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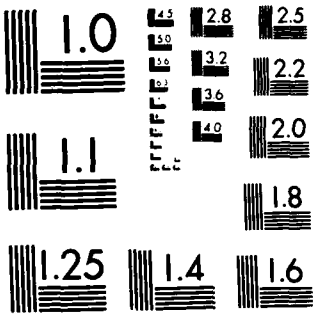

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Research was performed on the reactivity, spectroscopy, and dynamics of vibrationally excited small polyatomic molecules. Infrared multiple-photon excitation of chlorocyclobutane, chloroethane, and other species was investigated. Laser-induced fluorescence excitation spectroscopy was used to probe vibrational distributions following IRMPE in thiophosgene. Master-Equation and Block-Equation calculations were used to analyze experimental results.

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AFOSR-TR- 83-0123

FINAL REPORT

to the

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

on

Grant No. AFOSR-78-3725

"Spectroscopy and Chemistry of Molecules with High Vibrational Energy Content"

by

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(15 October 1982)

The overall objectives in this program were to characterize the reactivity, spectroscopy, and dynamics of vibrationally excited small polyatomic molecules. For convenience, we summarize here the principal findings arising from the research carried out. Further details can be found in the cited reference(s) from the publications list which follows.

The reactivity of a variety of molecules excited to dissociation by infrared multiple-photon absorption (IRMPA) has been investigated. The species $R_2C{=}CHCl$ ($R = CH_3$, F) were found to produce the vinylidenecarbene intermediate, $R_2C = C:$, which rearranged to the substituted acetylene except in the case of R = F, where the rearrangement was hindered. (Reiser and Steinfeld, 1980). The species C_4H_7Cl (cyclobutyl chloride) was found to possess three competitive dissociation channels, viz., HCl elimination, ring scission, and C=Cl homolysis. (Francisco and Steinfeld, 1981; Lawrance et al., 1981). The species CF_3OOCF_3 (bis(trifluoromethyl)peroxide) dissociated by cleavage of the O-O bond; the resulting CF_3O radicals underwent secondary dissociation to CF_2O + F. (Francisco et al., 1981; Zhang et al., 1982). The most extensive series of investigations was carried out on normal ($-d_0$) and deuterated ($-2-d_1$, $-2,2,2-d_3$) chloroethane. By the use of a Master-Equation model, we were able to estimate the energy-dependent infrared absorption cross-section $\sigma(E)$; both increasing deuteration and increasing energy within the molecule have the effect of enhancing the statistical behavior of $\sigma(E)$. (Francisco et al., 1982; Francisco et al., to be published). Spectroscopic and kinetic investigations were also carried out on these molecules. (Francisco et al., 1981; Francisco et al., 1982; Zhu et al., 1982).

Infrared-optical double-resonance methods have been employed to probe the excitation dynamics and distributions in IRMPA. In a collaboration with Dr. D. Brenner of the Brookhaven National Laboratory, vibrational levels of thiophosgene were probed by laser-induced fluorescence excitation spectroscopy under both collision-free (beam) and bulk-gas conditions. The dominant feature in this

system appears to be highly efficient on-resonant pumping of very weak overtone and combination bands; the most astonishing result is the apparently huge effect of collisions in suppressing this pumping process. (Brenner et al., 1981; Brenner et al., in press). We are also developing a Coherent Anti-Stokes Raman method for probing vibrational distributions following IRMPA.

We also attempted to investigate the reactivity of single-photon-excited molecules, using a DF chemical laser oscillating at 3.4 μm to excite C-H stretching modes in alkanes. (Frankel and Frankel, 1982). Although laser operation at these wavelengths was achieved, and excitation cross-sections measured, difficulties with sample purity and analytical procedures prevented us from obtaining a definitive result in this particular area.

Towards the conclusion of the present research grant, increasing emphasis was placed on laser-initiated reactions taking place at or near surfaces, particularly of fluorocarbon radicals generated by IRMPA with silicon surfaces. Optical diagnostic techniques, particularly laser-induced fluorescence, have been developed for studying these reactions, and work is now proceeding along these lines.

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