Three-body dissociation of OCS^{3+} : separating sequential and concerted pathways

Herendra Kumar*[1], Pragya Bhatt† , C. P. Safvan† and Jyoti Rajput*[2]

* Department of Physics and Astrophysics of University of Delhi, Delhi-110007, India.
† Inter University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi-110067, India.

Synopsis Three body fragmentation pathways of OCS^{3+} molecular ion leading to detection of $C^+ + O^+ + S^+$ in coincidence have been studied using the technique of recoil ion momentum spectroscopy. This fragmentation can occur either via a one step concerted process or a two step sequential process. In the first step of the sequential pathway either CO^{2+} or CS^{2+} is formed. By separating the events coming from the two processes, branching ratios are determined and the possible electronic states associated with the intermediate CO^{2+} or CS^{2+} have been identified.

Studying many-body fragmentation of poly-atomic molecules is a big challenge to both theory and experiment. One of the questions in the field which seeks resolution is the separation of events based on concerted or sequential mechanism. Even in a simple case of a tri-atomic molecule, the three-body dynamics can be very complicated. Working towards the same goal we have studied the three-body dissociation pathways of a simple tri-atomic molecule OCS.

The experiment was conducted at the Low Energy Ion Beam Facility (LEIBF) of Inter University Accelerator Centre (IUAC), New Delhi, India in an ion-molecule collision setup. A beam of Xe^{9+} ions at an energy of 200 kV/q, extracted from an electron cyclotron resonance ion source was made to interact with neutral OCS molecules effusing from a needle. All the fragmentation products resulting from the interaction were collected using a multi-hit recoil ion momentum spectrometer. More details of the experimental setup can be found in reference [1].

The three-body breakup of OCS^{3+} molecular ion, which is the focus of the present work, can be broadly categorized in terms of concerted and sequential mechanisms. In the case of concerted fragmentation process , the reaction products are generated in one step,

$OCS^{3+} \rightarrow C^+ + O^+ + S^+$

while the sequential breakup is a two step process,

$OCS^{3+} \rightarrow CO^{2+} + S^+ \rightarrow C^+ + O^+ + S^+$

or

$OCS^{3+} \rightarrow CS^{2+} + O^+ \rightarrow C^+ + O^+ + S^+$

Since the final products in both these cases are the same set of three ions in coincidence, it becomes difficult to separate events coming from the two different mechanisms. A new method was recently developed in the group of *Prof. Itzik Ben-Itzhak* (JRM Laboratory, Kansas State University, USA) which enables the separation of events based on the fragmentation mechanism. The method is based on analysing the three-body fragmentation data set in two different frames of reference, one in the centre of mass frame of OCS^{3+} and other in the frame of reference of the intermediate molecular ion, CO^{2+} or CS^{2+}. Upon following the procedure, the kinetic energy release spectra associated with the breakup of the intermediate ion is obtained which enables identification of possible electronic states of the intermediate populated during the first step of the sequential process. The kinetic energy release spectra of the CO^{2+}intermediate is shown in the figure below. Some of the electronic states [2, 3] which may be populated are also marked. Further, using this new method, we have determined the branching ratio of all the fragmentation pathways observed in our data.

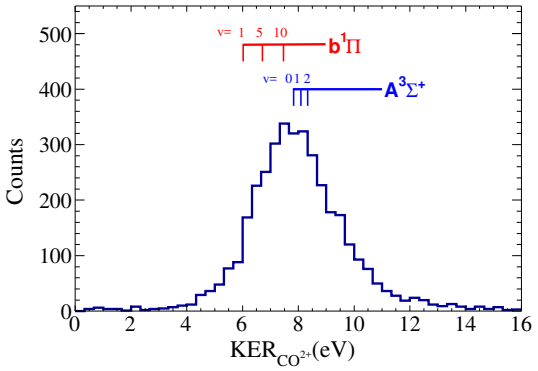

Figure 1. Kinetic energy release spectrum associated with the second step of sequential breakup of OCS^{3+} via CO^{2+} as intermediate.

References

[1] Kumar *et al.* 2014 *J. Mass Spect.* **374** 44

[2] M. Lundqvist *et al.* 1995 *Phys. Rev. Lett.*, **75** 1058

[3] F. Mrugala 2008 *J. Chem. Phys.* **129** 064314

[1]E-mail: harendraamu@gmail.com
[2]E-mail: jrajput.du@gmail.com