

VIBRATIONAL STATE DISTRIBUTION AND RELAXATION OF VINOXY RADICALS

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To the red of B-X band origin, the LIF excitation spectra were recorded for vinyloxy radicals (CH_2CHO) produced from photodissociation of alkyl vinyl ether or reactions of $\text{O}(^3\text{P})$ with terminal alkenes. The nascent radicals display rich hot bands from which the vibrational state distribution is determined. For the reactions of $\text{O}(^3\text{P})$ with ethylene, propene, 1-butene and 1-pentene, the average vibrational energy released to vinyloxy is 2100, 1800, 1570 and 1180 cm^{-1} respectively. This remarkable cooling with the lengthening of hydrocarbon chain indicates that the reaction complex lives long enough for the IVR to occur prior to the formation of vinyloxy. Following the time dependence of the hot band intensities, the relaxation rate of vinyloxy were measured as a function of vibrational energy and buffer gases. The relaxation process is found to be stepwise with a 200-300 cm^{-1} step.