APPLICATIONS OF STEP-SCAN TIME-RESOLVED FOURIER-TRANSFORM INFRARED SPECTROSCOPY TO REACTION DYNAMICS AND INTERMEDIATES

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With the multiplex advantage associated with FTIR spectroscopy, the step-scan time-resolved Fourier-transform infrared (ss-TRFTIR) spectroscopy provides valuable information about gaseous reaction intermediates and their reaction dynamics. Infrared emission observed upon ultraviolet laser irradiation of gaseous precursors, under either continuous flow or pulsed supersonic-expansion conditions, provides information about the internal (rotational and vibrational) distributions of photoproducts or parents. For instance, the internal distributions of HF produced via a four-center elimination channel upon irradiation of fluorobenzene and other fluorocompounds at 193 nm were determined. Upon excitation at 248 nm, the emission from highly internally excited fluorobenzene provides evidence of mode-selective excitation in its ground electronic state that might reflect the geometry near the transition-state region for four-center elimination. We also developed ss-TRFTIR in an absorption mode by coupling an absorption reactor with multipassed UV photolysis beam and IR probe beam to record infrared absorption spectra of transient species. Infrared spectra of several reactive species such as ClCS and CH_3SO_2 were thus detected for the first time. Observed spectra are consistent with quantum-chemical calculations and simulation of rotational contours. Related reaction kinetics were also investigated with these absorption features.