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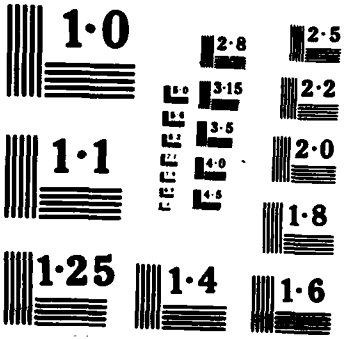
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An excimer laser based dye laser system has been purchaed and integrated into a experiments which involve DOD funding. The laser system is currently used in several important experiments: photodissociation of aliphatic nitro and nitroso alkanes, and halogen cyanides; bimolecular reactions of C_2H, and cluster reactions of H with CO_2; laser induced infuorescence studies in pulsed power switches such as thyratrons. The laser system has already become an integral part of these studies, and will be used in other funded research in the future.

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A PRECISION LASER SPECTROMETER SYSTEM

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ABSTRACT

An excimer laser based dye laser system has been purchased and integrated into experiments which involve DoD funding. The laser system is currently used in several important experiments: photodissociation of aliphatic nitro and nitroso alkanes, and halogen cyanides; bimolecular reactions of C_2H, and cluster reactions of H with CO_2; laser induced fluorescence studies in pulsed power switches such as thyratrons. The laser system has already become an integral part of these studies, and will be used in other funded reserach in the future.

I. INTRODUCTION

This final report outlines our research results obtained on AFOSR Grant AFOSR-83-0306 during the period 15 August 1983 through 31 August 1984. The funding obtained on this equipment grant was used to construct an excimer laser based spectrometer system to be used in several DoD supported projects of the PI's. The system is now fully integrated and is used effectively in several experiments. Although it usually takes several years for the completion of the initiated projects, several studies using the excimer laser based system are already underway and the results of these experiments are summarized below.

II. RESEARCH PROJECTS: CURT WITTIG AND HANNA REISLER

1. Laser kinetic spectroscopic studies of unimolecular reactions of 2-nitropropane

Initial results concerning the different photodissociation pathways which accompany the UV photolysis (excimer laser, 222, 249, and 308 nm) of 2-nitropropane (2NP), under collision-free conditions were obtained. Since there are no nitrogen atom lone pair electrons, excitation involves the promotion of an oxygen atom lone pair electron into an antibonding -group orbital. Even though the subsequent radiationless transition out of S_1 is rapid, the nuclear motions which commence upon absorption of a photon cause the nuclei to reconfigure, particularly in the vicinity of the NO_2 group. The radical-like nature of the oxygen can facilitate the formation of a five-membered ring, which can lead to products such as OH and HONO, and NO_2 can also be liberated efficiently before the nuclear energies dissipate into the vibrational reservoir of the propyl radical. We find that all three of these products are produced at each of the photolysis wavelengths, and that OH is a nascent product in all instances. This capacity of the system to produce a well known chain carrier such as OH may be a key to understanding the initial stages of the decomposition of energetic materials in condensed phases.

2. Laser kinetic studies of unimolecular processes

a. Spin-aligned CN($X^2\Sigma^+$) from the photodissociation of ICN and BrCN

We reported the first observation of a nascent photodissoiation product of $^2\Sigma$ symmetry, whose electron spin is aligned preferentially relative to the fragment rotational angular momentum.ICN and BrCN were dissociated by an excimer laser operating on the 193 and 248 nm lines, and the population of the spin-rotation compoenents of CN($X^2\Sigma^+$,N") was determined by LIF. Spin-orbit interaction can align spins during the dissociation process, and electron correlation can couple this spatial information to the $^2\Sigma$ species.

b. Collisional metastability of high rotational states of CN($X^2\Sigma^+$, v"=0)

We have shown that CN($X^2\Sigma^+$,v"=0) high rotational states relax slowly via 300 K collisions with Ar and Kr. CN population was probed by LIF using the output of an excimer pumped dye laser. Relaxation decreases with increasing rotation, and the partially relaxed distributions are bimodal, with low N'' thermalized (300 K), and $N'' \geq 80$ unrelaxed after 1000 collisions. Relaxation by N_2, CO, and Xe is similar to Ar and Kr, but more efficient. He and NO remove many quanta in a single collision.

c. NCNO→CN+NO: Complete NO(E,V,R) and CN(V,R) nascent population distributions from well-characterized monoenergetic unimolecular reactions

We reported detailed vibrational, rotational, and electronic (V,R,E) distributions of nascent NO($X^2\pi$) deriving from monoenergetic unimolecular ractions of jet-cooled NCNO. Excitation is via the $\tilde{A}^1A'' \leftarrow \tilde{X}^1A'$ system above dissociation threshold (17085±5 cm^{-1}), and vibrational predissociation occurs following radiationless decay of the initially excited $\tilde{A}^1A''$ state. The NO($X^2\pi$) was probed via photon LIF using an excimer pumped dye laser. These results are combined with data on the corresponding CN($X^2\Sigma^+$) nascent V,R distributions, thereby providing a complete description of the energy partitioning into the various degrees of freedom of both products. The data support our previous conclusion that dissociation is "statistical." All the V,R distributions of both products can be predicted accurately using a modification of the phase space theory of unimolecular reactions (PST), which we call the separate statistical ensembles (SSE) method; it is expected that this method will have quite general applicability. NO spin-orbit excitation is "cold" relative to the V,R degrees of freedom, and although no detailed explanation is offered, the origin of this observation was discussed.

3. Bimolecular reactions in the gas phase and in clusters

a. The photolytic production of C_2H: Collisional quenching of $A^2\pi \rightarrow X^2\Sigma^+$ IR emission, and the removal of excited C_2H

We reported the observation of time-resolved C_2H $A^2\pi \rightarrow X^2\Sigma^+$ infrared emission (1-5 μm) following the 193 nm photolyses of C_2H_2 and C_2HBr. Quenching of this emission by numerous collision partners (M) under pseudo-first-order conditions leads to large bimolecular 'rate coefficients' (e.g. $>10^{-11}$ cm^3 $molec^{-1}$), except when M is a rare gas or N_2). although such 'rate coefficients' can be assigned to the quenching of fluorescence, they do not represent state-to-state processes, since quenching is due to an intricate combination of reactive, radiative, and energy transfer processes. In separate experiments, rate coefficients were determined by monitoring the time resolved CH $A^2\Delta \rightarrow X^2\pi$ chemiluminescence which is produced directly by the reaction of C_2H with O_2, and the C_2H species responsible for the CH emissions was identified as electronically and/or vibrationally excited C_2H. The above results are in agreement with recent molecular beam experiments which show that nascent C_2H contains considerable internal energy following the 193 nm photolysis of C_2H_2.

b. Orienting reactants using van der Waals precursors:

$OCO\cdot HBr + h\nu \rightarrow \{OCO + H\} + Br \rightarrow CO + OH + Br$

We reported the results of an experimental study in which the reaction of atomic hydrogen with carbon dioxide was examined under conditions wherein the reagents are highly oriented relative to one another. Orientation is achieved using nozzle expansions to prepare a precursor of the form CO_2+HBr, which is best described as a weakly bound van der Waals or hydrogen bonded complex. The weak bond insures that the CO_2 and HBr moieties are separable insofar as electronic excitations and HBr dissociation are concerned. Translationally hot H atoms are produced by the 193 nm photolysis of the HBr constituent of the nearly linear $CO_2\cdot HBr$ complex. Dissociation is direct, and the initial H-atom velocity is directed primarily along the HBr axis. Because the HBr is complexed with the CO_2, the initial conditions for the ensuing reaction are quite restricted relative to cases in which there is no selective orientation i.e., bulk or molecular beam conditions. $OH(X^2\pi)$ is detected under experimental conditions which minimize effects due to uncomplexed bimolecular processes and/or contributions from higher clusters, and vibration, rotation spin-orbit, and Λ-doublet populations are determined. The $OH(X^2\pi)$ deriving from the complexed reaction appears instantly on the time scale of the measurement, in contrast to the clear rise time observed under bulk conditions, and the rotational population distributions differ measurably from those obtained under bulk conditions. This difference can be due to the short lifetime of the HOCO intermediate, and/or interactions of the OH fragment with the nearby Br atom from the CO_2•HBr complex.

III. RESEARCH PROJECTS: MARTIN GUNDERSEN

1. Measurement of excited-state densities during high-current operation of a hydrogen thyratron using laser-induced fluorescence

The population of the n=2 level of atomic hydrogen and the collisional relaxation rates of the n=3 and n=4 levels during the conductive phase in the positive column of a high-current ($J \sim 100-400$ A/cm^2) pulse in a hydrogen thyratron were measured using laser induced fluorescence.

Knowledge of plasma excited-state populations is necessary for calculation of electron production and recombination rates, and for the analysis of steady-state discharge behavior as well as breakdown and plasma quenching. Excited-state relaxation rates are also important in this type of analysis, since any rate equation-based plasma model must take into account collisionally induced transition rates, which are not well known; experimentally obtained rates therefore provide a useful check on those obtained theoretically.

For the LIF measurments we use a short (5 ns) laser pulse with 10 MW/cm^2 intensity, using the Balmer α and β lines for pumping. The absolute population of the lower state (n=2 level of atomic hydrogen) is found through measurement of the LIF signal under conditions of pump saturation, while those of the upper states (n=3 and 4, respectively, for the Balmer α and β lines) are found through measurement of spontaneous emission in the absence of laser irradiation.

An excimer-pumped dye laser supplied the pump beam, which was tunable and had an energy of up to 10 mJ in 5 ns. The laser linewidth was 0.03 Å. The laser beam entered and excited the thyratron through baffling discs. Emission from the plasma passed through an interference filter before being detected by a photomultiplier. The amount of laser light scattered directly into the detector was very small and could be neglected, as was verified by the lack of LIF signal well after the current.

The results demonstrate the laser-induced fluorescence is a useful in situ diagnostic for high-current switch plasmas. In these devices, the plasma carry current densities of order 100 A/cm^2; the electron temperature and density are close to 10,000 ^{o}K and 10^{14} cm^{-3} respectively.

2. Comparison of calculated and measured GaP:N luminescence spectra

We derived an expression for the luminescence intensity due to indirect transitions between particular impurity-related energy levels, and related it to the k-space charge densities, $|\psi(k)|^2$, of the impurity levels. The expression can then be used to estimate $|\psi(k)|^2$ from a measured luminescence spectrum. We presented results obtained for an exciton bound to nitrogen in GaP.

IV. PUBLICATIONS

1. G. Radhakrishnan, T. Parr and C. Wittig, "Multiple product channels in the collision free UV photodissociation of 2-nitropropane," Chem. Phys. Lett. **111**, 25 (1984).
2. F. Shokoohi, S. Hay and C. Wittig, "Spin-aligned CN($X^2\Sigma^+$) from the photodissociation of ICN and BrCN, Chem. Phys. Lett. **110**, 1 (1984).
3. S. Buelow, G. Radhakrishnan, J. Catanzarite, and C. Wittig, "The use of van der Waals forces to orient chemical reactions: H+CO_2 reaction," J. Chem. Phys. **83**, 444 (1985).
4. S. Hay, F. Shokoohi, S. Callister, and C. Wittig, "Collisional metastability of high rotational states of CN($X^2\Sigma^+$,v"=0), Chem. Phys. Lett. **118**, 6 (1985).
5. C.X.W. Qian, M. Noble, I. Nadler, H. Reisler, and C. Wittig, "NCNO $\rightarrow$CN+NO: complete NO(E,V,R) and CN(V,R) nascent population distributions from well-characterized monoenergetic unimolecular reactions, J. Chem. Phys, **83**, 5573 (1985).
6. G. Radhakrishnan, S. Buelow, and C. Wittig, "Orienting reactants using van der Waals precursors: $CO_2HBr + h\nu \rightarrow (OCO \leftarrow H) + Br \rightarrow CO+OH+Br$," J. Chem. Phys. **84**, 727 (1986).
7. S. Shokoohi, T.A. Watson, H. Reisler, F. Kong, A.M. Renlund, and C. Wittig, " The photlytic production of C_2H: Collisional quenching of $A^2\pi \rightarrow X^2\Sigma^+$ IR emission, and the removal of excited C_2H," J. Phys. Chem, submitted (1986).
8. P. Snyder, ;M.A. Gundersen, and C.W. Myles, "Comparison of calculated and measured GaP:N luminescence spectra," J. Luminescence **31 & 32**, 448 (1984).

9. D.A. Erwin and M.A. Gundersen, "Measurements of excited-state densities during high-current operation of a hydrogen thyratron using laser-induced fluorescence," submitted (1986).

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