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STUDIES OF ENERGY STORAGE AND TRANSFER IN GAS LASERS
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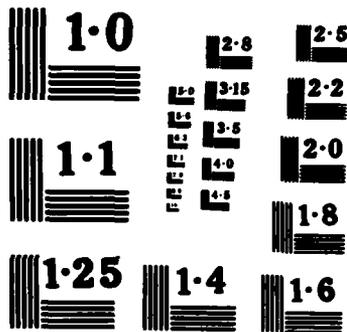
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FINAL TECHNICAL REPORT

**Studies of Energy Storage and Transfer
in Gas Lasers**

1 March 1982 - 28 February 1985

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Abstract

This experimental program was designed to elucidate the behavior of electronically excited atoms and molecules in gases and examine methods by which these species might generally be detected using laser-based spectroscopic techniques. To that end, several atomic and molecular states were observed using Resonance Enhanced Multiphoton Ionization. In addition, the photodissociative production of electronically excited states was investigated and the subsequent deactivation of excited atoms in collisional encounters with molecules studied.

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Introduction

The search for electronic transition lasers pumped by chemical reaction continues unabated. Recent interest in the application of such devices to a continental defence against ballistic missiles requires the accurate assessment of their potential utility. At the current time, it is probably still too early to reach a conclusive opinion regarding their viability as practical systems; more research into possible candidate reactions for attainment of electronic population inversion is clearly in order.

During the course of the subject grant, we examined several aspects of energy storage and transfer phenomena as they might apply to the development of electronic transition chemical lasers. Of special interest was the refinement of our understanding of the mechanism by which laser action can be achieved in the chemical oxygen-iodine laser (COIL) and the development of novel diagnostic techniques for the characterization of complex chemical mixtures of atoms and small molecules in defined quantum states. To this end, some of the work reported here was carried out in collaboration with Professor Paul Houston of Cornell University, a colleague in the Department of Chemistry.

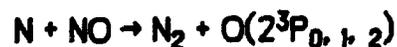
Laser Induced Resonance Enhanced Multiphoton Ionization of Atoms and Small Molecules

Increasing attention is being paid to the use of REMPI in the analysis of complex systems and the state-specific characterization of atoms and small molecules. The applicability of this technique to the low-pressure regime below $\sim 1 \mu$ is now well established; single atom detection has been claimed under these conditions.¹ At higher pressures, REMPI offers a special attraction: Collisional quenching, which routinely wreaks havoc with laser induced fluorescence measurements made under conditions where collisions occur frequently with respect to the optical emission lifetime, plays no role in REMPI because excited states are ionized before they can be quenched. With this in mind we set about to investigate the REMPI of the following atoms and small molecules.

Atomic iodine The REMPI spectra obtained following exposure of alkyl iodides to intense laser irradiation in the vicinity of 300 nm have been presented in a previous progress report. Both $I^*(5^2P_{1/2})$ and $I(5^2P_{3/2})$

were detected in this way. This observation has also been reported in work from other laboratories² and has recently been extended to the chlorine and bromine atoms.³

Atomic oxygen We prepared atomic oxygen both by direct discharge through O₂ in a microwave discharge and, somewhat more elegantly, by the reaction



The latter avoids the formation of excited molecular oxygen and also permits the production of O in the absence of NO which strongly interferes with O atom detection. Indeed, it is the reaction with N that causes the removal of the nitric oxide!

Our experimental results clearly demonstrated (see previous report) the capability of REMPI to detect the different spin-orbit levels of O even though they are separated by only 16 cm⁻¹. Our efforts to establish the REMPI technique as a quantitative measure of the J level distribution and hence the electronic temperature of atomic oxygen were not successful. No quantitative relationship between observed REMPI signal intensity and state population was obtained. In retrospect, this may have resulted from a number of different causes:

Poorly understood line strength factors involving the unresolved real intermediate 3²P_J state leading to ionization.

Nonlinearities induced by failure to achieve an electron collection "plateau".⁴

Actual nonthermal J level distributions in the O atoms generated in these flow systems.

We suspect that a more careful study under a wider range of bias voltages in which the ion collection efficiencies are better controlled might well be successful.

Molecular nitrogen The REMPI spectrum of molecular nitrogen was obtained at P_{N₂} ≈ 1 torr using a simple pair of biased electrode plates. A recent report from JILA⁵ of the same spectra suggests that this method

will be widely applicable to the detection of N_2 at low pressures. As was mentioned for the case of O atoms, considerable care must be exercised before the REMPI technique can be applied to detection at moderate pressures due to problems arising from electron-ion recombination and secondary electron excitation in the proportional counting regime.

Molecular oxygen Our most successful effort in the area of REMPI studies of small molecules involved the detection of O_2 in the $X^3\Sigma^+$ and $a^1\Delta_g$ states. A schematic of the observed transitions is presented in Figure 1. A manuscript reporting these results is currently in preparation. Specific features of a number of O_2 Rydberg states have been identified and will be discussed at length in that document.

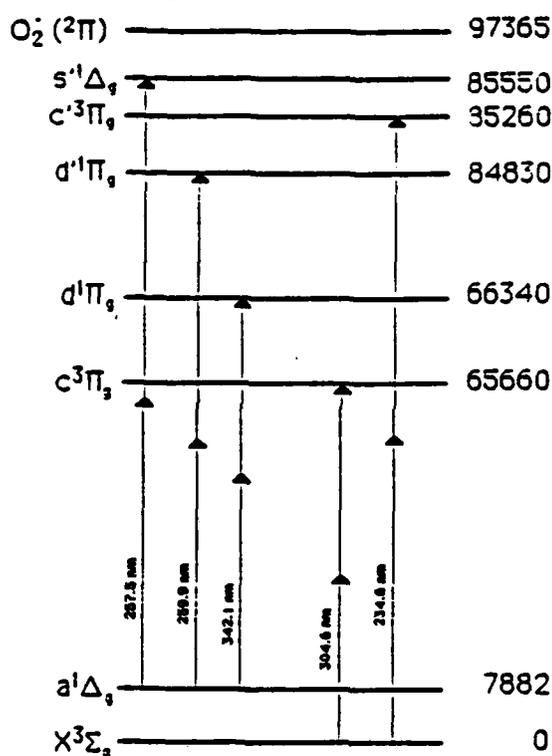


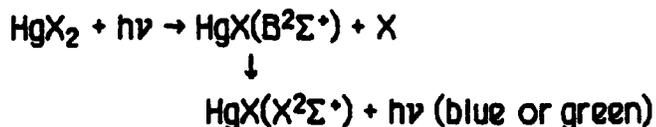
Figure 1. Schematic representation of the observed REMPI transitions in molecular oxygen.

State specific pathways for excited state production in metal halide photodissociation

Because of the known state selective behavior of photochemical effects as in the dissociation of alkyl iodides to form predominantly I^* , metal halide photochemistry can fruitfully be examined in order to better understand those atomic and molecular phenomena which govern the

course of gas phase chemical reactions. Two systems were examined in some detail.

Mercuric halides The photolysis or electric discharge induced dissociation of HgX_2 is the basis of an important molecular electronic transition laser. Following an earlier study of HgBr_2 ,⁶ we set up a new apparatus to measure the degree of polarization observed in the spontaneous emission from HgX^* following 193 nm photodissociation of the source molecule



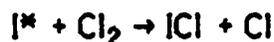
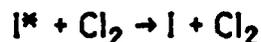
By paying careful attention to detail, it was possible to observe a B \rightarrow X polarization of 13.1% following HgBr_2 photodissociation, close to the value of 14.7% derived from classical theory. Quite surprisingly, the degree of polarization is much smaller in the case of HgCl_2 photodissociation to yield $\text{HgCl}(\text{B}^2\Sigma^+)$, roughly 5%. This seems hard to understand because the correlation arguments on which one may base the treatment of these photodissociations do not take into account spin-orbit coupling, i.e., one expects the correlations to be better for the lighter atoms.⁷ This observation suggests that multiple dissociating states may be involved in the case of HgCl_2 , a factor not hitherto realized.

Alkali metal iodides Our work in this area concentrated on KI which was previously shown⁸ to yield $\text{K}(4^2\text{P})$ following photolysis at 248 nm and $\text{K}(5^2\text{P})$ at 193 nm. Followup experiments designed to elucidate the mechanism by which $\text{K}(5^2\text{P})$ deactivation might occur (this will be discussed below) clearly supported the view that it is in fact $\text{K}(5^2\text{P})$ which is formed virtually exclusively at 193 nm.

Collisional Deactivation of Electronically Excited Atoms

The efficiency of any electronic transition chemical laser would be strongly affected by the collisional deactivation of the upper lasing level or by a selective population of a potentially inverted state. In the course of the subject grant, we addressed important issues on both sides of this question.

Quenching of I(5²P_{1/2}) by Cl₂* The chemical generation of O₂(a¹Δ) in the H₂O₂/Cl₂ system currently used in the COIL unavoidably results in the presence of molecular chlorine in the gas stream. If as had been reported,⁹ the rate coefficient for I* deactivation by Cl₂ were as large as 1.7 x 10⁻¹² cm³ sec⁻¹, the presence of Cl₂ in the laser cavity would significantly affect the extractable power. This had not been observed so it was decided to investigate the kinetics of



further.

Typical infrared emission profiles at 1.315 μ (Figure 2) reveal that the rate of I* quenching by Cl₂ is strongly dependent upon the photolysis power used in dissociating the CF₃I source (and coincidentally the Cl₂). The apparent rate of quenching also increases dramatically if instead of using a flowing mixture, a static photolysis cell is used. From these studies, we concluded that:

The rate coefficient for I* deactivation by Cl₂ at 300 K is less than 8x10⁻¹⁵.

The deactivation of I* by chlorine *atoms* is very efficient with an estimated rate near gas kinetic.

At present a clear explanation for the observed rates of I* deactivation by the halogens is not apparent.

*Selective Deactivation of K**(5²P) by H₂* Collisional deactivation of the lowest resonance states of the alkali metals has been studied for some time. In general, the quenching of these states is dominated by long-range attractive forces with concomitant multiquantum energy transfer to the collision partner.¹⁰ Prior to our work, no such studies had been made on the higher resonance levels nor had there been an attempt to understand the possible role chemistry might play in these deactivation processes.

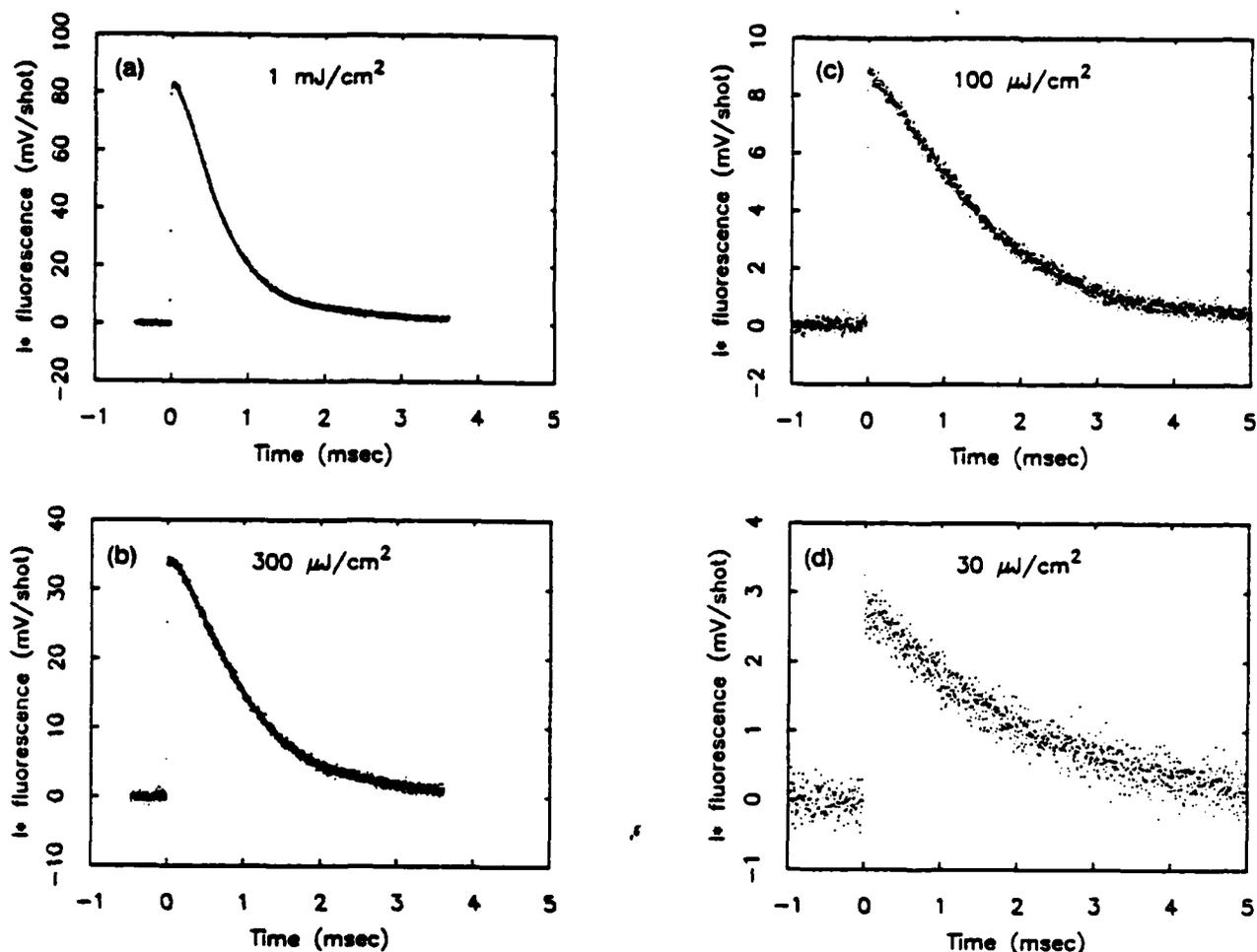
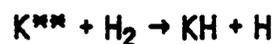


Figure 2. Time-resolved infrared emission from I^* in the presence of Cl_2 . In each case the sample is a flowing mixture of 4.0 torr Ar, 1.0 Torr CF_3I and 1.2 Torr Cl_2 . The 266 nm laser photolysis energy was varied as indicated and the number of shots averaged at 0.1 Hz varied from 20 at 1mJ to 100 at 0.03 mJ.

Photolysis of KI at elevated temperatures using an ArF laser resulted in the exclusive production of K^{**} . Addition of H_2 to the reaction cell caused the expected decrease in the K^{**} lifetime ($\tau_{\text{optical}} = 138 \pm 1 \text{ nsec}$) along with an *increase* in the observed emission from the lower lying $K^*(4^2P)$ resonance levels (Figure 3). On the basis of a careful kinetic analysis, it was concluded that:

The rate coefficient for K^{**} deactivation by H_2 at 791 K is $2.2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$.

The reaction



while exothermic for the second resonance state plays no discernible role in the overall deactivation.

The predominant pathway for deactivation involves near resonant energy transfer



with possible vibrational excitation of the product.

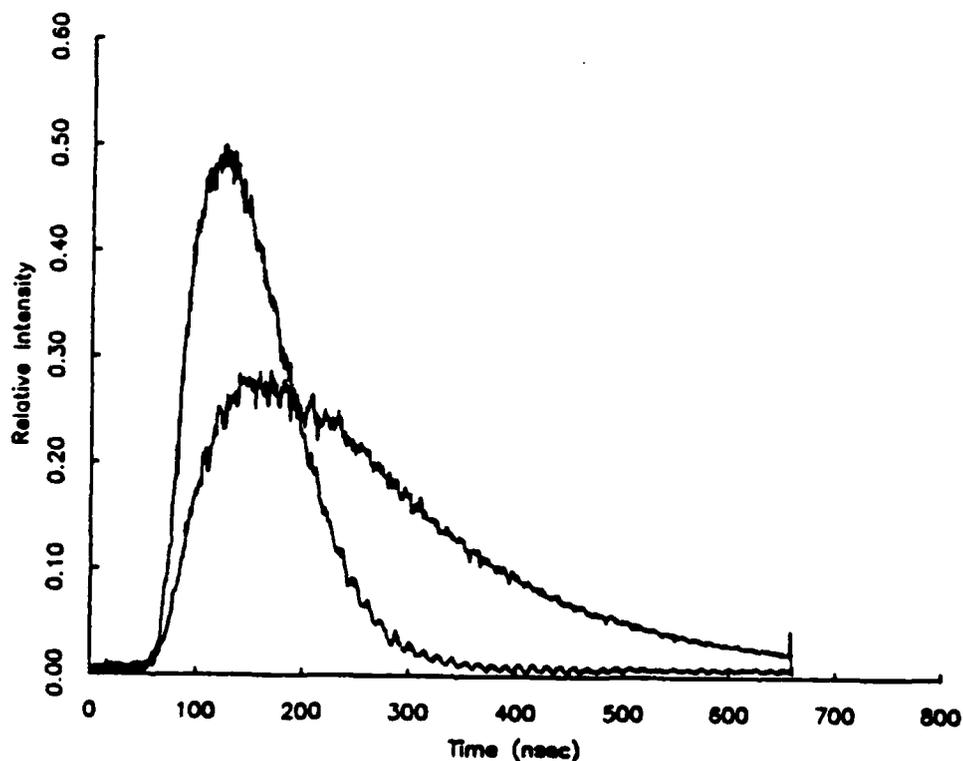


Figure 3. Temporal dependence of the 767 nm emission $K(4^2P_{1/2} \rightarrow 4^2S_{1/2})$ at $P(H_2) = 0$ (lower intensity, longer-lived) and $P(H_2) = 5$ Torr (more sharply peaked and shorter-lived).

Because the cross-sections of resonance state deactivation are so large, it is hard to understand why the second resonance state is deactivated in a near-resonant process. It is interesting to note however, that this provides a way in which to *selectively* populate the upper state of the known lasing transition $K(5^2S,3^2D) \rightarrow K(4^2P)$.

Conclusions

During the course of this work an number of useful techniques for the detection of species important to the COIL were developed and some questions concerning the kinetics of this laser answered. In addition, new questions regarding the chemistry of electronically excited atom behavior in the gas phase were raised; these and others will have to be addressed before a sufficient knowledge of the relevant chemistry will permit the development of new electronic transition chemical lasers.

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