Statistical Molecular Fragmentation model for studying the decomposition of molecules

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The fragmentation of molecules under conditions that result in yields of products that are thermodynamically controlled can be readily studied with statistical models. In this context, we have developed the statistical molecular fragmentation (SMF) model which describes molecular fragmentation by building the microcanonical ensemble of all possible configurations of the fragments and by deriving the probabilities of all fragmentation channels from the laws of classical and quantum mechanics. The input data for the SMF model are the structural, electronic, and vibrational properties of the parent molecule and its fragments. These can be obtained from *ab initio* electronic structure calculations. We explore which properties influence the branching ratios using our SMF model and apply it to the decomposition of propane. We find that the fragmentation process has low sensitivity to the differences between the molecular descriptions given by commonly used ab initio methods (B3LYP, CCSD(T), and composite methods with different atom-centered basis sets). However, the branching ratios are most influenced by the vibrational frequencies of the molecules and radicals present in the decomposition pathways.

The SMF model was also used to analyze the 306 fragmentation channels (containing 611 different species) that result from the fluorene ($C_{13}H_{10}^+$) cation losing up to three hydrogen atoms (neutral radicals and/or a proton). Breakdown curves from such analysis permit one to extract experimentally inaccessible information about the fragmentation of the fluorene cation, such as the locations of the lost hydrogen atoms (or proton), yields of the neutral fragments, electronic states of the residues, and quantification of very low probability channels that would be difficult to detect. Charge localization during the fragmentation pathways was studied to provide a qualitative understanding of the fragmentation process. Breakdown curves for both the fluorene cation and neutral fluorene were compared. The SMF results match the rise and fall of the one hydrogen loss yield experimentally measured by imaging photoelectron-photoion coincidence spectroscopy using a VUV synchrotron.
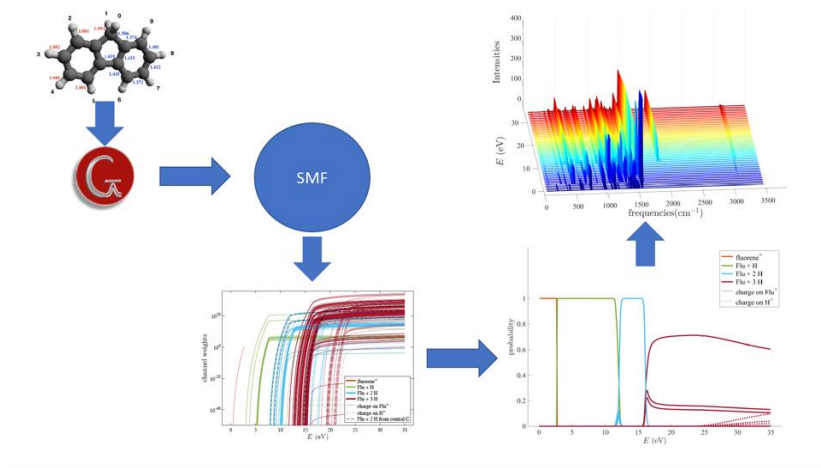
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