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Study of the Stability and Hydration of Doubly Charged Ions in the Gas Phase: SO_4^{2-}, $S_2O_6^{2-}$, $S_2O_8^{2-}$, and Some Related Species

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Abstract: Many ions that are of paramount importance in solution chemistry could not be produced in the gas phase until the advent of electrospray. The doubly charged ions $SO_4^{2-}{\cdot}nH_2O$ (sulfate), $S_2O_6^{2-}{\cdot}nH_2O$ (dithionate) and $S_2O_8^{2-}{\cdot}nH_2O$ (peroxydisulfate) were produced in the gas phase by electrospray of solutions containing the disodium salts. The ions were detected with a triple quadrupole mass spectrometer. The primary gas phase ion species selected with Q_1 can be subjected to collision induced dissociation (CID) in Q_2 and the products detected with Q_3. CID of $SO_4^{2-}{\cdot}nH_2O$ led to loss of H_2O down to $n \approx 3$. For $n < 3$ an intramolecular proton transfer from HOH to SO_4^{2-} led to the products HSO_4^- and OH^-. The naked SO_4^{2-} ion could not be detected and could be unstable in the gas phase. CID of the $S_2O_6^{2-}{\cdot}nH_2O$ and $S_2O_8^{2-}{\cdot}nH_2O$ led to loss of H_2O down to the naked ions. The greater stability of $S_2O_6^{2-}$ and $S_2O_8^{2-}$ is expected because of the more extensive charge dispersal possible for these species. CID of $S_2O_8^{2-}$ led to the singly charged species SO_4^-, SO_5^-, and SO_3^-.

Introduction

Recently,[1] we reported the production and study in the gas phase of multiply charged metal ions such as $M^{2+}(L)_n$, coordinated to water molecules or other ligands, L. Solvated or coordinated multiply charged ions such as the alkaline earths and transition metal and rare earth ions in solution are of great importance in chemistry and biochemistry, but such species have been difficult to produce in the gas phase. Since these ions exist in solution a method for their production in the gas phase is the "transfer" from solution to the gas phase, and such a "transfer" has become possible by means of electrospray.[2−4]

Doubly or multiply charged negative ions are obviously also of interest. Thus, the sulfate (SO_4^{2-}) and phosphate (HPO_4^{2-}) ions are of paramount importance in chemistry and biochemistry. The present work describes results for several anions deriving from sulfur−oxo acids, such as SO_4^{2-}, $S_2O_6^{2-}$, $S_2O_8^{2-}$, and other species. Observations of multiply charged negative ions obtained with electrospray are routinely reported in analytical mass spectrometric work. However, these ions are polymeric molecules which have many acidic functional groups, and the acidic groups are separated from each other by at least several carbon atoms. For example, electrospray mass spectra of 40-mer, deoxy nucleotides containing some 40 acidic units exhibit an envelope of multiply charged anions which peaks in the 20 negative charges region.[5] Obviously, these are systems in which the repulsive interactions of the charges are greatly reduced by the very large distances between the single, isolated charges.

The situation is very different for anions like SO_4^{2-} or HPO_4^{2-} where the two charges are localized on a much smaller entity. In fact, the question can be asked whether SO_4^{2-} is stable at room temperature with regard to thermal electron detachment (autodetachment) in the gas phase.

$$SO_4^{2-} = SO_4^{-} + e \qquad (1)$$

Thermal detachment at room temperature would be expected when the electron affinity of SO_4^- is positive but quite small (a few kilocalories per mole).[6,7] The electron affinity of SO_4^- even may be negative, *i.e.*, the SO_4^{2-} may be only a temporary ion state.[8]

Since SO_4^{2-} is a very stable species in protic solvents like water or methanol, it is expected that ion−solvent molecule clusters such as $SO_4^{2-}{\cdot}nH_2O$ will be stable in the gas phase, and if the value of n for which SO_4^{2-} remains stable is quite low, information on the electron affinity of SO_4^- and the binding energies of the solvent molecules to SO_4^{2-} could still be obtained by electron photodetachment methods,[9,10] ion−molecule equilbria measurements[11,12] and collision induced decomposition, (CID) threshold measurements.[13]

The present experimental results provide only qualitative information which is of interest in its own right. However, we do believe that the present results will also serve as stepping stones to quantitative measurements.[9−13]

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1994.

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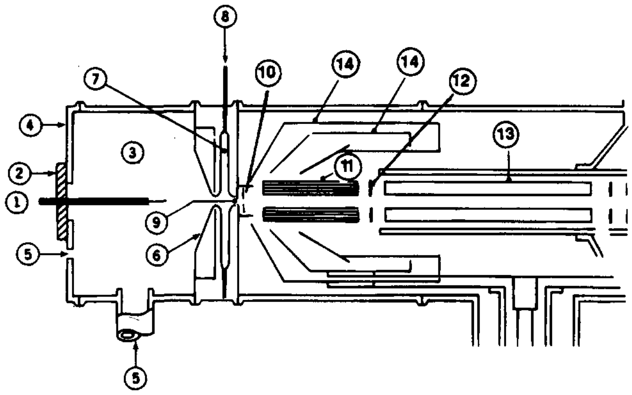

Figure 1. Front end of apparatus: (1) electrospray capillary movable via two-axis positioner (2); (3) electrospray chamber with ambient air at 1 atm; (4) plexiglass lid; (5) ports for air circulation; (6) interface plate; (7) interface chamber with interface gas; (8) interface gas entry; (9) orifice into vacuum 100 μm in diameter; (10) electrode; (11) AC quadrupole lens (Brubaker lens); (12) electrode; (13) first quadrupole Q1; (14) cryobaffles.

Experimental Section

The experiments were performed with ions produced by Electrospray. A triple quadrupole mass spectrometer,[14] SCIEX TAGA 6000 E, which can sample ions present in gases at atmospheric pressure, was used for detection of the ions and the CID experiments. The apparatus and procedure were described previously[1b] in some detail. Only a brief account will be given here.

The ions generated by the spray from the capillary (1, Figure 1) in ambient air, in the plenum chamber (3, Figure 1), drift, due to the applied electric field, into a conditioning chamber (the interface chamber, 7 in Figure 1). The ions entering the chamber are quite heavily clustered with solvent molecules. In the present case the molecules are methanol, due to the methanol solvent used for the electrospray and water due to the water vapor present in the ambient air. A partial exchange of methanol for water in the clusters occurs in the plenum chamber. Additional exchange and some declustering occur in the interface chamber which contains dry N_2 (~3 mTorr of H_2O).

A very weak electric field drifts the ions through the interface chamber and ions coming in the vicinity of an 100 μm diameter orifice (9, Figure 1) are entrained by the fast flow into the vacuum of the mass spectrometer.

It is possible to obtain a good ion signal with the mass spectrometer even when the potential drop between the orifice (9, Figure 1) and the subsequent electrodes: (10, 11, 12, Figure 1) is very low. Under these conditions, the ions do not experience CID due to collisions in this still relatively high gas density region. Under such *mild* conditions, the ions have thermal energies and the extent of clustering observed with the mass spectrometer is approximately equal to that present in the interface chamber. Such ions can be subjected to CID studies, when a collision gas (Ar) is supplied to the second quadrupole Q_2 operated in the AC only mode. The parent ions are mass selected with Q_1 while the CID products are detected with Q_3.

When larger potential drops are applied to electrodes 10–12 (Figure 1), CID occurs in the space between the orifice and the electrodes. Partial or complete declustering of the ions can be achieved in this stage. Ions obtained under such *harsh* conditions can then be subjected to conventional CID in Q_2.

Typical conditions for the generation of electrospray were the following: 10^{-4} mol/L solutions of the given salt in methanol, with ~1% water; flow rate through the electrospray capillary, 3 μL/min; distance of capillary tip to interface plate (6, Figure 1), 4 cm; potential of the capillary, 4 kV.

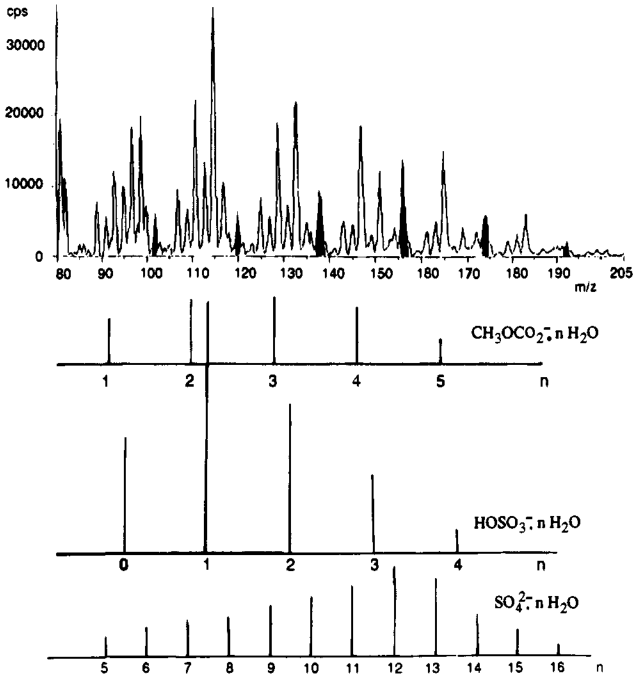

Figure 2. Ions observed with a 10^{-4} mol/L solution of Na_2SO_4 in methanol. Three major series of ions are present: $HSO_4^-\cdot nH_2O$, $SO_4^{2-}\cdot nH_2O$, and $CH_3OCO_2^-\cdot kH_2O$. The $CH_3OCO_2^-$ is due to a bicarbonate impurity, see text. The mass-to-charge ratio *m/z* for $CH_3OCO_2^-\cdot kH_2O$ is the same as that for $SO_4^{2-}\cdot nH_2O$ when *n* is odd. The $SO_4\cdot nH_2O$ peaks with *n* = even, which are free of overlap, are shown in black. The intensity distribution of these peaks is used to estimate the approximate contributions of $CH_3OCO_3^-\cdot kH_2O$and $SO_4^{2-}\cdot nH_2O$ where these peaks superimpose. Mass spectrum obtained under mild front end conditions.

Methanol rather than water was used as solvent since methanol is more easy to spray, due to its lower surface tension.[4]

Results and Discussion

(a) **The Sulfate Anion, SO_4^{2-}.** The ions observed when a 1 × 10^{-4} mol/L solution of Na_2SO_4 in methanol is electrosprayed are shown in Figure 2. Superficially the results appear complex, because a large number of ions are observed. However, most of the total ion intensity derives from three series of ions: $HSO_4^-\cdot nH_2O$, $SO_4^{2-}\cdot nH_2O$, and $CH_3OCO_2^-\cdot nH_2O$. The first two series are expected, considering the solution used. As explained in the Experimental Section, the predominantly methanol solvated clusters $HSO_4^-\cdot n$MeOH and $SO_4^{2-}\cdot n$MeOH that are formed by the electrospray process experience an exchange of methanol for H_2O in the atmospheric region between the ES capillary and the orifice leading to the vacuum of the mass spectrometer.

The identity and origin of the $CH_3OCO_2^-$ ion was traced to the presence of sodium carbonate impurities in the Na_2SO_4 salts used. When perdeuterated methanol was used, the $CH_3OCO_2^-$ derived peaks shifted up in mass by 3 units as expected for $CH_3OCO_2^-$. Furthermore, this series was not present when an acidic solution such as H_2SO_4 in methanol was used.

The SO_4^{2-} hydrates are easily spotted because, due to the double charge, they appear at *m/z* intervals of only 9 units.

The hydrate intensity distribution of the three ions, observed under the mild conditions used in the experiments, Figure 2, is also of interest. The doubly charged ion intensity reaches a maximum at a very much higher solvent number, *n* = 12, relative to *n* = 2 for $CH_3OCO_2^-$ and *n* = 1 for $HOSO_3^-$. This difference illustrates the very much higher solvation needs of the doubly charged ions. Comparing the $SO_4^{2-}\cdot nH_2O$ intensity

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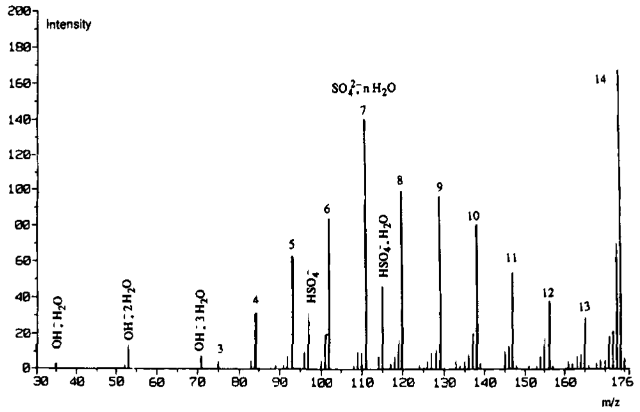

Figure 3. Mass spectrum showing daughter ions obtained from CID of $SO_4^{2-} \cdot 14H_2O$. Consecutive single H_2O loss leads to daughter hydrates $SO_4^{2-} \cdot kH_2O$ down to $k \approx 4$. At this point, charge separation reaction leading to HSO_4^- and OH^-, both of which may be hydrated, becomes dominant. The "stick" spectrum representation used in this figure results from ion counts collected only at nominal integral m/z masses. Because the resolution used in Q_3 was quite low, broadening of a high intensity peak can extend over adjacent nominally integral m/z values, see for example, $SO_4^{2-} \cdot 14H_2O$, $m/z = 174$, which extends over lower masses, $m/z = 173, 172, 171$.

envelope with that observed previously[1b] under very similar conditions for the doubly charged positive ions M^{2+}, one finds that the maximum for SO_4^{2-} at $n = 12$ is higher than that of $n = 9$ for Sr^{2+}, $n = 10$ for Ca^{2+}, and $n \geq 10$ for Mg^{2+}. It is also found that the SO_4^{2-} envelope spreads over a wider range of hydrates than was the case for the M^{2+} ions. Probably, this is due to the relatively strong HOH••O−S hydrogen bonding promoted by the electrostatic effect of the negative charge and the relatively large number of sites, 2, for each H bonded O atom, where a direct interaction can occur. The primary hydration shell of the SO_4^{2-} ion is expected to be much less crowded than is the case for the M^{2+} ions.

The observed intensities of the $SO_4^{2-} \cdot nH_2O$ ions are quite high, some 16 000 ion counts/s for $n = 12$. Beams of that intensity could be used for diverse measurements.[9−13]

The daughter ions observed on CID in Q_2, collision gas Ar, of the mass selected parent, $SO_4^{2-} \cdot 14H_2O$, are shown in Figure 3. The dominant CID products are due to H_2O loss:

$$SO_4^{2-} \cdot 14H_2O \xrightarrow{CID} SO_4^{2-} \cdot kH_2O + (14 - k)H_2O \qquad (2)$$

Observations of the relative cross sections for the product ions as a function of center of mass collision energy for this and other hydrates indicate that reaction 2 proceeds predominantly by consecutive single ligand (H_2O) loss. Thus, the $SO_4^{2-} \cdot 13H_2O$ product assembly contains ions which are highly internally excited and decompose unimolecularly to $SO_4^{2-} \cdot 12H_2O$, and these in turn decompose to $SO_4^{2-} \cdot 11H_2O$ and so on. The maximum at $k = 7$ in Figure 3 occurs at a point where the consecutive ligand loss begins to slow down. The position of the maximum depends on the average internal energy supplied to the parent ions by the collisions. The higher the energy is, the lower the value of k is.

The $SO_4^{2-} \cdot 14H_2O$ ions entering the collision cell were accelerated by 46 V, which for doubly charged ions of mass 348 D corresponds to a center of mass energy of 9.5 eV. The Ar collision gas pressure was $\sim 10^{-3}$ Torr for a collision cell length of 5 cm. For these conditions, the average doubly charged ions will have experienced one to two low impact parameter collisions, acquiring typical internal energies in the ~5−19 eV range (~115−440 kcal/mol). The water to ion bond energies are expected to be ~15 kcal/mol, per ligand, in the $SO_4^{2-} \cdot 14H_2O$−$SO_4^{2-} \cdot 8H_2O$ (outer shell solvation) range and to be rapidly increasing for the inner shell molecules.[1] The observed CID yields, Figure 3, are rougly consistent with these expectations.

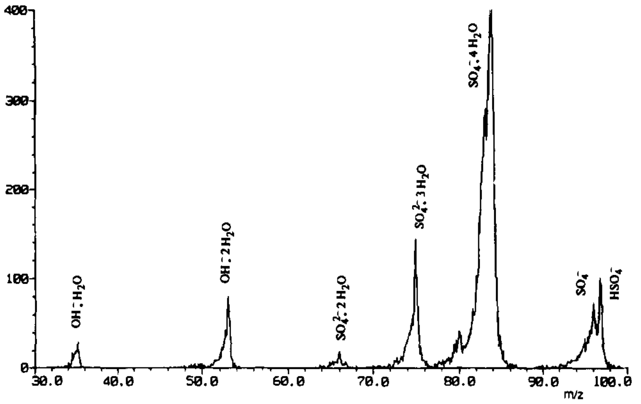

Figure 4. CID of $SO_4^{2-} \cdot 4H_2O$, giving additional information on the charge separation reaction. Ion at $m/z = 80$ is SO_3^-, probably formed by decomposition of vibrationally excited HSO_4^-. The ion at $m/z = 96$ is probably SO_4^-.

An additional reaction leading to $HOSO_4^-$ and OH^- is also observed in Figure 3. This reaction becomes dominant when parent ions, $SO_4^{2-} \cdot nH_2O$, with low n are subjected to CID, as shown in Figure 4. The parent ion, $SO_4^{2-} \cdot 4H_2O$, decomposes to $SO_4^{2-} \cdot 3H_2O$ but probably also undergoes the charge separation reaction:

$$SO_4^{2-} \cdot 14H_2O = HOSO_3^- \cdot H_2O + OH^- \cdot 2H_2O \qquad (3)$$

Only a very low intensity for the $SO_4^{2-} \cdot 2H_2O$ daughter ion is observed in Figure 4, which indicates that $SO_4^{2-} \cdot 3H_2O$ decomposes predominantly by the charge separation pathway.

The charge separation reaction, eq 3, and the analogous reaction involving $SO_4^{2-} \cdot 3H_2O$ can be viewed as intramolecular proton transfer reactions from HOH to SO_4^{2-}. In solution these reactions are strongly endoergic, *i.e.*, $HSO_{4(aq)}^-$ is a very much stronger acid than HOH, but the Coulombic repulsion in the clusters, which increases rapidly as the number of water molecules is decreased, makes the proton transfer become less endoergic than the H_2O ligand loss.

It is interesting to note in Figure 2 and 3 that of the two products of the charge separation $HOSO_3^-$ and OH^-, it is the hydroxide ion that is more hydrated. Note the virtual absence of $HOSO_3^- \cdot 2H_2O$ at $m/z = 133$ in Figure 3 while both $OH^- \cdot 2H_2O$ and $OH^- \cdot 3H_2O$ are observed. Energetically one expects the hydration of OH^- to be much more exothermic than that $HOSO_3^-$ of because the charge in $HOSO_3^-$ is delocalized over three oxygens. A similar situation was observed earlier for the OH^- and NO_3^- hydration,[15] where it was found that the dissociation of H_2O from $OH^- \cdot H_2O$ required 27 kcal/mol, while the dissociation of H_2O from $NO_3^- \cdot H_2O$ required only 12.4 kcal/mol. Evidently minimum energy requirements favor formation of highly hydrated OH^- in the charge separation reactions. One might consider that the minimum energy path should not be necessarily favored because the most stable form of the reactant, $SO_4^{2-} \cdot 4H_2O$, will have one H_2O on each of the SO_4 oxygens. To form a product like $OH^- \cdot 2H_2O$, three water molecules have to come together. It appears that the water molecules in the highly vibrationally excited $SO_4^{2-} \cdot 4H_2O$ are sufficiently mobile to be able to achieve this feat.

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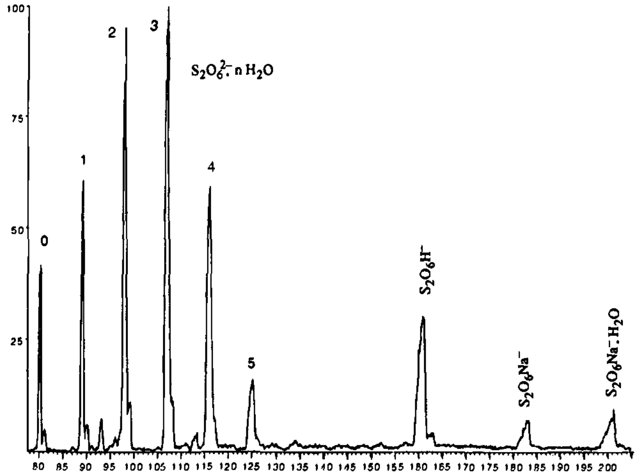


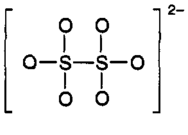
Figure 5. Mass spectrum of ions from electrospray of a 10^{-4} mol/L solution of $Na_2S_2O_6$. The relatively harsh front end conditions used have led to significant declustering (dehydration) of the ions. $S_2O_6^{2-}\cdot nH_2O$ with $n = 5$ to 0 are observed as the major ion series.

The ion of $m/z = 80$ observed in Figure 4 is SO_3^-. It probably originates from CID of $HOSO_3^-$. This is supported by experiments in which $HOSO_3^-$ was obtained under harsher front end conditions and subjected to CID in Q_2. The major product observed was SO_3^-, presumably due to the decomposition

$$\mathrm{HOSO_3^-} \xrightarrow{\mathrm{CID}} \mathrm{SO_3^-} + \mathrm{OH} \qquad (4)$$

The ion observed at $m/z = 96$, Figure 4, is probably SO_4^-. The reaction mechanism leading to this product is not clear. It is conceivable that some SO_4^{2-} is formed as a minor product from a complete dehydration of $SO_4^{2-}\cdot 4H_2O$ and then SO_4^- results by electron detachment from SO_4^{2-}. The observed intensity of SO_4^- is not much lower than that of the $HOSO_3^-$ product. The rather relatively large intensity of SO_4^- is surprising because the $SO_4^{2-}\cdot H_2O$ precursor of SO_4^{2-} is completely absent from the spectrum of Figure 4. A study of the energy threshold of the products observed in Figure 4 is presently underway and we hope to be able to report some more detailed information on the interesting thermochemistry of this reaction system.

(b) **The Dithionate, $S_2O_6^{2-}$, and the Dithionite, $S_2O_4^{2-}$, Anions.** The ions observed from a 10^{-4} mol/L solution of $Na_2S_2O_6$ are shown in Figure 5. The major species are due to the $S_2O_6^{2-}\cdot nH_2O$ series. The mass spectrum was obtained with a potential drop of 18 V between the orifice (9, Figure 1) and the first electrode (10, see Figure 1). CID in the region between the electrodes leads to partial declustering of $S_2O_6^{2-}\cdot nH_2O$. The observation of the "naked" $S_2O_6^{2-}$, whose structure[17] is



$$\left[\mathrm{O{-}\overset{\displaystyle O}{\underset{\displaystyle O}{S}}{-}\overset{\displaystyle O}{\underset{\displaystyle O}{S}}{-}O} \right]^{2-}$$

demonstrates that this anion is stable even in the complete absence of solvation. This was not the case for the SO_4^{2-} anion. The additional stability of the $S_2O_6^{2-}$ must be due to the ability of the charge to delocalize over a larger number of oxygen atoms which are also, on the average, at larger distances from each other than is the case for SO_4^{2-}.

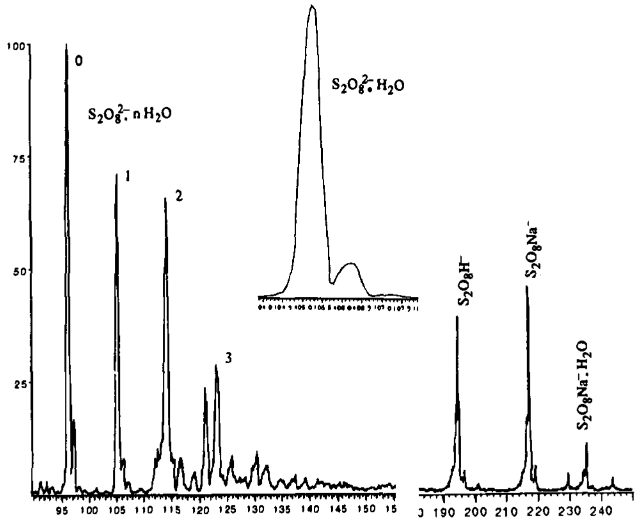


Figure 6. Mass spectrum of ions from electrospray of a 10^{-4} mol/L solution of $Na_2S_2O_8$. The relatively harsh front end conditions used have led to significant declustering (dehydration) of the ions. The major series observed is $S_2O_8^{2-}\cdot nH_2O$, with $n = 4$ to 0. The insert at the top gives details of the isotopic distribution of $S_2O_8^{2-}\cdot nH_2O$, which is quite different from that observed for $S_2O_8^{2-}$. The much larger $m/z = 97$ in that group reveals the presence of HSO_4^- at $m/z = 97$.

Also observed in Figure 5 is the $S_2O_6H^-$ ion, the $S_2O_6Na^-$ ions, and the $S_2O_6Na^-\cdot H_2O$ ion. The presence of these ions in the electrospray spectrum can be expected. It is of interest that the hydrate, $S_2O_6H^-\cdot H_2O$, is missing. This indicates that the bonding of H_2O to the negative ion is significantly weaker for $S_2O_6H^-$ relative to $S_2O_6Na^-$. Similar findings were made also for some of the other species such as $S_2O_8H^-$ and $S_2O_6Na^-$, see section c below, where a probable explanation is provided.

We were not able to observe the doubly charged dithionite, $S_2O_4^{2-}$, and also the singly charged $S_2O_4H^-$ ion from solutions of $Na_2S_2O_4$ in methanol. The only observed ions that could be identified were $CH_3OSO_2^-$ and HSO_4^-. Although the dithionite anion has been well characterized[16] in the crystalline state of its alkali salts, this ion is known to be relatively unstable in solutions because of the occurrence of disproportionation reactions as well as oxidation by air.[17] Our inability to observe dithionite ions in the gas phase is probably due to the intervention of such processes in solution.

(c) **The Peroxydisulfate $S_2O_8^{2-}$, and the Pyrodisulfate $S_2O_7^{2-}$, Anions.** The ions observed with a 10^{-4} mol/L solution of $Na_2S_2O_8$ in methanol are shown in Figure 6. The series $S_2O_8^{2-}\cdot nH_2O$ where $n = 0, 1, 2, 3, 4$ makes a dominant contribution to the total ion intensity. The peak at $m/z = 121$ should be to $S_2O_8^{2-}\cdot nH_2O\cdot CH_3OH$, and it is due to incomplete exchange of the methanol molecules with water molecules in the atmospheric region and the interface chamber, see Experimental Section.

Some of the $S_2O_8^{2-}\cdot nH_2O$ ions were mass selected with Q_1 and exposed to CID in Q_2. In all cases, a clean decomposition to lower $S_2O_8^{2-}$ clusters and ultimately to $S_2O_8^{2-}$ was observed. These experiments demonstrate that $S_2O_8^{2-}$ is relatively stable in the gas phase and is not prone to thermal electron detachment. This result was expected because the charge delocalization in $S_2O_8^{2-}$ onto the oxygens is more extensive than that for $S_2O_6^{2-}$, which was found in the previous section to be stable.

The mode of decomposition of $S_2O_8^{2-}$ exposed to CID in Q_2 was examined. Two major daughter ions were observed, at $m/z = 80$ and 112 at a ratio of ~3:1. These ions are probably

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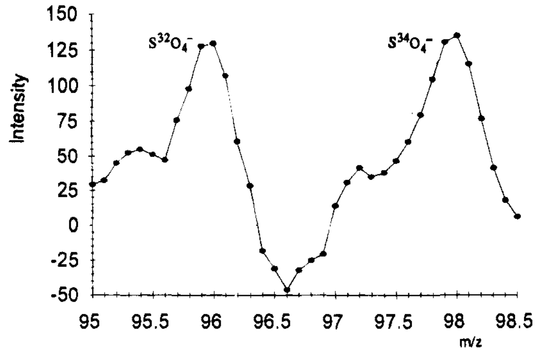
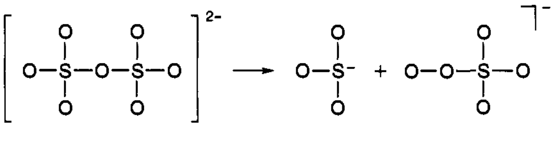


Figure 7. Ion intensities obtained from CID of *m/z* = 97 ions largely due to the $S^{32}S^{34}O_8^{2-}$ species. Peaks observed at *m/z* 96 and 98 are due to CID products $S^{32}O_4^-$ and $S^{34}O_4^-$.

SO_3^- and SO_5^-. The formation of these products suggests the fragmentation path



$$\left[\mathrm{O{-}\overset{O}{\underset{O}{S}}{-}O{-}\overset{O}{\underset{O}{S}}{-}O}\right]^{2-} \longrightarrow \mathrm{O{-}\overset{O}{\underset{O}{S}}^{-}} + \left[\mathrm{O{-}O{-}\overset{O}{\underset{O}{S}}{-}O}\right]^{-} \qquad (5)$$

which is followed by some fragmentation of the SO_5^-:

$$SO_5^- \rightarrow SO_3^- + O_2 \qquad (6)$$

It may be noted that the peroxo bisulfate anion, HSO_5^-, is known[17] to exist in the condensed phase, *e.g.*, in salts like $KHSO_5$. The SO_5^- species detected in the present work may be viewed as a peroxo sulfate anion, SO_5^{2-}, that has detached one electron.

Another possible fragmentation pathway of $S_2O_8^{2-}$ is the cleavage of the central, peroxy O–O bond:

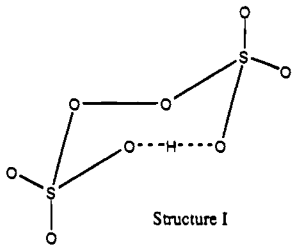
$$S_2O_8^{2-} \rightarrow 2SO_4^- \qquad (7)$$

The SO_4^- products can be easily missed, since the major ^{32}S isotopic components of $S_2O_8^{2-}$ and SO_4^- have the same *m/z* = 96. The possible occurrence of reaction 7 should be detectable on the basis of the isotopic intensities in the *m/z* (96, 97, 98) region.

The two species have the following predicted intensity patterns: SO_4^- (100, 0.74, 4.4); $S_2O_8^{2-}$ (100, 10, 0.2) (based on the natural abundances: ^{32}S, 0.95; ^{33}S, 0.007; ^{34}S, 0.042 and ^{16}O, 0.998; ^{18}O, 0.002). The *m/z* = 97 ion from $S_2O_8^{2-}$ is mostly due to the $S^{32}S^{34}O_8^{16}$ species. CID of this ion should lead to two products: $S^{32}O_4^{16}$, at *m/z* = 96, and $S^{34}O_4^{16}$, at *m/z* = 98, if reaction 7 is occurring. Experiments in which *m/z* = 97 was selected with Q_1 and exposed to CID in Q_2 led to the results shown in Figure 7. The two ion peaks at *m/z* = 96 and 98 were obtained from the ion intensities at *m/z* = 96, 97, 98 observed with Q_3, where the ion intensities detected with the collision gas absent were subtracted from those with the collision gas present. The intensity at *m/z* = 97 was normalized to equal height in the two groups before the subtraction. Both *m/z* = 96 and 98 in Figure 7 have a distorted peak shape which tails to lower mass. A similar shape also was present for the parent ion and is of instrumental origin. The results in Figure 7 were obtained by signal averaging over 50 mass scans. Two other such measurements reproduced well the essentail features seen in Figure 7. Therefore the observed equal intensity product peaks at *m/z* 96 and 98 in Figure 7 can be considered to provide good evidence for the decomposition of $S_2O_8^{2-}$ to two SO_4^- ions.

It should be noted that the *m/z* = 97 ion used in the above experiment did not consist entirely of the $S^{32}S^{34}O_8^{2-}$ ion. This is indicated by the ion abundances for *m/z* = 96, 97, 98 in Figure 6. The intensities observed are (100, 17, 1.2) while those predicted for $S_2O_8^{2-}$, see above, are (100, 10, 0.2). The observed intensities for $S_2O_8^{2-}\cdot H_2O$ (100, 12, 1.2), see insert in Figure 6, are much closer to the expected pattern. The excess intensity at *m/z* = 97 in the $S_2O_8^{2-}$ spectrum is most likely due to the HSO_4^- ion. This ion was observed in the studies of the sulfate ion, see section a above, and is probably observed here because of a sulfate impurity in the $Na_2S_2O_8$ used. The CID of HSO_4^- was shown to lead to SO_3^- and OH. Therefore, the presence of this species at *m/z* = 97 should not have interfered with the proof for the occurrence of reaction 7, see Figure 7.

Spectra obtained with $Na_2S_2O_8$ solution and $K_2S_2O_8$ solution showed the presence of a hydrate for the ions $NaS_2O_8^-\cdot H_2O$ and $KS_2O_8^-\cdot H_2O$ only but not for the $HS_2O_8^-$ species, see Figure 6. The observed difference in the tendency to form a hydrate, indicates that $HS_2O_8^-$ is cyclized due to the formation of a strong intramolecular hydrogen bond as shown in structure **I**.



Structure I

Structure **I** is nonplanar and similar to the boat conformation of cyclohexane. It is based on the fact that the SO_4 conformations in $S_2O_8^{2-}$ are essentially tetrahedral.[17] For structure I to be undistorted, the hydrogen O···H···O bond must be of a length that is similar to the peroxy O–O bond length. The hydrogen bond could be expected to be longer, but not very much so, because the presence of negative charge will lead to a strong hydrogen bond. The hydrogen bond formation will reduce the negative charge density on the remaining four oxygens and thus reduce the tendency of $HS_2O_8^-$ to hydrate. On the other hand, because the $NaS_2O_8^-$ and $KS_2O_8^-$ cannot form stable cyclic structures, the negative charge density on the oxygens will be high and promote hydration.

Solutions of the pyrodisulfate anion, $S_2O_7^{2-}$ (10^{-4} mol/L), $K_2S_2O_7$ or $Na_2S_2O_7$, were subjected to electrospray. The ions detected did not include the $S_2O_7^{2-}$ ion or its hydrates. The observed spectra were very similar to those obtained with Na_2SO_4 in methanol. The pyrodisulfate ion is known to undergo rapid hydrolysis (halflife ~2 min) in aqueous solution.[18]

$$SO_3{-}O{-}SO_3^{2-} + H_2O = 2HOSO_3^- \qquad (8)$$

Evidently hydrolysis was occurring also in the not completely dry (reagent grade) methanol solution used in the present experiments. Attempts were made to suppress the hydrolysis by using dry acetonitrile solutions and dried air in the electrospray chamber. However, the ions obtained did not contain the pyrodisulfate species. The major ions were HO_4^-, $HSO_4^-\cdot CH_3CN$, $HSO_4^-\cdot H_2SO_4$, and $CH_3SO_4^-\cdot H_2SO_4$. The same ions were obtained also from a solution of Na_2SO_4 in acetonitrile. These results show that the conditions used were not sufficiently dry to suppress the hydrolysis, eq 8.

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[18] Hofmeister, H. K.; van Wazer, J. R. *Inorg. Chem.* **1962**, *1*, 811.

Conclusions

A number of interesting ion species were observed for the first time in the gas phase. These include the doubly charged ions $SO_4^{2-}{\cdot}nH_2O$, $S_2O_6^{2-}{\cdot}nH_2O$, and $S_2O_8^{2-}{\cdot}nH_2O$ and the singly charged ions SO_4^- and SO_5^-.

The $SO_4^{2-}{\cdot}nH_2O$ ion could be desolvated down to $n \approx 3$. At this and lower n, the intramolecular proton transfer from HOH to SO_4^{2-} leading to formation of $HOSO_3^-$ and OH^- became dominant. The "naked" SO_4^{2-} ion could not be observed. The hydrates of $S_2O_6^{2-}$ and $S_2O_8^{2-}$ could be decomposed down to the "naked" ions. The above results demonstrate that $S_2O_6^{2-}$ and $S_2O_8^{2-}$ are stable in the gas phase. On the other hand, SO_4^{2-} may not be stable.

The SO_4^- and SO_5^- species were obtained by CID from the peroxidisulfate ion $S_2O_8^{2-}$. They may be viewed as a sulfate and a peroxysulfate dianion that have lost one electron.

The gas-phase ions observed with electrospray and sampled under mild front end conditions correspond quite closely to the species expected to be present in solution. The absence of given ions from the mass spectrum can indicate the removal of these ions by reactions in the solution. The two instances where gas phase ions were not observed in the present work—dithionites, ($S_2O_4^{2-}$) and pyrodisulfate ($S_2O_7^{2-}$)—correspond to cases where the dianion species are known to react rapidly in the solution.