
C	0.51	0.79	0.91	0.80
R15	1.36	1.53	1.26	1.30
R35	2.68	2.74	2.84	2.68
2-thiouracil				
Anion	ΔE_{MP2}	ΔE_{PMP2}	ΔE_{CCSD}	$\Delta E_{\text{CCSD(T)}}$
C	0.58	0.69	0.77	0.71
R15	1.49	1.72	1.77	1.66
R35	2.44	2.50	2.63	2.45
Dithiouracil				
Anion	ΔE_{MP2}	ΔE_{PMP2}	ΔE_{CCSD}	$\Delta E_{\text{CCSD(T)}}$
C	0.75	1.04	1.17	1.06
R15	1.75	1.99	1.78	1.77
R35	2.48	2.56	2.69	2.51

reverse process, where electron detachment from an anion occurs, therefore should produce broad peaks in the photoelectron spectrum that represent many vibrational excitations in the final, uncharged state. The spectra of Bowen and coworkers¹² confirm these predictions. CCSD(T) results may be improved with zero-point-energy corrections obtained with MP2 to produce the following predictions for adiabatic electron affinities: 0.61 (4-thiouracil), 0.26 (2-thiouracil), and 0.87 eV (2,4-dithiouracil). The thresholds observed in the photoelectron spectra of 4-thiouracil and 2,4-dithiouracil are, respectively, 0.7 and 1.0 eV (Ref. 12) and agree closely with the calculations. Relative stabilities that accompany tautomerization are summarized in Table VI. For 4-thiouracil and 2,4-dithiouracil, the R15 forms are unlikely to be present in an equilibrium sample, for their relative energies at the CCSD(T) level exceed 5 kcal/mol. Consideration of zero-point-energy corrections at the MP2 level reinforces this conclusion. The R35 forms are even less stable. However, the conditions under which anions have been produced prior to the measurement of their photoelectron spectra are far from equilibrium.¹²

The relative stability of the R15 form with respect to the canonical isomer of 2-thiouracil is noteworthy. In fact, the canonical and R15 anions of 2-thiouracil are predicted at the CCSD(T) level to be more stable than the R15 anion

TABLE V. Electron affinities of 4-thiouracil, 2-thiouracil, and 2,4-dithiouracil, in eV.

Vertical				
Molecule	ΔE_{MP2}	ΔE_{PMP2}	ΔE_{CCSD}	$\Delta E_{\text{CCSD(T)}}$
4-TU	-0.05	0.24	0.18	0.24
2-TU	-0.22	-0.05	-0.20	-0.17
DiTU	0.17	0.47	0.54	0.48
Adiabatic				
Molecule	ΔE_{MP2}	$\Delta E_{\text{MP2+ZPE}}$	ΔE_{CCSD}	$\Delta E_{\text{CCSD(T)}}$
4-TU	0.19	0.29	0.44	0.51
2-TU	0.03	0.12	0.17	0.17
DiTU	0.44	0.53	0.85	0.78

TABLE VI. Relative stabilities of 4-thiouracil, 2-thiouracil, and 2,4-dithiouracil anions, in kcal/mol.

4-thiouracil				
Anion	ΔE_{MP2}	$\Delta E_{\text{MP2+ZPE}}$	ΔE_{CCSD}	$\Delta E_{\text{CCSD(T)}}$
C	0	0	0	0
R15	3.51	11.09	13.46	10.05
R35	10.31	10.00	14.80	13.62
2-thiouracil				
Anion	ΔE_{MP2}	$\Delta E_{\text{MP2+ZPE}}$	ΔE_{CCSD}	$\Delta E_{\text{CCSD(T)}}$
C	1.88	1.98	6.29	5.81
R15	0	0	0	0
R35	6.31	5.92	9.73	9.32
Dithiouracil				
Anion	ΔE_{MP2}	$\Delta E_{\text{MP2+ZPE}}$	ΔE_{CCSD}	$\Delta E_{\text{CCSD(T)}}$
C	0	0	0	0
R15	3.56	5.68	11.73	8.82
R35	10.45	10.00	15.37	13.55

of 4-thiouracil. High barriers to conversion between the 2-thiouracil and 4-thiouracil trios of structures are likely to prevent the former set of species from being represented in the anion photoelectron spectrum, for the synthetic precursor employed in this experiment is 4-thiouracil.¹²

VEDEs predicted at various levels of electron propagator theory are listed in Table VII for 4-thiouracil. (Valence molecular orbitals of anions are enumerated in Tables VII–X.) For the lowest final state, corrections to KT results provided at the OVGf, P3, and P3+ levels are large (0.6–0.7 eV), consistent, and in close agreement with the experimental peak at 1.05 eV.¹² Three triplet final states, corresponding to β spin-orbitals in the reference configuration, are considered as well. Results for the first two triplet final states near 3.1 eV are in good agreement with the features seen in the spectrum at 3.21 and 3.32 eV. A separation of approximately 0.1 eV is predicted between two triplets by the OVGf, P3, and P3+ methods.

TABLE VII. Electron propagator VEDEs of 4-thiouracil conventional anion, in eV.

MO	α				β			
	KT	OVGF	P3	P3+	KT	OVGF	P3	P3+
22	1.84	1.00	1.22	1.14				
		1.01						
		1.13						
21					3.63	3.07	3.17	3.13
						3.17		
						3.23		
20					3.89	3.17	3.12	3.07
						3.37		
						3.37		
19					6.04	4.93	5.23	5.12
						4.94		
						5.09		

TABLE VIII. Electron propagator VEDEs of 4-thiouracil tautomer anion (R15), in eV.

MO	α				β			
	KT	OVGF	P3	P3+	KT	OVGF	P3	P3+
22	1.67	1.24 1.32 1.42	1.69	1.62				
21					4.81	3.91 4.00 4.06	3.96	3.90
20					5.06	4.23 4.26 4.36	4.38	4.31
19					6.65	5.27 5.37 5.48	5.50	5.32

Results obtained with the same methods for the R15 tautomer are given in Table VIII. All of the VEDEs are shifted to higher values. For the first VEDE, the OVGF predictions lie within the experimental envelope (0.7–1.5 eV), but the P3 and P3+ values do not. For the triplet final states, all predicted transitions lie beyond the observable range established by the photon energy of 3.49 eV.¹²

The present results imply that only the R15 isomer could be making a small contribution to the observed photoelectron spectrum. However, it is not necessary to invoke its presence in the experimental sample to explain any feature of the spectrum. Given the high relative energy of the R15 isomer of 4-thiouracil and the poorer correspondence of its first VEDE with the observed spectrum, there are no grounds to establish its presence in the experiment of Bowen and coworkers.¹² Electron propagator results on the canonical isomer suffice to explain the features of this spectrum.

Table IX shows electron propagator results for the canonical form of 2,4-dithiouracil. Excellent agreement with the experimental peak at 1.40 eV is obtained for OVGF, P3, and P3+ levels of theory. Results for three triplet final states are

TABLE IX. Electron propagator VEDEs of 2,4-dithiouracil conventional anion, in eV.

MO	α				β			
	KT	OVGF	P3	P3+	KT	OVGF	P3	P3+
22	2.18	1.30 1.32 1.44	1.50	1.42				
21					3.90	3.34 3.45 3.51	3.44	3.39
20					4.17	3.44 3.63 3.64	3.37	3.32
19					5.20	4.46 4.47 4.55	4.60	4.56

TABLE X. Electron propagator VEDEs of 2,4-dithiouracil tautomer anion (R15), in eV.

MO	α				β			
	KT	OVGF	P3	P3+	KT	OVGF	P3	P3+
22	2.32	1.77 1.84 1.94	2.16	2.09				
21						4.41 3.77 3.84 3.92	3.92	3.86
20						4.63 3.83 4.00 4.02	3.76	3.72
19						5.28 4.36 4.47 4.51	4.35	4.30

also listed. The first two of these transitions lie tantalizingly close to the limit imposed by the photon energy. Whereas a shoulder appears near this limit in the reported spectrum,¹² its presence may represent a technical artifact that makes definite assignment premature.

Electron propagator predictions on the R15 tautomer of 2,4-dithiouracil given in Table X cast doubt on the presence of this isomer in the experimental sample. The P3 and P3+ results lie outside the 1.0–1.9 eV envelope, although the OVGF values are barely within these limits. The high relative energy of this tautomer and the larger discrepancy between its predicted VEDE and experiment provide no justification for invoking its presence in the experimental spectrum. The results of Table IX suffice to explain the principal features of the anion photoelectron spectrum of 2,4-dithiouracil.

IV. CONCLUSIONS

Whereas 4-thiouracil, 2-thiouracil, and 2,4-dithiouracil have a plane of symmetry in their equilibrium, canonical structures, their anions do not. Positive, vertical electron affinities are obtained only for 4-thiouracil and 2,4-dithiouracil, but all three molecules have bound anions. Adiabatic electron affinities of 0.61, 0.87, and 0.26 eV were determined at the CCSD(T) level of theory of 4-thiouracil, 2,4-dithiouracil, and 2-thiouracil, respectively. These values differ by several tenths of an eV from vertical electron affinities of the uncharged molecules and confirm the valence character of the anions. Tautomeric forms of the anions exhibit shifts of a proton to the C5 from the N1 or N3 ring positions. These forms are less stable than their canonical counterparts by more than 5 kcal/mol for 4-thiouracil and 2,4-dithiouracil anions. However, the canonical form of the 2-thiouracil anion is less stable than the tautomer with the N1 to C5 proton shift.

Electron propagator and CCSD(T) predictions of the vertical electron detachment energies of the canonical anions suffice to explain the principal features of the photoelectron spectra observed by Bowen and coworkers.¹² Electron propagator predictions at 1.1 eV for the VEDE of 4-thiouracil agree closely with the 1.05 eV experimental peak. Predictions of

triplet states at 3.1–3.2 eV also coincide closely with spectral features seen at 3.21 and 3.32 eV. Results obtained for the next most stable tautomer produce inferior agreement with experiment.

For 2,4-dithiouracil, electron propagator predictions on the canonical anion are in close agreement with the observed spectral peak at 1.4 eV. Two triplet states are predicted to be close to the edge of the experimental range of electron binding energies imposed by the 3.49 eV photon source. VEDES corresponding to the next most stable tautomer are outside the range of the envelope seen in the spectrum.

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