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During the last year we have been performing experiments that will lead to the development of quantitative remote diagnostics for atomic and molecular fluorine, using ultraviolet multiphoton excitation followed by the detection of fluorescence or ionization. In this report, we describe the first demonstration of resonant multiphoton excitation of molecular fluorine and the construction of a new apparatus for high-sensitivity detection of atomic fluorine using two-photon absorption of 170-nm radiation from a narrow-band tunable ArF laser, Raman shifted in liquid-nitrogen-cooled HD.

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INTRODUCTION

The goal of this work is to develop quantitative detection techniques for F and F₂ based on multiphoton excitation of high-lying atomic or molecular states. Because of their high ionization potentials, F and F₂ are among the most difficult neutral chemical species to detect spectroscopically. Our research program includes (1) development of the necessary high-power narrow-band ultraviolet radiation sources, (2) identification and experimental observation of appropriate multiphoton transitions, (3) measurement and calculation of absolute cross sections for multiphoton absorption and photoionization, and (4) measurement of radiative lifetimes, quenching rates, and branching ratios.

In our studies of F₂, vibrational levels $v' = 0, 1, 2$ of the $F^1\Pi_g$ state and $v' = 3$ of the $f^3\Pi_g$ state have been excited from the ground $X^1\Sigma_g^+$ by two photons near 207 nm and detected by vuv fluorescence or by ionization by a third photon. In addition to providing a means of detecting ground state of F₂, the two-photon excitation scheme we have developed should also be especially useful in investigating the kinetics of the 157 nm F₂ laser, which is believed to arise from a transition from the outer well of the $f^3\Pi_g$ state to a weakly bound $^3\Pi_u$ state correlating to ground state atoms.

In order to make practical the quantitative detection of atomic fluorine by two-photon excited fluorescence (TPEF) using a 170-nm pump laser, we had to develop a new laser source that is much more intense than the sixth-order anti-Stokes Raman shifted doubled dye laser we had used previously. Such a laser system has now been assembled, along with an appropriate experimental cell and detection equipment. It is based on using both a stronger ultraviolet primary laser (ArF) and lower order Raman shifting (only two shifts).



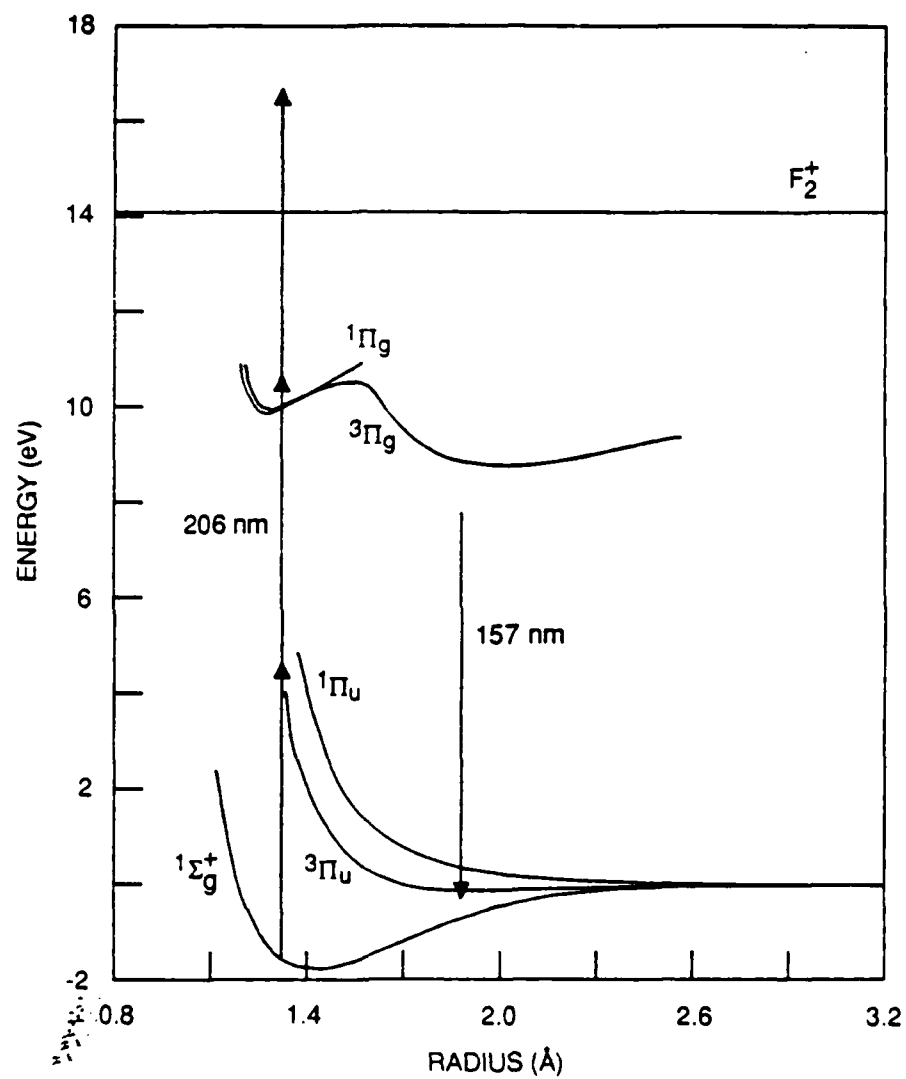
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PROGRESS

TWO-PHOTON SPECTROSCOPY OF THE $F^1\Pi_g$ AND $f^3\Pi_g$ STATES OF F_2

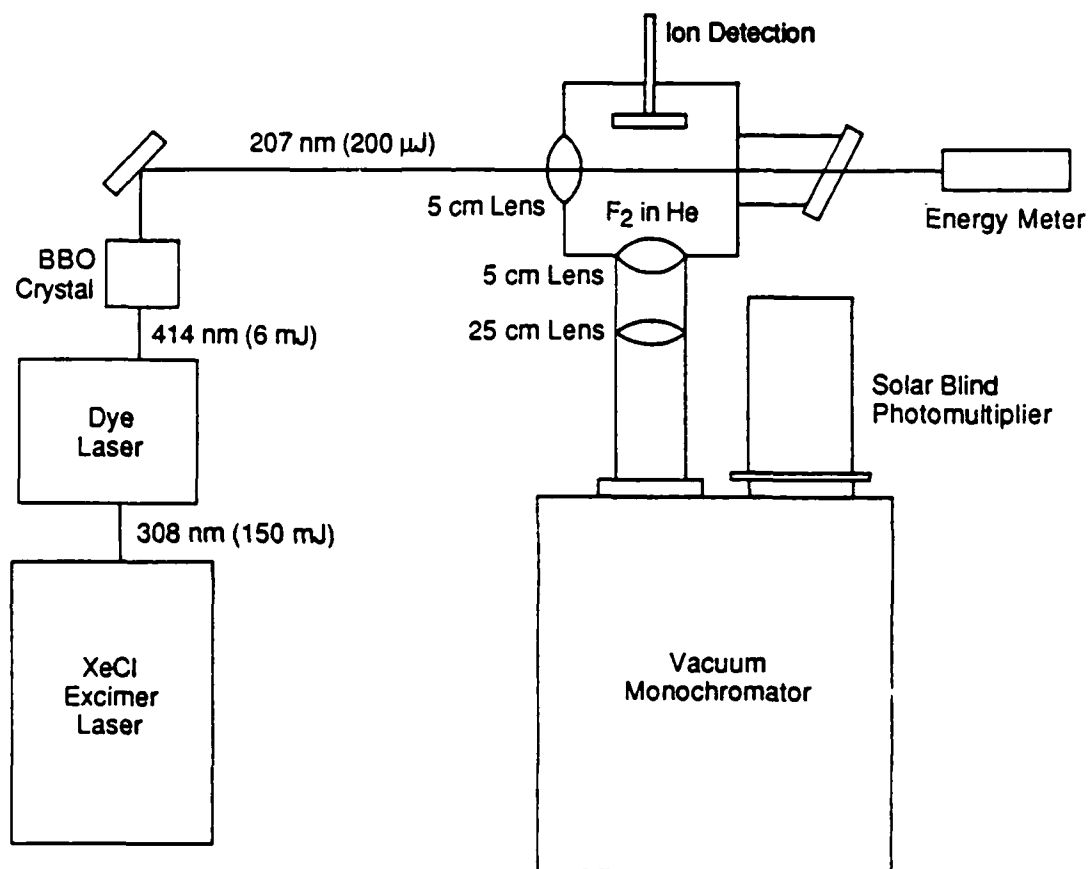
Spectroscopic detection of molecular fluorine is difficult because the lowest spin-allowed bound state lies some $94,000\text{ cm}^{-1}$ above the ground state. Calculated potential energy curves for F_2 are given in Figure 1. The lower states are taken from Cartwright and Hay [CH79], while the upper two states are taken from Sakai *et al.* [STM88]. The upper states have been lowered from the position given by Sakai *et al.* to give the proper energy spacing for the $^1\Pi_g \leftarrow ^1\Sigma_g^+$ and $^3\Pi_g \leftarrow ^1\Sigma_g^+$ transitions (the outer well of the shifted $^3\Pi_g$ state is still too high compared to the 157-nm transition to the lower $^3\Pi_u$ state). We have performed the first optical excitation from the ground state to both the lowest bound singlet state, the $^1\Pi_g$ state, as well as the nearby $^3\Pi_g$ state. Both states are reached by two-photon excitation and detected by fluorescence or by ionization by a third photon. Our observation of the $f^3\Pi_g$ state is, to our knowledge, the first two-photon transition from a singlet state to triplet state.

The experimental arrangement for two-photon excitation of F_2 is shown in Figure 2. An excimer-pumped dye laser (Lambda Physik EMG102 and FL3002) with PBBO dye produces about 6 mJ at 414 nm. This light is frequency doubled in a $\beta\text{-BaB}_2\text{O}_4$ crystal to give about 200 μJ at 207 nm. This light is focused with a 5-cm lens into a stainless steel cell containing a mixture of fluorine and helium. Ions are detected with a single electrode biased at 100 V relative to the cell. The ion signals are amplified with an Ortec model 142 PC charge-integrating preamplifier. Fluorescence is collected with a 5-cm MgF_2 lens and focused with a 25-cm MgF_2 lens onto the slits of a vacuum monochromator. Fluorescence was detected with a CsI solar blind photomultiplier. The positions of the lenses are set to image the focal volume of the laser onto the slits, thus enhancing the contrast between the fluorescence and the scattered laser light in the cell. For most of the fluorescence measurements, the vacuum monochromator was not used. One set of slits (removed from the vacuum monochromator) was placed at the image of the second lens, and the photomultiplier was placed directly behind the slits. In all cases, it was necessary to evacuate the entire fluorescence optical path to detect the VUV fluorescence. The 207-nm light that passes through the cell passes either through a calibration cell containing NO or



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Figure 1. Calculated potential curves of some states in F_2 .



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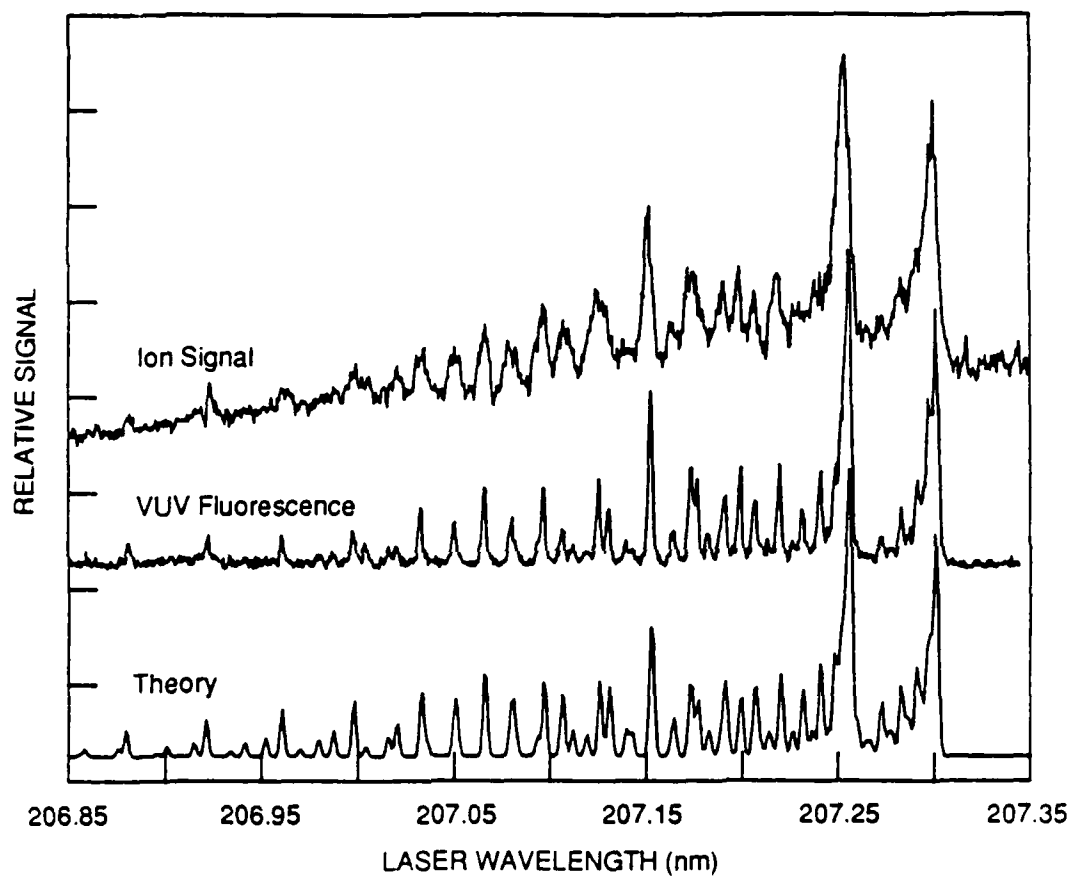
Figure 2. Experimental schematic for F₂ detection.

onto a pyroelectric energy meter. The 1+1 REMPI signal from the $B^2\Pi \leftarrow X^2\Pi$ (3,0) band in NO is used as a wavelength calibration. The NO band was later calibrated against iodine fluorescence by operating the dye laser at about 621 nm, doubling the frequency in a KDP crystal, and mixing the doubled and fundamental beams in the same β -BaB₂O₄ crystal. Part of the remaining fundamental beam was directed to an iodine cell, while the mixed beam passed through the NO cell.

Ionization and fluorescence excitation spectra of the $F^1\Pi_g(v'=2)$ state are shown in Figure 3. We have also observed the lower vibrational levels $v' = 0$ and 1, but with poorer signal-to-noise. We have assigned the observed transitions based on previous fluorescence [HH79] and electron-impact excitation experiments [HFK85]. Five rotational bands ($\Delta J = 0, +1, +2$) are expected for this two-photon transition. The O and P branches form heads, while the other three branches are degraded to the blue, indicating that the rotational constant of the upper state is greater than that of the ground state. Also shown in Figure 3 is a spectral simulation. The line intensities are calculated from the two-photon Hönl-London factors given by Halpern *et al.* [HZW80], while the rotational energies for the $X^1\Sigma_g$ ground state are from Huber and Herzberg [HH79]. A room temperature Boltzmann population is assumed, and the linewidth, vibrational energy, and rotation constants for the upper $F^1\Pi_g$ state are used as fitting parameters. The agreement in structure between the theoretical and fluorescence spectra is good.

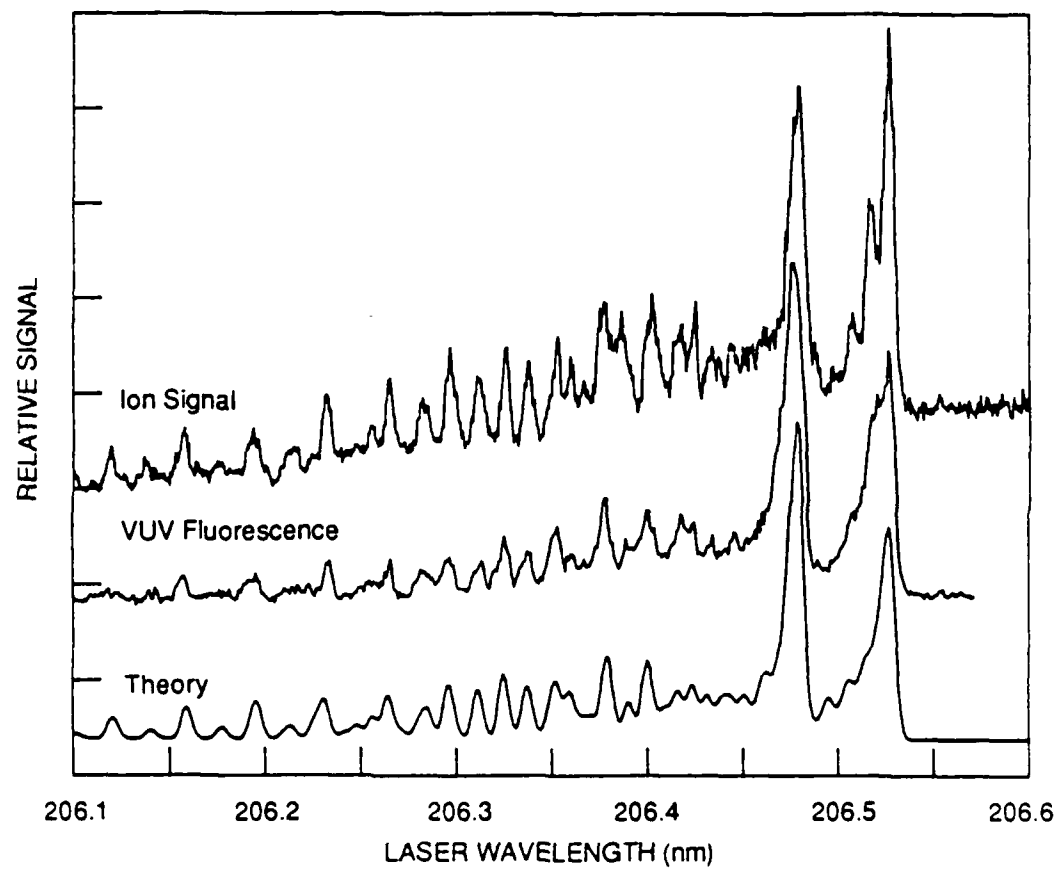
In Figure 4 are shown ionization and fluorescence excitation spectra for the transition $f^3\Pi_g(v'=3) \leftarrow X^1\Sigma_g^+$. These constitute the first two-photon singlet to triplet transition to our knowledge. A theoretical spectrum calculated in the same manner as for that in Figure 3 is also shown in Figure 4. The calculation does not take into account spin-orbit fine structure of the $f^3\Pi_g$ state. The agreement between the experimental and simulated spectra is not as good as for singlet state, but the qualitative agreement suggests that the main source of transition probability is spin-orbit mixing of the $f^3\Pi_g(\Omega=1)$ spin component with the $F^1\Pi_g(\Omega=1)$ state.

The emission spectrum obtained, using the vacuum spectrometer, when we excite $v' = 2$ of the $F^1\Pi_g$ state is shown in Figure 5. This spectrum agrees very well with those observed in electron excited F₂-rare gas mixtures [RHW77, Di80]. Thus, we conclude that our initially excited $F^1\Pi_g$ levels are being collisionally transferred into the outer well of the $f^3\Pi_g$ state (see Figure 1). This conclusion is supported by increase in the fluorescence signal as the He pressure is increased, and by the time dependence of the fluorescence signal, which is shown in Figure 6 for various total pressures. Similar fluorescence time histories are obtained for excitation of either the $F^1\Pi_g$ or the $f^3\Pi_g$. The peak fluorescence



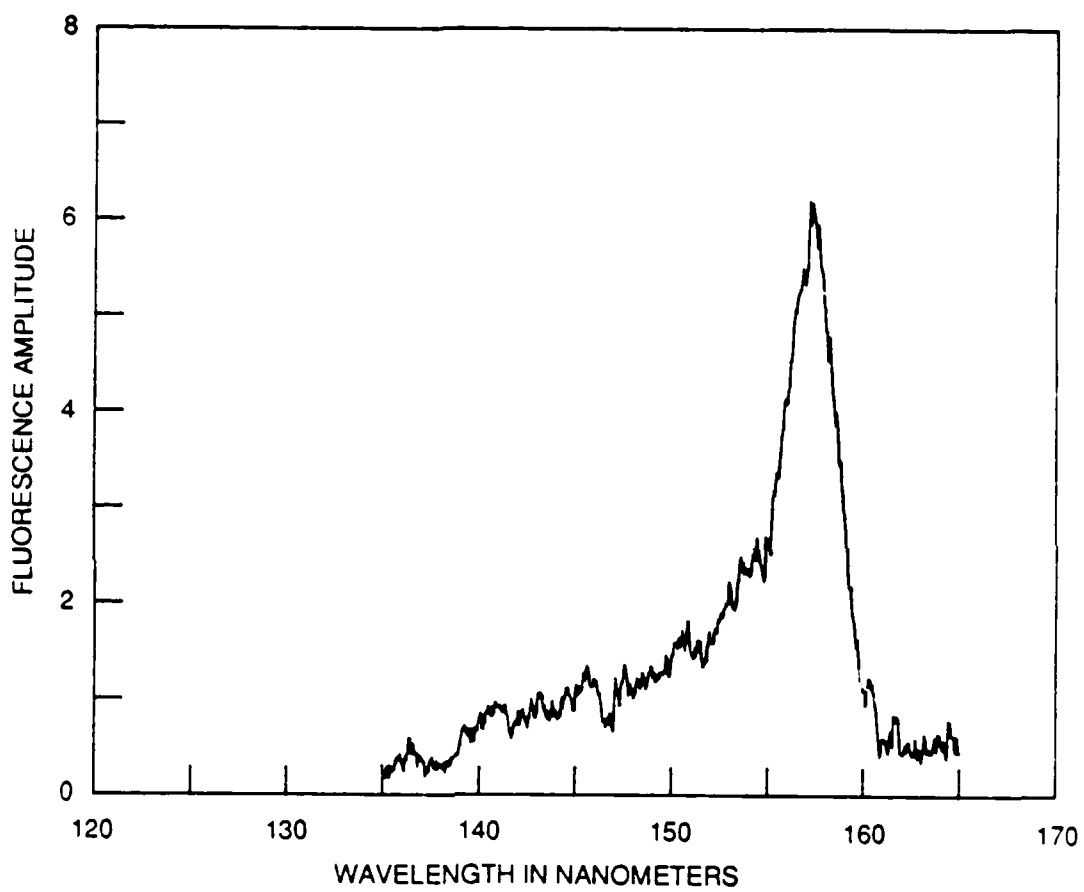
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Figure 3. $F_2 F^1\Pi_g (v' = 2) \leftarrow X^1\Sigma_g$ two-photon spectra.



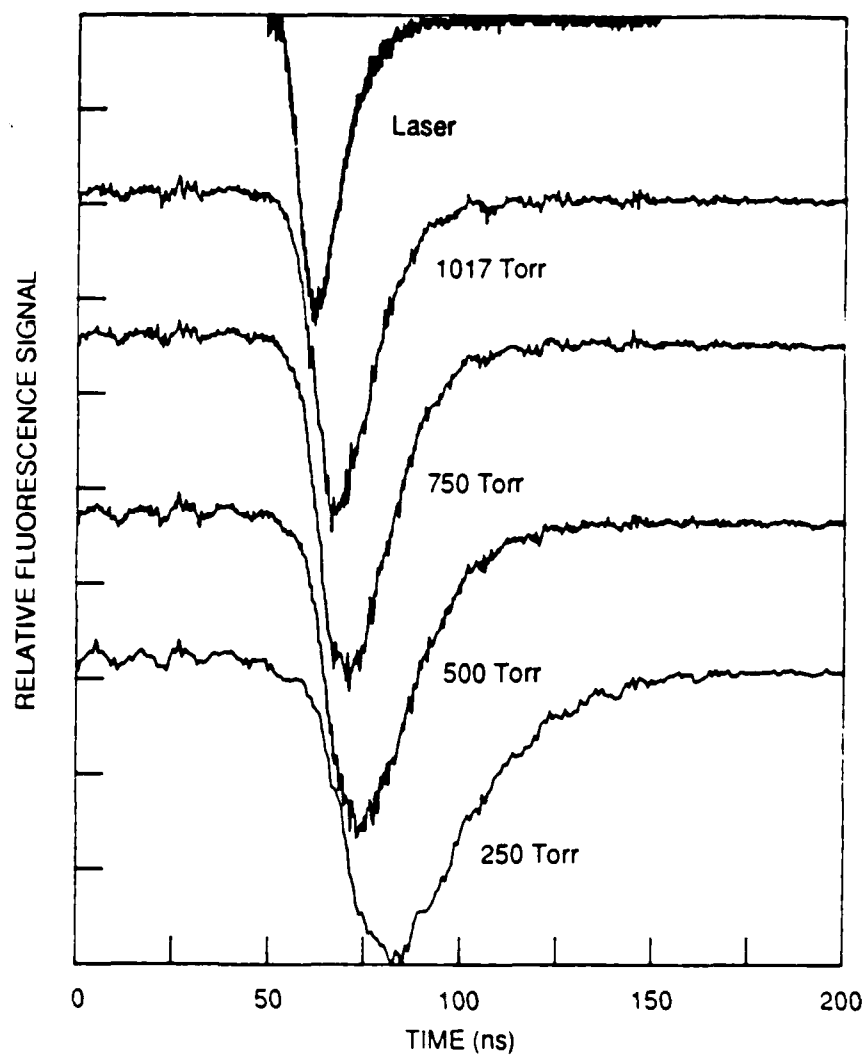
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Figure 4. F_2 $1^3\Pi_g (v' = 3) \leftarrow X^1\Sigma_g$ two-photon spectra.



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Figure 5. VUV emission on excitation of the $F_2 F^1\Pi_g (v' = 2)$ state.



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Figure 6. Pressure dependence of $F_2 F^1\Pi_g (v' = 2)$ fluorescence signal.

signal is always delayed with respect to the laser pulse, the delay increasing as the total pressure in the cell decreased. We interpret this as being due to the changing rate, as the He density is changed, of collisional transfer from the inner well of either the $F^1\Pi_g$ or $f^3\Pi_g$ state to the outer well of the $f^3\Pi_g$ state. The time scale of the fluorescence decay also changes with pressure. We interpret this as being due to the changing the rate of quenching as the F_2 density is changed.

These discoveries are important because they establish with high certainty the origin of the F_2 laser transition (about which there has been some controversy [STM88]). In addition, because this state can now be accessed optically, the kinetics of the laser may be studied in an environment which can be controlled much better than that of electron beam or discharge excitation.

An additional interesting result was found when the ionization signal was measured as a function of pressure. A set of such measurements is shown in Figure 7. The relative intensities of the different rotational lines change with pressure in a way that is not currently understood. This behavior was not present in the fluorescence spectra.

GENERATION OF 170 nm RADIATION FROM AN ArF LASER RAMAN SHIFTED IN HD

A suitable detection scheme for atomic fluorine was demonstrated during the previous AFOSR contract (No. F49620-85-K-0005) [Bi88,HDJ88]. This scheme involves two-photon excitation with 170-nm light followed by detection of fluorescence at 776 nm. In the previous experiments the 170-nm light was generated by sixth-order anti-Stokes (AS) Raman shifting in H_2 of the 30-mJ output at 280 nm of a doubled Nd:YAG pumped dye laser. The resulting laser energy at 170 nm was on the order of 10 μ J.

The sensitivity of the detection technique depends on the square of the pump laser intensity. It is therefore important to obtain as large an energy at 170-nm as possible in order to maximize the detection sensitivity. We have designed and constructed a new apparatus for generating intense narrow-band 170 nm radiation using the technique of multiwave Raman mixing in HD to produce the second AS wave at 170 nm starting with a tunable, narrow-band ArF excimer laser at 193 nm. The advantage of this approach is that the ArF laser is much closer to the desired wavelength, allowing us to use only second-order anti-Stokes Raman shifting (previous experience suggests at least a factor of three reduction in output for each anti-Stokes order). A technical problem that we have to solve is that the gas that has the appropriate Raman shift energy is HD, which under normal conditions has a smaller Raman gain and conversion efficiency than H_2 . We believe that

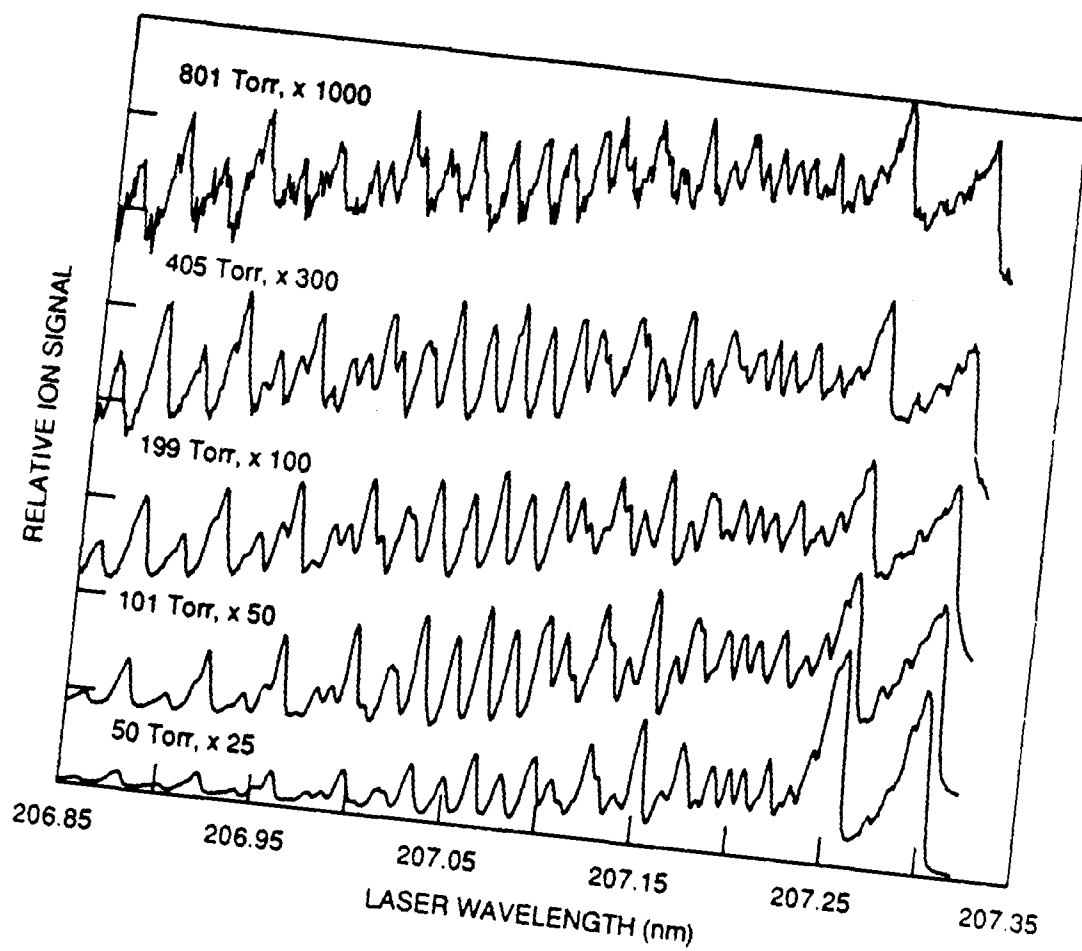
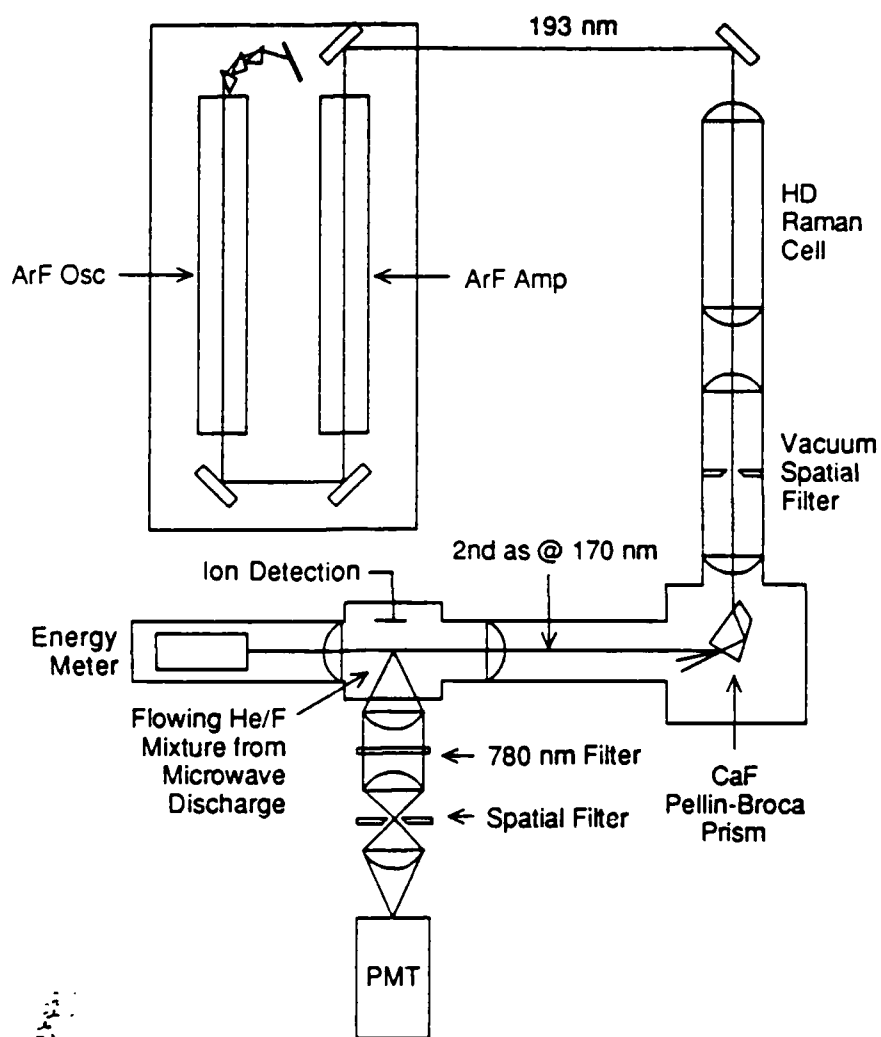


Figure 7. $F_2 F^1\Pi_g (v' = 2) \leftarrow X^1\Sigma_g$ MPI spectra versus pressure.

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by cooling the HD Raman cell to liquid nitrogen temperature (77 K) the Raman gain in HD will be equivalent to that of H₂ at room temperature, and thus the multiwave mixing technique should efficiently (approximately 1%) generate the second AS wave at 170 nm. We hope to generate at least 100 times more energy than was available previously. If successful, this could be an important technological advance in making the TPEF technique portable and easy to use.

The apparatus for this Raman-shifting of an excimer has been set up and is shown in Figure 8. The tunable oscillator-amplifier ArF laser (Lambda Physik 150 MSC) is well suited for this type of measurement. The oscillator provides a narrow-band (approximately 1 cm) output, tunable over about 1 nm. This narrow-band radiation is used as a seed for an amplifier with its own resonator to give high-power tunable radiation in a fairly good spatial mode suitable for Raman shifting. From the liquid-nitrogen cooled Raman cell on, the entire optical path is in a vacuum system, including a spatial filter to improve the spatial mode for absolute cross section measurements as well as to reject most of the unshifted excimer laser and the other, unwanted shifted Raman orders. A spatial filter has also been set up between the fluorine cell and the photomultiplier tube (PMT), as in the previous measurement [HDJ88], to minimize background signals from outside the focal volume. To date, no measurements have been made.



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Figure 8. Experimental schematic for F-atom detection.

FUTURE WORK

Our first priority is to demonstrate high-sensitivity detection of atomic fluorine using the Raman-shifted excimer laser. Since the equipment is in place, preliminary tests of feasibility should be completed quickly. To achieve high power in the second AS beam, we may have to modify the cavity of the ArF laser to improve the spatial mode quality. If this goes well, we should have enough time to measure absolute two-photon cross sections. These measurements would be compared to theoretical calculations of these cross sections performed by Roberta Saxon. Funds for these theoretical calculations have been set aside.

Many interesting and important measurements can be performed using the TPEF detection technique that we have developed for F_2 . The first of these is further experiments and analysis to understand the pressure dependence of the different rotational branches in three-photon ionization. Such a dependence makes more complicated the inference of species concentrations from ionization signals. Next in importance is a general investigation of the collisional kinetics of the excited states of F_2 . Only limited information is presently available [HHN78], principally because of the lack of a convenient excitation scheme, a problem we have just solved. Such studies should provide valuable information about various kinetic processes in the F_2 laser at 157 nm, the brightest spectral source in the VUV today. Just as we are now using the ArF excimer laser in our studies of the F-atom, improvement in the performance of the F_2 laser would make practical development of additional optical diagnostics farther into the vacuum ultraviolet.

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LIST OF PUBLICATIONS

None.

LIST OF CONFERENCE PRESENTATIONS

1. "Multiphoton detection techniques for F and F₂," W. K. Bischel, presented at the 1988 AFOSR Contractors' Meeting, 14-16 June, 1988, Monrovia, CA.
2. "Two-photon spectroscopy of the F¹Π_g and f³Π_g states of molecular fluorine," G. W. Faris and W. K. Bischel, presented at the Annual Meeting of the Optical Society of America, July 1988, Anaheim, CA.