REACTION DYNAMICS OF VIBRATIONALLY EXCITED CH_3D MOLECULES WITH CHLORINE

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State-resolved reactions of CH_3D molecules with Cl atoms probe the consumption and disposal of vibrational and translational energy. Using state-resolved detection it is possible to determine the relative effects of these on the reaction and gain a better understanding of the reactivity differences between modes.

In one recent experiment, we explored the effect of exciting either the combination of the C-H symmetric stretch and the C-D stretch ($\nu_1 + \nu_2$), the combination of the C-D stretch and the C-H antisymmetric stretch ($\nu_2 + \nu_4$), or the combination of the C-D stretch and the first overtone of the CH_3 bend ($\nu_2 + 2\nu_5$). The reaction dynamics largely follow a spectator picture in which the surviving bond retains its initial vibrational excitation. In at least 80% of the reactive encounters of vibrationally excited CH_3D with Cl, cleavage of the C-H bond produces CH_2D radicals with an excited C-D stretch, and cleavage of the C-D bond produces CH_3 radicals with an excited C-H stretch. Deviations from the spectator picture seem to reflect mixing in the initially prepared eigenstates and, possibly, collisional coupling during the reaction.