

Dissociation of OCS upon various S(2p) Auger decay transitions

K. Saha, S. B. Banerjee and B. Bapat

Physical Research Laboratory, Ahmedabad, 380009, India

E-mail: koushik@prl.res.in

Abstract. Dissociation of OCS upon various Auger decay transitions due to ionization at sulphur $2p_{1/2}$ threshold is studied. A combination of Recoil Ion Momentum Spectroscopy and electron energy analysis are employed to perform these studies. It is observed that the dissociation channels and their branching ratios vary with the binding energy of the Auger decay state. The kinetic energy release distribution (KERD) upon fragmentation of the molecule for various Auger transitions have also been examined.

1. Introduction

Dissociation of molecules upon photon impact have been studied extensively in last few decades. Photo-ionization is an excellent tool for studying the molecular dissociation process, owing to the energy selectivity of photon beams which give us a handle to selectively ionize a specific electronic shell in a molecule. Resulting dissociations following various electronic decay processes have been routinely studied by electron-ion coincidence techniques in the past [1]. Though studies have been done to understand molecular fragmentation corresponding to a particular electronic de-excitation mechanism [2, 3, 4], the study of complete kinematics of the dissociation process is rare. We have built a spectrometer which is capable of revealing the complete kinematics of dissociation upon different electronic decay mechanisms of molecule. Kinematically complete study of fragmentation of OCS corresponding to various Auger decay transitions upon photo excitation at S(2p) edge were done using our spectrometer. The fragmentation of the molecule was found to be highly dependent on different Auger decays through which the precursor molecular ions are formed.

2. Experiment

Monoenergetic photon beam from Indus-1 synchrotron facility at RRCAT, Indore was used to perform the experiments. The photon beam had a flux of 10^{10} s^{-1} with an energy resolution of $E/\Delta E = 300$. The energy of the photon beam was set at 172 eV (sulphur $2p_{1/2}$ ionization threshold in OCS) which produced a core hole at S(2p) orbital hence triggering a subsequent Auger decay. A cross beam geometry was maintained between the photon beam and the effusive target gas beam. The target gas jet was placed in between two spectrometers, a Cylindrical Mirror Analyser (CMA) and a Recoil Ion Momentum Spectrometer (RIMS) [5]. Electrons ejected from the target OCS molecule due to photo ionization were energy analysed by the CMA. By varying the potential applied to the CMA, electrons of different energies could be detected hence generating the Auger electron spectrum of OCS. Once the electron spectrum was obtained,



the CMA was set to appropriate voltage so as to admit electrons of specific kinetic energies corresponding to a certain Auger decay transition. The identification of resultant fragment ions along with the determination of their momenta was done by the RIMS set-up . A double field time of flight (ToF) spectrometer with a continuous ion extraction and acceleration electric fields of 166 V/cm and 1000 V/cm respectively coupled with a position sensitive micro channel plate (MCP) detector was used for this purpose. The time of flight of the ions was recorded taking START from the electron detection pulse while the STOP was marked by the ion detection at the MCP. Along with the time of flight, the position information of the ion hit was used to obtain the momenta of the fragment ions. Correlated time of flight and momentum information of all the fragment ions was recorded on an event by event basis in a list mode file which was analysed to obtain the kinematics of the fragmentation process. Further details about the spectrometer and the experimental procedure followed is reported in reference [6].

3. Results

The S(2p) Auger electron spectrum of OCS is shown in Figure 1. A high resolution electron spectrum is not achievable by our spectrometer due to the finite width of the gas beam – photon beam overlap and the continuous electric field applied in the interaction zone for ion extraction. Nevertheless, board features in the spectrum are still identifiable and are fitted with Gaussians. The centroids of the fit are found to match within 2 eV of the value reported in literature [7, 8]. The electronic configuration of the molecular ion formed due to each Auger decay transition is unique and is shown by the horizontal lines. Subtracting the Auger electron kinetic energy from the sulphur 2p_{1/2} ionization energy yields the binding energy of the final Auger states which is shown as the top scale in Fig. 1. The binding energy gives us a measure of the energy gained by the excited molecular ion due to a particular Auger decay. Ionization to lower binding energy state signifies lesser energy available to the internal degrees of freedom of the residual molecular ion, while ionization to higher binding energy states signifies greater energy for the same.

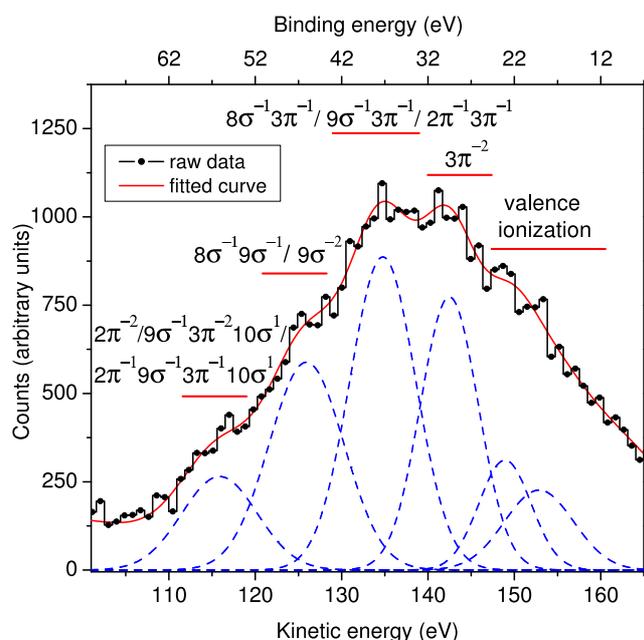


Figure 1. S(2p) Auger spectrum of OCS. The (---) curve is raw data, (—) curve is the cumulative curve of multiple Gaussian fits. Gaussian fits corresponding to various states are shown by (---) curves.

The ion time of flight spectra for each Auger decay state was analysed and it was found that OCS²⁺ and ionic fragments arising from break-up of unstable OCS²⁺ were the dominant products due to S(2p) Auger decay. In S(2p) Auger decay of OCS, following a core ionization

at 2p orbital of sulphur, the core vacancy is filled up by an electron from valence orbital while another valence electron (*i.e.* the Auger electron) is emitted in the process. Thus two electrons are emitted in the ionization and subsequent decay mechanism, the 2p core electron and the Auger electron, producing doubly ionized molecular ion. Hence we observe OCS^{2+} and fragments due to its dissociation to be the major products. In an Auger decay the OCS^{2+} is mostly stable when ionization to $3\pi^{-2}$ state occur while the propensity to dissociate increases as higher binding energy states are accessed. The cross-section of OCS^{2+} is highest for ionization to lowest binding energy Auger state, because the energy gained by the molecular ion for these ionizations are insufficient to break the molecular bonds. On the other hand, as ionization to higher binding energy states occur the molecular ion gains sufficient energy required for bond rupture, thus fragmentation inevitably follows.

The fragmentation channels can be identified by a two dimensional ion-ion coincidence map using the time of flight data of first and the second fragment from the same dissociation event. Each island in such a plot corresponds to a certain fragmentation channel. Figure 2 shows the ion-ion coincidence map for various Auger states. Various information about the fragmentation mechanism can be gained by studying the structure of the islands itself. In general, diagonal island like structure with slope of -1 signifies two body break-up of the molecule producing two fragment ions with equal and opposite momenta. This can be seen in Figure 2 for two body break-up of OCS^{2+} via $\text{OC}^+:\text{S}^+$ and $\text{O}^+:\text{CS}^+$ channels. Three body break-up on the other hand produce islands having different shapes with various slopes due to complex dissociation mechanisms [10].

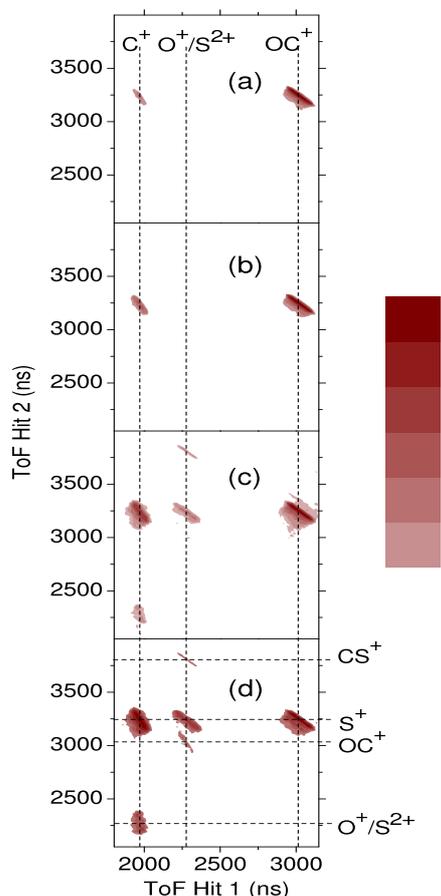


Figure 2. Ion-ion coincidence map of OCS fragments corresponding to different final Auger states. a, b, c and d represent $3\pi^{-2}$, $(9\sigma^{-1}3\pi^{-1}, 8\sigma^{-1}3\pi^{-1}, 2\pi^{-1}3\pi^{-1})$, $(9\sigma^{-2}, 8\sigma^{-1}9\sigma^{-1})$ and $(2\pi^{-2}, 9\sigma^{-1}3\pi^{-2}10\sigma^1, 2\pi^{-1}9\sigma^{-1}3\pi^{-1}10\sigma^1)$ Auger states respectively. Color bar indicates intensity. The maximum of the intensity scale is normalized to 1 in each panel. However, there is no normalization across the panels.

The appearance energy of two body break-up channel of OCS^{2+} is 34 eV while for three body break-up it is 42.5 eV [9]. Thus the $\text{OC}^+:\text{S}^+$ island for ionization to $3\pi^{-2}$ state and the faint $\text{C}^+:\text{S}^+:\text{O}$ island for ionization to $3\pi^{-2}$ and $(9\sigma^{-1}3\pi^{-1}, 8\sigma^{-1}3\pi^{-1}, 2\pi^{-1}3\pi^{-1})$ states may be attributed to the contribution from higher binding energy states owing to the moderate resolution of the CMA. It is evident from the coincidence map that unstable OCS^{2+} , formed due to ionization to low binding energy Auger states, fragments mainly via two body break-up. Since more energy is required to break both the molecular bonds in OCS than a single bond, three body break-up only becomes prominent when ionization to higher binding energy Auger states occur. This is in agreement with a previous work [11] which studies the break-up patterns of OCS^{2+} due to S(2p) Auger decay. Among the two possible two body fragmentation channels namely $\text{OC}^+:\text{S}^+$ and $\text{O}^+:\text{CS}^+$, the former is the dominant channel while the three body dissociation mostly occur via $\text{C}^+:\text{S}^+:\text{O}$ channel. For ionization to $(2\pi^{-2}, 9\sigma^{-1}3\pi^{-2}10\sigma^1, 2\pi^{-1}9\sigma^{-1}3\pi^{-1}10\sigma^1)$ Auger states, along with fragmentation channels from doubly ionized precursor ion, a small signature of $\text{S}^{2+}:\text{CO}^+$ channel is observed which may arise due to triple ionization of OCS through double Auger decay. In our experiment the triple ionization channel may get mixed with the $(2\pi^{-2}, 9\sigma^{-1}3\pi^{-2}10\sigma^1, 2\pi^{-1}9\sigma^{-1}3\pi^{-1}10\sigma^1)$ state, because of the overlap of the electron energy distributions corresponding to the two channels.

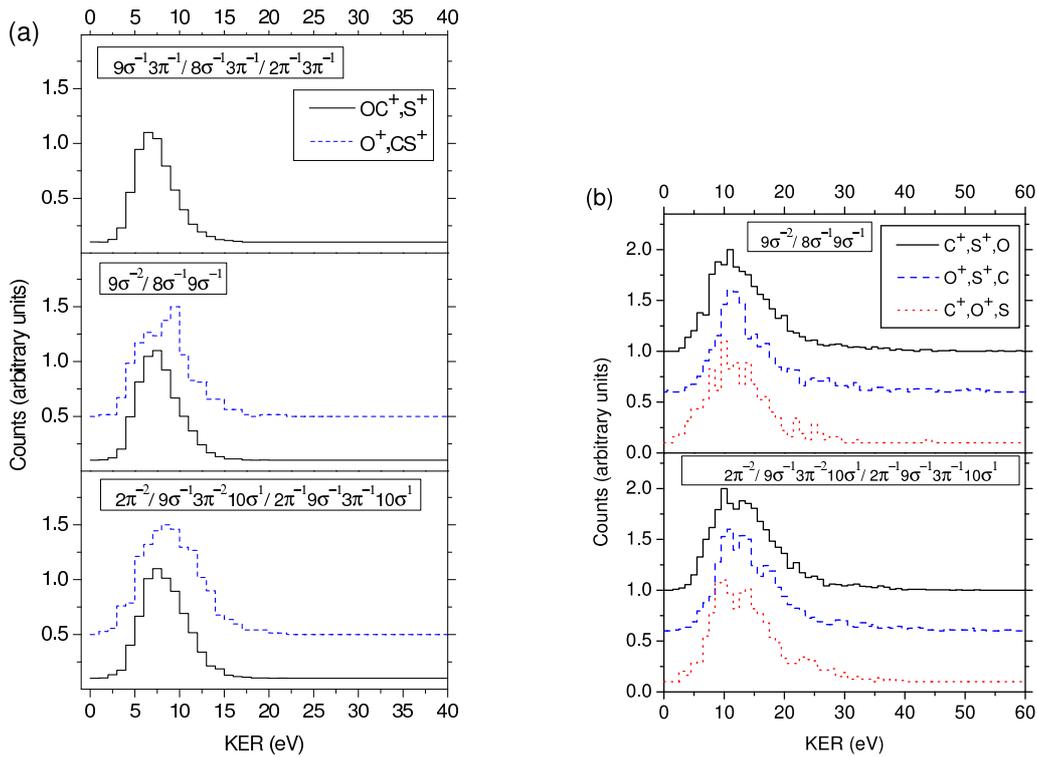


Figure 3. Kinetic Energy Release (KER) distribution for (a) two body break-up and (b) three body break-up channels of OCS^{2+} corresponding to various final Auger states. Curves are offset for clarity.

We now turn our attention towards the kinetic energy release distribution (KERD) of various fragmentation channels. The kinetic energy of each fragment ion in a dissociation process is evaluated from the experimentally measured momenta of the ion. The correlated momenta information of all the ions produced in the dissociation event yields the correlated kinetic energy information of the fragments ions. Kinetic energy of any neutral fragment can be estimated using

energy conservation rules provided kinetic energy of all the other fragments are known. The sum of the kinetic energy of all the fragments produced in the dissociation event gives the total kinetic energy that is released in the fragmentation process. Figure 3 shows the KERD upon fragmentation of OCS^{2+} through different channels due to ionization to various Auger decay states.

For each fragmentation channel the mean KER is calculated from the observed KERD. We find a gradual increase in the mean KER value as we go from lower to higher binding energy Auger states. The mean KER for all the fragmentation channels of OCS^{2+} due to various S(2p) Auger decay is given in Table 1.

Table 1. Mean KER value in eV upon fragmentation of OCS^{2+} for different Auger states.

	$\text{OC}^+:\text{S}^+$	$\text{O}^+:\text{CS}^+$	$\text{C}^+:\text{S}^+:\text{O}$	$\text{O}^+:\text{S}^+:\text{C}$	$\text{C}^+:\text{O}^+:\text{S}$
$9\sigma^{-1}3\pi^{-1}, 8\sigma^{-1}3\pi^{-1}, 2\pi^{-1}3\pi^{-1}$	6.3	–	–	–	–
$9\sigma^{-2}, 8\sigma^{-1}9\sigma^{-1}$	6.9	7.6	12.0	11.5	11.9
$2\pi^{-2}, 9\sigma^{-1}3\pi^{-2}10\sigma^1, 2\pi^{-1}9\sigma^{-1}3\pi^{-1}10\sigma^1$	7.6	8.3	12.7	12.3	13.1

The estimated error in the measurement of KER of ion pairs is 0.46 eV. The increase in mean KER value is attributed to excitation of the neutral molecule to higher lying repulsive molecular ion states following ionization of deep electronic states of molecule. These states may then dissociate directly or predissociate [12], yielding higher KER values than in the case of dissociation from lower molecular ion states that are accessed following ionization of weakly bound electronic states.

4. Summary

We have studied the dissociation of OCS due to S(2p) Auger decay upon ionization at sulphur $2p_{1/2}$ threshold. The kinematics of dissociation is studied in coincidence with various Auger decay transitions which yields different final electronic states of the transient molecular ion. Ionization to low binding energy Auger decay state yields stable OCS^{2+} as energy gained by the molecular ion is not enough to break the molecular bonds. Probability of dissociation increases as ionization to high binding energy Auger decay states occur, rendering the molecular ion with sufficient energy for bond breakage. Since more energy is required to break both the bonds than a single bond in OCS, three body fragmentation only occur due to Auger decay from highly bound electronic orbitals. We also observe a increase in mean KER value from lower to higher binding energy states for all fragmentation channels, indicating that Auger decay involving weakly bound electronic orbitals excites the molecule to low energy ion states while decay from high binding energy orbitals promotes the molecule to higher energy repulsive molecular ion states.

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