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TWO-PHOTON DETECTION TECHNIQUES FOR ATOMIC FLUORINE(U)
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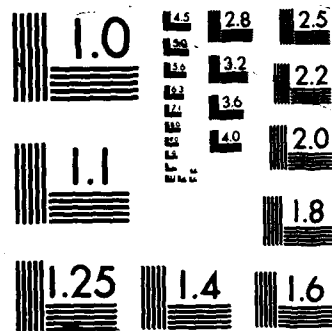
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TWO-PHOTON DETECTION TECHNIQUES FOR ATOMIC FLUORINE

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During the first year of the project, the multiphoton spectroscopy of atomic fluorine was investigated to determine if three-photon excitation could be used for remote detection applications. The first observation of resonantly enhanced multiphoton ionization (REMPI) of atomic fluorine is reported. Four excited states are observed for dye laser wavelengths in the range of 286 nm corresponding to a three-photon resonant transition in a 3+2 photon ionization process. REMPI spectra of molecular fluorine in a 3+1 photon process are also observed. The resonant excited states in the spectra have been identified using absorption spectra published in the literature. In the present experiment, it is estimated that 0.03 millitorr of fluorine atoms can be detected with a signal-to-noise ratio of two. An apparatus is under development to test the techniques of two-photon excited fluorescence and coherent anti-Stokes Raman spectroscopy for detection of atomic fluorine.			
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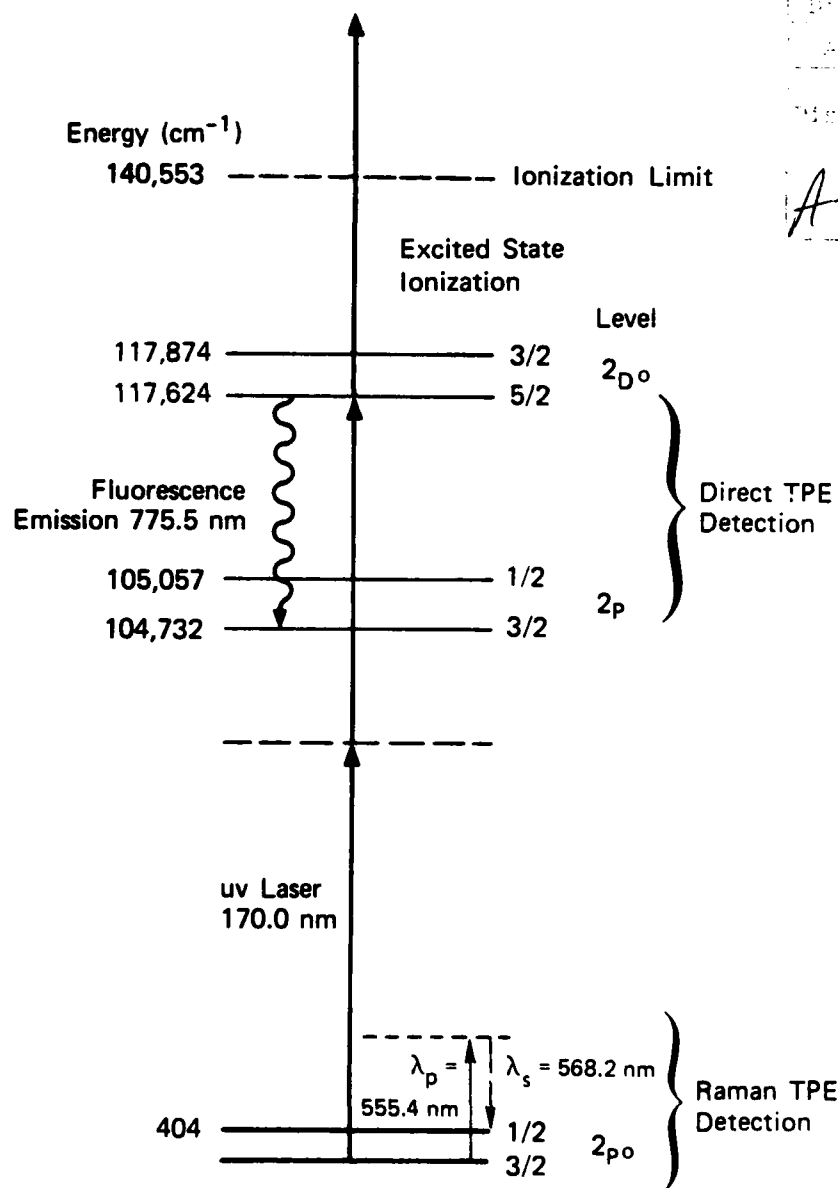
TWO-PHOTON DETECTION TECHNIQUES FOR ATOMIC FLUORINE

Statement of Work

The objective of the research project is to understand the fundamental physical processes that determine the sensitivity and versatility of a fluorine atom detection technique based on two-photon excitation methods. We plan to examine both direct two-photon excitation processes and Raman excitation processes. Fundamental measurements detailing the spectroscopy and kinetics of the fluorine atomic system will be performed. Applications of the research include the development of a sensitive F-atom detection technique that has good spatial and temporal resolution.

Status of the Research

Figure 1 shows the fluorine excited states relevant to the two-photon detection technique for both the direct excitation process and the Raman excitation process. We chose to concentrate on the direct multiphoton excitation of excited states during the first year of the project. The basic concept for the two-photon excited fluorescence technique is to excite states in the region of $118,000 \text{ cm}^{-1}$ with a laser with a wavelength around 170 nm and observe visible fluorescence from that excited state at 776 nm. Signal estimates given in the proposal indicated that only 1-10 μJ of energy at 170 nm were necessary to see an adequate fluorescence signal. However, we anticipated that the development of this laser source at this energy level would take a significant amount of development time. We therefore started a two-part research program: first, to investigate methods of producing 170 nm, and second, to see if three-or-more photon excitation could lead to a detection technique where fluorescence could be observed. The development of the 170-nm laser source is currently in progress and we anticipate results will be reported in the next annual report. The remainder of this report concentrates on our recent multiphoton excitation experiments.



JA-330583-268

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

Three-photon excitation with the subsequent observation of fluorescence has been successfully demonstrated in the detection of H atoms and may prove to be useful in the detection of F as well. The main advantage of the three-photon excitation scheme is that it requires a laser wavelength in the region of 220-286 nm, depending on what level is excited. Since these wavelengths can be generated using standard nonlinear techniques with millijoules of energy, there is a big advantage to be gained in the simplicity of the experiment. We therefore set up an experiment to observe the first multiphoton excitation spectra of F.

The results of this experiment are given in the Appendix and this report summarizes the most important points. Because we wanted to obtain the largest signal-to-noise ratio for this first experiment, we decided to use the ionization signal rather than a fluorescence signal to monitor the multiphoton excitation process. From these experiments, we reported the first observation of resonantly enhanced multiphoton ionization (REMPI) of atomic fluorine. Four excited states were observed in the region of $105,000\text{ cm}^{-1}$ corresponding to the $2P_{1/2,3/2}^0 \rightarrow 2P_{1/2,3/2}$ three-photon transition in a 3+2 photon ionization process. The dye laser wavelength used in these experiments was 286 nm. We also observed REMPI spectra of F_2 in a 3+1 photon process. Using absorption spectra from the literature, we have identified the resonant excited states as $H^1\Sigma_u$ and $h^3\Sigma_{1,u}$. We estimated an F-atom detection sensitivity for the present experiment of $\sim 10^{12}\text{ cm}^3$.

The signal strengths in the experiment were much stronger than anticipated, indicating that three-photon excitation may be a viable alternative to two-photon excitation for remote detection applications of F. We plan to probe for shorter wavelength three-photon allowed transitions to higher lying states that would fluoresce in the visible.

During the next year, we also plan to try to detect F atoms using both direct two-photon excitation and the Raman excitation. Results of these experiments will be given in the next annual report.

List of Publications

1. William K. Bischel and Leonard E. Jusinski, "Multiphoton Ionization Spectroscopy of Atomic Fluorine," Chem. Phys. Lett. 120, 337 (1985).

List of Conference Presentations

1. W. K. Bischel and L. E. Jusinski, "Multiphoton Ionization Spectroscopy of Atomic Fluorine," in Laser Spectroscopy VII, eds. T. W. Hänsch and Y. R. Shen (Springer-Verlag, Berlin, 1985), pp. 94-95. Post-deadline paper presented at the Seventh International Conference on Laser Spectroscopy, Hawaii, June 24-28, 1985.
2. W. K. Bischel and L. E. Jusinski, "Multiphoton Ionization Spectroscopy of Atomic Fluorine," presented at the OSA Annual Meeting, Washington, DC, October 14-18, 1985.

MULTIPHOTON IONIZATION SPECTROSCOPY OF ATOMIC FLUORINE

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The first observation of resonantly enhanced multiphoton ionization (REMPI) of atomic fluorine is reported. Four excited states are observed in the region of 105000 cm^{-1} corresponding to the $2P_{1/2,3/2} \rightarrow 2P_{1/2,3/2}$ three-photon transition in a $3+2$ -photon ionization process. REMPI spectra of F_2 in a $3+1$ -photon process is also observed. The resonant excited states in the spectra have been identified as the $H^1\Sigma_u$ and $h^3\Sigma_u$ levels using absorption spectra. We estimate an F-atom detection sensitivity for the present experiment of $\approx 10^{12}\text{ cm}^{-3}$.

1. Introduction

The study of the electronic spectrum of atomic fluorine is extremely difficult since all the single-photon transitions from the ground state require wavelengths that are below the LIF window cutoff at 106 nm. The resonance transition occurs at 95.5 nm, and all other allowed absorption transitions are at shorter wavelengths. Because of the inaccessibility of these electronic states, there have been few experiments reporting the detection and spectroscopy of atomic fluorine [1,2]. This situation presents an ideal application for the techniques of multiphoton excitation, followed by either fluorescence or ionization detection.

We report here the first observation of resonantly enhanced multiphoton ionization (REMPI) of atomic fluorine in a $3+2$ -photon process. The excited states that are three-photon resonant in this experiment are the $2P_{3/2,1/2}$ states at 104731.0 cm^{-1} and 105056.3 cm^{-1} , respectively [3] and are illustrated in fig. 1. These states are then ionized by the absorption of two additional photons forming a five-photon ($3+2$) process. Since the ground-state fine-structure splitting between the $2P_{3/2,1/2}$ states is 404.1 cm^{-1} ($3/2$ lower), we expect that the REMPI spectrum would have four transitions if both these states were populated (observation of the hyperfine structure [2] is below our resolution limit). Thus the observation of these four transitions would form unambiguous evidence that atomic fluorine has been detected using REMPI. The

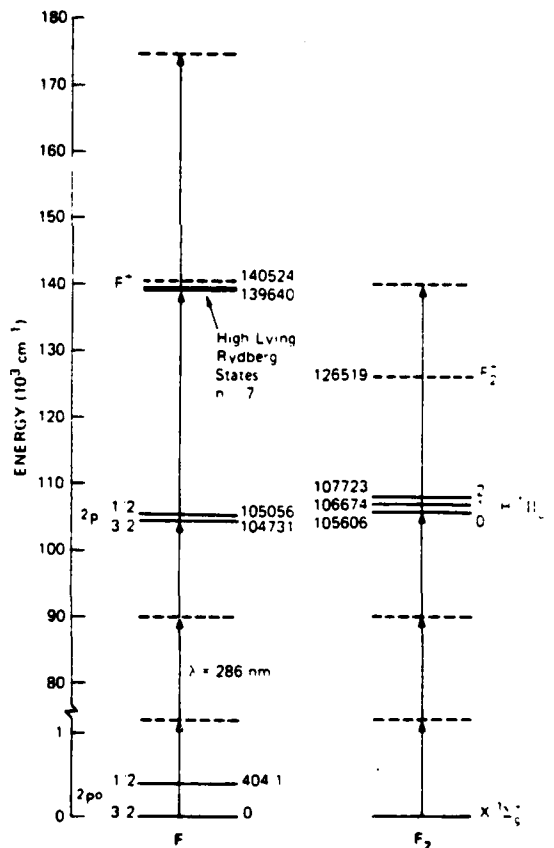


Fig. 1. Energy levels of F and F_2 involved in the REMPI spectrum shown in fig. 2.

four transition wavelengths correspond to vacuum dye laser wavelengths of: 287.56 nm ($1/2 \rightarrow 3/2$), 286.67 nm ($1/2 \rightarrow 1/2$), 286.45 nm ($3/2 \rightarrow 3/2$), and 285.56 nm ($3/2 \rightarrow 1/2$).

Since the ionization limit [3] occurs at 140524.5 cm^{-1} , the possibility of $4 + 1$ REMPI process also exists as is illustrated in fig. 1. Starting from the $2p_{3/2}^0$ ground state, the equivalent energy of four UV laser photons accesses excited states in the $2S_j^0$, $2p_j^0$, $2D_j^0$ manifolds that are $\approx 880 \text{ cm}^{-1}$ below the ionization limit. These states could also be observed if there were near coincidences with the wavelengths for the three-photon resonant states. We give evidence below that we also observe these states in our REMPI experiments.

2. Experimental

The experimental apparatus is relatively simple. The laser photons at 285 nm are produced by doubling a Quanta Ray YAG-pumped dye laser giving a maximum UV energy of approximately 15–20 mJ. This energy is varied to obtain approximate power dependences of the ion yields by turning an achromatic half-wave plate before the doubler crystal. This allows us to change laser intensity in the cell without changing the beam quality or divergence.

The UV laser was initially focused into the experimental cell with a 20 cm focal length suprasil lens. The laser energy was measured after the cell with a calorimeter, and the temporal pulse shape was measured (fwhm of 5.5 ns) using a fast photodiode and Tek 7104 oscilloscope. The spatial profile of the laser beam at the focus was measured by scanning a $10 \mu\text{m}$ diameter pinhole through the laser beam. For the 20 cm focusing lens, the maximum peak intensity used in this experiment was $\approx 5 \times 10^{11} \text{ W/cm}^2$. The intensity was reduced to $\approx 10^9 \text{ W/cm}^2$ later in the experiment to obtain high-resolution spectra.

The cell is constructed of pyrex with suprasil Brewster windows. In the cell are two electrodes biased at +90 V. The negative electrode collects the positive ions produced in the focal volume of the laser and is grounded through an Ortec 142PC charge amplifier. The resulting signal is recorded using a boxcar averager and strip chart recorder. We estimate that it is necessary to produce approximately 10^4 ions per laser pulse in the focal volume to achieve a 1:1 signal to background ratio.

We flow a mixture of 10% F_2 in He into the cell at a slow rate to prevent F_2 loss to the pyrex walls of the cell. There is an activated charcoal F_2 filter between the roughing pump and the cell. All data presented here were taken with a total pressure of 1 Torr (0.1 Torr F_2) as measured with a 10 Torr Baraton capacitive manometer.

The F atoms are produced by UV photolysis of F_2 at 286 nm, using the same laser used to excite the multiphoton transition. The absorption cross section for the transition $\text{F}_2 + h\nu \rightarrow 2\text{F}$ peaks at approximately 280 nm with a value of approximately $2 \times 10^{-20} \text{ cm}^2$ [4]. We estimate that the F_2 is completely dissociated at the highest intensities used in our experiment while only $\approx 15\%$ is dissociated at 10^9 W/cm^2 . However, we note here that REMPI signals from F_2 were observed at all intensities, resulting from ionization in the wings of the spatial profile of the laser.

3. Results and discussion

The MPI spectrum for a low-resolution scan of the UV laser from 291 to 278 nm (equivalent three-photon energy of $103000\text{--}108000 \text{ cm}^{-1}$) is given by the solid line in fig. 2 for tight focusing conditions ($f = 20 \text{ cm}$). The laser energy is given by the dashed line. There are three prominent resonances in this spectrum that correspond to the above three-photon resonant transitions in F, thus confirming that F atoms are being observed. The fourth transition, barely observable in this spectrum, is obscured by background signals. These transi-

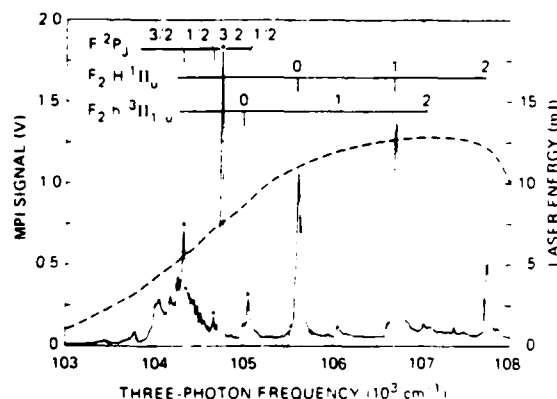


Fig. 2. Low-resolution REMPI spectrum of F and F_2 . The dashed line is the laser energy.

tions are labeled in the figure by the J of the excited 2P state. If the peak laser energy is reduced from 13 mJ to 3.5 mJ, the F-atom REMPI signals disappear completely from the spectrum while the F_2 signals are reduced by only a factor of 15. This is additional evidence that we have properly identified the four transitions in fig. 2 as F-atom signals.

Note in fig. 1 that the F-atom transition $2p_{3/2}^o \rightarrow 2p_{3/2}$ at 104731 cm^{-1} is more than five times larger than any of the other atomic transitions. This effect is much larger than can be explained by differences in three-photon line strength factors and relative ground-state populations. We interpret this enhancement as due to accidental resonances with Rydberg states near the ionization limit, thus making the REMPI signal a $3 + 1 + 1$ -photon process instead of a $3 + 2$ -process. The intensity dependence of this transition is discussed below.

The other features observed and labeled in the spectrum given in fig. 2 correspond to transitions to the $H^1\Pi_u$ and the $h^3\Pi_{1,u}$ states in F_2 that have previously been observed in single photon absorption [5]. An analysis of these transitions will be given in a subsequent paper.

The broad feature in the region of 104000 cm^{-1} has been identified [6–8] as a background signal from $2 + 1$ photoionization of O_2 (resonant state is the $3\Pi_g(v' = 2)$) by putting pure O_2 into the cell and taking a REMPI spectrum. In the same manner, we also tested for background signals from the REMPI of N_2 [9]. None of the features in fig. 2 could be assigned to the transitions observed in N_2 . All the transitions in fig. 2 are severely broadened due to the ac Stark effect. The laser intensity had to be reduced in order to increase the resolution and accurately measure the intensity dependence of the signal.

To achieve this, the spatial profile of the laser intensity was defined by inserting a spatial filter before the cell and imaging the pinhole ($300 \mu\text{m}$ diameter) into the cell with a 2:1 lens system. The intensity distribution in the focal volume was measured to be circularly symmetric by scanning a pinhole through the beam at different points along the propagation axis. At the focus the fwhm beam diameter was 0.017 cm with a Rayleigh range of approximately 1.8 cm . Assuming a Gaussian form for the spatial profile, the peak laser intensity was 800 MW/cm^2 for every mJ of measured laser energy.

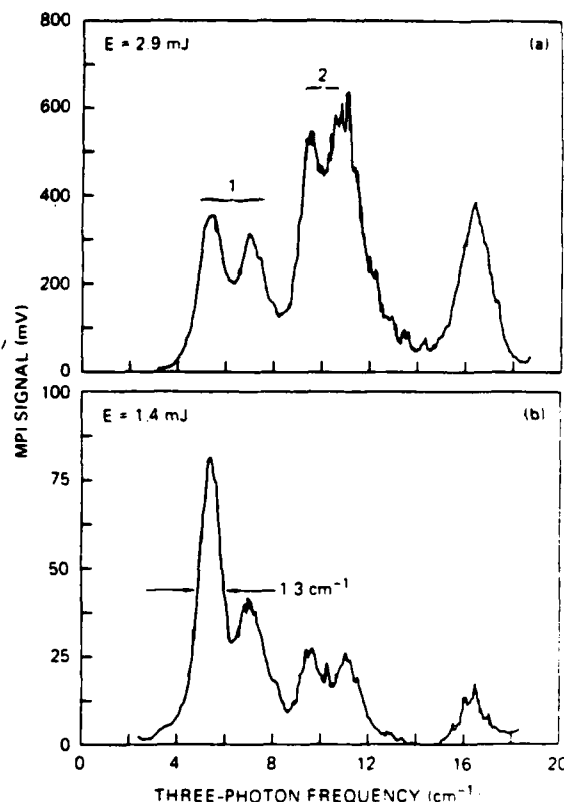


Fig. 3. High-resolution scan of the $2P_{3/2}^o \rightarrow 2P_{3/2}$ transition at 104731 cm^{-1} for two different laser energies.

With the intensity reduced, we have taken high-resolution scans of the strong feature at 104731 cm^{-1} identified as the $2P_{3/2}^o \rightarrow 2P_{3/2}$ three-photon resonant transition in F. These data are given in fig. 3 for two different laser energies. Note from fig. 3b that the resolution is approximately 1.3 cm^{-1} limited by the linewidth of the fundamental dye laser ($\approx 0.25 \text{ cm}^{-1}$). We observe five different peaks (instead of one). We interpret this observation as a combination of the $3 + 2$ and $4 + 1$ (near $3 + 1 + 1$) ionization processes discussed above. In addition, the ion signals labeled by 1 and 2 in fig. 3a have a different dependence on the laser intensity. Given our REMPI signals, we were able to vary the laser intensity from 800 to 2400 MW/cm^2 (laser energy of $1\text{--}3 \text{ mJ}$). Over this limited range, the order n intensity dependence of feature 1 is $n = 2.6$ while the order for feature 2 is $n = 5.0$. If we could have obtained signals at low enough intensity, the

order of the process would have been between 5 and 6, depending on how much of the F_2 has been dissociated in the experiment.

The intensity dependence of MPI transitions is difficult to accurately measure and interpret, even for non-resonant processes [9,10]. In addition to the shot-to-shot changes in the laser beam profile (both temporal and spatial) that plague all MPI experiments [10], the intensity dependence of the REMPI signals in this experiment are complicated by two other factors. First, the single-photon resonant steps in the $3 + 2$ (near $3 + 1 + 1$) processes may be saturated at these intensities, thus reducing the order of the observed intensity dependence. In addition, the ac Stark effect can shift levels into (or out of) resonance [11], thereby changing the apparent order of the intensity dependence. However, we can detect no change in the position of the peaks of the transitions given in fig. 3 at the different laser intensities. Thus, we conclude that only saturation plays a significant role in determining the order for the intensity dependence of the data in fig. 3.

Second, the ground-state F-atom density is varying during the laser pulse and thus the order of the intensity dependence will reflect the degree of dissociation of F_2 . Both of these effects make the modelling of the ionization process unproductive without data over a much larger intensity range (several orders of magnitude). If such data were available, effective cross sections for each step of the ionization process could, in principle, be determined by fitting the entire intensity dependence of the ionization yield curve as has been done in the case of the $3 + 1$ REMPI of xenon [12]. Experiments of this type are necessary if REMPI is ever to be used to measure absolute F-atom concentrations for an arbitrary laser intensity.

We can, however, make estimates of the F-atom detection sensitivity in the present experiment. The slope of the ion yield curve for feature 2 in fig. 3a is 6.0 mV/mJ [5]. At 3 mJ of laser energy, we estimate that we have a ground-state density at the time of peak laser intensity of approximately 10^{15} F atoms/cm³. For this density, we can obtain a signal/background ratio of greater than 1000:1, giving a F-atom detection sensitivity of approximately 10^{12} cm⁻³. This is unoptimized with respect to a number of parameters and thus could be significantly improved. Since 1 mV of signal corresponds to approximately

5×10^3 ions, the signal in fig. 3b corresponds to $\approx 4 \times 10^5$ ions. In this experiment, the excitation volume is $\approx 2 \times 10^{-4}$ cm³ and thus approximately $\approx 2 \times 10^{-6}$ of the ground-state F-atoms have been ionized.

We plan to modify the apparatus to include time-of-flight mass analysis of the ion signal to eliminate background signals from F_2 and O_2 and enhance the detection sensitivity. This should allow two-color experiments to study the odd parity Rydberg states near the ionization limit. In addition, the enhanced detection sensitivity will allow the intensity dependence of the ionization yield to be determined over a much larger range. And finally, we plan to look for third and fifth harmonic radiation at 95 and 57 nm which should compete with the ionization process at higher F-atom densities [13].

4. Conclusion

In conclusion, we have unambiguously demonstrated for the first time the detection of atomic fluorine using REMPI with a sensitivity limit of approximately 10^{12} cm⁻³ for the present experimental arrangement. This limit can probably be reduced by several orders of magnitude in a two-color experiment. We anticipate that these results can be utilized in a number of research areas requiring the sensitive detection of spatially and temporally resolved F-atom distributions.

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