

## Intramolecular particle exchange in the fragmentation of methanol upon valence photo double ionization

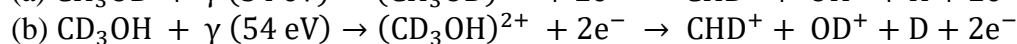
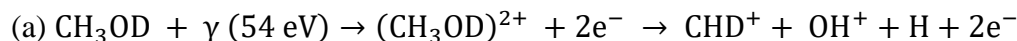
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We investigated the valence photo double ionization (54eV) of two isotopologues of methanol molecules (CH<sub>3</sub>OD and CD<sub>3</sub>OH), by measuring the final 3D momenta of 2 electrons and 2 cation fragments in coincidence, using the COLTRIMS (COLd Target Recoil Ion Momentum Spectroscopy) technique at the Advanced Light Source. Here we report on the comparison of two specific 3-body fragmentation channels that show a clear signature of intramolecular particle exchange, which we trace via deuterium scrambling in the two different isotopologues of methanol:



For both reactions, the momentum of the neutral fragment is determined via momentum conservation. The goals of our investigation are to track and understand state-selectively the influence of nuclear dynamics on intramolecular particle exchange and roaming during the dissociation process. This is achieved through the analysis of the relative branching ratios with respect to the most intense 2-body breakup channels, CH<sub>3</sub><sup>+</sup> + OD<sup>+</sup> or CD<sub>3</sub><sup>+</sup> + OH<sup>+</sup>, respectively. Moreover, electron-ion energy correlation maps are used to identify and isolate the participating electronic states along the C-O internuclear distance of the dication potential energy surfaces, which we calculated using the Multi-Reference Configuration Interaction (MRCI) method. In addition, by exploiting the measured electron energy sharing and the electron angular distributions, we are able to distinguish between contributions from autoionization and direct double ionization. Employing this differential insight, we interpret observables like the pairwise ionic and neutral fragment momentum sharing and Newton plots, and apply the native frames analysis, in order to retrace the fragmentation processes and identify the intermediates of the 3-body breakups (a) and (b).

**Keywords:** Methanol, Native frames, COLTRIMS, molecular dynamics, valence photo double ionization, roaming, particle exchange.

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