Disentangling sequential from concerted three-body fragmentation of molecules

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Synopsis Many times the three-body fragmentation of polyatomic molecules proceeds via two competing pathways, either a concerted fragmentation or a sequential breakup. Since in both cases the final products are the same set of ions, it becomes difficult to disentangle events coming from the two. We propose a novel method to separate events belonging to the two pathways by analyzing the data in two frames of reference associated with each of the breakup steps. Such an analysis reveals information about the electronic states of the molecular intermediate formed in the sequential mechanism, yields branching ratios of all the competing pathways, and enables plotting spectra for each pathway separately.

Advances in imaging techniques have always led to better understanding of molecular fragmentation induced by either photons or collisions. A long-standing goal is the experimental distinction between concerted and sequential (sometimes called "stepwise") fragmentation mechanisms in polyatomic molecules. For example, the sequential breakup of triply-charged triatomic molecules may involve an intermediate dication which later undergoes unimolecular dissociation, such as $OCS^{3+} \rightarrow CO^{2+} + S^{+}$ followed by $CO^{2+} \rightarrow C^{+} + O^{+}$.

In particular we focus on pathways involving metastable dication states which survive much longer than their rotational period, i.e. $\tau \gg T_R$. This "delayed" sequential breakup has been invoked [1] to explain the observation of a circular feature in a Newton diagram, which shows the correlation between momenta of the three final fragments measured in coincidence.

We further explore the identity of these metastable dication states by analyzing the coincidence three-dimensional momentum imaging data of the three fragment ions in two frames of reference associated with each of the breakup steps. This method allows clear identification of sequential breakup of states with $\tau \gg T_R$, separating them from the other competing breakup mechanisms, and thus providing branching ratios. More importantly, the evaluated kinetic energy release (KER) during each step opens the door to pinpointing the specific electronic, or with improved resolution, vibrational states involved. In addition, it allows for exploring any measured distribution for each mechanism independent of the other.

Our method is demonstrated using ionization of an OCS target by ultrashort intense laser pulses. However, it is applicable to other processes leading to three-body breakup, like electron and ion impact, as long as the momenta of the three fragments are detected in coincidence. By using the proposed method, we have identified the possible electronic states of intermediate CO^{2+} formed during the first step of sequential breakup (see figure below).

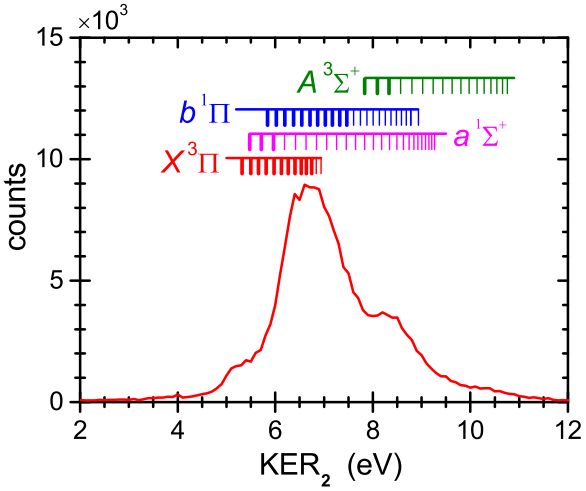

Figure 1. Kinetic energy release upon dissociation of the intermediate CO^{2+} formed in the first step of sequential breakup of OCS^{3+}.

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References

[1] N. Neumann *et al.* 2010 *Phys. Rev. Lett.* **104** 103201

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