

# Dissociation of multiply ionized carbonyl sulfide due to electron impact

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The dissociation of singly to triply ionized carbonyl sulfide has been studied through electron impact ionization at an electron energy of 200 eV. Two- and three-dimensional covariance mapping techniques are used, accompanied by a focusing time-of-flight mass spectrometer. The absolute cross sections for the various dissociation channels of up to triply ionized carbonyl sulfide (OCS) have been obtained. The unstable OCS dications dissociate mostly into ion pairs, while the OCS trications dissociate into ion triple or ion pair with comparable probabilities. The total single ionization cross section agrees with the result of the binary-encounter-Bethe method. A metastable decay trace corresponding to  $\text{OCS}^{2+} \rightarrow \text{CO}^+ + \text{S}^+$  is observed on the covariance map.

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## I. INTRODUCTION

Multiply ionized molecules exist in some physically important processes such as photoionization, electron impact ionization, neutral beam collision, and ion beam collision. In many cases these ions are abundant and contribute substantially to the final ionic products (see, for example, Refs. 1–4). Most of these multiply ionized molecules are transient and dissociate through various pathways. The dissociation of multiply ionized molecules is interesting in the research areas such as plasma physics and planetary atmospheric chemistry.<sup>5–7</sup> The dissociation dynamics of these ions contain valuable information on the electronic states and potential energy surfaces of the parent ions. The investigation on the dissociation of multiply ionized molecules requires one to distinguish different dissociation pathways through a coincidence method, such as photoion–photoion coincidence (PIPICO),<sup>8</sup> photoelectron–photoion–photoion coincidence (PEPIPICO),<sup>9</sup> position-sensitive photoelectron–photoion–photoion coincidence (PSD-PEPIPICO),<sup>10</sup> three-ion coincidence,<sup>3</sup> and covariance mapping.<sup>11</sup>

Carbonyl sulfide (OCS) is an important molecule that contributes to our global atmospheric sulfur cycling. It also exists in the atmospheres of other planets and is astrophysically interesting.<sup>12</sup> The dissociation of OCS ions has been extensively studied through photoionization. Masuoka *et al.* studied the dissociation of OCS ions using synchrotron radiation.<sup>2,13–15</sup> Eland and co-workers investigated the dissociation dynamics of OCS ions using atomic discharge lamps.<sup>10,16,17</sup> Busch *et al.* studied the dissociation of core-electron excited OCS using synchrotron radiation.<sup>4,18,19</sup> Compared to photoionization, the work on electron impact ionization of OCS is rather limited. Early works<sup>20,21</sup> reported on the appearance potentials and the ion kinetic energies. Hagan and Eland showed a three-ion coincidence mass spectrum at high energies.<sup>3</sup> The cross sections of electron impact

ionization are currently urgently needed in the areas such as plasma modeling in semiconductor manufacturing.<sup>22,23</sup> We have recently studied the dissociation of multiply ionized CO,<sup>24</sup> CO<sub>2</sub>,<sup>25</sup> C<sub>3</sub>H<sub>8</sub>,<sup>26</sup> and other alkanes<sup>27</sup> through electron impact ionization, which reveals a wealth of new information on these molecules.

In this paper we report the dissociation of OCS after single, double, and triple ionization using electron impact at 200 eV, probed by two- and three-dimensional covariance mapping techniques. This energy is used because we expect that like in other molecules, such as CO,<sup>24</sup> CO<sub>2</sub>,<sup>25</sup> N<sub>2</sub>, and O<sub>2</sub>,<sup>28</sup> at this energy most dissociation channels may have cross sections close to their maxima and thus can be easily detected. Also above 200 eV the relative cross sections of most of the dissociation channels have no significant variations.<sup>24,25,28</sup> The experimental apparatus and the methods on deducing the various cross sections are described in Sec. II. The cross sections for the different dissociation channels are presented in Sec. III.

## II. EXPERIMENTAL METHODS

The experimental setup has been described elsewhere,<sup>25</sup> thus only a brief description is given here. The molecular beam is provided by a continuous gas flow from a long needle passing through a skimmer. The electron beam is provided by a pulsed electron gun. The two beams cross each other perpendicularly. A focusing time-of-flight (FTOF) mass spectrometer<sup>29</sup> is used to collect the ions. The shield plates in the interaction region of the FTOF mass spectrometer focuses the ions close to the axis, and a mesh between two flight tubes focuses the ions onto the microchannel plate detector. In the present experiment the pulsed voltage on the extraction mesh is  $-1.20$  kV. The voltage on the flight tubes is  $-2.06$  kV, and on the focusing mesh is  $-2.60$  kV. Ion trajectory simulations<sup>29</sup> have shown that using this voltage setting the ions with initial energies as high as 25 eV/charge can be collected with the same efficiency as the thermal ions. The output of the microchannel plate is preamplified and sent to a constant fraction discriminator. The ion signals are fi-

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nally recorded by a multichannel scaler. OCS (>99%) is purchased from Praxair. The experiment runs at a repetition rate of 4 kHz. It lasts for 48 h with totally  $7 \times 10^8$  pulses. The counting rate is about 1 ion/pulse.

The principle of covariance mapping<sup>11</sup> is as follows. Let  $X_n(i)$  be the single pulse TOF spectrum of the  $n$ th pulse, where  $i$  is the time bin of the multichannel scaler. The second order covariance function of the single pulse spectrum is given by

$$C_2(i,j) = \overline{N(X_n(i) - \overline{X_n(i)})(X_n(j) - \overline{X_n(j)})} \\ = \sum_{n=1}^N X_n(i)X_n(j) - \frac{1}{N} \sum_{n=1}^N X_n(i) \sum_{n=1}^N X_n(j). \quad (1)$$

Here  $N$  is the total number of pulses, and the averages are taken over all the pulses. The first term of Eq. (1) is the total coincidence between the ions, and the second term corresponds to the false coincidence. Removing the false coincidence can be achieved in an alternative way.<sup>30–32</sup> Briefly, the autocorrelation function of the single-count spectrum, i.e.,  $\sum_{n=1}^N X_n(i)$ , is normalized so that its count in a completely false coincidence area (such as  $S^+ + OCS^+$ ) is equal to that in the same area of the total coincidence, and then it is subtracted from the total coincidence. Statistically as shown in Eq. (1) the normalization factor is close to the reciprocal of the total number of pulses. In our experiment this factor is  $1/6.97 \times 10^8$ , which satisfies this requirement. If we plot  $C_2(i,j)$  on a plane we get a covariance map. Similarly the third order covariance function of  $X_n(i)$  is described by

$$C_3(i,j,k) \\ = \overline{N(X_n(i) - \overline{X_n(i)})(X_n(j) - \overline{X_n(j)})(X_n(k) - \overline{X_n(k)})} \\ = \sum_{n=1}^N X_n(i)X_n(j)X_n(k) - \frac{1}{N^2} \sum_{n=1}^N X_n(i) \sum_{n=1}^N X_n(j) \\ \times \sum_{n=1}^N X_n(k) - \frac{1}{N} \sum_{n=1}^N (C_2(i,j)X_n(k) \\ + C_2(i,k)X_n(j) + C_2(j,k)X_n(i)). \quad (2)$$

The first term of Eq. (2) is the total coincidence between three ions, and the other terms represent the false coincidence. If we plot  $C_3(i,j,k)$  in the space we get a three-dimensional covariance map, or a covariance volume.

The highest order ionization of OCS occurring in our experiment is thought to be triple ionization. Higher order ionizations are found to be much less and negligible. As a result all the ions are supposed to be produced from OCS monocations, dications or trications. The possible dissociation channels for these ions are listed in Table I, which have been divided into 5 groups according to the charges of the parent ion and the ionic fragments. No considerable trication has been observed in the spectrum, so they are omitted in the table. The neutral fragments are not recorded in the present experiment. For the sake of brevity we use the symbol “ $n$ ” to stand for all the neutral fragments if they exist, and “ $n$ ” vanishes if there is no neutral product. The cross section for each dissociation channel is denoted in the last column.

TABLE I. The possible dissociation channels for OCS monocations, dications, and trications. The symbol “ $n$ ” denotes the neutral fragments if they exist.

Parent ion	Dissociation channel	Cross section
OCS <sup>+</sup>	$\rightarrow X^+ + n$	$\sigma_1(X^+)$
OCS <sup>2+</sup>	$\rightarrow X^{2+} + n$	$\sigma_2(X^{2+})$
	$\rightarrow X^+ + Y^+ + n$	$\sigma_2(X^+, Y^+)$
OCS <sup>3+</sup>	$\rightarrow X^{2+} + Y^+ + n$	$\sigma_3(X^{2+}, Y^+)$
	$\rightarrow X^+ + Y^+ + Z^+ + n$	$\sigma_3(X^+, Y^+, Z^+)$

The absolute partial cross section of a specific ion is obtained by comparing the ion count to argon, whose cross sections have been well established. The result of Straub *et al.*<sup>33</sup> is used in our study. In the course of calibration argon is mixed in the reservoir with the same pressure as OCS. The pressure of the gas in the chamber above the needle is kept low enough so that the gas flow is in the effusive flow regime. The absolute partial cross section of a particular ion  $X^+$  (or  $X^{2+}$ , etc.) is given by

$$\sigma(X^+) = \frac{n_1(X^+)}{n_1(Ar^+)} \sigma(Ar^+), \quad (3)$$

where  $n_1(X^+)$  is the ion count of  $X^+$  in the single-count spectrum.

The absolute cross sections for the dissociation channels that produce an ion pair or an ion triple can be calculated as follows:

$$\sigma_2(X^+, Y^+) = \left( \frac{n_2(X^+, Y^+)}{T\eta} - \sum_{Z^+} \frac{n_3(X^+, Y^+, Z^+)}{(T\eta)^2} \right) \frac{\sigma_{\text{total}}}{n_{\text{total}}}, \quad (4)$$

$$\sigma_3(X^{2+}, Y^+) = \frac{n_2(X^{2+}, Y^+)}{T\eta} \frac{\sigma_{\text{total}}}{n_{\text{total}}}, \quad (5)$$

$$\sigma_3(X^+, Y^+, Z^+) = \frac{n_3(X^+, Y^+, Z^+)}{(T\eta)^2} \frac{\sigma_{\text{total}}}{n_{\text{total}}}. \quad (6)$$

Here  $n_2$  is the ion-pair count inside the corresponding island on the covariance map, and  $n_3$  is the ion-triple count inside the corresponding region in the covariance volume. Note that since  $n_3(X^+, Y^+, Z^+)$  always contributes to  $n_2(X^+, Y^+)$ , it must be subtracted when calculating  $\sigma_2(X^+, Y^+)$ . The value of  $\sigma_{\text{total}}$  is the total cross section of the ions, and  $n_{\text{total}}$  is the total ion count in the single-count spectrum.  $T$  is the total transmission of the meshes in the mass spectrometer, and  $\eta$  is the detection efficiency of the microchannel plate.  $T$  is calculated from the open area ratio, which is 58.1% and agrees with the optical transparency of the meshes. For  $\eta$  we use the open area ratio, which is 54.5%. It has been shown that the detection efficiency of the microchannel plate is equal to its physical open area ratio.<sup>33–35</sup>

The remaining cross sections, i.e.,  $\sigma_1(X^+)$  and  $\sigma_2(X^{2+})$  can be derived as follows. Since any ionic species detected in the experiment should come from one or more channels listed in Table I, we have the sum rules

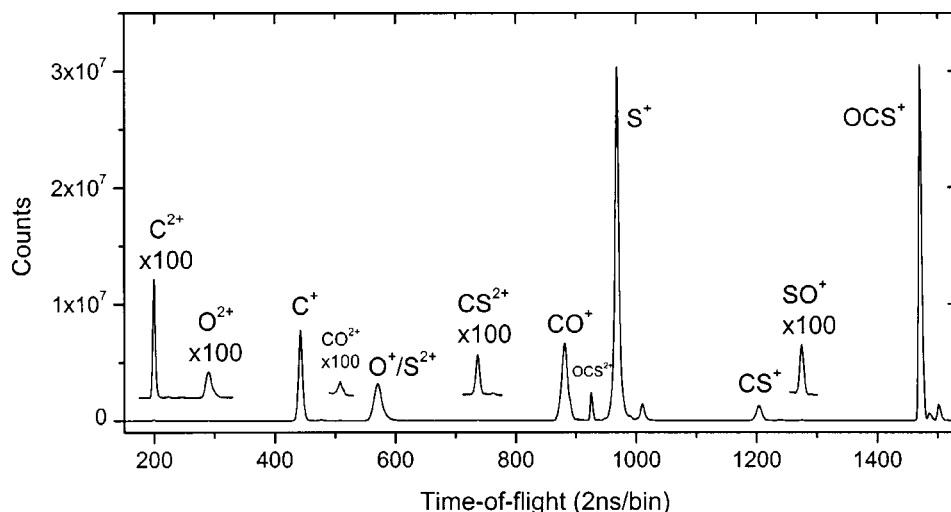


FIG. 1. The time-of-flight mass spectrum of OCS. The electron energy is 200 eV.

$$\sigma(X^+) = \sigma_1(X^+) + \sum_{Y^+} \sigma_2(X^+, Y^+) + \sum_{Y^{2+}} \sigma_3(Y^{2+}, X^+) + \sum_{Y^+, Z^+} \sigma_3(X^+, Y^+, Z^+), \quad (7)$$

$$\sigma(X^{2+}) = \sigma_2(X^{2+}) + \sum_{Y^+} \sigma_3(X^{2+}, Y^+). \quad (8)$$

From these equations  $\sigma_1(X^+)$  and  $\sigma_2(X^{2+})$  can be easily obtained.

The ion count from the background gases is measured without OCS. It is less than 5% of the total ion count of OCS, and is subtracted from the single-count spectrum and the covariance map. The errors in the cross section data have been estimated elsewhere.<sup>27</sup> The error in the absolute partial cross section of a single ion is generally 10%. The error in the cross section for an ion pair is about 20%. For the ion triple, and for the dissociation channels that produce only one ionic fragment, the errors are expected to be about 25%, and it may be more for very weak channels.

### III. RESULTS AND DISCUSSIONS

#### A. Covariance map and covariance volume

The single-count mass spectrum of OCS is shown in Fig. 1. Some minor mass peaks have been amplified and shifted to show the details. All the mass peaks are well resolved except some isotope peaks due to  $^{13}\text{C}$ ,  $^{33}\text{S}$ , and  $^{34}\text{S}$ . The covariance map of OCS is shown in Fig. 2. The positions of the mass peaks are displayed on the bottom and left. Since the false coincidence has been subtracted, the counts in the completely false coincidence areas such as  $\text{CO}^+ + \text{CS}^+$  and  $\text{S}^+ + \text{CS}^+$ , etc., are very small.

The geometrical properties of an island on the covariance map, e.g., the shape, size and orientation contain useful information on the dissociation dynamics.<sup>17,25,30,36,37</sup> Theoretical analysis has shown that the structure of the island is a momentum contour, and the slope of the island can be approximated by<sup>30</sup>

$$k = P_y Q_x / P_x Q_y, \quad (9)$$

where  $Q$  and  $P$  are the charge and initial momentum of the ions. In order to show the details, some islands on the covariance map are expanded and shown in Fig. 3, which corresponds to the dissociation channels  $\text{OCS}^{2+} \rightarrow \text{O}^+ + \text{CS}^+$ ,  $\text{OCS}^{3+} \rightarrow \text{S}^{2+} + \text{CO}^+$ ,  $\text{OCS}^{3+} \rightarrow \text{O}^+ + \text{CS}^{2+}$ ,  $\text{OCS}^{2+} \rightarrow \text{C}^+ + \text{S}^+ + \text{O}$ ,  $\text{OCS}^{2+} \rightarrow \text{O}^+ + \text{S}^+ + \text{C}$ , and  $\text{OCS}^{2+} \rightarrow \text{C}^+ + \text{O}^+ + \text{S}$ , respectively. Note that the islands (d)–(f) also contain some contaminations from  $\text{OCS}^{3+} \rightarrow \text{O}^+ + \text{C}^+ + \text{S}^+$ . The islands (a)–(c) are two-body separations, the slope of each island reflects the charge ratio between the ions. For false coincidence since it happens accidentally the orientation of the island should be horizontal or vertical. The islands (a)–(c) indicate that false coincidence has been effectively removed.

The interpretation of the shape of the island for a three-body separation is more complicated.<sup>17</sup> Briefly, one must first distinguish between simultaneous three-body dissociation and sequential dissociation. Sequential dissociations can be further divided into initial charge separation and deferred charge separation. The slope of the island in Fig. 3(d) is measured to be  $-2.5 \pm 0.2$ . This supports a sequential dissociation through initial charge separation as  $\text{OCS}^{2+} \rightarrow \text{CO}^+ + \text{S}^+ \rightarrow \text{C}^+ + \text{O} + \text{S}^+$ , in which the slope of the island is supposed to be  $-m_{\text{CO}}/m_{\text{C}} = -2.33$ . For Fig. 3(e), the measured slope is  $-1.2 \pm 0.2$ . This is very likely caused by a simultaneous dissociation, of which the carbon atom serves as a neutral spectator, and thus the slope of the island is nearly  $-1$ . Figure 3(f) is more complex, besides the contamination from  $\text{OCS}^{3+} \rightarrow \text{O}^+ + \text{C}^+ + \text{S}^+$ , it also includes the dissociation  $\text{OCS}^{3+} \rightarrow \text{C}^+ + \text{S}^{2+} + \text{O}$ . Since the islands from the dissociation of trications are generally broader, we measured the slope of the central part of the island, which is  $-3.8 \pm 0.3$ . This is in good agreement with a sequential dissociation through  $\text{OCS}^{2+} \rightarrow \text{O}^+ + \text{CS}^+ \rightarrow \text{O}^+ + \text{C}^+ + \text{S}$ , where the estimated slope is  $-m_{\text{CS}}/m_{\text{C}} = -3.67$ .

The island  $\text{CO}^+ + \text{S}^+$  has a tail which ends on the diagonal at the time bin of  $\text{OCS}^{2+}$ , as shown in Fig. 4. This is caused by the decay of some metastable  $\text{OCS}^{2+}$  ions, which have lifetimes comparable to the TOF scale of the experiment, and decay through  $\text{OCS}^{2+} \rightarrow \text{CO}^+ + \text{S}^+$ . Detailed analysis<sup>27</sup> has shown that for a two-body ion-pair separation

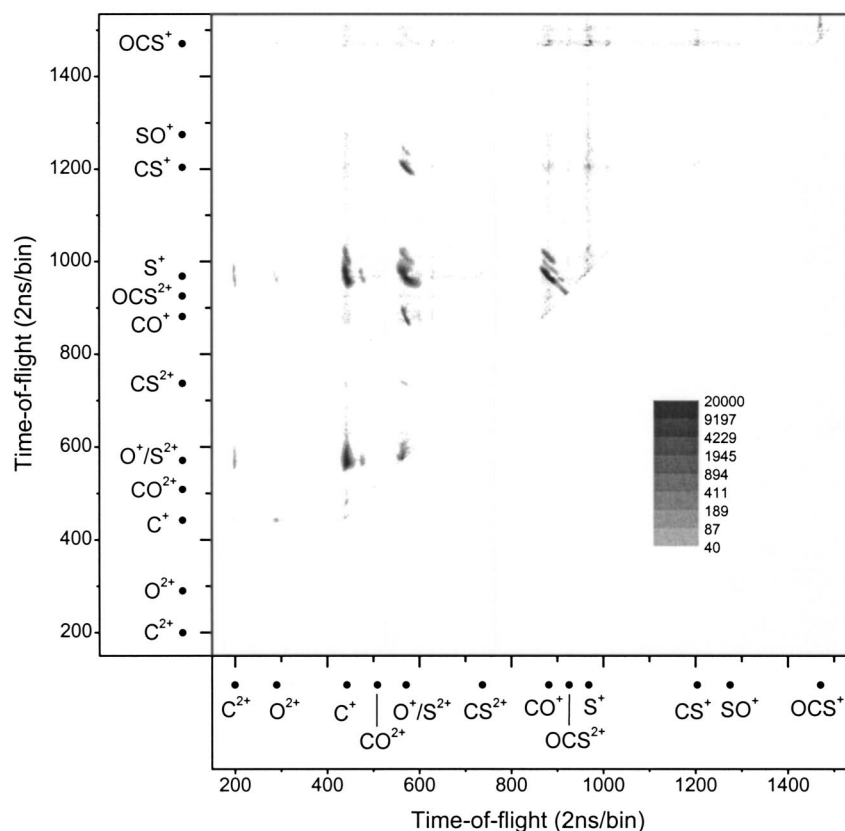


FIG. 2. The covariance map of OCS. The positions of the mass peaks are displayed on the bottom and left.

of a dication the initial slope of the decay trace should be  $-1$ , and the end of the decay trace is a V-shape with slopes equal to the mass ratios of the fragments. For  $\text{OCS}^{2+} \rightarrow \text{CO}^+ + \text{S}^+$  this means that at the end of the trace we

should have two arms with slopes of  $-7/8$  and  $-8/7$ . Due to the low resolvability the whole decay trace in Fig. 4 appears as a broad line with a slope close to  $-1$ .

The covariance volume for the dissociation channel

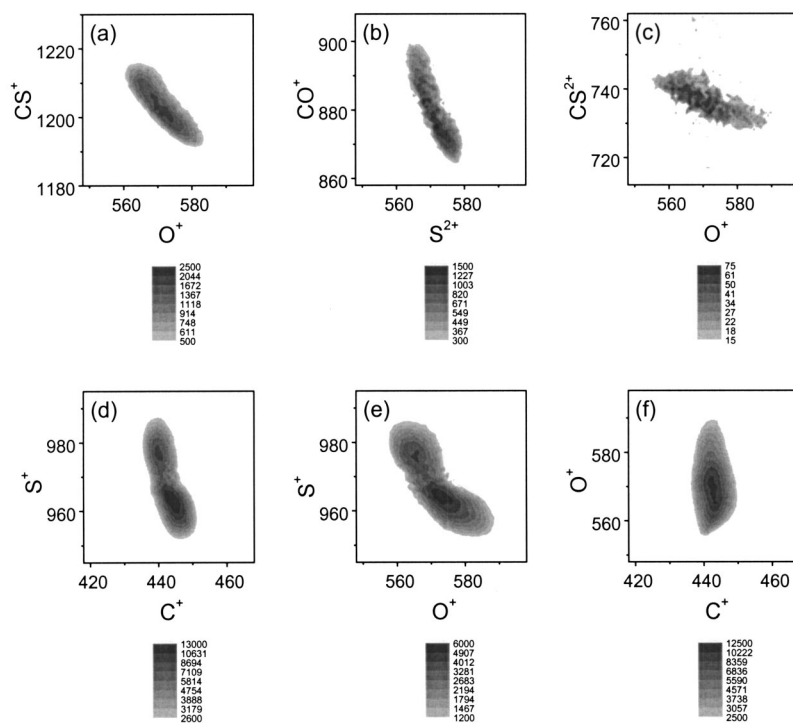


FIG. 3. The covariance maps for the dissociation channels (a)  $\text{OCS}^{2+} \rightarrow \text{O}^+ + \text{CS}^+$ , (b)  $\text{OCS}^{3+} \rightarrow \text{S}^{2+} + \text{CO}^+$ , (c)  $\text{OCS}^{3+} \rightarrow \text{O}^+ + \text{CS}^{2+}$ , (d)  $\text{OCS}^{2+} \rightarrow \text{C}^+ + \text{S}^+ + \text{O}$ , (e)  $\text{OCS}^{2+} \rightarrow \text{O}^+ + \text{S}^+ + \text{C}$ , and (f)  $\text{OCS}^{2+} \rightarrow \text{C}^+ + \text{O}^+ + \text{S}$ . Note that the islands (d)–(f) contain contaminations from  $\text{OCS}^{3+} \rightarrow \text{O}^+ + \text{C}^+ + \text{S}^+$ , and (f) also includes  $\text{OCS}^{3+} \rightarrow \text{C}^+ + \text{S}^{2+} + \text{O}$ .

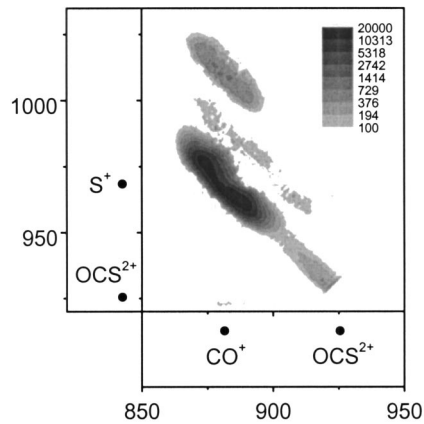


FIG. 4. The metastable decay trace caused by  $\text{OCS}^{2+} \rightarrow \text{CO}^+ + \text{S}^+$ .

$\text{OCS}^{3+} \rightarrow \text{O}^+ + \text{C}^+ + \text{S}^+$  cannot be directly drawn on paper. In Fig. 5 we show the projections of this covariance volume on three planes. The actual shape of the covariance volume can be imagined if one folds up the  $x$ - $z$  and  $y$ - $z$  planes along the dashed lines. The projections on the  $x$ - $y$  and  $x$ - $z$  planes have orientations near the vertical line, while the projection on the  $y$ - $z$  plane has a slope close to  $-1$ . This implies that the dissociation is nearly a spontaneous explosion, where  $\text{C}^+$  serves as a spectator ion. It is notable that the projection on the  $x$ - $y$  plane has a slight tilt with a positive slope, while the projection on the  $x$ - $z$  plane has also a slight tilt but with a negative slope. This indicates that after the explosion  $\text{C}^+$  has a small momentum and flies in the direction closer to  $\text{O}^+$ , but further from  $\text{S}^+$ .

B. Cross sections for the different dissociation channels

The partial cross sections for electron impact ionization of OCS are listed in column a of Table II. For monocations all the possible seven compositions ( $\text{OCS}^+$ ,  $\text{CS}^+$ ,  $\text{SO}^+$ ,  $\text{CO}^+$ ,  $\text{O}^+$ ,  $\text{C}^+$ , and  $\text{S}^+$ ) have been observed. For dications

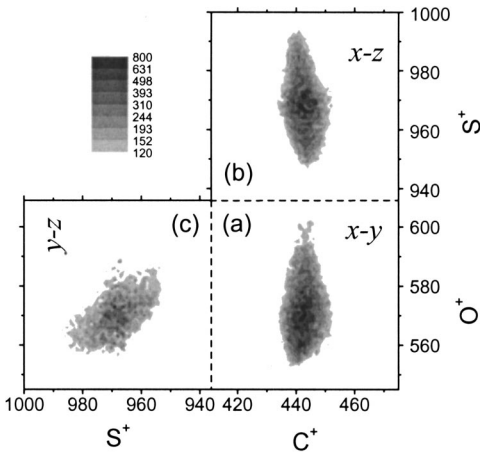


FIG. 5. The projections of the covariance volume  $\text{OCS}^{3+} \rightarrow \text{C}^+ + \text{O}^+ + \text{S}^+$  on the (a)  $x$ - $y$ , (b)  $x$ - $z$ , and (c)  $y$ - $z$  planes.

we observed all the compositions except  $\text{SO}^{2+}$ . Note that the present setup cannot distinguish  $\text{O}^+$  and  $\text{S}^{2+}$  due to their intrinsically equal  $m/q$  ratios. The  $\text{SO}$  ions can only be produced through rearrangement of OCS ions before dissociation, thus they exist in very small quantities. To our knowledge there is no available partial electron impact cross sections of OCS that can be used to compare with our results. The total cross section is  $5.34 \times 10^{-16} \text{ cm}^2$ , which is about 8% higher than the unpublished data of Srivastava quoted by Kim *et al.*<sup>38</sup>

The cross sections for the dissociation of OCS monocations, i.e.,  $\sigma_1(X^+)$  for  $\text{OCS}^+ \rightarrow X^+ + n$  are listed in column b of Table II. Note that we cannot distinguish  $\text{OCS}^+ \rightarrow \text{O}^+ + n$  and  $\text{OCS}^{2+} \rightarrow \text{S}^{2+} + n$ . Because electron impact double ionization is much less than single ionization, we tentatively neglect the latter. The total cross section of single ionization, by summing up  $\sigma_1(X^+)$ , is  $4.75 \times 10^{-16} \text{ cm}^2$ . About one-third of the OCS monocations stabilize into  $\text{OCS}^+$ , and others will dissociate, of which  $\text{S}^+$  and  $\text{CO}^+$  are the main prod-

TABLE II. The cross sections ( $10^{-19} \text{ cm}^2$ ) for electron impact dissociative ionization of OCS (a), for the dissociation channels  $\text{OCS}^+ \rightarrow X^+ + n$  or  $\text{OCS}^{2+} \rightarrow X^{2+} + n$  (b), and for the dissociation channels  $\text{OCS}^{2+} \rightarrow X^+ + Y^+ + n$  or  $\text{OCS}^{3+} \rightarrow X^{2+} + Y^+ + n$  (remaining columns). The electron energy is 200 eV

	a	b	$\text{C}^{2+}$	$\text{O}^{2+}$	$\text{C}^+$	$\text{CO}^{2+}$	$\text{O}^+$	$\text{S}^{2+}$	$\text{CO}^+$
$\text{OCS}^+$	1520	1520							
$\text{SO}^+$	2.58	2.44			0.14				
$\text{CS}^+$	116	107		0.05			9.00		
$\text{S}^+$	2090	1920	0.69	0.43	45.8	0.26	26.9		78.6
$\text{OCS}^{2+}$	101	101							
$\text{CO}^+$	637	553						5.57	
$\text{CS}^{2+}$	2.15	1.74					0.41		
$\text{S}^{2+}$							5.22		
$\text{O}^+$	396 <sup>a</sup>	284 <sup>b</sup>	0.76		41.5 <sup>c</sup>				
$\text{CO}^{2+}$	0.70	0.44							
$\text{C}^+$	474	369		0.33					
$\text{O}^{2+}$	2.13	1.32							
$\text{C}^{2+}$	3.90	2.45							

<sup>a</sup>Including  $\text{S}^{2+}$ .  
<sup>b</sup>Including  $\text{OCS}^{2+} \rightarrow \text{S}^{2+} + n$ .  
<sup>c</sup>Including  $\text{OCS}^{3+} \rightarrow \text{C}^+ + \text{S}^{2+} + \text{O}$ .



ucts. It is obvious that the C–S bond cleavage plays a dominant role in the dissociation of  $\text{OCS}^+$ .

There has been much progress in the theoretical calculation on the absolute total electron impact ionization cross sections of molecules, among which the Deutsch–Märk (DM) formalism<sup>39,40</sup> and the binary-encounter-Bethe (BEB) formalism<sup>41</sup> have been well developed. Both methods use the quantum mechanically determined molecular parameters and sum up the ionization cross sections from each orbital. We compared our result with that calculated from the BEB method. Using the parameters in Ref. 38 the BEB cross section for single ionization of OCS is found to be  $4.24 \times 10^{-16} \text{ cm}^2$ , which agrees with our total single ionization cross section, i.e.,  $4.75 \times 10^{-16} \text{ cm}^2$ .

The cross sections for the dissociation channels  $\text{OCS}^{2+} \rightarrow \text{X}^{2+} + n$ , i.e.,  $\sigma_2(\text{X}^{2+})$  are also listed in column b of Table II. The cross sections for  $\text{OCS}^{2+} \rightarrow \text{X}^+ + \text{Y}^+ + n$ , i.e.,  $\sigma_2(\text{X}^+, \text{Y}^+)$  are listed in the remaining columns. Note that we cannot distinguish  $\text{OCS}^{2+} \rightarrow \text{O}^+ + \text{C}^+ + \text{S}$  and  $\text{OCS}^{3+} \rightarrow \text{O} + \text{C}^+ + \text{S}^{2+}$ . Since triple ionization is much less than double ionization, we tentatively neglect the latter. The total cross section of double ionization, by summing up  $\sigma_2(\text{X}^{2+})$  and  $\sigma_2(\text{X}^+, \text{Y}^+)$ , is  $0.309 \times 10^{-16} \text{ cm}^2$ . About one-third of the OCS dications are stable, others will dissociate. Among these dissociations  $\text{OCS}^{2+} \rightarrow \text{X}^{2+} + n$  contribute only a small portion. The ion-pair dissociation channels, i.e.,  $\text{OCS}^{2+} \rightarrow \text{X}^+ + \text{Y}^+ + n$  are the dominant pathways. The top three abundant dissociation channels are  $\text{OCS}^{2+} \rightarrow \text{CO}^+ + \text{S}^+$ ,  $\text{COS}^{2+} \rightarrow \text{C}^+ + \text{S}^+ + \text{O}$ , and  $\text{OCS}^{2+} \rightarrow \text{C}^+ + \text{O}^+ + \text{S}$ . The first two abundant channels are in accordance with the photoionization experiments of Masuoka *et al.*<sup>2</sup> and Ankerhold *et al.*<sup>4</sup> For the third channel, more specifically, the coincidence between mass 12 and 16, a problem occurs because Ankerhold *et al.* treated it as  $\text{OCS}^{3+} \rightarrow \text{C}^+ + \text{S}^{2+} + \text{O}$ , while Masuoka *et al.* treated it as a contamination from  $\text{OCS}^{3+} \rightarrow \text{C}^+ + \text{O}^+ + \text{S}^+$ . To solve this problem one needs to resolve  $\text{O}^+$  and  $\text{S}^{2+}$  ions. However, we suppose that  $\text{OCS}^{2+} \rightarrow \text{C}^+ + \text{O}^+ + \text{S}$  exist with a considerable abundance. The reasons are as follows. First, the coincidence between mass 12 and 16 has been observed at 48.4 eV (Ref. 10) and near 50 eV,<sup>2</sup> both are well below the triple ionization threshold of OCS, which is 60.0 eV.<sup>42</sup> Therefore it is evident that  $\text{OCS}^{2+} \rightarrow \text{C}^+ + \text{O}^+ + \text{S}$  should exist. Second, by comparing the double and triple coincidence counts we find that  $\text{C}^+ + \text{O}^+ + \text{S}^+$  contributes less than 30% to Fig. 3(f). Therefore in this coincidence pure ion pairs are much more abundant than ion triples. Third, since  $\text{OCS}^{3+}$  is subjected to Coulomb repulsions, which generally favor the separation of the total charge, the channel  $\text{C}^+ + \text{S}^{2+} + \text{O}$  should be less than or comparable with  $\text{C}^+ + \text{O}^+ + \text{S}^+$ . As a result  $\text{C}^+ + \text{O}^+ + \text{S}$  is suspected to have a considerable abundance.

All the OCS trications are unstable. The cross sections for  $\text{OCS}^{3+} \rightarrow \text{X}^{2+} + \text{Y}^+ + n$ , i.e.,  $\sigma_3(\text{X}^{2+}, \text{Y}^+)$  are listed in Table II. The cross section for ion-triple dissociation, i.e.,  $\text{OCS}^{3+} \rightarrow \text{O}^+ + \text{C}^+ + \text{S}^+$ , is measured to be  $17.4 \times 10^{-19} \text{ cm}^2$ . The total triple ionization, by summing up  $\sigma_3(\text{X}^{2+}, \text{Y}^+)$  and  $\sigma_3(\text{X}^+, \text{Y}^+, \text{Z}^+)$ , is  $31.1 \times 10^{-19} \text{ cm}^2$ . The ion-triple dissociation is a major pathway, which contributes more than half to the dissociation of  $\text{OCS}^{3+}$ . However, al-

though each  $\text{X}^{2+} + \text{Y}^+ + n$  is relatively small, the total ion-pair dissociation is comparable with  $\text{O}^+ + \text{C}^+ + \text{S}^+$ .

#### IV. CONCLUSIONS

We have studied the dissociation of up to triply ionized carbonyl sulfide molecules through electron impact ionization at 200 eV. Two- and three-dimensional covariance mapping techniques are used to measure the ionic fragments in double and triple coincidence. A focusing time-of-flight mass spectrometer is used to collect all the ions. The absolute cross sections for the ion-pair and ion-triple dissociation channels have been measured directly, while the cross sections for the dissociation channels that have only one ionic product are derived. The unstable OCS dications dissociate mostly through ion-pair dissociation channels. The channel  $\text{C}^+ + \text{O}^+ + \text{S}$  is expected to exist with a considerable abundance. The OCS trications dissociate into ion triple or ion pair with comparable probabilities, although the ion-triple separation channel contributes a major part. A metastable decay trace caused by  $\text{OCS}^{2+} \rightarrow \text{CO}^+ + \text{S}^+$  has been observed on the covariance map. The total electron impact single ionization cross section of OCS agrees with the total cross section calculated from the BEB method.

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