

# Reactivity of a sodium atom in vibrationally excited water clusters: An ab initio molecular dynamics study

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## Abstract

We investigated the reaction between a sodium atom and water molecules in both small and medium-size vibrationally excited water clusters using ab initio molecular dynamics simulations. Formation of NaOH was observed in small ( $n = 4, 5$ ) clusters, while water dissociation and subsequent geminate recombination accompanied by a transient formation of a  $\text{Na}^+ - \text{OH}^-$  pair occurred in a 34 water cluster. Our results show that the initial step of the vibrationally excited reaction between a single sodium atom and water does not shut off in larger clusters and that it can also occur in the bulk water, however, more sodium atoms are likely required to stabilize the product.

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## 1 Introduction

The reaction of sodium in water is a textbook example of a vigorous oxidation process. Nevertheless, the microscopic mechanism of this reaction is still an open issue to which cluster studies are shedding new light [1–5]. Based on both experimental and theoretical investigations of clusters, a complex mechanism involving at least three sodium atoms was proposed, consequently water clusters containing a single Na atom were shown to be unreactive [6,7]. Recently, based on density functional theory (DFT) calculations, a new mechanism requiring only one sodium atom and characterized by a relatively low (below 20 kcal/mol) activation barrier was suggested [8–10]. The reaction, however, becomes feasible at ambient conditions only upon effectively vibrationally exciting a water O-H bond. It was also predicted that  $\text{Na}(\text{H}_2\text{O})_n$  clusters should preserve their reactivity beyond the largest studied clusters of  $n = 17$ , whereas in isoelectronic  $\text{Mg}^+$ -doped clusters the hydrogen loss reaction shuts off for  $n > 17$  [10,11]. However, such large sodium doped clusters have not been yet investigated computationally regarding their reactive properties.

In this work we focus on the dynamics of the reaction between a sodium atom and water molecules in  $\text{Na}(\text{H}_2\text{O})_n$  clusters of increasing size using “on-the-flight” ab initio molecular dynamics (MD) simulations. In previous DFT studies the reaction  $\text{Na} + (\text{H}_2\text{O})_n \rightarrow \text{Na}^+ + \text{OH}^- + \text{H} + (\text{H}_2\text{O})_{n-1}$  was characterized along the minimum potential energy path, i.e., effectively at  $T=0$  K [10]. Here, we study this reaction at finite temperature conditions and facilitate it via a sizable vibrational excitation of a water OH bond. Our previous ab initio MD calculations showed that both in small and large (up to  $n = 34$ ) vibrationally ‘cold’ clusters containing only a single sodium atom the

reaction does not occur at the picosecond timescale thermally at 350 K [12]. Nevertheless, DFT results suggest that the reaction path is connected with an elongation of the O-H bond in a water molecule located in the vicinity of sodium atom in the cluster [10]. In this study, we vibrationally excite such an O-H bond and computationally investigate the feasibility of the subsequent chemical reaction.

## 2 Computational details

We studied the reactivity of a sodium atom in water clusters using ab initio MD where atoms followed classical equations of motion, while forces were calculated at each step using a quantum mechanical electronic structure method. We employed the cp2k/Quickstep software package which describes the electronic structure using the density functional theory (DFT) with a mixed gaussian and plain waves basis [14,15]. We used the BLYP functional combined with the DZVP basis set and the GTH-type pseudopotential [16–18]. The plain-waves energy cutoff was set to 400 Ry. This choice of parameters was based on our previous study of collisions of a sodium atom with a water cluster [12]. We employed the unrestricted Kohn-Sham scheme for the open-shell neutral sodium-water clusters.  $\text{Na}(\text{H}_2\text{O})_n$  clusters with  $n = 4, 5$ , and 34 were studied. We used simulation boxes of sizes of  $16 \times 16 \times 16 \text{ \AA}$  for  $n = 4, 5$  and  $20 \times 20 \times 20 \text{ \AA}$  in the case of  $n = 34$ , employing the cluster boundary conditions. Each simulation was started from a cluster pre-equilibrated in a canonical ( $NVT$ ) ensemble at  $T=300 \text{ K}$ . Then, in order to model vibrational excitation, we elongated one O-H bond of a selected water molecule close to sodium to a chosen initial length ( $r_{init}$ ) and then continued the simulation within the mi-

crocanonical ( $NVE$ ) ensemble observing the subsequent non-equilibrium time evolution of the system. Additionally, for selected clusters we performed geometry optimization runs using the DFT method with the BLYP functional and the aug-cc-pVDZ basis set employing Gaussian software package [19].

### 3 Results and Discussion

#### 3.1 Small water clusters

In order to identify the conditions required for reaction and to elucidate the possible vibrationally excited reaction mechanisms we started with studies of relatively small ( $n = 4, 5$ ) neutral water clusters doped with a sodium atom. For both values of  $n$  we performed an extended search of initial configurations (varying the initial value of the O–H bond elongation  $r_{init}$  and the location of an excited water molecule) that would lead to water dissociation and creation of NaOH. We systematically tested different O–H bond elongation values starting from  $r_{init} = 1.0 \text{ \AA}$  with a  $0.1 \text{ \AA}$  step (an equilibrium O–H distance in water molecule in the gas phase calculated with the BLYP/aug-cc-pvDZ method is equal to  $0.98 \text{ \AA}$ , the experimental value being equal to  $0.96 \text{ \AA}$  [13]). We observed the reaction occurring typically for  $r_{init} = 1.7 \text{ \AA}$ , the shortest 'reactive' O–H bond elongation was found to be  $1.6 \text{ \AA}$  for  $n = 5$ . The reaction was not observed at the picosecond timescale for  $r_{init} \leq 1.5 \text{ \AA}$ .

As an example, Fig. 1 (solid line) presents the time evolution of the O–H distance of the initially elongated bond for one of the  $n = 5$  clusters for the case when the reaction was observed. The  $t = 0$  point corresponds to the moment when the bond was elongated ( $r_{init} = 1.7 \text{ \AA}$ ). Additionally, in order to test if

the presence of sodium was the factor inducing reactivity we followed a trajectory for an analogical cluster with the sodium atom removed from the system, and with the trajectory started with identical positions and velocities of atoms of water molecules (dashed line in Fig. 1). In the presence of the sodium atom the hydrogen from the elongated bond was ejected from the cluster after 2 periods of oscillation (at  $t \approx 40 fs$ ) and the NaOH product was formed. In contrast, in the system without sodium the energy from the elongated bond was dissipated within the cluster and water dissociation was not observed (the amplitude of O-H bond oscillations decreases with time). Similar time evolution patterns and the same behavior in the absence of sodium atom were observed for other reactive  $n = 4, 5$  clusters investigated during this study. Therefore, we can conclude that the presence of sodium was the necessary condition for water dissociation in our simulations.

We studied also another reaction scenario starting from the sodium-doped  $n = 5$  cluster with  $r_{init} = 1.7 \text{ \AA}$  and a fully relaxed geometry of the remaining water molecules to model an adiabatic vibrational excitation of the cluster. These initial conditions corresponded to the transition state studied by Chan *et al.* [10]. In this case, as for the reactive cases described above, we also observed dissociation of a water molecule. However, a hydrogen atom was not ejected from the cluster, and the dissociated water molecule recombined in the final stage of the trajectory.

### 3.2 Medium-size water clusters

The  $n = 34$  system was studied as an example of a medium-size water cluster. We collected 4 trajectories, each with a single sodium atom inside the cluster.

As in the case of smaller clusters, one O-H bond of a water molecule in the vicinity of sodium atom was initially elongated to 1.7 Å, corresponding to a vertical vibrational excitation. In each trajectory a different water molecule was chosen to be vibrationally excited. Fig. 2 presents time evolution of the excited O-H bond length along each of the four trajectories. In three cases (“B”, “C”, “D”) the reaction was not observed, rather the O-H bond length oscillated between about 0.8 and 1.6 Å with the period of about 30 fs. In the trajectory “A” we observed more significant variations of the bond length. Namely, shortly after the beginning of the simulation the excited O-H bond was strongly elongated reaching more than 2 Å at  $t = 30$  fs. To test if the presence of the sodium atom influences these results we calculated analogical trajectories with sodium atom removed from the cluster. The absence of sodium did not change the behavior of ‘non-reactive’ trajectories “B”, “C” and “D”. In contrast, evolution of O-H distances for the trajectory corresponding to the trajectory “A” changed qualitatively (see Fig. 3): without sodium atom the extreme elongation of O-H bond was not longer observed and thus this trajectory resembled the three remaining ones. Therefore, we can conclude that the presence of the sodium atom was directly connected with the extreme elongation of O-H bond observed in trajectory “A”.

We analyzed the electronic structure of the system along the trajectory “A” for clusters both with and without the sodium atom. We focused on two characteristic points in both trajectories, defined by the shortest and the longest values of the O-H bond length. In the case of the sodium doped cluster these characteristic points occurred at  $t = 10$  fs and  $t = 30$  fs (see Fig. 2A), while for the system without sodium they were located at  $t = 7$  fs and  $t = 30$  fs (see Fig. 3). Fig. 4 presents two snapshots of the system without sodium atom in

both characteristics points of the trajectory. The spin polarization (i.e., the difference between alpha and beta spin densities) is depicted on the plots and the water molecule that was initially vibrationally excited is highlighted. At  $t = 7$  fs the O-H distance was equal to  $0.81 \text{ \AA}$  and no spin polarization can be seen, i.e., all electrons in the system were paired. At  $t = 30$  fs, as the O-H distance reached  $1.8 \text{ \AA}$ , a qualitatively different situation occurred. The hydrogen atom was close to dissociation and there was a non-negligible unpaired spin density located near both the hydrogen and the oxygen atom of the remaining OH fragment with an opposite sign between both spin density differences. Thus, near  $t = 30$  fs for about 10 fs we observe a near-dissociation of a water molecule. The difference in the sign of spin polarization reveals that the dissociation products have a partially radical character.

Two corresponding snapshots displaying the difference between alpha and beta spin densities for the open-shell cluster doped with sodium atom are depicted in Fig. 5 (here, only positive values occur). At the step with the shortest O-H distance ( $t = 10$  fs,  $r_{OH} = 0.78 \text{ \AA}$ ) the spin density reveals the presence of the solvated electron shared both by sodium and the excited water molecule in the cavity formed by surrounding water molecules, i.e., a pair of a sodium cation and a solvated electron is formed. This picture is consistent with the results from our previous study concerning a sodium atom in vibrationally unexcited water clusters [12]. As the O-H distance in the excited water molecule increased the distribution of electrons changed dramatically. The hydrogen atom from the elongated bond penetrated the cavity where the solvated electron previously resided and the spin density then became localized on this dissociating hydrogen atom. Moreover, some part of the spin density was localized in the vicinity of the oxygen atom of the OH fragment. This observations revealed



that in the presence of sodium the dissociation reaction occurred according to the overall scheme:



In other words, within this trajectory we observed the reaction of a neutral sodium atom with a vibrationally excited water molecule and the formation of dissociated sodium hydroxide. The reaction mechanism involves the following steps:

- creation of solvated electron in the cavity formed by water molecules next to sodium; this electron originates from the 3s electron of the sodium atom,
- interaction between the hydrogen atom of vibrationally excited water molecule with the solvated electron which causes the breaking of the O-H bond in the excited water molecule,
- creation of hydrogen radical located in the cavity previously occupied by solvated electron.

This mechanism can be summarized by the following set of elementary processes:



The mechanism is similar to the one proposed by Chan and co-workers [10]. It should be stressed that in the end for  $n = 34$  we observed neither hydrogen loss nor the NaOH formation. The time scale of the reactive process was in a range of tenths of femtoseconds and the products lived for about 100 fs, afterwards they recombined forming back a water molecule, a sodium cation, and

a solvated electron. Chan’s studies suggest that the activation barrier for this reverse reaction is very low, about 2 kcal/mol, therefore, the products quickly recombined. The recombination was also possible because the hydrogen atom was not ejected from the cluster and resided near the reaction site. We, therefore, observe a classical example of a cage effect leading to geminate recombination. It is likely that in order to stabilize  $\text{Na}^+$  and  $\text{OH}^-$  more sodium atoms are required in order to provide additional hydrogen atoms that can form  $\text{H}_2$  molecules and thus shut off the reverse process. The necessity of having more than a single sodium atom for reaction has been proposed previously for vibrationally unexcited clusters [6] and is also observed macroscopically when gaseous hydrogen is formed as a product.

### 3.3 Activation energy

For the reactive trajectory in the  $n = 5$  cluster presented in Fig. 1 we calculated a vertical vibrational excitation energy of  $\Delta E_{vert} = 83$  kcal/mol as an energy difference between the vibrationally excited system (the configuration at  $t = 0$  with  $r_{init} = 1.7 \text{ \AA}$ ) and a fully optimized one. This energy can be viewed as an activation energy of the studied reaction in the vertical excitation scenario. We also performed a partial geometry optimization with the length of the excited O-H bond kept unchanged, optimizing only the geometry of the remaining atoms. The energy change during this optimization which corresponds to the relaxation of water molecules around the vibrationally excited one was equal to  $\Delta E_{relax} = 67$  kcal/mol. The difference  $\Delta E_{vert} - \Delta E_{relax} = 16$  kcal/mol is the energy of excitation from the fully optimized system to the one with both an elongated O-H bond and with relaxed geometry of the system, which

corresponds to the transition state of the process studied by Chan and co-workers in [10]. Therefore, the energy difference  $\Delta E_{vert} - \Delta E_{relax} = E_{act}^{adiabatic}$  can be viewed as the activation barrier of the reaction in the adiabatic reaction scenario. Note that it correlates well with the value of 16 kcal/mol of the minimal energy barrier for water dissociation in sodium-doped  $n = 5$  clusters [10].

In the case of  $n = 34$  system we calculated the energy difference between the vertically excited doped cluster and a similar system with the O-H distance in the previously excited water molecule shortened to 0.98 Å. This quantity  $\Delta E'_{vert} = 47$  kcal/mol is a measure of the vertical excitation energy, however, it is not exactly equal to  $\Delta E_{vert}$  defined above because here the non-excited reference state was unrelaxed.  $E'_{vert}$  is significantly lower than the corresponding  $\Delta E_{vert} = 83$  kcal/mol for  $n = 5$ . This suggests that also the adiabatic activation energy  $E_{act}^{adiabatic}$  for the  $n = 34$  cluster shall be lower than the corresponding value of 16 kcal/mol calculated for the smaller clusters. This is also supported by the study of Chan *et al.*, where activation barrier drops to 8 kcal/mol for  $n = 9$  [10]. These results indicate that upon moving from small ( $n = 4, 5$ ) to medium size ( $n = 34$ ) clusters the activation energy of the reaction between sodium and water possibly goes down below 16 kcal/mol, and that in bulk water the barrier for the reaction involving a single sodium atom mechanism can also be below this value. Note that experimentally it is difficult to vertically excite vibrational modes of water above some 60 kcal/mol, however, adiabatic excitations above 16 kcal/mol are accessible [20].

## 4 Conclusions

Using ab initio molecular dynamics we confirmed the possibility of both water dissociation and NaOH formation in small vibrationally excited water clusters ( $n = 4, 5$ ) doped with a single sodium atom. We demonstrated that a vertical vibrational excitation of about 80 kcal/mol is needed in order to initiate the reactive process but if water molecules are allowed to relax a low-barrier reaction path is possible with an activation energy of about 16 kcal/mol. We also observed water dissociation and a transient formation of a  $\text{Na}^+\text{--OH}^-$  pair in a 34 water vibrationally excited cluster. This shows that the initial step of the vibrationally excited reaction between a single sodium atom and water does not shut off in larger clusters and that it can also occur in the bulk water. However, in our simulations the reverse process of geminate recombination occurs in the larger cluster due to the cage effect. This suggests that although the investigated microscopic mechanism can involve in the very first step only a single sodium atom, more sodium atoms are likely required to stabilize the product.

## 5 Acknowledgment

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## References

- [1] U. Buck, C. Steinbach, *J. Phys. Chem. A* 102 (1998) 7333.
- [2] L. Bewig, U. Buck, S. Rakowsky, M. Reymann, C. Steinbach, *J. Phys. Chem A* 102 (1998) 1124.
- [3] C. Bobbert, C.P. Schulz, *Eur. Phys. J. D* 16 (2001) 95.
- [4] C. Steinbach, U. Buck, *PCCP* 7 (2005) 986.
- [5] U. Buck, I. Dauster, B. Gao, Z.-F. Liu, *J. Phys. Chem. A* 111 (2007) 12355.
- [6] C. Mundy, J. Hutter, M. Parrinello, *JACS* 122 (2000) 4837.
- [7] F. Mercuri, C. Mundy, M. Parrinello, *J. Phys. Chem. A* 105 (2001) 8423.
- [8] Y. Ferro, A. Allouche, *J. Chem. Phys.* 118 (2003) 10461.
- [9] Y. Ferro, A. Allouche, V. Kempter, *J. Chem. Phys.* 120 (2004) 8683.
- [10] K.W. Chan, S.Y. Wong, Z.-F. Liu, *J. Chem. Phys.* 123 (2005) 124313.
- [11] C.-K. Siu, Z.-F. Liu, *PCCP* 7 (2005) 1005.
- [12] L. Cwiklik, U. Buck, W. Kulig, P. Kubisiak, P. Jungwirth, *J. Chem. Phys.* 128 (2008) 154306.
- [13] A.R. Hoy, P.R. Bunker, *J. Mol. Struct.* 77 (1979) 1.
- [14] CP2K version 2.0.0, the CP2K Development group, <http://cp2k.berlios.de/>
- [15] J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, J. Hutter, *Comp. Phys. Comm.* 167 (2005) 103.
- [16] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [17] C.T. Lee, W.T. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.

- [18] S. Goedecker, M. Teter, J. Hutter, Phys. Rev. B 54 (1996) 1703.
- [19] M. J. Frisch et al., Gaussian 03, Revision C.02, Gaussian Inc., Wallington CT, 2004
- [20] P. Theule, A. Callegari, T.R. Rizzo, J. Chem. Phys. 122 (2005) 124312.

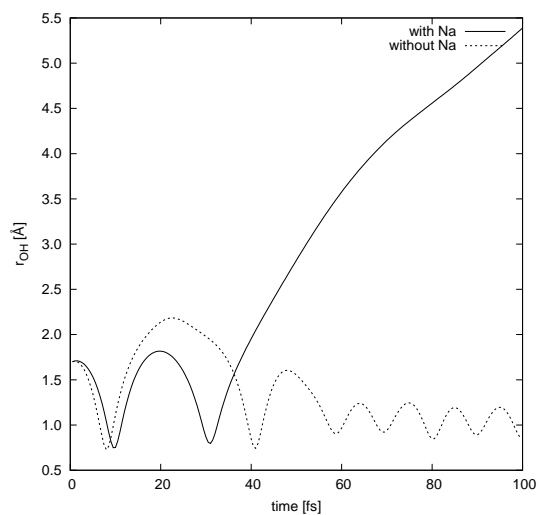


Fig. 1. Time evolution of O-H distance in the bond that was initially elongated for two small ( $n = 5$ ) water clusters: doped with sodium and a neat water one.

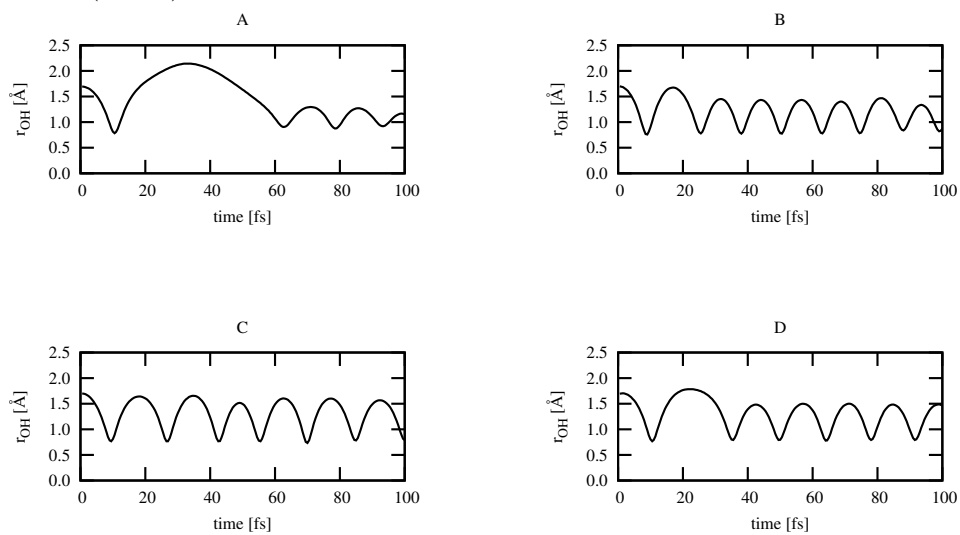


Fig. 2. Time evolution of O-H distance in the elongated bond in medium-size ( $n = 34$ ) water clusters doped with sodium atom.

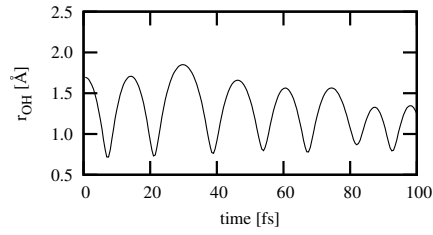


Fig. 3. Time evolution of O-H distance in the elongated bond in the system corresponding to trajectory “A” in Fig. 2 without sodium atom. cluster.

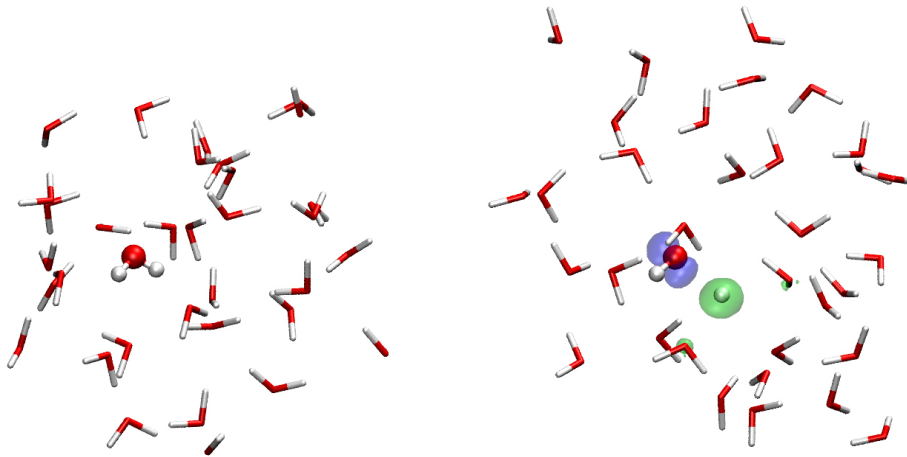


Fig. 4. Spin polarization for the shortest ( $t = 7$  fs, left-hand-side plot) and the longest ( $t = 30$  fs, right-hand-side plot) O-H distance in the tagged water molecule for  $n = 34$  water cluster without sodium. Positive (green) and negative (blue) differences between 0.0025 isovalues of alpha and beta spin densities are presented.



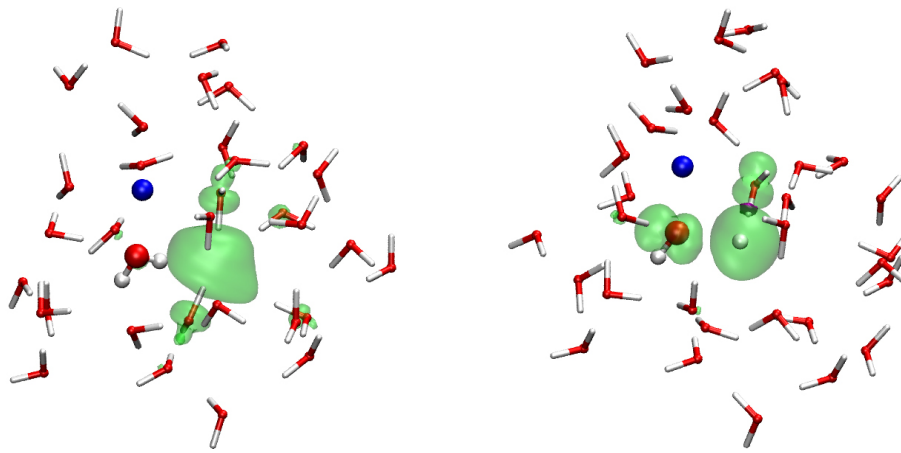


Fig. 5. Spin density (0.0025 isovalue) for the shortest ( $t = 10$  fs, left-hand-side plot) and the longest ( $t = 30$  fs, right-hand-side plot) O-H distance in the tagged water molecule for  $n = 34$  water cluster doped with sodium atom (blue ball).