

An excess electron bound to urea oligomers. II. Chains and ribbons

Piotr Skurski

Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, and 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

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The possibility of electron binding to chain- and ribbon-like urea oligomers was studied at the second-order Møller–Plesset perturbation theory level as well as at the coupled cluster level with single, double, and noniterative triple excitations. It was found that all the chains form stable dipole-bound anions whose electron binding energies grow rapidly with chain length, while ribbon-type oligomers bind an excess electron only when they contain an odd number of urea monomer units. Moreover, the chain oligomers support bound excited anionic states of Σ and Π symmetry. © 2001 American Institute of Physics. [DOI: 10.1063/1.1418441]

I. INTRODUCTION

This is the second 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 has not been examined thus far. We previously studied the possibility of excess electron binding to a single OCN_2H_4 molecule.¹ In fact, we considered not only the canonical urea with two amino groups ($\text{O}=\text{C}(\text{NH}_2)_2$) but also (i) the zwitterionic form [created by moving an H atom from one amino group to the other ($\text{O}=\text{C}(\text{NH})\text{NH}_3$)] and (ii) so-called isourea [created by moving an H atom from one amino group to the oxygen atom ($\text{HOC}(\text{NH})\text{NH}_2$)]. Briefly, we found that none of the urea isomers form stable valence-bound anion, however, some of them do form electronically stable dipole-bound anions. In particular, the nonplanar C_{2v} -symmetry canonical urea, known as the global minimum on the neutral ground-state potential-energy surface (PES),^{1,2} supports a dipole-bound anion with 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 site.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} .

In this work, we consider binding an extra electron to

urea oligomers (from dimer to pentamer). In particular, we follow the extensive study of the neutral aggregates by Masunov and Dannenberg,³ and we focus on two types of structures: (i) chains (see Fig. 1), 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 (see Fig. 2), with each monomer oriented oppositely to the neighboring molecule and forming two hydrogen bonds with it. Both types of aggregates are 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.⁴ Moreover, the planar structure is of particular interest since the crystal structures published indicate planar character⁵ and because recent microwave spectroscopic gas-phase studies show zero-point vibrations to exceed the planarization barrier.⁶ Therefore, we decided to use planar urea as the building block for all of the aggregates studied in this work. Moreover, we view the small oligomers examined here as prototypes for defects and surface sites that may occur in the crystalline state or in microcrystals.

II. METHODS

As explained in the previous section, to mimic solid-phase structures, we used the C_{2v} planar urea geometry given in Ref. 1 as the building block to construct the initial geometries of all oligomers. This monomer unit is held fixed in internal structure in all the systems studied, but we optimized the intermonomer distances for each chain- or ribbon-like structure. In particular, we allowed all of the intermonomer distances to vary while preserving the symmetry of the species.

We studied small chain oligomers (from dimer to tet-

^{a)}Author to whom correspondence should be addressed. Electronic mail: simons@chemistry.utah.edu

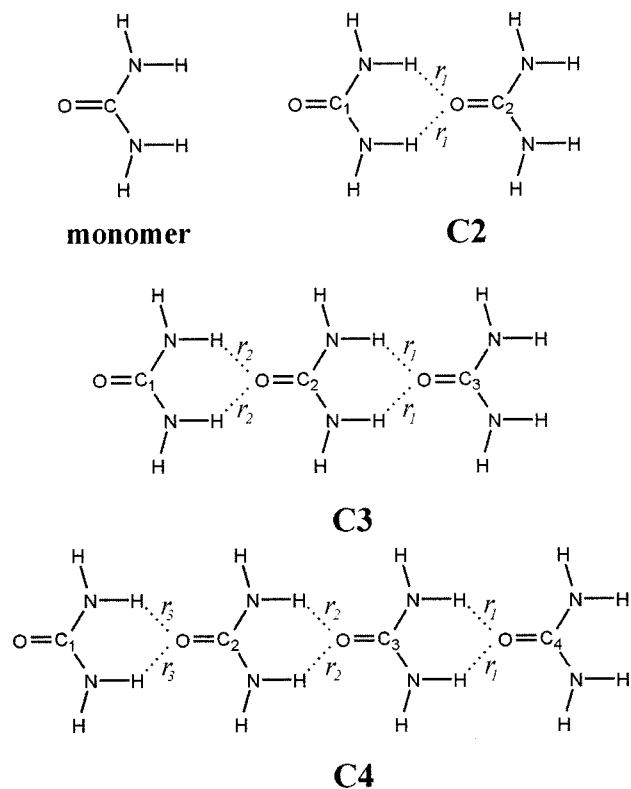


FIG. 1. Hydrogen bonding patterns of chains of urea.

ramer) and ribbons (from dimer to pentamer). All the structures are planar and possess relatively high symmetry. In particular, all chain structures possess C_{2v} symmetry, while the symmetry of the ribbons depends on the number of

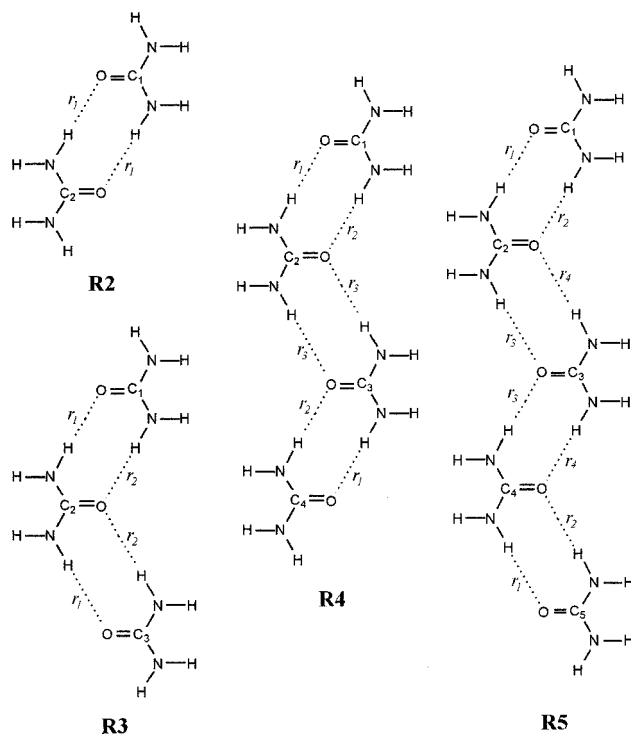


FIG. 2. Hydrogen bonding patterns of ribbons of urea.

monomer units (i.e., the dimer and tetramer have C_{2h} symmetry and the trimer and pentamer possess C_{2v} symmetry).

The intermonomer separations (see Figs. 1 and 2) within each neutral structure were optimized at the Hartree–Fock level of theory. Subsequently, we calculated the electron binding energies (D) for each species at various levels. 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 relevant rotational energy level spacings for the species studied 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 energies 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)).⁷ In addition, D was analyzed within the perturbation framework described elsewhere.⁸ Since the “size” of the numerical problem increases rapidly with each additional monomer unit, we were able to perform CCSD(T) calculations only for the dimers, while we had to limit our calculations to the CCSD level for the trimers, and to the MP2 level for the tetramers and the ribbon pentamer.

The simplest theoretical approach to estimate D is based on Koopmans’ theorem (KT).⁹ 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

$$\Delta D_{\text{ind}}^{\text{SCF}} = D^{\text{SCF}} - D^{\text{KT}} \quad (1)$$

where

$$D^{\text{SCF}} = E_N^{\text{SCF}} - E_A^{\text{SCF}} \quad (2)$$

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 ap-

proximated here by $\Delta D_{\text{disp}}^{\text{MP2}}$, which takes into account proper permutational symmetry for all electrons in the anion

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

where ϕ_a and ϕ_{lbe} are *spinorbitals* 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 spinorbital.

The total MP2 contribution to D defined as

$$\Delta D^{\text{MP2}} = D^{\text{MP2}} - D^{\text{SCF}} \quad (4)$$

is naturally split into dispersion and non-dispersion terms

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

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

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

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

$$\Delta D^{\text{CCSD}} = D^{\text{CCSD}} - D^{\text{MP4}}, \quad (7)$$

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

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

The diffuse character of the orbital describing the loosely bound electron necessitates the use of extra diffuse basis functions having very low exponents.¹⁰ All the calculations presented here were performed with the 6-31+G(d,p) basis sets¹¹ supplemented with a 7(sp)5 d set of diffuse functions. This additional diffuse set was centered (i) in chain structures: on the carbon atom at the positive end of the molecular dipole (i.e., C₂ for the dimer, C₃ for the trimer, and C₄ for the tetramer; see Fig. 1); or (ii) in the ribbon structures: on a ghost atom localized in the center of the system for the dimer and tetramer, on C₂ atom for the trimer, and on the C₃ atom for the pentamer (see Fig. 2). The extra diffuse s and p functions share exponent values and we used even-tempered¹² seven-term sp , and five-term d basis sets. The geometric progression ratio was equal to 3.2,¹³ and for sp and d symmetry, and we started to build up the exponents of the extra diffuse functions from the lowest exponent of the same symmetry included in 6-31+G(d,p) basis set designed for carbon. As a consequence, we achieved the lowest exponents of $1.274\,748 \times 10^{-5}$ and $2.384\,186 \times 10^{-3}$ a.u., for the sp , and d symmetries, respectively. Our attempts to use two sets of such diffuse basis sets (on two centers) led to extremely small eigenvalues of the overlap matrix ($\sim 1 \times 10^{-8}$) even for the ribbon pentamer, which could cause erroneous results, so we decided to use only one additional diffuse basis set for all the species.

In computing correlation energies, all orbitals except the 1s orbitals of carbon, oxygen and nitrogen were included.

TABLE I. Inter-monomer hydrogen bond lengths (in Å) and SCF and MP2 dipole moments (in Debye) of the neutral chain- and ribbon-like urea oligomers calculated with the 6-31+G**+7(sp)5 d basis set.

Species	μ^{SCF}	μ^{MP2}	Inter-monomer H-bond lengths
Monomer ^a	4.849	4.421	...
Dimer (chain) C2	11.053	10.241	$r_1 = 2.258$
Trimer (chain) C3	17.598	16.448	$r_1 = 2.215, r_2 = 2.216$
Tetramer (chain) C4	24.254	22.785	$r_1 = 2.204, r_2 = 2.174, r_3 = 2.206$
Dimer (ribbon) R2	0.000	0.000	$r_1 = 1.991$
Trimer (ribbon) R3	4.840	4.356	$r_1 = 2.012, r_2 = 2.012$
Tetramer (ribbon) R4	0.000	0.000	$r_1 = 2.017, r_2 = 2.017, r_3 = 2.015$
Pentamer (ribbon) R5	4.741	4.292	$r_1 = 2.020, r_2 = 2.020, r_3 = 2.019, r_4 = 2.019$

^aResults for C_{2v} planar monomer.

All calculations were performed with the GAUSSIAN 98 program¹⁴ on AMD Athalon 950 MHz computers and a SGI Origin2000 numerical server. The three-dimensional plots of molecular orbitals were generated with the MOLDEEN program.¹⁵

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 considered two types of urea aggregates: chains and ribbons. Both are planar and consist of identical monomer units. The only difference is the H-bond network. Namely, in the chain structure each monomer forms *two* bifurcated hydrogen bonds—it uses its oxygen atom lone pairs as proton acceptors while connecting to a neighboring monomer. As a consequence, a symmetrical chain of urea monomers is formed with all the subunits oriented in the same direction (see Fig. 1). In the ribbon structures, each monomer forms four hydrogen bonds—two with one neighbor and two with another (see Fig. 2).

Both chains and ribbons possess relatively high symmetry. All the chains have C_{2v} symmetry while the symmetry of a given ribbon depends on the number of monomer units (i.e., C_{2h} or C_{2v} for “even” and “odd” ribbons, respectively). That the urea monomers are oriented in the same direction in the chainlike structure leads to large dipole moments in the resulting oligomer. We observe the dipole moment growing by ca. 6.5 Debye with each urea unit that is added to the chain (see Table I), which is consistent with the result reported by Masunov and Dannenberg.³ The situation for the ribbons is completely different. The opposite orientation of each monomer with respect to its two neighbors causes considerable cancellation of the dipole moments. In particular, the dipole moments of the ribbons containing an even number of monomers vanish by symmetry. For the “odd” ribbons, however, we find total dipole moments similar to that found for the monomeric urea (see Table I).

TABLE II. Components of the vertical electron binding energies D (in cm^{-1}) of the anions based on urea chain and ribbon oligomers calculated with the 6-31+G**+7(sp)5d basis set.

Species	D^{KT}	$\Delta D_{\text{ind}}^{\text{SCF}}$	$\Delta D_{\text{disp}}^{\text{MP2}}$	$\Delta D_{\text{no-disp}}^{\text{MP2}}$	ΔD^{MP3}	ΔD^{MP4}	ΔD^{CCSD}	$\Delta D^{\text{CCSD(T)}}$	Sum
Monomer ^a	103	8	98	-56	13	6	43	14	229
Dimer C2 (chain)	990	92	479	-223	46	34	97	76	1591
Trimer C3 (chain)	1740	130	639	-279	54	2 ^b	161 ^c	...	2447
Tetramer C4 (chain)	2236	139	712	-301	2786
Trimer R3 (ribbon)	64	7	70	-37	9	1 ^b	46 ^c	...	160
Pentamer R5 (ribbon)	37	6	45	-20	68

^aResults for C_{2v} planar monomer.

^bThe difference between $D^{\text{MP4(SDQ)}}$ and D^{MP3} .

^cThe difference between D^{CCSD} and $D^{\text{MP4(SDQ)}}$.

Moreover, the total dipole moment of the “odd” ribbons slightly decreases with the size of the oligomer. These findings are important when one considers the possibility of forming stable dipole-bound anionic states based on these chains and ribbons.

Finally, the optimized length of the H-bond is ca. 2.2 Å for the chains and approximately 2.0 Å for ribbons (see Table I). Within a given structure, the H-bonds have almost the same length and the differences are almost negligible (the largest difference we found for the chain tetramer—0.03 Å).

Let us now move to the discussion of the stable negatively charged species based on the chain and ribbon oligomers of urea.

B. Anionic species

1. Electron binding energies

Since the dipole moments of the ribbon dimer (**R2**) and tetramer (**R4**) shown in Fig. 2 vanish by symmetry (see Table II), these systems were not expected to bind an excess electron. However, one might anticipate that even though the net dipole moment is zero, the relatively strong local dipoles could support anionic states, as was observed for other systems.^{16,17} On the other hand, the local dipoles are very close to one another, which causes strong destabilizing effects. However, we found neither **R2** nor **R4** to bind an extra electron, and we expect this to be the case for any ribbon-like oligomer containing an even number of urea monomers (**R_{2n}**, $n = 1, 2, 3, \dots$).

Among “odd” ribbon urea oligomers, the simplest cases studied by us [i.e., the trimer (**R3**) and pentamer (**R5**)] possess small but nonvanishing total dipole moments and are able to support stable anionic states. As far as the chain oligomers are concerned, all have nonzero net dipole moment. Moreover, because all the monomers are oriented in the same direction, the total dipole moment increases from the dimer (**C2**) to tetramer (**C4**), which causes the electron binding energy to grow (see Table II).

As has been observed earlier for other dipole-bound anions, the excess electron is localized in the vicinity of the positive end of the molecular dipole [see Fig. 3 where the

singly occupied molecular orbitals (SOMO) holding the excess electron are shown]. Although the localization and shape of the SOMO for each anion supported by the chain structure was quite predictable, the distributions of the extra electron densities for the ribbon structures may seem unusual. In particular, one might expect more localization of the SOMO's in the vicinities of each local dipole. Instead, the character of the SOMO's for **R3**⁻ and **R5**⁻ resembles the typical situation where the excess electron is bound by one, well-defined dipole moment of the parent neutral (see Fig. 3).

The electron binding energy was partitioned into incremental contributions calculated at “successive” levels of theory [KT, SCF, $\text{MP}n$ ($n = 2, 3, 4$), and CCSD(T)] as discussed in Sec. II, and the results for the chain and ribbon structures of urea 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 in-

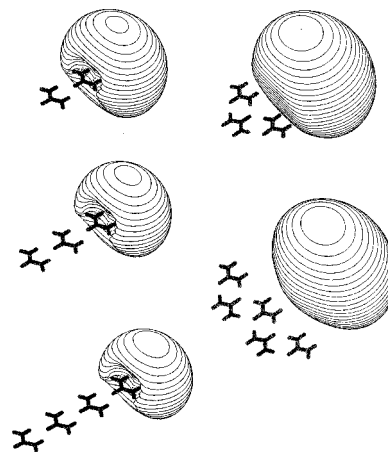


FIG. 3. Singly occupied molecular orbital (SOMO) holding the excess electron in the ground electronic states of anions supported by urea chains: dimer, trimer, and tetramer (left column), and ribbons: trimer and pentamer (right column). SOMO's for chain and ribbon structures were plotted with 0.0070 and 0.0030 bohr^{-3/2} contour spacing, respectively.

teractions with higher permanent multipoles and penetration effects are also included). For all three chain conformers, the D^{KT} values are relatively large: 990 cm^{-1} for **C2**⁻, 1740 cm^{-1} for **C3**⁻, and 2236 cm^{-1} for **C4**⁻ and consistent with the near linear growth in dipole with chain length (see Table I). For the **R3** and **R5** ribbon structures, however, D^{KT} is small (64 and 37 cm^{-1} for **R3** and **R5**, respectively) and the dipole moments are nearly identical (Table I). Compared to the monomer, the chain-type orientation of the urea building blocks leads to significant growth of the electron binding energy (by ~ 10 – 20 times for **C2**–**C4**), while the D values of the odd ribbon structures are smaller than for the monomer structure and decrease as the number of urea building blocks increases. As a result, as demonstrated in Fig. 3, the anion's singly occupied molecular orbital (SOMO) becomes more and more compact as D^{KT} increases for **C2**–**C4**. In contrast, the SOMO of the ribbon anions becomes more diffuse as the structure grows, which is consistent with the corresponding D^{KT} values.

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 (Table II) these contributions (which can be interpreted as orbital relaxation corrections to D^{KT} , denoted $\Delta D_{\text{ind}}^{\text{SCF}}$) to be relatively small for all **C** and **R** structures, and only 5–15% of the corresponding D^{KT} . Although usually significant for valence-bound anions, orbital relaxation effects are usually small 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.¹⁸

The contributions denoted $\Delta D_{\text{disp}}^{\text{MP2}}$ in Table II results from dynamical correlation between the loosely bound excess electron and the electrons of the neutral molecule. This stabilization is caused by quantum mechanical charge fluctuations, and is larger than D^{KT} for **R3** and **R5** while for the chain oligomers its significance decreases as the total binding energy increases. This finding is consistent with our earlier results for other dipole-bound anions.^{18,19}

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 $\Delta D_{\text{no-disp}}^{\text{MP2}}$. In all **C** and **R** cases, MP2 electron correlation effects reduce the dipole moment of the neutral system in comparison with the SCF value (see Table I). For the ribbon **R3** and **R5** structures, this change is comparable to the change observed for the urea monomer (~ 0.4 – 0.5 Debye) while for the chain oligomers it is much larger (0.81 , 1.15 , and 1.47 Debye, for **C2**, **C3**, and **C4**, respectively). This indicates that the SCF description of the charge density distribution of the neutral molecule becomes more and more incorrect as the size of the chain oligomer grows. Therefore the value of $\Delta D_{\text{no-disp}}^{\text{MP2}}$ 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 the **C2**, **C3**, and **R3** structures.

Since the MP2 level was the highest level of theory for

the largest oligomers studied in this work (i.e., **C4** and **R5**), the MP2 electron binding energies are our best estimates of the vertical electron attachment energies for these species. Namely, we predict the **C4**⁻ and **R5**⁻ anions to be stable by 2786 and 68 cm^{-1} , respectively, although we are aware that these numbers are likely to be underestimated because, for the majority of dipole-bound anions, higher-than-second-order effects are usually stabilizing.^{18,19}

As also shown in Table I, the contributions from ΔD^{MP3} and ΔD^{MP4} are stabilizing but small (2–5% of D). Clearly, the relative $\Delta D^{\text{MP4(SDQ)}}$ contributions are much smaller than the full ΔD^{MP4} (i.e., $\Delta D^{\text{MP4(SDTQ)}}$) which suggests the importance of the triple excitations at this level of treatment. Higher-order correlation effects, calculated here as ΔD^{CCSD} [the difference between CCSD and MP4(SDTQ) or MP4(SDQ) binding energies] and $\Delta D^{\text{CCSD(T)}}$ [the difference between CCSD(T) and CCSD binding energies], are stabilizing in all cases and amount to 3–7% of the total D .

Combining all of these calculated contributions produces our final predictions for the vertical electron attachment energies of 1591 , 2447 , and 2786 cm^{-1} for **C2**⁻, **C3**⁻ and **C4**⁻, respectively, as well as 160 and 68 cm^{-1} for **R3**⁻ and **R5**⁻, respectively. We again note that increasing the size of the system leads to rapidly increasing electron binding energy for the chain structures and decreasing electron binding energy for the ribbon structures. While the former is obviously caused by the growth in dipole moment of the neutral parent molecule, the latter seems to be a consequence of the destabilizing interactions among strong local dipoles located close to one another as dictated by the ribbon-like conformation.

2. Bound excited states

The ability of a given neutral to support bound excited anionic states is always of interest since only a few anions are known to possess such states.²⁰ In particular, the systems that have been characterized experimentally are primarily atomic or diatomic.^{21–24} Even more interesting are polyatomic anions that possess this property. Valence bound excited anionic states of tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ),^{25–27} as well as lithium substituted double-Rydberg anions^{28,29} offer examples of such species. In the case of chain urea oligomers, however, we found electronically stable excited anionic states of dipole-bound nature.

Closed-shell neutral molecules having very large dipole moments can sometimes support more than one dipole-bound anionic state.³⁰ For the urea chain structures, the dipole moment of the neutral system increases when the number of urea monomers increases, thus one expects to find bound excited anionic states for these species. Indeed, we found that although the urea monomer ($\mu^{\text{SCF}} = 4.849$ Debye) has only one stable anionic state (i.e., the ground-electronic 2A_1 state), the chain dimer ($\mu^{\text{SCF}} = 11.053$ Debye) can also support one excited anionic state of the same A_1 symmetry. Since the neutral dipole moment rapidly grows with the size of the chain, we found that the trimer ($\mu^{\text{SCF}} = 17.598$ Debye) and tetramer ($\mu^{\text{SCF}} = 24.254$ Debye) possess four and five bound excited anionic states, respectively. The corresponding

TABLE III. Symmetries and KT vertical electron binding energies (in cm^{-1}) of bound anionic states supported by chain urea oligomers.

Species	Electronic state	KT binding energy
Dimer ⁻ (chain) C2	1 2A_1	990
	2 2A_1	40
Trimer ⁻ (chain) C3	1 2A_1	1740
	1 2B_2	222
	2 2A_1	158
	3 2A_1	15
	1 2B_1	9
Tetramer ⁻ (chain) C4	1 2A_1	2236
	1 2B_2	593
	2 2A_1	309
	1 2B_1	259
	3 2A_1	46
	4 2A_1	7

electronic states and their KT binding energies are collected in Table III and the five corresponding virtual molecular orbitals of the neutral tetramer are shown in Fig. 4. Here we see that the trimer and tetramer support two Π states (2B_2 and 2B_1) and two and three excited Σ states, respectively (see Table III and Fig. 4). This phenomenon is relatively rare; to the best of our knowledge $^2\Pi$ -symmetry dipole-bound states of anions were found only for linear $(\text{HCN})_5^{-30}$ and $(\text{NaCl})_2^{-,31}$ with the latter being geometrically unstable with respect to a bending distortion. In the case of chain urea oligomers, the number of supported bound excited anionic states is large and the corresponding virtual orbitals indicate that the extra electron in each case is localized in the vicinity of the positive pole of the molecular dipole, as expected for

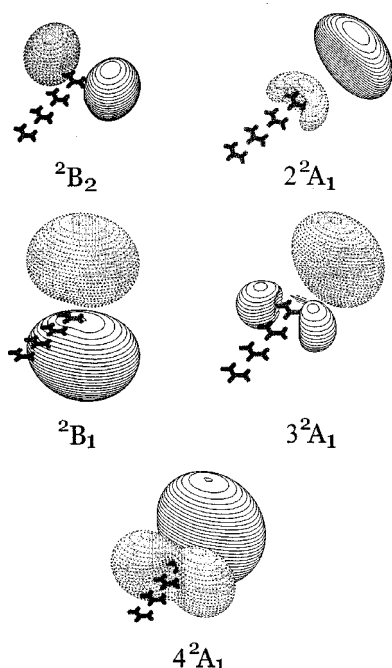


FIG. 4. Low-energy 1^2B_2 , 2^2A_1 , 1^2B_1 , 3^2A_1 , 4^2A_1 virtual orbitals of chain urea tetramer corresponding to bound excited states of the anion plotted with 0.0038, 0.0035, 0.0030, 0.0015, and 0.0005 bohr^{-3/2} contour spacing, respectively.

the dipole-bound species (see Fig. 4). Finally, we should note that the diffuse basis we employed in the present study was designed primarily to offer a good description of the lowest anion state. As such, it does not have sufficient radial or angular flexibility to guarantee that the energy ordering of the excited states discussed above is quantitatively accurate. It was not our intention here to accurately determine this ordering, but, rather, to suggest that longer chains of urea may possess some excited dipole-bound states.

IV. SUMMARY

We studied the possibility of binding an excess electron to chain and ribbon urea oligomers (from dimer to pentamer) constructed from planar monomers. On the basis of our *ab initio* calculations with 6-31+G**+7(sp)5d basis sets, we found that:

- (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) electron binding energies for ribbon-like anions (containing an odd number of monomers) vary only slightly with the size of the system and are close to the isolated monomer's anion electron binding energy;
- (iv) chain urea oligomers support also bound excited anionic states; in particular, the chain dimer supports an excited 2^2A_1 state (in addition to the ground 1^2A_1), and the trimer and tetramer support four and five bound excited states, respectively (in addition to their ground 1^2A_1 states); and
- (v) 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).

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