

Competing Atomic and Molecular Hydrogen Pathways in the Photodissociation of Methanol at 157 nm

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Abstract

With the advent of various high power lasers and the third generation of synchrotron light source, molecular beam photofragmentation translational spectroscopy has become an extremely powerful tool for the investigation of dynamics and mechanism of dissociation of polyatomic molecules.

Precise measurements of recoil velocity distributions and angular distributions not only provide detailed information about the dynamics of dissociation processes, but also give definitive answers to the identifies of dissociation products. The problem related to the failure to observe the parent ions from highly internally excited radical products by mass spectrometric detection can be overcome by applying the conservation of linear momentum and total mass number in the dissociation process in spite of the fact that only daughter ions are detectable.

Photofragment translational spectra at $m/e = 1(\text{H}), 2(\text{H}_2, \text{D}), 3(\text{HD})$ and $4(\text{D}_2)$ have been obtained for CH_3OH , CH_3OD and CD_3OH at 157nm excitation. Analysis of the time-of-flight (TOF) spectra reveals two different atomic H loss channels: hydroxyl H elimination, and methyl H elimination. While the hydroxyl H elimination seems to be a single fast process, the methyl H loss exhibits clearly two significantly different mechanisms: one fast and one slow. Experimental results also show two molecular hydrogen elimination channels: 3-center elimination from the methyl group, which displays two different micro-pathways, and 4-center elimination involving hydrogen atoms on both the C and O sites. The relative branching of the atomic versus molecular hydrogen elimination channels was found to be 1:0.15. These results present a uniquely clear picture of methanol photodissociation at 157nm, and thus provide an excellent case for quantitative theoretical investigations.

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