IMPLEMENTATION OF FLASH PHOTOLYSIS AND ELECTRIC DISCHARGE APPROACHES FOR FREE RADICAL ABSORPTION SPECTROSCOPY IN SUPERSONIC JET

Y. G. UTKIN, JIA-XIANG HAN, HONG-BING CHEN, N. T. HUNT and R. F. CURL, *Rice University, Department of Chemistry and Rice Quantum Institute, Houston, Texas 77005, USA*.

An IR pulsed supersonic jet spectrometer for the investigation of cold free radicals has been developed using a DFG probe. The novel feature of this spectrometer is that radicals can be produced by either flash photolysis or electric discharge providing significant versatility. With methyl bromide precursor, both radical production methods gave comparable S/N for CH_3 ν_3 R(0) with the discharge method yielding a somewhat better S/N ratio. Flash photolysis tends to produce higher radical concentrations, and the production of a specific radical species is more predictable with this approach. In addition, with flash photolysis, the temperature can be controlled to some extent: increasing the backing pressure lowers the temperature in the probe region with a consequent reduction in spectral congestion. Electric discharge production has a much higher duty cycle. In each gas pulse, data can be taken over a 2ms time window as compared with of 4-8 μs for flash production, and concentration modulation with lock-in detection dramatically increases sensitivity in the discharge approach. With this spectrometer, the previously unobserved rotationally resolved spectra of the ν_1, ν_2 and ν_{14} vibrations of allyl radical were measured by using both techniques. Flash photolysis radical production was more recently employed to record the high resolution low temperature spectrum of methoxy radical in the region 2800-3000 cm^{-1}.