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Ion–Molecule Reactions in Helium Nanodroplets Doped with C_{60} and Water Clusters[**]

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Helium nanodroplets, which contain some 10^3 to 10^8 atoms, provide an avenue for important new experiments.[1] In a low-pressure environment, the droplets cool within microseconds to 0.37 K by evaporation of weakly bound helium atoms. Molecules captured in collisions with a superfluid droplet will quickly aggregate in the droplet's interior into novel, often metastable structures.[2] These "personal nanocryostats"[1] may be used to explore chemical reactions. For example, Müller et al. reported that ionization initiates complete hydrolysis of cesium–water complexes within the droplets.[3]

Herein we report ion–molecule reactions between C_{60} and small water clusters. Water is an integral part of biomolecular organization; its bioactivity can be further understood by characterization of its function at the C_{60}–H_2O interface.[4] C_{60} is hydrophobic; its hard-core radius of 0.5 nm is close to the crossover point beyond which the breakage of hydrogen bonds becomes unavoidable.[5] Molecular dynamics simulations show that fullerenes strongly bind to single and double-strand DNA;[6] addition of hydrated C_{60} to drinking water has been found to mitigate damage of ethanol to brain cells of rats without causing any adverse biological effects.[7]

In the present work, helium droplets were doped with C_{60} and water, and subsequently ionized by electron impact ionization. The interpretation of experimental results was aided by ab initio Hartree–Fock calculations. Two observations stand out: Firstly, the weak interaction between neutral C_{60} and water extends to the cationic system. Desorption of entire water clusters rather than evaporative loss of water molecules occurs for certain water cluster sizes. Secondly, $C_{60}OH^+$ is a major product ion. We postulate that this ion results from doubly charged $[C_{60}(H_2O)]^{2+}$ intermediates that form by charge transfer from a primary He^+ ion. The existence of doubly charged intermediates in doped helium droplets and their role in subsequent ion–molecule reactions has so far been ignored; these intermediates provide a compelling rationale for previous observations of hydrogen loss from clusters of organic molecules and biomolecules.[8–10]

We first summarize results obtained by ionization of helium droplets doped with water (either H_2O or D_2O) but no C_{60}. In agreement with a previous report,[11] electron impact ionization results in a prominent series of protonated water cluster ions. Unprotonated water cluster ions are observed with a 10% abundance relative to the protonated cluster ions. Unprotonated ions are not observable upon electron impact or multiphoton ionization of bare water clusters, but they occur if water clusters are complexed with heavy rare-gas atoms.[12] These trends are well understood—the ground state of $(H_2O)_2^+$ corresponds to the proton-transferred isomer $OH–H_3O^+$, and its dissociation to $OH + H_3O^+$ is energetically much more facile than dissociation to $H_2O + H_2O^+$.[13] Direct ab initio dynamics studies of water clusters show that vertical ionization is followed by one or more barrierless proton transfer reactions within 100 fs; solvent reorganization leads to a highly excited cluster ion and ejection of the OH radical within sub-picoseconds; enough energy remains for the evaporation of several more water molecules.[14]

The composition of cluster ions changes drastically when helium droplets are co-doped with C_{60}. The most prominent ion series in Figure 1 arises from $C_{60}(D_2O)_n^+$, $n = 0, 1, 2$. Dehydrogenated ions, that is, ions with the stoichiometry $C_{60}(D_2O)_{n-1}OD^+$ are also observed, while the abundance of protonated ions is weak.

For a quantitative analysis, we fitted the distribution of C_{60} isotopologues by sets of four Gaussians with fixed ratios of amplitudes computed from the 1.11% natural abundance of

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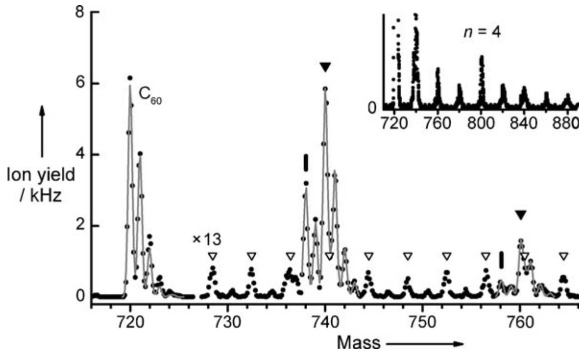

Figure 1. Mass spectrum of helium droplets doped with C_{60} and D_2O. Solid lines indicate Gaussian fits. Symbols represent unprotonated $^{12}C_{60}(D_2O)_n^+$ ions (▼), He_n^+ ions (▽), and dehydrogenated $^{12}C_{60}(D_2O)_{n-1}OD^+$ (|). The inset shows an extended mass range.

^{13}C. For example, the mass range from 737.5 to 744 Da is fitted by one quadruplet for $C_{60}OD^+$, one for $C_{60}D_2O^+$, and one for $C_{60}D_3O^+$. Two free parameters (amplitude and width) are needed for the first quadruplet, and one more parameter (the amplitude) for each additional quadruplet. The fit also accounts for He_{185}^+ at 740.481 Da, with fixed amplitude and width interpolated from He_{184}^+ and He_{186}^+.

The results of the analysis are compiled in Figure 2. Two features are particularly intriguing: 1) The dominance of unprotonated ions and the appearance of dehydrogenated ions, and 2) the local abundance maximum for $C_{60}(D_2O)_4^+$ (see the inset in Figure 1) and a similarly strong maximum for $(C_{60})_2(D_2O)_4^+$ (not shown).

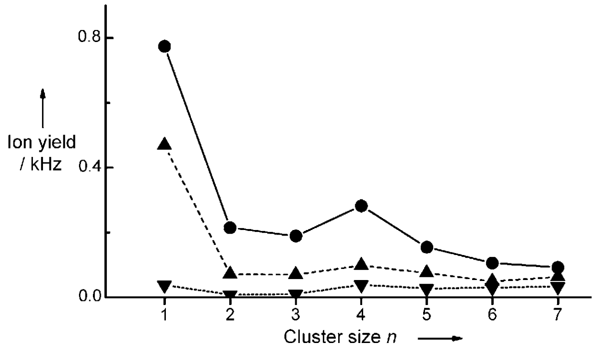

Figure 2. The yield of protonated (▼), unprotonated (■), and dehydrogenated (▲) cluster ions. For example, $n=2$ corresponds to $C_{60}H_2OH_3O^+$, $C_{60}(H_2O)_2^+$, and $C_{60}H_2OOH^+$.

The unprotonated ions $(H_2O)_n^+$ are stable but the autoprotonation reaction initiated upon vertical ionization leads to ejection of the OH radical within subpicoseconds.[14] Ionization near the adiabatic threshold is not possible because of unfavorable Franck–Condon factors. We investigated why the presence of C_{60} suppresses the ejection of OH (or OD) to a much greater extent than complexing water clusters with argon atoms, or embedding them in helium.[12]

It is tempting to view $C_{60}(D_2O)_n^+$ as a C_{60}^+ plus a more or less weakly bound neutral water cluster because the first ionization energy of H_2O (12.621 eV) greatly exceeds that of C_{60} (7.60 eV).[15] We tested the hypothesis by analyzing neutral and cationic $C_{60}(H_2O)_n$ by means of Hartree–Fock calculations and the 3-21G double-zeta basis set. The interaction of water molecules with neutral C_{60} has been the subject of several theoretical studies that employed semi-empirical interaction potentials[16] or density functional methods.[17] To the best of our knowledge, the work presented herein is the first ab initio study of charged $C_{60}(H_2O)_n^+$. While calculations of systems with the neutral C_{60} or C_{60}^+ cations alone pose no problems, we found that both unrestricted Hartree–Fock or DFT calculations of the unsymmetrical C_{60}^+/H_2O clusters led to artificial 'spin waves' in the fullerene unit and therefore to unphysical high expectation values of the total spin operator S^2 (often exceeding 10). Therefore, the restricted open-shell level of theory was chosen which guarantees the correct spin state. According to our experience, the modest 3-21G basis set is best used with the Hartree–Fock level calculations and is at least qualitatively quite adequate for a system that consists of C, O, and H atoms where electrostatic interactions dominate. It should be mentioned that, because of the floppy and large systems, many energy and gradient evaluations are necessary and that calculations with large basis sets show nearly always cumbersome SCF convergence problems because of the multitude of energetically close molecular orbitals of C_{60} cation. We have also tried to establish the preferred orientation of one water molecule towards C_{60}/C_{60}^+ and its preferred binding site by exploring different binding sites and orientations of the water dipole; these results will be discussed elsewhere. However, it should be kept in mind that the experimental procedure used in the current work is likely to result in metastable configurations of the neutral C_{60}–H_2O complex.

The results of these calculations are as follows: The presence of neutral C_{60} does not disturb the $(H_2O)_n$ entities compared to their normal hydrogen-bonded structures. For the cations, the water clusters rearrange in such a way that their oxygen atoms point towards C_{60}^+ while keeping their hydrogen bonds mostly intact; their deformation energies remain small. The total energies of $C_{60}(H_2O)_n^+$ relative to $C_{60}^+ + nH_2O$ are listed in Table 1. The small (0.18 eV) binding energy of the water monomer explains why no reaction could be identified in gas-phase collisions between H_2O and C_{60}^+.[18,19] The adduct simply desorbs too quickly, even at room temperature.[19] In both neutral and cationic systems, the Mulliken partial charges do not show substantial charge transfer between water and C_{60}. The largest charge transfer

Table 1: Energies of $C_{60}(H_2O)_n^+$ calculated at the HF/3-21G level.[a]

Size *n*	E_{total}	ΔE_{vap}	$\Delta E_{fission}$
1	−0.18	0.18	0.18
2	−0.55	0.37	0.26
3	−1.04	0.49	0.18
4	−2.13	1.09	0.30
5	−2.30	0.17	0.28
6	−2.95	0.65	0.36

[a] Energies given in eV. E_{total} is relative to $C_{60}^+ + n\,H_2O$, ΔE_{vap} is relative to $C_{60}(H_2O)_{n-1}^+ + H_2O$, and $\Delta E_{fission}$ is relative to $C_{60}^+ + (H_2O)_n$.

was found to be 0.05 *e* for the system with two water molecules. Charge localization on C_{60} does indeed suppress the autoprotonation reaction in the attached water cluster.

Why are $C_{60}(D_2O)_4{}^+$ and $(C_{60})_2(D_2O)_4{}^+$ particularly abundant? The most common mechanism for the appearance of such "magic numbers" is an enhanced thermodynamic stability of cluster ions, that is, an increased evaporation energy for loss of a monomer from a cluster. According to several theoretical studies isolated, neutral $(H_2O)_4$ features an enhanced evaporation energy.[20] Given the concentration of the positive net charge on $C_{60}{}^+$, this energy value suggests that $n = 4$ is a magic number for $C_{60}(H_2O)_n{}^+$ as well.[21]

This suggestion is confirmed by ab initio calculations. Table 1 reveals a maximum for the evaporation energy of $C_{60}(H_2O)_4{}^+$. However, a competing reaction is conceivable, namely desorption of the complete water cluster, or "fission". The adiabatic energies calculated for this reaction are listed in Table 1. For $n = 3$, 4, and 6, $\Delta E_{\text{fission}}$ is much less than ΔE_{vap}.[22]

The hypothesis that "fission" may be favored over evaporation is testable. As observed in several previous studies, cations formed by electron impact ionization of doped helium droplets often contain enough excess energy to undergo spontaneous (unimolecular) dissociation on the timescale of microseconds to milliseconds. The reaction is most likely due to vibrational predissociation. Figure 3 displays mass-analyzed kinetic energy (MIKE) scans of size-selected $C_{60}(H_2O)_n{}^+$ clusters that undergo unimolecular dissociation in the second field-free region of the magnetic mass spectrometer.[23] The ion yield is plotted versus the mass of transmitted ions relative to the mass of their parent ion. All traces show loss of $x = 1$ molecules from $C_{60}(H_2O)_n{}^+$. For $n = 3$, 4, and 6 we also see an intense signal for loss of all water molecules; this signal is absent for $n = 2$, 5, and (not shown) 7, or 8. That is, cluster ions of size $n = 3$, 4, and 6 have a large propensity to shed all their water molecules during the brief time that they spend between the magnetic and electric sector. These sizes agree with the values for which the computed fission channel are energetically most competitive compared to evaporation.[22] (Experimentally we cannot distinguish between sequential loss of all monomers and fission, but multiple sequential loss is extremely unlikely, because it is energetically costly.)

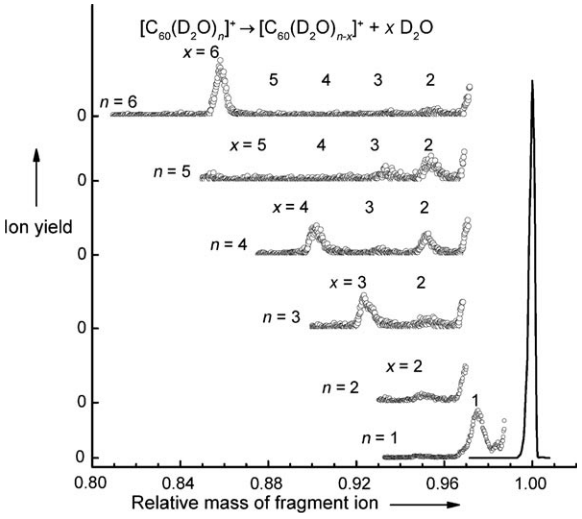

Figure 3. MIKE scans of $C_{60}(D_2O)_n{}^+$ for $1 \leq n \leq 6$. Numbers *x* above the traces indicate the expected position of fragment ion peaks corresponding to loss of $x\,D_2O$ molecules from a parent ion of size *n*. Ion yield is given in arbitrary units.

The dehydrogenated cluster ions, which are particularly abundant for $C_{60}OH^+$, seem to be a counterexample to the notion that fragmentation of clusters embedded in helium is suppressed.[1,24] How do they form? Electron-impact ionization of doped helium droplets starts with formation of He^+, which migrates through the droplet by charge hopping until charge exchange with the dopant occurs. The ionization energy of He (25.4887 eV[15]) exceeds the energy for double ionization of C_{60} (19.00 eV). Thus $C_{60}{}^{2+}$ may form, followed by the reaction shown in Equation (1)

$$[C_{60}{}^{2+}(H_2O)_x] \rightarrow [C_{60}{}^{+}(H_2O)_x{}^{+}] \rightarrow C_{60}{}^{+}OH(H_2O)_{x-2}H_3O^+ \rightarrow [C_{60}OH]^+ + (H_2O)_{x-2}H_3O^+ \tag{1}$$

Electron transfer from H_2O to $C_{60}{}^{2+}$ in the gas phase is endothermic by 1.22 eV, but $C_{60}OH^+$ has been observed upon gas-phase collisions between vibrationally hot $C_{60}{}^{2+}$ and H_2O at hyperthermal collision energies.[18] (No reaction has been reported under thermal conditions.[19] In our experiments, C_{60} is initially at 0.37 K, but the high exothermicity of charge transfer from He^+ to C_{60} will produce electronically or vibrationally excited $C_{60}{}^{2+}$.)

Is there any direct evidence for the proposed formation of $C_{60}{}^{2+}$? The ion is indeed observed (at *m*/*z* 360) in relatively large amounts in the absence of H_2O and if the C_{60} vapor pressure is low, in order to avoid the formation of doubly charged C_{60} aggregates that would charge-separate into singly charged ions.

Doubly charged intermediates X^{2+} may also play a role for dopants other than C_{60}, provided that the energy IE_2 of forming X^{2+} from X is less than 25.49 eV. This requirement will be met for most large molecules or clusters. In fact, the appearance of dehydrogenated cluster ions formed from haloalkanes,[9] alcohols,[10] and valine[8] has been reported, even though ionization of the corresponding bare molecules does not lead to dehydrogenated ions. Ellis and co-workers attributed their finding to a differential cage effect which favors loss of a single hydrogen atom because the tightly bound helium solvation shell was thought to suppress competing molecular elimination channels.[9] In our view, ionization via a doubly charged intermediate provides a more plausible mechanism.

In conclusion, we have identified novel ion–molecule reactions between C_{60} and water clusters upon electron impact ionization. The composition of ions produced in these helium "nanoreactors" differs significantly from those produced upon ionization of pure clusters. The interaction between C_{60} and water remains weak even in the cationic complex, as demonstrated by complete desorption of the water trimer, tetramer, and hexamer from $C_{60}{}^+$. We postulate that charge transfer from the initial He^+ produces $C_{60}{}^{2+}$, subsequent charge transfer to the cluster and charge separation reactions results in ions that are not formed in the absence of helium. Doubly charged intermediates could also explain previous observations of dehydrogenated cluster ions, and they may play a role in molecular synthesis in interstellar clouds and solar nebula where gas-phase reactions and surface catalysis on dust nanoparticles represent the major pathways.[26]

Experimental Section

Neutral helium nanodroplets were produced by expanding helium from 15 to 20 bar through a 5 μm nozzle at 10 K into a vacuum.[8] The average number of He atoms per droplet was a few times 10^4. The skimmed supersonic beam traversed a 10 cm long pick-up region. C_{60} was vaporized at around 460 °C; most droplets picked up either zero, one, or two C_{60} molecules. H_2O or D_2O vapor was also introduced in this region, or directly into the ionization chamber of a high resolution two-sector field mass spectrometer; the data showed no systematic differences between the two approaches (the lack of an experimentally detectable difference does not necessarily imply that the configuration of the C_{60}–H_2O complexes are independent of the order in which species are added[27]). Doped helium droplets were ionized by electron impact at 100 eV. The pressure in the mass spectrometer is less than 8×10^{-6} Pa; in the ion source it is approximately 10^{-4} Pa.

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