

TURNING REACTIONS OFF AND ON WITH VIBRATIONAL EXCITATION

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Vibrational excitation can control the course of a bimolecular H-atom abstraction reaction. The bond-selected reaction of HOD with H, Cl, or O atoms is a prototypical example in which excitation of a stretching overtone vibration of either the O-H or the O-D bond leads to preferential cleavage of that bond. The energy available in the reaction preferentially appears in the new bond with the bond that breaks being essentially a spectator to the reaction. The ability to drive these direct reactions by exciting vibrational eigenstates that closely resemble bond stretching vibrations and involve motion along the reaction coordinate raises the question of the role of vibrations that are "perpendicular" to the reaction coordinate.

Preparation of well-characterized vibrational states in the region of three quanta of N-H stretching excitation ($3\nu_1$) in isocyanic acid (HNCO) permits experimental investigation of the extent to which vibrations perpendicular to the reaction coordinate can direct the bimolecular reaction of Cl atoms with HNCO to form HCl and NCO. Angular momentum states corresponding to different amounts of a-axis rotation in HNCO are well separated in energy, and perturbations by background states make each of the eigenstates a different mixture of zero-order states. Molecules in the essentially unperturbed $K = 1$ and 4 states, which are nearly pure N-H stretching excitation, react efficiently, but those in the perturbed states, $K = 0, 2,$ and 3 , which are a mixture of N-H stretching and bending excitation, react only half as fast. Detailed analysis of resolved, perturbed eigenstates for $J = 6$ and 7 of $K = 3$ reveals the reactivity of the two interacting zero-order states separately. The less reactive zero-order state, which most likely contains only two quanta of N-H stretch and several quanta of bending excitation, reacts only 10% as well as the pure N-H stretch zero-order state. Ab initio calculations suggest that bending excitation inhibits the reaction by changing the interaction potential between HNCO and the approaching Cl atom.