

Cold Reactions of Alkali and Water Clusters inside Helium Nanodroplets

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The reaction of alkali (Na, Cs) clusters with water clusters embedded in helium nanodroplets is studied using femtosecond photo-ionization as well as electron impact ionization. Unlike Na clusters, Cs clusters are found to completely react with water in spite of the ultracold helium droplet environment. Mass spectra of the $Cs_n+(H_2O)_m$ reaction products are interpreted in terms of stability with respect to fragmentation using high-level molecular structure calculations.

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Chemical reactivity at very low temperatures is a topic of increasing interest both for theory and for experiment [1, 2, 3, 4]. On the one hand, this is due to new phenomena which arise as the reaction dynamics enters the quantum scattering regime, *e.g.* quantum scattering resonances in the reaction cross sections [1]. On the other hand, the recent progress in developing experimental techniques for producing and trapping cold and ultracold molecules allows for extending experiments on reactive scattering to the quantum regime. Cold reactive ion-molecule collisions have recently been reported [4] and experiments aiming at studying cold reactive neutral molecule-molecule collisions using Stark-decelerated molecular beams are in preparation [2, 5].

Helium (He) nanodroplets are particularly well suited as a nearly ideal cryogenic matrix for studying reactions at sub-Kelvin temperatures [3, 6]. The high mobility of dopant atoms and molecules inside the superfluid droplets allows to bring together atoms or molecules of rather different nature, the inert He environment causing only negligible perturbations [6, 7]. Fast dissipation of internal excitations by evaporation of He atoms leads to efficient cooling of the internal degrees of freedom and allows to prepare weakly-bound precursor states as starting conditions prior to initiating a chemical reaction, *e.g.* by shining in a laser pulse. Thus, using femtosecond (fs) pump-probe spectroscopy, the formation dynamics of alkali metal (M)-He exciplexes on He nanodroplets has been studied in real time [8, 9]. The dynamics of photo-induced dissociation inside He nanodroplets has recently been investigated using ion imaging techniques [10].

So far, the only chemical reaction involving neutral heterogeneous reactant molecules inside He nanodroplets is $Ba + N_2O \rightarrow BaO + N_2$, which was characterized by chemiluminescence spectroscopy [11]. Recently, some efforts for exploring chemical reactions in He droplets have been made *e.g.* on the reaction $F + CH_4$ [12]. However, no reactive process was found indicating that at the low temperature of the He droplet environment even small energy barriers may impede chemical reactions. Beside the reaction of neutrals, a rich ion-molecule chemistry inside ionized He droplets has been reported [6]. *E.g.*, secondary reactions of N_2^+ , D_2^+ and CH_4^+ fragment ions created by electron impact ionization (EII) of the He have

been identified, thus evoking the term 'flying nano-cryo-reactors' [13].

The showcase reaction $Na+H_2O$ has been studied in great detail at high temperatures to solve the long-standing puzzle [14, 15, 16, 17, 18, 19]: While M metals are well-known to react with water in a violent exothermic reaction at the macroscopic scale, single Na atoms colliding with water molecules or even with clusters do not react besides being solvated. Only when combining Na_n clusters with $(H_2O)_m$ clusters, chemical reactions were found to take place and products $Na(NaOH)_n^+$ appeared in the product mass spectra [18, 19]. Both experimental and theoretical results point at a complex elementary reaction involving three Na atoms and six H_2O molecules [17, 19]. In this Letter we report on the chemical reaction of alkali (M=Na, Cs) clusters with water (H_2O) clusters inside He nanodroplets. We have done similar studies using K and Rb; these results nicely go along with the interpretations given below and will be published elsewhere.

Our experiment combines a beam of He nanodroplets, consecutively doped with water molecules and with M atoms, with fs laser ionization or with EII. The experimental setup is described in detail elsewhere [8, 9]. In short, ultrapure He gas is expanded at high pressure (60 bar) out of a cryogenic nozzle (diameter $10 \mu m$) into high vacuum. At the nozzle temperature of 13 K the average droplet size amounts to about 20,000 atoms. In the doping chamber the beam passes through two scattering cells for the droplets to pick up water molecules and subsequently M atoms. For reaction products to appear in the photo ionization (PI) mass spectrum, the vapor pressures in the pick-up cells have to be increased significantly above the levels needed for doping one M atom or H_2O molecule. At a vapor pressure corresponding to maximum probability for picking up 10 M atoms per droplet, cluster sizes up to M_6 are detected without adding H_2O mainly due to fragmentation induced by the ionization process. The H_2O doping conditions are chosen such that a broad (FWHM $\approx \bar{N}$) cluster size distribution peaked around the prominent mass peak at $N=20$ water molecules per cluster is observed in the EII mass spectrum without doping with M atoms.

In order to obtain a realistic picture of the compounds

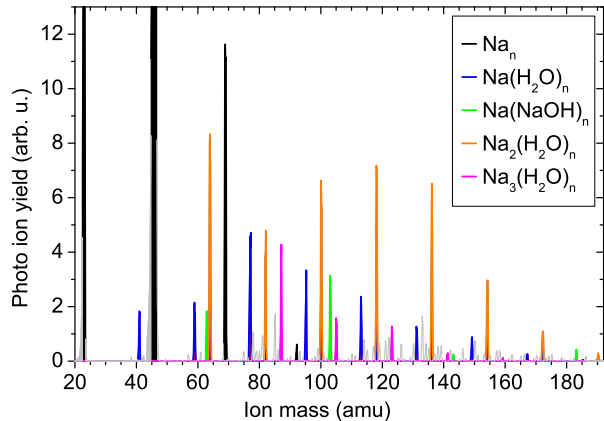


FIG. 1: Photo ionization mass spectrum of mixed sodium (Na)-water (H_2O) clusters in He nanodroplets. The dominant cluster series $\text{Na}(\text{H}_2\text{O})_n$, $\text{Na}(\text{NaOH})_n$ and $\text{Na}_2(\text{H}_2\text{O})_n$ are highlighted.

produced in the reaction, two complementary ionization schemes are employed, non-resonant multi-photon PI using laser pulses of 150 fs duration at 860 nm (755 nm) for the Cs (Na) experiments and EII at 30 eV electron energy. While fs photo ionization acts on the M atoms and clusters due to their low ionization potentials (~ 2.7 – 5 eV), it is completely inefficient for pure water clusters. In contrast, EII proceeds in a two-step process mediated by the He atoms. Thus, $(\text{H}_2\text{O})_m$ clusters, which are immersed into the droplets, are easier to ionize by EII than the neat clusters M_n , which stay bound to the droplet surface.

The resulting PI mass spectrum of He droplets simultaneously doped with Na_n and $(\text{H}_2\text{O})_m$ is displayed in Fig. 1. It is clearly dominated by small clusters Na_{1-3} carrying up to 8 water molecules reflecting weakly bound van der Waals-complexes (blue and red lines) [20]. The only compounds originating from the reaction with H_2O are low-abundant Na hydroxide masses, $\text{Na}(\text{NaOH})_n$, the most prominent peak being the one of $\text{Na}(\text{NaOH})_2$ (green line). This finding is in line with cluster reactions being largely frozen out in the ultracold droplet environment, except for a small fraction that has not completely thermalized to 0.4K before initiating the reaction.

However, a totally different picture presents itself when Cs_n clusters are combined with H_2O clusters inside He droplets. The PI mass spectrum, shown in Fig. 2, features a number of additional peaks aside from the pure Cs_n masses, which follow a strikingly regular pattern: Roughly speaking, every Cs_m cluster mass peak is augmented by $m - 1$ satellites with additional masses of about 1 to $m - 1$ water molecules. Except for the Cs_2 -satellite, the last peak of each series, corresponding to $\text{Cs}(\text{CsOH})_m$, shows extraordinarily high abundance, in

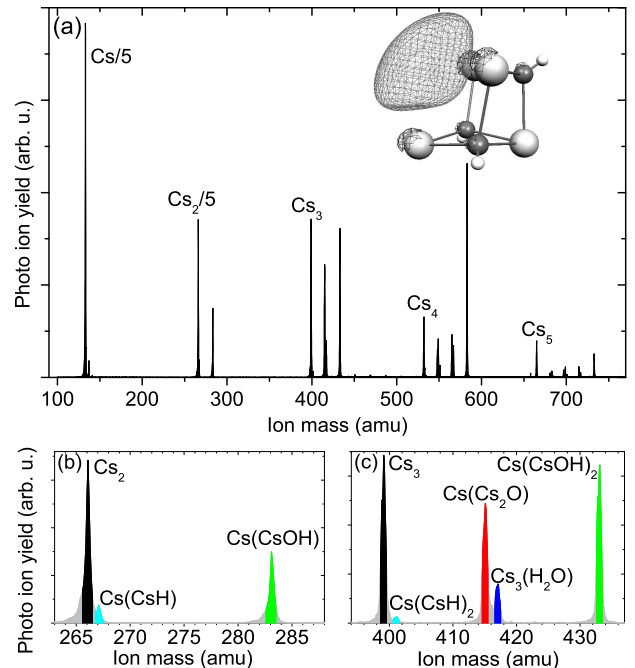


FIG. 2: a) Photo ionization mass spectrum of mixed cesium-water clusters in He nanodroplets. The vertical scale is shrunk by factor 5 in the mass range 100 to 300 amu for the sake of clarity. The inset illustrates the molecular structure of the prominent compound $\text{Cs}(\text{CsOH})_3^+$ (see text). b) and c) Detailed views of the mass spectrum showing Cs_2 and Cs_3 , respectively, and associated reaction products.

the case of $\text{Cs}(\text{CsOH})_3$ even exceeding the one of the corresponding neat cluster Cs_4 . However, no van der Waals-bound complexes, $\text{Cs}_n(\text{H}_2\text{O})_m$ with $m \geq n$ are observed under any conditions, in contrast to the Na+ H_2O system.

Upon closer inspection the satellite peaks reveal a more complex composition reflecting different reaction products, shown in Fig. 2 b) and c). Besides the dominating $\text{Cs}(\text{CsOH})_m$ -peaks we find various Cs oxide, hydride, and hydroxide compound clusters as well as reaction products involving H_2O complexes, which have not been observed in earlier experiments. These compounds are found to follow odd-even alternations in terms of the number of Cs atoms involved. *E. g.*, Cs_nO and $\text{Cs}_n\text{H}_2\text{O}$ are most abundant for odd n , whereas Cs_nOH mass peaks are more pronounced for even n . This suggests the notation used in legends of Fig. 2 a)-c), in accordance with valencies of the atomic and molecular constituents. These compounds may reflect intermediate states of the reaction which are stabilized by the dissipative He droplet environment. Note that NaH formation was identified as the rate determining step with a reaction barrier of 0.6 eV in the $\text{Na}_n + (\text{H}_2\text{O})_m$ reaction [17].

The surprising result of this experiment is that small

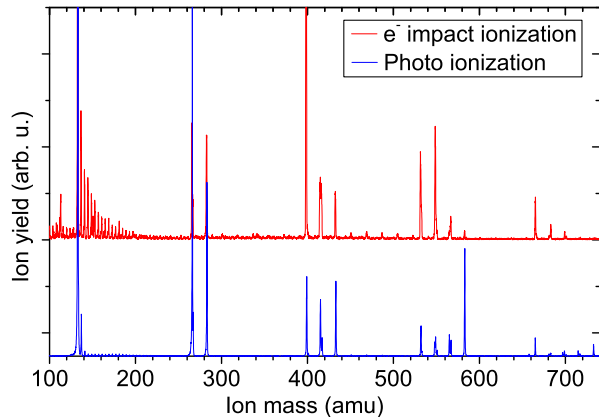


FIG. 3: Mass spectra of mixed cesium-water clusters in He nanodroplets, recorded using electron impact ionizations (upper trace) vs. fs photo ionization at 860 nm (lower trace). Despite the different ionization mechanisms (see text) the spectra show great qualitative resemblance.

clusters Cs_n actually react very efficiently with water inside He nanodroplets, despite the low temperature environment. This implies nearly vanishing activation energy for cluster reactions involving Cs, in contrast to the findings for the elementary Na reaction [17]. Possibly, surplus energy from the ionization energy or high-spin states of Cs clusters, as expected from the aggregation process in He droplets, may facilitate reactions. The lack of H_2O appendages may also be related to the lower hydration energy of Cs atoms (2.86 eV per molecule for bulk water) as compared to the one of Na atoms (4.21 eV). While water molecules are bound rather tightly to Na_n , the surplus energy from ionization may boil off the excess water from Cs_n clusters more easily. Strong reactivity of Cs_n with H_2O in He droplets is even more unexpected since Cs atoms and molecules are located in surface states whereas water molecules are immersed inside the droplets. Apparently, long-range attractive forces bring the Cs and H_2O clusters together, as previously observed with M atoms and HCN molecules [20].

In order to investigate to what extent the observed mass spectra depend on the particular detection scheme, EII is applied under identical conditions as the PI measurements. Fig. 3 illustrates the remarkable qualitative agreement of the mass spectra obtained for the two complementary ionization schemes. In both cases the mass spectra consist of progressions of neat clusters Cs_m with $m-1$ 'water' satellites. Thus, the interpretation of the excess Cs atom in terms of serving as a chromophore which enhances the PI cross section of the compound can be ruled out [19]. The similarity of PI and EII spectra show that these spectra actually reproduce the abundance distributions of ionized compounds and that reactions take

place among neutral precursor clusters before ionization. The differences in the mass spectra can be attributed to varying degrees of fragmentation of the individual compound clusters due to the differing excess energies deposited in the clusters. Furthermore, ionization spectra of the individual components (not shown here) clearly confirm this interpretation.

In order to draw more quantitative conclusions, high-level quantum chemical calculations are performed to determine equilibrium structures, ionization potentials (IPs), and stabilities with respect to fragmentation for the observed clusters. All calculations are done with the Gaussian 03 program package [21] using Hybrid-HF-DFT with the PBE1PBE [22, 23] functional. On Cs, a semi-relativistic [24] and a relativistic core potential [25] with the corresponding basis sets are used for the geometry optimizations and for single point calculations on the optimized geometries, respectively. On H and on second row atoms the 6-31++G(d,p) basis is applied for the geometry optimizations and the 6-311++G(3df,3pd) basis is used for the single point calculations. This method is found to reproduce the experimental atomization energies of Cs_2 , Cs_2O , CsOH , CsH , CsF and CsCl with a mean deviation of ≤ 0.2 eV.

The theoretical results show that all detected compound masses feature low vertical $\text{IP} < 3.3$ eV and are thus amenable to efficient ionization by 2 or 3 photons from our fs-laser. In contrast, the likely reaction products $(\text{CsOH})_n$, have large vertical $\text{IP} > 6.4$ eV for $n \leq 5$, thus requiring at least 5 photons for laser ionization. However, the fact that these cluster masses are absent in the EII mass spectra as well demands further explanations. It turns out that while $(\text{CsOH})_n$ clusters require high energies $\Delta E > 3$ eV for fragmentation, the ionization products $(\text{CsOH})_n^+$ are quite unstable with respect to the likely fragmentation channel, the loss of OH. For all cluster masses with $n \leq 5$ fragmentation energies are $\Delta E < 1$ eV and fall below the excess energy upon 5-photon ionization. We conclude that while $(\text{CsOH})_n$ are most likely produced in the M- H_2O reactions, reaction products fragment into the observed cluster masses $\text{Cs}(\text{CsOH})_n^+$ upon ionization.

The stability of neutral $\text{Cs}(\text{CsOH})_n$ and of cationic $\text{Cs}(\text{CsOH})_n^+$ clusters, which dominate the mass spectrum, is theoretically analyzed with respect to the most probable fragmentation channel, the loss of $(\text{CsOH})_m$. Fig. 4 depicts the fragmentation energies ΔE . Interestingly, for the neutral clusters the fragmentation channel requiring lowest fragmentation energy is the loss of the entire hydroxide compound, $(\text{CsOH})_{m=n}$, (dashed line in Fig. 4 (a)), whereas for the cations this channel is highest in ΔE (dashed line in Fig. 4 (b)), except for $\text{Cs}(\text{CsOH})_4^+$. This is due to the large binding energies of neutral $(\text{CsOH})_m$, and to the tendency of the positive charge to spread out over a large cluster to minimize Coulomb repulsion, respectively.

While ΔE for cationic $\text{Cs}(\text{CsOH})_n^+$ is substantially larger than ΔE for neutral $\text{Cs}(\text{CsOH})_n$, surprisingly both

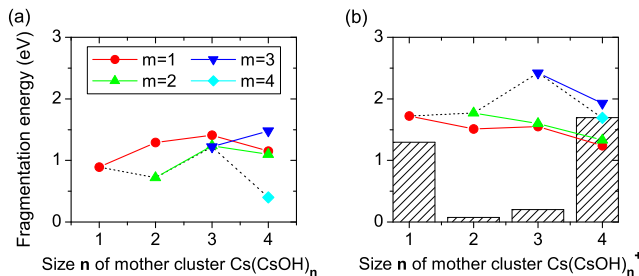


FIG. 4: (a) Fragmentation energies for the endothermic fragmentation reaction of neutral clusters $\text{Cs}(\text{CsOH})_n \rightarrow \text{Cs}(\text{CsOH})_{n-m} + (\text{CsOH})_m$ and (b) of cationic clusters $\text{Cs}(\text{CsOH})_n^+ \rightarrow \text{Cs}(\text{CsOH})_{n-m}^+ + (\text{CsOH})_m$. The bars represent the excess energy after multi-photon ionization of the neutral clusters.

the neutrals and the ions show an enhanced stability for $n = 3$; ΔE is particularly high with respect to all 3 possible fragmentation channels. This is due to the regular geometric structure of $\text{Cs}(\text{CsOH})_3^{0/+}$, which matches the cuboid rock salt lattice with one unoccupied site, where an electron is localized in the case of neutral $\text{Cs}(\text{CsOH})_3$ (see inset in Fig. 2). In particular, ΔE by far exceeds the excess energy deposited in the cluster upon 2-photon ionization, depicted as hatched bars in Fig. 4 (b). The same is true for $n = 1, 2$. The enhanced stability for $n = 3$ and the expected fragmentation of $\text{Cs}(\text{CsOH})_4^+$ into $\text{Cs}(\text{CsOH})_3^+$ nicely explains the extraordinarily high abundance of that compound observed by laser ionization

(Fig. 2).

The abundance of cluster masses of the type Cs_nH^+ , Cs_nO^+ , $\text{Cs}_n(\text{H}_2\text{O})^+$, and $\text{Cs}_n(\text{OH})^+$, which show alternating abundance patterns, may be rationalized using the following simple picture. High stability is determined by the number n of valence electrons of the Cs_n -part, which either form chemical bonds or pair up in even numbers. *E. g.*, Cs_2OH^+ (Cs_3O^+) are particularly stable, since one (two) electrons are needed for Cs binding to OH (O), and the remaining electron is ejected upon ionization. This picture, which applies here due to predominantly ionic bonding of these small compound clusters, is confirmed by our theoretical results in terms of cluster stabilities with respect to fragmentation.

In conclusion, we find that while Na and H_2O clusters in He droplets predominantly form van der Waals complexes, Cs_n clusters completely chemically react with H_2O to form a variety of compounds despite the ultracold droplet environment. The peculiar abundance pattern of reaction products is largely independent of the detection scheme applied. All prominent features are interpreted in terms of stabilities of individual compound clusters with respect to fragmentation, as obtained from high-level molecular structure calculations. In particular, the high abundance of $\text{Cs}(\text{CsOH})_3^+$ is found to be related to the extraordinary stability of neutral $\text{Cs}(\text{CsOH})_3$ and of its cation as a result of their regular cuboid structure. These experiments demonstrate the potential of He nanodroplets to serve as nanoscopic cryo-reactors for probing elementary reactions at ultralow temperatures.

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