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Evidence for Water Rings in the Hexahydrated Sulfate Dianion from IR Spectroscopy

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Multiply charged anions, such as sulfate, play important roles in interfacial and condensed-phase chemistry. Sulfates act as nuclei for cloud formation,[1] and the presence of water on the Martian surface has been inferred from sulfate geochemistry.[2] Despite the stability of sulfate in many condensed-phase environments, calculations indicate that the isolated dianion is unstable, with an electron tunneling lifetime of 1.6×10^{-10} s.[3] This may explain why the isolated dianion has not been observed experimentally.[4−6] Sulfate dianions solvated by three or more water molecules can be formed by electrospray ionization (ESI)[4−7] via evaporation from more extensively hydrated droplets.[8] The structures and reactivities of these hydrated dianions have been extensively studied.[4−7,9−12] Activation of $[SO_4(H_2O)_n]^{2-}$ results in fragmentation either by the loss of a water molecule or by the loss of a solvated hydroxide ion.[4,6] The latter is the only pathway observed during blackbody infrared radiative dissociation (BIRD) at room temperature for $n \leq 4$, whereas water loss is the only pathway observed for $n > 6$.[6] Water loss is entropically favored,[6] and the formation of $[SO_4(H_2O)_2]^{2-}$ has been reported from more energetic activation methods.[4] This ion has been inferred to be electronically unstable based on photoelectron spectra of slightly larger clusters.[5]

BIRD experiments indicated that $[SO_4(H_2O)_6]^{2-}$ and $[SO_4(H_2O)_{12}]^{2-}$ are more stable than neighboring hydrates,[6] although equilibrium measurements indicated no special stability for the latter ion at elevated internal energies.[9] The stability of these ions indicates that they may have complete solvent shells or especially stable networks of hydrogen bonds.[6] Multiple structures of $[SO_4(H_2O)_6]^{2-}$ have been proposed to account for its special stability. In one of these, all of the water molecules donate two hydrogen bonds to the sulfate core (T_d symmetry).[6] In the remaining structures, water molecules interact with each other in addition to solvating the ion. $[SO_4(H_2O)_6]^{2-}$ can adopt structures containing one (C_3 symmetry)[5] or two (C_2 symmetry)[10] trimeric water rings, in which each water molecule donates one hydrogen bond to an oxygen atom of the sulfate core and one hydrogen bond to a neighboring water molecule. Additional structures have been proposed that have larger water rings and more inter-water hydrogen bonding (e.g., structure $C_1{}^a$).[11]

The structures of hydrated sulfate dianions were recently investigated by Zhou et al. using elegant infrared (IR) action spectroscopy experiments in the 540−1850 cm^{-1} region.[7] For $[SO_4(H_2O)_6]^{2-}$, the calculated spectra for the T_d and C_3 symmetry structures in this region are similar, but the photodissociation spectrum was assigned to the T_d symmetry structure based on the absence of a band near 865 cm^{-1} calculated for the C_3 symmetry structure. Similarly, the spectrum for $[SO_4(H_2O)_7]^{2-}$ was assigned to a structure in which the seventh water molecule binds to the T_d symmetry core found for $[SO_4(H_2O)_6]^{2-}$, although the presence of an alternative structure that has a water ring could not be ruled out.[7] The spectrum of $[SO_4(H_2O)_{12}]^{2-}$ was assigned to a T symmetry structure with a water trimer on each of the four faces of the sulfate core, like that found computationally by molecular mechanics[6] and ab initio[10,12] calculations.

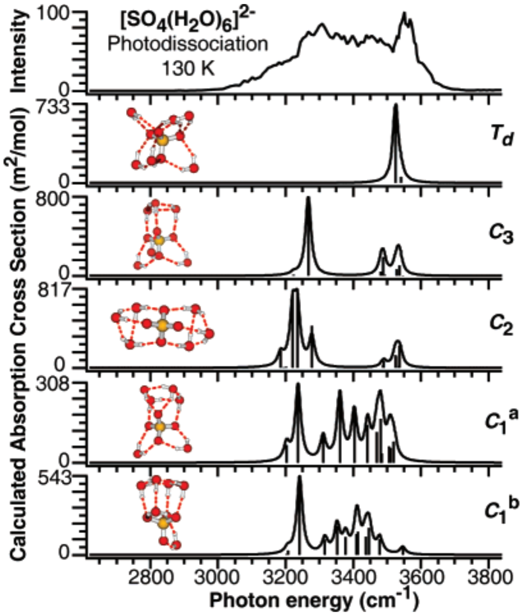

Figure 1. Photodissociation spectrum of $[SO_4(H_2O)_6]^{2-}$ and the spectra for five low-energy conformers from B3LYP/AUG-cc-pVDZ calculations. Calculations use the harmonic oscillator approximation, and vibrational frequencies are scaled by 0.962, a factor used previously to compare results from similar calculations with photodissociation spectra of $[H(H_2O)_n]^+$ in this frequency region.[18] Individual oscillators are broadened using 20 cm^{-1} fwhm Lorentzian distributions.

Here, an IR action spectrum of $[SO_4(H_2O)_6]^{2-}$ in the hydrogen stretch region and complementary calculations provide new insights into the structure of this ion (Figure 1). Experiments were performed on a Fourier-transform ion cyclotron resonance instrument,[13−15] and general experimental methods are described elsewhere.[14] $[SO_4(H_2O)_n]^{2-}$ ions formed by ESI are trapped in a cylindrical ion cell, which is cooled to 130 K with a regulated flow of liquid nitrogen.[15] $[SO_4(H_2O)_6]^{2-}$ is isolated and subsequently exposed to 70−1200 pulses of IR radiation (8−21 mJ per ~7 ns pulse) from a tunable 10 Hz optical parametric oscillator/amplifier (LaserVision, Bellevue, WA). The IR action spectrum includes all product channels[16] and is obtained by plotting the power- and time-corrected photodissociation intensity as a function of laser frequency.[14] All calculations were performed using Gaussian 03,[17] and initial structures were based on previously proposed structures.[6,10,11]

Comparisons between the photodissociation spectrum and spectra calculated for candidate structures provide insights into the structure of this ion (Figure 1, relative energies in Table 1). All structures are energetically competitive (within 8 kJ/mol with zero-point energy corrections). The structures with water rings are slightly lower in energy than the T_d symmetry structure, but this result

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Table 1. Relative Energies (in kJ/mol) of the $[SO_4(H_2O)_6]^{2-}$ Conformers from B3LYP/AUG-cc-pVDZ Calculations. Corrections Are Sequentially Added and Use Unscaled Harmonic Oscillators

	T_d	C_3	C_2	$C_1{}^a$	$C_1{}^b$
E_{elec}	20.5	4.9	0.2	3.8	0.0
+ZPE	8.4	0.0	3.1	3.3	3.2
$+\Delta \boldsymbol{H}_{130\,K}$	9.8	0.0	1.4	2.3	1.2
$-\Delta \boldsymbol{S}_{130\,K}$	8.5	0.0	5.8	4.1	5.4

depends on the type and level of theory used.[7] Calculations indicate that the T_d symmetry structure has only two modes above 2000 cm^{-1} (nearly degenerate symmetric and asymmetric water stretches), and these are consistent with the measured band at $\sim$3550 cm^{-1}. However, the observed photodissociation intensity broadly centered at $\sim$3300 cm^{-1} is inconsistent with this structure. The remaining structures all contain cyclic water rings and are calculated to have intense absorbance in this region, which originates from the stretching modes for water molecules that donate a hydrogen bond to another water molecule. No single calculated spectrum matches the observed spectrum, but a superposition of some of these do, indicating that at least two or more structures are present and contribute to the observed spectrum. These results thus provide strong evidence that the observed ions contain water rings, although contributions from a population of ions with T_d symmetry may be indicated by the feature at $\sim$3550 cm^{-1}.

The bands in the measured spectrum are quite broad. Broad bands are commonly observed in water-loss action spectra of hydrated anions in the hydrogen stretch region.[19] This is associated with ions that are in excited torsional and librational states or transitions with short life times. Multiple conformers appear to be present in this experiment, making it more challenging to definitively establish which structures contribute to the observed photodissociation intensity.

Both the C_3 and T_d symmetry structures are calculated to have intense bands at $\sim$1050 and $\sim$1700 cm^{-1}, corresponding to sulfate asymmetric stretches and water bending modes, respectively.[7] These bands were observed experimentally.[7] However, the C_3 symmetry structure is also calculated to have a concerted water torsional mode at $\sim$865 cm^{-1} that was not observed.[7] It is possible that the calculated frequency and/or intensity for the water torsional mode in the C_3 symmetry structure have significant uncertainties due to anharmonicity or other effects. Also, the sulfate asymmetric stretch appears as a single band at $\sim$1100 cm^{-1}, yet it is broader than the corresponding bands in some of the other $[SO_4(H_2O)_n]^{2-}$ spectra; this may indicate the presence of more than one conformer in the previous experiment. The lower symmetry structures were not considered in the previous report,[7] but calculations performed here indicate that the spectra for those structures would contain additional bands (caused by reduced degeneracy for many classes of oscillators) that are not observed experimentally (Supporting Information Figure 1). For example, the three sulfate asymmetric stretches are essentially degenerate for the C_3 and T_d symmetry structures, whereas those same oscillators for the C_2 and $C_1{}^b$ symmetry structures have large splittings that would likely have been resolved in the Zhou et al. spectrum.[7]

It is also possible that the two experiments probe different populations of structures. In our experiments, ions are stored in an ion cell at $\sim$130 K,[15] whereas the ions in the Zhou et al. experiments were at $\sim$17 K.[7] The difference between the calculated free energies of the T_d and C_3 symmetry structures at 130 K (8.5 kJ/mol) is essentially the same as that at 0 K, and the remaining structures are only slightly disfavored at the higher temperature (Table 1), suggesting that any temperature effect should be small over this range. At higher internal energy (roughly 1000 and 10 cm^{-1} at 130 and 17 K, respectively), additional states may contribute to the photodissociation spectrum. Although some heating of the ion population occurs over the many second time frame of laser irradiation, the persistence of structure in the spectrum seems to indicate that this effect is minimal. In these two experiments, both the time scale and ion generation method are different. In the Zhou et al. study, ions were generated by ionspray from a solution of 1 mM *tert*-butylammonium sulfate in 15:85 water/acetonitrile,[7] whereas ions in this study are formed by nanoESI of 1 mM $MgSO_4$ in pure water. Ions may be kinetically trapped in higher-energy conformers, but this is unlikely in the experiments described here due to elevated internal energies and the 4 s storage time prior to laser irradiation. The Zhou et al. experiments also required significantly more photons to observe photodissociation, due to very low ion internal energies and the lower-energy photons used, which may affect the comparison between the two experiments.

The high- and low-frequency vibrational spectra of $[SO_4(H_2O)_6]^{2-}$ provide complementary information. The hydrogen stretch region spectrum provides strong evidence for a significant population of structures in which inter-water hydrogen bonds are energetically favored over additional hydrogen bonds to the dianion core. Similar spectra of additional, size-selected clusters should provide a more detailed understanding of the early and extended solvation of the sulfate dianion.

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Supporting Information Available: Cartesian coordinates for all structures, Supplemental Figure 1, and the full citation for references for 2, 7, 17, and 18. This material is available free of charge via the Internet at http://pubs.acs.org.

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