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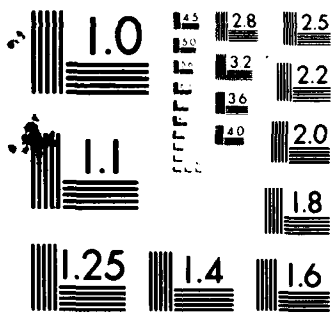
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# MEASUREMENT OF FLUORINE ATOM CONCENTRATIONS AND REACTION RATES IN CHEMICAL LASER SYSTEMS

## ANNUAL TECHNICAL REPORT

by

Alan C. Stanton

Center for Chemical and Environmental Physics
Aerodyne Research, Inc.
Crosby Drive, Bedford Research Park
Bedford, MA 01730

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The line positions of two components of the fluorine-atom ground state fine structure transition have been measured with diode laser absorption spectroscopy, using a water vapor pure rotational line at 404.077 $cm^{-1}$ as a wavelength reference. These results imply a spin orbit splitting for fluorine of 404.142 ± 0.01 $cm^{-1}$. Further experiments planned in the program will provide data on the temperature-dependent line broadening parameters →

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for foreign gas broadening of the F atom transitions. In addition, F atom recombination rates will be studied using the diode laser measurement technique. It is anticipated that the results of this program will provide all data required for implementation of this technique as an in-situ F atom diagnostic in chemical laser systems.

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# 1. RESEARCH OBJECTIVES

The basic objective of this research effort is to investigate and characterize the $^2P_{3/2} \rightarrow ^2P_{1/2}$ magnetic dipole transition of atomic fluorine, using diode laser absorption spectroscopy. All parameters required for the application of this technique to in-situ measurement of atomic fluorine concentrations in chemical lasers are to be measured in the present program. The Statement of Work includes the following tasks:

Task A

Experimentally identify the hyperfine components of the $^2P_{3/2} - ^2P_{1/2}$ absorption transition near 404 $cm^{-1}$ in atomic fluorine, using diode laser absorption spectroscopy.

Task B

Measure the absolute F atom absorption line positions, using a suitable wavelength reference.

Task C

Characterize the room temperature pressure broadening of the strongest atomic fluorine absorption line near 404 $cm^{-1}$.

Task D

Develop reliable diode laser wavelength calibration techniques for use in locating the atomic fluorine absorption lines near 404 $cm^{-1}$.

Task E

Fully calibrate the diode laser fluorine atom absorption measurement technique for a range of temperatures and gas compositions applicable to cw chemical laser flows. These tests shall include measurements of the temperature-dependent F-atom line broadening coefficient for important broadening species.

Task F

Utilize the diode laser F-atom diagnostic to measure F-atom reaction rates of importance in chemical laser systems, using existing flow reactor facilities. Emphasis will be placed on measurement of the rates of F-atom recombination reactions over a temperature range of 300 - 1000 K.

Under previous AFOSR sponsorship (Contract F49620-79-C-0107), the first direct absorption measurement of the $^2P_{3/2} \rightarrow ^2P_{1/2}$ magnetic dipole transition of atomic fluorine was performed at Aerodyne Research, Inc. in November 1979. In these initial experiments, one hyperfine component of the transition was identified, its absorption strength was measured by comparison with a $C\ell_2$ titration measurement of the F-atom concentration, and the wavelength of the transition was measured relative to a pure rotational line of $H_2O$ at 404.077 $cm^{-1}$. The atmospheric-broadened $H_2O$ line (~0.15 $cm^{-1}$ linewidth) was used in these initial experiments. The results of these experiments were presented in a final report for the contract(1) and in a journal publication.(2)

The present work was undertaken in order to measure the detailed spectroscopic parameters which would be required to implement the diode laser technique as a diagnostic for a chemical laser system. In particular, in the original work mentioned above, only one of the three F-atom transitions which would arise from hyperfine splitting was observed, due to tuning limitations of the available diode laser. Task "A" of the present work is directed toward the measurement of all three F-atom lines. Also, use of a pressure broadened line as the wavelength reference in the initial experiments resulted in a relatively imprecise determination of the F-atom wavelengths due to possible pressure shifting of the $H_2O$ line center as well as other factors which contribute to measured intensity variations as a function of wavelength. Tasks "B" and "D" of the present work are intended to improve the wavelength calibration techniques. Tasks "C" and "E" will result in measurement of the temperature-dependent absorption linewidths. These data are required for quantitative interpretation of the F-atom concentration from the measured diode laser absorption. Finally, in Task "F", the diode laser technique will be used as an F-atom monitor in measurement of rates of recombination, such as

$$F + F + M \rightarrow F_2 + M \quad (M = He, Ar) \quad .$$

These rates, although slow, are poorly known, and improved values for the rate constants would be desirable for kinetic modeling of chemical lasers.

# 2. RESEARCH STATUS

## 2.1 Research Results

In work to date under the present contract, two of the three F-atom transitions have been measured and identified, and their wavelengths have been measured relative to the $H_2O$ pure rotational line at 404.077 $cm^{-1}$.* For these measurements, a room temperature flow reactor with F-atoms produced by microwave discharge dissociation of $F_2$ was utilized. A 40-pass White cell was used in order to facilitate measurement of the two relatively weaker F-atom lines. The measurements of the $H_2O$ reference line were made in the same White cell/flow tube system immediately prior to F-atom measurements. All measurements (of either F or $H_2O$) were made in a near-Doppler pressure regime (5 - 10 torr), resulting in sharp absorption features in the spectral scans. The calibration of the laser tuning rate was made using an accidental etalon produced by the White cell mirrors (free spectral range = $1.19 \times 10^{-2} cm^{-1}$).

The experimental results obtained to date in this program are summarized in Table 1. The assignment of the hyperfine designations for the observed transitions is based on the measured relative line strengths of the two lines. (The ratios of the line strengths may be calculated from the degeneracies of the hyperfine levels.[4] The strongest line is the (J=3/2, F=2)→(J=1/2, F=1) line, which is the middle transition in the hyperfine triplet.) The measured separation between the two observed lines, $\Delta\nu$=0.208 $cm^{-1}$, is in exact agreement

*The absolute frequency assigned to this reference line is determined from $H_2O$ energy level assignments obtained from high-resolution Fourier transform flame spectra by Camy-Peyret, et al.[3] The estimated uncertainty in the line position is $\pm$ 5 x $10^{-3} cm^{-1}$.

Table 1 - Results of Fluorine Atom Spectroscopy Experiments

Observed line positions:

$^2P_{3/2}(F=1) \rightarrow {}^2P_{1/2}(F=0)$ $\nu = 403.969 \pm 0.01\ cm^{-1}$

$^2P_{3/2}(F=2) \rightarrow {}^2P_{3/2}(F=1)$ $\nu = 404.177 \pm 0.01\ cm^{-1}$

F-atom spin-orbit splitting:

$$E_o(^2P_{1/2}) - E_o(^2P_{3/2}) = 404.142 \pm 0.01\ cm^{-1}$$

Transition probability:

$$A(^2P_{1/2} \rightarrow {}^2P_{3/2}) = 1.52 \times 10^{-3} s^{-1} \pm 25\%$$

Pressure broadening coefficient (argon), FWHM (T=300 K)

$$\Delta\nu(F=2 \rightarrow F=1) \cong 2.3 \times 10^{-4}\ cm^{-1}/Torr$$

$$(0.175\ cm^{-1}/atm)$$

with results for the $^2P_{3/2}$ and $^2P_{1/2}$ zero field hyperfine splittings which have been obtained in electron paramagnetic resonance experiments.[5,6] Observation of the third magnetic dipole-allowed transition, (J=3/2, F=1)→ (J=1/2, F=1), with an expected location 0.134 $cm^{-1}$ to the blue side of the strong F=2→F=1 line, has so far been prevented by gaps in the tuning range of the diode laser used in these experiments. A new laser has recently been obtained, however, and observation of all three F-atom lines is an immediate goal of the continuing effort.

The other results shown in Table 1 are consistent with previous measurements or calculations regarding the $^2P_{3/2} \rightarrow {}^2P_{1/2}$ transition. The spin-orbit splitting, inferred from the measured line positions and therefore based on the $H_2O$ wavelength reference, is the most precise measurement of the F-atom spin orbit splitting available. This measurement is consistent with the approximate splitting of 404 ± 1 $cm^{-1}$, which had been inferred from measured vacuum UV line positions.[7-9] The measured transition probability is in good agreement with the previously calculated value of $A = 1.18 \times 10^{-3} s^{-1}$.[10] Finally, the preliminary value for the foreign gas broadening coefficient by argon is typical of broadening coefficients for infrared optical transitions. Much of the emphasis in the remainder of the present program will be placed on measurement of the broadening coefficient as a function of temperature and broadening species.

The relative positions of the three F-atom lines and the $H_2O$ reference line are shown schematically in Figure 1. The $H_2O$ line should provide a convenient wavelength calibration line in any implementation of the diode laser technique as an in-situ F-atom diagnostic, as its location relative to the F-atom lines is well within the ~ 0.5 $cm^{-1}$ tuning range of typical diode laser modes. A pressure of ~ 5 torr $H_2O$ has proved to be a suitable value in experiments to date in obtaining strong absorption by a relatively narrow line. (At higher pressures, self-broadening of the $H_2O$ line dominates the lineshape, and no advantage is gained in adding more $H_2O$). The measured linewidth at 1 torr pressure is approximately $3 \times 10^{-3}$ $cm^{-1}$, compared with a

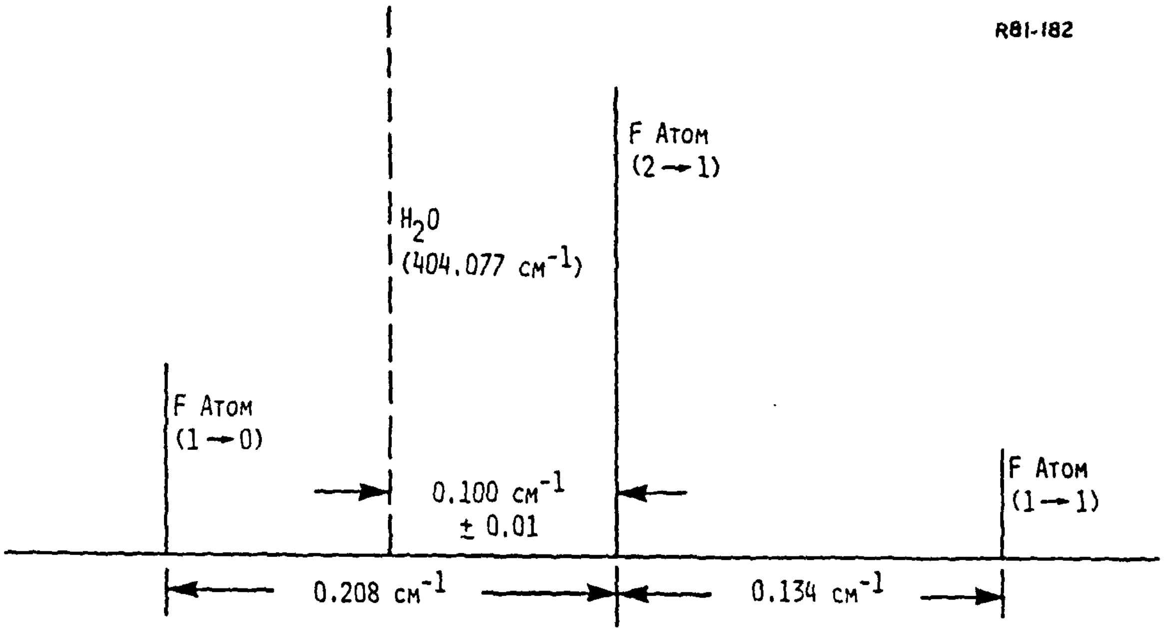


Figure 1. Locations of Fluorine Atom Absorption Lines Relative to $H_2O$ Line at 404.077 cm$^{-1}$. The 1→0 and 2→1 F-atom lines have been observed in diode laser experiments at Aerodyne. The positions of these two lines with respect to the $H_2O$ line were measured by etalon calibration of the diode laser tuning rate.

Doppler width of 1.2 x $10^{-3}$ $cm^{-1}$. At this pressure, the measured line-center absorption coefficient is approximately 4.5 x $10^{-5}$ $cm^{-1}$, compared with an expected value of 5.5 x $10^{-5}$ $cm^{-1}$, based on parameters given in the HITRAN compilation.(11)

## 2.2 Further Experiments

At present, a new optical arrangement is being assembled to permit measurements in the high temperature flow reactor at Aerodyne Research. This facility may be operated at controlled gas temperatures over the range 300 K to 1500 K(12) and will be suitable for the temperature-dependent measurements of line broadening and F-atom recombination rates in this program. F-atom production will again be by microwave discharge dissociation of $F_2$, and the F-atom concentration may be independently measured by the $C\ell_2$ titration technique used in the earlier experiments.

A diagram of the new optical design for use with the high temperature facility is shown in Figure 2. The 40-pass White cell will again be used for measurements of F-atom absorption. Two new elements in the optical layout are a commercial air-spaced etalon (Spectra-Physics) with a free spectral range of 0.015 $cm^{-1}$, and a water vapor absorption cell. This system will permit measurement of the $H_2O$ reference line while the F-atom flow is maintained through the White cell. The etalon will be used to monitor possible nonlinearities in the diode laser tuning rate as a function of laser current. This element is removable from the optical system. The $H_2O$ absorption cell is a three-pass cell (70 cm/pass) and will be in the optical path at all times. The expected line center absorption for the $H_2O$ reference line at 404.077 $cm^{-1}$ is 5%, for 5 torr $H_2O$.

Assembly of this system is currently under way and alignment and calibration of the new diode laser and optics will begin within the current month. The initial emphasis will be on accurately measuring the positions and relative intensities of all three F-atom lines. Following these

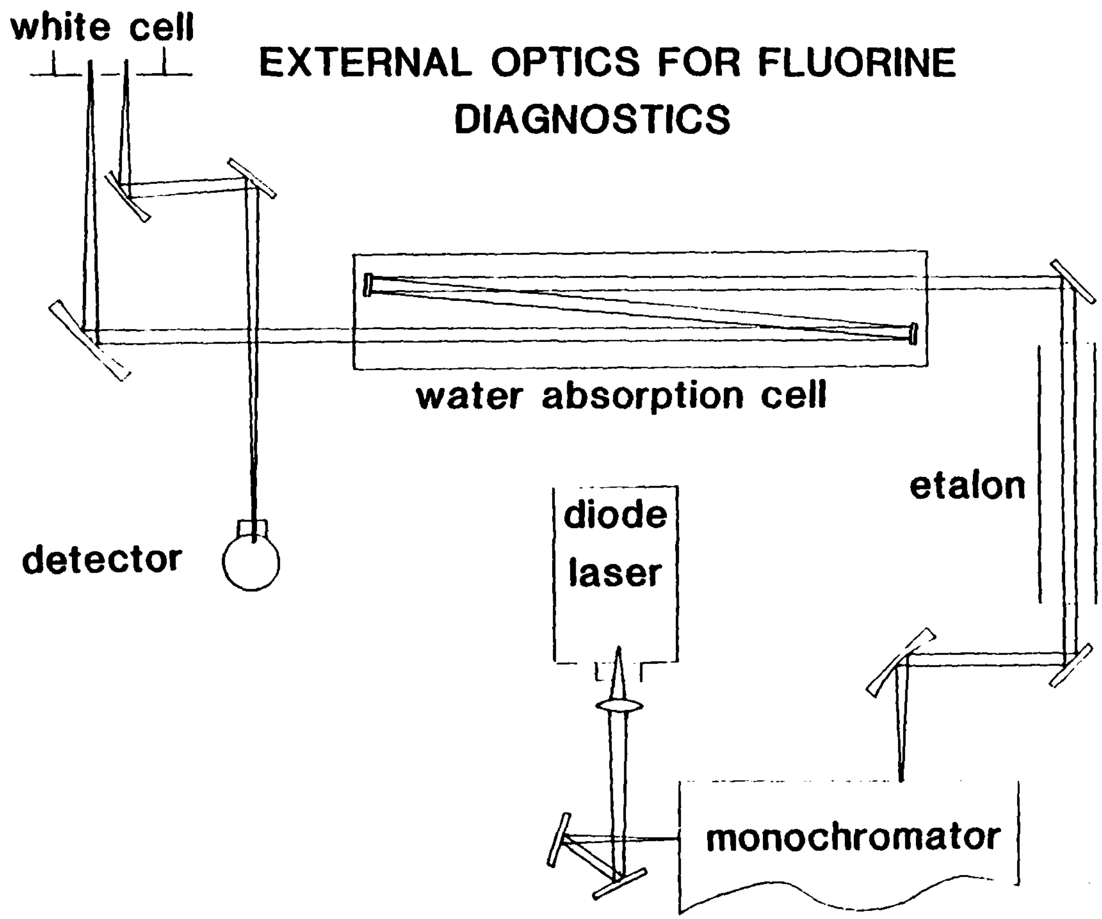


Figure 2. Schematic of Optical Layout for Fluorine Atom Measurements in High Temperature Flow Tube.

measurements, the temperature dependent line broadening measurements will be made, and finally, use of the diode laser technique to measure F-atom recombination rates will be studied.

# 3. PERSONNEL

The Principal Investigator for this work has been Dr. Alan Stanton, who is a Senior Research Scientist in the Applied Sciences Division of Aerodyne Research, Inc. He has been assisted in the laboratory by Mr. Robert Brown, Laboratory Research Associate.

In addition, Dr. Charles Kolb, Director of the Applied Sciences Division, has advised the project on matters related to fluorine atom production techniques. Dr. Morton Camac, Chairman of the Board of Directors of Aerodyne Research, Inc., has consulted on questions of optical design for the program.

# 4. PUBLICATIONS, PRESENTATIONS, AND INTERACTIONS

## 4.1 Publications

The results of the previous contract study, Contract No. F49620-79-C-0107, were published in the Journal of Chemical Physics:

Alan C. Stanton and Charles E. Kolb, "Direct Absorption Measurement of the Spin-Orbit Splitting and $^2P_{1/2}$ Radiative Lifetime in Atomic Fluorine ($2p^5$)," J. Chem. Phys. 72, 6637 (1980).

When detailed measurements of the line positions, relative intensities, and collisional broadening coefficients are completed, the results will be submitted for publication as an article in the Journal of Chemical Physics. Measurements of recombination rates will be reported in a separate article.

## 4.2 Presentations

Results of the work performed under this contract were presented by Dr. Stanton at the 28th Congress of the International Union of Pure and Applied Chemistry, Vancouver, B.C., August 1981.

## 4.3 Interactions

Possible applications of this technique for in-situ measurements in chemical lasers, along with optical design considerations and operational procedures, have been discussed with Captain Ralph Hill of the Chemical Lasers Branch, Air Force Weapons Laboratory. It is anticipated that Captain Hill or other AFWL personnel will interact with the upcoming experimental measurements program at Aerodyne.

# 5. DISCOVERIES AND APPLICATIONS

The measurements performed thus far under this program are the first direct observations of the fine structure transitions in atomic fluorine and provide the most accurate measurement of the line positions and F-atom spin orbit splitting available. It is anticipated that the techniques developed under this contract will be applicable to development of a fluorine atom diagnostic for in-situ F-atom concentration measurements in high power chemical lasers.

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