

First Steps Towards Dissolution of NaSO_4^- by Water

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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 molecules¹⁻⁴ and acids,⁵⁻⁷ 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.⁸⁻¹⁰ Very recently, the hydration energies and the dissolution processes of charged salt clusters, such as $(\text{NaI})_n\text{Na}^+$, have been reported.^{11,12} 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,⁸ ~ 6 for NaCl and Na_2I^+ ,^{2,12} which is qualitatively consistent with simple saturation concentration data in the respective bulk solutions.⁹ Here we examine the microdissolution of a complex salt, Na_2SO_4 . Sulfate is ubiquitous in solids, solutions, and atmosphere aerosols.¹³⁻¹⁵ 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 SO_4^{2-} dianion allows us to produce contact ion pairs (CIP), such as MSO_4^- ($M = \text{alkali atoms}$),¹⁵ which provide a convenient handle for detection in the gas phase. Both CIP and SSIP are present in sulfate solutions depending on the concentration.^{16,17} Our goal is to follow the microhydration of CIP toward the onset of conversion to SSIP as a function of water in hydrated clusters, $\text{NaSO}_4^-(\text{H}_2\text{O})_n$.

We produced $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ clusters from a 10^{-3} M Na_2SO_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.¹⁸ Our previous studies^{13,19,20} 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 NaSO_4^- and $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ with $n = 1, 2$ were generated, but no $n = 3, 4$ species could be observed (Figure 1, top). Tuning the Na_2SO_4 concentration and the ESI source humidity, we were able to produce $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ with n up to 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 $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ ($n = 0 - 4$) are shown in Figure 2. The bare NaSO_4^- spectrum shows three well-separated and rather broad features, labeled X', X and A, which have been reported before.¹⁵ The weak X' band is due to detachment from the $(\text{NaSO}_4)_2^{2-}$ 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 (t_1) an HOMO-1 (t_2) of 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 $n > 1$.

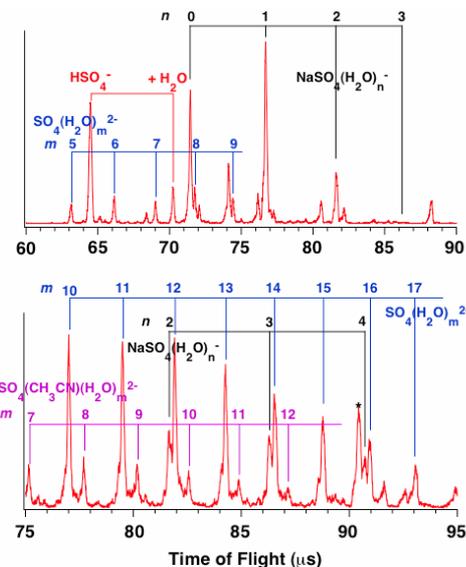


Figure 1. Mass Spectra of $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ ($n = 0 - 4$) under dry (top) and relative humid (bottom) ESI conditions. All major species are labeled. The mass peak with "*" is an unidentified impurity.

The incremental increase of electron binding energies, defined as $\text{VDE}(n) - \text{VDE}(n-1)$, where $\text{VDE}(n)$ is the vertical detachment energy measured from the peak of X for $\text{NaSO}_4^-(\text{H}_2\text{O})_n$, is 0.5, 0.4, 0.2, and 0.2 eV for $n = 1 - 4$, respectively. Because of the broadness of the X peaks, the estimates of the VDEs are rather rough. The X' feature in each spectrum is due to the corresponding $(\text{NaSO}_4)_2^{2-}(\text{H}_2\text{O})_{2n}$ dimer clusters. The strong low binding energy band centered at 3.5 eV (denoted as *) in the spectrum of $\text{NaSO}_4^-(\text{H}_2\text{O})_4$ is due to contamination by an unknown species 1 m/z below $\text{NaSO}_4^-(\text{H}_2\text{O})_4$ (Figure 1). This contaminant could not be completely eliminated because it is too close to the $\text{NaSO}_4^-(\text{H}_2\text{O})_4$ mass peak to allow us for a clean mass selection. We confirmed that the contaminant has no contributions to features beyond 4.5 eV.

To obtain detailed molecular structures and understand how water interacts with NaSO_4^- we performed ab initio calculations. We computed VDEs to compare with the experiment at the MP2/aug-cc-pvdz level using the Gaussian03 package.²¹ For each $\text{NaSO}_4^-(\text{H}_2\text{O})_n$ cluster we did geometry optimization without pre-imposed symmetry. For the larger clusters we started from several different chemically reasonable structures in order to locate the global minimum. The VDE was calculated as the difference between energy of the optimized anionic structure and that of the corresponding neutral at the anionic geometry. In the case of neutral species, which are open-shell systems, projected MP2 energies were considered.

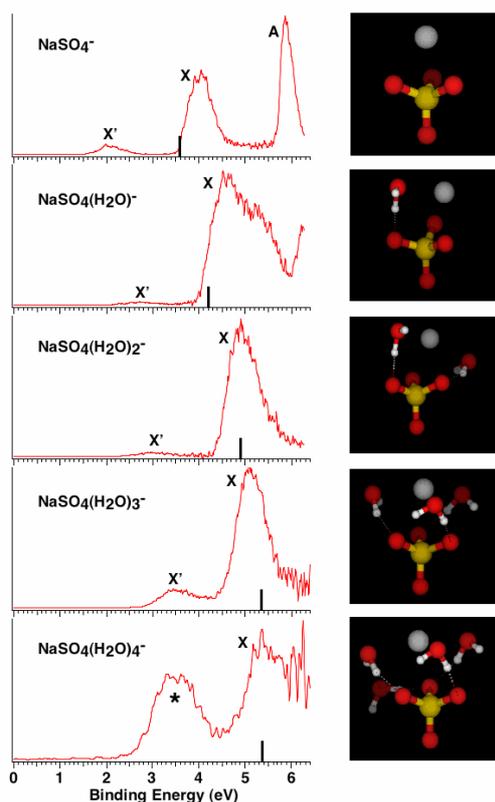


Figure 2. PES spectra of $\text{NaSO}_4(\text{H}_2\text{O})_n$ ($n = 0-4$) at 193 nm (6.424 eV) and their optimized structures. Calculated VDEs are shown as vertical bars. The feature noted with "*" for the $n = 4$ is due to an impurity (see Figure 1).

The first water was found to bind between the SO_4^{2-} and Na^+ parts of the ion-pair. This water molecule is orientated in such a way that it binds both to SO_4^{2-} and Na^+ by optimizing the $\text{O}-\text{H}\cdots\text{O}$ H-bond and water $\text{O}\cdots\text{Na}$ 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 $\text{O}-\text{H}\cdots\text{O}$ 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 dissolution of diatomic salt and acids.^{5,6} When the fourth water is added, it has to bind elsewhere. The best site for this water is next to SO_4^{2-} but further from Na^+ (Figure 2). The binding of this water is significantly lower than that of the first three H_2O , dropping to ~16 kcal/mol, but it still results in an additional increase of the Na-S distance to 2.93 Å.

The calculated VDE of NaSO_4^- is 3.58 eV (Table 1), comparable with our previous study.¹⁵ The calculation also predicted successive increases of the VDE's, by 0.62 eV for the first water, 0.71 eV for the second, 0.43 eV for the third, and 0.03 eV for the fourth water. The calculated VDEs are compared with the experimental data in Figure 2 as vertical bars. Good agreement is obtained between the calculated VDEs and the experiment, providing credence to the solvated structures.

The obtained solvated structures for $\text{NaSO}_4(\text{H}_2\text{O})_n$ ($n = 0-4$) have direct connections with the processes occurring in concen-

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

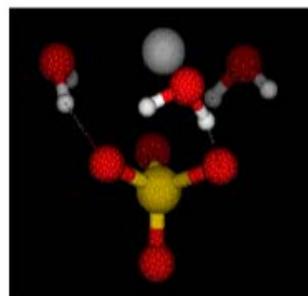
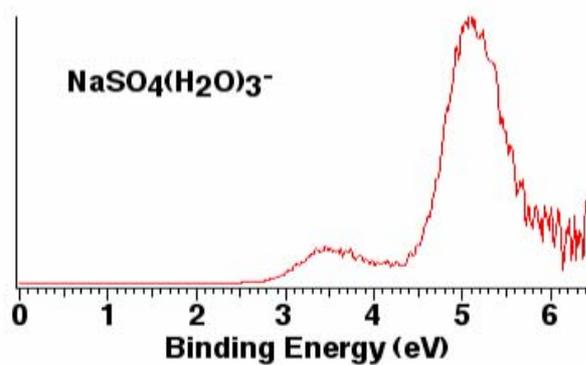
n	VDE (eV)	E_{bind} (kcal/mol)	$R_{\text{Na-S}}$ (Å)
0	3.58	-	2.50
1	4.20	29.6	2.71
2	4.91	27.1; 21.7	2.81
3	5.34	21.1; 21.1; 21.1	2.84
4	5.37	23.2; 20.9; 18.9; 16.2	2.93

trated sulfate solutions. The CIP and SSIP were proposed to coexist in solutions from previous computational and experimental investigations.^{16,17} 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

- (1) Woon, D. E.; Dunning, T. H., Jr. *J. Am. Chem. Soc.* **1995**, *117*, 1090.
- (2) Jungwirth, P. *J. Phys. Chem. A* **2000**, *104*, 145.
- (3) Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. B* **2001**, *105*, 10468.
- (4) Peshlherbe, G. H.; Ladanyi, B. M.; Hynes, J. T. *J. Phys. Chem. A* **2000**, *104*, 4533.
- (5) Lee, C.; Sosa, C.; Planas, M.; Novoa, J. J. *J. Chem. Phys.* **1996**, *104*, 7081.
- (6) Milet, A.; Struniewicz, C.; Moszynski, R.; Wormer, P. E. S. *J. Chem. Phys.* **2001**, *115*, 349.
- (7) Al-Halabi, A.; Bianco, R.; Hynes, J. T. *J. Phys. Chem. A* **2002**, *106*, 7639.
- (8) Hurley, S. M.; Dermota, T. E.; Hydutsky, D. P.; Castleman, A. W. Jr. *Science*, **2002**, *298*, 202.
- (9) Gregoire, G.; Mons, M.; Dedonder-Lardeux, C.; Jouvet, C. *Eur. Phys. J. D* **1998**, *1*, 5.
- (10) Gregoire, G.; Mons, M.; Dimicoli, I.; Dedonder-Lardeux, C.; Jouvet, C.; Martrenchard, S.; Solgadi, D. *J. Chem. Phys.* **2000**, *112*, 8794.
- (11) Blades, A. T.; Peschke, M.; Verkerk, U. H.; Kebarle, P. *J. Am. Chem. Soc.* **2004**, *126*, 11995.
- (12) Zhang, Q.; Carpenter, C. J.; Kemper, P. R.; Bowers, M. T. *J. Am. Chem. Soc.* **2003**, *125*, 3341.
- (13) Wang, X. B.; Yang, X.; Nicholas, J. B.; Wang, L. S. *Science*, **2001**, *294*, 1322.
- (14) Gopalakrishnan, S.; Jungwirth, P.; Tobias, D. J.; Allen, H. C. *J. Phys. Chem. B* **2005**, *109*, 8861.
- (15) Wang, X. B.; Ding, C. F.; Nicholas, J. B.; Dixon, D. A.; Wang, L. S. *J. Phys. Chem. A* **1999**, *103*, 3423.
- (16) Buchner, R.; Capewell, S. G.; Heftler, G.; May, P. M. *J. Phys. Chem. B* **1999**, *103*, 1185.
- (17) Mason, P. E.; Dempsey, C. E.; Neilson, G. W.; Brady, J. W. *J. Phys. Chem. B* **2005**, *109*, 24185.
- (18) Wang, L. S.; Ding, C. F.; Wang, X. B.; Barlow, S. E. *Rev. Sci. Instrum.* **1999**, *70*, 1957.
- (19) Yang, X.; Wang, X. B.; Wang, L. S. *J. Phys. Chem. A* **2002**, *106*, 7607.
- (20) Wang, X. B.; Nicholas, J. B.; Wang, L. S. *J. Chem. Phys.* **2000**, *113*, 10837.
- (21) Frisch, M. J. T. et al., Gaussian03, Pittsburgh PA, 2003.



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NaSO₄⁻(H₂O)_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.
