The lowest electronically excited state of small Na(H\textsubscript{2}O\textsubscript{n})\textsuperscript{n} clusters have been investigated experimentally and theoretically. The excitation energy as determined by the depletion spectroscopy method drops from 16950 cm\textsuperscript{-1} for the sodium atom down to 9670 cm\textsuperscript{-1} when only three water molecules are attached to the Na atom. For larger clusters the absorption band shifts back towards higher energies and reaches 10880 cm\textsuperscript{-1} for \( n = 12 \). The experimental data are compared to quantum chemical calculations at the MP2 and MRSDCI levels. We found that the observed size-dependence of the transition energy is well reproduced by the interior structure where the sodium atom is surrounded by water molecules. The analysis of the radial charge distribution of the unpaired electron in these interior structures gives a new insight into the formation of the “solvated” electron.

I. INTRODUCTION

Complexes containing alkali-atoms surrounded by polar solvent molecules are interesting species to study the behavior of loosely bound metal valence electrons in polar environment. Since the first report of the solvation of alkali metal in liquid ammonia by Weyl in 1864,\textsuperscript{1} the solvation phenomena of metals in liquid ammonia and other polar solvents has been studied extensively.\textsuperscript{2} It has been found that in liquids solvated electrons are formed when alkali metal is dissolved. These solvated electrons are completely detached from the alkali metal ions and exhibit spectroscopic properties of their own. On the other hand, in very small complexes with only a few solvent molecules attached to the alkali atom the valence electron is still bound in the coulomb field of the metal ion core. Thus, research on the formation of solvated electrons in model systems is of fundamental interest for the understanding of elementary chemical processes such as solvation, electron transfer, charge induced reactivity and the structure of the liquid phase in general.

A variety of clusters have been studied to gain information at the solvation process on a molecular level. Negatively charged (H\textsubscript{2}O\textsubscript{n})\textsuperscript{−} and (NH\textsubscript{3}\textsubscript{n})\textsuperscript{−} clusters were one of the first species, where photo detachment energies have been determined.\textsuperscript{3} Later absorption spectra of (H\textsubscript{2}O)\textsuperscript{−} have been reported.\textsuperscript{4} Sr\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{n}, Ca\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{n} and Mg\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{n} clusters have been studied and photo dissociation spectroscopy to understand the ion solvation.\textsuperscript{5–8} Fuke et al. reported photoelectron spectra of the anion complexes Li(H\textsubscript{2}O)\textsuperscript{+}\textsubscript{n} and Na(H\textsubscript{2}O)\textsuperscript{+}\textsubscript{n}.\textsuperscript{9,10}

On theoretical side the energetics and structures of negatively charged (H\textsubscript{2}O)\textsuperscript{−} and (NH\textsubscript{3})\textsuperscript{−} clusters have been studied by applying a modified continuum model.\textsuperscript{11,12} Quantum mechanical calculations were carried out to elucidate the geometric and electronic structures of Ca\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{n} and Mg\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{n} clusters.\textsuperscript{13,14} The geometries and detachment energies of Li\textsuperscript{−}(H\textsubscript{2}O)\textsubscript{n}, Li\textsuperscript{−}(NH\textsubscript{3})\textsubscript{n}, Na\textsuperscript{−}(H\textsubscript{2}O)\textsubscript{n}, and Na\textsuperscript{−}(NH\textsubscript{3})\textsubscript{n} have been explored by \textit{ab initio} MO method.\textsuperscript{15–18}

In the past years, our group has investigated the spectroscopic properties of size selected neutral sodium-water and sodium-ammonia clusters. Ionization potentials (IP) for Na(H\textsubscript{2}O)\textsubscript{n} and Na(NH\textsubscript{3})\textsubscript{n} clusters up to \( n \approx 20 \) have been determined by one photon ionization.\textsuperscript{19–22} The measurements have shown that the IP decreases with increasing number of solvent molecules. While for Na(NH\textsubscript{3})\textsubscript{n} clusters the ionization potential decreases smoothly with increasing cluster size towards the bulk value of 1.5 eV, the IP of Na(H\textsubscript{2}O)\textsubscript{n} stays constant for \( n \geq 4 \) at 3.2 eV. A similar behavior was found when sodium was replaced by cesium or lithium.\textsuperscript{10,23} The interesting difference in the size dependence of IPs in M(H\textsubscript{2}O)\textsubscript{n} and M(NH\textsubscript{3})\textsubscript{n}, especially the unusual behavior of the IPs in the former clusters has motivated many theoretical studies.\textsuperscript{24–30} Among them, Hashimoto and Kamimoto have found for the first time the excess electron localization and the formation of the two center state in Li(H\textsubscript{2}O)\textsubscript{n} (\( n \geq 4 \)).\textsuperscript{28}

Another important spectroscopic quantity is the energy of the lowest electronically excited state, which asymptotically corresponds to the 3\( p \leftarrow 3s \) transition in the bare sodium atom. The energetics of this transition can give information on the charge density of the sodium valence electron. The first electronically excited state of Na(NH\textsubscript{3})\textsubscript{n} complexes has been studied extensively in our group.\textsuperscript{31–33} As a general result of these studies, it has been found that the 3\( p \leftarrow 3s \) excitation energy decreases from its atomic value (16950 cm\textsuperscript{-1}) with increasing number of ammonia molecules bound to the sodium atom and reaches 6000 cm\textsuperscript{-1} when the first solvation shell is filled at \( n = 4 \). This size dependence of the transition energy resembles that of the separation between the 3\( S^{2}\)(Na) \( \equiv 3^{1}S(Na^{−}) \) and 3\( P^{2}\)(Na) \( \equiv 3^{1}S(Na^{−}) \) type bands in the photoelectron spectra for the negatively charged Na(NH\textsubscript{3})\textsubscript{n}.\textsuperscript{17} The decrease of 3\( S^{2}\)–3\( P^{2} \) energy separations with increasing cluster size has been theoretically attributed to the growth of the Rydberg-like wavefunction of the valence electron in the clusters.\textsuperscript{17} For
Water clusters are prepared by expanding water vapor. The source and its properties can be found in a separate publication. Larger Na(NH$_3$)$_n$ clusters the excitation energy increases slightly towards the absorption of the "solvated" electron in liquid ammonia at 6300 cm$^{-1}$. As a second interesting result these spectroscopic studies revealed a strong interaction between the electronic excitation of the unpaired electron with vibrations of the solvent molecules: a strong absorption peak for all Na(NH$_3$)$_n$ clusters with $n > 3$ was observed at 6600 cm$^{-1}$ and assigned to the first overtone of the symmetric and/or asymmetric N–H$_3$ stretching vibration. The result was also confirmed by pump-probe experiments in our lab, which showed a decreasing lifetime for the exited state with an increasing number of solvent molecules.

In this paper we present for the first time a spectroscopic study of sodium-water clusters. The absorption bands for the first electronically excited state of Na(H$_2$O)$_n$ with $n = 1 - 12$ have been obtained experimentally by the depletion method as described in the next section. The structures and the vertical transition energies of these clusters with $n$ up to 8 were investigated by $ab$ initio MO calculations at the correlated level. The size and the structure dependence of the vertical transition will be presented in section III. In the final section we will not only compare the experimental and theoretical results on the excitation energies of sodium-water cluster but also discuss the relationship to our previous study on sodium-ammonia clusters.

II. EXPERIMENTAL

In contrast to our earlier studies, where the mixed clusters were formed in a pulsed crossed beam type pick-up source, in the experiments presented here a newly build continuous pick-up source was used. The design is similar to the setup used to dope large helium clusters with alkali metal atoms. A brief overview will be adequate here. A detailed description of the source and its properties can be found in a separate publication.

Figure 1 shows the experimental setup schematically. Water clusters are prepared by expanding water vapor through a 70$\mu$m diameter nozzle into the vacuum. The oven and the nozzle are heated to temperatures 115°C and 125°C, respectively, giving a water vapor pressure of 1.4 bar. A skimmer collimates the supersonic jet and the water cluster beam traverses to the sodium oven in a separate chamber. The number of sodium atoms picked up by the water clusters is controlled by the sodium vapor pressure. In this experiment an oven temperature of 200°C ($p_{Na} \approx 1 \cdot 10^{-4}$ mbar) gives the best condition to form complexes containing only one sodium atom. The formed mixed clusters enters the detection chamber further downstream. Here the clusters are excited and ionized with nanosecond laser pulses. The ions are mass analyzed in a time-of-flight mass spectrometer and detected with MSP (MicroSpherePlates).

In our earlier spectroscopic study of sodium-ammonia clusters it was found that the clusters fragment after excitation. We expect that sodium-water clusters exhibit the same behavior. Therefore the method of depletion spectroscopy have been used to determine the absorption band of Na(H$_2$O)$_n$ clusters. This method has been described in detail in Ref. 33. Sodium-water clusters are excited with a tunable laser beam counter propagating to the cluster beam. The laser radiation is generated by an optical parametric process. A commercial laser system (Spectra Physics MOPO 730-10) was used, which provides photon energies from 5500 to 24000 cm$^{-1}$ with a small gap around the degeneration point of the OPO between 13650 cm$^{-1}$ and 14500 cm$^{-1}$. The clusters are ionized 200 $\mu$s after excitation by photons of 4.66 eV (266 nm) energy (4th harmonic of a Nd:Yag laser, Continuum Surelight).

For the evaluation of our data it is important that the ionization does not introduce dissociation of the clusters and thus an incorrect assignment of $n$. In our earlier study of the ionization potentials we have found for Na(NH$_3$)$_n$ that most of the excess energy is carried by the photo electron. The remaining internal energy is small and does not lead to fragmentation due to the high binding energy between the ammonia molecules of about 0.3 eV. We can safely assume that this also holds for Na(H$_2$O)$_n$ clusters especially because the binding energy between the solvent molecules is even higher (0.5 eV).

The raw ion signal taken with ($S_{on}$) and without ($S_{off}$) excitation laser at each wavelength are converted to the absorption cross section $\sigma$ by the Beer-Lambert law $-\ln(S_{on}/S_{off}) = \sigma \phi$, where $\phi$ is the laser fluence also measured at each point. As a typical example Figure 2 shows $-\ln(S_{on}/S_{off})$ as a function of the laser fluence $\phi$ for the Na(H$_2$O)$_3$ cluster. The depletion signal increases linearly with the laser fluence as predicted by Lambert-Beer law up to 2.5 mJ/cm$^2$ and saturates for larger laser fluence. The slope gives the photo absorption cross section $\sigma$. The all measurements presented in this paper were taken in the linear part.
III. THEORETICAL

Molecular structures of Na(H$_2$O)$_n$ ($n = 1 - 6$ and 8) were optimized at MP2 level with the usual frozen core approximation. The basis sets used were the 6-311++G(d,p). Since the number of potential minimum configurations becomes very large for $n \geq 4$, we have optimized most $n \geq 4$ clusters by referring to the low-energy structures of Na(H$_2$O)$_n$ and Li(H$_2$O)$_n$ reported in the previous ab initio studies. We also referred to the anionic geometries of Na(H$_2$O)$_4$ and Na(H$_2$O)$_6$. The vibrational analyses were carried out at each optimized geometry to confirm the minima on the potential energy surfaces. Harmonic frequencies of all $n \leq 3$ clusters and a few $n = 4$ structures were evaluated by computing the second derivative matrices analytically, while those of other isomers were calculated by differentiating numerically the first derivatives along the nuclear coordinates. The program used for the geometry optimization and vibrational analyses was Gaussian-98. Total binding energies, $\Delta E(n)$, of the minimum structures were evaluated by the following formula.

$$-\Delta E(n) = E[^{1} \text{Na(H}_{2}\text{O)}]_{n} - E[^{1}\text{Na}] - n \cdot E[^{1}\text{H}_{2}\text{O}]$$  \hspace{1cm} (1)

We have taken the zero point vibrational correction (ZPC) into account by using the scaled harmonic frequencies. The scale factor, 0.956, was obtained from the average ratio of the experimental fundamental and the calculated harmonic frequencies of a free H$_2$O. We have also corrected the basis set super position error for the total binding energies by the counter-poise correction (CPC). From now on, we designate the $\Delta E$ with only CPC as $\Delta E_{\text{cpc}}$ and that with both CPC and ZPC as $\Delta E_{\text{zp}}$. The vertical transition energies (VTEs) of Na(H$_2$O)$_n$ were calculated by the multi reference single and double excitation configuration interaction (MRSDCI) method preceded by the complete active space self-consistent-filed (CASSCF) calculations. The active space for the CASSCF consists of five molecular orbitals (MOs) corresponding to the 3s, 3p and 4s orbitals of Na, and the ground and four low-lying excited states were averaged with equal weight. The natural orbitals (NOs) obtained by this method were used as one-particle functions in the MRSDCI calculations with the CASSCF reference. All single and double excitations from the five active orbitals and $n$ high-lying occupied MOs corresponding to lone pairs of H$_2$O molecules were included in the MRSDCI. We used the MOLPRO-2000 for the MRSDCI calculations.

IV. RESULTS

A. Spectroscopic Properties of Na(H$_2$O)$_n$

The photoabsorption of the Na(H$_2$O)$_n$ clusters has been investigated in a broad spectral range from the $3p \leftarrow 3s$ transition of the bare sodium atom (16950 cm$^{-1}$) to the infrared region (6000 cm$^{-1}$) except for a small gap between 13650 cm$^{-1}$ and 14500 cm$^{-1}$. Figure 3 shows the spectra of Na(H$_2$O)$_n$ with $n = 1 - 6$. The circle symbols present the experimental data. To guide the eye the full line has been added, which was obtained by a polynomial fit to the experimental data. Two vertical dotted lines give the limit of the laser gap.

For the Na(H$_2$O) cluster (1:1 complex) only a weak absorption is observed at the low energy side of the scanned spectrum. The absorption increases noticeable at 13400 cm$^{-1}$ close to the degeneration gap of the laser. From the decreasing absorption towards higher energies we assume that the main absorption band for Na(H$_2$O) clusters is in the laser gap around 14000 cm$^{-1}$. This would be a considerable red shift in comparison with the $3p \leftarrow 3s$ transition of the free sodium atom at 16950 cm$^{-1}$, which is similar to our earlier observation for the Na(NH$_3$)$_3$ complex. However, in contrast to the sodium-ammonia complex no sharp vibrational lines were resolved for Na(H$_2$O) even when the scan was repeated with higher spectral resolution. Apart from this main feature two very weak absorption bands are observed around 8850 cm$^{-1}$ and 12150 cm$^{-1}$. These bands coincide with transition energies to highly excited vibrational and rotational states of the water molecules, which have been observed in atmospheric water vapor.

The absorption for larger Na(H$_2$O)$_n$ complexes with $n \geq 2$ are much stronger. The absorption bands are broad, asymmetric without any distinct structures. For
Fig. 3: Absorption spectra of Na(H$_2$O)$_n$ clusters. The open are the experimental data while the full eye guiding line re-
sults from polynomial fit. The full vertical line at 9450 cm$^{-1}$
denotes maximum for $n = 3$.

$n = 2$ the onset of the absorption is at 7300 cm$^{-1}$. The maximum at 10085 cm$^{-1}$ is shifted strongly to the near infra red spectral region compared to the Na(H$_2$O) cluster. The maximum of the absorption for $n = 3$ and 4 are shifted further to the red spectral range and have more or less the same position. For easier comparison the full vertical line in Fig. 3 denotes the position of the ab-
sorption maximum for Na(H$_2$O)$_3$ at 9680 cm$^{-1}$. In the right column of Fig. 3 it is clearly visible that the ab-
sorption maxima for larger clusters than $n = 4$ slowly shifts to higher energies. This trend continues for even larger Na(H$_2$O)$_n$ clusters with $n = 6–12$ while the general shape of the absorption spectrum remains the same. Therefore they are not shown here. The shift towards the blue spectral range with increasing cluster size can be extrapolated to the absorption band of the hydrated electrons in liquids as it will be shown in Section V. Table I summarizes the on-
set and maxima of the absorption bands for all Na(H$_2$O)$_n$ clusters accessible in our experiment.

A closer inspection of Fig. 3 reveals a second absorp-
tion maximum around 16000 cm$^{-1}$ for Na(H$_2$O)$_n$ clusters with $n \geq 4$. This absorption peak increases for larger clusters. We tentatively assign this peak to the next higher electronic state of the Na(H$_2$O)$_n$ complex. For cluster larger than $n = 4$ the electronic states are no longer connected asymptotically to the electronic states of the sodium atom because the valence electron starts to localize outside the first solvation shell as it will be shown further below in the theoretical section.

For Na(H$_2$O)$_n$ ($n = 2–6$) we were able to determine the absolute absorption cross section. Although these values have a quite large error as can be seen in Fig. 2 we will use them to estimate the oscillator strength $f$ of the first electronically excited state between 6000 cm$^{-1}$ and 16000 cm$^{-1}$. As shown in Table II the oscillator strength decreases only by 30 to 50% compared to the $3p \leftarrow 3s$ transition in the bare sodium atom and remains relatively constant with the cluster size. Our values for neutral Na(H$_2$O)$_n$ clusters are in good agreement with measured oscillator strength $f \approx 0.77$ of negatively charged water cluster which is also nearly cluster size independent.

B. Optimized geometries and energetics

The optimized structures and the total binding ener-
gies of Na(H$_2$O)$_n$ ($n = 1–8$) have been calculated. Some selected isomers are shown in Figure 4. A com-
pletes overview about all optimized structures and tables of their frequencies are given in the electronic version (EPAPS). The labels of the form $p+q+(r)$ under each structure denote the numbers of the water molecules in the first ($p$), second ($q$), and third ($r$) shells.

Na(H$_2$O) has a C$_2v$ structure with a Na–O bond and the $\Delta E$ is about 4 kcal/mol. $2+0$ and $1+1$ type iso-
mers of Na(H$_2$O)$_2$ are as stable as each other. Their

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TABLE I: Energy of the absorption maxima and onset for Na(H$_2$O)$_n$ clusters. a: From Ref. 51

<table>
<thead>
<tr>
<th>$n$</th>
<th>$E_{\text{max}}$ / cm$^{-1}$</th>
<th>$E_{\text{onset}}$ / cm$^{-1}$</th>
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<tr>
<td>0</td>
<td>16960</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>14000</td>
<td>13450</td>
</tr>
<tr>
<td>2</td>
<td>10090</td>
<td>7300</td>
</tr>
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<td>7570</td>
</tr>
<tr>
<td>$\infty$</td>
<td>14100$^a$</td>
<td>-</td>
</tr>
</tbody>
</table>

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TABLE II: Estimated oscillator strength for Na(H$_2$O)$_n$ clusters

<table>
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<tr>
<th>$n$</th>
<th>$f_{6000–16000}$ cm$^{-1}$</th>
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<tr>
<td>0</td>
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</tr>
<tr>
<td>2</td>
<td>0.6(4)</td>
</tr>
<tr>
<td>3</td>
<td>0.7(4)</td>
</tr>
<tr>
<td>4</td>
<td>0.6(4)</td>
</tr>
<tr>
<td>5</td>
<td>0.5(4)</td>
</tr>
<tr>
<td>6</td>
<td>0.6(4)</td>
</tr>
<tr>
<td>$\infty$</td>
<td>0.75</td>
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</table>
FIG. 4: Optimized structures of Na(H₂O)ₙ (n = 1–8) calculated at MP2/6-31++G(d,p) level. Geometrical parameters are given in Å and degrees. Molecular symmetry and total binding energies (∆Eₑ, ∆Eₑₑ, ∆E) in kcal/mol are also given under each structure.
\[ \Delta E_{zpc} \] are 8.9 kcal/mol.

Three 3+0 structures (W3a-c) and two 2+1 isomers (W3d-e) were found for Na(H2O)3. The former clusters whose \( \Delta E_{zpc} \) values are 14.1 - 14.6 kcal/mol are only slightly more stable than the latter. A water molecule is bound to W2a by forming the third Na-O bond in W3a, while Na is located near the center of three equivalent O atoms in W3b which is similar to the cationic structure. Na is situated on a cyclic (H2O)3 in W3c; the O-Na-O angles are about 70 degrees. W3a and W3b can be regarded as the beginning of the so called interior structures in which Na is surrounded by the first-shell ligands from O sides, while W3c is the smallest surface complex where Na is situated on the surface of the hydrogen-bonded water clusters.

For \( n = 4 - 6 \), we also found interior (W4a-c, W5a-b and W6a-e) and surface (W4d-f, W5c and W6f-g) clusters as well as other isomers having one of the \( n = 3 \) structures in the first shell (W5d-f). We could find the 4+1 surface complex at the HF level, however, the optimization starting from the HF-optimized surface geometry converged to W5f by the MP2 method. The \( \Delta E_{zpc} \) values are around 20-23, 27-31 and 33-39 kcal/mol for \( n = 4 - 6 \), respectively.

Although it is practically impossible to examine all possible minimum configurations for \( n = 8 \) we have optimized thirteen equilibrium structures for this size in total. Fig. 4 shows only the lowest energy structure we have found for \( n = 8 \) (W8a) and in addition a typical surface isomer (W8b). All other optimized structures are given in the EPAPS.54 As we have seen already for the smaller clusters \( n = 2 - 6 \), there are several close-energy isomers for each \( n \) and the similar situation is naturally expected for \( n = 8 \). Thus, several isomers are considered to coexist in the molecular beam even for small \( n \).

C. Vertical transition energies

The calculated vertical transition energies (VTEs) and oscillator strengths to the 3\(^2\)P- and 4\(^2\)S-like states of Na(H2O)\(n\) for \( n = 0 - 6 \) and two isomers with \( n = 8 \) are listed in Table III. The results of all other \( n = 8 \) isomers are given in the EPAPS.54 The VTE for the transition to the 3\(^2\)P state of bare Na atom was calculated to be 2.00 eV, which agrees with the experiment within 0.1 eV. The calculated VTE for the \( A \leftarrow X \) transition decreases by 0.46 eV in the 1:1 complex, being in good agreement with the observed lowering of the absorption maximum from \( n = 0 \) to \( n = 1 \) (0.364 eV). Although the two \( n = 2 \) isomers are equally stable, the VTE value for the transition to the first excited state in W2a is lower than that of W2b. Since the W2a structure reproduces the observed lowering of the absorption maximum better we can assign the observed peak to the \( A \leftarrow X \) transition in W2a. The present calculations predict that the band for the \( B \leftarrow X \) transition in W2a and that of \( A \leftarrow X \) transition in W2b are expected to appear at around 1.39 eV (11200 cm\(^{-1}\)) and 1.42 eV (11500 cm\(^{-1}\)), respectively. The tail in the higher energy side of the observed band maximum may correspond to these transitions.

For \( n = 3 \), several transitions of the different isomers can contribute to the observed band because the VTEs of the low-energy structures are close to one another. The calculated VTEs of the 3\(^2\)P-type transitions in W3a-c whose \( \Delta E_{zpc} \) values deviate within 0.5 kcal/mol range from 0.88 eV (7100 cm\(^{-1}\)) to 1.25 eV (10100 cm\(^{-1}\)). They are between the lowest and the highest edges of the observed band, and the oscillator strengths of these transitions (0.2-0.4) are almost independent of the structures. Nevertheless, the present calculations show that VTEs for the \( A \leftarrow X \) transition of these 3+0 clusters decreases from the lowest VTE value for \( n = 2 \), which is consistent with the experimental observation.

The calculations also suggest that some lowest energy structures such as W4a-e can contribute to the observed band. The situation for \( n \geq 5 \) is similar to \( n = 3 \) and 4. It is worth noticing that the transition energies to 4\(^2\)S-like state in the low-energy structures are shifted down to 1.7-2.0 eV for \( n \geq 4 \) although the oscillator strengths are small due to its forbidden nature. This fact supports the tentative assignments of the second band around 16000 cm\(^{-1}\) observed for \( n \geq 4 \) to the 4\(^2\)S-type transitions.
TABLE III: Vertical transition energies and oscillator strength ($f$) corresponding to transitions from ground state to four low-lying excited states in Na(H$_2$O)$_n$ at the MRSDCI level.

<table>
<thead>
<tr>
<th>$n$ = 0</th>
<th>$n$ = 1</th>
<th>$n$ = 2</th>
<th>$n$ = 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>W3b</td>
<td>W3c</td>
<td>W3d</td>
<td>W3e</td>
</tr>
<tr>
<td>$C_3$</td>
<td>$eV$</td>
<td>$f$</td>
<td>$C_4$</td>
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<tr>
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<td>1$^2$B$_2$</td>
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<tr>
<td>2$^2$A</td>
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<tr>
<td>4$^2$S</td>
<td>3.08</td>
<td>0.00</td>
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</tr>
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</table>

$\text{only 1s orbital was frozen.}$
V. DISCUSSION

A. Comparison of experimental and theoretical results

Figure 5 shows the experimental and theoretical transition energies of the $\tilde{A} \rightarrow \tilde{X}$ transition as a function of $n$. The experimental transition energies for the band maximum and onset are taken from Table I. The figure visualizes the findings of section IV A: the strong red shift of the absorption energy for small clusters up to $n = 3$ and the slight shift towards higher absorption energies for larger clusters. Fig. 5 also shows the calculated vertical transition energies of the $\tilde{A} \rightarrow \tilde{X}$ transition for the lowest energy structures of Na(H$_2$O)$_n$ for each $n$.

Taking into account that the calculations tend to underestimate the VTEs, the agreement with the experimental data is remarkably good. The rapid decrease of the excitation energy for the small clusters containing up to three water molecules is reproduced reasonably well. Towards larger clusters the VTEs of these structures increase slightly in accordance with experimental data. Although it is difficult to assign the observed diffuse spectra definitely, the agreement between the experiment and theory suggests that the lowest energy structures at the present level are the major contributor to the spectra for each $n$. For a rigorous comparison the finite temperature of the clusters has to be taken into account. In earlier experiments a value of 200 K has been estimated for the vibrational temperature of Na(NH$_3$)$_n$ clusters.$^{52}$ We expect a similar value for Na(H$_2$O)$_n$ clusters. Since a full Monte-Carlo simulations to determine the isomer abundances is beyond the scope of this paper a simple estimate using the Boltzmann distribution will be sufficient: At a temperature of 200 K the main contribution to the observed spectra will come from isomers with an energy of up to 0.4 kcal/mol above the most stable structure. Thus, the lowest energy isomers for each $n$ will still be the main contributors to the observed spectra since the energy difference of most isomers is much larger.

B. Electronic states

Although we could not assign the observed bands definitely due to the diffuse spectra, it is instructive to investigate the electronic character of the stable clusters which should be an important contributor to the spectra. The electronic states of M(H$_2$O)$_n$ (M = Li and Na) have been studied by inspecting the contour surface of excess electron density or the space containing the half unpaired electron.$^{28,30}$ To get further insight about the electronic nature, we have examined the radial distribution function of the unpaired electron by dividing it into two components, $\rho_+(r)$ and $\rho_-(r)$. They are contributions to the total radial distribution function $\rho(r)$ from a half share with $z > 0$ and from that with $z < 0$, respectively, and evaluated using the singly occupied molecular orbital (SOMO) by unrestricted Hartree-Fock method with Na at the origin. We have taken the molecular symmetry axis as the $z$ axis except for W2a and W6a, with positive $z$ values in the direction opposite to the solvents. For W2a and W6a, the $z$ axis is set to a line passing through Na and the point with the maximum SOMO density. We have also calculated the number of electrons in the half spheres with a radius of $r$, $N_+(r)$ and $N_-(r)$, by integrating the $\rho_+(r)$ and $\rho_-(r)$ numerically. The results for small and the most stable interior clusters for $n \geq 4$ are shown in the left hand side of Figure 6. We also present the results of the typical surface clusters in the right column in Fig. 6 to examine the structure-dependence. The positions ($r_{\rho_{\pm\text{max}}} (\tilde{A})$, values of peaks for $\rho_{\pm\text{max}}$, and $N_\pm(\infty)$ at infinite separation from Na.

<table>
<thead>
<tr>
<th>label</th>
<th>$r_{\rho_{\pm\text{max}}} (\tilde{A})$</th>
<th>$\rho_{\pm\text{max}} (r)$</th>
<th>$r_{\rho_{\pm\text{max}}} (\tilde{A})$</th>
<th>$\rho_{\pm\text{max}} (r)$</th>
<th>$N_-(\infty)$</th>
<th>$N_+(\infty)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>1.78</td>
<td>0.130</td>
<td>1.78</td>
<td>0.130</td>
<td>0.500</td>
<td>0.500</td>
</tr>
<tr>
<td>W1a</td>
<td>2.11</td>
<td>0.068</td>
<td>1.93</td>
<td>0.157</td>
<td>0.329</td>
<td>0.671</td>
</tr>
<tr>
<td>W2a</td>
<td>2.35</td>
<td>0.045</td>
<td>2.09</td>
<td>0.155</td>
<td>0.244</td>
<td>0.756</td>
</tr>
<tr>
<td>W3c</td>
<td>2.34</td>
<td>0.035</td>
<td>2.16</td>
<td>0.157</td>
<td>0.212</td>
<td>0.788</td>
</tr>
<tr>
<td>W4a</td>
<td>3.90</td>
<td>0.155</td>
<td>3.57</td>
<td>0.009</td>
<td>0.931</td>
<td>0.069</td>
</tr>
<tr>
<td>W4d</td>
<td>2.44</td>
<td>0.027</td>
<td>2.26</td>
<td>0.157</td>
<td>0.168</td>
<td>0.832</td>
</tr>
<tr>
<td>W6a</td>
<td>4.01</td>
<td>0.159</td>
<td>3.43</td>
<td>0.002</td>
<td>0.981</td>
<td>0.019</td>
</tr>
<tr>
<td>W6f</td>
<td>2.31</td>
<td>0.023</td>
<td>2.40</td>
<td>0.156</td>
<td>0.133</td>
<td>0.867</td>
</tr>
<tr>
<td>W8a</td>
<td>5.61</td>
<td>0.168</td>
<td>2.36</td>
<td>0.000</td>
<td>0.966</td>
<td>0.004</td>
</tr>
<tr>
<td>W8b</td>
<td>2.31</td>
<td>0.025</td>
<td>2.41</td>
<td>0.154</td>
<td>0.131</td>
<td>0.869</td>
</tr>
</tbody>
</table>

TABLE IV: Positions ($r_{\rho_{\pm\text{max}}} (\tilde{A})$, values of peaks for $\rho_{\pm\text{max}}$, and $N_\pm(\infty)$ at infinite separation from Na.

In Fig. 6 top left, we see the high $\rho_+(r)$ and the low $\rho_-(r)$ for W2a in comparison with the bare Na atom. The water molecules bound to Na push the unpaired electron to the space in the direction opposite to the solvents. In W4a-W8a, $\rho_-(r)$ is a dominant component of $\rho(r)$. The $\rho_+(r)$ is very low in the whole $r$ region for these clusters and that for W8a is actually invisible. The $\rho_-(r)$’s for W4a, W6a and W8a are peaked at 3.90 Å, 4.01 Å and 5.61 Å with their values being 0.155, 0.159 and 0.168, respectively. As shown in the middle left, the values of the $\rho_+(r)$ and $\rho_-(r)$ in the $r \leq 1.0$ Å region for these three are very small. The contribution of Na 3s orbital to SOMO decreases and the unpaired electron is separated from Na$^{+}$ as $n$ grows. The bottom left panel shows that more than 90 percents of the unpaired electrons are distributed in space in the direction occupied by the water molecules. Note that the distance between the Na atom and the outermost first-shell H atom in the negative $z$ direction (3.029 Å (W4a), 3.052 Å (W6a) and 2.884 Å (W8a)) is shorter than the $r$ giving the maximum $\rho_-(r)$. The excess electron is mostly distributed outside the Na$^{+}$(H$_2$O)$_4$ core in these clusters. The Na is spontaneously ionized and the “solvated” electron is excited in the interior clusters. In addition, the height-
FIG. 6: Components of radial distribution function of unpaired electron in the most stable interior (left) and representative surface (right) clusters of Na(H₂O)ₙ (n = 0–8). Na is placed at the origin. ρ₊(r) and ρ₋(r) are contributions from a half sphere with the radius of r in space with z ≥ 0 and z < 0, respectively, (see text). Number of electrons in each half sphere, N₊(r) and N₋(r), are also presented in the bottom.

electron localization, which is similar to the formation of the two-center state in Li-water clusters. In contrast, in Fig. 6 top right, we see the polarization of the unpaired electron to the space free from waters not only in the small but also in the n ≥ 4 surface complexes. The hydration shifts the peak gradually from 1.93 Å (W1a) to 2.41 Å (W8b) with keeping its height almost unchanged (0.157 (W1a) - 0.154 (W8b)). The close examination of the functions in the r ≤ 1.0 Å region indicates that both ρ₊(r) and ρ₋(r) are zero at ρ = 0, 10 Å and at ρ ≈ 0.55 Å reflecting the character of the Na 3s orbital (see the middle right). In the bottom right, around 0.17 electrons move to the free space in the 1:1 complex, and about 80 percents or more unpaired electrons are distributed in the free space opposite to solvent molecules for n ≥ 3. N₊(r) and N₋(r) of the bare Na are nearly constant for r ≥ 4 Å, while those of W1a-W8b become insensitive to r at r ≥ 5 Å(W1a) - 7 Å(W8b). With all right panels together, the spatial expansion of the Na 3s electron occurs gradually with stepwise hydration in space opposite to the solvents in these clusters. The increasing Rydberg-like nature of the electron distribution results in the reduction of the ²S-²P energy separation, namely the red-shifts of the absorption bands.
FIG. 7: Absorption energy as a function of \((n+1)^{-1/3} \propto 1/r\) for \(\text{Na(H}_2\text{O)}_n\) and \(\text{Na(NH}_3\text{)}_n\) clusters.

In addition, the positions and values of the peaks for \(\rho_+(r)\) and \(\rho_-(r)\) as well as \(N_+(r)\) and \(N_-(r)\) do not depend very much on the cluster size for \(n \geq 4\), which is considered to be responsible for the near constancy of the VTEs in the surface clusters.

Finally, we present a comparison of the experimental absorption energies for the two solvents. Figure 7 shows the maximum of the absorption bands for \(\text{Na(H}_2\text{O)}_n\) along with our earlier data\(^{33}\) for \(\text{Na(NH}_3\text{)}_n\) as a function of \((n+1)^{-1/3}\), which is proportional to the inverse of the cluster radius. For both solvents the initial absorption energy of the bare sodium atom (2.1 eV) decreases by 1 eV with only three solvent molecules attached to the alkali metal atom. Towards larger complexes the behavior of the water and ammonia solvent differs. While the absorption energy for \(\text{Na(H}_2\text{O)}_n\) increases for larger clusters, as discussed above, the energy decreases further to approx. 0.7 eV for \(\text{Na(NH}_3\text{)}_4\) and then remains almost constant at this value in the investigated mass range up to \(n = 20\). For both solvents the experimental gas phase data can be extrapolated to the corresponding bulk values measured in liquid solvents. The different behavior of the two solvents can be attributed to the differences in the excess electron localization. Since the most stable forms of \(\text{Na(NH}_3\text{)}_n\) are known to have the interior structure,\(^{24,27}\) the analysis of their electronic states along the above line is expected to give further insight about the solvent dependence of the electron localization mode. One can assume that in ammonia the solvated electron is more diffused and the excitation energies will be lower than for \(\text{Na(H}_2\text{O)}_n\) clusters. A full theoretical analysis of the electronic wave functions in \(\text{Na(NH}_3\text{)}_n\) clusters is presently underway and will be given in a separate publication.

VI. CONCLUSION

The measured absorption spectra of small \(\text{Na(H}_2\text{O)}_n\) cluster in connection with the \textit{ab initio} calculations give new insights into the geometrical structure and charge distribution in these clusters. We have found that the observed absorption band can be mainly attributed to interior cluster structures, where the sodium atom is surrounded by the water molecules. The analysis of charge distribution shows an onset of the formation of the solvated electron already with only four solvent molecules bound to the alkali metal atom.

The results presented in this paper are the bases for extended experimental and theoretical studies. We have recently conducted time resolved pump-probe experiments on sodium-ammonia and sodium-water clusters. A strong dependence of the lifetime of the excited state on the number of solvent molecules surrounding the sodium atom has been observed.\(^{35}\) These dynamical studies in connection with theoretical calculation can give a deeper insight into the interaction of metal atoms with polar solvent molecules.

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