PRODUCT STATE AND SPEED DISTRIBUTIONS IN PHOTOCHEMICAL TRIPLE FRAGMENTATIONS

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The clearest dynamical signature of a roaming reaction is a very cold distribution of energy into the rotational and translational degrees of freedom of the roaming donor fragment (e.g. CO) and an exceptionally hot vibrational distribution in the roaming acceptor fragment (e.g. H_2, CH_4). These signatures were initially identified in joint experimental/theoretical investigations of roaming in H_2CO and CH_3CHO and are now being used to infer the presence of roaming mechanisms in other photodissociating molecules. In this seminar we present a phase space theory (PST) model of triple fragmentation (3F) and show that the dynamical signature of triple fragmentation is very similar to that of the roaming donor fragment.

The 3F-PST model assumes that the initial two-body fragmentation (2F) step occurs via a barrierless bond cleavage process (which is true for many many closed shell systems), and calculates the 2F-PST distribution of energy in each fragment. The 2F-PST model is benchmarked against $H_2CO \rightarrow H + HCO$, $CH_3CHO \rightarrow HCO + CH_3$, $CH_3CHO \rightarrow H + CH_3CO$, and $CH_3OCHO \rightarrow H + CH_3OCO$ and shown to provide a good representation of the available experimental data. Every fragment with sufficient internal energy to undergo subsequent spontaneous dissociation is allowed to dissociate and the 3F-PST distribution of energy into secondary products is calculated.

Using $CH_3CHO \rightarrow HCO + CH_3 \rightarrow H + CO + CH_3$ as an example, we calculate that the energy disposal into the product rotational and translational degrees of freedom of the secondary fragments is very low. In the case of the CO fragment this is similar to the dynamical signature for production of CO via a roaming mechanism. We compare the 3F-PST model with published experimental data for photodissociation of several molecules at energies above the 3F threshold, and demonstrate that, in some cases, 3F provides an alternative explanation for the observed product state distribution.