

Analysis of the coulombic explosion of the photoexcited DMS [$\text{CH}_3\text{-S-CH}_3$] molecule using statistical methods

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Synopsis. In this work we study the photoionization of DMS, using a Time of Flight Mass Spectrometer (TOFMS) and synchrotron radiation. Photoelectron-Photoion-Photoion Coincidence (PEPIPICO) spectra were obtained in selected photon energies, and a statistical method was applied to determine the slope parameter for each coincidence, which allowed us to propose mechanisms for ionic dissociation of DMS (CH_3SCH_3) dication.

Highly excited states in molecules, associated with single, double or multiple ionization usually lead to dissociation and fragmentation relaxation processes. The use of electron-ion coincidence techniques, such as PEPIPICO, allows for the discussion of the dissociation mechanisms.

In the present work, ionic dissociation of dimethylsulfide molecule (DMS – CH_3SCH_3) have been studied around the S 2p edge using synchrotron radiation (TGM beamline of LNLS [1]) and time-of-flight mass spectrometry techniques [2]. Here, we focus on triple coincidences spectra (PEPIPICO - photoelectron-photoion-photoion-coincidences).

DMS PEPIPICO spectra were recorded at 162 eV, 166 eV, 185 eV and 300 eV photon energies, respectively below, on and above the main resonance of S 2p NEXAFS DMS spectrum [3]. A new statistical methodology [4] is applied to the study of the fragmentation of the dimethylsulfide molecule. Briefly, the ion-ion coincidence spectrum may be represented as a Bi-variate Normal density function that is expressed as the combination of two matrices: the mean time expectation matrix for the two participating ions and the variance-covariance matrix.

Here, we focus in the coincidence $\text{CH}_3^+/\text{SCH}^+$, which corresponds to an island in the PEPIPICO spectrum, as shown in Figure 1 for 300 eV photons (T_1 refers to the flight time of the lighter fragment, CH_3^+ and T_2 refers to the flight time of the heavier fragment, SCH^+). This coincidence has a slope of -0.97 ± 0.18 , which suggests two possible dissociation mechanisms (Table 1) if we consider a three body dissociation model proposed by Eland [5].

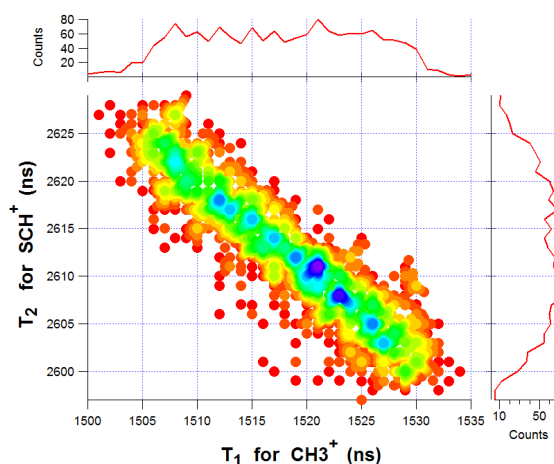


Figure 1: $\text{CH}_3^+/\text{SCH}^+$ coincidence island (300 eV)

Table 1: Possible dissociation mechanisms

Deferred charge separation	Initial charge separation (Secondary decay)
$\text{C}_2\text{H}_6\text{S}^{2+} \rightarrow \text{C}_2\text{H}_4\text{S}^{2+} + \text{H}_2$	$\text{C}_2\text{H}_6\text{S}^{2+} \rightarrow \text{CH}_3^+ + \text{SCH}_3^+$
$\text{C}_2\text{H}_4\text{S}^{2+} \rightarrow \text{CH}_3^+ + \text{SCH}^+$	$\text{SCH}_3^+ \rightarrow \text{SCH}^+ + \text{H}_2$
Theoretical slope: -1	Theoretical slope: -0.96

The $\text{CH}_3^+/\text{SCH}^+$ double coincidence slope in the other studied photon energies will be presented, along with proposed dissociation mechanisms. Besides, other DMS double coincidences will also be analyzed.

References

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