Dissociation pathways of two-body fragmentation of methane dication

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Synopsis The two-body fragmentation of methane dication has been studied using the technique of cold target recoil ion momentum spectroscopy. For the dissociation channel leading to detection of ($H^+ + CH_3^+$) the kinetic energy release distribution shows three different pathways, of which two are explained but the third, which appears only with particle impact excitation, remains unexplained. A discussion on the relative branching ratios of these three pathways as a function of specific ion-molecule interaction will be presented.

The methane molecule is the smallest hydrocarbon with a three-dimensional structure and thus provide a test bench for both experimental and theoretical methods. The dication of methane, CH_4^{2+}, formed upon a Frank-Condon transition from the ground electronic state of neutral methane has a tetrahedral geometry with T_d symmetry. On the other hand, the minimum energy equilibrium structure of methane dication is predicted to have planar geometry. Because of these different geometries of neutral methane and its dication, the dissociation of methane dication is expected to involve significant structural changes. We have addressed the two-body and three-body dissociation of methane dication $[CH_4]^{2+}$ using the technique of cold target recoil ion momentum spectroscopy (COLTRIMS) in an ion-molecule collision experiment.

For two body dissociation of methane dication, fragment pairs (H^+ , CH_3^+) and (H_2^+ , CH_2^+) are observed. For breakup into (H^+ , CH_3^+), results on four different data sets will be presented [1]. We observe three distinct dissociation pathways (I,II,III) for each data set with mean kinetic energy releases (KER) of around 4.7 eV, 5.8 eV and 7.9 eV, respectively (see figure 1). Of the three observed pathways, pathway II has been observed and its origin is explained in earlier reports. We have proposed an explanation for observation of pathway III using existing *ab-initio* calculations on electronic states of methane dication but the pathway I still remains unexplained [1]. We have also estimated the relative branching ratios for the three pathways, and a strong correlation with the specific nature of the ion-molecule interaction is noted. A discussion on the electronic states leading to these different pathways will be presented.

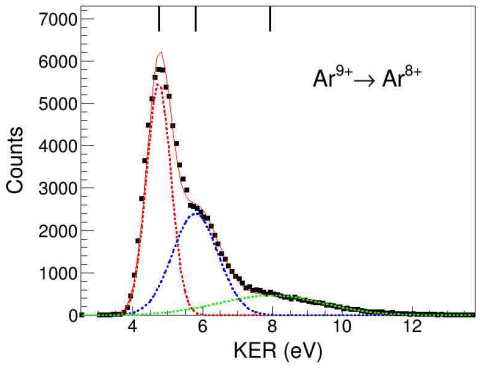

Figure 1. A typical fit for the KER distribution for the process, $CH_4^{2+} \rightarrow H^+ + CH_3^+$. The squares correspond to experimental data.

References

[1] J Rajput *et al.* 2022 *J. Chem. Phys.* **156** 054301

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