Detailed knowledge of how polar molecules are dissolved in a solvent is essential to understanding the chemistry taking place in salt solutions and the fate and transport of environmental pollutants. Despite significant theoretical efforts directed at elucidating the dissolution of simple diatomic salt molecules and acids, the molecular processes and the initial steps of dissolution are not well understood. Experimental techniques have been developed to probe the dissolution processes with hydrated clusters of diatomic molecules, such as NaI or HBr, by detecting chemical changes as a function of the number of water molecules. Very recently, the hydration energies and the dissolution processes of charged salt clusters, such as \((\text{NaI})_n\text{Na}^+\), have been reported. It has been suggested that only a few waters are required to form stable and characteristic solvent separated ion pairs (SSIP), i.e. \(-5\) for HBr, \(-6\) for NaCl and \(-8\) for NaI, which is qualitatively consistent with simple saturation concentration data in the respective bulk solutions. Here we examine the microdissolution of a complex salt, \(\text{Na}_2\text{SO}_4\). Sulfate is ubiquitous in solids, solutions, and atmosphere aerosols. Molecular level information about the dissolution of sulfate should prove valuable in understanding its behavior and chemistry in the bulk phases and in complex environments. The \(\text{SO}_4^{2-}\) dianion allows us to produce contact ion pairs (CIP), such as \(\text{MSO}_4^-(M = \text{alkali atoms})\), which provide a convenient handle for detection in the gas phase. Both CIP and SSIP are present in sulfate solutions depending on the concentration. Our goal is to follow the microhydration of CIP toward the onset of conversion to SSIP as a function of water in hydrated clusters, \(\text{Na}_2\text{SO}_4(\text{H}_2\text{O})_n\).

We produced \(\text{Na}_2\text{SO}_4(\text{H}_2\text{O})_n\) clusters from a \(10^{-3}\) M \(\text{Na}_2\text{SO}_4\) solution in a \(\text{H}_2\text{O}/\text{CH}_3\text{CN}\) mixed solvent using electrospray ionization (ESI) and studied their structures and energetics by photoelectron spectroscopy (PES) and ab initio calculations. The ESI-PES apparatus has been described in details before. Our previous studies showed that \(\text{SO}_4^{2-}(\text{H}_2\text{O})_n\) were the dominating species from our ESI source at relatively high humidity. However, under relatively dry conditions, bare \(\text{Na}_2\text{SO}_4\) and \(\text{Na}_2\text{SO}_4(\text{H}_2\text{O})_n\) with \(n = 1, 2\) were generated, but no \(n = 3, 4\) species could be observed (Figure 1, top). Tuning the \(\text{Na}_2\text{SO}_4\) concentration and the ESI source humidity, we were able to produce \(\text{Na}_2\text{SO}_4(\text{H}_2\text{O})_n\) with \(n \leq 4\) (Figure 1, bottom). The source conditions and the solution concentration were carefully tuned to optimize each species before recording its PES spectrum.

The PES spectra of \(\text{Na}_2\text{SO}_4(\text{H}_2\text{O})_n\) for \(n = 0 - 4\) are shown in Figure 2. The bare \(\text{Na}_2\text{SO}_4\) spectrum shows three well-separated and rather broad features, labeled \(X^*, X\) and \(A\), which have been reported before. The weak \(X^*\) band is due to detachment from the \((\text{Na}_2\text{SO}_4)_2^3\) dimer, which has the same m/z ratio as the monomer. The \(X\) and \(A\) features are assigned as due to detachment from the HOMO \((\epsilon_1)\) an HOMO-1 \((\epsilon_2)\) of \(\text{SO}_4^{2-}\). Upon adding water molecules, the binding energies of all features increase systematically due to solvent stabilization of the anion. The \(A\) band was not accessible for \(n > 1\).
The first water was found to bind between the SO$_4^{2-}$ and Na$^+$ parts of the ion-pair. This water molecule is oriented in such a way that it binds both to SO$_4^{2-}$ and Na$^+$ by optimizing the O-H $\cdots$ O bond and water O $\cdots$ Na interaction (Figure 2). The association of the first water is very strong, with binding energy of 29.6 kcal/mol (Table 1). The second and third water molecules behave in a similar way, each forming one O-H $\cdots$ O H-bond with a sulfate O atom while the water O atom points towards Na$^+$. The binding energies are also large, 27.1 and 21.7 kcal/mol for the two waters of the $n = 2$ cluster, and 21.1 kcal/mol for each water molecule of the $n = 3$ cluster (Table 1). Thus, the first three waters occupy all three O sites of SO$_4^{2-}$ facing Na$^+$, forming a solvation ‘ring’ between Na$^+$ and SO$_4^{2-}$ and moving apart the two ions from its tight CIP form. The Na–S distance gradually increases from 2.50 Å in the bare CIP to 2.71, 2.81, and 2.84 Å upon adding 1 to 3 water molecules, respectively (Table 1). Such a three-water solvation ring structure was also proposed in previous studies of hydrated sulfate solutions. The CIP and SSIP were proposed to coexist in solutions from previous computational and experimental investigations. Because of the unique framework of NaSO$_4$ the first three water molecules behave both as acid (donating H to sulfate) and base (O of water interacting with Na$^+$). The formed three-water solvation ring begins to separate the cation from the anion, which is a manifestation of the initial steps of dissolution. Additional water molecules further destabilize the sodium-sulfate bond, which will eventually lead to the formation of a SSIP.

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References


Table 1. Calculated vertical detachment energies (VDE’s), binding energies of individual water molecules, and Na-S distances for NaSO$_4$(H$_2$O)$_n$ ($n = 0$–$4$).

<table>
<thead>
<tr>
<th>$n$</th>
<th>VDE (eV)</th>
<th>$E_{bind}$ (kcal/mol)</th>
<th>R$_{Na-S}$ (Å)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>3.58</td>
<td>-</td>
<td>2.50</td>
</tr>
<tr>
<td>1</td>
<td>4.20</td>
<td>29.6</td>
<td>2.71</td>
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<tr>
<td>2</td>
<td>4.91</td>
<td>27.1; 21.7</td>
<td>2.81</td>
</tr>
<tr>
<td>3</td>
<td>5.34</td>
<td>21.1; 21.1; 21.1</td>
<td>2.84</td>
</tr>
<tr>
<td>4</td>
<td>5.37</td>
<td>23.2; 20.9; 18.9; 16.2</td>
<td>2.93</td>
</tr>
</tbody>
</table>

Figure 2. PES spectra of NaSO$_4$(H$_2$O)$_n$ ($n = 0$–$4$) at 193 nm (6.424 eV) and their optimized structures. Calculated VDEs are shown as vertical bars. The feature noted with ‘*’ for the $n = 4$ is due to an impurity (see Figure 1).
NaSO₄(νH₂O)ₙ (n = 0 – 4) clusters have been generated in the gas phase as model systems to simulate the first dissolution steps of sulfate salts in water. Photoelectron spectroscopy and theoretical calculation indicate that the first three water molecules strongly interact with both Na⁺ and SO₄²⁻, forming a three-water solvation ring to pry apart the Na⁺SO₄²⁻ contact ion pair.