Sulfate Ion Patterns Water at Long Distance

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In 1888, F. Hofmeister reported an ordering for salts based on their ability to precipitate hen egg albumin in aqueous solution.[1] This "Hofmeister series" that ranks how ions affect protein solubility is remarkably reproducible for a wide variety of proteins and salts, with anions generally having a stronger effect than cations. Among the anions, sulfate in particular has a strong ability to decrease protein solubility placing it at the kosmotropic (structure maker) end of the Hofmeister scale. In contrast, ions such as ClO_4^- or SCN^- are chaotropes (structure breakers) on the opposite end of the Hofmeister scale and these ions increase protein solubility. Hofmeister effects have been extensively investigated using a number of methods, including X-ray absorption spectroscopy,[2] nuclear magnetic resonance,[3] sum-frequency generation (SFG) spectroscopy,[4] and computational chemistry.[5] Despite significant progress, the precise chemical origins of the Hofmeister series are still debated over 120 years later. Evidence supporting both direct ion−protein interactions and long-range effects of ions on solvent structure has been reported,[2−6] but no clear consensus has been reached as to what extent either of these effects are responsible for the Hofmeister series. Although it is widely accepted that ions can have a very significant structuring effect on water molecules in the first solvation shell, the dynamic nature of liquid water presents a significant challenge in determining long-range structural effects beyond the first solvation shell. Ascribing ion-induced structural effects to a specific ion can also be complicated by counterions, which are always present in bulk salt solutions.

Effects of salts on water structure at interfaces have also been investigated, and rankings for how ions affect surface tension[6] and ion interfacial affinities[4] that are very similar to the Hofmeister series have been reported. Surface-sensitive methods, such as SFG, can provide information about the orientation of water molecules near surfaces, and effects of ions on these interfacial water molecules have been observed. For example, the intensity of the SFG signal in the frequency region 3000−3600 cm^{-1} for sodium salt solutions with different anions at an aqueous/polymer interface correlates with the Hofmeister series.[4] However, even phase-resolved SFG spectra can be difficult to interpret in terms of the water surface structure.[7,8]

Infrared photodissociation (IRPD) spectroscopy of gas-phase hydrated ions is a more direct probe of vibrational resonances than nonlinear spectroscopic methods. In many cases, IRPD spectra closely resemble linear absorption spectra and can provide detailed information about both the interior *and* surface hydrogen bond structure of water in these complexes.[9−11] This technique is especially well suited for investigating how ions affect water structure because the frequencies of OH stretching vibrations are highly sensitive to their hydrogen bonding environment. The structures of small, hydrated sulfate clusters have been investigated recently using both photoelectron[12] and IRPD spectroscopy.[10,11]
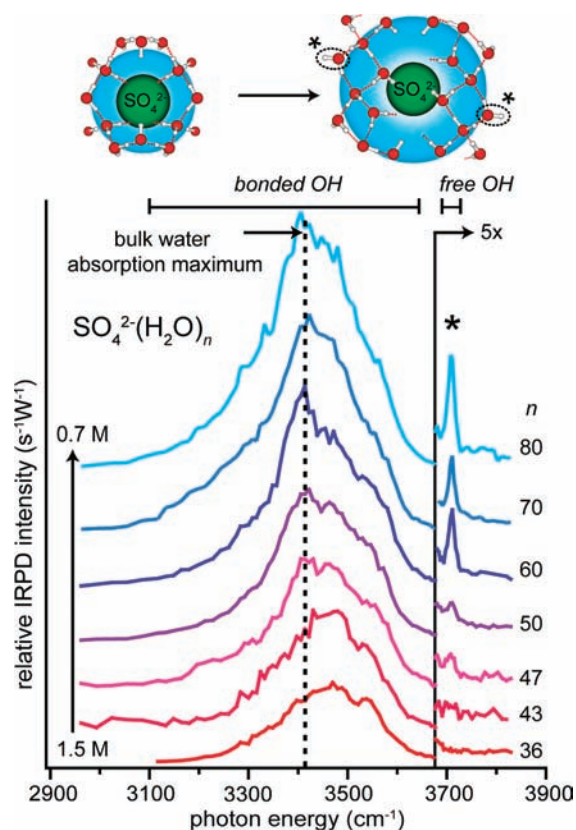

Figure 1. Ensemble average IRPD spectra of $SO_4^{2-}(H_2O)_n$ with up to 80 water molecules obtained at 130 K. The band at ∼3710 cm^{-1} (*) for $n > 43$ corresponds to outer-shell water molecules with "free" OH groups similar to those at the bulk water surface, indicating that the sulfate ion has a long-range effect on water structure. Equivalent molarity of SO_4^{2-} is indicated. Bulk water absorption maximum is from ref 16.

For sulfate ions surrounded by up to 14 water molecules, the ion patterns nearby water molecules such that each hydrogen atom interacts with the sulfate ion or the oxygen atom of another water molecule.[10−12] In contrast, many water molecules at the surface of bulk solutions are oriented so that a hydrogen atom protrudes from the surface and is not part of a hydrogen bond, i.e., such water molecules have a "free-OH" group. An important question in measuring the ability of sulfate to pattern the water hydrogen bond network and thus a benchmark for studying Hofmeister series effects is at what size does the surface of hydrated sulfate clusters exhibit these free-OH groups?

Here, we report the IRPD spectra of $SO_4^{2-}(H_2O)_n$ clusters with up to 80 water molecules measured at 130 K (Figure 1). IRPD spectra are acquired using a 2.7 T Fourier-transform ion cyclotron resonance mass spectrometer by measuring the frequency-dependent, laser-induced photodissociation rate constant of a mass-selected cluster(s).[13] Hydrated sulfate ions are generated from a 4 mM

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solution of $MgSO_4$ (Fisher Scientific, Pittsburgh, PA) by nanoelectrospray ionization and are trapped in a cylindrical ion cell surrounded by a copper jacket cooled to 130 K with a regulated flow of liquid nitrogen.[14] The clusters of interest are isolated using stored waveform inverse Fourier transform excitations. A single cluster size is isolated for the spectrum of $SO_4^{2-}(H_2O)_{36}$, and an ensemble of five adjacent cluster sizes is isolated for all other spectra. Each spectrum in Figure 1 is labeled with the weighted-average cluster size. The ions are photodissociated with IR radiation from a tunable 10 Hz OPO/OPA laser system (LaserVision, Bellevue, WA) for 1.5−5 s (15−50 pulses). For all of the clusters studied, sequential loss of water molecules is the only dissociation pathway observed. Under these conditions, absorption of a single photon increases the photodissociation rate, although absorption of more than one photon can also occur. IRPD spectra are obtained by plotting the laser-induced photodissociation rate constant versus the photon energy of the laser radiation. The photodissociation rate constants are calculated using the ensemble average method[15] which makes possible IRPD spectroscopy of large, hydrated clusters with improved signal-to-noise. All photodissociation rate constants are corrected for dissociation due to blackbody radiation and frequency-dependent variations in laser power.

There is a broad, intense feature from ∼3100 to 3700 cm^{-1} in the IRPD spectra of $SO_4^{2-}(H_2O)_n$ at all cluster sizes, which corresponds to hydrogen-bonded OH groups (Figure 1). At smaller cluster sizes, the maximum in this band is blue-shifted from the hydrogen-bonded OH-stretch absorption of bulk water.[16] This indicates less optimal water−water binding in these clusters presumably due to strong patterning of the first solvation shell by the ion. With increasing cluster size, the shape and central frequency of this band approach those of the OH-stretch absorption spectrum of bulk water. No band above ∼3700 cm^{-1} is observed in the spectra of $SO_4^{2-}(H_2O)_{36}$ and $SO_4^{2-}(H_2O)_{43}$, indicating that each surface water molecule donates two hydrogen bonds. Although a number of factors can affect band intensities, these results indicate that the vast majority of the cluster populations do not have free-OH groups. For $SO_4^{2-}(H_2O)_n$, $n > 43$, a new band appears at ∼3710 cm^{-1} that grows in intensity with increasing cluster size. This band corresponds to free-OH groups of water molecules at the nanodrop surface. The increasing relative intensity of this band with increasing cluster size is consistent with additional water molecules adopting a more intrinsic structure at the nanodrop surface. A similar effect for the hydrated electron is observed at a much smaller cluster size.[17]

The frequency of the free-OH band in the IRPD spectra of the clusters is slightly blue-shifted from a band in SFG spectra of pure water[18] (∼3700 cm^{-1}) and a band observed near 3700 cm^{-1} in vibrational predissociation spectra of neutral water clusters,[19] which are attributed to free-OH groups at the liquid−air interface and cluster surface, respectively. The slight blue shift in this band compared to that for neutral water clusters or at the air/water interface is consistent with a Stark shift in this frequency as a result of the electric field at the surface of these clusters that contain sulfate dianion. This blue shift decreases slightly (less than 3 cm^{-1} from $n = 47$ to 80) with increasing cluster size, consistent with decreasing electric field strength at the surface due to improved ion solvation for larger clusters.

The appearance of the free-OH band at ∼3710 cm^{-1} indicates that intrinsic water−water interactions begin to dominate over the ion-induced structure for cluster sizes greater than ∼43, which is equivalent to a bulk sulfate concentration of ∼1.3 M. These free-OH groups belong to water molecules *in the third or higher*

solvation shells of the sulfate dianion, indicating that an individual sulfate ion patterns water molecules to a distance much farther than the first solvation shell. Despite the significant patterning effects of the sulfate dianion, the hydrogen-bonded feature in these spectra is similar to both that of bulk water and that observed in the IRPD spectra of large, hydrated Ca^{2+} complexes.[9] This indicates that the patterning of the hydrogen-bond network does not significantly affect the local environment of fully hydrogen bonded water molecules, a conclusion that is supported by results from MD simulations of hydrated anions, which indicate that despite substantial perturbations of the spatial pattern of water molecules in outer solvation shells, the number and typical strength of hydrogen bonds are remarkably unaffected.[5] These results are also supported by spectroscopy experiments, which indicate that ions do not substantially affect the reorientation time of water molecules beyond the first solvation shell.[20] The results of these studies have been interpreted by some as evidence that ion-induced solvent structure effects are not the dominant factor behind the Hofmeister series. However, it appears unlikely that rotational dynamics of bulk water molecules reflect the presence or absence of large scale patterning of the hydrogen-bond network.

IRPD spectroscopy provides a unique measure of the water patterning ability of sulfate, and this technique has many advantages over condensed-phase methods for investigating the effects of ions on water structure. The free-OH band is sensitive to subtle changes in the patterning of the water hydrogen bond network and is more structurally informative than the bonded-OH region. By investigating these long-range patterning effects for other ions, new insight into the origins of the Hofmeister series could be obtained.

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