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# Solvation and chemical reaction of sodium in water clusters

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**Abstract.** $Na_m(H_2O)_n$ Clusters ($n = 1\ldots200$, $m = 1\ldots50$) are formed in a recently build pick-up arrangement. Preformed water clusters traverse a sodium oven, where sodium atoms are picked up. At low sodium vapour pressure ($< 1 \times 10^{-4}$ mbar) pure $Na(H_2O)_n$ clusters are observed in the mass spectra. At high sodium vapour pressure ($> 1 \times 10^{-3}$ mbar) the water cluster pick up more than 50 Na atoms and reaction products $Na(NaOH)_n$ ($n = 2, 4\ldots50$) dominate the mass spectra. The even number of NaOH units in the products indicate that also in a finite cluster the reaction occurs in pairs as in the macroscopic reaction.

**PACS.** 33.80.Eh Autoionization, photoionization, and photodetachment – 36.40.Jn Reactivity of clusters – 82.80.Rt Time of flight mass spectrometry

## 1 Introduction

The strongly exothermic reaction of alkali metal with liquid water is well known even beyond the scientific community. Despite this fact even nowadays the reaction mechanism is not yet fully understood on a microscopic scale. The investigations of the reaction in the liquid phase are dated back to the begin of the 19th century and the first measurement of exothermicity for the reaction $Na+H_2O \rightarrow \frac{1}{2}H_2+NaOH$ have been published in 1883 [1]. A first step into deeper understanding of the reaction mechanism was the observation that solvated electrons are formed when alkali metal is desolved in polar liquids (see *e.g.* [2] and references there in). The large differences in the reactivity of alkali metal with ammonia and water are closely related to the stability of the solvated electron. While in liquid ammonia the solvated electron is stable for days, the lifetime in water is less than 1 ms. To follow the course of the reaction alkaline aqueous solutions have been studied [3,4]. In these experiments neutral sodium atoms are formed as intermediates in a reaction with solvated electron produced by photolysis, which then react further to known reaction products.

A couple of years ago we have started to investigate the formation of the solvated electron by studying $Na(H_2O)_n$ and $Na(NH_3)_n$ clusters as model systems [5,6]. In these early experiments the clusters were formed by expanding an Ar-$H_2O$ mixture through a sodium beam. Here, mainly intact $Na(H_2O)_n$ clusters are observed with no additional NaOH units except for some small mass peaks [7]. This is in agreement with crossed beam experiments, where also no reaction products have been found after scattering of single Na atoms with water molecules [8]. Recently, Buck and Steinbach [9] have used a modified cluster source compared to ours, where the preformed water clusters undergo multiple collisions with the sodium vapour. They could observe reaction products of the type $Na^+(NaOH)_m(H_2O)_n$ with $m = 2, 4$ after photoionization with 360 nm. They suggest a two step mechanism to form $Na(NaOH)_2(H_2O)_n$, where first one sodium atom is captured to form $Na(H_2O)_n$ as precursor and then a dimer is attached to the complex to start the reaction. Barnett and Landman [10] found in their calculation of the reaction $Na_2(H_2O)_n \rightarrow (NaOH)_2 + H_2$ has an exothermicity of 1.22 eV and a reaction barrier of 1.56 eV. A decrease of the reaction barrier with increasing cluster size is expected. Very recently, Mundy *et al.* [11] suggest that the formation of $Na^-$ is an important step in the sodium-water reaction.

Here, we present a new experimental arrangement to prepare efficiently sodium-water-clusters containing more than one sodium atom. With this arrangement we were able to observe new series of reaction products leading to a new insight into the sodium-water reaction.

## 2 Experimental

A new continuous source has been build to prepare sodium-water-clusters using the pick-up method [12]. Figure 1 shows the scheme of the experimental setup. Water clusters are prepared by expanding pure water vapour through a nozzle of 70 $\mu$m diameter into the vacuum. The water oven can be heated up to a temperature of 200 °C, which corresponds to a stagnation pressure of 10 bar. To avoid clogging the nozzle is heated separately and kept 10 to 20 °C warmer than the oven temperature. Alternatively,

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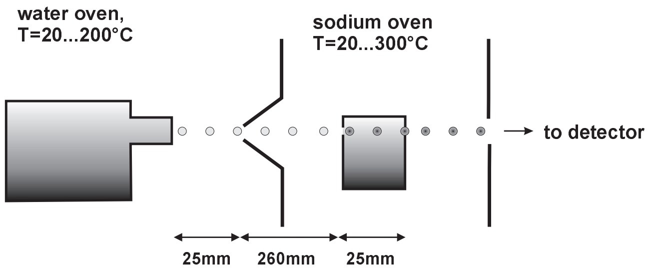

**Fig. 1.** Scheme of the pick-up source.

a conical shaped nozzle (diameter $d = 100\ \mu$m, half opening angle 15.6°) is used to obtain larger clusters [13]. Approximately 25 mm from the nozzle a skimmer collimates the supersonic beam and the water clusters enter a separately pumped chamber, where the sodium oven with a diameter of 25 mm is located. The beam of water-clusters traverses the oven through two holes, which are 3 mm in diameter. In the oven the water-clusters pick up one or more sodium atoms. The pick-up process is controlled by the sodium vapour pressure, which can be raised to $2 \times 10^{-2}$ mbar at 300 °C.

The thus formed sodium-water-clusters enter the detector chamber and are ionized 280 mm downstream with a pulsed laser beam. In the experiment presented here, we have used the 4th harmonic of a Nd:YAG laser (266 nm; 4.66 eV) with a pulse energy of 1.7 mJ. Since the clusters are ionized by a single photon [6] no focusing of the beam was necessary and the corresponding flux was 6 mJ/cm$^2$ at the cluster beam. The ions are mass selected in a time-of-flight mass spectrometer (TOF) and detected with microsphere plates (MSP). Since the ions are extracted perpendicular to the molecular beam axis large clusters are discriminated.

## 3 Results and discussion

The pick-up source enables us to produce sodium water clusters in a wide range of sizes and composition. Figure 2 shows four mass spectra taken at different temperatures of the sodium oven. The data are obtained by measuring a mass spectrum with water cluster beam and subtracting a mass spectrum taken without water cluster beam. This reduces spurious mass peaks from the sodium oven and other impurities (mainly pump oil) in the chamber. During the measurement the temperature of the water oven and the nozzle has been kept constant at 110 °C and 133 °C, respectively. Under these conditions the average water cluster size is 140, which has been calculated by the scaling law of Hagena [14,15]. When heating up the sodium oven the first $\mathrm{Na^+(H_2O)}_n$ clusters are observed at a temperature $T_{\mathrm{Na}} = 170$ °C (Figure 2a). This corresponds to a vapour pressure of $p_0 = 4 \times 10^{-5}$ mbar. At $T_{\mathrm{Na}} = 190$ °C the intensity of the sodium water clusters containing a single sodium atom reaches maximum (Figure 2b). In addition, new series of mass peaks occur. One is identified as $\mathrm{Na_2^+(H_2O)}_n$, which interestingly ends after only 10 water molecules are bound to the sodium dimer. The second series are the first appearance of the reaction products $\mathrm{Na^+(NaOH)_2(H_2O)}_n$. This series starts at $n = 0$ and is visible up to the resolution limit of the mass spectrometer at large masses. With further increasing temperature $T_{\mathrm{Na}} = 210$ °C the intensity of the $\mathrm{Na(H_2O)}_n$ clusters decreases, while the mass peaks of $\mathrm{Na^+(NaOH)_2(H_2O)}_n$ increases. Figure 2c shows distinct strong peaks, marked by arrows, at the masses 103, 183, 263 amu. These mass peaks correspond to reaction products $\mathrm{Na(NaOH)}_n$ ($n = 2$, 4, and 6) with no additional water molecules.

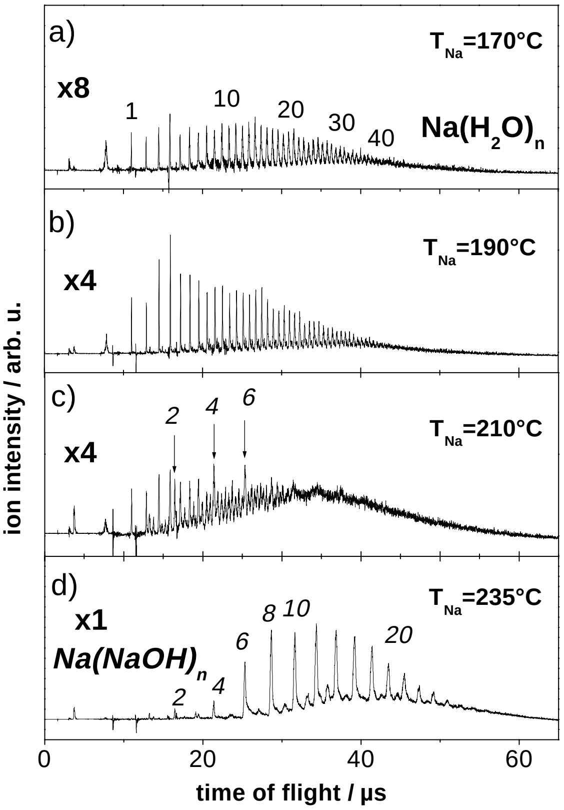

**Fig. 2.** Typical mass spectra taken by photoionization at 266 nm (4.66 eV). The average size of the water clusters is kept constant at 140. The temperature of the sodium oven has been varied. At the lowest temperature intact $\mathrm{Na(H_2O)}_n$ clusters are observed (a). Reaction products $\mathrm{Na(NaOH)}_n$ are detected higher sodium temperatures (d).

The observed mass spectra change dramatically at an oven temperature $T_{\mathrm{Na}} = 235$ °C which corresponds to a vapour pressure $p_0 = 1.2 \times 10^{-3}$ mbar (Figure 2d). The mass spectrum is now dominated by $\mathrm{Na(NaOH)}_n$ with $n$ up to 34. Small clusters are not longer detected, because they are scattered out of the beam, due to numerous collisions in the high sodium pressure of the oven. It should be noted here, that the observed reaction products always contains an even number of NaOH units and an additional sodium atom. To understand this massive reaction a closer inspection of the cluster formation process is necessary. The size distribution of the water clusters depends on the expanded gas, stagnation pressure, temperature of the nozzle and nozzle geometry and follows a log-normal distribution. The average cluster size for our experimental conditions is $\overline{n} \approx 140$. The water clusters enter the sodium oven, which acts as a gas cell. The sodium vapour is in thermal equilibrium with the sodium liquid. Thus, at the temperature $T_{\mathrm{Na}} = 235$ °C mainly sodium atoms are present in the gas. The density of sodium dimers is below 0.5% [16]. Therefore, the water clusters capture preferentially single sodium atoms. Assuming a capture probability of 1 one can easily determine the number of sodium atoms picked up in the sodium cell by calculating the number of collisions. For a cell of diameter $L$ the number of collisions is given as $k = n\sigma L$, where $n$ denotes the density of the sodium vapour and $\sigma$ is the cross section. As a rough estimate one can use the "hard-sphere-model" and the Wigner-Seitz radii to determine the cross section: $\sigma = \pi(r_{\mathrm{Na}} + r_n)^2$ with $r_n = n^{1/3} r_{\mathrm{H_2O}}$. For our experimental conditions we find $k \approx 2$ which is about 10 time lower than observed in the experiment. This is not too surprising since the hard-sphere only gives a lower limit for the collision cross section. Long range forces may play an important role. Also, the sodium vapour may also be present outside the cell, due to the 3 mm holes leading to a longer effective length $L$. We can conclude here, that the water clusters pick up a large number of single sodium atoms when traveling through the sodium vapour.

Recently, Buck and Steinbach [9] have suggested a two step reaction mechanism to explain their observation of $\mathrm{Na(NaOH)_2(H_2O)}_n$ and $\mathrm{Na(NaOH)_4(H_2O)}_n$ products. After the solvation of a single sodium atom an additional collision with a sodium dimer initiates the reaction. Since the exothermicity of the reaction leads to evaporation of water molecules the authors concluded, that the smallest reactive cluster is $\mathrm{Na_3(H_2O)_6}$. This was confirmed by theoretical calculation of Mundy *et al.* [11] suggesting, that a delocalized 3s electron from the solvated sodium atom aids the sodium dimer in the formation of a charge separated pair $\mathrm{Na^-Na^+}$ as reactive intermediate.

In general, this mechanism also describes the formation of the reaction products seen in our mass spectra (Fig. 2d). Although in our source the water clusters have multiple collisions with individual sodium atoms. It may well be, that during the redistribution of the excess energy of the collision sodium dimers or even larger clusters are formed prior the actual reaction. After the reaction water molecules are evaporated to compensate the reactive excess energy. This should be a statistical process in the sense of the "evaporative ensemble". In the reaction products we observe all remaining water molecules are evaporated. In the course of the reaction there should be also a certain probability for the evaporation of NaOH units. Surprisingly, we do not observe $\mathrm{Na(NaOH)}_n$ with an odd number of NaOH [17]. This observation suggests, that the NaOH molecules are stronger bound to each other forming a salt like ionic micro crystal.

In both experiments, Buck's and ours, the observed reaction products have a extra sodium atom. This sodium atom acts as a chromophor which enables the complex to be ionized with 3.44 eV and 4.66 eV photons, respectively. In Fig. 2b and c the series $\mathrm{Na_2(H_2O)}_n$, $n = 1 \ldots 10$, $\mathrm{Na_3(H_2O)}_n$, $n = 1 \ldots 4$ and $\mathrm{Na_4(H_2O)}_n$, $n = 1, 2$ are observed in the mass spectra. These clusters can be viewed as precursors of the reaction and the distinct cut off of these series of clusters hints at the onset of the spontaneous reaction within the sodium water complexes.

## 4 Conclusion

We have built a new pick-up source to form sodium-water clusters in a wide range of size and composition. By varying the temperature of the sodium oven we can produce different series of clusters: at low sodium vapour pressure intact $\mathrm{Na(H_2O)}_n$ clusters are present in the mass spectra while at high vapour pressure the spectrum is dominated by reaction products $\mathrm{Na(NaOH)}_n$ with only even number of NaOH units. This source enables detailed investigations of these metal-solvent-clusters, which are important building blocks for an microscopic understanding of solvation and reaction processes in liquids. Spectroscopic properties of electronically excited states of $\mathrm{Na(H_2O)}_n$ were determined in our lab [18]. Dynamical studies are presently underway.

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