An excess electron bound to urea. I. Canonical and zwitterionic tautomers

Piotr Skurski
Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah,
Salt Lake City, Utah 84112and Department of Chemistry, University of Gdańsk ul. Sobieskiego 18,
80-952 Gdańsk, Poland

Jack Simons[a]
Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah,
Salt Lake City, Utah 84112

The possibility of electron binding to urea was studied at the coupled cluster level of theory with single, double, and noniterative triple excitations. It was found that none of the urea isomers forms a valence anionic state although almost all of them can attach an excess electron and form a stable dipole-bound or Rydberg anion. Moreover, the canonical tautomers are the lowest energy structures of the neutral and anion. The zwitterionic isomer was found to be locally stable only when solvated with an "extra" electron and the corresponding anion is a Rydberg species perturbed by a neighboring negative charge. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1412003]

I. INTRODUCTION

Urea ($O=C(NH_2)_2$), the first synthetic organic compound and one of the simplest biological molecules,[1,2] is of great interest in inorganic chemistry due to its capability to form transition metal complexes[3] and because of its interesting nonlinear optical properties.[4] Also, urea-driven denaturation of proteins is widely used to study protein folding–unfolding equilibria.[5–7] As one of the simplest diamides, urea has been extensively studied by biologists, chemists, and material scientists. Its planar conformation in the solid state was determined by numerous x-ray studies[8–11] and theoretical calculations[12] as has been its vibrational spectrum in the gas and crystal phases.[13] In addition, its static and dynamic electric properties (e.g., the first-, second-, and third-order polarizabilities) have been studied theoretically at various levels of approximation.[14,15] One of the most recent works devoted to this species is that by Pluta and Sadlej who examined major linear and nonlinear electric properties (dipole moments, dipole polarizabilities, first and second hyperpolarizabilities) at the coupled-cluster (CCSD(T)) level of theory.[16] On the experimental side, recent work by Wang *et al.*[17] provided valuable information about the proton affinity and gas-phase basicity of urea, which were determined by using a kinetic method.

As far as computational studies on the molecular structure of urea are concerned, early *ab initio* calculations carried out with small basis sets predicted the molecule to be planar.[18–20] More recent calculations, however, have shown it to possess a global minimum at nonplanar geometry.[21–23] It is worth mentioning that recently two excellent theoretical papers by Masunov and Dannenberg appeared, the first[24] showing molecular structures of urea in various monomeric and dimeric forms [calculated at the Hartree–Fock (HF),

density functional theory (DFT) with the hybrid B3PW91 functional, and Møller–Plesset second-order perturbation theory (MP2) with basis sets up to D95++**], and the second[25] dealing with one-dimensional hydrogen-bonded aggregates corresponding to chains and ribbons.

Although urea has been so extensively studied, two issues remain that have not been addressed thus far: (i) the stability of its zwitterionic $O=C(NH)NH_3$ tautomer and (ii) its ability to bind an extra electron to form stable molecular anions. In this work, we present *ab initio* results for both canonical ($O=C(NH_2)_2$) and zwitterionic ($O=C(NH)NH_3$) urea tautomers together with a detailed study of an excess electron binding to those systems. For completeness, we also consider another structural isomer of urea–isourea ($HO–C(NH_2)=NH$).

We explored the ground-state potential energy surface (PES) of urea to search for a minimum corresponding to the zwitterionic (**Z**) form with a proton transferred from one $–NH_2$ group to another. Such an isomer ($O=C(NH)NH_3$) is expected to be much more polar than the canonical (**C**) $O=C(NH_2)_2$ system due to its larger charge separation. Since we have recently studied zwitterionic isomers of three other biologically important molecules (i.e., glycine,[26] arginine,[27] and betaine[28]) we are aware of the fact that, in the gas phase, the **Z** forms can be either unstable with respect to the canonical form (e.g., glycine) or competitive, as for arginine. Moreover, in cases such as betaine,[28] the zwitterionic form may be the lowest energy isomer due to the unique molecular constitution of the system.

Although one expects canonical forms of amino acids and other biological molecules to dominate in the gas phase, it is well known that zwitterionic tautomers are very common in solutions because of the differential stabilizing solvent effects.[29] We recently pointed out that, in the gas phase, a similar stabilizing role can be played by an excess electron.[26,30] Attachment of the extra electron to the **Z** tautomer leads to a negatively charged species whose energy

[a]Author to whom correspondence should be addressed. Electronic mail: simons@chemistry.utah.edu

should be lower than that of the parent neutral since the zwitterionic forms will attach an extra electron to the $-NH_3^+$ group forming an electronically stable anion of either dipole-bound[31] or Rydberg[32] nature.

We decided to undertake an extensive search for such negatively charged species. Our goal was to (i) determine their electronic stabilities, (ii) describe the nature of the electron binding, as well as to (iii) discuss the possible consequences of forming such anions. On the basis of the chemical structure of urea and its molecular orbital picture we were skeptical about the possibility of forming stable valence anions in this case. However, the dipole moments reported in the literature for the lowest conformers (being in the 3.7–4.7 Debye range)[23,25] made us consider the possibility of forming stable dipole-bound anions. As far as the zwitterionic tautomer is concerned, as noted above we expected even stronger excess electron binding than for the canonical form because of its significant charge separation.

II. METHODS

We first studied the ground-state potential energy surfaces of the neutral and anionic urea molecules at the second-order Møller–Plesset (MP2) level of theory.[33] Because the methods we used are based on an unrestricted Hartree–Fock starting point, it is important to make sure that little if any artificial spin contamination enters into the final wave functions. We computed the expectation value $\langle S^2 \rangle$ for species studied in this work and found values of 0.7500 in all anion cases. Hence, we are certain that spin contamination is not large enough to significantly affect our findings.

The electron binding energies (D) were calculated using a supermolecular approach (i.e., by subtracting the energies of the anion from those of the neutral). This approach requires the use of size-extensive methods for which we have employed Møller–Plesset perturbation theory up to the fourth order and the coupled-cluster method with single, double, and noniterative triple excitations (CCSD(T)).[34] In addition, D was analyzed within the perturbation framework described elsewhere.[35]

The simplest theoretical approach to estimate D is based on Koopmans' theorem (KT).[36] The KT binding energy (D^{KT}) is the negative of the energy of the relevant unfilled orbital obtained from a Hartree–Fock self-consistent-field (SCF) calculation on the neutral molecule. This is a static approximation to the electron binding energy which neglects both orbital relaxation and electron correlation effects. These effects were taken into account by performing SCF and CCSD(T) calculations for the neutral and the anion.

The polarization of the neutral host (N) by the excess electron and the effect of back-polarization are taken into account when the SCF calculation is performed for the anion (A), and the accompanying induction effects on D are given by

$$\Delta D_{ind}^{SCF} = D^{SCF} - D^{KT}, \tag{1}$$

where

$$D^{SCF} = E_N^{SCF} - E_A^{SCF} \tag{2}$$

and E_N^{SCF} and E_A^{SCF} stand for the SCF energies of the neutral and the anion, respectively.

The dispersion interaction between the loosely bound electron and N was extracted from the MP2 contribution to D. The dispersion term is a second-order correction with respect to the fluctuation–interaction operator and it is approximated here by ΔD_{disp}^{MP2} which takes into account proper permutational symmetry for all electrons in the anion

$$\epsilon_{disp}^{(02)} \approx \sum_{a \in N} \sum_{r < s} \frac{|\langle \phi_a \phi_{lbe} || \phi_r \phi_s \rangle|^2}{e_a + e_{lbe} - e_r - e_s} = -\Delta D_{disp}^{MP2} \tag{3}$$

where ϕ_a and ϕ_{lbe} are spin orbitals occupied in the unrestricted Hartree–Fock (UHF) anion wave function, ϕ_r and ϕ_s are unoccupied orbitals, and e's are the corresponding orbital energies. The subscript lbe denotes the loosely bound electron's spin orbital.

The total MP2 contribution to D defined as

$$\Delta D^{MP2} = D^{MP2} - D^{SCF} \tag{4}$$

is naturally split into dispersion and nondispersion terms

$$\Delta D^{MP2} = \Delta D_{disp}^{MP2} + \Delta D_{no\text{-}disp}^{MP2} \tag{5}$$

with the latter dominated by the correlation correction to the static Coulomb interaction between the loosely bound electron and the charge distribution of N.

The higher-order MP contributions to D are defined as

$$\Delta D^{MPn} = D^{MPn} - D^{MP(n-1)}, \quad n = 3,4. \tag{6}$$

Finally, the contributions beyond the fourth order are estimated by subtracting MP4 results from those obtained at the coupled-cluster level

$$\Delta D^{CCSD} = D^{CCSD} - D^{MP4} \tag{7}$$

while the contribution from noniterative triple excitations is calculated as the difference between $D^{CCSD(T)}$ and D^{CCSD}

$$\Delta D^{CCSD(T)} = D^{CCSD(T)} - D^{CCSD}. \tag{8}$$

The diffuse character of the orbital describing the loosely bound electron necessitates the use of extra diffuse basis functions having very low exponents.[37] In addition, the basis set chosen to describe the neutral molecular host should be flexible enough to (i) accurately describe the static charge distribution of the neutral and (ii) allow for polarization and dispersion stabilization of the anion upon electron attachment. All the calculations presented here (i.e., optimization of geometries, calculating frequencies, and evaluating the electron binding energies) were performed with the aug-cc-pVDZ basis set[38] supplemented with a $7s6p5d$ set of diffuse functions centered on the carbon atom.[39] The aug-cc-pVDZ basis set was chosen since we earlier showed its usefulness in describing dipole-bound anions compared to other commonly used one-electron basis sets.[37] The extra diffuse functions do not share exponent values and we used even-tempered[40] seven-term s, six-term p, and five-term d basis sets. The geometric progression ratio was equal to 3.2,[41] and for each symmetry we started to build up the exponents of the extra diffuse functions from the lowest exponent of the same symmetry included in aug-cc-pVDZ basis set designed for carbon. As a consequence, we achieved the

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lowest exponents of $1.364\,969\,6 \times 10^{-5}$, $3.763\,474\,5 \times 10^{-5}$, and $4.500\,150\,4 \times 10^{-4}$ a.u., for the s, p, and d symmetries, respectively.

In computing correlation energies, all orbitals except the $1s$ orbitals of carbon, oxygen and nitrogen were included. All calculations were performed with the GAUSSIAN98 program[42] on Intel Pentium III 500 MHz and AMD Athalon 950 MHz computers. The three-dimensional plots of molecular orbitals were generated with the MOLDEN program.[43]

In order to avoid erroneous results from the default direct SCF calculations with the basis sets with the large s, p, and d sets of diffuse functions, the keyword SCF=NoVarAcc was used and the two-electron integrals were evaluated (without prescreening) to a tolerance of 10^{-20} a.u.

III. RESULTS

A. Neutral urea—characterization of stationary points

In agreement with earlier studies,[24] we found that the global minimum of neutral urea corresponds to a nonplanar anti-conformation canonical structure ($\mathbf{C_{anti}}$) possessing C_2 symmetry with the H atoms of the NH_2 groups pyramidalized in opposite directions. Another local minimum corresponds to a less stable syn-conformation ($\mathbf{C_{syn}}$) of C_S symmetry with the hydrogen atoms of the NH_2 groups pyramidalized in the same direction. Even though the planar structure ($\mathbf{C_{planar}}$) of C_{2V} symmetry has been detected in the crystal structure, in fact, it does not correspond to a minimum on the gas-phase potential energy surface. Instead, as stated by Masunov and Dannenberg[24] and confirmed by our calculations at the same MP2 level but with the extended aug-cc-pVDZ$+7s6p5d$ basis set, the planar structure is a second-order saddle point connecting the two pairs of equivalent $\mathbf{C_{anti}}$ or $\mathbf{C_{syn}}$ nonplanar minima. Despite the fact that $\mathbf{C_{planar}}$ (i) is higher in energy and (ii) is a saddle point rather than a minimum, we also considered this structure while studying attachment of an extra electron because of its existence in condensed phases.[8–11]

As far as isourea ($\mathbf{I}$) is concerned (the urea isomer created by moving an H atom from one amino group to the oxygen atom), we found two minima on the PES, corresponding to $\mathbf{I_{syn}}$ and $\mathbf{I_{anti}}$ conformers, the former having the H atom (connected to the oxygen) directed in the same, and the latter in the opposite direction with respect to the $-NH_2$ functional group. We predicted the $\mathbf{I_{anti}}$ conformer to be lower in energy than the $\mathbf{I_{syn}}$, although both are thermodynamically unstable with respect to the canonical urea $\mathbf{C_{anti}}$.

To discuss the relative stabilities of these low-energy structures, we calculated their energies at the CCSD(T) level at the previously determined MP2 geometries. These energies and the geometrical parameters are shown in Table I and II, respectively. The structures of the anions (and of the $\mathbf{I_{anti}}$ neutral) are shown in Fig. 1; those of the corresponding neutrals are nearly identical, so they are not depicted. Finally, the energies of the anions and neutral species are summarized in Fig. 2.

The two canonical minima ($\mathbf{C_{anti}}$ and $\mathbf{C_{syn}}$) are close in energy, and so is the planar conformer $\mathbf{C_{planar}}$. The energy differences among those structures are less than 720 cm^{-1}

TABLE I. CCSD(T) energies (E in cm^{-1}) of the neutral and anionic species calculated with respect to the $\mathbf{C_{anti}}$ structure of the neutral (the energies, also in cm^{-1}, corrected for the MP2 zero-point vibrational energies, are denoted $E+E_{0,vib}$).

System	E	$E+E_{0,vib}$
neutral $\mathbf{C_{anti}}$[a,b]	0	0
neutral $\mathbf{C_{syn}}$	428	244
neutral $\mathbf{C_{planar}}$	718	306
neutral NH_3+HNCO	6621	4813
neutral $\mathbf{I_{anti}}$	5103	5008
neutral $\mathbf{I_{syn}}$	7420	7303
anion $\mathbf{C_{anti}^-}$	−111	−139
anion $\mathbf{C_{syn}^-}$	106	−73
anion $\mathbf{C_{planar}^-}$	433	3
anion $\mathbf{I_{syn}^-}$	7108	6990
anion $\mathbf{Z^-}$	9905	9601

[a]The CCSD(T)/aug-cc-pVDZ$+7s6p5d$ energy is −224.762 5579 a.u.
[b]The MP2 value of $E_{0,vib}$ is 39.963 kcal/mol.

and become even smaller when the zero-point energy corrections are included (see Table I). In fact, when averaged over zero-point vibrations, those conformers are separated by less than 1 kcal/mol, which leads to the conclusion that all of them can be present at room temperature.

Our extensive search for a local minimum corresponding to the zwitterionic structure $\mathbf{Z}$ of the neutral led us to the conclusion that the O=C(NH)NH$_3$ structure does not correspond to a stationary point on the MP2 potential energy surface. All geometry optimization attempts we undertook based on *ab initio* forces move downhill in energy to two species: ammonia and isocyanic acid (HNCO) which are the result of C–NH$_3$ bond breaking (see Fig. 2 and Table I for relative energies). After performing a *relaxed scan* of the variable corresponding to the distance between the carbon atom and the nitrogen connected to three H atoms, we are confident that the neutral zwitterion, if formed, would fall apart with no kinetic barrier producing NH$_3$ and HNCO.

Finally, we found the two ($\mathbf{I_{anti}}$ and $\mathbf{I_{syn}}$) conformers of isourea to be higher in energy by 5103 and 7420 cm^{-1}, respectively, than the most stable $\mathbf{C_{anti}}$ structure (see Fig. 2 and Table I). The zero-point energy corrections decrease these instabilities only by ca. 100 cm^{-1}.

B. Anions based on urea—characterization of geometries and electron binding energies

1. Stable anions supported by the conformers of urea and isourea

None of the urea conformers forms a valence-bound anion. However, the dipole moments calculated for the neutral system at the $\mathbf{C_{anti}}$, $\mathbf{C_{syn}}$, $\mathbf{C_{planar}}$, and $\mathbf{I_{syn}}$ geometries are larger than 2.5 Debye (see Table II), which suggests the possibility of binding an extra electron by the dipole potential to form stable dipole-bound anionic states. In this section we present detailed results for the canonical C_2-symmetry structure ($\mathbf{C_{anti}}$) that corresponds to the global minimum on the ground-state potential energy surface for both neutral and anionic species. We also discuss electron binding energies for other canonical ($\mathbf{C_{syn}}$, $\mathbf{C_{planar}}$) and zwitterionic ($\mathbf{Z}$) conformers, as well as for the isourea isomer ($\mathbf{I_{syn}}$).

TABLE II. MP2 geometries, dipole moments, and zero-point vibrational energies of the neutral and anionic (given in parentheses) structures of urea. Bond lengths (r) in Å, valence (α) and dihedral (δ) angles in degrees, dipole moments (μ) in Debyes, zero-point vibrational energies ($E_{0,\mathrm{vib}}$) in kcal/mol. All dipole moments were calculated for the neutral species either at the equilibrium geometry of the neutral or the anion (in parentheses). See Fig. 1 for atom numbering.

$\mathbf{C_{anti}}$ Neutral (anion)	$\mathbf{C_{syn}}$ Neutral (anion)	$\mathbf{C_{planar}}$ Neutral (anion)	$\mathbf{Z}$[a] (anion)	$\mathbf{I_{anti}}$ Neutral	$\mathbf{I_{syn}}$ Neutral (anion)
$r(C_1O_2)=1.230$ (1.231)	$r(C_1O_2)=1.231$ (1.233)	$r(C_1O_2)=1.233$ (1.235)	$r(C_1O_2)=(1.239)$	$r(C_1O_2)=1.366$	$r(C_1O_2)=1.371$ (1.373)
$r(C_1N_3)=1.394$ (1.393)	$r(C_1N_3)=1.389$ (1.388)	$r(C_1N_3)=1.380$ (1.379)	$r(C_1N_3)=(1.617)$	$r(C_1N_3)=1.386$	$r(C_1N_3)=1.408$ (1.407)
$r(N_3H_5)=1.014$ (1.014)	$r(N_3H_5)=1.012$ (1.013)	$r(N_3H_5)=1.009$ (1.009)	$r(C_1N_4)=(1.309)$	$r(C_1N_4)=1.288$	$r(C_1N_4)=1.283$ (1.282)
$r(N_3H_6)=1.014$ (1.014)	$r(N_3H_6)=1.012$ (1.013)	$r(N_3H_6)=1.008$ (1.009)	$r(N_4H_7)=(1.027)$	$r(N_4H_7)=1.023$	$r(N_4H_7)=1.024$ (1.024)
$\alpha(N_3C_1N_4)=113.50$ (113.58)	$\alpha(N_3C_1N_4)=114.66$ (114.65)	$\alpha(N_3C_1N_4)=114.77$ (114.79)	$r(N_3H_8)=(1.025)$	$r(N_3H_5)=1.014$	$r(N_3H_5)=1.018$ (1.018)
$\alpha(H_5N_3H_6)=114.02$ (114.22)	$\alpha(H_5N_3H_6)=115.83$ (115.67)	$\alpha(H_5N_3H_6)=119.44$ (119.37)	$r(N_3H_5)=(1.026)$	$r(N_3H_6)=1.013$	$r(N_3H_6)=1.016$ (1.016)
$\alpha(C_1N_3H_5)=112.41$ (112.68)	$\alpha(C_1N_3H_5)=113.80$ (113.89)	$\alpha(C_1N_3H_5)=117.04$ (117.16)	$\alpha(N_3C_1N_4)=(106.16)$	$r(O_2H_8)=0.971$	$r(O_2H_8)=0.969$ (0.969)
$\delta(H_8N_4C_1H_7)=134.22$ (135.21)	$\delta(H_8N_4C_1H_7)=-143.20$ (-142.81)		$\alpha(H_7N_4C_1)=(106.53)$	$\alpha(N_3C_1N_4)=130.23$	$\alpha(N_3C_1N_4)=129.47$ (129.49)
$\delta(H_6N_3C_1H_5)=134.22$ (135.21)	$\delta(H_6N_3C_1H_5)=143.20$ (142.81)		$\alpha(O_2C_1N_3)=(111.64)$	$\alpha(H_7N_4C_1)=111.00$	$\alpha(H_7N_4C_1)=109.81$ (109.83)
			$\alpha(H_5N_3H_6)=(107.16)$	$\alpha(O_2C_1N_3)=109.77$	$\alpha(O_2C_1N_3)=112.39$ (112.55)
			$\alpha(H_5N_3H_8)=(109.82)$	$\alpha(H_5N_3H_6)=114.29$	$\alpha(H_5N_3H_6)=110.91$ (110.92)
			$\delta(H_8N_3H_5H_6)=(119.24)$	$\alpha(C_1N_3H_5)=114.79$	$\alpha(C_1N_3H_5)=113.34$ (113.30)
				$\alpha(C_1O_2H_8)=104.94$	$\alpha(C_1O_2H_8)=108.12$ (108.30)
				$\delta(N_3C_1O_2N_4)=177.38$	$\delta(N_3C_1O_2N_4)=177.75$ (177.61)
				$\delta(H_5N_3C_1H_6)=-136.25$	$\delta(H_5N_3C_1H_6)=-127.45$ (-127.24)
				$\delta(N_3C_1N_4H_7)=2.44$	$\delta(N_3C_1N_4H_7)=8.41$ (8.45)
				$\delta(N_3C_1O_2H_8)=176.36$	$\delta(N_3C_1O_2H_8)=23.16$ (23.40)
$\mu^{SCF}=3.997$ (4.060)	$\mu^{SCF}=4.708$ (4.739)	$\mu^{SCF}=4.763$ (4.791)	$\mu^{SCF}=(5.868)$	$\mu^{SCF}=2.486$	$\mu^{SCF}=4.744$ (4.745)
$\mu^{MP2}=3.571$ (3.631)	$\mu^{MP2}=4.261$ (4.289)	$\mu^{MP2}=4.315$ (4.340)	$\mu^{MP2}=(5.447)$	$\mu^{MP2}=2.314$	$\mu^{MP2}=4.383$ (4.384)
$E_{0,\mathrm{vib}}=39.963$ (39.878)	$E_{0,\mathrm{vib}}=39.437$ (39.452)	$E_{0,\mathrm{vib}}=38.775$ (38.726)	$E_{0,\mathrm{vib}}=(39.091)$	$E_{0,\mathrm{vib}}=39.691$	$E_{0,\mathrm{vib}}=39.629$ (39.625)

[a]For the zwitterionic Z^- structure the c_s-symmetry plane contains C_1, O_2, N_3, N_4, and H_7 atoms.

According to our predictions based on the dipole moment of the neutral species, some of the isomers can bind an excess electron and form stable anions. The lowest energy structure on the anionic PES is the $\mathbf{C_{anti}^-}$, although the anions supported by other $\mathbf{C}$ conformers remain close in energy, in the 200–550 cm^{-1} range (see Fig. 2 and Table I). When
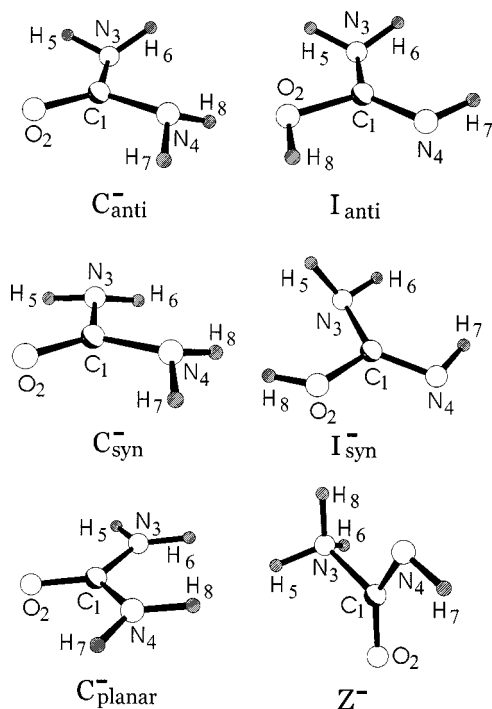

FIG. 1. Structures of anion stationary points (in the case of $\mathbf{I_{anti}}$ the neutral is depicted since the corresponding anion is not stable).

averaged over zero-point vibrations, the energy differences among all three canonical anions ($\mathbf{C_{anti}^-}$, $\mathbf{C_{syn}^-}$, and $\mathbf{C_{planar}^-}$) become very small (66–142 cm^{-1}).

Even though the zwitterionic $\mathbf{Z}$ tautomer of urea does not correspond to a stationary point on the ground-state potential energy surface of the neutral (see the preceding section) we found that a local minimum for $\mathbf{Z}^-$ develops when an excess electron is attached. It is much higher in energy than the most stable neutral form ($\mathbf{C_{anti}}$) by 9905 cm^{-1}, but may be detectable experimentally if successfully formed, since its vertical electron detachment energy (VDE) is predicted to be more than 10 times larger than VDE for $\mathbf{C_{anti}^-}$ (see Sec. III B 3 for detailed discussion of the electron binding energies). Moreover, the $\mathbf{Z}^-$ anion is geometrically stable and the kinetic barrier for its transformation to the $\mathbf{C}$-type anionic species (via proton transfer from $-NH_3$ to the $-NH$ group) is relatively high, as determined at the MP2 level, and equal to 7301 cm^{-1} (20.9 kcal/mol). We determined that $\mathbf{Z}^-$ should be electronically stable along the path of this tautomerization. In particular, at the transition state geometry connecting $\mathbf{Z}^-$ and $\mathbf{C}$, the dipole moment of the neutral parent molecule is 3.866 Debye, and the corresponding anion is bound at the electrostatic–exchange Koopmans (KT) level by 40 cm^{-1}.[44] Between two isourea conformers, $\mathbf{I_{anti}}$ and $\mathbf{I_{syn}}$, only the latter binds an extra electron and forms a dipole-bound anion. The dipole moment of the $\mathbf{I_{anti}}$ is only 2.486 Debye and we checked that, in this case, binding of an excess electron by more than 1 cm^{-1} is not possible. In contrast, $\mathbf{I_{syn}}$ possesses a dipole moment of 4.744 Debye which is similar to that of $\mathbf{C_{planar}}$ (see Table II), and it forms a dipole-bound anion having similar VDE to $\mathbf{C_{planar}^-}$ (see

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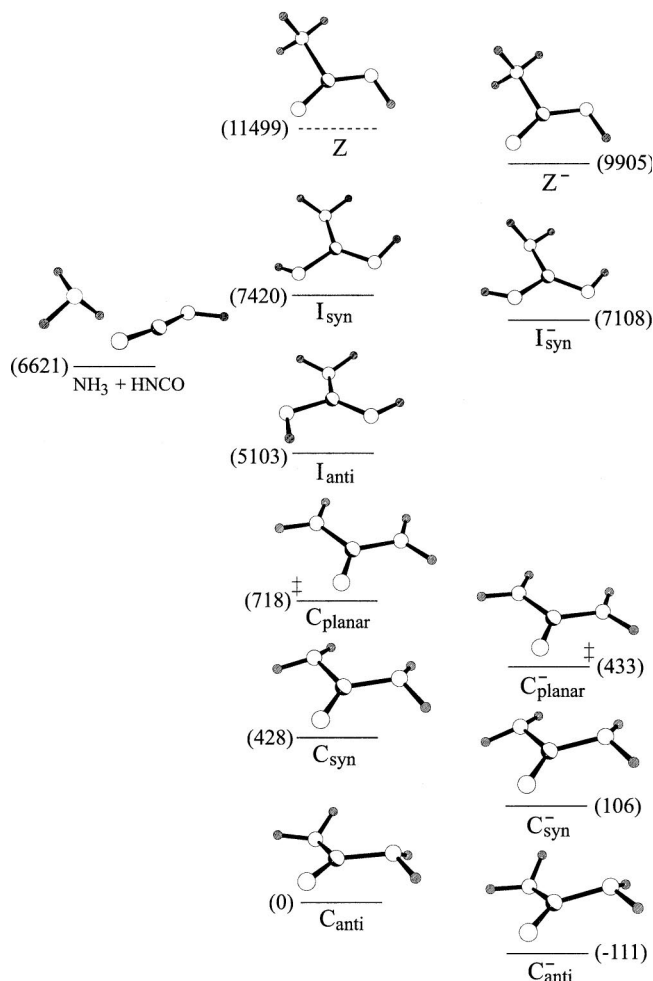Excess electron bound to urea   8377

FIG. 2. CCSD(T) energies (in parentheses, given in cm^{-1}) and MP2 equilibrium structures of stationary points on the anion (right) and neutral (left) ground-state potential energy surface. The **Z** neutral's energy is computed at the geometry of the stable **Z**$^-$; this **Z** spontaneously dissociates into NH$_3$+HNCO and the dashed line indicates **Z**$^-$ does not correspond to a stationary point on the neutral PES.

Table III). However, we predict **I**$^-_{\text{syn}}$ to be thermodynamically unstable with respect to **C**$^-_{\text{anti}}$ as was the case for **Z**$^-$.

2. Geometry relaxation upon excess electron attachment

An excess electron attachment, although crucial for the existence of the zwitterionic stationary point, has very little impact on the geometrical parameters characterizing other species. In Table II we collected the bond lengths and valence and dihedral angles for the equilibrium neutral and anionic structures. The bond lengths remain essentially the same upon electron attachment (the typical change is 0.001 Å and the largest change is only 0.002 Å), as do valence angles. The biggest change in a valence angle is 0.27 deg for $<$(C$_1$N$_3$H$_5$) in the **C$_{\text{anti}}$** structure (see Table II and Fig. 1). The changes in dihedral angles caused by attachment of an electron are small but noticeable, especially for **C$_{\text{anti}}$** and **C$_{\text{syn}}$**, but even here they never exceed 1.0 deg. One can also notice that the **I$_{\text{syn}}$** structure remains almost unaffected when the anion is formed.

Small geometry differences between the corresponding anionic and neutral species cause the dipole moments of the neutral to be almost the same when calculated at the negatively charged or parent neutral equilibrium geometries (see Table II). According to our experience with other dipole-bound anions,[26–28,31,35,37,45] the values of the dipole moments of the neutrals are always larger when calculated at the corresponding anionic geometries since the geometry relaxation upon electron attachment always allows for increasing the electrostatic stabilization of the resulting dipole-bound anion. For the urea and isourea conformers, we observe analogous trends but the changes in dipole moments are rather small, from +0.063 Debye for **C$_{\text{anti}}$** to only +0.001 Debye for **I$_{\text{syn}}$**.

3. Electron binding energies

The relevant rotational energy level spacings for these species are much smaller than the calculated values of D. Hence, non-BO coupling between the electronic and rotational degrees of freedom is expected to be of secondary importance for these anions and is not considered in this study.

The electron binding energy was partitioned into incremental contributions calculated at "successive" levels of theory [KT, SCF, MPn ($n=2,3,4$), and CCSD(T)] as discussed in Sec. II, and the results for the optimal **C**, **Z**, and **I** structures of urea are presented in Table III. In the KT approximation, the electron binding energy results from the electrostatic and exchange interactions of the loosely bound electron with the SCF charge distribution of the neutral molecule (primarily characterized by the dipole moment, but interactions with higher permanent multipoles and penetration effects are also included). For all three canonical conformers, the D^{KT} values are relatively small: 35 cm^{-1} for **C$^-_{\text{anti}}$**, 112 cm^{-1} for **C$^-_{\text{syn}}$**, and 103 cm^{-1} for **C$^-_{\text{planar}}$**. The KT binding energy for the isourea (**I$^-_{\text{syn}}$**) is similar (105 cm^{-1}). For the **Z** structure, however, D^{KT} is very large (683 cm^{-1}), even though its dipole moment is only 1.1 Debye larger than the dipole moment of the **C$_{\text{planar}}$**. As demonstrated in Fig. 3, the anion's singly occupied molecular orbital becomes more and more compact as D^{KT} increases (see the second column in Fig. 3 where two-dimensional orbital pictures are shown).

The SCF binding energies include orbital relaxation and thus take into account static polarization of the neutral molecule by the extra electron and the secondary effect of back polarization. We found these contributions (which can be interpreted as orbital relaxation corrections to D^{KT}, denoted $\Delta D_{\text{ind}}^{\text{SCF}}$) to be extremely small for all **C** tautomers and **I$_{\text{syn}}$**, and only 2–3 % of the total D. For **Z**$^-$, however, $\Delta D_{\text{ind}}^{\text{SCF}}$ is not negligible (124 cm^{-1}) and is responsible for 8% of D. Although usually significant for valence-bound anions, orbital relaxation effects are usually negligible and rarely responsible for more than a few percent of the total value of D for the majority of dipole-bound anions studied so far.[31]

The contribution denoted $\Delta D_{\text{disp}}^{\text{MP2}}$ results from dynamical correlation between the loosely bound electron and the electrons of the neutral molecule. This stabilization is caused by quantum mechanical charge fluctuations, and is larger than D^{KT} for all species studied here (see Table III). This finding is consistent with our earlier results for other dipole-bound

TABLE III. Components of the vertical electron binding energies D (in cm^{-1}) of the anions based on urea canonical and zwitterionic forms calculated with the aug-cc-pVDZ+$7s6p5d$ basis set. For each species D was calculated for the equilibrium geometry of the anion and the neutral (if it exists).

	C_{anti}		C_{syn}		C_{planar}		Z	I_{syn}	
	Geometry of the neutral	Geometry of the anion	Geometry of the neutral	Geometry of the anion	Geometry of the neutral	Geometry of the anion	Geometry of the anion	Geometry of the neutral	Geometry of the anion
D^{KT}	31	35	108	112	99	103	683	103	104
ΔD_{ind}^{SCF}	2	2	10	10	10	9	124	9	9
ΔD_{disp}^{MP2}	41	46	131	135	114	117	731	133	134
$\Delta D_{no-disp}^{MP2}$	−26	−28	−68	−69	−60	−61	−303	−55	−56
ΔD^{MP3}	5	5	11	11	12	13	50	10	10
ΔD^{MP4}	6	6	18	18	13	12	70	17	17
ΔD^{CCSD}	45	49	82	85	74	75	165	73	74
$\Delta D^{CCSD(T)}$	7	7	22	23	20	21	74	20	20
Sum	**111**	**122**	**314**	**325**	**282**	**289**	**1594**	**310**	**312**

anions.[31,45] Moreover, for each species the value of ΔD_{disp}^{MP2} increases when calculated for the anionic equilibrium geometry since the dispersion interaction between an excess electron and the electrons of the neutral parent molecule is stronger when the former is localized closer to the molecular core which is the case for the relaxed anion geometries.

In addition to the dispersion interaction, other electron correlation factors may also affect the charge distribution (and dipole moment) of the neutral molecule and thus its electrostatic interaction with the extra electron. This effect first appears at the MP2 level and is denoted by $\Delta D_{no-disp}^{MP2}$. In all C, Z, and I_{syn} cases, MP2 electron correlation effects reduce the dipole moment of the neutral system by ca. 0.4 Debye in comparison with the SCF value (see Table II). Therefore the value of $\Delta D_{no-disp}^{MP2}$ is always destabilizing, yet the total MP2 contribution to D is substantial and stabilizing due to the dominant role of the dispersion component. In particular, the total MP2 contribution is responsible for 15–20 % of D for C tautomers and I_{syn}, and for 27% of D for the zwitterion.

The convergence of the MP series for the electron binding energy is slow for all the systems. The contributions from ΔD^{MP3} are stabilizing but small (3–4 % of D). The contributions from ΔD^{MP4} are stabilizing and approximately as large as ΔD^{MP3}. Higher order correlation effects, calculated here as ΔD^{CCSD} (the difference between CCSD and MP4 binding energies) and $\Delta D^{CCSD(T)}$ [the difference between CCSD(T) and CCSD binding energies], are significant and stabilizing in all cases. ΔD^{CCSD} contributions are responsible for 26% of D for C_{syn}^- and C_{planar}^-, 40% of D for C_{anti}^-, and 24% of D for I_{syn}^-. However, this term is less important for the Z^- and responsible only for 10% of the total electron binding energy calculated for the Z^- anion. Finally, the contribution from noniterative triple excitation ($\Delta D^{CCSD(T)}$) is always stabilizing but small and amounts to 5–7 % of the total D for all species.

Combining all of these contributions produces our final predictions for the vertical electron detachment energies of 122, 325, and 289 cm^{-1} for C_{anti}^-, C_{syn}^-, and C_{planar}^-, respectively. For the anion based on the zwitterion, the vertical electron detachment energy is predicted to be much larger

(1594 cm^{-1}), and the anion formed by attaching an electron to isourea in its *syn* conformation is bound by 312 cm^{-1}.

We note that electron correlation effects represent 60–70 % of the electron binding energy for the C^- and I_{syn}^- anions and this finding is consistent with our recent results for other dipole-bound species, where the correlation contributions were always crucial and very often responsible for more than 50% of the total value of D.[31,45] For the Z^- however, the correlation contribution is much smaller and responsible for 49% of D.

4. Dipole-bound and Rydberg character of the anionic states

In all cases, the singly occupied molecular orbital holding the excess electron is fully symmetric and localized on the positive side of the molecular dipole in all the anionic species described in this work (see Fig. 3). This reflects the fact that the ground electronic state for C_{anti}^-, C_{syn}^-, C_{planar}^-, Z^-, and I_{syn}^- is a doublet state of A, A', A_1, A', and A symmetry, respectively. This observation suggests that all the anionic states described here display dipole-bound character. However, while analyzing the various contributions to the total electron binding energies, we noticed that for Z^- the significance of the certain terms is different than for the other anions. In particular we noticed much larger D^{KT} and ΔD_{ind}^{SCF} contributions, and significantly smaller ΔD^{CCSD} for Z^- in comparison with C^- and I_{syn}^- (see Table III). It is known[31] that D^{KT} values for dipole-bound anions usually correlate with the dipole moments of their neutral parent molecules. For a dipole moment of approximately 5.9 Debye (as calculated for Z), one would expect a KT electron binding energy in the 200–400 cm^{-1} range.[46] Instead, D^{KT} for Z^- is much larger (683 cm^{-1}). These observations bring into question the nature of the Z^- anionic state. We have concluded that this state exhibits Rydberg rather than dipole-bound character as we now explain. Z can be viewed as containing a $^+NH_3R$ functional group (R is $[-C(NH)O]^-$). Adding an electron then produces Z with one electron in a Rydberg orbital on the $^+NH_3R$ terminus perturbed by the negative charge (electron) localized in the vicinity of the other nitrogen atom. Noting that the ionization potentials (IP) for removing an
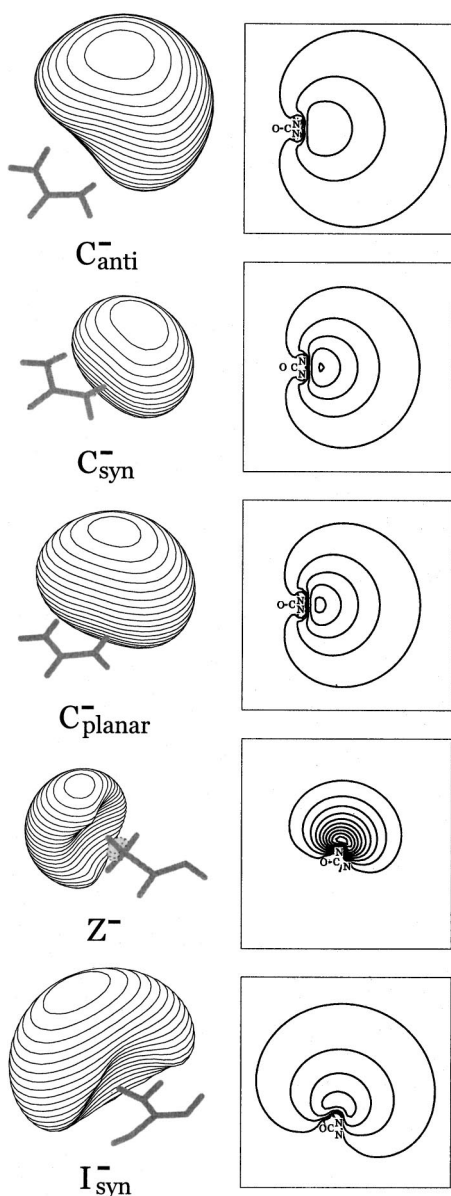
FIG. 3. Singly occupied molecular orbital of various anion stationary points (contour spacing is 0.004, 0.006, 0.006, 0.018, and 0.006 bohr$^{-3/2}$ for C_{anti}^-, C_{syn}^-, C_{planar}^-, Z^-, and I_{syn}^-, respectively, for the perspective plots in the left column, and 0.002 bohr$^{-3/2}$ for all plots in the right column).

electron from the Rydberg orbitals of NH_4, NH_3CH_3, $NH_2(CH_3)_2$, $NH(CH_3)_3$, and $N(CH_3)_4$ are 4.5, 4.0, 3.6, and 2.7 eV, respectively,[32,47–49] one observes how increasing the number of methyl groups decreases the energy needed to detach an electron. In Z^-, the destabilizing functional group is $-C(NH)^-O$, which holds an excess negative charge that can only further destabilize the system. If we assume that the vertical electron detachment energy for $O=C(NH)NH_3$ would be in the 3.6–4.0 eV range (where the upper limit is given by the IP of NH_3CH_3), we can estimate the electrostatic effect caused by the presence of the negative charge in $O=C(NH)^-NH_3$, that is, the electron binding energy for Z^- (1594 cm^{-1} ≈ 0.2 eV) may be considered as the IP of $O=C(NH)NH_3$ system (3.6–4.0 eV) lowered by the destabilizing electrostatic interaction with the negative charge in $O=C(NH)^-NH_3$. This e^2/r repulsion is thus responsible for

reducing the IP from 3.6–4.0 eV to 0.2 eV. This Coulomb repulsion corresponds to $r=3.8$–4.2 Å, which is close to the distance between two the most distant atoms in Z^- molecule (3.9 Å).

IV. SUMMARY

We studied the possibility of binding an excess electron to various urea and isourea isomers. On the basis of our *ab initio* CCSD(T)/aug-cc-pVDZ+$7s6p5d$ results we found the following:

(i)   The most stable conformer of neutral urea is non-planar (C_{anti}), but two other (C_{syn} and C_{planar}) structures are very close in energy (within 1 kcal/mol when averaged over zero-point vibrations).

(ii)   The zwitterionic form of urea is locally stable only when solvated by an excess electron (i.e., the neutral zwitterion does not correspond to a minimum on the potential energy surface but fragments to NH_3+HNCO).

(iii)   Neither canonical nor zwitterionic isomers of urea (or isourea) form valence anions. However, all of them (except isourea's *anti* conformer) can attach an "extra" electron due to the interaction with the dipole moment of the neutral species to form dipole-bound anions.

(iv)   As for the neutral species, the global minimum for the urea anion corresponds to the C_{anti}^- (canonical) C_2-symmetry nonplanar conformer.

(v)   The anion supported by the zwitterionic neutral urea should be viewed as a neutral Rydberg species perturbed by the presence of a nearby negative charge.

(vi)   Electron binding energies for the urea and isourea conformers are: 122, 325, 289, 312, and 1594 cm^{-1}, for C_{anti}^-, C_{syn}^-, C_{planar}^-, I_{syn}^-, and Z^-, respectively.

[1] F. Wöhler, Ann. Phys. (Leipzig) **12**, 253 (1828).
[2] R. A. Kuharski and P. J. Rossky, J. Am. Chem. Soc. **106**, 5786 (1984).
[3] T. Theophanides and P. D. Harvey, Coord. Chem. Rev. **76**, 237 (1987).
[4] I. Ledoux and J. Zyss, Chem. Phys. **73**, 203 (1982).
[5] C. Tanford, Adv. Protein Chem. **24**, 1 (1969).
[6] D. Neri, M. Billeter, G. Wider, and K. Wüthrich, Science **227**, 1559 (1992).
[7] E. Liepinsh and G. Otting, J. Am. Chem. Soc. **116**, 9670 (1994).
[8] S. Swaminathan, B. M. Craven, M. A. Spackman, and R. F. Stewart, Acta Crystallogr., Sect. B: Struct. Sci. **40**, 398 (1984).
[9] A. Kutoglu, C. Scheringer, H. Meyer, and A. Schweig, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **38**, 2626 (1982).
[10] A. W. Pryor and P. L. Sanger, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **26**, 532 (1970).
[11] D. Mullen and E. Hellner, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **34**, 1624 (1978).
[12] M. S. Miao, V. E. Van Doren, R. Keuleers, H. O. Desseyn, C. Van Alsenoy, and José Luis Martins, Chem. Phys. Lett. **316**, 297 (2000).

[13] B. Rousseau, C. Van Alsenoy, R. Keuleers, and H. O. Desseyn, J. Phys. Chem. A **102**, 6540 (1998).

[14] C. Adant, M. Dupuis, and J. L. Brédas, Int. J. Quantum Chem. **S29**, 497 (1995).

[15] H. Reis, M. G. Papadopoulos, and R. W. Munn, J. Chem. Phys. **109**, 6828 (1998).

[16] T. Pluta and A. J. Sadlej, J. Chem. Phys. **114**, 136 (2001).

[17] F. Wang, S. Ma, D. Zhang, and R. G. Cooks, J. Phys. Chem. A **102**, 2988 (1998).

[18] L. Snyder, J. Chem. Phys. **61**, 747 (1974).

[19] S. T. Elbert and E. R. Davidson, Int. J. Quantum Chem. **8**, 857 (1974).

[20] M. L. Williams and J. E. Gready, J. Comput. Chem. **10**, 35 (1989).

[21] M. Kontoyianni and J. P. Bowen, J. Comput. Chem. **13**, 657 (1992).

[22] A. Gobbi and G. Frenking, J. Am. Chem. Soc. **115**, 2362 (1993).

[23] T.-K. Ha and C. Puebla, Chem. Phys. **181**, 47 (1994).

[24] A. Masunov and J. J. Dannenberg, J. Phys. Chem. A **103**, 178 (1999).

[25] A. Masunov and J. J. Dannenberg, J. Phys. Chem. B **104**, 806 (2000).

[26] M. Gutowski, P. Skurski, and J. Simons, J. Am. Chem. Soc. **122**, 10159 (2000).

[27] P. Skurski, M. Gutowski, R. Barrios, and J. Simons, Chem. Phys. Lett. **337**, 143 (2001).

[28] J. Rak, P. Skurski, and M. Gutowski, J. Chem. Phys. **114**, 10673 (2001).

[29] C. R. Cantor and P. R. Schimmel, *Biophysical Chemistry* (W. H. Freeman, New York, 1980), Part I, pp. 41–53.

[30] P. Skurski, M. Gutowski, J. Rak, and J. Simons, J. Am. Chem. Soc. (to be published).

[31] M. Gutowski and P. Skurski, Recent Res. Dev. Phys. Chem. **3**, 245 (1999) and references therein.

[32] J. Simons and M. Gutowski, Chem. Rev. **91**, 669 (1991).

[33] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

[34] R. J. Bartlett and J. F. Stanton, in *Reviews in Computational Chemistry*, edited by K. B. Lipkowitz and D. B. Boyd (VCH, New York, 1994), Vol. V.

[35] M. Gutowski and P. Skurski, J. Phys. Chem. B **101**, 9143 (1997).

[36] T. Koopmans, Physica (Amsterdam) **1**, 104 (1934).

[37] P. Skurski, M. Gutowski, and J. Simons, Int. J. Quantum Chem. **80**, 1024 (2000).

[38] R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).

[39] We kept the extra $7s6p5d$ diffuse set centered on the carbon atom also for the **Z** and **I** isomers. We tested that doing so correctly describes the excess electron and verified that the resulting binding energies do not change when the $7s6p5d$ functions are moved to the nitrogen atom.

[40] M. W. Schmidt and K. J. Ruedenberg, Chem. Phys. **71**, 3961 (1979).

[41] M. Gutowski and J. Simons, J. Chem. Phys. **93**, 3874 (1990).

[42] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.7, Gaussian, Inc., Pittsburgh, PA, 1998.

[43] G. Schaftenaar and J. H. Noordik, J. Comput.-Aided Mol. Des. **14**, 123 (2000).

[44] Interestingly, when the additional diffuse functions possessing higher angular momentum (i.e., the d functions) are removed from the total basis set, the anion corresponding to the transition state structure becomes unbound. This is atypical for dipole-bound anions since, for all the species studied thus far, the inclusion of additional diffuse functions of d-symmetry were necessary only for saturating the electron binding energies, but their presence was never crucial to the stability of the dipole-bound anion.

[45] M. Gutowski, P. Skurski, A. I. Boldyrev, J. Simons, and K. D. Jordan, Phys. Rev. A **54**, 1906 (1996).

[46] The KT binding energies for the species possessing similar dipole moments, as uracil (5.39 Debye), HNNH$_3$ (5.50 Debye), and C$_5$H$_2$ (6.28 Debye), are 266, 377, and 216 cm^{-1}, respectively (see Ref. 31).

[47] S. Raynor and D. R. Hershbash, J. Phys. Chem. **86**, 3592 (1982).

[48] S. Havriliak and H. S. King, J. Am. Chem. Soc. **105**, 4 (1983).

[49] A. I. Boldyrev and J. Simons, J. Chem. Phys. **97**, 6621 (1992).