SPECTROSCOPIC PROBES AND VIBRATIONAL STATE CONTROL OF CHEMICAL REACTION DYNAMICS IN GASES AND LIQUIDS

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Vibrational energy plays a crucial role in chemical reactions because the relative motion of the constituent atoms transforms molecules from reactants into products. Thus, one means of controlling the course of a reaction is selective excitation of vibrations containing a significant component of motion along the reaction coordinate. Experiments on both bimolecular reaction and photodissociation of vibrationally excited molecules demonstrate this possibility by selectively breaking chemical bonds. These measurements raise the possibility of similar manipulations in liquids. Experiments using ultrashort laser pulses to prepare a bond vibration and to monitor the vibrationally excited molecule directly observe the flow of vibrational energy in molecules isolated in the gas phase or interacting in solution. They reveal the influence that the level of initial vibrational excitation, the vibrational state structure of the excited molecule, and the identity of the solvent have on the flow of energy within the excited molecule and into the solvent. The rates of these processes determine the characteristic times for control of bimolecular reaction or photodissociation in liquids.