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DETECTION OF TRANSIENT FLUORINE ATOMS

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ABSTRACT

A KrF excimer laser with a fluence of 50 mJ/cm^2 was used to photolyze either uranium hexafluoride or molecular fluorine, yielding a transient number density of fluorine atoms. The rise and decay of the atomic fluorine density was observed by transient absorption of a $25\text{-}\mu\text{m}$ Pb-salt diode laser. To prevent the diode laser wavelength from drifting out of resonance with the atomic fluorine line, part of the beam was split off and sent through a microwave discharge fluorine atom cell. This allowed a wavelength modulation-feedback technique to be used to lock the diode laser wavelength onto the atomic line. The remaining diode laser beam was made collinear with the excimer laser beam using a LiF window with a 45° angle of incidence to reflect the infrared beam while transmitting most of the uv beam. Using this setup along with a transient digitizer to average between 100 and 200 transient absorption profiles, fluorine atom number densities on the order of 10^{16} cm^{-3} in a 1.7 m pathlength were detected. The signals observed were about a factor of two less than expected from known photolysis and atomic fluorine absorption cross-sections.

INTRODUCTION

The absorption spectrum of atomic fluorine contains features only at $25 \mu\text{m}$ and at wavelengths shorter than 78 nm. The absorption at 404 cm^{-1} corresponds to the $^2P_{3/2} \rightarrow ^2P_{1/2}$ spin-orbital transition in atomic fluorine. The detection of fluorine atoms by absorption of a $25 \mu\text{m}$ diode laser beam has previously been demonstrated¹ and used to measure the hyperfine splitting² for a continuous source of fluorine atoms generated in a microwave discharge cell. We report here demonstration of a technique that allows transient fluorine atoms to be detected using the same diode laser absorption.

EXPERIMENTAL APPARATUS

The demonstration of transient fluorine atom detection was accomplished using a KrF excimer laser at 248 nm to photolyze either UF_6 or F_2 forming a nearly instantaneous density of fluorine atoms (10 ns lifetime), which then disappears due to recombination or diffusion out of the diode laser probe beam. The transient fluorine atoms absorbed part of a collinear diode laser beam, which was tuned to the strongest hyperfine line at 404.175 cm^{-1} . The excimer laser beam and diode laser beams were made collinear using a LiF window to transmit the excimer laser beam and reflect the diode laser beam (see figure 1). The excimer laser fluence was measured at several

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Fig. 1. Optical schematic of the equipment used to measure transient fluorine atom absorption and to wavelength stabilize the diode laser.

positions through the 1.7 m photolysis cell using a known aperture size and an energy meter. The diode laser beam diameter was kept smaller than the excimer laser beam so that the entire diode laser beam sampled the atomic fluorine number density. KBr windows were used to transmit the 25 μm diode laser beam. A monochromator was used to separate the diode laser modes and reject background IR from the LiF window produced by the excimer laser. Ge(Cu) detectors at 10K were used, and a cold filter was used to remove excess noise due to blackbody radiation. The response time of the detector was about 20 μs , which gave maximum gain. A shorter response time could have been used, as fast as 20 ns, but would have given a lower gain. The signal due to transmitted diode laser reaching the detector was sent to a transient digitizer that was triggered at the excimer laser pulse.

A Ge beamsplitter (50%T) before the photolysis cell was used to direct part of the beam into a fluorine atom absorption cell used to lock the diode laser wavelength onto the absorption line. The long term stability of the diode laser wavelength has been observed

by repetitive scans across the line to be several times larger than the room temperature fluorine atom Doppler linewidth. This drift of the diode laser wavelength would cause the detection of transient fluorine atoms to be extremely difficult. For this reason, the diode laser wavelength is locked onto the fluorine atom absorption line using wavelength modulation at 5 kHz, creating a first-derivative signal. This first-derivative signal is feed into the diode current power supply, causing wavelength stabilization (see figure 2).

Fig. 2. Diagram of the wavelength modulation (diode laser current modulation), feedback stabilization electronics.

Although this technique does keep the diode laser wavelength in resonance, it decreases the apparent absorption cross-section because it requires that the wavelength be modulated across the absorption line rather than sitting at the peak. The wavelength modulation also causes the transient absorption signal to be modulated. However, the excimer laser is triggered randomly relative to the phase of the modulation, so signal averaging will remove modulation of the signal to a large extent.

RESULTS

Two sets of data were obtained using either UF_6 or F_2 as the photolysis precursor. Averaged signals are shown in figures 3 and 4. When using UF_6 , a slower risetime for absorption is observed, and absorption is also seen when the diode laser wavelength is moved off resonance of the atomic fluorine absorption line. The suspected source of the interfering absorption is $(\text{UF}_5)_2$, which is created by collisions after photolysis of UF_6 .

The sensitivity of this technique can be estimated from the data shown in figures 3 and 4. From known photolysis cross sections and excimer laser fluence, including attenuation by absorption and beam divergence, the average fluorine atom density is about 10^{14} cm^{-3} , which corresponds to an absorption of about 0.05 of the diode laser. The observed absorption was about a factor of two less than the expected value. This is probably due to the diode laser wavelength being modulated across the absorption line rather than sitting on the peak. This problem is being addressed in ongoing experiments.

Fig. 3. Averaged transient absorption with 1.5T of UF_6 in and 5T of He in photolysis cell. a) Diode wavelength stabilized, b) 0.016 cm^{-1} resonance.

Fig. 4. Averaged transient absorption with 5T of F_2 photolysis cell. a) Diode wavelength stabilized, b) 0.017 cm^{-1} off off resonance.

Another effect that may be occurring is that photolysis may not form a room temperature population distribution in the $^2\text{F}_{3/2}$ and $^2\text{F}_{1/2}$ states, which affects the absorption cross section. If the fluorine atoms are formed hotter, i.e., more population in the upper state, the cross section would be smaller but would increase as collisional relaxation to the room temperature distribution occurred. The data suggests this is occurring, with more occurring in the F_2 photolysis.

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