An excimer laser with pulse duration of 28 ns FWHM and average power at 248 nm of 530 mJ per pulse was purchased and used as a photolysis source to accompany an existing nanosecond infrared spectrometer. With this system, transient molecular species with lifetimes as short as ten nanoseconds can be investigated. Gaseous CF3I was photolyzed to produce CF3 radicals whose infrared spectra around 1250 wavenumbers were taken at selected delay times. At very short delays highly vibrationally excited radicals are found, and a measure of vibrational relaxation rates can be made. Final report, AFOSR-87-0044, 22 Jun 88, 'Transient Behaviors in Chemical Reactions: Nanosecond Infrared Spectroscopy, Chemically Pumped Visible and Near-IR Lasers', Cang P. and Atwood, A.
AFOSR-TH. 88-0862

FINAL REPORT

DOD-University Research Instrumentation Program Grant AFOSR-87-0044

TRANSIENT BEHAVIORS IN CHEMICAL REACTIONS: NANOSECOND INFRARED
SPECTROSCOPY, CHEMICALLY PUMPED VISIBLE AND NEAR-IR LASERS.

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The purpose of this grant was to provide funds for acquisition of an excimer dye laser to serve as a dedicated photolysis source to accompany our nanosecond infrared spectrometer. This nanosecond infrared spectrometer provides a broad-band (~300 cm\(^{-1}\) band width) continuum infrared pulse near ten microns with pulse duration near one nanosecond. This pulse can be used as a diagnostic "probe" pulse to investigate transient molecular species with lifetimes as short as ten nanoseconds. The requested photolysis source produces the transient species we wish to study.

The funds have now been expended in the purchase of a Lambda Physik Model EMG 201 Excimer Laser with pulse duration of 28 nanoseconds (FWHM) and average power at 248 nm of 530 millijoules per pulse. It has been in successful operation now for several months. Figure 1 shows an example of its successful use. The sample photolyzed was a mixture of 0.5 torr CF\(_3\)I plus 25 torr of CO\(_2\) in a one meter path cell. The photolysis source was operated at 248 nm to photodissociate a fraction of the CF\(_3\)I, producing gaseous CF\(_3\) and I. With selected delay times, the IR probe pulse was used to examine the infrared spectrum of CF\(_3\) in the spectral region centered around 1250 cm\(^{-1}\). The figure shows that at modest delay times (1-5 microseconds), the CF\(_3\) spectrum has the classic P-R band contour of a rotationally and vibrationally relaxed molecule. At much longer times, this CF\(_3\) signal disappears due to the (relatively) slow binary recombination to form C\(_2\)F\(_6\), which is recorded as a final, stable product. What is most interesting in this study is the spectrum after short delays (less than 200 nsec). The CF\(_3\) spectrum plainly shows the presence of a high concentration of...
vibrationally excited molecules. The temporal changes between 10 and 1000 nanoseconds permit direct measurement of vibrational relaxation. In addition, enhanced reactivity of such vibrationally excited molecules with some added reactant can be sensed and measured.

This is but one example showing the successful and productive outcome of this grant. Publications are in preparation; all equipment details are included in the Ph.D. dissertation of Mark Young, University of California, Berkeley, California (December 1987).