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An excess electron bound to urea. III. The urea dimer as an electron trap

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The possibility of electron binding to urea dimers in the gas-phase was studied at the coupled cluster level with single and double excitations using aug-cc-pVDZ$+7s6p5d$ basis sets. It was found that two kinds of anions can be formed—dipole-bound anions and solvated-electron anions. The global minimum on the ground-state anionic potential energy surface corresponds to the dipole-bound anion whose adiabatic and vertical electron binding energies are 484 and 1443 cm^{-1}, respectively. It was also found that solvated electron structures, which are locally geometrically stable yet thermodynamically unstable, are considerably higher in energy than dipole-bound anions. However, the vertical electron detachment energies of the latter are significantly larger (i.e., 1267, 4129, and 7540 cm^{-1}, depending on whether two canonical, one canonical, and one zwitterionic, or two zwitterionic urea monomers are involved, respectively), so their presence in any experimental source should allow them to be identified.
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I. INTRODUCTION

A. The preceding studies

This is the third paper in a series dealing with excess electron binding to urea and urea clusters. Although urea is one of the simplest organic compounds, its ability to form stable anions had not been examined until recently when we studied the possibility of excess electron binding to a single OCN_2H_4 molecule.[1] In fact, we considered not only canonical urea with two amino groups $[O{=}C(NH_2)_2]$ but also (i) the zwitterionic form (created by moving an H atom from one amino group to the other $[O{=}C(NH)NH_3]$) and (ii) so-called isourea (created by moving an H atom from one amino group to the oxygen atom $[HOC(NH)NH_2]$). Briefly, we found that none of the urea isomers form a stable valence-bound anion. However, some of them do form electronically stable dipole-bound anions. In particular, the nonplanar C_2-symmetry canonical urea, which we earlier found to be the global minimum on the neutral ground-state potential energy surface (PES),[1] and which was studied earlier by others,[2] supports a dipole-bound anion. That anion has an electron binding energy of 122 cm^{-1}, and the resulting anion is electronically, geometrically, and thermodynamically stable. We also found that other conformations of canonical urea (i.e., the nonplanar C_s-symmetry "syn" conformation and the planar C_{2V} structure) also form stable anions of dipole-bound nature. Moreover, we determined that the zwitterionic form of urea can exist only when an extra electron is attached (the neutral zwitterion falls apart to ammonia and isocyanic acid with no kinetic barrier). Interestingly, the zwitterion-based anion binds its electron more strongly (by 1594 cm^{-1}) than any canonical structure, and the extra electron occupies a Rydberg, rather than a dipole-bound orbital.[1] Finally, we found that the syn conformation of isourea supports a dipole-bound anionic state with an electron binding energy of 312 cm^{-1}. The relative energies and qualitative structures of these species are shown in Fig. 1.

Next, we extended our studies to urea oligomers (from dimer to pentamer).[3] We followed the extensive study of the neutral aggregates by Masunov and Dannenberg,[4] and we focused on two types of structures: (i) chains, where the monomers are oriented in the same direction with each molecule forming a bifurcated hydrogen bond connecting its oxygen atom with two hydrogen atoms of the neighbor, and (ii) ribbons, with each monomer oriented oppositely to the neighboring molecule and forming two hydrogen bonds with it. Both types of aggregates were constructed from planar monomers. Although the planar conformer of the canonical urea monomer is a second-order saddle point on both its neutral and anion PES, it has been shown that the barrier to achieve planarity is extremely small and is systematically lowered by H-bond formation and application of external electric fields.[5] Moreover, the planar structure is of particular interest since the crystal structures published indicate planar character[6] and because recent microwave spectroscopic gas-phase studies show zero-point vibrations to exceed the planarization barrier.[7] Therefore, we decided to use planar urea as the building block for all of the aggregates studied in that work. Moreover, we view these small oligomers as prototypes for defects and surface sites that may occur in the crystalline state or in microcrystals. Briefly, we found that[3]

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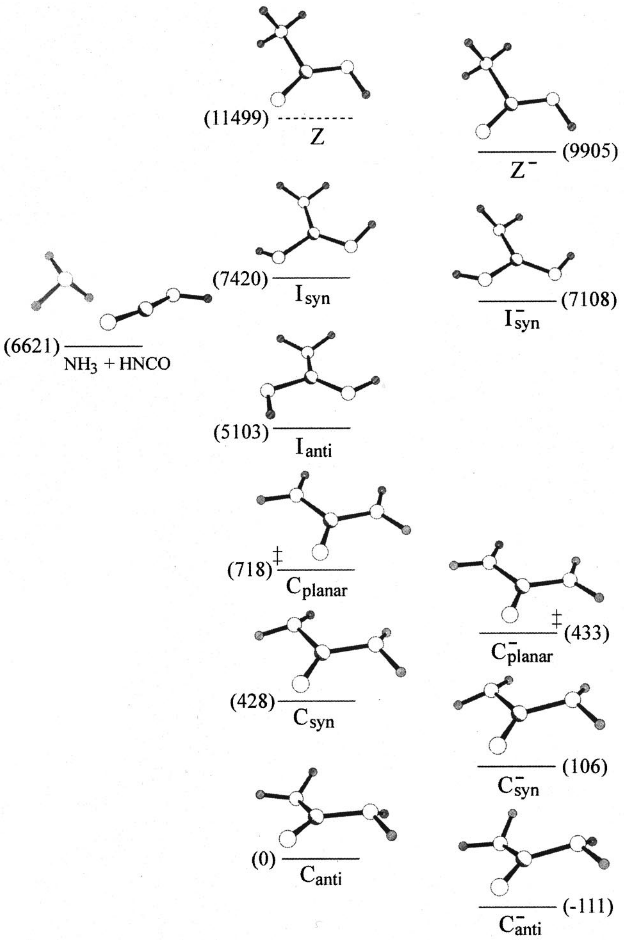

FIG. 1. CCSD(T) energies (in parenthesis, given in cm^{-1}) and MP2 equilibrium structures of stationary points on the anion (right) and neutral (left) ground-state potential energy surface. The zwitterion **Z** neutral's energy is computed at the geometry of the stable $\mathbf{Z}^-$; this **Z** spontaneously dissociates into NH_3+HNCO and the dashed line indicates $\mathbf{Z}^-$ does not correspond to a stationary point on the neutral PES. **C** and **Z** indicate canonical isomers, respectively, whereas **I** corresponds to isourea (taken from Ref. 1).

(i) chain urea oligomers form electronically stable dipole-bound anions whose electron binding energies rapidly grow with the size of the system;

(ii) ribbon urea oligomers bind an excess electron to form dipole-bound anions only when the number of urea monomer units is odd;

(iii) the electron binding energies for ribbonlike anions (containing an odd number of monomers) vary only slightly with the size of the system and are close to the isolated monomer anion's electron binding energy; and

(iv) the electron binding energies for the ground electronic states of the anions for the chain dimer, trimer, and tetramer are 1591, 2447, and 2786 cm^{-1}, while for the ribbon trimer and pentamer they are 160 and 68 cm^{-1} (the ribbon dimer and tetramer do not form stable anions).[3]

In the present work, we focus our attention on the urea dimer, but within a different context than considered in Ref. 3. In particular, we consider its ability to bind an excess electron in two different ways: by attaching it to the molecular dipole and by trapping it in between two urea monomers whose dipoles are both oriented toward the "solvated" electron. It should be mentioned that analogous situations occur in other anion clusters as we detail further in the next section. For example, in $(HF)_2{}^-$, one can bind the electron to the quasilinear FH··FH van der Waals dimer to produce a dipole-bound state, or one can trap the electron between two HF molecules oriented as FH··HF.

B. Dipole-bound anions and solvated electrons

The binding of electrons to polar molecules has been addressed in many theoretical studies.[8–21] It is that, within the Born–Oppenheimer (BO) approximation, a dipole moment greater than 1.625 Debye possesses an infinite number of bound anionic states.[22,23] However, a more practical critical value to experimentally observe a dipole-bound state (DBS) of anion bound by at least 1 cm^{-1} was found to be ca. 2.5 Debye.[8] In fact, this "practical" value depends on the size and chemical structure of the molecule as reflected in its valence-electron Coulomb and exchange repulsions. Jordan and Luken demonstrated that the loosely bound electron in a dipole-bound state occupies a diffuse orbital localized mainly on the positive side of the dipole.[11] This finding was confirmed by many more recent studies. The role of non-BO coupling has been studied by Garrett, who concluded that such couplings are negligible for dipole-bound states with electron binding energies much larger than the molecular rotational constants.[24] The electron binding energy (D) can be estimated based on Koopmans' theorem (KT)[25] as well as at other levels of theory. The orbital relaxation effects, which are neglected in the KT approximation, have been found to be quite small for a variety of dipole-bound anionic states.[12] In contrast, the role of electron correlation has proven to be very significant. In fact, in many cases, the electron binding energy of a dipole-bound anion is dominated by the contribution from electron correlation. In particular, the dispersion interaction of the excess electron with the electrons of the neutral parent molecule proved to be crucial for the stability of the dipole-bound anion[9,10,12–15] although higher order correlation effects were also significant.[12–15,20]

An excess electron may also be trapped inside a molecular cluster instead of being attached to the dipole moment of the neutral system. The existence of such species, very often referred to as *solvated electrons* (SE), has been known since 1864 when they were observed in liquid ammonia.[26] Since then many systems containing solvated electrons have been studied, such as $(NaCl)_n{}^-$ (n=2,3,4)[27] and $(HF)_n{}^-$ (n=2,3).[28] There are several important differences between SE systems and dipole-bound anions. The former contain an extra electron localized primarily *inside* a cluster of polar molecules whose dipoles are directed toward the excess electron.[29] In the latter, an excess electron is localized *outside* the molecular framework and the dipoles are aligned constructively. SE systems are known to usually possess relatively large vertical electron detachment energies (VDE) and to undergo large geometrical rearrangements upon electron detachment.[27–29]

Despite these differences, both solvated electron cluster anions and dipole-bound anions share a conceptual relationship in that they both involve the interaction of an excess electron primarily with the dipole potentials of the constituent polar molecules. For dipole-bound anions, the extra electron interacts with the dipole moment at a distance (i.e., it is tethered to the dipole), whereas for solvated electron cluster anions, the excess electron interacts with a set of polar molecules (either on the surface of a clustered collection or within a cavity of oriented polar molecules). However, the difference between dipole-bound anions and solvated electron cluster anions is a matter of the symmetry of the dipolar field encountered by the excess electron.[29]

II. METHODS

We first studied the ground-state potential energy surfaces of the neutral and anionic urea dimers at the Hartree–Fock (HF) level of theory. Because the methods we used are based on an unrestricted Hartree–Fock (UHF) 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 or 0.7501 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[30] up to the fourth order and the coupled-cluster method with single and double excitations (CCSD).[31] In addition, D was analyzed within the perturbation framework designed for dipole-bound anions and solvated electrons described elsewhere.[28]

The simplest theoretical approach to estimate D is based on Koopmans' theorem. The KT binding energy ($D^{\rm KT}$) 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 that neglects both orbital relaxation and electron correlation effects. These effects were taken into account by performing SCF and CCSD 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

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

where

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

and $E_N^{\rm SCF}$ and $E_A^{\rm SCF}$ 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 $\Delta D_{\rm disp}^{\rm MP2}$, which takes into account proper permutational symmetry for all electrons in the anion

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

where ϕ_a and $\phi_{\rm lbe}$ 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

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

is naturally split into dispersion and nondispersion terms

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

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

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

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

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

The diffuse character of the orbital describing the loosely bound electron necessitates the use of extra diffuse basis functions having very low exponents. Based on our extensive studies of a wide variety of such weakly bound anions,[32] we have developed a procedure for designing such extra diffuse bases. We have also described[32] how such basis functions need to be located on or near atoms that reside near the positive end of a polar molecule's dipole. 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[33] supplemented with a $7s6p5d$ set of diffuse functions centered on the carbon atom which was close to the positive pole of the molecular dipole (for dipole-bound species) or in the center of the system (for solvated electrons). 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.[32] The extra diffuse functions do not share exponent values and we used even-tempered[34] seven-term s, six-term p, and five-term d basis sets. The geometric progression ratio was equal to 3.2,[35] 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 lowest exponents of $1.364\,969\,6\times10^{-5}$, $3.763\,474\,5\times10^{-5}$, and $4.500\,150\,4\times10^{-4}$ a.u., for the s, p, and d symmetries, respectively.

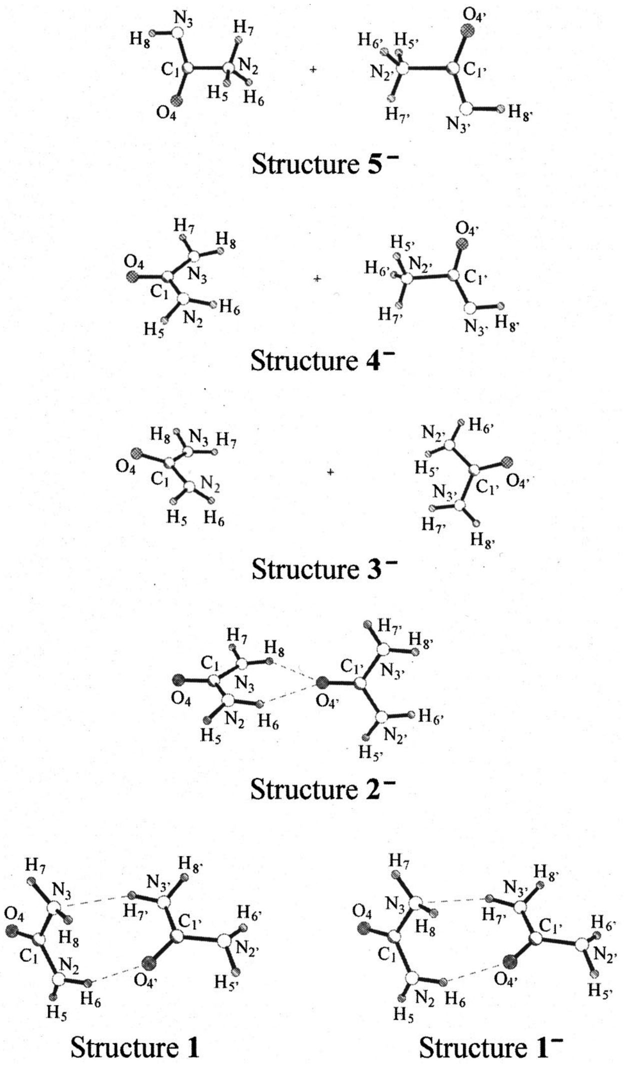

FIG. 2. Equilibrium structures corresponding to the neutral and anionic minima studied in this work.

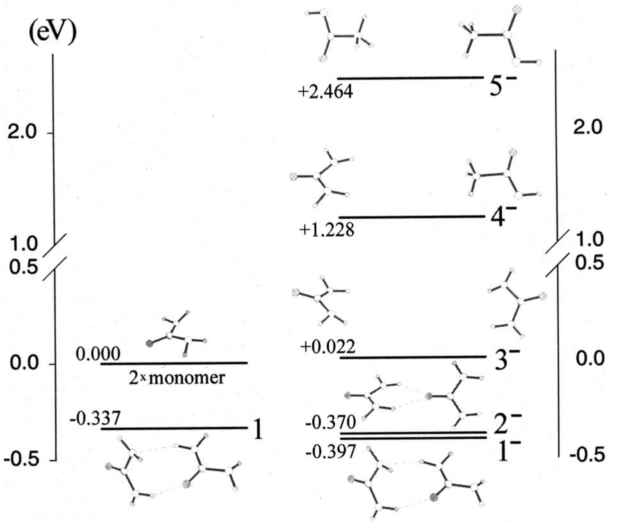

FIG. 3. Relative CCSD energies (in eV) and the corresponding structures of the stationary points (minima only) on the anion (right) and neutral (left) ground-state potential energy surface. The zero of energy is taken to be twice the CCSD energy of the most stable canonical urea monomer.

In computing correlation energies, all orbitals except the 1*s* orbitals of carbon, oxygen and nitrogen were included. All calculations were performed with the GAUSSIAN 98 program[36] on AMD Athalon 950 MHz computers, as well as on SGI Origin2000 and Compaq Sierra systems. The three-dimensional plots of molecular orbitals were generated with the MOLDEN program.[37]

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 species

We focused our investigation of the ground state potential energy surface (PES) of the neutral urea dimer on finding the structure corresponding to the global minimum. We followed the search undertaken previously by Masunov and Dannenberg[2] and we found a structure **1** (see Figs. 2 and 3). In this dimer, the urea monomers are linked by two hydrogen bonds and the amino groups of one monomer acts as both a proton donor and acceptor (see Fig. 2). We also found that the neutral structure where two urea monomers are aligned and one monomer donates its two H atoms to form two hydrogen bonds to the oxygen lone pairs is a first order saddle point that decays to structure **1**. In addition, as examined by Masunov and Dannenberg,[2] several other structures one can design are either geometrically unstable or of much higher energy than the global minimum **1** (see detailed discussion given in Ref. 2).

Our minimum-energy structure **1** lies 0.337 eV below the energy of two separated monomers (see Fig. 3), and contains two canonical urea monomers of *anti*character (see Fig. 1) stabilized by two relatively elongated (ca. 2.2–2.5 Å) hydrogen bonds. The intramonomer geometrical parameters (i.e., bond lengths, valence and dihedral angles) are similar to those we found previously for the isolated C_2-symmetry *anti*monomer.[1] For example, the largest differences in bond lengths are smaller than 0.05 Å and the differences in valence angles are in 1–2 deg range (see Table I where selected geometrical parameters are given).

The fact that the two hydrogen bonds connecting the monomers in structure **1** are relatively long gives rise to a significant dipole moment (6.818 Debye at the SCF level), which is important when forming anionic states.

B. Anionic species

1. Geometries and relative stabilities

We first consider the anions that result from attaching an excess electron to the dipole field of the parent neutral dimer. When the electron is attached to structure **1**, the dipole-bound anion $\mathbf{1}^-$ is formed (see Fig. 4 where the corresponding singly occupied orbital is shown), and we notice negligible geometry relaxation upon this process. In fact, the changes in bond lengths, valence angles, and dihedral angles are smaller than 0.0005 Å, 0.005 deg, and 0.015 deg, respec-

TABLE I. Selected geometrical parameters for the minima corresponding to neutral and anionic urea dimers studied in this work (bond lengths (r) and inter-monomer distances (R) in Å, valence (α) and dihedral (γ) angles in degrees). All the stationary points were calculated at the HF level with the aug-cc-pVDZ+$7s6p5d$ basis set. For each structure the corresponding value of the dipole moment μ^{N} (in Debye) of the neutral structure is also given (calculated from the SCF and MP2 densities). See Fig. 2 for atom numbering.

Structure **1** (C_1) neutral	Structure **l**$^-$ (C_1, DBS) anion	Structure **2**$^-$ (C_2, DBS) anion	Stucture **3**$^-$ (C_1, SE) anion (C⋯e⋯C)	Structure **4**$^-$ (C_1, SE) anion (C⋯e⋯Z)	Stucture **5**$^-$ (C_{2h}, SE) anion (Z⋯e⋯Z)
$r(\mathrm{C_1O_4})=1.203$	$r(\mathrm{C_1O_4})=1.203$	$r(\mathrm{C_1O_4})=1.210$	$r(\mathrm{C_1O_4})=1.205$	$r(\mathrm{C_1O_4})=1.208$	$r(\mathrm{C_1O_4})=1.214$
$r(\mathrm{C_{1,}O_{4,}})=1.211$	$r(\mathrm{C_{1,}O_{4,}})=1.211$	$r(\mathrm{C_{1,}O_{4,}})=1.214$	$r(\mathrm{C_{1,}O_{4,}})=1.205$	$r(\mathrm{C_{1,}O_{4,}})=1.213$	$r(\mathrm{C_{1,}O_{4,}})=1.214$
$r(\mathrm{C_1N_2})=1.358$	$r(\mathrm{C_1N_2})=1.358$	$r(\mathrm{C_1N_2})=1.361$	$r(\mathrm{C_1N_2})=1.368$	$r(\mathrm{C_1N_2})=1.365$	$r(\mathrm{C_1N_2})=1.561$
$r(\mathrm{C_{1,}N_{2,}})=1.366$	$r(\mathrm{C_{1,}N_{2,}})=1.366$	$r(\mathrm{C_{1,}N_{2,}})=1.357$	$r(\mathrm{C_{1,}N_{2,}})=1.368$	$r(\mathrm{C_{1,}N_{2,}})=1.565$	$r(\mathrm{C_{1,}N_{2,}})=1.561$
$r(\mathrm{C_1N_3})=1.384$	$r(\mathrm{C_1N_3})=1.384$	$r(\mathrm{C_1N_3})=1.361$	$r(\mathrm{C_1N_3})=1.368$	$r(\mathrm{C_1N_3})=1.365$	$r(\mathrm{C_1N_3})=1.277$
$r(\mathrm{C_{1,}N_{3,}})=1.360$	$r(\mathrm{C_{1,}N_{3,}})=1.360$	$r(\mathrm{C_{1,}N_{3,}})=1.357$	$r(\mathrm{C_{1,}N_{3,}})=1.368$	$r(\mathrm{C_{1,}N_{3,}})=1.277$	$r(\mathrm{C_{1,}N_{3,}})=1.277$
$\alpha(\mathrm{N_2C_1N_3})=114.42$	$\alpha(\mathrm{N_2C_1N_3})=114.42$	$\alpha(\mathrm{N_2C_1N_3})=114.71$	$\alpha(\mathrm{N_2C_1N_3})=114.84$	$\alpha(\mathrm{N_2C_1N_3})=115.04$	$\alpha(\mathrm{N_2C_1N_3})=108.51$
$\alpha(\mathrm{N_{2,}C_{1,}N_{3,}})=115.62$	$\alpha(\mathrm{N_{2,}C_{1,}N_{3,}})=115.62$	$\alpha(\mathrm{N_{2,}C_{1,}N_{3,}})=115.93$	$\alpha(\mathrm{N_{2,}C_{1,}N_{3,}})=114.85$	$\alpha(\mathrm{N_{2,}C_{1,}N_{3,}})=108.34$	$\alpha(\mathrm{N_{2,}C_{1,}N_{3,}})=108.51$
$\alpha(\mathrm{N_3C_1O_4})=121.93$	$\alpha(\mathrm{N_3C_1O_4})=121.93$	$\alpha(\mathrm{N_3C_1O_4})=122.65$	$\alpha(\mathrm{N_3C_1O_4})=122.58$	$\alpha(\mathrm{N_3C_1O_4})=122.47$	$\alpha(\mathrm{N_3C_1O_4})=140.02$
$\alpha(\mathrm{N_{3,}C_{1,}O_{4,}})=122.57$	$\alpha(\mathrm{N_{3,}C_{1,}O_{4,}})=122.57$	$\alpha(\mathrm{N_{3,}C_{1,}O_{4,}})=122.04$	$\alpha(\mathrm{N_{3,}C_{1,}O_{4,}})=122.59$	$\alpha(\mathrm{N_{3,}C_{1,}O_{4,}})=140.22$	$\alpha(\mathrm{N_{3,}C_{1,}O_{4,}})=140.02$
$R(\mathrm{N_3H_{7,}})=2.448$	$R(\mathrm{N_3H_{7,}})=2.449$	$R(\mathrm{H_6O_{4,}})=2.214$	$R(\mathrm{C_1C_{1,}})=11.048$	$R(\mathrm{C_1N_{2,}})=8.161$	$R(\mathrm{N_2N_{2,}})=6.017$
$R(\mathrm{H_6O_{4,}})=2.161$	$R(\mathrm{H_6O_{4,}})=2.162$	$R(\mathrm{H_8O_{4,}})=2.214$	$\gamma(\mathrm{O_4C_1C_{1,}O_{4,}})=1.98$	$\gamma(\mathrm{O_4C_1C_{1,}O_{4,}})=5.43$	$\gamma(\mathrm{O_4C_1C_{1,}O_{4,}})=180.00$
		$\alpha(\mathrm{H_6O_4H_8})=60.96$			
$\mu^{\mathrm{N}}(\mathrm{SCF})=6.818$	$\mu^{\mathrm{N}}(\mathrm{SCF})=6.818$	$\mu^{\mathrm{N}}(\mathrm{SCF})=10.489$	$\mu^{\mathrm{N}}(\mathrm{SCF})=3.778$	$\mu^{\mathrm{N}}(\mathrm{SCF})=1.705$	$\mu^{\mathrm{N}}(\mathrm{SCF})=0.000$
$\mu^{\mathrm{N}}(\mathrm{MP2})=6.221$	$\mu^{\mathrm{N}}(\mathrm{MP2})=6.221$	$\mu^{\mathrm{N}}(\mathrm{MP2})=9.733$	$\mu^{\mathrm{N}}(\mathrm{MP2})=3.427$	$\mu^{\mathrm{N}}(\mathrm{MP2})=1.651$	$\mu^{\mathrm{N}}(\mathrm{MP3})=0.000$

tively (see Table I). The resulting **1**$^-$ anion lies 0.397 eV below the two isolated neutral monomers and 0.060 eV below neutral **1** (see Fig. 3) and we believe this species corresponds to the global minimum on the anionic ground state potential energy surface.

Another dipole-bound anion we found (structure **2**$^-$, see Fig. 4) to have C_2 symmetry in which the canonical monomer units are aligned to maximize the dipole moment for the neutral. The **2**$^-$ anion is higher in energy than **1**$^-$ (by 0.027 eV) but lower than the lowest neutral structure by 0.033 eV (see Fig. 3), so its adiabatic electron affinity is positive and equals 0.033 eV when calculated at the CCSD level. In **2**$^-$, each amino group of one monomer forms an H bond with the oxygen atom of another urea monomer and the two units are twisted by ca. 90 deg with respect to each other (see Fig. 2). Even though the distance between the monomers in **2**$^-$ is slightly shorter than in **1**$^-$ (see the H bond lengths given in Table I), the fact that the C═O bonds are perfectly aligned leads to a much larger value of the dipole moment (10.489 Debye) for the neutral **2** calculated at this geometry. Unlike the situation we observed for **1** and **1**$^-$, where both the neutral and its underlying anion are minima on the PES, the parent **2** neutral structure is a saddle point that decays to structure **1**.

The excess electron can also be trapped between two local dipoles (each produced by the urea monomer), and we considered three structures of this kind (so-called solvated electron structures, SE): (i) structure **3**$^-$ containing two canonical urea monomers, (ii) structure **4**$^-$ where one canonical and one zwitterionic isomer is used, and (iii) structure **5**$^-$ constructed with two urea zwitterions. Although the neutral dimers in these configurations are geometrically unstable (they reorganize to form a hydrogen-bond linked structure), the presence of the excess electron stabilizes such minima on the anionic ground state PES to render them locally geometrically stable. By this we mean that these structures are local minima on the PES and possess all positive curvatures (i.e., all real harmonic vibrational frequencies).

In the SE structures, the excess electron is localized primarily inside the cluster, as indicated by the shape of the singly occupied molecular orbital (see Fig. 4). Such behavior has been previously observed for many other clusters [e.g., $(\mathrm{NaCl})_n^-$ ($n=2-4$) (Ref. 27) and $(\mathrm{HF})_n^-$ (Ref. 28)]. The distance between the two urea monomers forming SE structures has to be large enough to decrease the repulsion energy between them (since their dipole moments are directed inward) and the electron binding energy must be larger than this repulsion to support the geometrical stability of the system. Indeed, geometry optimizations of the SE structures led to three structures (**3**$^-$, **4**$^-$, and **5**$^-$) in which the distances between two monomers are rather large: 11.048, 8.161, and 6.017 Å, respectively (see Table I). The lowest energy SE structure is **3**$^-$, constructed with two canonical monomers and it lies 0.42 eV above the lowest-energy anion, the **1**$^-$ structure and even 0.022 eV above the energy of two isolated neutral urea monomers (see Fig. 3). However, as noted earlier, **3**$^-$ is a local minimum on the PES, so there must be some barrier to its geometrical rearrangement.

In Fig. 5, we further characterize the relative energy relations among the various low-energy anion structures. Note that **3**$^-$ (denoted U e U in Fig. 5) is vertically electronically stable by 0.157 eV. Further, note that U e U lies 0.42 eV above the lowest-energy (dipole-bound) anion **1**$^-$ (labeled U··U$^-$), although there is a barrier separating these two minima on the anion's ground-state energy surface. Finally, we note that at each geometry shown in Fig. 5, the anion lies below its neutral daughter; that is, the excess electron is bound at all geometries. These observations all indicate that the U e U species can rearrange, by passing over a saddle point, to generate U··U$^-$, but, in the absence of internal

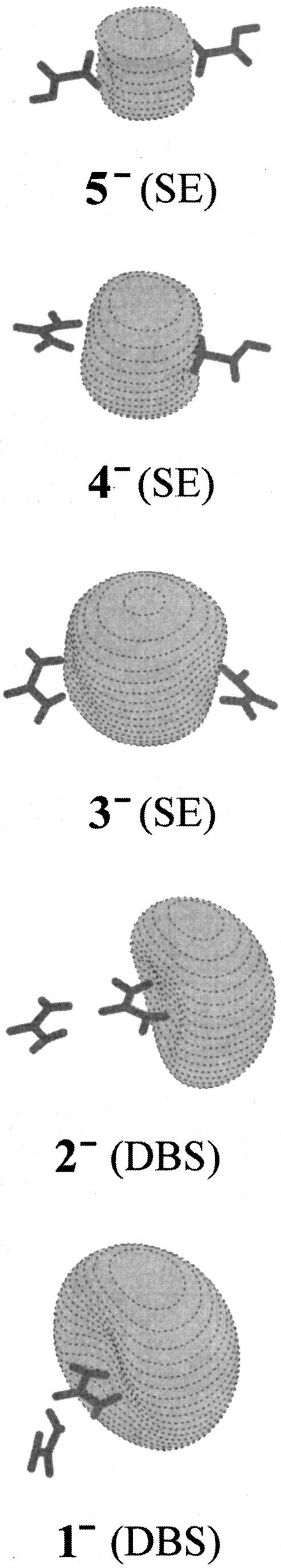

FIG. 4. Singly occupied molecular orbital (SOMO) holding the excess electron in the ground electronic states of anions supported by urea dimers plotted with 0.006 (for **1**$^-$), 0.009 (for **2**$^-$), 0.009 (for **3**$^-$), 0.015 (for **4**$^-$), and 0.021 (for **5**$^-$) bohr$^{-3/2}$ contour spacing, respectively.

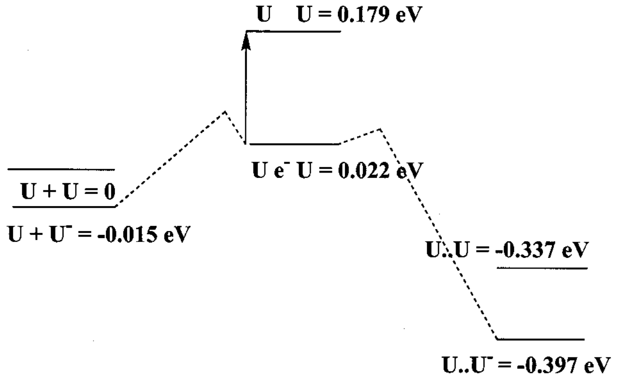

FIG. 5. Relative energies of dipole-bound **1**$^-$(U$\cdot\cdot$U$^-$) and solvated-electron **3**$^-$(U e U) anions and corresponding neutrals, showing electronic stability at all geometries.

energy, will remain kinetically stable and will not spontaneously lose its excess electron.

Because the U e U anion is thermodynamically unstable with respect to U$\cdot\cdot$U$^-$ as well as with respect to U+U$^-$ and even U+U (again, see Fig. 5), we decided to take special care to make sure the electronic stability of U e U was not an artifact of the limited atomic orbital basis that we employed. In particular, we carried out an *ab initio* calculation on the one excess electron alone, using exactly the same orbital basis as described earlier and centered on the atomic centers of the U e U anion. That is, we removed all of the other electrons as well as all of the nuclear charges and computed the energy of the one ‘‘excess’’ electron in the same atomic orbital basis. This calculation yielded an energy of +0.000 017 686 Hartrees, or 4 cm^{-1}. This means that the basis set we used does indeed confine the excess electron relative to a complete basis where the electron could ‘‘escape’’ and have zero kinetic energy. However, the extent to which our basis artificially confines the electron (ca. 4 cm^{-1}) is negligible compared to the extent to which the presence of the two U moieties in the U e U anion bind this electron (i.e., 0.157 eV or 1267 cm^{-1}). Hence, we can be relatively confident of the relative energies reflected in Figs. 3 and 5. The lowest energy SE structure is **3**$^-$, constructed with two canonical monomers and it lies 0.022 eV above the energy of two isolated neutral urea monomers (see Fig. 3), although, as noted earlier, it is a local minimum on the PES. This means that this species can rearrange, by passing over a saddle point, to generate one urea neutral and a urea anion, but, in the absence of internal energy, will remain kinetically stable.

The two other SE structures are even higher in energy, which is not surprising since they contain one (**4**$^-$) or two (**5**$^-$) zwitterionic tautomers whose energy was previously found to be much higher than that of the canonical isomer.[1] Structure **4**$^-$, in which one canonical and one zwitterionic isomers are used, lies 1.228 eV above the energy of two separated neutral monomers, while structure **5**$^-$, containing two zwitterionic monomers, is 2.464 eV above that level (see Fig. 3). Although these three SE structures possess higher energies than the global minimum of the neutral (which means their adiabatic electron affinities are not positive) or other anionic species, they correspond to local minima on the

TABLE II. Components of the vertical electron binding energies D(in cm^{-1}) of urea dimer anions of dipole-bound (DBS) and solvated electron (SE) character calculated with the aug-cc-pVDZ+$7s6p5d$ basis set.

	Structure $\mathbf{1}^-$ (C_1, DBS)	Structure $\mathbf{2}^-$ (C_2, DBS)	Structure $\mathbf{3}^-$ (C_1, SE)	Structure $\mathbf{4}^-$ (C_1, SE)	Structure $\mathbf{5}^-$ (C_{2h}, SE)
D^{KT}	236	810	645	2348	4504
$\Delta D_{\mathrm{ind}}^{\mathrm{SCF}}$	24	81	135	554	1052
$\Delta D_{\mathrm{disp}}^{\mathrm{MP2}}$	233	518	626	1567	2205
$\Delta D_{\text{no-disp}}^{\mathrm{MP2}}$	−99	−198	−278	−722	−1129
ΔD^{MP3}	17	32	44	120	229
$\Delta D^{\mathrm{MP4(SDQ)}}$	16	21	6	15	29
ΔD^{CCSD}	58	179	89	247	650
Sum	**485**	**1443**	**1267**	**4129**	**7540**

ground state anion potential energy surface and they are vertically electronically stable. Thus, they can be kinetically stable.

2. Vertical electron detachment energies (VDE)

The electron binding energy was partitioned into incremental contributions calculated at "successive" levels of theory [KT, SCF, MPn ($n=2,3,4$), and CCSD] as discussed in Sec. II, and the results for the optimal $\mathbf{1}^-$, $\mathbf{2}^-$, $\mathbf{3}^-$, $\mathbf{4}^-$, and $\mathbf{5}^-$ structures of urea dimer are presented in Table II. 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 five anions (of DBS: $\mathbf{1}^-$ and $\mathbf{2}^-$ or SE character: $\mathbf{3}^-$, $\mathbf{4}^-$, and $\mathbf{5}^-$) the D^{KT} values are relatively large: 236 cm^{-1} for $\mathbf{1}^-$, 810 cm^{-1} for $\mathbf{2}^-$, 645 cm^{-1} for $\mathbf{3}^-$, 2348 cm^{-1} for $\mathbf{4}^-$, and 4504 cm^{-1} for $\mathbf{5}^-$. These contributions are responsible for 50–60% of the total electron binding energies (see Table II). 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 $\Delta D^{\mathrm{SCF}}{}_{\mathrm{ind}}$) to be very small for two dipole-bound anions ($\mathbf{1}^-$ and $\mathbf{2}^-$) and only 5–6% of the total D. For SE species, however, $\Delta D^{\mathrm{SCF}}{}_{\mathrm{ind}}$ is larger and responsible for 11–14% of D (see Table II). 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.[12–15] For solvated electrons, however, orbital relaxation effects are usually important as was shown, for example, for HF clusters (dimer and trimer) solvating an excess electron.[28]

The contribution denoted $\Delta D_{\mathrm{disp}}^{\mathrm{MP2}}$ 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 responsible for ca. 50% (for $\mathbf{1}^-$ and $\mathbf{3}^-$) and 30–40% (for $\mathbf{2}^-$, $\mathbf{4}^-$, and $\mathbf{5}^-$) of the total D (see Table II). This finding is consistent with our earlier results for other dipole-bound anions and solvated electrons.[1,3,9,12–15,28]

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 $\Delta D_{\text{no disp}}^{\mathrm{MP2}}$. In all of the cases at hand, MP2 electron correlation effects reduce the dipole moment of the neutral system (see Table I). This effect is especially important for dipole-bound anions since it reduces the dipole moment of the neutral system by 0.6 and 0.8 Debye, for structure **1** and **2**, respectively (in comparison with the SCF value). For the SE systems this effect is only significant for **3**, for which the neutral dipole moment decreases by 0.35 Debye when calculated from the MP2 electron density. Therefore, the value of $\Delta D_{\text{no disp}}^{\mathrm{MP2}}$ is 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 20%–30% of D for all dipole-bound anions and solvated electrons except $\mathbf{5}^-$ where this contribution is smaller (14%).

The contributions from ΔD^{MP3} are stabilizing but small (2%–4% of D). The contributions from $\Delta D^{\mathrm{MP4(SDQ)}}$ are also stabilizing but small (ca. 2%–3% of D) for the dipole-bound anions $\mathbf{1}^-$ and $\mathbf{2}^-$, or almost negligible for the SE systems (ca. 0.5% of D). Higher order correlation effects, calculated here as ΔD^{CCSD} [the difference between CCSD and MP4(SDQ) binding energies] are stabilizing in all cases. In particular, ΔD^{CCSD} contributions are responsible for 12% of D for the dipole-bound anions and 6%–9% of D for the solvated electrons (see Table II).

Combining all of these contributions produces our final predictions for the vertical electron detachment energies of 485 and 1443 cm^{-1} for $\mathbf{1}^-$ and $\mathbf{2}^-$, respectively (whose nature we characterize as dipole bound), and 1267, 4129, and 7540 cm^{-1} for $\mathbf{3}^-$, $\mathbf{4}^-$, and $\mathbf{5}^-$, respectively (which are solvated electron systems).

The significant differences among the vertical electron detachment energies that we observe for the five anions studied in this work suggest that it may be convenient for experimentalists to study these anions based on the urea dimer. In fact, the only difficulty in assigning the measured electron detachment energies to the proper structures may be encountered when the VDEs corresponding to $\mathbf{2}^-$ and $\mathbf{3}^-$ are considered, since they both should be observed in the 1200–1450 cm^{-1} range (see Table II).

IV. SUMMARY

We studied the possibility of binding an excess electron to the urea dimer in the gas phase. On the basis of our *ab initio* calculations with aug-cc-pVDZ+$7s6p5d$ basis sets, we found that

- (i) urea dimers form electronically stable anions of either dipole-bound (DBS) or solvated electron (SE) nature;
- (ii) the global minimum on the ground-state anionic potential energy surface is suggested to be a C_2-symmetry DBS structure for which the vertical (VDE) and adiabatic (EA) electron affinities are 1443 and 484 cm^{-1}, respectively;
- (iii) solvated electron structures are higher in energy than dipole-bound anions supported by the urea dimer but their vertical electron detachment energies are significantly larger;
- (iv) solvated electron structures are not characterized by positive adiabatic electron affinities but are locally geometrically and vertically electronically stable species, so they may be kinetically stable;
- (v) electron binding energies for the ground electronic states of the dipole-bound anions based on the urea dimer are 485 and 1443 cm^{-1}, while for the solvated electron species they are 1267, 4129, and 7540 cm^{-1}.

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