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Microsolvation and Chemical Reactivity of Sodium and Water Clusters

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It has long been known that sodium and water react violently, yielding sodium hydroxide and hydrogen gas. Although this is a showcase reaction, the mechanism is still not fully understood. Motivated by recent experimental findings,[1,2] we report a novel mechanism of the reaction of sodium and water in a molecular beam through a detailed first principles molecular dynamics investigation. While it is clear that the bulk-phase reactions proceed without difficulty, special conditions are necessary in order for the same reaction to occur in a beam.

Recent experimental observations have indicated that at least three sodium atoms must be present to initiate the chemistry.[1,2] More specifically, it is the presence of a solvated sodium atom and its interaction with a sodium dimer that will give rise to the reactive species. To explain this unexpected observation, we used the Car−Parrinello molecular dynamics (CPMD) method.[3] Using the experimental conditions as a guide, we started with initial conditions (reactants) of an equilibrated sodium water cluster ($Na(H_2O)_6$) and a sodium dimer. We used plane waves as a basis within local spin density (LSD) functional theory with an energy cutoff of 70 Ry and a BLYP gradient-corrected functional.[4,5] Norm-preserving pseudopotentials were used to describe the oxygen, hydrogen,[6] and sodium cores. In the case of Na, the $2s^2 2p^6 3s^1$ electrons were included explicitly.[7] The CPMD dynamics were performed in an isolated cubic cell of length 15.87 Å using the Poisson solver of Martyna and Tuckerman.[8]

Our novel mechanism begins with the dissociation of the sodium dimer to yield a polarized Na^- and a solvated Na^+. To explain this prediction we examine the electronic structure of $Na(H_2O)_6$ cluster. To obtain a chemically intuitive description of the electronic structure we used the Boys localization[9] criterion which obtains localized orbitals that minimize the fluctuations in the position operator for each electronic state.[10,11] This methodology also affords us the centroid and spread of the orbital. It is known from a previous study of liquid water that the two lone-pair and bonding electrons have a spread of roughly 0.7 Å.[12] When we examine the electronic structure of the isolated $Na(H_2O)_6$ we find something quite different, namely the presence of an extended state with a spread of nearly 3 Å. This corresponds to the delocalized 3s electron of the sodium atom as shown in Figure 1 and previously reported from independent studies.[13,14] Figure 1 shows a snapshot of the density of the Boys localized 3s electron of the isolated $Na(H_2O)_6$ undergoing CPMD. This computation was performed under conditions identical to those previously stated with a cubic cell of length 13.32 Å. Note the local tetrahedral coordination of the Na. Minimum energy structures of $Na(H_2O)_6$ have been reported elsewhere[13] and are in good agreement with the structure depicted in Figure 1. Attention should be brought to the Boys localized state that is distributed over some of the solvating water molecules in Figure 1. This leads to a very interesting and dynamic electronic state.[15] During the finite temperature CPMD (roughly 100 K in accordance with experiment) this is a highly polarizable species. Through its interaction with this extended electronic state, the sodium dimer is aided in its dissociation. Thus, the reactive intermediate, Na^-, is formed (see Figure 2). From previous density functional theory calculations of the same accuracy we have inferred that indeed the charge-separated pair Na^- and Na^+ is stable under CPMD dynamics with six solvating molecules. It seems clear that the charge-separated dimer is a local minimum in the energy at finite temperature, but it is unlikely to occur spontaneously in the molecular beam without the aid of the solvated sodium acting as a catalyst.

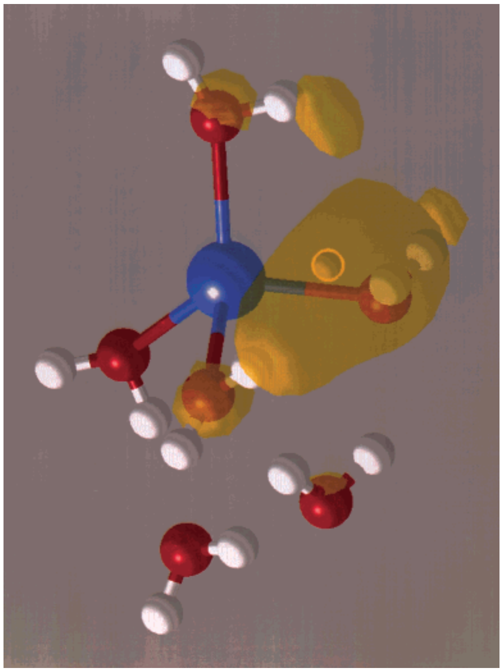

Figure 1. Snapshot of an isolated $Na(H_2O)_6$ cluster undergoing CPMD dynamics. Blue denotes sodium, red water, and white the hydrogens. The yellow sphere is the centroid of the localized function. The extended 3s electron of the sodium is represented by the transparent yellow mesh with isosurface value of 0.165 $e^-/Bohr^3$. The structure here is similar to the 6(4 + 2) structure observed by Barnett and Landman.[13]

Thus, after 3 ps of CPMD we can analyze the electronic structure of the full system (three sodiums and six waters) in the same fashion. Here we find that instead of one state with a large spread, there are three electronic states with a spread of roughly 3 Å. One of the extended states is the 3s electron of the solvated sodium (as shown in Figure 1), and the two others are the spin-polarized 3s states of the Na_2 (see Figure 2). Figure 2 depicts a typical configuration after 3 ps of CPMD. The spontaneous cleavage of the Na_2 is evident. It is this polarized Na^- that is the reactive intermediate. Thus, the dipolar Na^- acts as a Lewis base and will attack a proton to form sodium hydride (NaH), completing the chemical process and yielding NaOH and H_2.

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[15] It should be noted that the extended state gives rise to a very active infrared mode. The spectroscopy of these clusters will be discussed in a future publication.

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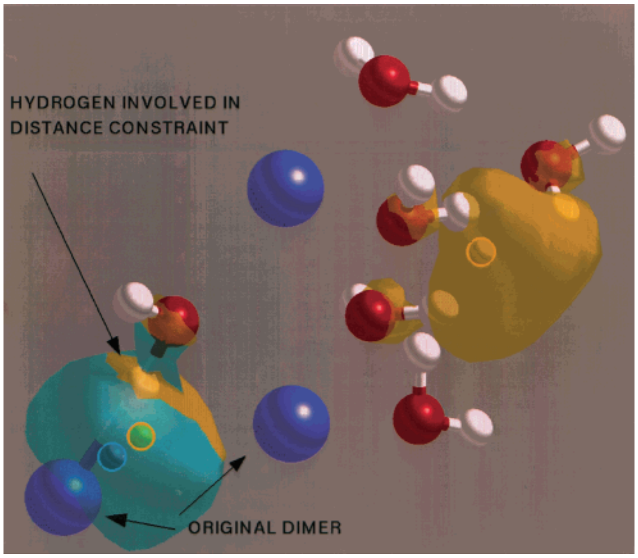

Figure 2. Snapshot of the full system, $Na_3(H_2O)_6$, during the formation of NaH. The color coding is the same as in Figure 1 except for the addition of a light blue sphere and transparent mesh denoting the "spin-down" centroid and localized electron, respectively. All electron densities are represented by an isosurface value of 0.397 $e^-/Bohr^3$. It is clear from this figure that the Na_2 is severed and the electrons are spin polarized (blue and yellow centroids are not overlapping as would be in a spin paired state) located closer to one sodium, thus forming the reactive intermediate, Na^-.

However, it is the formation of NaH that is the rate-determining step and thus requires some care to gain understanding into its mechanism.

Because of the time scales involved in the experiment (e.g., microseconds[1,2]), constraint algorithms must be employed to aid in sampling the reaction barrier. We would like to utilize a set of constraints that enable the reaction path to evolve in a natural way, rather than following the bias of the simulator. To this end, we use the coordination number constraint algorithm of Sprik.[16] Recall that our assumption is that the rate-determining step is the formation of NaH. One can think of this as requiring the oxygen in a water molecule to go from coordination number two (H_2O) to coordination number one (OH^-). This then gives the water molecule the freedom to choose which proton to liberate, as well as allowing this proton to choose its own path to the Na^-. Following the work of Sprik, we choose the coordination number of the oxygen to be given by $n_o(\mathbf{r}) = \sum_{i>0} S(|\mathbf{r}_i - \mathbf{r}_o|)$. Here, $S(r) = 1/(\exp[\kappa(r - r_c)] + 1)$. In the work presented here, we choose $r_c = 1.32$ Å and $\kappa = 1.58$ Å. The choice of our target oxygen can easily be deduced from Figure 2. It is clear from Figure 2 that the dipolar Na^- has a distinct directionality. It is this water, we believe, that is chosen in a natural way by the Na^- to be attacked. We believe that, by decreasing the coordination number by 3.5×10^{-5} every time step, the system is nearly equilibrated at every time step, and a reasonable upper bound to the reaction barrier to form NaH can be obtained either by integration of the Lagrange multiplier or by taking energy differences. Utilizing the coordination number constraint, we find a barrier of 14 kcal/mol that translates into a reaction time of roughly 1 μs at the temperatures realized in the simulation which is in line with experiment. It is of interest to note that another candidate for the transition state of this reaction has been postulated, albeit in a different context.[17] The structure of this transition state, based on studies of sodium chloride in water, leads to a concerted mechanism where the sodium hydroxide and hydrogen gas are formed in one step. This leads to a barrier roughly 3 times higher than what we report here, giving us confidence that our mechanism could be relevant. Furthermore, we have performed independent calculations using the more standard distance constraint (see Figure 2) where we assume that the reaction path is the O−H distance getting bigger and the H−Na distance becoming smaller simultaneously. This constraint was decreased at the same rate as the coordination number constraint and yielded almost quantitatively the same barrier.

After the formation of NaH, the reaction proceeds spontaneously to produce H_2 gas. The outline of the mechanism is as follows. First, a single sodium atom is solvated by six waters on the picosecond time scale: $Na + (H_2O)_6 \rightarrow Na(H_2O)_6$. Second, cleavage and solvation of a sodium dimer occur: $Na_2 + Na(H_2O)_6 \rightarrow Na_3(H_2O)_6$. Third, sodium hydride and sodium hydroxide are formed: $Na_3(H_2O)_6 \rightarrow (NaH)(NaOH)Na(H_2O)_5$. Fourth, a second sodium hydroxide and molecular hydrogen are formed: $(NaH)(H_2O)_5 \rightarrow (NaOH)(H_2O)_4 + H_2$. This reaction mechanism is able to explain experimental observations. Recall from refs 1 and 2 that in order to observe NaOH as a product the molecular beam interaction time must be on the order of a microsecond *and* molecular sodium (Na_2) must be present. The first criterion is corroborated by our upper bound on the reaction barrier. The second can be understood from the fact that the formation of Na^- is impossible from interactions of the cluster with neutral sodium atoms. It can be explained further by the novel observation that the role of the extended state of the $Na(H_2O)_6$ could act as a catalyst in "cleaving" the Na_2 bond. The analogy of a catalyst could be further emphasized by the fact that it is consumed during the chemical process and is seemingly regenerated after the final products are formed; i.e., the remaining sodium atom will be again stablized by solvating waters. This could lead to the additional formation of $(NaOH)_2$ that is observed in experiments.[1,2]

In conclusion, we have presented a novel mechanism for the reactions of sodium and water in a molecular beam. Not only does our mechanism explain experimental results, but our interpretation regarding the role of the outer solvated valence electron of Na leads to a picture that indicates that the solvation chemistry in clusters may differ from that in the bulk.

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