Intramolecular energy partitioning in multiphoton excitation by isotopic branching

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The IR multiphoton dissociation of CH_2DCH_2Cl was studied by observing the yields and the branching ratio R = [HCl]/[DCl] of the two unimolecular reaction channels. The yields and R were examined as a function of beam energy, beam geometry, excitation wavelength, irradiation time and the pressure of various added inert gases. It was found that R initially decreased with increasing inert gas pressure in the range 0 - 5 Torr and finally reached a plateau at higher pressures; the plateau corresponded to internal energies E^* up to 120 kcal mol^{-1} (about 40 photons) and lifetimes of about 10^{-10} - 10^{-11} s. The effects of various added inert gases, changes in excitation wavelength and the inert gas pressure were incompatible with a Boltzmann population but quantitatively compatible with a Rice–Ramsperger–Kassel–Marcus transition state model.

Energy pooling in laser CO_2 multiphoton dissociation

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Collision-induced energy pooling in laser CO_2 multiphoton dissociation is discussed. The number of molecules which are transported above the threshold energy for decomposition is calculated for two initial energy distributions. The effects on the final internal energy distribution of the degrees of freedom, the number of photons absorbed and the temperature are reported. It is found that collisional energy pooling does take place after the laser pulse and the number of molecules transported above a critical threshold depends on the initial energy distribution, the degrees of freedom and the number of photons absorbed.