A Sodium Atom in a Large Water Cluster: Electron Delocalization and Infrared Spectra

Lukasz Cwiklik,1,2 Udo Buck,3 Waldemar Kulig,4 Piotr Kubisiak,4 and Pavel Jungwirth1*

1Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic and Center for Biomolecules and Complex Molecular Systems, Flemingovo nám. 2, 16610 Prague 6, Czech Republic

2Fritz Haber Institute for Molecular Dynamics, Hebrew University, Jerusalem, Israel 91904

3Max-Planck Institut für Dynamik und Selbstorganisation, Bunsenstr. 10, D-37073 Göttingen, Germany

4K. Guminski Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30060 Krakow, Poland

*Corresponding author: pavel.jungwirth@uochb.cas.cz

Abstract

Ab initio molecular dynamics simulations modeling low energy collisions of a sodium atom with a cluster with more than thirty water molecules are presented. We follow the dynamics of the atom-cluster interaction and the delocalization of the valence electron of sodium together with changes in the electron binding energy. This electron tends to be shared by the nascent sodium cation and the water cluster. IR spectra of the sodium-water cluster are obtained both computationally and experimentally, with good agreement between the two approaches.
The formation of the solvated electron is an important and extensively studied process in solution chemistry. When alkali metals are dissolved in liquid ammonia or water the electron detaches and is embedded in the solvent with characteristic features ranging from optical and NMR spectra to intra-molecular vibrational modes.\textsuperscript{1,2} The interaction of the excess electron with the solvent molecules has been treated theoretically by methods ranging from the dielectric continuum model\textsuperscript{3} to a full evaluation of the dynamics using quantum path integral and local density functional approach.\textsuperscript{4-8} Despite of all these efforts a detailed understanding of its properties is still an open problem.

A step towards a better understanding has been the investigation of clusters. In this context, experiments with anionic water\textsuperscript{9} and ammonia\textsuperscript{10} clusters should be mentioned first. They were also accompanied by numerous calculations\textsuperscript{11-13} to rationalize the measured data. Recently, the advent of a new series of experiments on anionic water clusters\textsuperscript{14-17} has solicited also new theoretical investigations,\textsuperscript{18} mainly on the question of the position of the electron which can either go inside the cluster beyond a certain size or stay at the surface of the clusters.

Experiments on sodium doped neutral clusters which come close to the original idea of the solvated electron are mainly focused on the measurement of ionization potentials (IP). Results are available for water, ammonia, and very recently also for methanol.\textsuperscript{19-23} They reveal a reduction of the ionization potential for the first four or six solvent molecules. The IPs of the water and methanol clusters then stay roughly constant for larger cluster sizes, while for ammonia the IP drops, interrupted by flat parts, until it comes close to the bulk value. Recently, first experiments on the infrared spectra in the OH-stretch region of size selected Na(H₂O)$_n$ clusters in the size range from $n=8$ to $60$ were published.\textsuperscript{24} Size selection was achieved by coupling the UV radiation of a dye-laser below the threshold for ionization with the tunable IR radiation from an optical parametric oscillator. A different approach, namely depletion spectroscopy, has been applied in the measurement of the IR spectroscopy
of Li\((NH_3)_n\) for \(n=4-7\).\textsuperscript{25} A number of theoretical studies addressed sodium-water clusters.\textsuperscript{26-32} The largest size treated was \(n=8\). Recently, extended calculations became available on the ionization induced relaxation in \(Na(H_2O)_n\) and \(Na(NH_3)_n\) clusters\textsuperscript{33} in which the size range was extended to \(n=10, 16,\) and \(20\) for the water system and to \(n=11\) for the ammonia system. Here, we present ab initio molecular dynamics (MD) simulations of low-energy collisions of a sodium atom with a larger water cluster containing 34 water molecules. The applied methodology allows us to follow the dynamics of electron delocalization and binding upon landing of sodium on the cluster. In addition, we show the IR spectrum of the OH stretch motion of the \(Na(H_2O)_{34}\) cluster calculated using the dipole-dipole correlation function and compare it to molecular beam measurements of sodium-water clusters in this size range.

**Methodology**

**Computational**

We performed ab initio Born-Oppenheimer molecular dynamics simulations using CP2K/Quickstep software package.\textsuperscript{34} Electronic part of calculations in Quickstep is handled with the density functional theory (DFT) method employing a mixed Gaussian and plane waves (GPW) approach. We used the BLYP functional combined with double-zeta (DZVP) basis set and Goedecker-Teter-Hutter pseudo potentials.\textsuperscript{35} The energy cutoff for plane waves was equal to 400 Ry. This relatively high value was needed in order to properly describe the sodium atom/ion. The system under investigation was an open-shell one, which we described using the unrestricted Kohn-Sham scheme. In order to check the possible self-interaction error we also calculated additional trajectories with self-interaction correction (SIC) within a restricted open shell Kohn-Sham scheme.\textsuperscript{36} Cubic, non-periodic simulation boxes 20x20x20 Å or 25x25x25 Å were used and the Martyna-Tuckerman Poisson's equation solver was employed.\textsuperscript{37} Simulations were performed in either NVE or NVT ensemble and with the time step of 0.5 fs for integration of equations of motion.
The distribution of the excess electron density was calculated for selected snapshots along the molecular dynamics trajectory. We calculated both differential density (i.e., the difference between total electron density of the neutral system and the total electron density calculated for the cationic system at the same geometry as a neutral one) and spin density (i.e., the difference between the alpha and beta spin densities). Note that these all-electron properties are, unlike the one-electron frontier orbitals, unambiguously defined measurable quantities. We also monitored values of vertical ionization potentials (VIP) which were calculated as a difference between the energy of the neutral system and the energy of the corresponding cation at the neutral geometry.

In order to check the convergence of results with respect to augmentation of the basis set we performed additional test calculations for selected structures with DFT/BLYP method and both cc-pVDZ and aug-cc-pVDZ basis set in Gaussian03.\textsuperscript{38} Calculated excess electron densities and VIP values were matching very well CP2K/Quickstep results for the DZVP basis. We also tested the convergence of results with respect to the method employed by performing second order perturbation theory calculations in Turbomole package (in RIMP2 scheme) with 6-31* type basis set (SVP).\textsuperscript{39} These RIMP2 results for VIPs were also in very good agreement with the CP2K/Quickstep calculations. This justifies the use of the DFT method with the BLYP functional and double-zeta type basis set.

The vibrational spectrum of the system was calculated according to the scheme presented by Buch et al. based on a Fourier transform of the dipole-dipole autocorrelation function.\textsuperscript{40} We selected three typical snapshots from trajectory B and took them as starting configurations for further calculations. For each of them a trajectory of the length between 300 and 400 fs was calculated within the NVE ensemble and dipole-dipole autocorrelation function was collected. In this way, three spectra were calculated and averaged in order to obtain the final spectrum.
**Experimental**

The experiments were carried out in a molecular beam machine which has been described in detail elsewhere. Here we will present only a short account of the main parts. The machine consists of a source chamber, a buffer chamber and a detector unit. In a first step the water clusters are produced by expanding water vapor of 0.53 bar seeded in helium at 4 bar through a nozzle of conical shape with a diameter of 63 µm, an opening angle of 41°, and a lengths of 2 mm. These clusters are doped by a single sodium atom by passing the beam through a pick-up cell which is placed in the buffer chamber and kept at a pressure of 0.023 mbar. The clusters are detected by a reflectron time-of-flight mass spectrometer. The ionization is carried out by the photons of a dye laser pumped by an excimer laser with a pulse width of 28 ns. Under optimal conditions, a mass resolution of $m/\Delta m = 1600$ was obtained at $m = 200$ u, based on the drift length of 1820 mm. The ions are extracted in the direction of the beam and detected on a microsphere plate. The mass spectra are sampled using a digital storage oscilloscope in a special particle counting mode. The spectra are corrected for the size dependence of the detection probability, the ionization cross section, and the transformation from time to mass coordinates. By UV detection only a distribution of Na(H$_2$O)$_n$ clusters was measured with an average size of $\langle n \rangle = 30$. The cluster temperature is estimated to be around 70 K based on the result which has been obtained for pure water clusters under similar expansion conditions.

To achieve complete size selection, the UV radiation is first lowered below the ionization threshold and then the IR photons are added to produce in a double resonance experiment an enhancement of the ion signal. The method works because of the strong coupling of the vibrational motion with the solvated electron which, in turn promotes the ionization process. The optimal signal enhancement for the product ions is obtained when the UV laser operates at 400 nm. The infrared radiation used to excite the clusters is obtained from a Nd:YAG-laser-pumped optical parametric oscillator (OPO) in the spectral range from 2900 cm$^{-1}$ to 3800 cm$^{-1}$. It consists of a master oscillator
containing a LiNbO$_3$ crystal, which is pumped by the fundamental of a Nd:YAG laser. The master oscillator is seeded by the narrow-bandwidth infrared radiation obtained by difference frequency mixing the output of a pulsed dye laser and the 532 nm radiation of the same Nd:YAG laser in a LiIO$_3$ crystal. The typical output energy for the low frequency component (idler) is ~4 mJ per pulse in the entire spectral range covered in this study. The pulse width is 10 ns. The bandwidth of the infrared radiation, which is determined by the bandwidth of the dye laser, is chosen to be 0.5 cm$^{-1}$. We note that the wave number region between 3480 and 3510 cm$^{-1}$ cannot be reached in the experiment caused by water impurities in the crystal. The time synchronization of the two laser beams is achieved by triggering the IR-laser by a pulse delay generator. The UV pulse of the second laser is time delayed by about 80 ns with respect to the IR-laser. This value is adjusted by optimizing the enhancement signal.

**Results**

*Collision of sodium atom with water cluster*

We calculated three trajectories, in which a sodium atom collided with a 34 water cluster. Before each collision, the water cluster was equilibrated within an initial molecular dynamics run in the NVT ensemble at $T = 350$ K. Then, the sodium atom was added to the system at the distance of about 3.4 Å from the nearest water molecules with an initial velocity in the direction of the cluster. The value of the initial velocity was 0.013 Å/fs for trajectory A and 0.045 Å/fs for trajectories B and B/SIC, which corresponded to about 2 and 7.5 times the thermal velocity. These velocities roughly correlate with those relevant for the experiment. The trajectory B/SIC was performed using the same initial conditions as trajectory B, with SIC correction turned on.

Fig. 1 depicts the distance of sodium atom from the geometric center of the system vs. time for the three simulated collisions. In each case the collision took place after about 50 fs from the beginning of the corresponding simulation. In the trajectory A the velocity of sodium atom was decreased shortly
after the collision (at about 100 fs) whereas in trajectories B and B/SIC the higher speed of the sodium atom resulted in a significant slow down of velocity only after about 200 fs. In the trajectory A the sodium atom was trapped on the surface of water cluster, at the distance of about 3.8 Å from the cluster's center. In the trajectories B and B/SIC, due to the high value of initial velocity, sodium was able to penetrate deeper into the cluster and, in the case of the trajectory B, to get even to the opposite side of the water cluster.

In Figure 2 the spin density for four snapshots taken along trajectory A (i.e., for a sodium atom with the smaller initial velocity) is presented together with calculated VIP values. In the snapshot taken before the collision (0 fs) the excess electron density is located spherically on the sodium atom. In snapshot taken after the collision (395 fs snapshot) the excess density is located asymmetrically, mainly on one side of sodium, forming a cloud outside the cluster, and also a small part of this density is delocalized and placed on hydrogen atoms of few water molecules. In the snapshot taken about 1 ps later (1367 fs), 4 water molecules which are the nearest neighbors of sodium are oriented in such a way that their oxygen atoms are directed toward sodium and a small part of excess electron density resides on their hydrogen atoms. Most of the excess density is located in a cavity next to sodium. Excess density still mostly resides on the surface of the cluster. In the last snapshot (1545 fs) a qualitatively new behavior of excess density can be observed. Most of it is still located in the cavity next to sodium, however, a significant part of excess density is placed into a small, second cavity located after the first solvation shell of sodium. Also, small yet more significant than in the previous snapshots parts of excess density are delocalized onto almost all water molecules in the cluster. A similar distribution of excess density, i.e., the presence of the cavity after the first solvation shell was previously observed in smaller clusters.\textsuperscript{30-32} VIP changes from an initial value of about 5.7 eV to about 4.0 eV in the second snapshot and then rises slightly to 4.6 eV. The experimental value of VIP for sodium atom in the gas phase is 5.14 eV.\textsuperscript{20}
Figure 3 presents the comparison between differential and spin densities for two representative snapshots from Figure 2. The discrepancies between differential and spin density are minor, generally, spin density is slightly more localized than the differential one. We made the same comparison for each trajectory discussed in this work and, since the differences between spin and differential plots were negligible, in the following we are presenting only spin densities.

Figure 4 depicts the spin density and VIP values for snapshots taken along trajectory B (i.e., the trajectory with higher value of the initial velocity of the sodium atom), calculated without the self-interaction correction. Just before the collision (the 5 fs snapshot) the excess density is located mainly around the sodium atom, however, a small fraction of it is also delocalized on the nearest-distant water molecules. After less that 200 fs after the collision (the 233 fs snapshot) sodium is able to penetrate the cluster and the excess density is located in the cavity between sodium and the first solvation shell. In contrast to the 1367 fs snapshot from Fig. 2, this cavity is not on the surface of the cluster but more hidden inside. In the following snapshots (438 and 645 fs) there are two cavities where the excess density resides, the first one placed between sodium and the first solvation shell and the second one just after the first solvation shell. The last snapshot (645 fs) presents the moment when sodium is already moving out of the interior of the cluster. It is clearly seen that the excess density from the second cavity, which is still inside the cluster, is following sodium, whereas the density that was located in the cavity next to sodium is now almost at the cluster's surface. VIP values are decreasing from 5.25 eV (slightly above VIP for sodium in the gas phase) to 3.66 eV (which is above the value of 3.17 eV obtained for clusters larger than n = 4). For the 438 fs snapshot VIP is slightly increased in comparison to the previous and the next snapshot.

**Self-interaction correction**

To eliminate the influence of the self-interaction error we performed calculations starting...
from the same initial state as trajectory B but employing the SIC scheme (trajectory B/SIC). Spin
densities and VIP values for snapshots taken along this trajectory are presented in Figure 5. The
snapshots are taken at the same time frames as those for trajectory B (Figure 4). The introduction of the
self-interaction correction does not cause qualitative changes of spin density. The main difference is a
small increase in VIP of 0.2-0.4 eV, indicating a slightly stronger transfer of the excess electron from
sodium to water (see Table 1). Table 1 also demonstrates that the values of VIP calculated along
trajectory B/SIC decrease from 5.67 eV to 3.79 eV.

Additionally, we calculated the total volume of spin density limited by isosurfaces corresponding to
the given isovalue (the same as the isosurfaces presented on snapshots in Figure 4), and the distance
between the nuclei of sodium atom and the “center of mass” of the spin density (spin density shift), the
latter being defined as \[ \int dr (\rho_A(r) - \rho_B(r))r \]. These results are collected in Table 2. Along with the
decreasing VIP (Table 1) values all other quantities are also changing monotonically. The volume of
spin density decreases from 318 at 5 fs up to 197 Å³ at 450 fs, remaining roughly constant afterwards.
Similarly, the spin density shift increases for the three first snapshots and then slightly decreases. The
snapshots from 5 to 450 fs show the initial delocalization of the excess electron in the cluster, the spin
density becoming divided into several smaller elements. Additionally, the increasing spin density shift
shows that the excess electron is asymmetrically located in the neighborhood of sodium. In the last
snapshot the spin density volume increases whereas the shift decreases which corresponds to the
localization of the excess electron in the two cavities described above, with the first cavity located next
to sodium atom (density shift equal to 1.5 Å).

**Dynamics of electron delocalization**

In order to study the dynamics of delocalization of excess electron density and to eliminate the
dependence on the initial velocity of sodium atom we performed an additional simulation with no
collision (trajectory C). To this end, we first took the 34 water cluster with one sodium cation located in the center and locally minimized the system with CP2K/Quickstep geometry optimization run (200 optimization steps) in order to have a proper orientation of water molecules in the nearest neighborhood of sodium cation. Then, we changed the total charge of the system from +1 to 0 and ran molecular dynamics trajectory (NVT ensemble, T=300K, without self-interaction correction). Fig. 6 presents spin density contours and VIP values for few points along trajectory C. In the initial phase of the trajectory the excess electron density was completely spread among water molecules in the whole cluster. This density was mainly located on oxygen atoms of solvent molecules. The VIP value was relatively low (about 2 eV) which corresponds to the fact that the initial geometry, which stabilizes the cation, is not that favorable for the neutral system. As the trajectory continued, the excess electron density started to be localized in the cavity formed by water molecules and separated from the sodium cation by its first solvation shell (see snapshots from 70 up to 275 fs). VIP values rose up to about 4 eV. After 275 fs the density started to flow from the cavity to the direction of sodium. Finally (see 590 fs snapshot), it became delocalized between sodium and water molecules from the first solvation shell of the sodium cation, although part of it was still residing in that cavity located behind first solvation shell of Na\(^+\). The value of VIP amounted at that point to 3.6 eV. The locations of the excess electron density in the final phase of the present simulation and in the corresponding states of two previous trajectories are very similar to each other. Moreover, the final value of VIP corresponds very well with that reached in the two previous MD runs.

We note that the error of the ionization potential determination is around 0.3 eV for the BLYP method with double zeta type basis set.\(^{45}\) The experimental value for Na(H\(_2\)O)\(_n\) clusters drops for the first four values of \(n\) and then stays constant at 3.17 eV.\(^{21}\) This is somewhat lower than the calculated values of this work. They are, however, in agreement with previous calculations of the largest cluster of this kind for \(n=20\).\(^{33}\) Very recent measurements and calculations for the similar system Na(CH\(_3\)OH)\(_n\)
reveal the same trends and demonstrate that the measured ionization potentials for these type of systems are adiabatic and not vertical.\textsuperscript{23} In a tentative explanation the electron distribution is excited below the vertical ionization threshold. This excitation is followed by a local structural relaxation that is coupled to an autoionization process. The time of the simulation is probably not long enough to account for these processes. It is interesting to note that also in the calculation of trajectory C, in which initially the correct ionic configuration is artificially introduced, the trajectory once changed into a neutral system develops along the same lines as trajectory B which starts directly from the neutral system.

We also monitored for the present run the position of sodium nuclei with respect to the geometric center of the cluster. The result, showing the displacement between sodium nuclei and the center of the cluster along the trajectory, is presented in Fig. 7. In the first phase (from 0 to about 120 fs) the sodium atom shifts from the center of the cluster towards the surface. This corresponds to the first localization of the excess electron density (compare with Fig. 6). Between 120 and about 230 fs, the excess electron density starts to be localized into the cavity which is separated from Na\textsuperscript{+} by solvent molecules which causes a return of sodium into the cluster. After about 230 fs the electron density starts to flow into the cavity located between sodium and its first solvation shell. In the present trajectory, in contrast to simulations where we collided sodium with the cluster, sodium stays inside the cluster. We note in passing that a prohibitively long trajectory would be needed to fully explore the position of sodium within the cluster, nevertheless the last trajectory indicates that once it get partially stripped of its valence electron density it tends to prefer the cluster interior.

Additionally, we analyzed the size of the sodium cavity. To this end we monitored positions of both oxygen and hydrogen atoms with respect to sodium along the trajectory. An average distance between oxygens in the first solvation shell and sodium is changing only slightly, whereas the distance between hydrogens of neighboring waters is increasing. This reflects the fact that water molecules
reorient from the situation where oxygen atoms were pointing toward the sodium atom to the state where hydrogen atoms are pointing in the direction of effectively a sodium cation. This reorientation is also observed in our previous trajectories, as well as in previous computational studies. The time scale of this process, characterized also by delocalization and redistribution of the excess electron density is in a range of hundreds of femtoseconds.

We also calculated a trajectory analogous to C including, however, the self-interaction correction (trajectory C/SIC). We collected a 400 fs trajectory, with spin density isosurfaces and VIP values presented in Fig. 8. The slight qualitative difference from the non-corrected run was that the spin density was more compact and, therefore, the calculated VIP values were somewhat higher. In Table 3 we collected the volume of spin density and the spin density shift for trajectory C/SIC. The spin density volume was increasing significantly, from 65 up to about 204 Å³ which corresponded to the formation of a large cavity where a big, single cloud of spin density resided. Later, the volume decreased slightly due to the formation of the three small cavities. Spin density shift from sodium was stabilized at about 2.4 Å.

Vibrational spectrum

Both the calculated and the experimental spectrum for n=34 in the range of the O-H stretch are presented in Fig. 9. To be on the safe side and to avoid single outliers of the measured points we have averaged the results over two further sizes n=34±2. The resulting spectrum is dominated by the peaks around 3400 and 3550 cm⁻¹. At larger frequencies smaller peaks at 3640 and 3725 cm⁻¹ are observed. At the other end of the spectrum between 3000 and 3300 cm⁻¹ several more or less pronounced peaks appear at 3230, 3130, and 3000 cm⁻¹.

The result of the calculation based on the dipole-dipole correlation function is also shown in
Fig. 9. Given the fact that there is no adjustment or flexible parameter in the calculation, the agreement between measurement and calculation in the intensity distribution is remarkable. The main peaks in the range between 3400 and 3500 cm$^{-1}$ and the two shoulders at 3700 and 3300 cm$^{-1}$ are well reproduced. As a whole, the experimental spectrum appears to exhibit more structure. One of the reasons might be the lower temperature in the experiment. We estimate, based on the measurement of pure water clusters, a temperature of 70 K. Even if the capture of the Na atom will lead to a somewhat higher value, it will be definitely lower than the temperature of 350 K assumed in the simulation. This would explain in a natural way the smooth curve of the calculation.

In principle, it would be possible to decompose the spectrum into solvent-solvent and solvent-solvated electron contributions using a scheme similar to that proposed for water recently.$^{46}$ Due to the large degree of delocalization of the solvated electron a possible way to proceed is it to identify the Wannier orbital that corresponds to this electron and to extract its contribution to the dipole moment. Such an analysis, which is beyond the scope of the present paper, will a a subject of future efforts.

A different and more practical approach is to compare the present results with those obtained from the analysis of the vibrational spectra of smaller clusters.$^{47}$ Although such a result can obtained in an unambiguous way only for small clusters like $n=8$, some qualitative conclusion can also be drawn for the larger ones. Thus the peaks at 3400 and 3550 cm$^{-1}$ are mainly caused by the interaction of the corresponding H atoms with the electron distribution. They also contribute to the signal around 3300 cm$^{-1}$. In addition, fingerprints from the pure hydrogen bonded molecules are observed all over the frequency range. The peaks around 3700 cm$^{-1}$ are attributed to free OH bond and those at the other end of the spectrum at 3000 cm$^{-1}$ originate from 3-coordinated single donor DAA molecules. Here the hydrogen bonded donor is indicated by D and the acceptor by A. Contributions of the 3-coordinated double donors DDA and 4-coordinated DDAA molecule are observed with decreasing frequency all over the place and cannot be distinguished from the interaction with the electron. We note that the
intensity distribution observed in this experiment does not agree with that one measured for negatively charged water cluster \((H_2O)_n^+\) with the largest \(n=21\).\(^{14}\) Although both clusters contain the electron distribution, but with and without the counter-ion \(Na^+\) present, the two spectra have their peak intensities in completely different frequency ranges. The peaks of the \(Na(H_2O)_{34}\) spectrum occur between 3400 and 3600 cm\(^{-1}\) while the peak intensity of the \((H_2O)_{21}^-\) cluster ion is found in the range of 3100 to 3300 cm\(^{-1}\). Both spectra share the general appearance with no spectacular peak structure, certainly a results of different structures and the coupling of the many oscillators which contribute to the spectrum.

**Conclusions**

In this paper we present results of ab initio molecular dynamics simulations of a collision of a low energy sodium atom with a medium-sized water cluster at 350 K, together with calculated and experimental IR spectra of the sodium-water system. Computational results show that after the collision of \(Na\) with the cluster, the valence electron of sodium becomes delocalized between the alkali cation and water molecules. This electron delocalization is connected with a decrease of its binding energy, which becomes close to that of a hydrated electron. Nevertheless, in this finite size system the excess electron cannot become fully decoupled from its parent sodium and remains delocalized between water molecules and \(Na^+\). Present simulations also show that the time scale of the relaxation of electron density to the final distribution is in the range of hundreds of femtoseconds. The location of the excess density in the cluster (surface vs. bulk) depends somewhat on the initial velocity of the sodium atom. Nevertheless, present trajectories show that after relaxation the excess electron density (together with sodium) tend to be located mostly in the interior the cluster, which is different from the situation in water cluster anions of comparable size with a preferentially surface-bound excess electron.\(^{48,49}\) However, the relatively small number of (time consuming) trajectories does not provide statistically
converged data in this respect. We note that this behavior is different from that observed for water cluster anions in this size range where in most of the results a surface position is predicted. Values of the vertical ionization potential and location of excess density correlate well with the data published previously for smaller clusters.

A very good agreement was also obtained between the calculated and experimental IR spectra of the sodium-water cluster. The IR spectrum of Na(H$_2$O)$_{34}$ is dominated by peaks in the hydrogen bonding region around 3430 and 3550 cm$^{-1}$. Aside from the interaction with the electron distribution in this frequency range, we also observe the typical motifs of a hydrogen bonded network, namely with decreasing wavenumbers and increasing strength of the hydrogen bond, the free, the 3-coordinated double donor DDA, the 2-coordinated DA, the 4-coordinated DDAA, and finally the 3-coordinated DAA molecules. The clear separation of the hydrogen and the electron bonded contributions is lost for this large cluster and we observe a mixture of both interactions.

Together with previous studies the present simulations open way for investigating in detail the following two issues. First is the process of separation of the excess electron from its parent sodium core and its transformation to a hydrated electron upon increasing the cluster size and approaching the bulk limit. Second is the chemical reactivity of the sodium atom with water toward hydroxide, which becomes particularly relevant and interesting in larger systems with higher concentration of sodium. We will attempt to touch upon these issues in our subsequent study.

Acknowledgment

Support by the Czech Ministry of Education and the Czech Science Foundation (projects LC512 and 202/06/0286) is gratefully acknowledged.
References


Figure captions:

Fig. 1. Distance of sodium atom from the geometric center of the system vs. time for simulated collisions.

Fig. 2. Spin density contours (isovalue equal to 0.001) and values of vertical ionization potential for snapshots taken from trajectory A.

Fig. 3: Comparison of the spin density and differential electron density contours for two snapshots from trajectory A.

Fig. 4. Spin density contours (isovalue equal to 0.001) and values of vertical ionization potential for snapshots taken from trajectory B.

Fig. 5. Spin density contours (isovalue equal to 0.001) and values of vertical ionization potential for snapshots taken from trajectory B/SIC.

Fig. 6. Spin density contours (isovalue equal to 0.001) and values of vertical ionization potential for snapshots taken from trajectory C.

Fig. 7. Distance of sodium atom from the geometric center of the system vs. time for trajectory C.

Fig. 8. Spin density contours (isovalue equal to 0.001) and values of vertical ionization potential for snapshots taken from trajectory C/SIC.

Fig. 9. Experimental (black points) and calculated (red curve) IR spectrum.
Table 1. Comparison of vertical ionization potential (VIP) values calculated both with and without self-interaction correction (SIC). Trajectory B was calculated without SIC therefore in 3rd column we put VIP calculated for snapshots from B but with SIC. Trajectory B/SIC was calculated with SIC and hence in 6th column there are values for snapshots from B/SIC without SIC.

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>B/SIC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>time [fs]</td>
<td>VIP [eV]</td>
</tr>
<tr>
<td>5</td>
<td>5.25</td>
<td>5.67</td>
</tr>
<tr>
<td>233</td>
<td>3.76</td>
<td>4.21</td>
</tr>
<tr>
<td>438</td>
<td>4.44</td>
<td>4.98</td>
</tr>
<tr>
<td>645</td>
<td>3.66</td>
<td>4.09</td>
</tr>
</tbody>
</table>
Table 2. Summary of results obtained for trajectory B/SIC (time corresponding to a snapshot, vertical ionization potential, the volume of spin density enclosed inside 0.001 isodensity surfaces, and the shift between the center of spin density and sodium nuclei).

<table>
<thead>
<tr>
<th>time [fs]</th>
<th>VIP [eV]</th>
<th>spin density volume [Å³]</th>
<th>spin density shift [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5.67</td>
<td>318</td>
<td>0.5</td>
</tr>
<tr>
<td>233</td>
<td>4.48</td>
<td>258</td>
<td>1.6</td>
</tr>
<tr>
<td>450</td>
<td>4.22</td>
<td>197</td>
<td>2.5</td>
</tr>
<tr>
<td>625</td>
<td>3.79</td>
<td>235</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Table 3. Summary of results obtained for trajectory C/SIC (time corresponding to a snapshot, vertical ionization potential, the volume of spin density enclosed inside 0.001 isodensity surfaces, and the shift between the center of spin density and sodium nuclei).

<table>
<thead>
<tr>
<th>time [fs]</th>
<th>VIP [eV]</th>
<th>spin density volume [Å$^3$]</th>
<th>spin density shift [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.07</td>
<td>65</td>
<td>1.9</td>
</tr>
<tr>
<td>50</td>
<td>3.32</td>
<td>151</td>
<td>2.6</td>
</tr>
<tr>
<td>100</td>
<td>5.04</td>
<td>171</td>
<td>3.2</td>
</tr>
<tr>
<td>200</td>
<td>4.38</td>
<td>204</td>
<td>2.6</td>
</tr>
<tr>
<td>300</td>
<td>4.94</td>
<td>186</td>
<td>2.8</td>
</tr>
<tr>
<td>400</td>
<td>4.54</td>
<td>213</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Fig. 1.
Fig. 2.

$t=5\text{fs}, \text{VIP}=5.65\text{eV}$
$t=395\text{fs}, \text{VIP}=4.04\text{eV}$
$t=1367\text{fs}, \text{VIP}=4.40\text{eV}$
$t=1545\text{fs}, \text{VIP}=4.61\text{eV}$
Fig. 3.

$t=5\text{fs}$, spin density $t=1367\text{fs}$, spin density

$t=5\text{fs}$, differential density $t=1367\text{fs}$, differential density
Fig. 4.

$t=5\text{fs}$, VIP=$5.25\text{eV}$

$t=233\text{fs}$, VIP=$3.76\text{eV}$

$t=438\text{fs}$, VIP=$4.44\text{eV}$

$t=645\text{fs}$, VIP=$3.66\text{eV}$
Fig. 5.

$t=5\text{fs}, \ VIP=5.67\text{eV}$

$t=233\text{fs}, \ VIP=4.48\text{eV}$

$t=450\text{fs}, \ VIP=4.22\text{eV}$

$t=625\text{fs}, \ VIP=3.79\text{eV}$
Fig. 6.

$t=5\text{fs}$, VIP=2.02eV

$t=70\text{fs}$, VIP=2.71eV

$t=125\text{fs}$, VIP=3.78eV

$t=275\text{fs}$, VIP=4.05eV

$t=575\text{fs}$, VIP=3.30eV

$t=590\text{fs}$, VIP=3.59eV
Fig. 7.
Fig. 9.

\[ n = 34 \pm 2 \]