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Formation of a Reactive Intermediate in Molecular Beam Chemistry of Sodium and Water

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The aim of this work is a theoretical study of the initial steps in the reaction of sodium and water clusters in a molecular beam. Recent experimental and theoretical works have indicated that the presence of both sodium atoms and Na_2 dimers in the molecular beam give rise to a chemical reaction yielding sodium hydroxide and molecular hydrogen. Furthermore, experiments seem to indicate that at least three sodium atoms are present (e.g. a dimer and a solvated neutral atom). In this study, we take a step toward answering the question of why it is necessary to have three sodium atoms present to initiate the chemistry. By means of Car−Parrinello molecular dynamics simulations we investigate the formation of the dipolar reactive intermediate using a sodium dimer and a small water clusters, $(H_2O)_n$ ($n = 6, 8$), as reagents. This stable reactive intermediate is then able to initiate the reaction, yielding sodium hydroxide and a sodium hydride. To our surprise, our findings indicate that that formation of the dipolar atom is a natural state of the dimer/water cluster system; lending credibility to it being the only channel for the reactive process.

Introduction

Although the reaction of sodium metal with water is a show case exothermic reaction yielding sodium hydroxide and molecular hydrogen, there is not a full understanding of the mechanism of its bulk chemistry. To this end experimental works have been carried out by Buck et al.[1] on the reaction of sodium and water clusters in a molecular beam. In these studies, evidence of NaOH formation in the beam only occurs under special conditions, namely, when both sodium and sodium dimers are generated in the beam source. Moreover, the reactive process in the beam seems to be due to the interaction with *at least* three sodium atoms: a sodium dimer and a solvated sodium atom.

In a recent theoretical work, we have given one possible mechanism for this reaction in the beam.[2] We proposed a mechanism where three sodium atoms are involved, starting from an initial configuration of a sodium dimer in the environment of a sodium water cluster, $Na(H_2O)_6$. In this study it was found that the reactive intermediate resembles an Na^+ ion and two spin-polarized electrons that are located off of the atom center. The resulting structure resembles a dipolar, or an extremely polarized Na^- (see Figure 2 of ref 2). We will refer to this species in the remaining text as a dipolar sodium anion. This stable reactive intermediate was found to form spontaneously under Car−Parrinello Molecular Dynamics (CPMD).[2] Furthermore, the dipolar sodium anion was always found to be the stable final state when starting from different geometries of the stoichiometry $Na_3(H_2O)_6$. For example, with an initial condition of three collinear sodium atoms decorated with six solvating water molecules, the resulting stable state contained the dipolar sodium anion. Moreover, the geometry and energy of this configuration were nearly identical geometry to that obtained under the initial conditions used in ref 2. We also found that the dipolar sodium anion acts as a Lewis base and extracts a proton from a water molecule yielding NaH. Within CPMD the formation of NaH seems to be the rate determining step with an upper bound to a barrier of 14 kcal/mol. The last step of the process is the spontaneous reaction of NaH with water yielding sodium hydroxide and molecular hydrogen. This mechanism is consistent with the product distribution found in the experimental mass spectra[1] and demonstrates that the presence of three sodium atoms is a sufficient condition to initiate the chemistry of sodium in water clusters.

The aim of this paper is to clarify, by means of ab initio molecular dynamics simulations, the initial steps in the formation of the dipolar sodium anion intermediate. Thus, we address the possible transition states for forming the dipolar sodium anion with the starting reagents being a sodium dimer and water. We believe this is one step in gaining further understanding into the question of why it is necessary to have three sodium atoms present to initiate the chemistry, as indicated by experiment.[1] To our surprise, we find that indeed the global minimum for a system of a sodium dimer and a small water cluster must contain this dipolar anion, leading one to conclude that the chemistry could proceed with one dimer. Thus, we present a detailed analysis of this alternative reaction pathway involving the Na_2 species and $(H_2O)_n$ clusters, emphasizing the conditions that allow the formation of the dipolar intermediate giving rise to the observed chemistry.

Models and Computational Details

The models for our molecular dynamics simulations have been based on the product distribution of the molecular beam experiment.[1] These mass spectra show a large probability to observe the $Na(H_2O)_4$ cluster, proving that the sodium atom prefers to coordinate with four water molecules. Furthermore, small water clusters, $(H_2O)_n$ with $n = 6$ and 8, are known to be very stable, assuming three-dimensional conformations for $n \geq 6$.[3]

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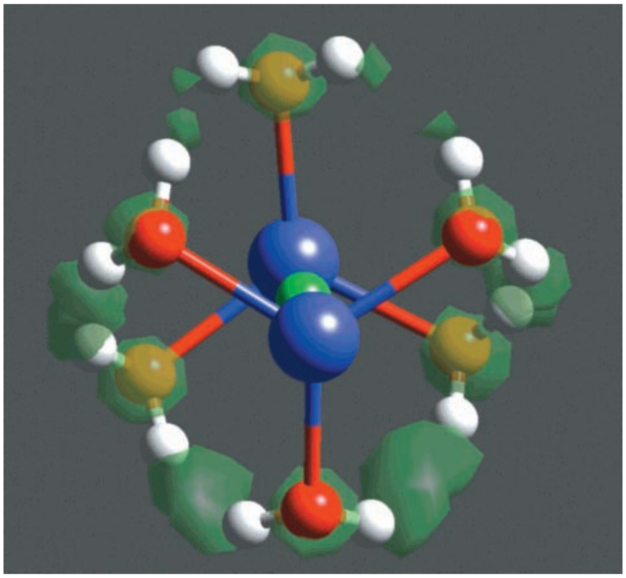

Figure 1. Optimized geometry for the $Na_2(H_2O)_6$ system (staggered-C_{3v}). Here blue represents sodium, red oxygen and white hydrogen. The green mesh represents an Wannier density iso-surface of 0.1647 electron/bohr^3 pertaining to the two spin-paired 3s electrons. The green sphere represents the Wannier centroid of these densities.

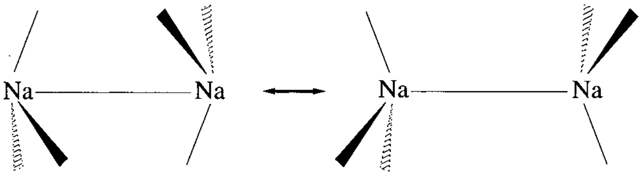

Figure 2. Thermal fluctuations for the structure of the symmetric $Na_2(H_2O)_6$ system under molecular dynamics at around 100 K. This figure shows the collective change in the Na−Na−O angles.

TABLE 1: Geometrical Parameters for the Symmetric $Na_2(H_2O)_6$ System (Staggered-C_{3v})

bonds	bond lengths [Å]
Na−Na	4.28
Na−O	2.33
O−H	0.99
bond angles	**bond angles [degrees]**
Na−$\hat{\text{Na}}$−O	87.1
Na−$\hat{\text{O}}$−H	112.0
H−$\hat{\text{O}}$−H	103.3

TABLE 2: Energies for the $Na_2(H_2O)_n$ (n = 6, 8) Complexes

species	energies [hartree]	ΔE [Kcal mol^{-1}]
$Na(H_2O)_3-Na(H_2O)_3$ (Figure 1)	−192.074	6.28
$Na(H_2O)_2-Na(H_2O)_4$ (Figure 3)	−192.084	
$Na(H_2O)_4-Na(H_2O)_4$ (Figure 7)	−226.398	7.53
$Na(H_2O)_2-Na(H_2O)_6$ (Figure 8)	−226.410	

It is also worth noting that in our previous theoretical work we observed the experimental products for initial conditions containing six water molecules and we remarked on the important role of the $Na(H_2O)_6$ cluster to achieve this. Specifically, the dipolar sodium anion reactive intermediate could only be formed with the dissociation of a sodium dimer which we believe was catalyzed by the $Na(H_2O)_6$ cluster. In the present work we carry out simulations involving six and eight water molecules interacting with a sodium dimer.

We used the CPMD method,[4] with a plane-wave basis set and an energy cut off of 70 Rydbergs, using the local spin density functional (LSD) within the BLYP gradient correction[5,6] norm preserving pseudopotentials were used to describe the oxygen, hydrogen[7] and the sodium core. In the case of sodium, the $2s^22p^63s^1$ electrons were included explicitly.[8] The CPMD dynamics were performed in an isolated cubic cell of length 15.87 Å using the Poisson solver of Martyna and Tuckerman.[9] A detailed description of the electronic structure was performed using the Boys localization criterion,[10] which obtains localized orbitals that minimize the spread for each electronic state.[11,12]

Results and Discussion

As alluded to above, both experimental results and our previous theoretical calculations show that a dipolar sodium anion can be observed only in the presence of a sodium dimer. Thus, calculations were carried out using models of sodium dimers in the environment of six and eight water molecules, allowing us to make comparisons between the two cases and identifying possible solvation effects.

We first investigated the stability of a sodium dimer solvated with six water molecules e.g. $Na_2(H_2O)_6$. A minimum energy structure was obtained using both the CPMD and Gaussian98 programs.[13] The results were consistent, and the optimized energy structure is shown in Figure 1 together with the Wannier functions and centroids with the two largest spreads. The geometrical parameters are given in Table 1. Given the high degree of symmetry for this structure, this result is not surprising. The salient feature of this configuration is that the sodium dimer is solvated in a staggered-C_{3v} symmetry. However, the bonding electrons of the Na_2 moiety deserves some attention. Looking at the overlapping spin-paired 3s Wannier centroids in Figure 1, it is clear that they lie in the center of the Na_2 bond. However, Figure 1 also shows the corresponding Wannier densities, indicating that the majority of the electron density of the two sodium 3s states are distributed evenly among the solvating waters, thus weakening bonding character. Another indication of this high delocalization comes also from the high spread value (5.7 Å) of the spin-paired 3s electrons. The high degree of delocalization is reflected in the large equilibrium bond length (4.28 Å compared to 3.1 Å in the free dimer). It is interesting to note that the extended state for the 3s electron is also reminiscent of the extended states observed for the 3s electron in the solvated neutral sodium clusters.[2,14] Furthermore, this result foreshadows our findings stated in the Introduction that the solvated dimer (Figure 1) is not a global minimum structure.

To test the stability of the solvated dimer configuration shown in Figure 1, we performed CPMD at finite temperature. This also allows one to assess whether a dipolar sodium anion can be formed spontaneously. The dynamic evolution of the solvated dimer system shown in Figure 1, at an average temperature of 100 K (in accordance with the beam temperature), shows the occurrence of an “umbrella” movement (Figure 2) in which there is a collective change of the Na−Na−O angles in the staggered configuration. However, the structure remains stable under thermal fluctuations. Thus, this symmetric local minimum will not spontaneously polarize to yield a dipolar sodium anion and a solvated Na^+ over the time scale of the simulation.

To probe the energetics of the dipolar sodium anion we artificially prepare the initial state. This is done by inserting a neutral sodium atom next to a equilibrated neutral cluster ($Na(H_2O)_6$) and performing a wave function minimization followed by CPMD dynamics under the same conditions as the solvated dimer. The resulting dipolar sodium anion was shown to be

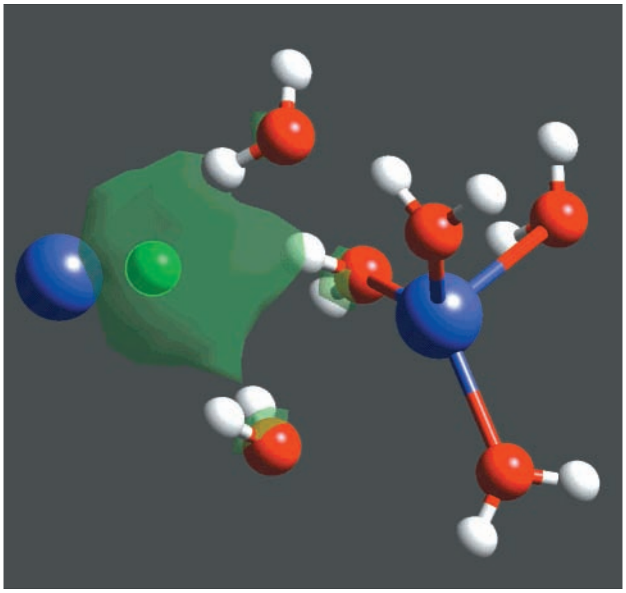

Figure 3. Geometry and Wannier densities at an iso-surface value of 0.3955 electrons/Bohr^3 (green mesh) for the two 3s electrons in the dipolar sodium anion system (atom color coding the same as in Figure 1). The Wannier density and Wannier centroid (green sphere) indicate a negative charge localization off the center of one sodium atom giving it a dipolar character. It is also possible to see the arrangement of the protons around this negative charge.

stable, with the negative charge localized between the unsolvated sodium atom and the solvated Na, hence giving it its dipolar character (see Figure 3). From Figure 3, it is clear that this negative charge is stabilized by a proton cage due to the specific orientation of the solvating waters, and the tetrahedral arrangement of the solvating lone pair electrons on the oxygens around Na^+. It is important to note that this dipolar structure will also give rise to the formation of sodium hydroxide under the same constrained CPMD dynamics as employed in ref 2, yielding qualitatively the same barrier (14 kcal/mol). However, the fragments involved in this configuration *are not* detected in molecular beam experiments.[1] This leads us to investigate the relative stability of the solvated dimer (Figure 1) and the dipolar sodium anion (Figure 3) structures under CPMD. To our surprise, we found that the equilibrium energy of the dipolar system is lower in energy (see Figure 4). The energy difference is estimated to be roughly 6.3 kcal/mol (see Table 1).

Now, the question concerns the search for a suitable reaction coordinate that can bring the high-energy solvated dimer configuration to the low-energy dipolar structure. It is instructive to use the distance between sodium atoms as a trial reaction coordinate, performing a constrained CPMD by slowly pulling apart the two sodium atoms. This pulling process was initiated on the equilibrated solvated dimer structure (Figure 1) at a maximum rate of $1.56 \cdot 10^{-3}$ Å/fs, to ensure adiabaticity.[2] The energy profile as a function of time is given in Figure 5. It is clear from the energies reported in Figure 5 that the stable configuration of the dipolar sodium anion was not obtained. Although the Na−Na distance was 4.20 Å, the distance coordinate is not relevant to the formation of the dipolar sodium anion.[15] However, by a closer examination of Figure 5 it is clear that there is a fluctuation to lower energies observed in the pulling process. We investigated this configuration (shown in Figure 6). This low energy fluctuation corresponds to instantaneous movement to an asymmetric charge separated configuration whose energy is −192.081 hartree, close to the average energy obtained for the dipolar geometry depicted in Figure 3.

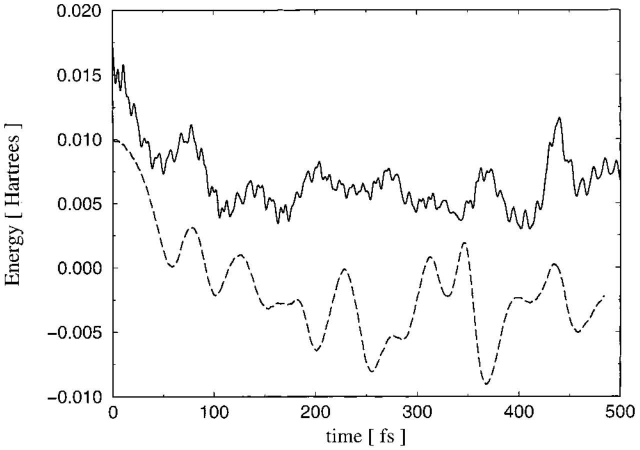

Figure 4. Kohn−Sham energies as a function of time of the solvated sodium dimer system (solid line) and dipolar sodium anion system (dashed line) relative to the average Kohn−Sham energy of the dipolar sodium anion geometry. The CPMD simulations were conducted at a temperature $T \approx 100$ K.

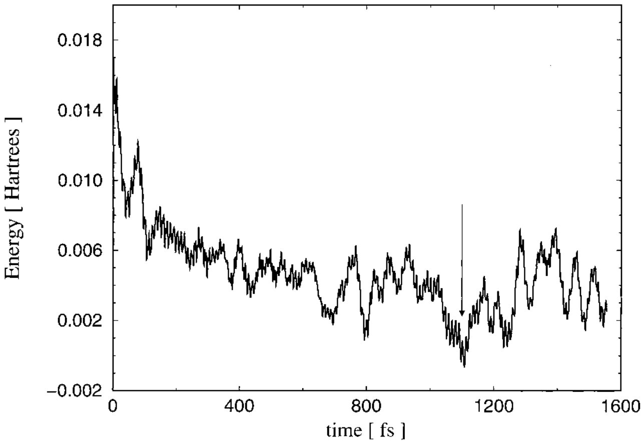

Figure 5. Kohn−Sham energy of the solvated sodium dimer subject to a constrained molecular dynamics at a temperature $T \approx 100$ K. The reaction coordinate is the sodium−sodium bond length, which is constrained to be an increasing function of the time (see text).

The Wannier function analysis carried out on this configuration shows the two 3s electrons delocalized among the solvating waters, but biased toward charge separation as further indicated by the location of the Wannier centroid (see Figure 6). Furthermore, as in the dipolar anion geometry shown in Figure 3, the system is stabilized by the tetrahedral water coordination of the Na^+. Thus, a rearrangement of the solvating water molecules in the solvated dimer geometry of Figure 1 could give rise to a charge polarization leading one to conclude that a change in water coordination number for the sodium atoms as a likely reaction coordinate. However, an entropic barrier may prevent the spontaneous formation of the dipolar anion on the time scales of the simulation.

The dominance of entropic factors on the charge separation process has also been analyzed by studying the interaction of an isolated sodium dimer with an equilibrated $(H_2O)_6$ water cluster, approximating the molecular beam geometry. We find that the propensity for charge separation of a sodium dimer in the neighborhood of an equilibrated water cluster of six molecules is strongly dependent on the initial configuration. As in the case previously discussed, the CPMD run for this system shows only instantaneous fluctuations to the charge separated state for which a lowering of the total energy can be observed. We also find that a complete transition to the charge polarized

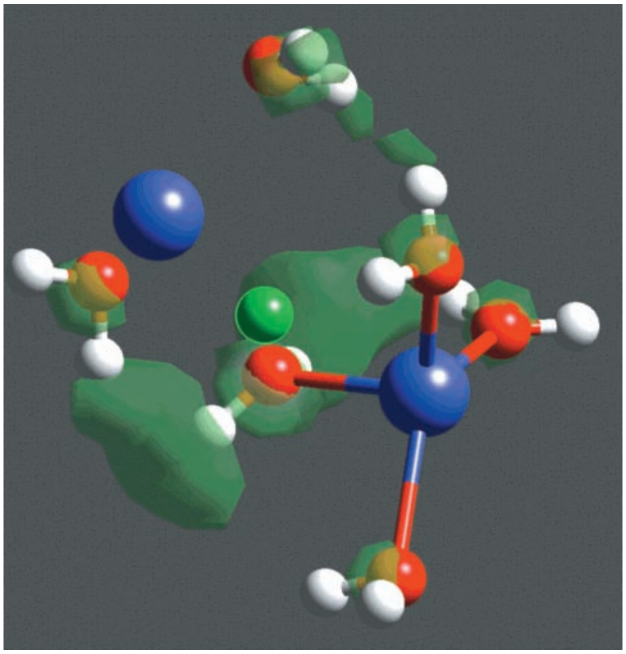

Figure 6. Configuration of the solvated sodium dimer during the constrained CPMD for a sodium−sodium distance of 4.027 Å (atom color coding the same as in Figure 1). This still frame corresponds to a point on the energy landscape denoted by the arrow in Figure 5. The green mesh represents a Wannier density at an iso-surface value of 0.1647 electrons/Bohr^3 pertaining to the two spin-paired 3s electrons. It is possible to see a difference in the coordination number (two and four) for each of the two sodium atoms, which we believe facilitates charge separation. The Wannier centroid (green sphere) is located 0.42 Å closer to the doubly coordinated sodium also indicating a fluctuation toward charge separation.

configuration is achievable within a CPMD run time scale when more drastic conditions are employed for the initial state, namely the sodium dimer placed at the surface of the equilibrated water cluster. This confirms that kinetic factors prevent the transition from a sodium dimer to the energetically more favored dipolar state as indicated by our pulling process.

To see if our previous results hold under the condition of additional solvent (water molecules), we investigated the behavior of the sodium dimer in the environment of eight water molecules, reflecting the well-known stability of $Na(H_2O)_4$ complexes and the $(H_2O)_8$ cluster.[3] We checked for the occurrence of a dipolar state starting from a symmetrical $Na(H_2O)_4-Na(H_2O)_4$ staggered configuration. The CPMD run at a temperature of about 100 K has shown a collective movement of the solvating waters around the sodium dimer in an umbrella-like fashion, as in the case of the solvated dimer as depicted in Figure 1. In this structure, both sodium atoms are tetrahedrally coordinated and the two bonding electrons of the sodium dimer are stabilized in a proton cage from the coordinating waters (see Figure 7). By examining Figure 7 it is possible to see, by means of the Wannier function localization scheme, that the bonding character of the 3s electrons are more localized between the two sodium atoms which is reflected in the shorter Na−Na distance. However, in agreement with our earlier results, we find that it is not possible to achieve spontaneous formation of a dipolar anion in with the addition of two more water molecules.

As in the case with six waters we must artificially create the dipolar geometry by inserting a neutral sodium atom next to an equilibrated neutral cluster ($Na(H_2O)_8$). Under the same conditions as the solvated dimer with eight surrounding waters, we performed a wave function minimization followed by CPMD dynamics, again confirming the dipolar sodium anion is stable under thermal fluctuations as shown in Figure 8. Similar to the $Na_2(H_2O)_6$ case, the stability of the dipolar anion is due to the formation of a $Na^+(H_2O)_4$ complex, with the remaining four water molecules in the second shell of solvation. Moreover, water molecules in the second shell are oriented in order to solvate the electrons localized near the dipolar sodium anion by means of the proton cage.

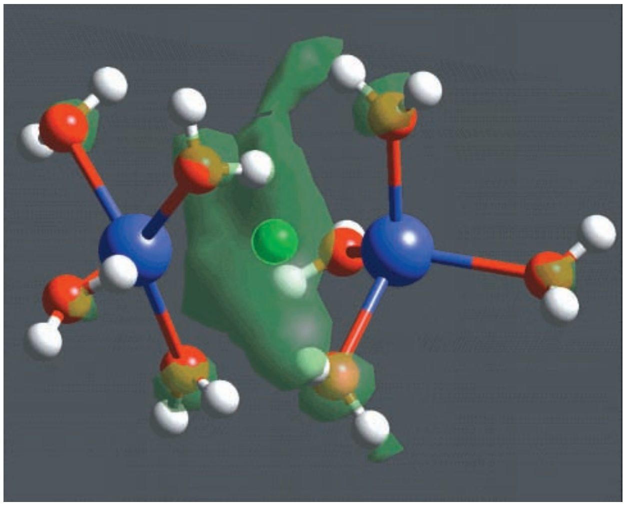

Figure 7. Equilibrium configuration for the symmetric $Na_2(H_2O)_8$-system under molecular dynamics at temperature $T \approx 100$ K (atom color coding the same as in Figure 1). The green mesh represents an Wannier density at an iso-surface value of 0.1647 electrons/Bohr^3 for the two spin-paired 3s electrons. Along with the Wannier centriod (green sphere), it clearly indicates the positioning of the two sodium−sodium bonding electrons nearly at the center of the bond axis and the tetrahedral coordination of both the sodium atoms.

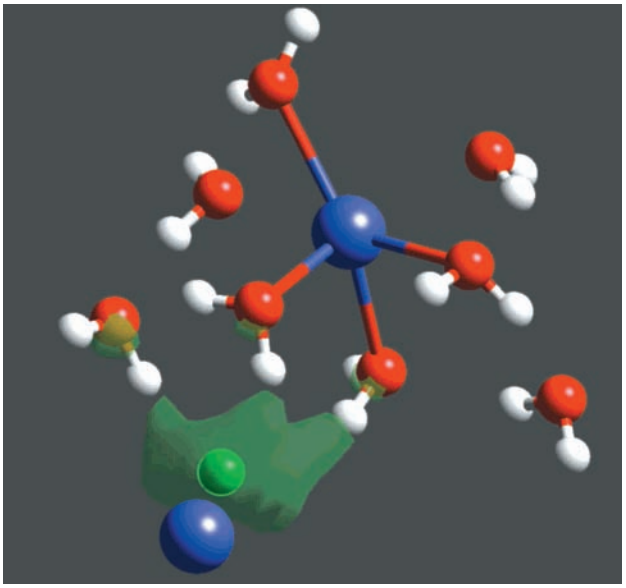

Figure 8. Equilibrium configuration for the asymmetric $Na_2(H_2O)_8$-system under molecular dynamics at temperature $T \approx 100$ K (color coding the same as in Figure 1). The green mesh represents the Wannier density at an iso-surface value of 0.3955 electron/bohr^3. The Wannier density and Wannier centroid (green sphere) indicate a negative charge localization off the center of one sodium atom, again giving a dipolar character.

In analogy to the $Na_2(H_2O)_6$ study, we compare the relative stability of the solvated dimer and dipolar sodium anion with eight solvating water molecules. The results are consistent with our previous findings that the dipolar geometry is more stable.

Thus, the additional water molecules do not affect this qualitative finding. The quantitative agreement is indicated in Table 1. Finally, we investigated the interaction of a sodium dimer and an equilibrated $(H_2O)_8$ water cluster. Our findings are identical with the $(H_2O)_6$ case pointing again to entropic factors dominating the kinetics of the formation of the dipolar species.

Conclusions

In conclusion, we investigated the question concerning the propensity of a solvated sodium dimer to spontaneously form the reactive dipolar intermediate in molecular beam chemistry of sodium and water. Our findings indicate that indeed the charge separated dimer configuration is the most stable leading to products of sodium hydroxide and molecular hydrogen. Moreover, our findings indicate that a single dimer is sufficient to form the reactive intermediate spontaneously under special circumstances. The formation of the dipolar sodium anion depends on the specific configuration of the sodium dimer and water cluster arrangement. However, these special circumstances are unlikely to occur in the molecular beam. To form the dipolar sodium anion intermediate from a stable solvated dimer requires a rearrangement of waters that corresponds to a loss of entropy. Thus, the formation of a dipolar intermediate from the sodium dimer is kinetically unlikely. We find that the only energy barrier to the formation of the reactive dipolar intermediate is entropic, with a reaction coordinate dictated by the water coordination number of the resulting Na^+. This barrier may prevent formation of the dipolar sodium anion within the time scale of the experiment. In the case of three sodium atoms, as investigated in our previous study, the presence of an additional delocalized 3s electron leads to an asymmetric charge distribution yielding the spontaneous formation of the dipolar sodium anion.[2] Thus, the high symmetry in the charge distribution that takes place in the case of a solvated dimer corresponds to a lower propensity for spontaneous formation of the reactive dipolar intermediate.

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References and Notes

(1) Buck, U.; Steinbach, C. *J. Phys. Chem. A* **1998**, *102*, 7333.

(2) Mundy, C. J.; Hutter, J.; Parrinello, M. *J. Am. Chem. Soc.* **2000**, *122*, 4837.

(3) Liu, K.; Cruzan, J. D.; Saykally, R. J. *Science* **1996**, *271*, 929.

(4) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.

(5) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(6) Lee, C.; Yang, W.; Parr, R. C. *Phys. Rev. B* **1988**, *37*, 785.

(7) Sprik, M,; Hutter, J.; Parrinello, M. *J. Chem. Phys.* **1996**, *105*, 1142.

(8) Hartwigsen, C.; Goedecker, S.; Hutter, J. *Phys. Rev. B* **1998**, *58*, 3641.

(9) Martyna, G.; Tuckerman, M. *J. Chem. Phys.* **1999**, *110*, 2810.

(10) Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296.

(11) Silvestrelli, P. L.; Marzari, M.; Vanderbilt, D.; Parrinello, M. *Solid State Commun.* **1998**, *7*, 107.

(12) Berghold, G.; Mundy, C. J.; Romero, A.; Hutter, J.; Parrinello, M. *Phys. Rev. B.* **2000**, *61*, 10040.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr., Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian98, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998. We used basis set 6-31G supplemented by diffuse functions, three sets of d functions and one set of f functions on heavy atoms, and supplemented by two sets of p functions on hydrogens. The exchange−correlation functional used was BLYP.

(14) Barnett, R. N.; Landman, U. *Phys. Rev. Lett.* **1993**, *70*, 1775.

(15) We also requenched the wave function to ascertain whether the electronic ground state was changed during the pulling process. As expected, the 3s electrons remained spin paired with the Wannier centroid in the centre between the sodium atoms.