## Title
Characterization of Multiphoton Ionization Processes in the Ultraviolet

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### Abstract
This report describes results of research directed toward a better understanding of multiphoton ionization (MPI) processes of molecules expected to have large MPI processes in the near ultraviolet region of the spectrum. The motivation for this work was to develop methods of optically controlling diffuse discharges. During the three-year period of this research, such processes were investigated in a variety of molecules, including NO, the methylamines, ferrocene, SO₂, and SO₃. In addition, some work on the use of photodetachment processes to control diffuse discharges was performed in collaboration with researchers at Texas Tech University, and a workshop on optical control of diffuse discharges was held at the University of Oregon.
CHARACTERIZATION OF MULTIPHOTON IONIZATION PROCESSES IN THE ULTRAVIOLET

Final Report on Contract No. DAAG 29 81 K 0117

by

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INTRODUCTION

This report describes results of research directed toward a better understanding of multiphoton ionization (MPI) processes of molecules expected to have large MPI processes in the near ultraviolet region of the spectrum. The motivation for this work was to develop methods of optically controlling diffuse discharges. During the three-year period of this research, such processes were investigated in a variety of molecules, including NO, the methylamines, ferrocene, $SO_2$, and $SO$. In addition, some work on the use of photodetachment processes to control diffuse discharges was performed in collaboration with researchers at Texas Tech University, and a Workshop on Optical Control of Diffuse Discharges was held at the University of Oregon. The subsequent sections of this report describes the results of this work.

MULTIPHOTON IONIZATION OF NITRIC OXIDE

The large multiphoton ionization cross section for the NO molecule in the region around 450 nm has resulted in a large number of MPI studies on this molecule. The primary process investigated is a four-photon ionization in which the second step is resonant with ro-vibrational levels of the $A^2E$ state. In spite of the relatively large cross section for this process, it
is not sufficiently large to be useful as a control mechanism for a diffuse discharge. However, three other processes related to the A state have been suggested as being even more efficient. We have investigated two of these, and are the originators of the third suggestion, which has not yet been studied.

**MPI of NO from the A state**

Schaefer and Schoenback from Texas Tech University have suggested (1) that it might be possible to produce NO(A) state molecules by excitation transfer with N$_2$(A), and to ionize the excited NO molecules with two visible photons through a resonant level in the E state. Modeling calculations indicate that this can be done with high but perhaps feasible laser powers under discharge conditions. Unfortunately, careful experiments in our laboratory using a flowing afterglow and an excimer-pumped high power tunable dye laser failed to observe this process (2). To make this technique work requires a delicate balance between excitation transfer, deexcitation by radiation and collisions, and the desired photoionization. Before the potential of this technique can be definitively assessed, the process must be observed under conditions which can be adequately modeled, so that the rates for the various processes listed above can be better determined.

**Double Enhancement of the MPI of NO**

During the course of these experiments aimed at studying the photoionization from the NO(A) state, both the two-photon ionization of the ground state using 193 nm ArF radiation, and the previously-described four-photon ionization from the ground
state using tunable radiation around 450 nm were very easily observed. It was also observed that a few lines in the four-photon ionization spectrum had anomalously strong intensities. A further investigation of these lines (3) revealed that these strong lines were due to a further accidental enhancement at the third step of the ionization via high-lying Rydberg states, which we were able to identify. The double resonance was sufficiently strong that for some lines the enhancement in intensity at around 1 mJ of dye laser power was greater than an order of magnitude.

It seems feasible that through the use of two tunable dye lasers to optimize the double enhancement effect, perhaps through the already mentioned E state which should have a very large cross section, this process might be useful in optical control. Unfortunately, we did not have the appropriate lasers to further investigate this process. We have recently been awarded a laser system through the DoD-URIP program which, when used with our existing laser, will allow a further investigation of this process. If funding is available, we intend to carry out this investigation in 1985.

Resonant Two-Photon Ionization of NO

An even more efficient scheme to photoionize NO would be a two-photon resonance ionization via the A state. In fact, many of the same A state levels observed in the study described above can be reached using radiation from a KrF laser, Raman-shifted in H₂. We performed calculations based on reasonably well known cross sections and published commercial specifications for Raman-shifted KrF radiation, with the result that it should be possible to ionize 1% of the NO molecules in a large volume during a laser
pulse. The volume is determined by the length of the gas
irradiated times the area of the laser beam. We plan to pursue
this process experimentally with the new laser system.

MPI MASS SPECTROMETRY OF METHYLMINES

Mass spectra of methylamine, dimethylamine, and trimethyl-
amine were obtained by resonant multiphoton ionization using a
pulsed molecular beam source and the excimer laser wavelengths
193 and 248 nm. Power dependence measurements were made for the
most intense fragment ions, and a rate equation model was
employed to interpret the results. In cases where fragmentation
was small, the mass resolved ions exhibit the expected integral
exponential power dependences; where fragmentation was extensive,
non-integral power dependences were observed. Total ionization
of trimethylamine was studied using 248 nm and tunable radiation
around 440 nm, in an attempt to improve the determination of the
ionization potential of this molecule. Although this was not
successful, an anomalously strong ionization, possibly due to a
two photon resonance, was observed using only dye laser radiation
near 439 nm. The results of this work (4) are now in press in
the Journal of Chemical Physics. Three copies of a preprint of
this journal article are submitted to ARO with this report.

PHOTODISSOCIATION AND MPI OF FERROCENE

Many organometallic compounds photodissociate upon absorp-
tion of light, and this process can dominate their photophysics
in an intense radiation field. In one or several multiphoton
dissociation (MPD) steps, the central metal atom can shake off
its ligands, leaving it as a bare metal atom. In spite of the
relatively low ionization potentials for many organometallic compounds, the rate of this MPD often exceeds the rate of direct ionization of the molecule by several orders of magnitude. Thus it is possible to produce high concentrations of metal atoms in the gas phase, essentially instantaneously, using a laser. These metal atoms, which are very easily resonantly ionized, can be useful in pulsed power applications. The goal of our research was to investigate the MPD and MPI of one of these compounds, ferrocene. This molecule is a prototypical metalloconene, which are composed of transition metal atoms sandwiched between two cyclopentadienyl (Cp) rings.

**MPI Spectra of Ferrocene**

Multiphoton ionization spectra of ferrocene were obtained as a function of dye laser wavelength in the region around 440 nm, with the dye laser alone, and with the dye laser output combined with 351 nm and with 248 nm radiation from the excimer laser which was pumping the dye laser. Power dependences were obtained under a variety of conditions. The results of this study are being prepared for publication,(5) and will be briefly summarized here. Reprints will be submitted to the contractor as soon as they are available.

As has been previously observed in other laboratories, the spectrum with the dye laser alone was dominated by easily identifiable atomic Fe lines due to two-photon resonances between the ground a^5D and the excited e^5D state. With the addition of the 351 nm radiation, new peaks were observed which were shown to arise from the resonant mechanism a^5D--z^7F--e^7G. It was also determined that the 351 nm radiation played no significant role
in the MPD of the ferrocene.

The addition of 248 nm radiation to the dye laser changed the spectrum dramatically, due to the participation of the excimer radiation in both the MPD and the MPI processes. Even though the 248 nm radiation can efficiently lead to ionization without the presence of the dye laser, a tunable spectrum with strong resonances was observed. No assignments for this new structure have yet been possible.

Iron Atom Recoil Energy

All of the dissociation processes mentioned above can lead to significant excess energy, which can be partitioned between internal energy in the Cp rings, and kinetic energy of these molecules and of the iron atom. A determination of this energy partition would be helpful in understanding the dissociation mechanism. It is possible to obtain some information on this energy partitioning by observing the width of the iron lines. If the width of these lines is greater than can be explained by the natural linewidth of the dissociating state, and by the normal room temperature Doppler width, this excess line width can be attributed to the recoil of the iron atom in the dissociation process.

Crudely, if the dissociation process is "concerted" in the sense that both Cp rings break off at the same time, the iron atom would be left in the center of mass, essentially at rest. If the process is one of "unimolecular decomposition", energy would be very significantly partitioned into the many vibrational modes of the molecule, resulting in a low, but suprathermal, iron
atom recoil energy. In striking contrast to these mechanisms, if the ferrocene dissociates in two steps, first to FeCp + Cp, followed by Fe + Cp, via electronically repulsive states, most of the available energy can end up in translational recoil.

Measurements of the iron atomic line widths revealed both lifetime broadening, due to the short lifetime of the dissociating state, as well as broadening due to the kinetic energy of the iron atom. Deconvolution of the resulting Voight profile into its Lorentzian (due to saturation broadening) and Gaussian (due to recoil broadening) components led to the conclusion that most of the excess energy goes into recoil of the fragments, thus supporting the third mechanism described above. The results of this work are also being prepared for publication,(6) and reprints will be submitted to the contractor when they are available.

MPI OF SULPHUR OXIDES

A brief study was made of the MPD and MPI of SO2 with a dye laser in the region of 360 nm. A weak, resonantly enhanced MPI spectrum was found, which was identified with transitions between the X3Σg and D3Π states of the SO molecule. Just above the three-photon ionization threshold, the (1,0) band was observed. Below this threshold, some relatively strong, isolated peaks were observed. Although a positive identification has not yet been made, it is likely that these peaks arise from the (0,0) band, with enhancement of the four-photon transition by Rydberg levels just below the ionization limit. This is a double enhancement similar to that observed in NO. Research is being continued under other sponsorship, and will eventually result in a
PHOTODETACHMENT AS AN OPTICAL CONTROL METHOD

The use of photodetachment as a mechanism for increasing the conductivity of a diffuse discharge has received little consideration so far, even though it appears to offer some interesting advantages over photoionization. A brief study was performed in collaboration with G. Schaefer, P. F. Williams, and K. H. Schoenbach of Texas Tech on the possibility of using the photodetachment of $O^-$ as a control mechanism. Experiments performed at Texas Tech were encouraging, and were reported in a journal article (7).

WORKSHOP ON OPTICAL CONTROL OF DIFFUSE DISCHARGES

A workshop was held at the University of Oregon on December 2 and 3, 1982, on the subject of the optical control of diffuse discharges. The primary objective of this workshop was to assess the current state of research in this area, and to consider new ideas for optical control. The workshop involved seventeen participants, including representatives from most of the groups currently working in this field. A Scientific Report was submitted to the Army Research Office describing the results of this workshop. This report gives an overview of the research situation as of the date of the workshop, and lists criteria developed at the workshop which molecules under consideration for various control schemes should meet. Opening switch, closing switch, and modeling studies are each considered in detail.

PARTICIPATING SCIENTIFIC PERSONNEL

Professors John Moseley, Physics, and Paul Engelking, Chemistry, Research Associates Timothy Steimle, J. D. Ganiere,
and Yoshi Ono, and Graduate Research Associate H. T. Liou participated in this research. No advanced degrees were awarded to those employed on the project, however, Mr. Liou expects to receive the PhD degree in Physics from the University of Oregon during 1985, based primarily on research he performed under this contract.

BIBLIOGRAPHY, INCLUDING PUBLICATIONS AND REPORTS

This Bibliography includes all publications and reports submitted under this contract.

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