Dissociation pathways of sulfur dioxide clusters and mixed sulfur dioxide-water clusters

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Abstract

A reflectron-time-of-flight mass spectrometer (RTOFMS) coupled with a femtosecond multiphoton ionization technique is used to study the combined metastable and collision-induced dissociation of sulfur dioxide clusters and mixed sulfur dioxide-water clusters. From the dissociation patterns, the general structural arrangement of the clusters is clearly identified: $(SO_2)_m^{\cdot+}$ clusters have a $SO_2^{\cdot+}$ core solvated by SO_2 molecules; $[SO(SO_2)_n]^{\cdot+}$ and $[S(SO_2)_{n+1}]^{\cdot+}$ have a structure of $SO^{\cdot+} \cdot (SO_2)_n$ and $(SO)_2^{\cdot+} \cdot (SO_2)_n$, respectively. For $[HSO_2(SO_2)]^+$ clusters, the ion core is HSO_2^+. $H_3SO_3^+$ appears to have two isomeric structures: one $HSO_2^+ \cdot H_2O$, the other $H_3O^+ \cdot SO_2$. (Int J Mass Spectrom 185/186/187 (1999) 905–911) © 1999 Elsevier Science B.V.

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1. Introduction

Cluster science has flourished since the advent of laser and molecular beam techniques. Indeed, studies of the properties, reactivity, and structure of molecular clusters contribute greatly to our understanding of reaction dynamics at the molecular level [1]. Many cluster systems have been well studied, both experimentally and theoretically [1–3]. Among those, the sulfur-containing compounds [4], and the interaction between acid gases [5–9] (e.g. NO_2, NO, SO_2, etc.) and water has been of particular interest because of their importance in atmospheric chemistry.

Acid rain is one of the biggest ecological problems facing the world today [8]. One major component of acid rain is sulfuric acid. As we know, SO_2, coming from the combustion of sulfur-containing fossil fuels, can be oxidized to form sulfuric acid after being incorporated into the cloud water. Only a few studies have been performed on sulfur dioxide-water clusters. Castleman and Kay [10] studied the polarity of $(SO_2)_m(H_2O)_n$ clusters by an electric deflection method and concluded that $(SO_2)_m(H_2O)_n$ clusters are nonpolar except for the $m = n = 1$ species. Le Duc Vacher and Fitaire [9] used a quadrupole mass spectrometer to study the stability of the mixed anionic sulfur dioxide-water clusters, and found that substitution of a sulfur dioxide molecule by a water molecule in $SO_2^- (SO_2)_m(H_2O)_n$ clusters for a rank $r = m + n$ is always stabilizing. Vincent et al. [8] investigated the mechanism of the oxidation of sulfur dioxide by hydrogen peroxide in water clusters by an ab initio

method, and found that the large reaction barrier for the bimolecular reactions of sulfur dioxide and hydrogen peroxide is considerably reduced upon the inclusion of catalytic water molecules, which provide a proton shuttle mechanism [11] to facilitate the reaction. In order to further an understanding of the interactions between sulfur dioxide and water, we studied the structure and the dissociation dynamics of sulfur dioxide clusters and mixed sulfur dioxide-water clusters with our RTOFMS, using a cut-off method [12].

2. Experimental methods

The RTOFMS, combined with a supersonic molecular beam and a femtosecond laser ionization technique is used in this experiment. Briefly, pure neutral sulfur dioxide clusters are generated by expanding a sample gas containing 20% SO_2 in Ar at a total stagnation pressure of about three atmospheres, through a pulsed nozzle with a 150 μm diameter orifice. The mixed sulfur dioxide-water clusters are generated by crossing the neutral sulfur dioxide clusters with an effusive water vapor beam, which comes from a pick-up source [13]. The pick-up source has four concentric orifices, each with an opening of 250 μm in diameter. The pick-up gas beam crosses the supersonic cluster beam at an angle of 30° at 1.5–2 cm downstream from the pulsed nozzle. In order to get larger water clusters, the pick-up source is heated to obtain higher water vapor pressure, and the flow of the water vapor is controlled by a precision needle valve.

The resulting clusters are ionized by a femtosecond laser beam with a wavelength centered around 400 nm. The laser system consists of a mode-locked Ti:sapphire laser pumped by a CW argon ion laser, which generates a 82 MHz pulse train, centered at 800 nm, with a pulse duration of approximately 60 fs and a pulse energy of about 8 nJ. The pulses are amplified by a regenerative Ti:sapphire amplifier pumped by the second harmonic output of a 10 Hz Nd:YAG laser. After amplification, the laser beam is frequency doubled with a potassium dihydrogen phosphate (KDP) crystal. The femtosecond laser beam is focused by a

40 cm focal lens before entering the center ionization chamber. Details can be found in previous publications [13,14].

Using a high flux (10^{26} photons per second) femtosecond laser, the multiphoton absorption occurs within the femtosecond pulse duration so that the dissociation of intermediate states is dramatically decreased; therefore ionization is much more efficient and involves considerably less fragmentation than in the case of nanosecond nonresonant multiphoton ionization. During the ionization event, because of the extensive heating by the laser beam, the ionized clusters are left with a significant amount of excess energy; consequently extensive evaporation occurs, resulting in cooler clusters. After the excess energy in the cluster ions is removed by evaporation, and the remaining energy is partitioned among the internal cluster modes, the cluster ions can survive long enough to enter the field-free region where their ensuing metastable fragmentations can be observed under collisionless conditions. When the vacuum chamber is operated at a higher pressure, collision-induced dissociation can be observed as well as the metastable dissociation.

3. Results and discussion

3.1. Sulfur dioxide clusters

Fig. 1(a) shows a typical mass distribution of sulfur dioxide clusters using the femtosecond ionization technique. When the nozzle is running, the ionization chamber is at a pressure of approximately $3 \sim 4 \times 10^{-6}$ Torr. The pressure of the field-free region and the detection chamber is at around 1×10^{-6} Torr. Sulfur has four naturally occurring isotopes, with ^{32}S and ^{34}S having abundance of 95.0% and 4.2%, respectively. Because of the mass overlap of two ^{16}O atoms with one ^{32}S atom, the peaks involving ^{34}S isotope are used in identifying the number of the sulfur atoms contained in one species.

As can be seen in Fig. 1(a), besides intense intact $(SO_2)_n^{\cdot+}$ clusters, $[SO(SO_2)_n]^{\cdot+}$ clusters and $[S(SO_2)_n]^{\cdot+}$ clusters also have very strong intensities.
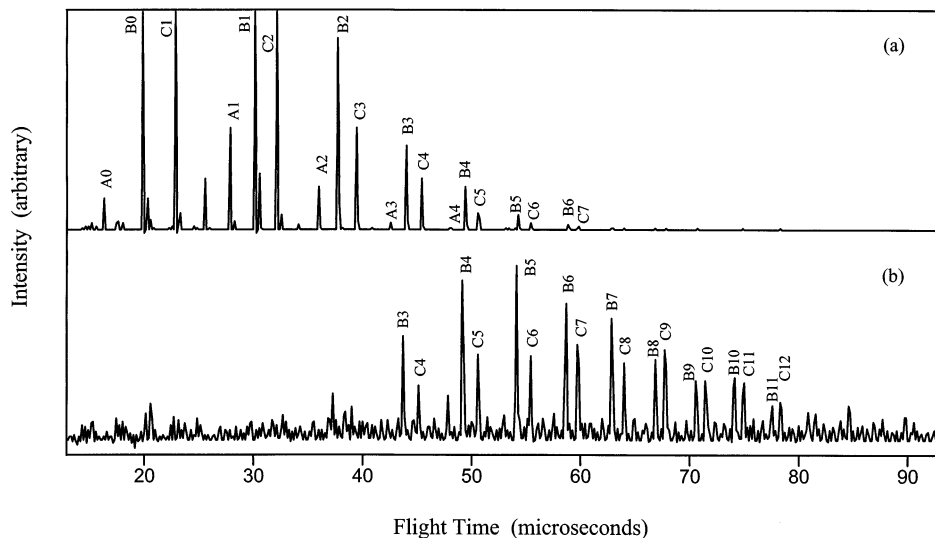
Fig. 1. (a) Mass spectrum of parent sulfur dioxide cluster ions. *The birth potential of the parent ions is 4460 V, the voltage setting on the reflectron is at 5100 V.* (b) Mass spectrum of daughter sulfur dioxide cluster ions. *The voltage setting on the reflectron is at 4420 V.* A: $[S(SO_2)_m]^{\cdot +}$ clusters, $m = 0, 1, 2, \ldots$; B: $[SO(SO_2)_n]^{\cdot +}$ clusters, $n = 0, 1, 2, \ldots$; C: $(SO_2)_x^{\cdot +}$ clusters, $x = 1, 2, 3, \ldots$. The two traces are not on the same scale.

Notice the intensity of the $[SO(SO_2)_n]^{\cdot +}$ clusters is stronger than that of the $(SO_2)_n^{\cdot +}$ clusters. From a previous high-resolution photoionization study of SO_2 and $(SO_2)_2$ dimer done by Erikson and Ng [15], $SO^{\cdot +}$ is shown to form readily from the predissociation of SO_2^+ on excited ionic states. A binding energy of 0.66 eV for $SO_2^{\cdot +} \cdot SO_2$ and 0.60 eV for $SO^{\cdot +} \cdot SO_2$ have been obtained from the appearance energies of $SO^{\cdot +}$, $SO_2^{\cdot +}$, $SO_2^{\cdot +} \cdot SO_2$, and $SO^{\cdot +} \cdot SO_2$ from neutral SO_2 dimer [15]. The ground state dissociation energy of $SO_2^{\cdot +}$ into $SO^{\cdot +}$ and O is 3.61 eV, and the dissociation of $SO^{\cdot +}$ into $S^{\cdot +}$ and O is endothermic by 5.43 eV based on a calculational result [16]. Because the binding strength of solvent SO_2 molecules with the core ions in $[SO(SO_2)_n]^{\cdot +}$ and $(SO_2)_n^{\cdot +}$ cluster ions are rather similar, the key to greater intensity of the observed $[SO(SO_2)_n]^{\cdot +}$ signal is probably because the higher dissociation energy of the core $SO^{\cdot +}$ ion, compared to the $SO_2^{\cdot +}$ ion.

Fig. 1(b) shows a daughter mass spectrum obtained under the condition that the reflectron voltage is set lower than the birth potential of the parent cluster ions. In this case, all the parent ions penetrate through

the reflectron instead of being reflected toward the MCP detector, while the daughter ions are reflected and detected. As can be seen, there are two dominant daughter ion series: one comes from the $(SO_2)_n^{\cdot +}$ cluster ions; the other from the $[SO(SO_2)_n]^{\cdot +}$ cluster ions. In general, the decay fraction of the two cluster series increases with the cluster size. Because of the low intensity, no fragmentation channels have been observed for the $[S(SO_2)_n]^{\cdot +}$ cluster ion series. For small cluster ions ($n < 3$), because of fewer cluster modes to accommodate the internal excitation energy, they don't go through spontaneous metastable dissociations within our experimental observation time window.

When the vacuum chamber pressure is raised (because of the opening of the pick-up source), the probability of collision-induced dissociation increases. Thus, some clusters experience collision-induced dissociation before and after entering the field-free region. Under this condition, fragments of the small cluster sizes are also observed. Fig. 2(b) is a daughter mass spectrum taken when the pick-up source is open. The center ionization chamber has a pressure of around 5×10^{-5} Torr, and the field-free
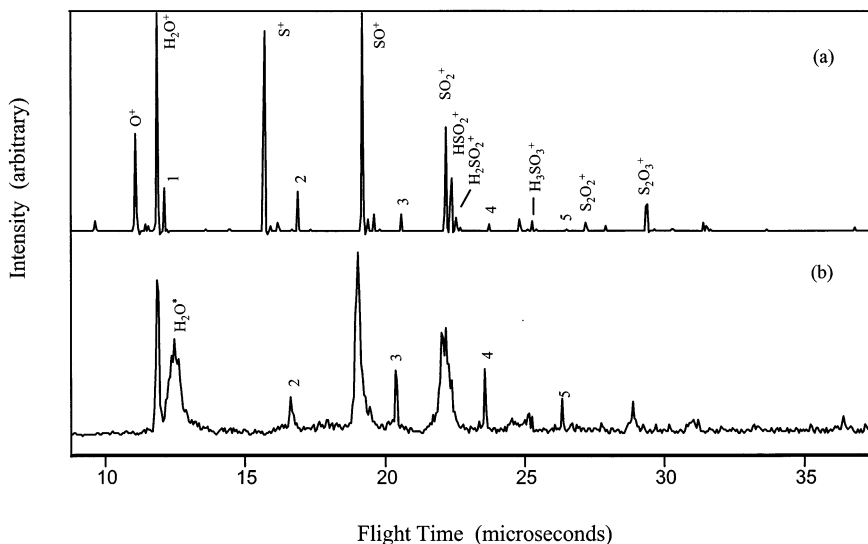
Fig. 2. (a) Mass spectrum of mixed sulfur dioxide-water parent cluster ions. *The birth potential of the parent ions is 4630 V, the voltage setting on the reflectron is 4700 V.* (b) Mass spectrum of mixed sulfur dioxide-water daughter cluster ions. *The voltage setting on the reflectron is at 4400 V.* The numbered peaks are pure water clusters $H^+(H_2O)_z$, $z = 1, 2, 3, \ldots$. The two traces are not on the same scale.

region and the detection chamber has a pressure of approximately 6×10^{-6} Torr. Notice, as expected, the daughter ions of $SO^{\cdot+}$ and $SO_2^{\cdot+}$ have much broader peaks than other cluster ions, because the binding energy of the $SO^{\cdot+}$ ion and the $SO_2^{\cdot+}$ ion is at least one order of magnitude higher than that of the van der Waals bonded clusters (e.g. $(SO_2)_n^{\cdot+}$) or the hydrogen bonded clusters (e.g. $(H_2O)_n H^+$). As is well established by previous studies, the degree of peak broadening of the fragments in the TOF mass spectrum often reflects the amount of kinetic energy released during the dissociation processes [17–19].

From the time overlap and the cut-off voltages [12], the metastable fragments can be identified. The intact $(SO_2)_{n \geq 2}^{\cdot+}$ cluster ions lose a neutral SO_2 molecule, indicating that they have a structure of a SO_2^+ ion core solvated by loosely bound SO_2 molecules. For the smallest cluster ion in this series, the $SO_2^{\cdot+}$ monomer, two fragmentation channels are observed. The primary decay channel is an O atom loss, and the secondary channel is an O_2 loss. This agrees with the previous observation [15] that O loss and O_2 loss are the two lowest photodissociation channels for the $SO_2^{\cdot+}$ ion.

The $[SO(SO_2)_{n \geq 1}]^{\cdot+}$ clusters all lose a neutral SO_2 molecule, down to cluster size $n = 1$, indicating that the charge carrier in this series is the $SO^{\cdot+}$ ion. The bare core ion $SO^{\cdot+}$ loses an O unit in the collision-induced dissociation process, as expected, because neutral O atom loss is the lowest exit channel for the $SO^{\cdot+}$ ion [16].

$S_2O_2^{\cdot+}$ ion did not show any observable dissociation fragment under both collision and collisionless conditions, which is somewhat surprising. Snodgrass et al. [16] studied the photodissociation dynamics of the $S_2O_2^{\cdot+}$ ion, and found out that $S_2O_2^{\cdot+}$ has two isomeric structures. One is the $(S \cdot SO_2)^{\cdot+}$ structure, and the other the more stable $(SO)_2^{\cdot+}$ structure. Our data strongly suggest that the $S_2O_2^{\cdot+}$ ion should have the tightly bound $(SO)_2^{\cdot+}$ structure rather than the loosely bound $(S \cdot SO_2)^{\cdot+}$ structure, because the loosely bound $(S \cdot SO_2)^{\cdot+}$ complex, having a low dissociation energy, would dissociate readily under our collision-induced dissociation conditions. Because of the stability of the $(SO)_2^{\cdot+}$ ion, it is concluded that all the large $[S(SO_2)_{n \geq 2}]^{\cdot+}$ clusters probably have an ion core of the $(SO)_2^{\cdot+}$ ion, not the $S^{\cdot+}$ ion.

Table 1
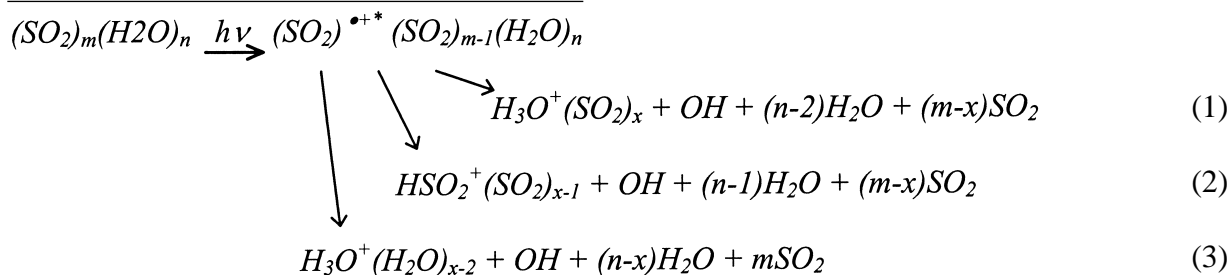Dissociation fragments of sulfur dioxide clusters and mixed sulfur dioxide-water clusters.

Parent ions	Ionic fragment	Neural loss
$SO^{\cdot+}$	$S^{\cdot+}$	O
SO_2^+	$SO^{\cdot+}$, $S^{\cdot+}$ (minor)	O, O_2
$SO_3^{\cdot+}$	$SO^{\cdot+}$	O_2
$S_2O_2^+$	*not observed*	
$(SO_2)_n^{\cdot+}$ $n > 1$	$(SO_2)_{n-1}^{\cdot+}$	SO_2
$[SO(SO_2)_y]^{\cdot+}$ $y \geq 1$	$[SO(SO_2)_{y-1}]^{\cdot+}$	SO_2
H_2O	OH^+	H
HSO_2^+	$SO^{\cdot+}$	H_2O
$H_3SO_3^+$	HSO_2^+, H_3O^+	H_2O, SO_2
$[H(SO_2)_n]^+$ $n > 1$	$[H(SO_2)_{n-1}]^+$	SO_2
$[HSO_2(SO_2)_y]^+$ $y \geq 1$	$[HSO_2(SO_2)_{y-1}]^+$	SO_2
$H_3O^+(H_2O)_n$ $n \geq 1$	$H_3O^+(H_2O)_n$	H_2O

The dissociation channels discussed earlier are listed in Table 1.

3.2. Mixed sulfur dioxide-water clusters

The mixed sulfur dioxide-water clusters are formed by expanding the SO_2/Ar gas through the pulsed nozzle and the water vapor through the pick-up source. The pick-up source is heated to above 50 °C,

mixed clusters. Besides the $(SO_2)_n^{\cdot+}$ clusters, the mixed $[SO(SO_2)_n]^{\cdot+}$ and $[S(SO_2)_n]^{\cdot+}$ clusters are observed as in the pure SO_2/Ar expansion case; some additional peaks, like $[H(SO_2)_n]^+$, $[H(H_2O)(SO_2)_n]^+$, and the $H_3O^+(H_2O)_n$ cluster ion series are also observed. The photon absorption cross section of the SO_2 molecule is much higher than that of the H_2O molecule for 400 nm radiation [20,21]. Here the SO_2 molecule functions as the chromophore that absorbs the photon energy and gets ionized. The ionization energies for SO_2 [15] and H_2O [22] are 12.60 eV and 12.74 eV, respectively. The close value of the ionization energy of the two molecules leads to efficient charge transfer between SO_2^+ and H_2O. Because of the high proton affinity of both sulfur dioxide (7.01 eV) and water (7.22 eV) molecules [23], protonation reactions always accompany charge transfer and dominate over other fragmentation channels. A similar reaction has been observed in a drift tube study by Rakshit and Warneck [24], in which a proton transfer between $H_2O^{\cdot+}$ and SO_2 occurs, producing HSO_2^+ and OH with unit efficiency. The mixed cluster ions observed here are generated as follows:

$$(SO_2)_m(H_2O)_n \xrightarrow{h\nu} (SO_2)^{\bullet+*}(SO_2)_{m-1}(H_2O)_n$$

$$H_3O^+(SO_2)_x + OH + (n-2)H_2O + (m-x)SO_2 \tag{1}$$

$$HSO_2^+(SO_2)_{x-1} + OH + (n-1)H_2O + (m-x)SO_2 \tag{2}$$

$$H_3O^+(H_2O)_{x-2} + OH + (n-x)H_2O + mSO_2 \tag{3}$$

and the center ionization chamber pressure is controlled to be $\sim 5 \times 10^{-5}$ Torr. The neutral sulfur dioxide-water clusters are formed through "pick-up" reactions, in which, by colliding with the sulfur dioxide clusters, the water molecules replace one or more of the sulfur dioxide molecules. Because of the high center vacuum chamber pressure, clusters also experience collisions with surrounding backing gases before and after the ionization event.

Fig. 2(a) shows a typical mass spectrum of the

Fig. 2(b) shows the daughter mass spectrum taken under the same conditions as that of Fig. 2(a) except that the reflectron voltage is set lower than the birth potential of the parent ions. Because the water line and the pick-up source are heated to above 50 °C, but the lens optics are at room temperature, there is some water condensation on the lens optics, including the meshes mounted on the second TOF lens and the ground TOF lens. The condensed water on the mesh can be ionized by ions passing in close proximity. The

peak marked H_2O^* in Fig. 2(b) comes from the ionization of the water molecules condensed on the mesh of the second TOF lens, as confirmed by determining the flight times and also the birth potentials. There should be some ionization of the water condensed on the mesh of the ground TOF lens as well, but because of the low kinetic energy gained, the water molecules ionized by this mechanism cannot be detected in the current TOF set-up.

As shown in Table 1, from the cut-off and time overlap results, it is found that protonated water clusters lose a water molecule as their primary dissociation channel, which agrees with previous investigations [25]. Protonated sulfur dioxide clusters lose a sulfur dioxide molecule, indicating that protonated SO_2 forms the ion core. $H_3SO_3^+$, which originates through the channel shown in Eq. (1), has two dissociation channels, one is a SO_2 loss, the other is an H_2O loss, as follows:

$$H_3SO_3^+ \longrightarrow H_3O^+ + SO_2 \qquad (4)$$
$$\searrow HSO_2^+ + H_2O \qquad (5)$$
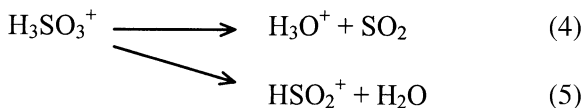
Because the proton affinity of water and sulfur dioxide are fairly close, protonation of SO_2 and H_2O are both favored. This indicates that two stable isomers could exist for $H_3SO_3^+$ ion: one $H_2OH^+ \cdot SO_2$, the other $SO_2H^+ \cdot H_2O$. The proposed structures are in agreement with the observed dissociation channels of the $H_3SO_3^+$ ion shown above.

4. Conclusion

Because of the intracluster ion-molecule reactions of sulfur dioxide-water clusters, different cluster species are formed, including the pure protonated water clusters, the protonated sulfur dioxide clusters, and the mixed protonated water-sulfur dioxide clusters. Because of the high proton affinity of both the sulfur dioxide and the water molecules, all mixed cluster ions are protonated species.

The structure and bonding of these clusters are studied by metastable dissociation and collision-induced dissociation. Experimental findings indicate that the $(SO_2)_m^{\cdot+}$ clusters have a structure of an SO_2^+ ion core solvated by SO_2 molecules; the $[SO(SO_2)_n]^{\cdot+}$ clusters have an $SO^{\cdot+}$ ion core, solvated by SO_2 molecules; the $[S(SO_2)_n]^{\cdot+}$ clusters have a structure of $(SO)_2^{\cdot+} \cdot (SO_2)_m$. For the $[HSO_2(SO_2)]^+$ clusters, the ion core is the protonated SO_2. The findings suggest that the $H_3SO_3^+$ cluster probably has two isomeric structures, one is $OSOH^+ \cdot OH_2$, the other is $H_2OH^+ \cdot OSO$.

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