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Electronic instability of isolated SO_4^{2-} and its solvation stabilization

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Despite its ubiquity in nature, SO_4^{2-} as an isolated dianion has never been detected because of its electronic instability as a result of the two negative charges. This study shows how the first few waters solvate and stabilize an isolated SO_4^{2-}, molecule-by-molecule, using photodetachment spectroscopy and theoretical calculations. We find that the minimum number of water required to stabilize a free SO_4^{2-} is three. The first four waters bind tightly to SO_4^{2-}, each forming two H-bonds with SO_4^{2-} without inter-water H-bonding. The charges of the dianion are stabilized sufficiently that additional waters form only single H-bonds with SO_4^{2-} and that inter-water H-bonding is observed starting at $n=5$. © *2000 American Institute of Physics.* [S0021-9606(00)01748-7]

Sulfate (SO_4^{2-}) is an important inorganic dianion commonly found in solutions, solids, atmospheric aerosols,[1] or in extraterrestrial bodies.[2] Due to its ubiquity in nature, the existence of SO_4^{2-} as a chemical structural unit has been taken for granted. However, claims of experimental observation of SO_4^{2-} in the gas phase have long been controversial. A definite answer has been reached only theoretically—because of the strong Coulomb repulsion between the two excess electrons, a free SO_4^{2-} was found to be unstable by ~1.6 eV with respect to autodetachment (to $SO_4^-+e^-$).[3] On the other hand, SO_4^{2-} is stabilized through solvation in solution and counterions in solids. Indeed, only solvated SO_4^{2-} has been observed as a gaseous species.[4] An interesting question concerns how an isolated SO_4^{2-} is solvated and stabilized. Answers to this question will provide molecular-level information about the solvation of a complex dianion, as well as help understand its properties in electrolyte solutions, on surfaces, and at interfaces. In this communication, we report the first spectroscopic characterization of water-solvated SO_4^{2-} and determine its electronic stability and the nature of the solvated complexes, using photodetachment spectroscopy and theoretical calculations.

Gas-phase cluster spectroscopy combined with theoretical calculations has become a powerful means of obtaining atomic-level information about ion solvation and structural metastability.[5] Solvated halide anions have attracted particular attention.[6–10] Beyond the halide anions, the most complicated hydrated anions that have been experimentally characterized are diatomic species, CN^- and O_2^-.[11,12] Dynamic processes such as the ‘‘cage’’ effect and cluster relaxation have been revealed using ultrafast spectroscopy.[13,14] Investigation of hydrated sulfate clusters is challenging experimentally. The most common means of generating solvated anions, i.e., electron attachment in a supersonic free jet, cannot generate $SO_4^{2-}(H_2O)_n$ clusters, even though it is successful in making singly charged solvated anions.[6–14] This is because: (1) isolated SO_4^{2-} is electronically unstable by 1.6 eV against autodetachment (to $SO_4^{2-}+e^-$)[3] and (2) the dianion nature of the clusters would require successive electron attachment, which is difficult due to the strong Coulomb repulsion between the second attaching electron and a singly charged anion. The electrospray ionization technique[15] has been shown to be a powerful soft ionization technique to transport ionic species from the solution to the gas phase. It can produce not only gaseous multiply-charged anions, but also solvated species.[4] We have recently developed an experimental technique, using electrospray and photodetachment photoelectron spectroscopy,[16] to investigate the properties of free multiply charged anions,[17–20] as well as solution phase chemistry in the gas phase.[20,21] This technique is uniquely and ideally suitable to probe the electronic stability and microsolvation of SO_4^{2-}.

In our mass spectra of $SO_4^{2-}(H_2O)_n$ clusters measured using an ion-trap time-of-flight technique,[16,22] the smallest cluster observed was $n=3$. We could not detect any clusters with one or two H_2O, consistent with a previous experiment, in which the smallest cluster observed was $n=4$.[4] The mass spectrum indicated that SO_4^{2-} needs at least three H_2O to be stabilized. This was quantified in the photodetachment experiments and confirmed by our theoretical calculations. Figure 1 displays a set of photoelectron spectra for $SO_4^{2-}(H_2O)_n$

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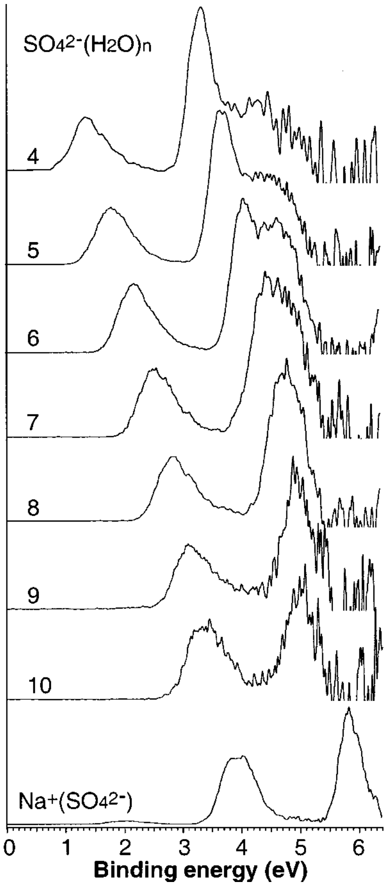

FIG. 1. Photoelectron spectra of $SO_4^{2-}(H_2O)_n$ ($n=4-10$) at 193 nm (6.424 eV) (Ref. 22). The 193 nm spectrum of $Na^+[SO_4^{2-}]$ is also shown for comparison (Ref. 21).

($n=4-10$), taken at a 6.424 eV (193 nm) photon energy.[22] The spectra for $n=4-8$ were also taken at several other photon energies (355, 266, and 157 nm). Due to the extremely weak mass signal for $SO_4^{2-}(H_2O)_3$, we were only able to measure its spectrum at 266 nm with very low count rates. We obtained photoelectron spectra for n up to 13, but the signal-to-noise ratios became poor at large n, due to the decreasing mass signals. Several observations can be made from the data. First, the electron binding energy [Table I and Fig. 2(a)], i.e., the electronic stability of $SO_4^{2-}(H_2O)_n$, increases steadily, but not linearly with the number of waters, from $\sim 0.4\,\text{eV}(n=3)$ to $\sim 3.5\,\text{eV}(n=13)$. Second, the spectral shift as a function of solvent number is rather rigid, i.e., all the spectra were very similar, exhibiting two strong features. Third, all the spectra seemed to be cut off at ~5 eV, due to the repulsive Coulomb barrier, which is universally present in gaseous multiply charged anions.[17–21] In the spectra of the larger clusters ($n>7$), the barrier appeared to cut off the third band, which was observable in the spectra of the smaller clusters. Fourth, the spectra of $SO_4^{2-}(H_2O)_n$ are all similar to that of $Na^+[SO_4^{2-}]$,[21] suggesting that SO_4^{2-} remains intact in the hydrated clusters, i.e., there is no proton transfer, $SO_4^{2-}(H_2O)_n \rightarrow HSO_4^- \cdot (H_2O)_{n-1} \cdot OH^-$. This result is consistent with the fact that HSO_4^- is a stronger acid than H_2O.

From the previously calculated electron binding energy of −1.6 eV for free SO_4^{2-},[3] our measured electron binding energy of 1.0 eV for $n=4$ implies that the first four H_2O stabilize SO_4^{2-} by ~2.6 eV, giving an average stabilization of ~0.65 eV per H_2O. The measured increase of electron binding energy from $n=3$ to 4 is ~0.6 eV, suggesting that each of the first four waters has approximately the same stabilizing effect on SO_4^{2-}. From the 0.4 eV binding energy measured currently for $SO_4^{2-}(H_2O)_3$, we extrapolate that one or two H_2O are not sufficient to stabilize SO_4^{2-}, each is still electronically unstable by roughly −0.9 and −0.2 eV, respectively. The photodetachment results thus provide the most conclusive evidence that *three* is the minimum number of H_2O needed to stabilize a free SO_4^{2-}. The first four waters seem to have the strongest stabilizing effect. As shown in Table I and Fig. 2(b), the incremental stabilization drops to ~0.4 eV for $n=5$ and 6. For the larger clusters, the stepwise stabilization becomes even smaller, decreasing smoothly: ~0.3 eV for $n=7$ and 8; ~0.25 eV for $n=9$ and 10, and ~0.2 eV for $n>10$.

We further performed theoretical calculations[23] to determine the minimum energy structures of $SO_4^{2-}(H_2O)_n$ and to obtain a more quantitative picture about how SO_4^{2-} is solvated by H_2O. Figure 3 shows the lowest energy optimized structures for the hydrated clusters with $n=1-6$. The calculated adiabatic (ADE) and vertical (VDE) electron binding energies[24] corresponding to these structures are in excellent agreement with the experimental data (Table I and Fig. 2), lending considerable credence for the validity of these structures. The theoretical results confirmed indeed $SO_4^{2-}(H_2O)$ and $SO_4^{2-}(H_2O)_2$ are electronically unstable; the calculated ADEs for them are −0.91 and −0.22 eV, respectively, in excellent agreement with our extrapolated ADEs discussed above. The calculations further confirmed that SO_4^{2-} exists as a distinct structural unit with minimal perturbations in all the solvated clusters; the S–O bond lengths and angles differ only slightly from the ideal tetrahedral structure (calculated S–O bond lengths are 1.52 Å in isolated SO_4^{2-}). Consistent with this interpretation, there is little delocalization of charge from the SO_4 species to the surrounding waters; the calculated charge on SO_4 ranges from $-1.92|e|$ with one water bound, to $-1.90|e|$ in the complex with six waters.

A clear picture of stepwise solvation and stabilization of SO_4^{2-} emerges from the structures shown in Fig. 3. The first water strongly binds to SO_4^{2-} (calculated binding energy $=27.7\,\text{kcal/mol}$), forming two strong H-bonds. The second, third, and fourth H_2O also form two strong H-bonds each with SO_4^{2-}. Thus in $SO_4^{2-}(H_2O)_4$ each oxygen on SO_4^{2-} is bonded to two H_2O, forming a symmetric solvated cluster (C_{2v}). The incremental binding energies for the second, third, and fourth H_2O are 26.4, 24.9, and 23.5 kcal/mol, respectively. We expected that the fifth H_2O would continue the same pattern and double H-bond to SO_4^{2-}. However, the lowest energy structure (Fig. 3) instead contains a water–water H-bond, with one of the waters forming only a single H-bond with SO_4^{2-}. The predicted binding energy of the fifth water is 22.4 kcal/mol. Finally, we similarly expected that $SO_4^{2-}(H_2O)_6$ would be tetrahedral, with all six H_2O double H-bonded to SO_4^{2-}. However, the lowest energy structure of $SO_4^{2-}(H_2O)_6$ (Fig. 3) has only three H_2O double H-bonded to

TABLE I. Experimental and theoretical adiabatic (ADE) and vertical (VDE) electron binding energies for $SO_4^{2-}(H_2O)_n$ in eV.[a]

	ADE		ΔADE[b]		VDE		ΔVDE[c]	
n	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.
0		−1.60[d]						
1		−0.91		0.69		−0.38		
2		−0.22		0.69		0.30		0.68
3	0.4 ± 0.2	0.32		0.54	0.8 ± 0.2	0.85		0.55
4	1.00 ± 0.10	0.90	0.60 ± 0.05	0.58	1.33 ± 0.10	1.47	0.53 ± 0.10	0.62
5	1.38 ± 0.10	1.27	0.38 ± 0.05	0.37	1.80 ± 0.10	1.82	0.47 ± 0.10	0.35
6	1.75 ± 0.10	1.69	0.37 ± 0.05	0.42	2.18 ± 0.10	2.18	0.38 ± 0.10	0.36
7	2.10 ± 0.10		0.35 ± 0.05		2.54 ± 0.10		0.36 ± 0.10	
8	2.43 ± 0.10		0.33 ± 0.05		2.84 ± 0.10		0.30 ± 0.10	
9	2.69 ± 0.10		0.26 ± 0.05		3.08 ± 0.10		0.24 ± 0.10	
10	2.93 ± 0.10		0.24 ± 0.05		3.33 ± 0.10		0.25 ± 0.10	
11	3.12 ± 0.10		0.19 ± 0.05		3.60 ± 0.10		0.27 ± 0.10	
12	3.31 ± 0.10		0.19 ± 0.05		3.80 ± 0.10		0.20 ± 0.10	
13	3.49 ± 0.10		0.18 ± 0.05		4.01 ± 0.10		0.21 ± 0.10	

[a] The VDEs were measured from the peak maximum of the first photodetachment feature in each spectrum. The ADEs were estimated by drawing a straight line at the leading edge of the first photodetachment feature and then adding a constant to the intersect with the binding energy axis to take into account the resolution and the thermal effect.

[b] $\mathrm{ADE}(n)-\mathrm{ADE}(n-1)$.

[c] $\mathrm{VDE}(n)-\mathrm{VDE}(n-1)$.

[d] Reference 3.

SO_4^{2-}. Interestingly, the remaining three H_2O form a cyclic H_2O trimer, with each H_2O donating one H to H_2O and one to SO_4^{2-}, and thus also acting as a single H-bond receptor. The calculated binding energy for the sixth H_2O is 21.8 kcal/mol. The stepwise solvation mechanism observed here for free SO_4^{2-} is interesting. We see a delicate balance between $H_2O-SO_4^{2-}$ interactions and H_2O–H_2O interactions. When the solvent number is between one to four H_2O, the two

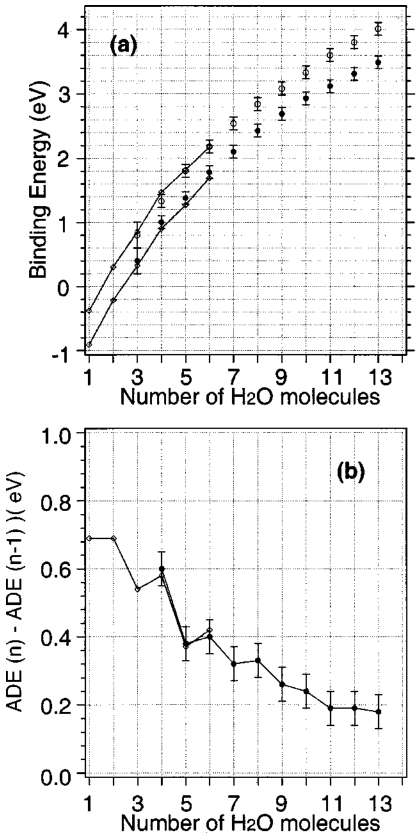

FIG. 2. Experimental and theoretical electron binding energies. (a) Experimental adiabatic (solid circle) and vertical (open circle) binding energies of $SO_4^{2-}(H_2O)_n$ ($n=3-13$), along with the calculated values for $n=1-6$ (lines with open diamond). (b) The experimental (solid circle) and calculated (open diamond) incremental increase of binding energies, $\mathrm{ADE}(n)-\mathrm{ADE}(n-1)$, as a function of solvent number.

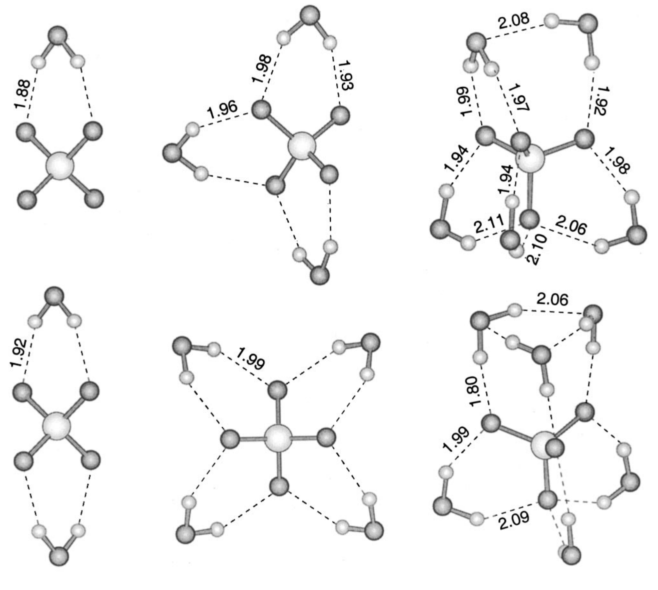

FIG. 3. Optimized structures for the lowest energy isomers of $SO_4^{2-}(H_2O)_n$ ($n=1-6$) at the B3LYP/TZVP+ level. The H-bond lengths (Å) are indicated.

negative charges on SO_4^{2-} attract water strongly enough that two H-bonds are formed with each water. As the solvent number increases $(n>4)$, the negative charges on SO_4^{2-} are sufficiently screened that single H-bonds, plus H_2O–H_2O interactions, are favored. These hydrated clusters may provide good model systems to elucidate the molecular mechanisms of SO_4^{2-} solvation in bulk solutions.[25–27]

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[22] The $SO_4^{2-}(H_2O)_n$ clusters were produced by spraying a 10^{-3} M tetra-butyl ammonium sulfate solution in a water/methanol mixed solvent at neutral pH. The anions produced from the electrospray were accumulated and stored in a quadrupole ion-trap for 0.1 s at a pressure of 10^{-4} Torr before being analyzed by a time-of-flight mass spectrometer. For photodetachment experiment, a mass-selected $SO_4^{2-}(H_2O)_n$ anion was decelerated and intercepted by a Nd:YAG laser beam (355 and 266 nm) or an excimer laser beam (193 and 157 nm). Photoemitted electrons were analyzed by a magnetic-bottle time-of-flight photoelectron spectrometer. Photoelectron time-of-flight spectra were measured and converted to kinetic energy spectra, calibrated by the known spectra of I^- and O^-. The electron binding energy spectra were obtained by subtracting the kinetic energy spectra from the detachment photon energies.

[23] The final geometries of all complexes were optimized using density functional theory, the B3LYP exchange-correlation functional [A. D. Becke, J. Chem. Phys. **98**, 5648 (1993)] and the TZVP+ basis set. The TZVP+ basis set was derived from the DFT-optimized TZVP basis set [N. Godbout, D. R. Salahub, J. Andzelm, and E. Wimmer, Can. J. Chem. **70**, 560 (1992)] by addition of a diffuse *s* function to each H (exponent $=0.0457$), and diffuse *s* and *p* functions to O and S (exponents 0.0814 and 0.0481 on O, 0.0509 and 0.0342 on S). The exponents of the diffuse functions were obtained from an even-tempered extrapolation of the outer exponents of the original basis set. Frequency calculations were done to verify that the optimized geometries were stable points on the potential energy surface. We then obtained more accurate energies from single-point B3LYP calculations using the aug-cc-pVTZ basis set [R. A. Kendall, T. H. Dunning, Jr., and R. A. Harrison, J. Chem. Phys. **96**, 6796 (1992)] on all oxygens and sulfur, the cc-pVTZ basis set on all hydrogens [T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989)], and the B3LYP/TZVP+ geometries. The aug-cc-pVTZ basis set adds a diffuse *s*, *p*, *d*, and *f* function on both O and S. The single-point energies were converged to 10^{-8} a.u. to insure accuracy. In order to locate the lowest dianion energy minima, ~ 10 initial geometries of each complex were first optimized at low levels of theory (typically RHF/3−21+G*). Many of the initial geometries optimized to the same final structure, generally giving ~ 3 geometries for use as input to the higher level optimizations. The geometries of the singly charged anions were optimized using the corresponding dianion geometries as starting points. We used GAUSSIAN98 [M. J. Frisch *et al.*, Gaussian 98, Revision A: Gaussian, Inc., Pittsburgh, PA (1998)] for all of the computations.

[24] We define the theoretical vertical electron binding energy as the difference in total energy between the optimized dianion complex and the singly charged anion calculated at the dianion geometry. We define the adiabatic electron binding energy as the difference in energy between the optimized geometries of the dianion and singly-charged anion complexes.

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