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Dissociation of Methanol and Acetylene by slow Highly Charged Ion Collision

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Abstract.

We report here the results of dissociation of multiple charged methanol and acetylene molecules in collision with 1.2 MeV Ar^{8+} projectiles. We observed a wide range of dissociation products from the TOF spectrum starting from undissociated molecular ions, fragments losing an hydrogen atom due to breakage of C–H and/or O–H bonds, to complete rupture of C–C and C–O skeletons for the respective molecules. From the coincidence map of the fragments, we could separate out the different dissociation channels between carbon and oxygen ionic fragments as well as complete two-body dissociation events. The most striking feature in the breakup of CH_3OH is the formation of H_2^+ and H_3^+ due to intramolecular rearrangement of the C–H bonds within the methyl group. In dissociative ionization studies of C_2H_2 , we observed a diatom-like behaviour of the C–C charged complex as evidenced from the measured slopes of the coincidence islands for carbon atomic charged fragments and theoretical values determined from the charge and momentum distribution of the correlated particles. The shape and orientation of the islands give further information about the momentum balance in the fragmentation process in two-body dissociation.

1. Introduction

Study of the dynamics of formation and subsequent dissociation of multiply charged molecules produced by collision with highly charged atomic ions (HCI) have been an active field of research in the last decade [1]. The field of ion-molecule fragmentation using polyatomic molecules is not much studied probably due to the complex nature of the analysis arising from different dissociation pathways of the multiply charged molecular ions formed. Recently, with the extensive use of multihit coincidence methods employing a position sensitive time-of-flight (TOF) measurement system, HCI impact studies on polyatomic molecules has gained momentum [2, 3, 4, 5].

We choose simple polyatomic species containing methyl group in order to observe the dynamics of the hydrogen atoms within the multiply charged parent molecular ion that leads to bond rearrangement or proton migration products. In the present study, we have chosen methanol as the first step of our investigation of characteristic ejection of diatomic and triatomic hydrogen molecular ions from hydrocarbon molecules induced by intense HCI-induced fields.

Dissociative studies of multiple charged acetylene in collision with highly charged ions are rare. So far dissociative studies of low energy proton impact on C_2H_2 [6] have only been done. The authors have measured the total and differential cross sections for various electron capture and ionization channels but no analysis was done on two-particle correlations. A detail study of the coincidence map, especially in the case of polyatomic molecules like acetylene, is very much needed to gain knowledge on multi-particle fragmentation dynamics induced by HCl impact.

2. Experimental details

Details of the experimental apparatus for molecular fragmentation studies has been described elsewhere [7]. Here we shall only give a brief account of the setup. The experiment has been carried out in the Low Energy Ion Beam Facility (LEIBF) of Inter-University Accelerator Centre (IUAC), New Delhi, India. In the experiment, 1.2 MeV Ar^{8+} projectiles produced from the electron cyclotron resonance (ECR) ion source were transported to the collision chamber where they interact with the target molecules effusing from a needle at right angle to the ion beam. Methanol molecules reach the needle through a clean vacuum line degassed by means of several freeze-pump-thaw cycles. The all metal gas line with the fine control valve was kept warm to avoid condensation of the vapours. Typical operating pressures were in the range of 7×10^{-7} Torr whereas the ultra high vacuum chamber was kept at a base pressure of 9×10^{-8} Torr. The dissociated fragments were extracted from the interaction region into the linear, two-field time-of-flight mass spectrometer (TOFMS) by applying a uniform electric field perpendicular to both the ion beam and molecular gasjet. At the end of TOFMS, the dissociation products were detected by a position sensitive micro-channel plate (MCP) detector. Ejected electrons were extracted in the opposite direction of TOFMS and detected by a Channeltron detector which gives the trigger for starting the coincidence data acquisition. The stop signals from the MCP were recorded after proper amplification and discrimination from noise using standard nuclear electronics used for fast pulses. The TOF spectrum is acquired in the multi-hit mode by a CAMAC-based time-to-digital converter (TDC) interfaced to a computer where several fragment ions were recorded in coincidence to obtain information on correlated dissociation products.

3. Dissociation of methanol

3.1. Time-of-flight spectrum

From the TOF spectrum (figure 1) of methanol molecules, we observe a wide range of dissociation products starting from undissociated molecular ion (CH_3OH^+), fragments losing a hydrogen atom in steps due to breakage of C–H and O–H bonds (CH_2OH^+ , $CHOH^+$, COH^+ , CO^+) keeping the C–O part intact, to complete rupture of C–O skeleton producing charged atomic species like C^{q+} and O^{q+} where q varies from 1 to 3. One can also take a note of the relative intensities of the m/q peaks from 28 to 32 in the TOF spectrum. From the highest count of CO^+ , we can infer that a large number of multiply charged parent molecules loses all its C–H and O–H bonds rather than step by step bond cleavage. It also shows that loss of all the hydrogen atoms from the methyl group is preferred over the O–H bond cleavage. Probability of one proton loss from the CH_3 group is more than loss of two, although intensity is maximum when all the C–H bonds are broken. Another striking feature in the TOF spectrum is the detection of hydrogen molecular ions at $m/q = 2$ and 3, origin of those will be described later.

To closely investigate the branching ratios of the different fragmentation channels and identify the two-body and three, four or many-body dissociation pathways, we have generated a ‘coincidence map’ from the offline analysis of the acquired multi-hit data. This map is a 2D spectrum between the TOF of the first fragment ion versus that of the second. It is a useful tool for the identification and separation of multi-particle events representing inter-particle correlations.

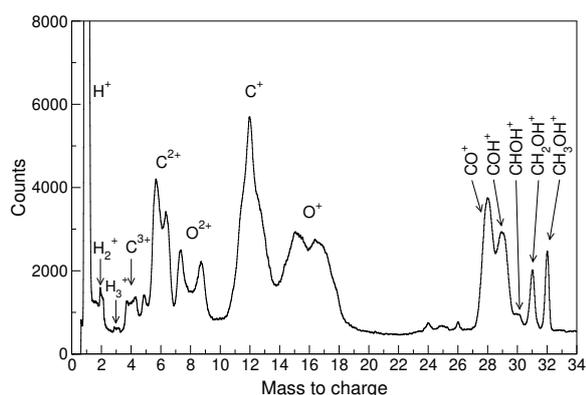


Figure 1. Mass calibrated TOF spectrum of dissociative products of CH₃OH.

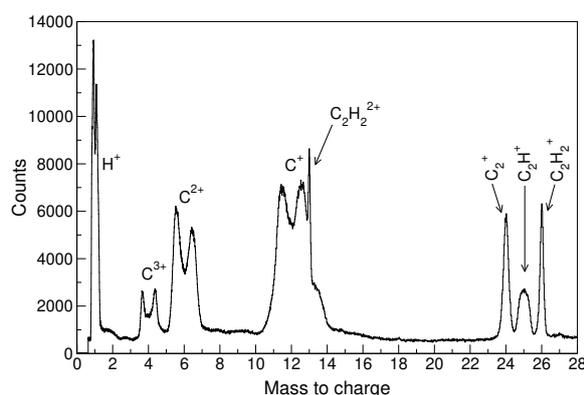
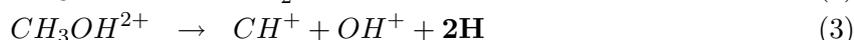
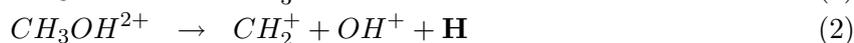


Figure 2. Mass calibrated TOF spectrum of dissociative products of C₂H₂.

3.2. Coincidence map

In the 2-dimensional coincidence map (figure 3), we had separated out the different dissociation channels corresponding to C^{q+} (q = 1 – 3) and O^{p+} (p = 1 – 3) fragments produced from complete rapture of C–O skeleton. Even two-body, three-body and four-body dissociation events such as:

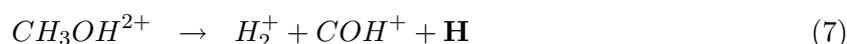


respectively are observed where the C–O bond is broken keeping the OH part intact with the loss of hydrogen at every step. For more than two-body events the missing fragments (i.e. the ones that are in **boldface** in the equations) are either undetected neutrals or H⁺ ions detected as a third or fourth hit in the MCP.

Concentrating on a specific area of the coincidence map, we observed different fragmentation pathways leading to the breakage of one or many of the C–H bonds or the O–H bond in the multiply ionized methanol resulting in the formation of H⁺, H₂⁺ and H₃⁺. There are three two-body Coulomb explosion processes that form hydrogen atomic and molecular ions from doubly charged methanol:

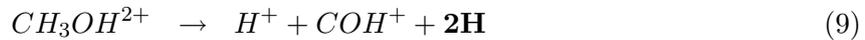
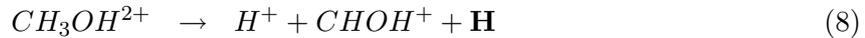


It was observed that H₃⁺ is ejected from doubly charged methanol due to two-body fragmentation process (Eqn. 6) after intramolecular bond rearrangement has taken place in the methyl group of the molecule. But H₂⁺ is formed due to both two-body (Eqn. 5) and three-body



dissociation pathways. It should be noted that as soon as the O–H bond is disrupted and CO⁺ is formed neither H₂⁺ nor H₃⁺ is recorded. It seems that the formation of H₂⁺ and H₃⁺ is a delicate phenomenon which gets disturbed as soon as COH part is broken. These results have

been published elsewhere [8]. Other than the above mentioned two-body channel (Eqn. 4), H^+ formation pathways are through many-body processes:



4. Dissociation of acetylene

4.1. Time-of-flight spectrum

The dissociation products observed from the TOF spectrum (figure 2) of acetylene molecules shows undissociated molecular ions like $C_2H_2^+$ and doubly ionized $C_2H_2^{2+}$. The spectrum further shows C_2H^+ and C_2^+ fragments produced after losing hydrogen atoms due to the breakage of C–H bonds keeping the C–C triple bond intact. Even complete rupture of C–C and C–H skeleton producing charged atomic species like H^+ and C^{q+} where q varies from 1 to 3 are also observed. Existence of stable dication $C_2H_2^{2+}$ hints at the metastability of such ionic species. Coulomb explosion of highly charged parent molecular ions give rise to large kinetic energy releases of charged atomic fragments. As an example, the splitting of carbon and hydrogen atomic fragments into double peaks demonstrate that these ions were expelled with a relatively large kinetic energy in the forward and backward directions to the detector. A shoulder on the higher mass side of $m/q = 13$ is a signature of the broad CH^+ peak produced from different breakup channels. The other interesting feature in the TOF spectrum is the width of the C_2H^+ peak which is broader than its nearest neighbours, $C_2H_2^+$ and C_2^+ . A broad peak of C_2H^+ exhibits a relatively larger kinetic energy distribution than C_2^+ . C_2H^+ is formed from complete two-body breakup ($C_2H^+ + H^+$) where H^+ and C_2H^+ takes away equal and opposite momentum. In case of C_2^+ , two H^+ fragments break away with equal momentum from the two opposite sides of the linear molecule leaving the inner C_2^+ part typically at rest. As a result, this peak narrows down due to less energy imparted to the central C–C moiety.

4.2. Coincidence map

From figure 4, we had separated out correlations between different dissociation channels corresponding to C^+ , C^{2+} and C^{3+} fragments produced from the complete rupture of C–C triple bond. Detection of backward component of CH^+ in coincidence with its forward counterpart confirms that the triple bond C–C although stronger than the C–H bond can break independently leaving the C–H part intact following the two-body reaction:



Also observed is the coincidence between C^+ and CH^+ which can be formed according to two dissociation pathways. One of them is from the secondary breakup of C_2H^+ after a three-body reaction:



Another pathway is through a further dissociation of CH^+ into C^+ following the process:



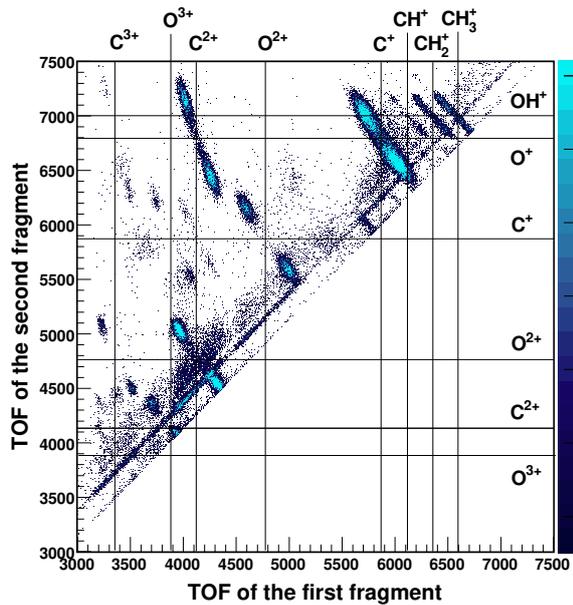


Figure 3. Coincidence map showing dissociation channels between C^{q+} ($q = 1 - 3$) and O^{p+} ($p = 1 - 3$) ions and events like $CH_3OH^{2+} \rightarrow CH_{(3-n)}^+ + OH^+ (n = 0 - 2) + nH$.

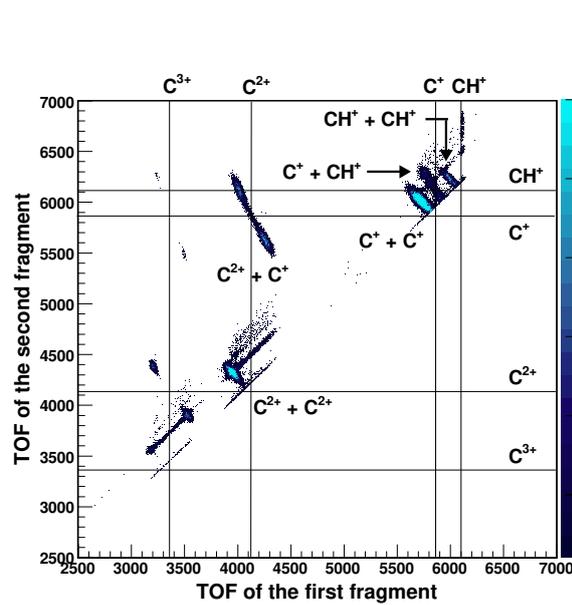


Figure 4. Coincidence map of the dissociative products of C_2H_2 . Islands corresponding to different breakup channels are shown.

4.3. Slope of islands in the coincidence map

The geometrical properties of an island, i.e. the shape, size and orientation, etc., contain useful information for studying the dynamics of dissociation, such as the kinetic energy release (KER) distribution, ejection direction of the dissociated fragments and the dissociation sequence. Theoretical analysis of covariance mapping in mass spectrum has shown that the structure of the island is a momentum contour [9, 10]. The length of the island reflects the kinetic energy of the ion pair and the slope gives information about the charge and momentum of the involved particles. If one or more fragments are not detected, the structure is broadened due to the momentum carried away by the undetected fragments.

The ion time-of-flight T is a linear function of the projection of the ion's initial momentum \mathbf{P} along the spectrometer axis $P_d = P \cos(\theta)$, where P is the modulus of \mathbf{P} and θ is the angle between \mathbf{P} and the ion detection direction. The momentum distribution $\Delta P_d(A^{Q+})$ for a particular A^{Q+} ion is related to the time-of-flight distribution $\Delta T(A^{Q+})$ following the equation:

$$\Delta P_d(A^{Q+}) = Q \Delta T(A^{Q+}) \quad (16)$$

Using the above relationship, we can define a slope between the TOF distributions of correlated ionic species in the coincidence map:

$$\tan \theta = \frac{T_x}{T_y} = \frac{P_x Q_y}{P_y Q_x} \quad (17)$$

where P and Q are the momentum and charge state of the ions displayed along the x - and y -TOF axis.

The shape of the islands gives information about the fragmentation dynamics of two-body as well as three- or many-body dissociation processes. Figure 4 shows the coincidence map

corresponding to the two-body fragmentation pathway:



Here the ions dissociate in opposite directions with equal momenta $|P_x| = |P_y|$ and the island is aligned along $\theta = -45^\circ$ or -1 slope. Therefore due to conservation of momentum, complete two-body fragmentation into equally charged ions result in a narrow structure perpendicular to the diagonal. In case of a stepwise fragmentation, the measured slope is influenced by the momenta of the intermediate dissociation products [9].

We observe a slight change in slope from -1 for the coincidence island between C^+ and CH^+ in figure 4. This deviation is due to the unaccounted momentum carried away by the undetected hydrogen fragment.

4.3.1. Measurement of slope The interpretation of peak slopes is central to the discussion of three-body; sometimes, four-body reaction mechanisms. The peaks are not lines, nor are they generally ellipses nor any figures with unique long axes of symmetry. As a result, the experimental slopes attributed to them depend on how the data are analyzed. Thissen *et al.* [11] have shown the impossibility of defining a straightforward mathematical algorithm to derive the slope of a measured coincidence peak without already knowing the associated fragmentation pathway. To avoid this problem and to obtain information relevant for the interpretation, we have generally taken slopes as manual fits to the long straight contours.

Table 1. Slopes (negative) obtained for the dissociation channels due to C_2H_2 breakup involving the carbon atomic charged fragments. These values were compared with that calculated from Eqn. 17 (see text).

Dissociation products	Slope	
	Expt.	Theory
$C^+ + C^+$	45°	45°
$C^+ + C^{2+}$	65°	63.4°
$C^+ + C^{3+}$	73°	71.5°
$C^{2+} + C^{2+}$	45°	45°
$C^{2+} + C^{3+}$	56°	56°
$C^{3+} + C^{3+}$	45°	45°

Table 1 lists the slopes measured for different dissociation channels involving $C^{q+} + C^{q'+}$ ($q, q' = 1 - 3$) breakup for acetylene. Theoretical slopes were calculated from Eqn. 17 considering equal momenta but different charge states for the correlated carbon fragments. The experimental slopes match very well with the theoretical ones. Observing such agreement one can predict that the carbon ions are ejected with equal and opposite modulus initial momenta similar to diatomic molecules. Due to the symmetry of acetylene, the two H^+ fragments might have broken away initially with equal momentum from the two opposite sides of the linear molecule leaving the inner C_2^{q+} part with minimum KER. This isolated C_2^{q+} part further dissociates in a diatom-like fashion.

5. Conclusion

In this article, we have described in detail the different dissociation pathways of multiply charged methanol and acetylene molecules in collision with HCl. We observed a wide range of dissociation

products from the TOF spectrum and discussed the relative intensities and widths in the peaks in accordance with different breakup phenomenon. From the coincidence map, complete two-body dissociation events such as $\text{CH}_3\text{OH}^{2+} \rightarrow \text{CH}_3^+ + \text{OH}^+$ and $\text{C}_2\text{H}_2^{2+} \rightarrow \text{CH}^+ + \text{CH}^+$ were observed along with three-, four- and many-body ones. The interesting feature in the breakup of CH_3OH is the formation of H^+ , H_2^+ and H_3^+ due to cleavage of the C–H bonds. The geometrical properties of the islands gives further information about the momentum balance in the fragmentation dynamics of two- or many-body dissociation. On careful study of the slopes of the islands we can even deduce whether the fragmentation process is concerted or sequential. We measured the slopes of the coincidence islands for carbon ionic fragments and observed a diatom-like behaviour of the C–C charged complex in dissociative C_2H_2 .

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