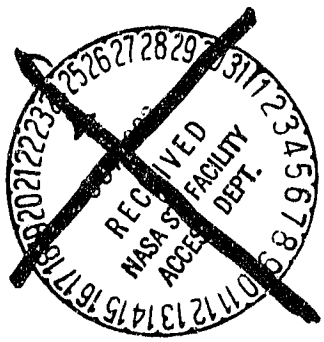

Final Report

NAG 5-17

Two Photon Excitation as a Tool for Atmospheric and Kinetic Research

Principal Investigator: Dr. Joshua B. Halpern
Howard University
Department of Chemistry
Washington, D.C. 20059

Covering the period June 1, 1982 - July 31, 1983

Although this constitutes the final project report, there are still several experiments underway which we anticipate will result in publications, and in which the support of NASA under grant NAG 5-17 will be acknowledged. Reprints and preprints of completed work are attached to this report as an appendix, and completely describe the finished studies. Only the incomplete work will be described below.

I. RESEARCH PROJECTS STILL UNDERWAY

A. Two Photon Excitation Cross-Section of Hydroxyl

Although in the last year's progress report we gave the results of a preliminary measurement of this cross-section as 2×10^{-51} cm^4-sec, this was subject to great uncertainty because the laser was not completely characterized. The primary problem in measuring multi-photon cross-sections is dealing with the phase relationship between the photons that are absorbed. Unless the illuminating laser is single mode this problem is intractable.

Four approaches have been taken to this problem. Firstly, one can with great effort construct a single mode laser system (1). Secondly, if a good cross-section measurement is available in the same spectral region, one can compare the signal from the standard against that of the unknown. In this case one must be sure that the quantum yield of excited state is known. (2). Thirdly, one can use a non-linear process which depends linearly on the strength of the exciting laser to measure $\chi^{(2)}$ (3). Fourthly, one may take advantage of the fact that the intensity dependence of the doubled light produced in the first Marker fringe is the same as that in two photon absorption (4). Thus the two photon cross-section may be obtained by comparing the amount of signal from the doubled light, to that from two

photon excitation. The ratio is simply that of the one and two photon cross-sections multiplied by the ratio of the amount of doubled light (very small) to the undoubled light.

The Marker fringes are the angular maxima of two photon generation in a non-linear crystal, where there is no phase matching. The first observed doubling in crystal quartz was an example of Marker fringe production of frequency doubled light (5).

In large molecules one must always worry about reaching different (unknown) states in the two photon excitation as opposed to those reached by single photon excitation. Such states can have very different fluorescent lifetimes and emissions, which would confuse the measurement. In small, well characterized molecules such as hydroxyl, such confussion does not exist. Although the actual levels reached will be different because of symmetry consideration, they will belong to the same electronic state and their radiative lifetimes and quantum yields for fluorescence will be well known.

We have set up an apparatus which will use the first Marker fringe doubling as a standard for two photon cross-section measurements. The doubling will be done in a thin piece of crystal quartz, where the doubling phenomina is well understood and the non-linear index of refraction has been measured. A sketch of the apparatus is shown in Figure 1. By using

appropriate filters the two and one photon excitation signals can be measured in cell 1 and compared to the one photon signal in cell 2. Cell 2 serves as a reference for laser mode and intensity stability and stability in the generation of OH radicals. These measurements are currently underway.

B. Marker Fringe Generation of Deep UV and VUV radiation.

Phase matching allows doubling efficencies of 0.5 and more. However frequency doubling is a quite general phenomina requiring only a non-centrosymmetric uniaxial optical crystal. Indeed one of the most interesting new surface analysis techniques is the second harmonic generation in thin films deposited on conductors (6). The price that one pays is efficency, which can drop to 10^{-6} or so, depending on the second order index of refraction of the optical crystal. In regions of the spectrum where phase matched frequency mixing is not possible, the Marker fringe maxima may provide the most efficent source of doubled light.

The problem is to find a non-linear crystal that transmits in the VUV. Surprisingly, MgF_2 may be such a material. The crystal is uniaxial, with the C axis having a different index of refraction than the other two axes. At 1064 nm, a small, but finite second order index of refraction has been measured (7). Moreover, the elements of the stress tensor are very small, indicating that the non-linearity might be increased by putting the crystal in a vise. (8).

We have obtained a MgF_2 single crystal, and are in the process of polishing it. (Almost all MgF_2 windows are provided with the C axis perpendicular to the face to avoid polarization effects.)

It should be pointed out that such techniques as third harmonic generation in gases provides about 1 J to 10 nJ depending on the frequency. These levels (and perhaps more) could be achieved using the MgF_2 plate. Possible improvements would be phase matching using pressure on the MgF_2 crystal. There would be a great improvement in the efficency if this worked, however it would never approach the efficency of doubling crystals without the pressure because of inhomogeneities introduced by the pressure. One should also check whether BaF crystals are more efficent, because of the heavier Ba atom.

C. $CN(A^2\Pi_i)$ Radiative Lifetimes

The CN red system is among the most prominent emission in cometary spectra and the spectra of cold stars. Interpretation of these spectra is hindered by a lack of knowledge about the radiative lifetime of the A state, especially with respect to the vibrational quantum numbers of the upper state. The best measurements of $CN(A^2\Pi_i, v > 2)$ lifetimes are those of Miller (9) which used laser excitation of $CN(X^2\Sigma^+)$ and monitored the decay as a function of time. Their method of production was the action of Ar metastables colliding with

BrCN. This meant that the pressure in their system was always 1 torr or higher. Under such conditions there is a rapid exchange of population between the vibrational levels of the A and X states of CN. The data in this experiment was analyzed in terms of a complicated kinetic scheme and the lifetimes were obtained as one of several parameters from the best overall fit to the data.

We have compared the efficency of production of CN from

a. Ar metastables colliding with BrCN,
b. active nitrogen colliding with CCl_4 and a variety of haloginated hydrocarbons,
c. and excimer laser photolysis of C_2N_2 and BrCN as developed in our laboratory.

We find the absolute signal to be at least two orders of magnitude higher for the last method and the signal-to-noise to be about three orders higher.

Measurements are underway to obtain the A state lifetimes for levels $v > 2$. We anticipate being easily able to go to the v=9 level and hope to reach the v=11 level which is perturbed by the $CN(B^2\Sigma^+)$ v=0 level. The CN will be excited by various dye lasers available in our laboratory and we will measure the decay with a boxcar analyzer.

Publications which acknowledge the support of NAG 5-17:

Papers published since the last report:

1. "Partitioning of Excess Energy in the Photolysis of Cyanogen Chloride and Cyanogen Bromide at 193 nm." Joshua B. Halpern and William M. Jackson. Journal of Physical Chemistry 86, 3528 (1982).

2. "Production of CS and S in Comet Bradfield (1979X)." W.M. Jackson, J.B. Halpern, P.D. Feldman and J. Rahe. Astronomy and Astrophysics 107, 385 (1982).

3. "Scanning Delay Generator for Measurement of Kinetic Decays Using Laser Induced Fluorescence Techniques." Joshua B. Halpern and Theodore G. Towns. Review of Scientific Instruments 53 1786 (1982).

4. "Oscillator Strength of the CN $A^2\Pi_i \leftarrow B^2\Sigma^+$ (0,0) Transition." Joshua B. Halpern and Xiao Tang. Chemical Physics Letters 97, 170 (1983.

Papers submitted for publication or in press:

1. "Photodissociation of C_2N_2, ClCN and BrCN in a Pulsed Molecular Beam." Richang Lu, J.B. Halpern and W.M. Jackson. Submitted to the Journal of Physical Chemistry, (1983).

2. "Photodissociation Dynamics in a Pulsed Molecular Beam". Richang Lu, J.B. Halpern and W.M. Jackson. To be published in Lasers as Reactants and Probes in Chemistry, Howard University Press (1983).

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JOSHUA B. HALPERN
514 11th Street, S. E.
Washington, D. C. 20003

Born January 21, 1946
Brooklyn, New York
Married, no children

Telephone: (202) 636-6883 Office
(202) 547-2337 Home

EDUCATION

Ph.D.; Physics, Brown University, Providence, Rhode Island
June 1972

B.A.; Physics, The Johns Hopkins University, Baltimore, Maryland,
June 1966

CURRENT POSITION

July 1979 - Present	Assistant Professor of Chemistry Department of Chemistry Howard University

PROFESSIONAL EXPERIENCE

October 1976 - July 1979	Assistant Research Professor Howard University Department of Chemistry
July 1973 - October 1976	Wissenschaftlicher Mitarbeiter (Scientific Assistant) Universitaet Bielefeld Fakultaet fuer Physik
July 1971 - June 1973	Post-Doctoral Assistant Radiation Laboratory University of Notre Dame

MEMBERSHIP IN PROFESSIONAL SOCIETIES

American Association for the Advancement of Science
American Chemical Society
Optical Society of America
North American Photochemical Society

RESEARCH

Energy partitioning in the photodissociation and reactions of small molecules and radicals.

Multiphoton spectroscopy of small molecules and radicals.

THESIS

A new method for detecting and discriminating zero field level crossing signals applied to measurement of resonant collision broadening at very high densities in the $^3P_1(6p7s)$ state of Pb(208).

SCIENTIFIC PUBLICATIONS

1. "Rotating Polarizer Technique for Measuring the Coherent Relaxation Rates of Excited Atomic States," E. B. Saloman, A. Baghdadi and J. B. Halpern. Review of Scientific Instruments 41 (8), 1148 (1970).

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5. "Dissociation of NH_3 to Ground Electronic State Fragments by High Intensity CO_2 Laser Radiation," J. D. Campbell, G. Hancock, J. B. Halpern and K. H. Welge. Optics Communications 17 (1), 36 (1976).

6. "Infrared Multiple Photon Dissociation into Ground Electronic State Fragments," J. D. Campbell, G. Hancock, J. Halpern and K. H. Welge. Optics Communications 18 (1), 34 (1976).

7. "Two Photon Excitation and Single Level Lifetime Measurements in the NO (A^{2+}) State," H. Zacharias, J. B. Halpern and K. H. Welge. Chemical Physics Letters 43 (1), 41 (1976).

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9. "Off Resonant Dissociation of NH_3 to Ground State Fragments by Pulsed CO_2 Laser Radiation," J. D. Campbell, G. Hancock, J. B. Halpern and K. H. Welge. Chemical Physics Letters 44 (3), 404 (1976).

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11. "Multiphoton Ultraviolet Photochemistry," W. M. Jackson , J. B. Halpern and C. S. Lin. Chemical Physics Letters 55 (2), 254 (1978).

12. "Tunable VUV Photofragment Monochromator," G. E. Miller, J. B. Halpern and W. M. Jackson. Applied Optics 17 (7), 2821 (1978).

13. "Vibronic Effects in the Photodissociation of Cyanogen," W. M. Jackson, G. E. Miller and J. B. Halpern. J. of Photochem. 9 (2-3), 137 (1978).

14. "Multiphoton Ultraviolet Photodissociation of C_2N_2," W. M. Jackson and J. B. Halpern. Journal of Chemical Physics 70, 2373 (1979).

15. "Multiphoton Sequential Photodissociation Excitation, A New Method of Remote Atmospheric Sensing," J. B. Halpern, W. M. Jackson and V. McCrary. Applied Optics 18, 590 (1979).

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19. "The Dynamics of the C + NO Reactions," W. M. Jackson, C. N. Beugre and J. B. Halpern. Journal of Photochemistry 13, 319 (1980).

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24. "Partitioning of Excess Energy in the Photolysis of ClCN and BrCN at 193 nm," Joshua B. Halpern and William M. Jackson. Journal of Physical Chemistry, 86, 3528 (1982).

25. "Scanning Delay Generator for Measurement of Kinetic Decays Using Laser Induced Fluorescence Techniques", J. B. Halpern and T. G. Towns. Review of Scientific Instruments, 53, 1786 (1982).

26. "Photodissociation Dynamics in a Pulsed Molecular Beam", R. Lu, J. B. Halpern and W. M. Jackson. To be published in Lasers as Reactants and Probes in Chemistry, W. M. Jackson and A. B. Harvey editors. Howard University Press, Washington D.C. Scheduled to appear Spring 1983.

27. "Laser Irradiation of SV40 DNA", J. B. Halpern, M. Johnson-Thompson W. M. Jackson and J. George. To be published in Lasers as Reactants and Probes in Chemistry, W. M. Jackson and A. B. Harvey editors. Howard University Press, Washington, D. C. Scheduled to appear in Spring 1983.

28. "Oscillator Strength of the CN $A^2 i$ $B^2 +$ (0,0) Transition", J. E. Halpern and X. Tang. Chemical Physics Letters 97, 170 (1983).

29. "Photodissociation Signature Analysis for Detection of Ammonia and Hydrazine", J. B. Halpern, E. B. Koker and W. M. Jackson. To be published in Analytical Chemistry.

30. "Photodissociation of Simian Virus 40 DNA by an ArF Laser", M. Johnson-Thompson, J. B. Halpern and W. M. Jackson. To be published in Photochemistry and Photobiology.

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