

AD-A179 596

TWO-PHOTON DETECTION TECHNIQUES FOR ATOMIC FLUORINE(U)
SRI INTERNATIONAL MENLO PARK CA W K BISCHEL ET AL.
04 MAR 87 AFOSR-TR-87-0454 F49620-85-K-0005

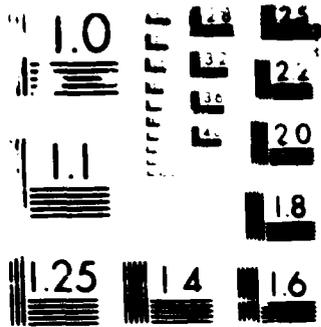
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REPORT DOCUMENTATION PAGE

AD-A179 596

			1b RESTRICTIVE MARKINGS None	
			3 DISTRIBUTION/AVAILABILITY OF REPORT Distribution unlimited; approved for public release	
4 PERFORMING ORGANIZATION REPORT NUMBER(S)			5 MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR-87-0454	
6a NAME OF PERFORMING ORGANIZATION SRI International		6b OFFICE SYMBOL (if applicable)	7a NAME OF MONITORING ORGANIZATION Air Force Office of Scientific Research	
6c ADDRESS (City, State, and ZIP Code) 333 Ravenswood Avenue Menlo Park, CA 94025			7b ADDRESS (City, State, and ZIP Code) Bolling AFB, DC 20332-6448	
8a NAME OF FUNDING SPONSORING ORGANIZATION Air Force Office Sci. Research		8b OFFICE SYMBOL (if applicable) AFOSR/NA	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F49620-85-K-0005	
8c ADDRESS (City, State, and ZIP Code) Bolling AFB, DC 20332-6448			10 SOURCE OF FUNDING NUMBERS	
			PROGRAM ELEMENT NO 61102F	PROJECT NO 2308
			TASK NO A3	WORK UNIT ACCESSION NO *
11 TITLE (Include Security Classification) TWO-PHOTON DETECTION TECHNIQUES FOR ATOMIC FLUORINE				
12 PERSONAL AUTHOR(S) William K. Bischel and Gregory C. Herring				
13a TYPE OF REPORT Annual Technical		13b TIME COVERED FROM 1/01/86 TO 12/31/86	14 DATE OF REPORT (Year, Month, Day) 1987 March 4	15 PAGE COUNT 12
16 SUPPLEMENTARY NOTATION				
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number) multiphoton ionization spectroscopy, atomic fluorine	
FIELD	GROUP	SUB-GROUP		
20	05			
21	02			
19 ABSTRACT (Continue on reverse if necessary and identify by block number) During the last year, we focused on experiments that will lead to a quantitative and remote diagnostic for atomic fluorine using multiphoton excitation followed by the detection of fluorescence or ionization. Three experimental investigations are summarized in this report. First, we describe an experiment to generate the sixth anti-Stokes (AS) wave at 170 nm from a tunable 285-nm beam for use in a two-photon absorption experiment. Second, we report the first observation of 3+1 resonantly enhanced multiphoton ionization (REMPI) of atomic F at 233 nm and experiments to detect fluorescence from the excited intermediate state. Finally, we describe the development of a time-of-flight (TOF) mass spectrometer to help interpret the combined F ₂ ⁺ and F ionization spectra at 286 nm and 233 nm.				
20 DISTRIBUTION AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a NAME OF RESPONSIBLE INDIVIDUAL Julian M. Tishkoff			22b TELEPHONE (include Area Code) 202/767-4935	22c OFFICE SYMBOL AFOSR/NA

DTIC SELECTED
APR 24 1987

AFOSR-TR- 87 - 0 4 5 4

March 4, 1987

Annual Technical Report
Covering the Period 1 January 1986 thru 31 December 1986

TWO-PHOTON DETECTION TECHNIQUES FOR ATOMIC FLUORINE

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SRI Project 8320
Contract No. F49620-85-K-0005
MP 87-033

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Approved for public release;
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87 4 27 1 7

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INTRODUCTION

The primary goal of this work is to develop a quantitative technique for remotely detecting atomic fluorine. Our approach to this problem is to detect the fluorescence from an excited state prepared by multiphoton absorption. During the first year of this project, we recorded¹ the first observation of 3+1 resonantly-enhanced multiphoton ionization (REMPI) in atomic fluorine at 285 nm. Because the lowest lying excited states ($3s^2P_J$ at $105,000\text{ cm}^{-1}$) are the intermediate states at 285 nm, no lower lying states are available for fluorescence in the visible wavelength region. Thus, a fluorescence detection technique must be used to observe states higher than $3s^2P_J$. This report summarizes three experimental investigations that were performed during the second year of the project. Each of these experiments represents one step towards the goal of demonstrating that these higher lying states can (1) be populated using either two- or three-photon absorption and (2) that fluorescence can be observed from these excited states.

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¹William K. Bischel and Leonard E. Jusinski, Chem. Phys. Lett. 120, 337 (1985).

PROGRESS

Experiments to Generate the Sixth Anti-Stokes Wave at 170 nm

A 170-nm beam is necessary to excite atomic fluorine to the $3p$ ($^2D^{\circ}_J$) states at $118,000 \text{ cm}^{-1}$ in a two-photon excitation technique. A series of experiments were performed to test if we could generate this VUV wavelength using multiwave Raman mixing in H_2 . A Raman cell in a purged beam line was constructed to measure conversion efficiencies to the higher order anti-Stokes waves in the VUV. To date, we have been able to generate only up to the fifth anti-Stokes (AS) at 185 nm using a tunable doubled dye laser at 286 nm as the pump. Recently, we discovered that cooling the Raman cell to liquid N_2 temperatures and freezing any impurities that may be in the H_2 may allow the generation of the sixth AS wave at 170 nm. A liquid N_2 cooled Raman cell has been constructed and will be tested during the third year of the project.

3+1 REMPI of the 2P_J State

Three-photon excitation may also be a viable technique for populating the high-lying states in atomic F that fluoresce. We can determine whether these states are populated by observing the 3+1 REMPI spectrum. For these experiments, we chose the $3d^2P_J$ state at $128,000 \text{ cm}^{-1}$ to excite in an 3+1 REMPI experiment. The experiment consisted of tuning a laser to 233 nm and observing the ionization signal while searching for fluorescence in the 700-800 nm region. A gas mixture (5% F_2 in He) flows through a cell that is equipped with an electrode for monitoring the total ion current and with collection optics for monitoring the fluorescence in the 700-800 nm region. We mixed the frequency-doubled output of a tunable dye laser with a $1.06\text{-}\mu\text{m}$ YAG output to produce the tunable 233-nm light. This light is used for both the photodissociation of the F_2 and the REMPI of the F.

Using this apparatus, we obtained the first 3+1 REMPI ionization spectra in the 233-nm region. The spectra show lines where most of the atomic fluorine

lines are expected to be and also contain extra lines that may be due to impurities in the compound. All these lines lie on top of a background signal that is wavelength independent and produces the dominant noise. The fluorine lines are roughly linear with gas density, whereas the impurity lines are somewhat independent of gas pressure.

To date we have been unable to detect any clear sign of fluorescence from any of the intermediate fluorine states. We detected very weak fluorescence signals for the same laser wavelength regions where the strongest ionization lines appear, but this fluorescence signal may be due to one of the impurity lines. Because we were able to observe only two fluorescence lines, we cannot unambiguously assign them to the expected atomic fluorine spectrum. Although the ionization signals are relatively large, it appears that three-photon excitation followed by the detection of fluorescence will not be a sensitive detection technique for atomic F. Further research with larger F-atom densities is necessary to determine if the fluorescence that was observed can be assigned to F-transitions.

Experiments Using a Time-of-Flight Mass Spectrometer

Because impurity ion signals precluded a clear analysis of the fluorine ion spectrum in all our REMPI experiments, we decided to build a time-of-flight (TOF) mass spectrometer to aid in the analysis of the fluorine REMPI data. In addition, the atomic fluorine beam developed for the TOF spectrometer might be usable as the high-density atomic fluorine source in our fluorescence detection experiments.

The TOF spectrometer is used in conjunction with a pulsed gas jet that allows the highest possible gas densities in the probing volume and the lowest possible densities at the detector. The 20-cm free-flight region gives a mass resolution of approximately 50 for our simple TOF mass spectrometer design.

With the TOF apparatus, we again obtained the $3s^2P_J$ spectrum at 285 nm.¹ We found that the 3+1 REMPI of F_2 at 284 nm produces only F^+ and no F_2^+ within the sensitivity limits of our detector. This result implies that the ionization of F_2 is immediately followed by the photodissociation of F_2^+ and thus the TOF mass spectrometer is unable to separate the F^+ and the F_2^+ spectra. Additional details of this work are described in the Appendix.

We also used the TOF spectrometer, along with an excimer laser (248 nm) used to dissociate the F_2 , to develop a high-density atomic fluorine beam. The primary drawback to this approach with the current apparatus is that light from the dissociation laser produces a large ion background that masks the signals at the F_2 and F mass positions. We plan to modify the TOF apparatus to eliminate this background signal and thus allow single-atom detection sensitivity for F^+ .

FUTURE WORK

We are currently setting up an experiment to excite fluorine atoms using a two-photon transition since the larger two-photon cross section will produce a larger fluorescence signal. This transition is shown in Figure 1. A 157-nm beam from an excimer laser and a tunable 185-nm beam (fifth anti-Stokes from 285 nm) will be overlapped in a cell to populate the $3p^2D^0_J$ state near $118,000 \text{ cm}^{-1}$. The 750-800 nm fluorescence to the $3s^2P_J$ states will then be monitored. A microwave discharge will be used to dissociate the F_2 . The larger two-photon cross section (compared with the three-photon) and the higher density of atomic fluorine from the discharge (compared with the photodissociation at 233 nm) should provide a greater chance of success for this approach than the three-photon excitation technique.

In addition, if cooling of the Raman cell allows the generation of the sixth AS at 170 nm, then we can use a single laser to access these same states with a two-photon transition.

Simultaneous with this two-photon effort, we will modify the TOF spectrometer in an effort to produce a high-density atomic fluorine beam. Modifications under consideration include

- (1) Geometry changes that will reduce the stray photodissociation light that produces the large ion background.
- (2) Use of a heated nozzle to dissociate the F_2 , which would eliminate the need for a photodissociation laser.
- (3) A differential pumping scheme to reduce the F_2 exposure to the detector.
- (4) Replacement of the current detector (a standard electron multiplier) with a microchannel plate detector.

The successful generation of a high-density atomic fluorine beam with known parameters will be an important step in the development of a fluorine diagnostic technique.

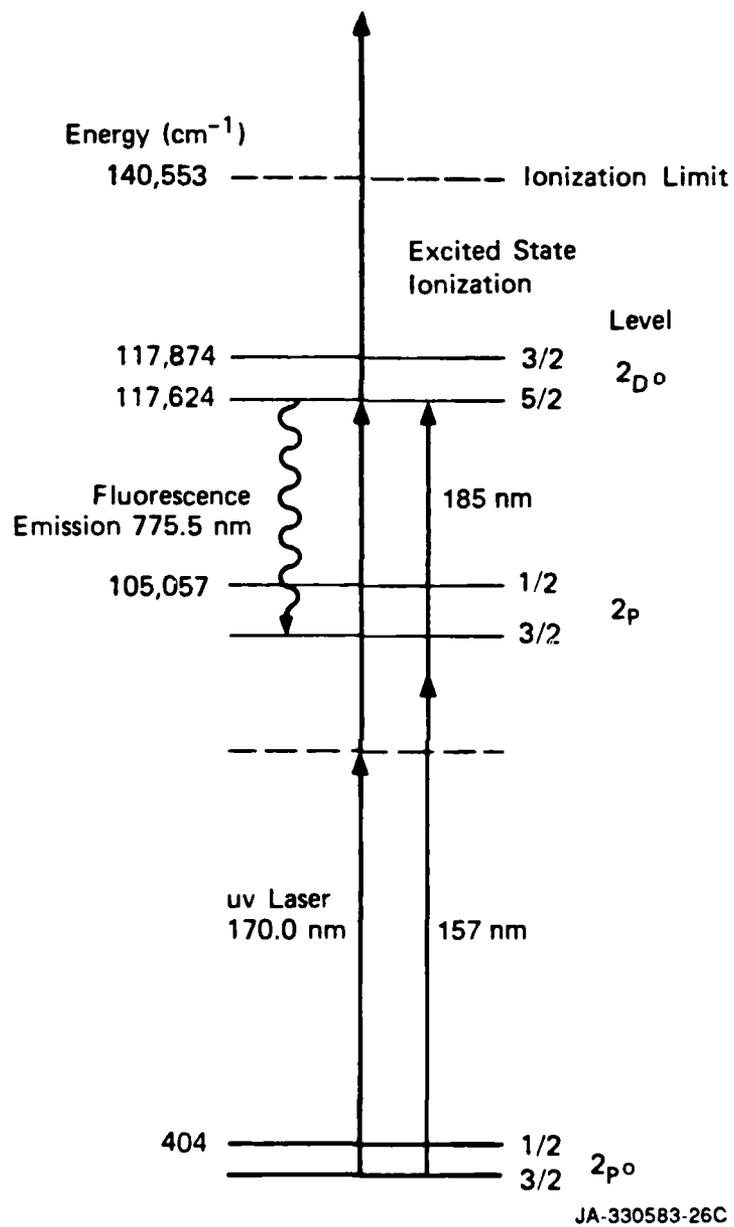


FIGURE 1 FLUORINE EXCITED STATES RELEVANT TO THE TWO-PHOTON DETECTION TECHNIQUE

Appendix

MULTIPHOTON IONIZATION SPECTROSCOPY OF F AND F₂
USING A TIME-OF-FLIGHT MASS SPECTROMETER

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ABSTRACT

Using a time-of-flight mass spectrometer, multiphoton ionization (MPI) spectra of F and F₂ have been obtained. We observe that the MPI of F₂ at 284 nm produces F⁺ instead of F₂⁺ thus complicating the interpretation of data obtained in F atom MPI experiments.

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SUMMARY

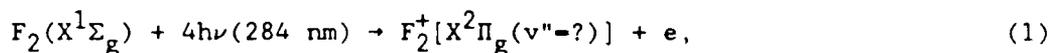
Recent studies¹ of the resonantly-enhanced multiphoton ionization (REMPI) of F and F₂ were performed in a bulb experiment where the total ion current was observed. When the laser was tuned through the spectral region around 286 nm, spectra from both F and F₂ were observed. Since we had difficulty interpreting some of the data from these experiments due to spurious signals resulting from overlapping F and F₂ MPI transitions and the background ionization of impurities, we developed a time-of-flight (TOF) mass spectrometer to allow the observation of just the F⁺ or F₂⁺ ion signals. We report here the results of these experiments.

Our current apparatus uses a tunable UV laser light source and a time-of-flight mass spectrometer. We have found that the 3+1 REMPI of F₂ at 284 nm produces only F⁺ and no F₂⁺ within the sensitivity limits of our detector. This surprising result implies that the ionization of F₂ is immediately

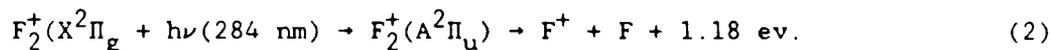
Herring et. al., "Multiphoton Ionization"

followed by the photodissociation of F_2^+ with a cross section that is estimated to be larger than 10^{-21} cm^2 . This observation limits the utility of TOF technique in interpreting the REMPI spectra of F and F_2 .

The TOF signal at the F^+ mass shows double-peaked signals resulting from the forward/backward translational energy release in the photodissociation process. When the laser is tuned to a 3+1 REMPI transition in F_2 at 284.1 nm [resonant state is the $H^1\Pi_u(v'=0)$]¹, the double-peak structure is evident when the laser polarization is parallel to the TOF detection axis indicating that the photodissociation transition is a parallel transition. We have tentatively identified the mechanism for F^+ atom production as a two-step process of

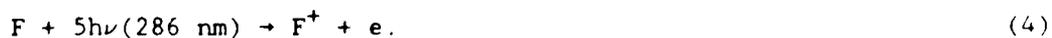
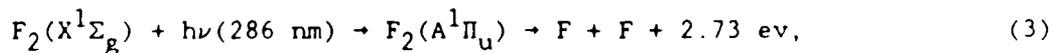


and



In determining the kinetic energy release given in Equation 2 we have assumed that the F_2^+ X state is formed with $v''=0$. We have measured the peak separation as a function of plate voltage and determined that the kinetic energy release is $1.0 \pm 0.2 \text{ ev}$, consistent with the energy release shown in Equation 2.

When the laser is tuned to the 3+2 REMPI transition in atomic F at 286.1 nm (resonant state is the $^2P_{3/2}$ state),¹ the double-peaked structure is only evident when the laser polarization is perpendicular to the TOF detection axis indicating that the photodissociation transition is a perpendicular transition. We have identified the mechanism for F^+ production as a two step transition of



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Again, measuring the peak separation as a function of plate voltage yields a kinetic energy release of 3.0 ± 0.3 eV, consistent with the kinetic energy release given in Equation 3.

We have used this information to separate the F atom REMPI signal from the the F₂ REMPI signal by using a laser polarized perpendicular to the TOF detection axis and two detection channels. The double peaked structure occurs when the laser is tuned through an F atom REMPI transition and is absent when the laser is tuned through an F₂ REMPI transition. This method allows the simultaneous measurement of F atom and F₂ REMPI spectra with minimal interference.

This work was supported by the Air Force Office of Scientific Research.

1. W. K. Bischel and L. E. Jusinski, Chem. Phys. Lett. 120, 337 (1985).

END

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