

Supplementary Materials for

Sequential Mechanism in H_3^+ Formation Dynamics on the Ethanol Dication

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Mass-scaled Dalitz plot representation

Three-body dissociation of ethanol dication can undergo complex dissociation processes such as concerted and sequential dynamics. In such a process, total energy and momentum conservation laws limit the maximal kinetic energy of any single fragment and create trivial momentum correlations. Thus, it is possible to identify non-trivial correlations that do not originate simply from total momentum and energy conservation. Dalitz-plot representation of three-body momentum correlations is a useful tool in investigating detailed insight into such underlying complex dissociation dynamics.^{37,40,47,52} Therefore, it is essential to obtain the momenta of the cationic fragments as well as the undetected neutral product. In our studies, the cationic momenta in the lab frame are directly obtained from their momentum images whereas undetected neutrals momentum in the laboratory frame are evaluated by momentum conservation from the measured recoil of the detected cationic products in the center of mass frame of the molecular beam. The Dalitz plot representation of the momentum correlation allows mapping the phase space of these correlations onto a 2D plane. The original Dalitz plot⁵¹ representation was developed for 3 equal masses using

$$\eta_1 = \frac{2}{\sqrt{3}}(KE_1 - KE_2)$$
$$\eta_2 = 2KE_3 - 1$$

where KE_1 , KE_2 and KE_3 are the kinetic energies of the three fragments in the center of mass frame. In this representation, 3-body fragmentation with no correlation beyond total momentum conservation maps to a uniform distribution within a unit circle. Luzon et al, generalized the Dalitz plot coordinates for any three different masses by scaling the kinetic energy by the maximal kinetic energy it can obtain while conserving total momentum.³⁷ A kinetic energy fraction is defined as:

$$\varepsilon_i = \frac{M}{M - m_i} \times \frac{KE_i}{KER}$$

Where, M is the total mass of the parent molecule and m_i and KE_i are the fragment masses and kinetic energies. The vertical coordinate, defined as $\eta_2 = 2\varepsilon_3 - 1$ indicates the kinetic energy fraction of the third fragment, while the horizontal $\eta_1 = a(\varepsilon_1 - \varepsilon_2) - b\eta_2$ coordinate reflects the energy partitioning between the other two products.³⁷

Where,

$$a = \frac{(M - m_1)(M - m_2)(M - m_3)}{\sqrt{m_1 m_2 m_3 M(M + m_3)}}$$

and

$$b = \sqrt{\frac{M m_3}{m_1 m_2}} \frac{(m_1 - m_2)}{(M + m_3)}$$

In the case of equal masses, $a = 2/\sqrt{3}$ and $b = 0$, the mass-scaled coordinates are reduced to the original Dalitz plot coordinates.⁵¹

Each point on the Dalitz plot represents a unique dissociation geometry. In the following figures S1-S5 shows how different velocity triangles map to different points on the mass scaled Dalitz plot representation for the masses corresponding to the channels discussed in the main text: $\text{COH}^+ + \text{CH}_3^+ + \text{H}_2$, $\text{CH}_3^+ + \text{CH}_2^+ + \text{OH}$, $\text{CH}_3^+ + \text{CO} + \text{H}_3^+$, $\text{CH}_3^+ + \text{COH} + \text{H}_3^+$ and $\text{C}_2\text{H}_2\text{O}^+ + \text{H} + \text{H}_3^+$. In each plot, the fragmentation patterns are represented by red, green, and blue circles that indicate the velocities of the three fragments. Also indicated by arrows are the three axes corresponding to the mass scaled energy fractions and color coded with red, green, and blue. While the ϵ axes depend on the particular mass, the longitudinal lines indicated on the Dalitz plot have a mass-independent meaning and signify contours of equal Jacobi angle $\beta = 0, \frac{\pi}{3}, \frac{\pi}{2}, \frac{2\pi}{3}$, and π . Where the β angle is defined as the angle of the 3rd fragments dissociation velocity from the center of mass the two other fragments with respect to the axis between them. For example, in the case of $\text{COH}^+ + \text{CH}_3^+ + \text{H}_2$ presented in figure S1, β is the angle between the dissociation velocity of H_2 and the $\text{COH}^+ - \text{CH}_3^+$ axis. Note that the co-linear dissociation patterns are mapped onto the circumference of the unity circle. Where the $\beta = 0$ limit ($\eta_1 > 0$) corresponds to a co-linear dissociation of the $\text{COH}^+ - \text{CH}_3^+ - \text{H}_2$ and $\beta = \pi$ limit ($\eta_1 < 0$) corresponds to a co-linear $\text{COH}^+ - \text{H}_2 - \text{CH}_3^+$ fragmentation.

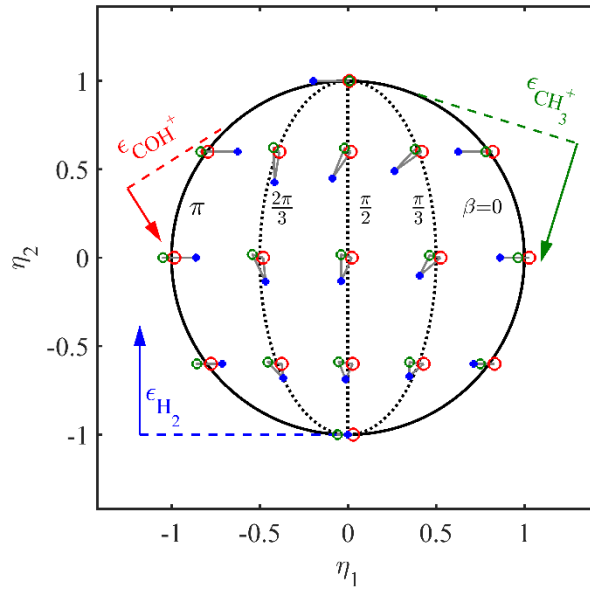


Fig. S1: Mass-scaled Dalitz plot representation 3-body $\text{COH}^+ + \text{CH}_3^+ + \text{H}_2$. ϵ_{COH^+} , $\epsilon_{\text{CH}_3^+}$, and ϵ_{H_2} indicate the energy fraction axis corresponding to each fragment. For different positions on the Dalitz plot plane, red, green, and blue circles indicate the velocity vectors of COH^+ , CH_3^+ and H_2 respectively. The longitudinal lines indicate contours of equal Jacobi angles $\beta = 0, \frac{\pi}{3}, \frac{\pi}{2}, \frac{2\pi}{3}$, and π .

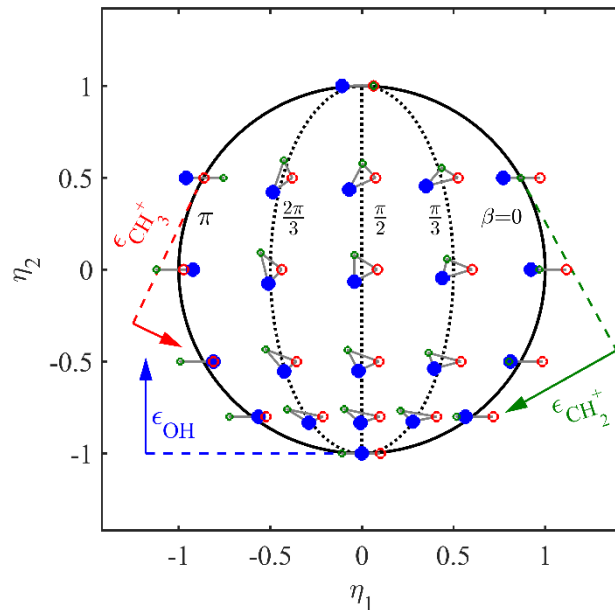


Fig. S2: Representation for $\text{CH}_3^+ + \text{CH}_2^+ + \text{OH}$. $\epsilon_{\text{CH}_3^+}$, $\epsilon_{\text{CH}_2^+}$, and ϵ_{OH} indicate the energy fraction axis corresponding to each fragment. The red, green, and blue circles indicate the velocity vectors of CH_3^+ , CH_2^+ and OH respectively. Longitudinal lines indicate equal Jacobi angle contours.

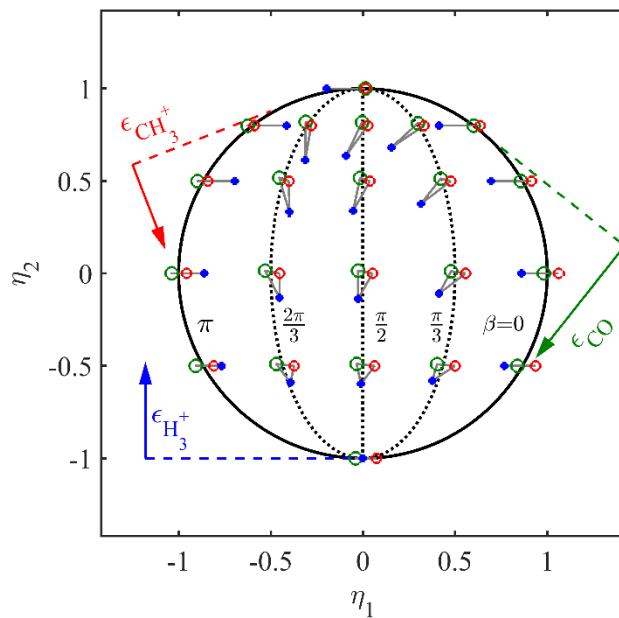


Fig. S3: Representation for $\text{CH}_3^+ + \text{CO} + \text{H}_3^+$. $\epsilon_{\text{CH}_3^+}$, ϵ_{CO} , and $\epsilon_{\text{H}_3^+}$ indicate the energy fraction axis corresponding to each fragment. The red, green, and blue circles indicate the velocity vectors of CH_3^+ , CO and H_3^+ respectively. Longitudinal lines indicate equal Jacobi angle contour.

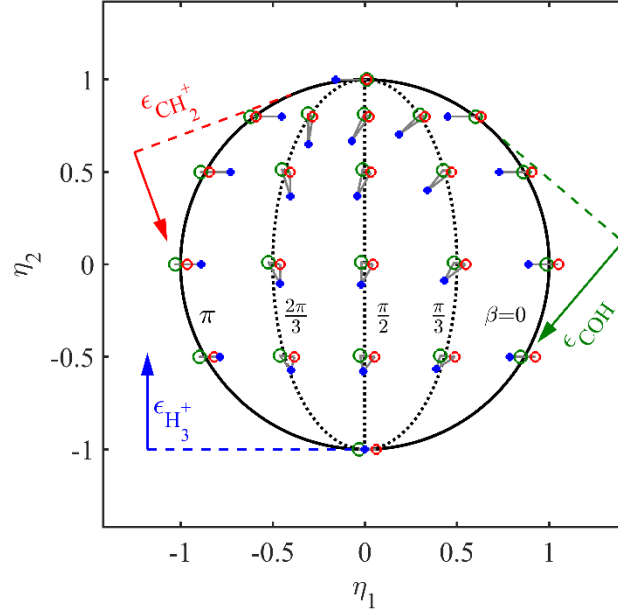


Fig. S4: Mass-scaled Dalitz plot representation 3-body $\text{CH}_3^+ + \text{COH} + \text{H}_3^+$ fragmentation of the methanol cation. $\epsilon_{\text{CH}_3^+}$, ϵ_{COH} , and $\epsilon_{\text{H}_3^+}$ indicate the energy fraction axis corresponding to each fragment. For different positions on the Dalitz plot plane, red, green, and blue circles indicate the velocity vectors of CH_3^+ , COH and H_3^+ respectively. The longitudinal lines indicate contours of equal Jacobi angles $\beta = 0, \frac{\pi}{3}, \frac{\pi}{2}, \frac{2\pi}{3}$, and π .

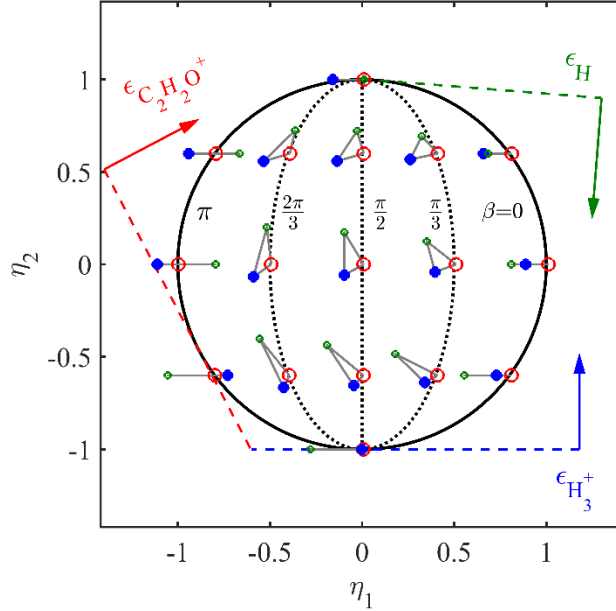


Fig. S5: Mass-scaled Dalitz plot representation 3-body $\text{C}_2\text{H}_2\text{O}^+ + \text{H} + \text{H}_3^+$ fragmentation of the methanol cation. $\epsilon_{\text{C}_2\text{H}_2\text{O}^+}$, ϵ_{H} , and $\epsilon_{\text{H}_3^+}$ indicate the energy fraction axis corresponding to each fragment. The red, green, and blue circles indicate the velocity vectors of CH_3^+ , COH and H_3^+ respectively. The longitudinal lines indicate contours of equal Jacobi angles $\beta = 0, \frac{\pi}{3}, \frac{\pi}{2}, \frac{2\pi}{3}, \text{ and } \pi$.

Three-body momentum correlations in the $\text{H}_3^+ + \text{C}_2\text{H}_2\text{O}^+ + \text{H}$ channel:

Fig. S6 shows the Mass-scaled weighted Dalitz plot representation of $\text{H}_3^+ + \text{C}_2\text{H}_2\text{O}^+ + \text{H}$ channel. The measured correlations are consistent with the sequential 3-body H_3^+ formation mechanism described in the manuscript text for the other H_3^+ formation 3-body breakup channels. In this channel that consists of one heavy and two light fragments, the reconstruction of the neutral fragment momentum is particularly sensitive to the momentum spread in the effusive molecular beam. It is possible that the larger spread in $\epsilon_{\text{H}_3^+}$, compared with the other two channels is at least partially due to the velocity spread in the molecular beam and not only due to a the distribution of momentum correlations according to the mapping depicted in Fig. S5.

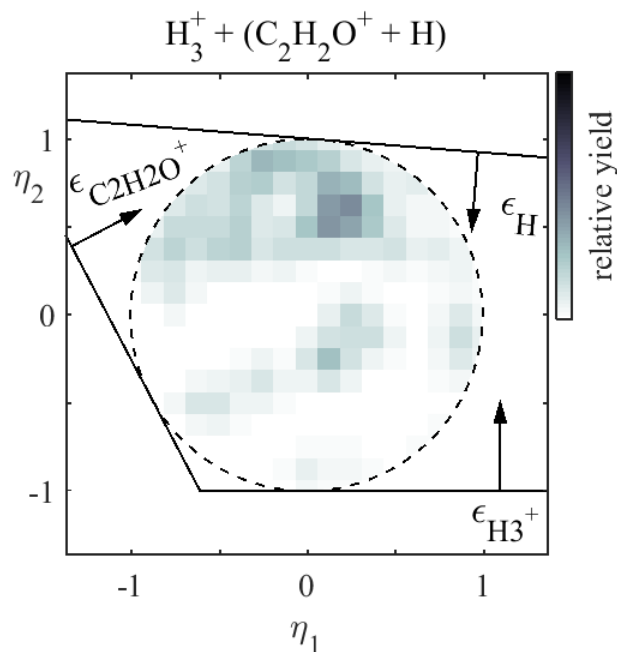


Fig. S6: Mass-scaled weighted Dalitz plot representation of three-body dissociation of $CH_3CH_2OH^{2+}$ into: $H_3^+ + C_2H_2O^+ + H$, assigned to a sequential mechanism. In each panel, three ϵ axis correspond to the fraction of the KER of each fragment relative to the maximal fraction allowed by total momentum conservation.

Dalitz plot representation of two typical sequential mechanisms:

In a purely sequential mechanism $ABC \rightarrow A + BC$, the transient BC can complete a rotation before the 2nd dissociation of $BC \rightarrow B + C$. Thus, the kinetic energy carried by fragment A does not depend on the energy partitioning between fragments B and C . Such an uncorrelated sequential mechanism in the mass-scaled weighted Dalitz plot would exhibit a stripe structure perpendicular to the kinetic energy axis of fragment A . Figure S7 shows simulated Dalitz plot of two types of sequential dissociation mechanisms.

One mechanism, in which the KER in the initial breakup into $A + BC$ is small relative to the KER in the 2nd dissociation of $BC \rightarrow B + C$. The contribution of this process is colored in blue and appears as a stripe at a particular KER fraction of fragment A , with no correlation with the energy partitioning between fragments B and C . In the second mechanism, indicated by the red distribution, the KER in the 1st dissociation is much higher than in the second step. Here the stripe appears at high KER fractions for fragment A .

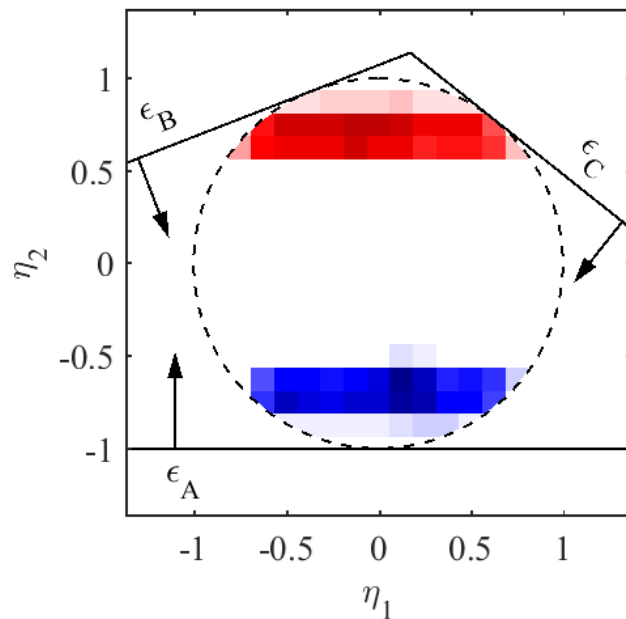


Fig. S7: Mass-scaled weighted Dalitz plot representation of a purely sequential mechanism $ABC \rightarrow A + BC \rightarrow A + B + C$. The blue strip feature shows the expected three-body correlation in a sequential dissociation mechanism in which initial KER of $A + BC$ is $15 \pm 5\%$ relative to the total KER, whereas the red strip shows a simulated correlation in a mechanism with an initial KER of $A + BC$ is $85 \pm 5\%$ relative to the total KER.

Mass spectrum:

The mass spectrum of photoionization of ethanol is presented in figure S8. Several masses of interest are indicated with corresponding arrows. In addition to the masses related to ethanol ionization, a prominent Ne^+ peak can be observed, originating from the HHG semi-infinite gas cell.

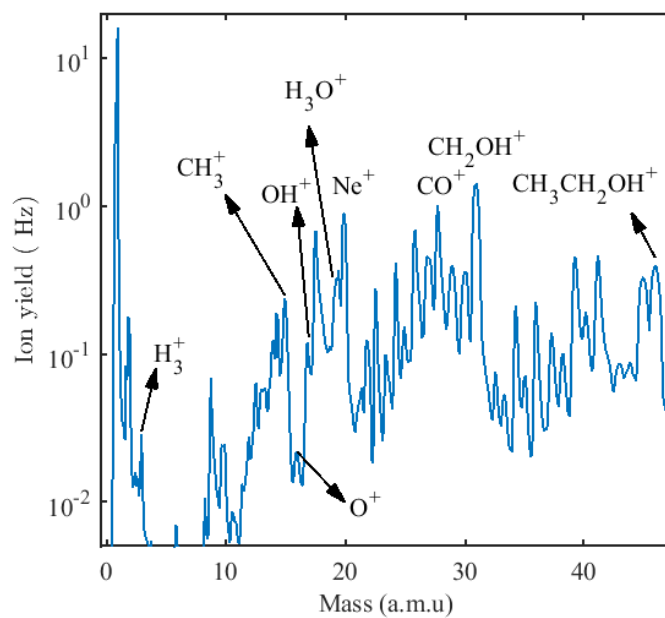


Fig. S8: Mass spectrum obtained from single ion counts, attributed primarily to dissociative photoionization of ethanol by EUV pulses.