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LETTERS

Formation of Sodium Hydroxyde in Multiple Sodium−Water Cluster Collisions

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In a pickup arrangement, the reactive scattering of sodium atoms and dimers with water clusters $(H_2O)_m$, $m \leq 140$, is investigated. The water cluster beam is generated in a pure supersonic expansion and crosses an atmosphere of sodium vapor. The reaction products are detected by photoionization at a wavelength of 360 nm (3.45 eV) and mass analyzed in a reflectron time-of-flight mass spectrometer. Doping the H_2O clusters with Na atoms results in the formation of solvated sodium atoms $Na(H_2O)_m$, representing the distribution of the pure water clusters. At higher sodium pressures also Na_2 dimers are produced, which then react in a second step with the solvated Na atoms to products of the type $Na(NaOH)_2(H_2O)_m$ and, to a lesser extent, also to $Na(NaOH)_4(H_2O)_m$. The size range follows that of the precursors with a pronounced maximum of intensities between $m = 6$ and 14 in the former case.

1. Introduction

The details of the well-known reaction of solid sodium with liquid water leading to solvated Na^+ and OH^- ions and molecular hydrogen are not yet understood. Macroscopic experiments have been conducted in sodium hydroxide solutions. Here, after the production of solvated electrons by photolysis of OH^-_{aq}, neutral metal atoms are found as intermediates that are rapidly decaying to the known reaction products.[1,2] On the other hand, it was observed that the scattering of single Na atoms with isolated H_2O molecules in a crossed molecular beam experiment did not lead to any reaction products.[3] Therefore clusters were thought to be the key in solving the problem microscopically. But also these experiments did not produce any remarkable concentration of species containing NaOH. The first results have been obtained in a pickup experiment in which a pulsed water cluster beam seeded in Ar was crossed with a supersonic sodium cluster beam under multiple collision conditions. Solvated sodium in water $Na(H_2O)_n$ and with much lesser intensity also solvated sodium dimers $Na_2(H_2O)_n$ were the only products observed.[4] Recently, we have investigated the scattering of sodium clusters Na_n, $n \leq 21$, with water clusters $(H_2O)_m$, $m \leq 40$, in a very detailed crossed molecular beam experiment under single-collision conditions.[5] To detect the products, they have to be formed in the collision region that corresponds to a time scale of picoseconds. The only products observed were solvated sodium atoms in water clusters $Na(H_2O)_n$. By measuring the angular and velocity distribution after the collision, the reaction mechanism could be clarified, namely, the formation of a complex $Na(H_2O)_{n+x}$ being stabilized by isotropic evaporation of $x = 2$ or 3 water molecules. Products containing Na clusters or NaOH did not appear in the mass spectra.

An experimental limitation in the search for products in these two experiments should be mentioned. The measured ionization potential of $Na(H_2O)_n$, $n \geq 4$, is 3.2 eV,[6] which is confirmed by calculations.[7−9] This low value makes them accessible for photoionization by a single laser photon. Probably the ionization potential of the $(NaOH)_n(H_2O)_m$ clusters is higher than the applied photon energies of 3.5−4.7 eV. On the other hand, these products are accessible for detection if additional Na atoms are attached. Thus, some very spurious amounts of masses that might be assigned to $Na_n(NaOH)(H_2O)_m$, n, $m = 1,2$,[4] and products of the type $Na_n(OH)_m$ arising from surface reactions with water impurities[10] were reported.

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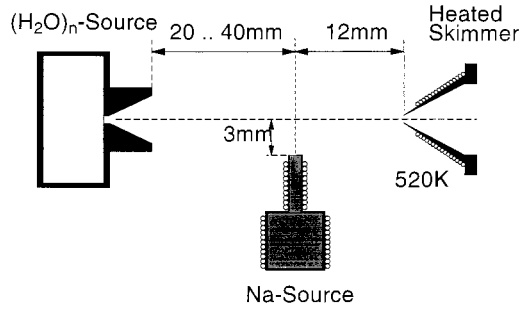

Figure 1. Pick-up arrangement. For the conditions of the beams, see text.

These experimental results are supplemented by a recent theoretical study of the direct reaction[11]

$$Na_2 + 2H_2O \rightarrow (NaOH)_2 + H_2 \qquad (1)$$

Although this reaction is exothermic by 1.81−2.0 eV, it is hindered by a barrier of 1.28−1.56 eV, depending on the method of calculation. This is caused by the fact that the minimum energy configuration of Na_2 and the chain $(H_2O)_2$ is far away from the transition state of the reaction.

Thus, we were looking for an experimental arrangement in which some of the solvations properties of the macroscopic experiments are still present and multiple collisions can occur. Therefore, a new Na pickup source was built with a nozzle diameter of 2 mm and capacities for heating to 1000 K. Raising the Na vapor pressure results in the formation of dimers leaving the source. Thus, the continuous water cluster beam crosses a vapor of about 1 cm length before passing the skimmer. It contains Na atoms or a mixture of Na atoms and Na_2 dimers depending on the pressure. In this way the interaction time is enlarged to several microseconds. The products are ionized by 360 nm single-photon ionization and mass analyzed in a reflectron time-of-flight (RETOF) mass spectrometer. Indeed, in this experimental arrangement we were able to detect solvated NaOH products that we propose of being produced in two sequential collisions.

2. Experiment

The experiment was performed in a molecular beams machine with a reflectron time-of-flight mass spectrometer (RETOF) that is described elsewhere.[12,13] Briefly, a supersonic water cluster beam crosses an atmosphere of Na atoms or atoms and dimers, respectively, under multiple-collision conditions. The actual arrangement is shown in Figure 1. The products generated in the interaction region are extracted through a skimmer and an additional differential pumping stage. They are detected by photoionization, mass resolved in the RETOF with a mass resolution of $m/\Delta m = 1300$, and sampled on a microsphere plate (MSP). The water clusters are generated in a continuous supersonic expansion of water vapor from an oven heated to 453 K corresponding to a vapor pressure of 10 bar. To obtain a stable cluster beam, the nozzle was kept at the higher temperature 621 K. The conical nozzle has a diameter of 70 μm, an aperture angle of 35°, and a length of 2 mm. The water cluster source can be refilled externally by excess pressure of rare gas. The continuous Na pickup source is heated between 745 and 919 K, corresponding to pressures of 3−66 mbar. The 2 mm diameter orifice is kept at 923 K. For the photoionization of the products at an ionizing wavelength of 360 nm, a pulsed excimer laser (Lambda Physics LPX200i) is used for pumping a dye laser (Lambda Physics LPD3000). The pulse energy at the ionizing volume was 4 mJ/pulse corresponding to a flux of 120 mJ/cm^2. The effective repetition rate is lowered to 4.2 Hz owing to a special method of counting the particles that is used because the signal rate proved to be rather low. If the digital scope (Tektronix TDS 744A) is operated in the average mode and masses do not show up at every laser shot, they easily disappear in the bit noise of the scope. Furthermore, the line of zero intensity is influenced by electric stray fields. The way to get nearly noise-free spectra is as follows. Every single-shot spectrum is read out and filtered with a value U_F, thus counting a pulse of intensity $nU_F + x$, $x \leq U_F$ as n particles. Then the resulting integer arrays are added.

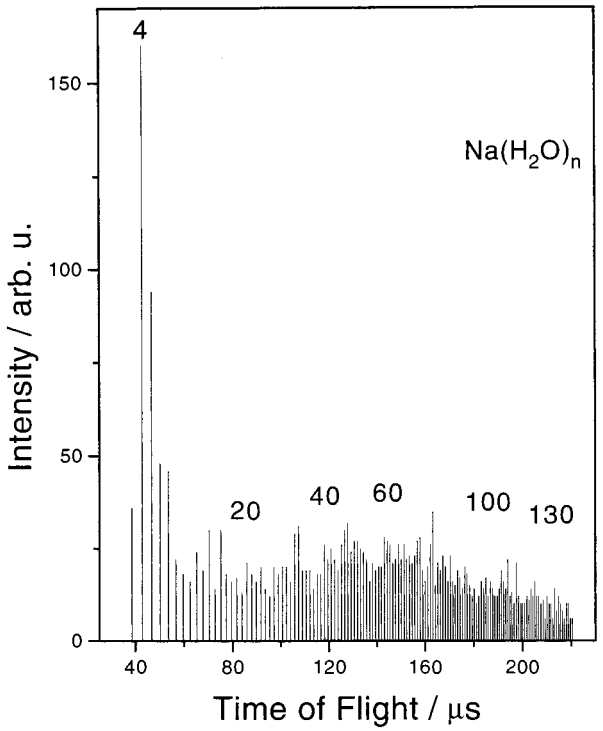

Figure 2. Mass spectrum taken at an oven temperature of 745 K corresponding to a sodium pressure of 3 mbar. The only masses seen are the complexes $Na(H_2O)_n$.

3. Results and Analysis

At a temperature of 745 K corresponding to a Na pressure of 3 mbar, only Na atoms leave the pickup source. The result of the product measurement, which is shown in Figure 2, is what we would have expected from the previous experiments.[4,5] The scattering of the water cluster beam by the Na atoms results in the formation of complexes $Na(H_2O)_{n+x}$, which are known to be stabilized by subsequent isotropic evaporation of $x = 2$ or 3 water molecules.[5] Thus, the result obtained by ionization with 360 nm photons (3.45 eV) is a spectrum of Na-doped water clusters that represents the nearly undisturbed size distribution of the pure water cluster beam. The mean cluster size of the water cluster beam at the given conditions turns out to be $\bar{n} = 63$ with the extension to clusters $n = 140$. The smallest complex detected is $Na(H_2O)_3$. With an IP of 3.48 eV, the 360 nm photons just reach the energy required, whereas $Na(H_2O)$ (IP 4.38 eV) and $Na(H_2O)_2$ (IP 3.80 eV) cannot be ionized. Since the corresponding ions could not be detected, their formation by ionization induced fragmentation of larger complexes can also be excluded.

At a temperature of 919 K corresponding to a sodium vapor pressure of 66 mbar, Na atoms and dimers are generated in the pickup source. This was confirmed by a measurement in which

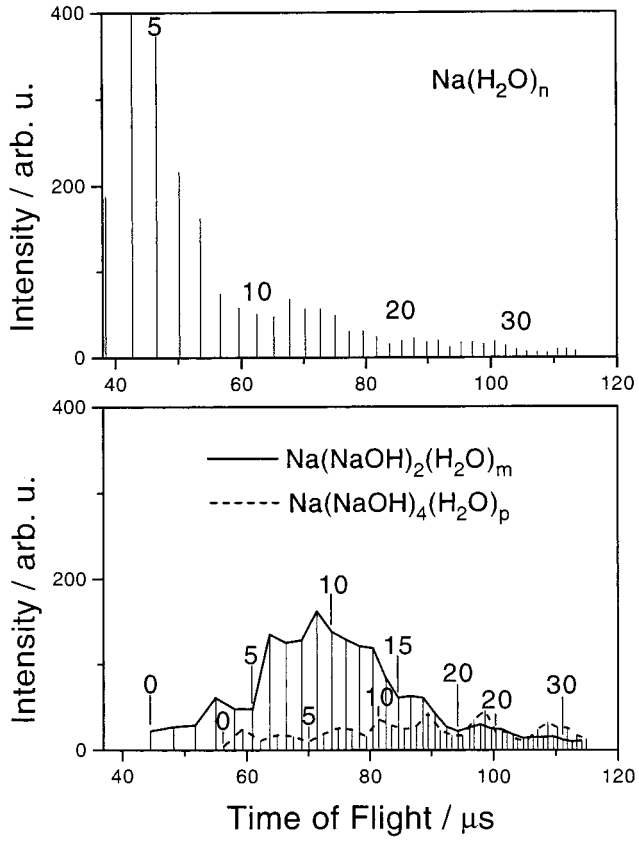

Figure 3. Mass spectrum taken at an oven temperature of 919 K corresponding to a sodium pressure of 66 mbar. Upper panel: $Na(H_2O)_n$ clusters. The peak at $n = 4$ has to be multiplied by 2. Lower panel: $Na(NaOH)_2(H_2O)_m$ clusters, connected by the solid line; $Na(NaOH)_4(H_2O)_p$ clusters, connected by the dashed line.

the pickup source was mounted in front of the skimmer. The product spectrum taken at this higher Na pressure is depicted in Figure 3. In the upper part, the Na doped water clusters are shown. Their mean cluster size has decreased to $\bar{n} = 14$, mainly caused by collisions of the increased sodium vapor pressure. In addition, we observe new masses in the spectrum that are assigned to products $Na(NaOH)_2(H_2O)_m$ and $Na(NaOH)_4(H_2O)_p$. These are shown in the lower part of Figure 3. Their intensities are even higher than those of the primary products $Na(H_2O)_n$. The onset for both reactive species is at $m = 0$ (no solvating water molecules). The high intensities of the reactive products indicate very large reaction cross sections. It is striking that only products with an even number of NaOH are found, thus pointing to H_2 molecules as further products leaving the complex aside from the water molecules. This is also inferred from the macroscopic reaction and eq 1.

Raising the sodium vapor pressure from 3 to 66 mbar leads to the following development of the mass spectra: As soon as Na_2 is present in the interaction region, the products $Na(NaOH)_2(H_2O)_m$ appear. The range of masses covered corresponds roughly to that of the $Na(H_2O)_n$ clusters. With increasing intensity of Na_2, the reactive products become more dominant with peak intensities between $m = 6$ and 14, and, in addition, $Na(NaOH)_4(H_2O)_p$ is observed with smaller intensities. Thus we write the two-step reaction equations as follows: In the first step $Na(H_2O)_n$ is formed according to

$$Na + (H_2O)_{n+x} \rightarrow Na(H_2O)_n + xH_2O, \quad x = 2, 3 \qquad (2)$$

which then react with Na_2 to the final products

$$Na_2 + Na(H_2O)_n \rightarrow Na(NaOH)_2(H_2O)_m + H_2 + (n - m - 2)H_2O \qquad (3)$$

$$2Na_2 + Na(H_2O)_n \rightarrow Na(NaOH)_4(H_2O)_p + 2H_2 + (n - p - 4)H_2O \qquad (4)$$

4. Discussion

Under the present multiple-collision conditions, reaction products containing NaOH are formed according to the multistep reaction 2 and 3 or 4. Aside from some spurious masses in the pickup experiment of Schulz et al., this is the first cluster experiment in which NaOH-containing products with large intensities have been observed. In the single-collision experiment no such products have been seen. Apparently for their production previous solvation of a Na atom in the water clusters is necessary. The large intensities of the reactive products indicate very large reaction cross sections for the second step, whereas the first step, the solvation of the Na atoms, takes place with relatively small cross sections.[5]

Interestingly, these products have not been observed in the experiments of ref 4. The main difference from our experiment is the presence of argon atoms with a pressure ratio $p_{argon}:p_{water}$ of 100:1 in the collision region. Apparently, the very efficient Na_2-Ar collisions prevent the occurrence of the reactions 3 and 4. The presence of Ar also explains why the products $Na_2(H_2O)_n$ are neither observed in the single-collision experiment nor in the present experiment. Obviously, in the high-pressure regime of the expansion, these clusters are stabilized by collisions with argon atoms. This argument is supported by the fact that also the products $Na(H_2O)$ and $Na(H_2O)_2$, which are quite prominent in the experiment with Ar, are not or only weakly observed in the experiment of ref 5, even for ionization energies up to 4.7 eV. The authors of ref 4 claim that these two products are stabilized by Ar collisions. On the basis of the results of ref 5 also processes of the kind $Na_3 + (H_2O)_{m+x+2} \rightarrow Na(NaOH)_2(H_2O)_m + H_2 + xH_2O$ are excluded. Thus we propose the reaction mechanism of two sequential steps and consider the reaction of eq 1 as an unlikely process.

These general results are in line with recent theoretical calculation that the direct exothermic reaction 1 is forbidden by a barrier of 1.28−1.56 eV.[11] The reason is that the minimum configurations of Na_2 and $(H_2O)_2$ are far away from the structure of the transition state that leads to the reaction products. Similar mechanisms might be valid for the larger cyclic water clusters. Apparently, the structure of the water clusters doped with one sodium atom brings them in a position closer to the transition state to overcome this barrier more easily and to generate in the reaction with Na_2 the products of reactions 3 and 4. For the understanding of this second reaction step it is necessary to know the structure of the precursor $Na(H_2O)_n$. In the detailed ab initio molecular orbital study, interior and surface states are found with the latter ones becoming more important for $n \geq 4$.[9] Especially these surface structures with several direct bonds between the O atoms of water and Na present an arrangement of water molecules with shorter distances of neighbored H atoms compared with the pure water clusters which favors the insertion of Na_2 and the formation of $(NaOH)_2$ and H_2.

We note that because of the exothermicity of the reaction very probably a couple of water molecules evaporate so that even the smallest product $m = 0$ stems from a precursor with $n \geq 6$. The product sizes of maximal intensities $m = 6-14$ are therefore traced back to the correspondingly larger initial clusters.

More detailed calcuations in this direction as well as a further crossed-beam experiment with $Na(H_2O)_n$ and Na_2 beams should give more insight in this interesting process. It would also be helpful to investigate these new products spectroscopically in order to get some information about their structure and their charge distribution.

In summary, the reactions of Na and Na_2 with water clusters under multiple collision conditions are investigated in a pickup experiment. Reactive products of the form $Na(NaOH)_{2,4}(H_2O)_m$ are found with H_2 as second product. $Na(H_2O)_n$ is proposed to be the precursor reacting with sodium dimers to the products noted above.

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References and Notes

(1) Telser, T.; Schindewolf, U. *J. Phys. Chem.* **1986**, *90*, 5378.

(2) Gopinathan, C.; Hart, E. J.; Schmidt, K. H. *J. Phys. Chem.* **1970**, *74*, 4169.

(3) Düren, R.; Lackschewitz, U.; Milošević, S.; Waldapfel, H.-J. *Chem. Phys.* **1990**, *140*, 199.

(4) Schulz, C. P.; Haugstätter, R.; Tittes, H.-U.; Hertel, I. V. *Phys. Rev. Lett.* **1986**, *57*, 1703. Schulz, C. P.; Haugstätter, R.; Tittes, H.-U.; Hertel, I. V. *Z. Phys. D* **1988**, *10*, 279.

(5) Bewig, L.; Buck, U.; Rakowsky, S.; Reymann, M.; Steinbach, C. *J. Phys. Chem. A* **1998**, *102*, 1124.

(6) Hertel, I. V.; Huglin, C.; Nitsch, C.; Schulz, C. P. *Phys. Rev. Lett.* **1991**, *67*, 1767.

(7) Dhar, R.; Kestner, N. R. *Radiat. Phys. Chem.* **1988**, *32*, 355. Dhar, R.; Kestner, N. R. In *Large Finite Systems*; Jortner, J., et. al., Eds.; Reidel: Dordrecht, 1987; p 209.

(8) Barnett, R. N.; Landman, U. *Phys. Rev. Lett* **1993**, *70*, 1775. Barnett, R. N.; Yannouleas, C.; Landman, U. *Z. Phys. D* **1993**, *26*, 119.

(9) Hashimoto, K.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 11436; *Chem. Phys. Lett.* **1994**, *223*, 423.

(10) Honea, E. C.; Homer, M. L.; Whetten, R. L. *Phys. Rev. B* **1993**, *47*, 7480.

(11) Barnett, R. N.; Landman, U. *J. Phys. Chem.* **1996**, *100*, 13950.

(12) Schütte, S. Max-Planck-Institut für Strömungsforschung, Göttingen, Germany, Bericht 7/1997.

(13) Hobein, M. Max-Planck-Institut für Strömungsforschung, Göttingen, Germany, Bericht 20/1994.