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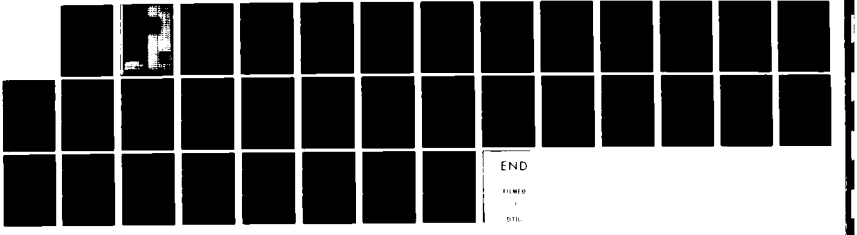

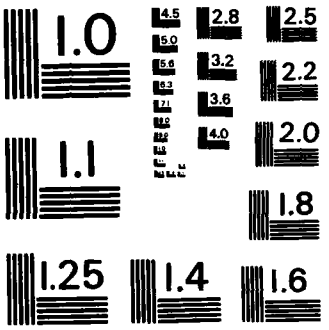

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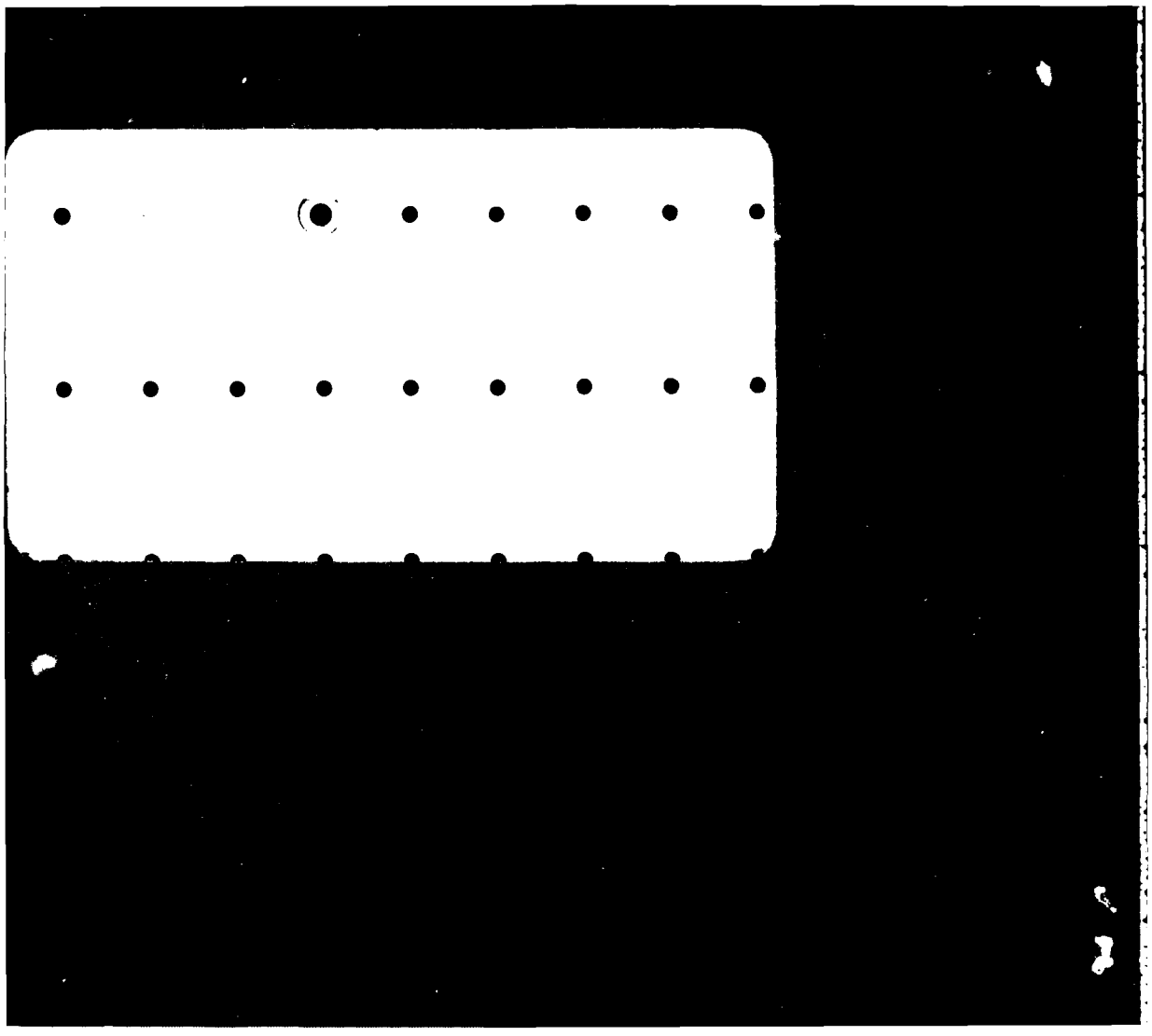

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MEASUREMENT OF FLUORINE ATOM CONCENTRATIONS AND REACTION RATES IN CHEMICAL LASER SYSTEMS

Final Technical Report

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The line positions of all three components of the fluorine atom ground state fine structure transition have been measured by 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 $\pm$ 0.005 cm^{-1}. The results for the line positions are in excellent agreement with independent, concurrent measurements performed at the Los Alamos

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National Laboratory, using vibration-rotation lines of CS_2 as the wavelength references. The line separations observed in both sets of experiments agree with the F atom zero-field hyperfine splittings obtained from electron paramagnetic resonance studies.

Collisional broadening of the strongest fluorine atom transition (the 1 ← 2 hyperfine component) was measured in this study for helium (T = 300 K to 800 K), argon (T = 300 K) and nitrogen (T = 300 K) perturbers. The measured room temperature broadening coefficients (FWHM) are 0.062 cm^{-1}/amagat (He), 0.067 cm^{-1}/amagat (Ar), and 0.11 cm^{-1}/amagat (N_2). The line width data for broadening by helium are fit by a temperature dependence of $T^{0.47}$.

The experimental results for fluorine atom line widths are compared with predictions from the classical Lindholm-Foley theory, using available ab initio and experimentally-derived fluorine atom-rare gas interaction potentials, as well as semiempirical Lennard-Jones potentials. Good agreement is obtained for broadening by argon and for the temperature dependence of broadening by helium.

The results of this study show that adequate sensitivity and time response for measurement of F atom concentrations in cw chemical lasers may be obtained using the diode laser absorption technique as a diagnostic. All spectroscopic parameters which are required to implement such a diagnostic have been obtained in this work.

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1. RESEARCH OBJECTIVES

The basic objective of this research effort has been to investigate and characterize the $^2P_{1/2} \leftrightarrow {}^2P_{3/2}$ magnetic dipole transition of atomic fluorine, using diode laser absorption spectroscopy. The emphasis of the program has been the measurement of all spectroscopic parameters which are required to implement the diode laser absorption technique as a quantitative diagnostic of F atom concentrations in HF/DF chemical lasers. The Statement of Work included the following tasks:

Task A

Experimentally identify the hyperfine components of the $^2P_{1/2} \leftarrow {}^2P_{3/2}$ 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 at Aerodyne.

Under previous AFOSR sponsorship (Contract F49620-79-C-0107), the first direct absorption measurement of the $^2P_{1/2} \leftarrow {}^2P_{3/2}$ 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 ($\sim$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. By completion of Tasks A, B, and D of the present contract, all three hyperfine components have been identified and their line positions have been accurately determined. In addition, through completion of Tasks C and E, experimental results for the F atom collisional line broadening cross sections for several perturbing species have been

obtained. These results have been compared with calculated F atom line widths, using the available calculated and experimentally derived fluorine - rare gas interaction potentials. In Task F, work in the present program has established that the diode laser absorption technique may be used as a sensitive monitor of F atom concentrations, in a flow reactor environment, over a temperature range of 300 K to $T \geq 1000$ K. Although specific F atom reactions have not been studied to date with this technique, it is anticipated that additional work at Aerodyne with this measurement system will include fluorine atom reaction kinetics.

2. RESEARCH RESULTS

2.1 Summary of Spectroscopic Results

In the work performed under this contract, the three hyperfine components of the $^2P_{1/2} \leftarrow {}^2P_{3/2}$ fluorine atom transition were identified, and the positions of these three lines were measured relative to the H_2O pure rotational line at 404.077 cm^{-1}. (The position of this reference line is believed accurate to within ±0.005 cm^{-1}.[3]) For these measurements, a high 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) to determine line positions were made in a near-Doppler pressure regime (5 to 10 Torr), resulting in sharp absorption features in the spectral scans. The calibration of the laser tuning rate was made using an air-spaced etalon (Laser Analytics) with a free spectral range of 0.015 cm^{-1}. Further details of the experimental technique are discussed in Subsection 2.4. X-Y recorder traces of diode laser current scans across the fluorine atom lines and the H_2O reference line are shown in Fig. 1. The upper trace in the figure is a scan over the three F atom lines (refer to Fig. 2 for identification of the F-atom transitions). The middle trace is a scan over the H_2O reference line, while the bottom trace is the air spaced etalon transmission. The diode laser current (x-axis of the figure) is correlated for the three traces.

The experimental results obtained in this program for the F atom line positions, line strength (transition probability), and pressure broadening coefficients are presented in Table 1. Concurrently with the present contract effort, results for the F atom line positions were also obtained in a similar measurements effort at the Los Alamos National Laboratory by Laguna and Beattie[4]. In these experiments, vibration-rotation lines in the ν_2 band of

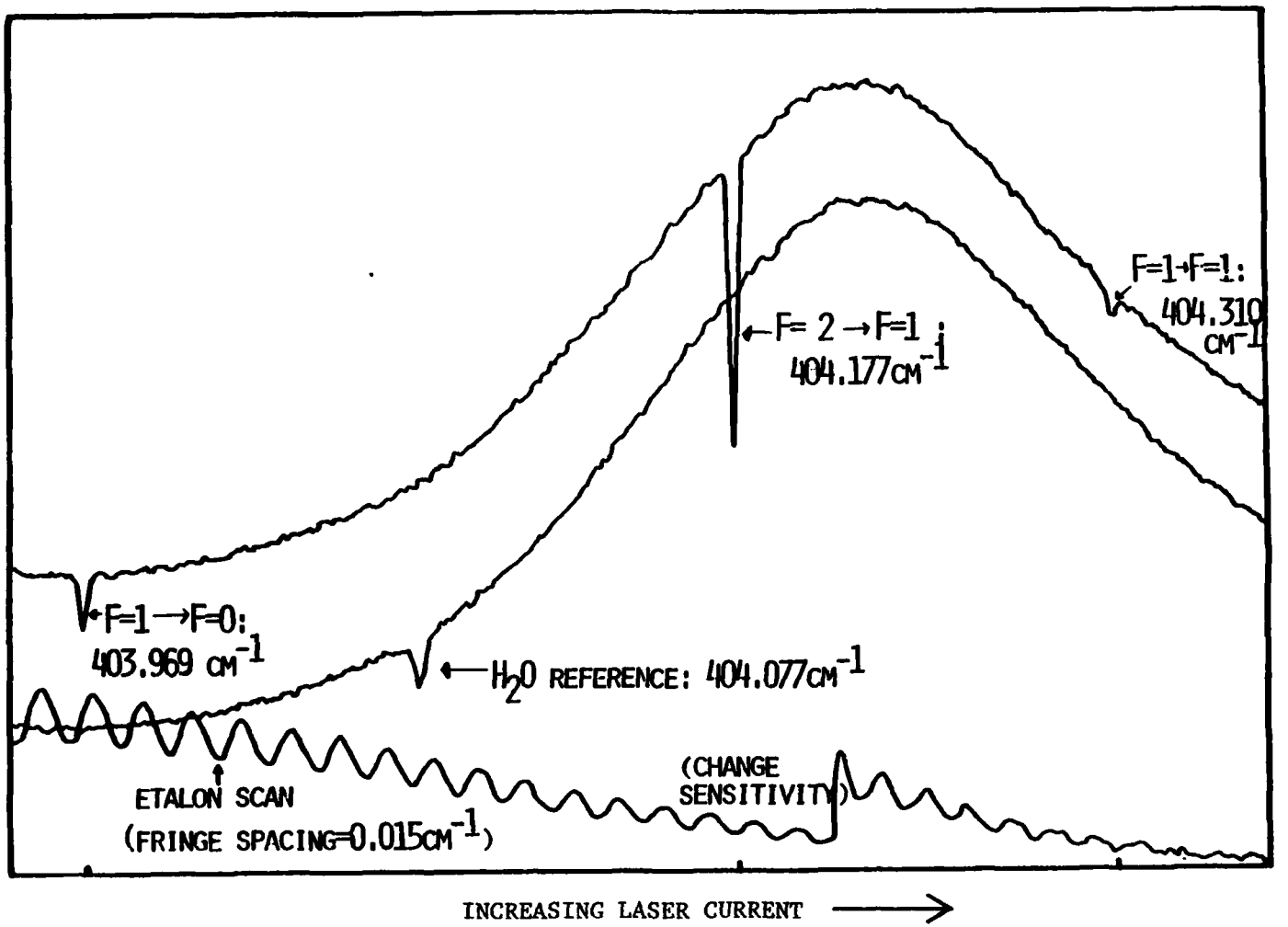

Figure 1. Diode Laser Current Scans: Upper Scan - Hyperfine Components of Fluorine Atom Transition, Middle Scan - H_2O Reference Absorption Line, Lower Scan - Air Spaced Etalon.

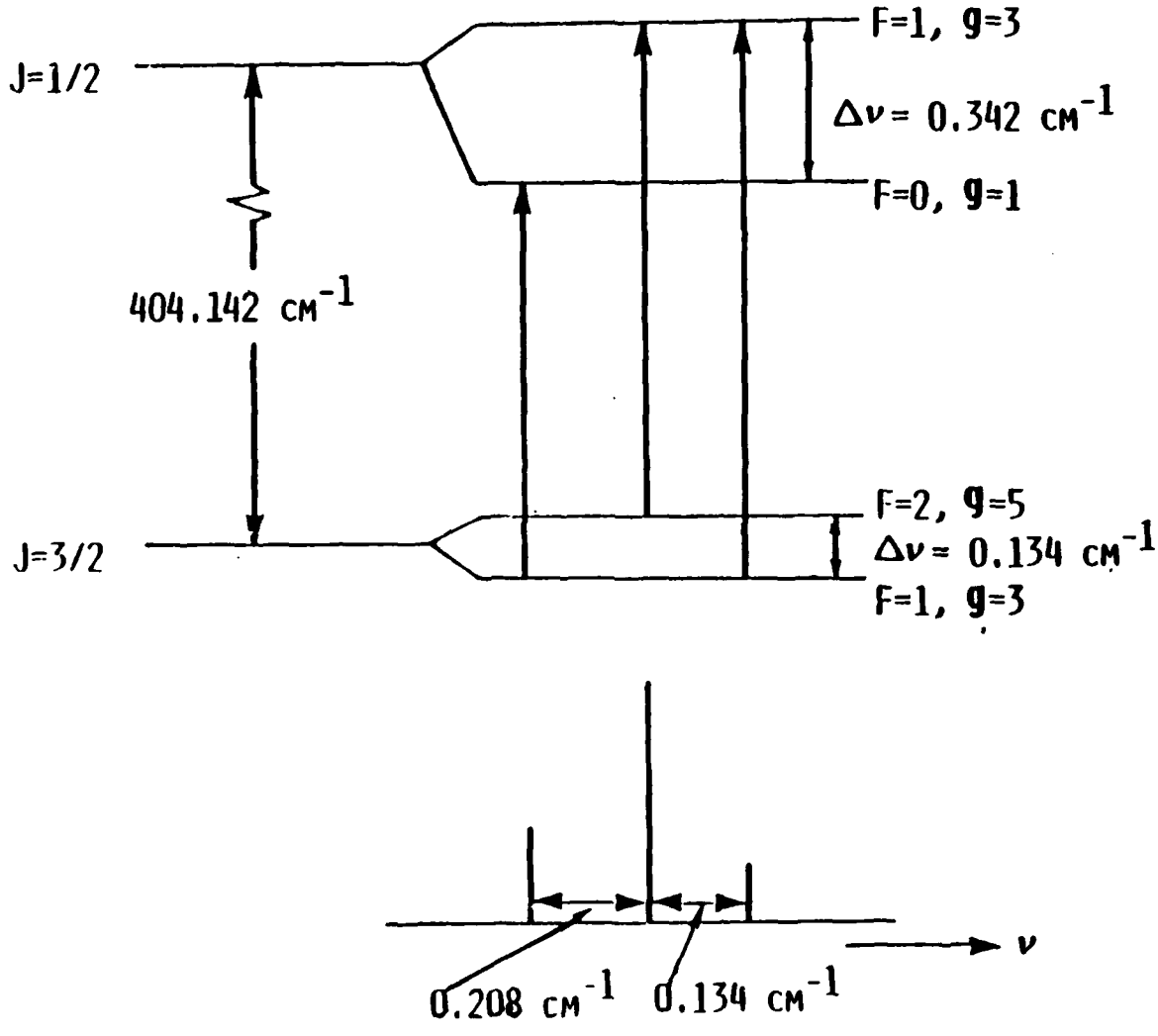

Figure 2. Energy Level Diagram Showing the Fluorine Atom $^2P_{1/2} \leftrightarrow {}^2P_{3/2}$ Transition, with Hyperfine Splitting.

Table 1 - Summary of Experimental Results

A. Line Positions

Transition	Line Center Frequency (cm^{-1}) Present Study	Ref.4
F = 0 ← F = 1	403.969	403.969
F = 1 ← F = 2	404.177	404.175
F = 1 ← F = 1	404.310	404.310

B. Transition Probability

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

C. Collisional Broadening Coefficients

Perturbing Gas	$\Delta\nu$ (FWHM, cm^{-1}/amagat) T = 300 K	575 K	800 K
He	0.062	0.083	0.098
Ar	0.067		
N_2	0.110		

CS_2 were used for wavelength references. As can be seen from Table 1, agreement between the two sets of values for the line positions is excellent, and the line positions can be considered to be well established, within an accuracy of at least ± 0.005 cm^{-1}. The line spacings are also in excellent agreement with the 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]

The result for the transition probability was obtained by measurement of the diode laser absorption by a known concentration of fluorine atoms, as determined by chemical titration with $C\ell_2$.[2] This experimental result is in good agreement with the previously calculated value of $A = 1.18 \times 10^{-3}$ s^{-1}.[7]

As discussed in detail in Subsection 2.4, the measured results for F atom collisional line widths are in good agreement with calculations based on classical impact theory, utilizing available experimentally derived interatomic potentials.

2.2 Comments on a Wavelength Reference for Diagnostic Applications

The relative positions of the three F atom lines and the H_2O reference line are shown schematically in Figure 3. The H_2O line may provide a convenient wavelength calibration line in many applications 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 line shape.) The measured line width at 1 Torr pressure is approximately 3×10^{-3} cm^{-1}, compared with a Doppler width of 1.2×10^{-3} cm^{-1}. At this pressure, the measured line-center absorption coefficient is approximately 4.5×10^{-5} cm^{-1}.

In some diagnostic applications where little time is available for acquisition of the F atom absorption signal (for example in a pulsed system or

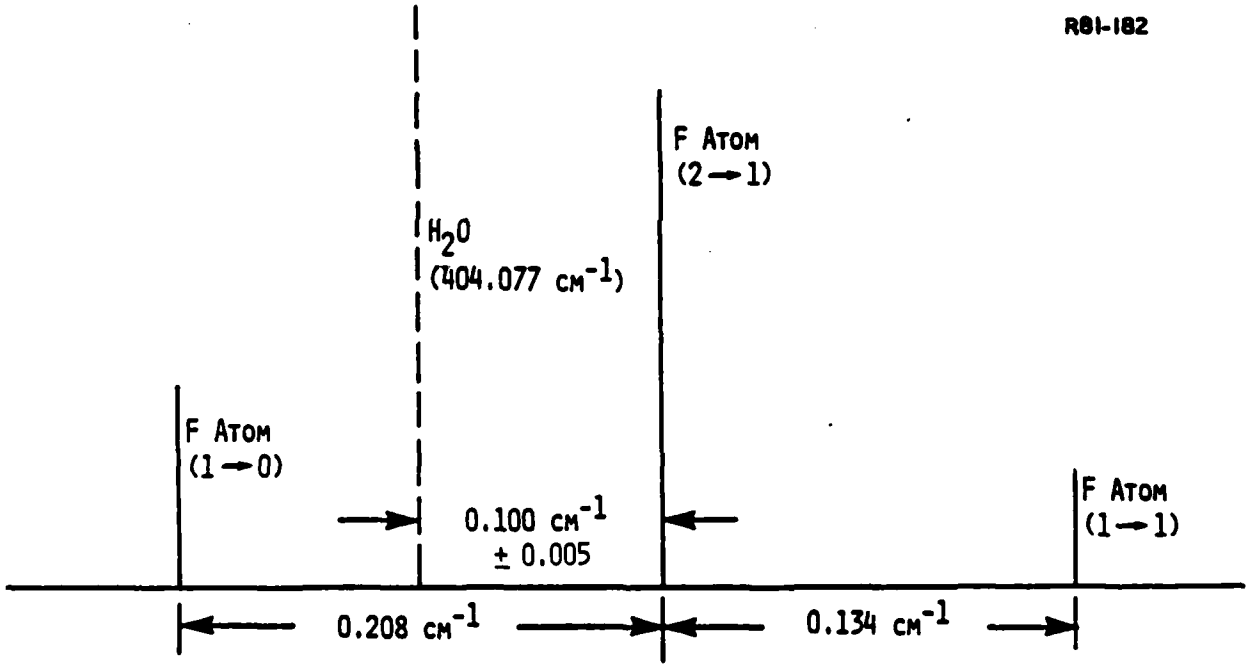

Figure 3. Locations of Fluorine Atom Absorption Lines Relative to H_2O Line at 404.077 cm^{-1}.

short-duration cw experiments), a more suitable wavelength reference could be obtained by constructing a flowing F atom cell using a microwave discharge source, in a design similar to the sources used in the present experimental program. Such a system could be used in a two-beam optical system to lock the laser wavelength to line center of the F atom line, if desired.

2.3 References

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2.4 Collisional Line Broadening Results

The results for collisional broadening of the $^2P_{1/2}$ (F=1) $\leftarrow$ $^2P_{3/2}$ (F=2), F atom absorption line by He (300 K to 800 K), Ar (300 K), and N_2 (300 K) which were obtained in this study are described in the following paper, which was prepared for the 6th International Conference on Spectral Line Shapes, Boulder, Colorado, July 12-16, 1982.

COLLISIONAL BROADENING OF THE ATOMIC FLUORINE $^2P_{1/2} \leftrightarrow {}^2P_{3/2}$ SPIN ORBIT TRANSITION

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Introduction

Direct absorption or emission measurements of the ground state spin-orbit transitions in the halogen atoms ($^2P_{1/2} \rightarrow {}^2P_{3/2}$ magnetic dipole transitions) have been reported for iodine (1), bromine (2), chlorine (3), and fluorine (4, 5). In the case of atomic fluorine, tunable diode laser absorption measurements have established accurate values for the spin-orbit splitting (reported as 404.141 cm^{-1} by Laguna and Beattie (5), and as 404.142 cm^{-1} in work associated with the present study (6)) and positions of the three hyperfine components of the transition (5, 6). A value of 660 s ±25% has been measured for the radiative lifetime of the $^2P_{1/2}$ level (4).

Studies of collisional line broadening of the atomic fluorine spin-orbit transition are of interest because of the availability of interatomic interaction potentials for both the $^2P_{3/2}$ and $^2P_{1/2}$ F atom levels with the rare gases (Ne, Ar, Kr, Xe). Ab initio potentials for these interactions have been calculated by Dunning and Hay (7), and Lee et al. (8, 9) have derived potentials for the fluorine-rare gas interactions from molecular beam scattering experiments. The availability of these potentials offers the opportunity for comparison of measured collisional line broadening with calculated collisional broadening utilizing classical impact approximation theories.

As a more practical matter, measurement of absorption by the hyperfine components of this transition in fluorine has been proposed as a diagnostic technique for F atom concentration measurements in HF/DF chemical laser systems (4, 10). In order to accurately determine fluorine atom

concentrations from measured line center absorption in such systems, a knowledge of collisional line broadening by several perturbers (rare gases, N_2, and HF) over the relevant temperature range in the laser systems (200 to 800 K) is required.

In the present study, tunable diode laser absorption measurements of collisional line broadening of the $^2P_{1/2}$ (F=1) ← $^2P_{3/2}$ (F=2) hyperfine component of the fluorine atom spin-orbit transition centered at 404.177 cm^{-1} have been carried out for He (T = 300 to 800 K), Ar (T = 300 K), and N_2 (T = 300 K) perturbers. The experimental results are compared with line widths calculated from the classical Lindholm-Foley theory (11), utilizing the available ab initio and experimentally derived interatomic potentials, as well as Lennard-Jones potentials where the C_{12} coefficient is obtained from a semi-empirical correlation.

Experimental Approach

The technique of diode laser absorption measurements of the 404 cm^{-1} fluorine atom transitions has been discussed previously (4, 5). In the present experiments, fluorine atoms are produced by microwave discharge dissociation of F_2 (10 to 20% F_2 concentrations in He or Ar buffer gas). For the flow rates utilized in these experiments, approximately 75% fractional dissociation of the F_2 is achieved, as demonstrated by titration with $C\ell_2$. The flow downstream of the microwave discharge is introduced into a high temperature flow reactor, as indicated in the diagram in Figure 1. The flow reactor may be operated at temperatures between 300 and 1500 K. The features and design of this reactor are described in detail in Reference 12.

The perturbing gases are added to the main flow of the reactor,which for these experiments was operated in the pressure range of 0.5 to 25 Torr with F atom partial pressure of approximately 0.01 Torr. Flow rates of F_2, He, or Ar buffer gases and the perturbing gases were measured with Tylan mass flow meters with digital readout. For measurements with N_2, the ratio of N_2 to He discharge buffer gas partial pressures was maintained at 10 to 1 or greater.

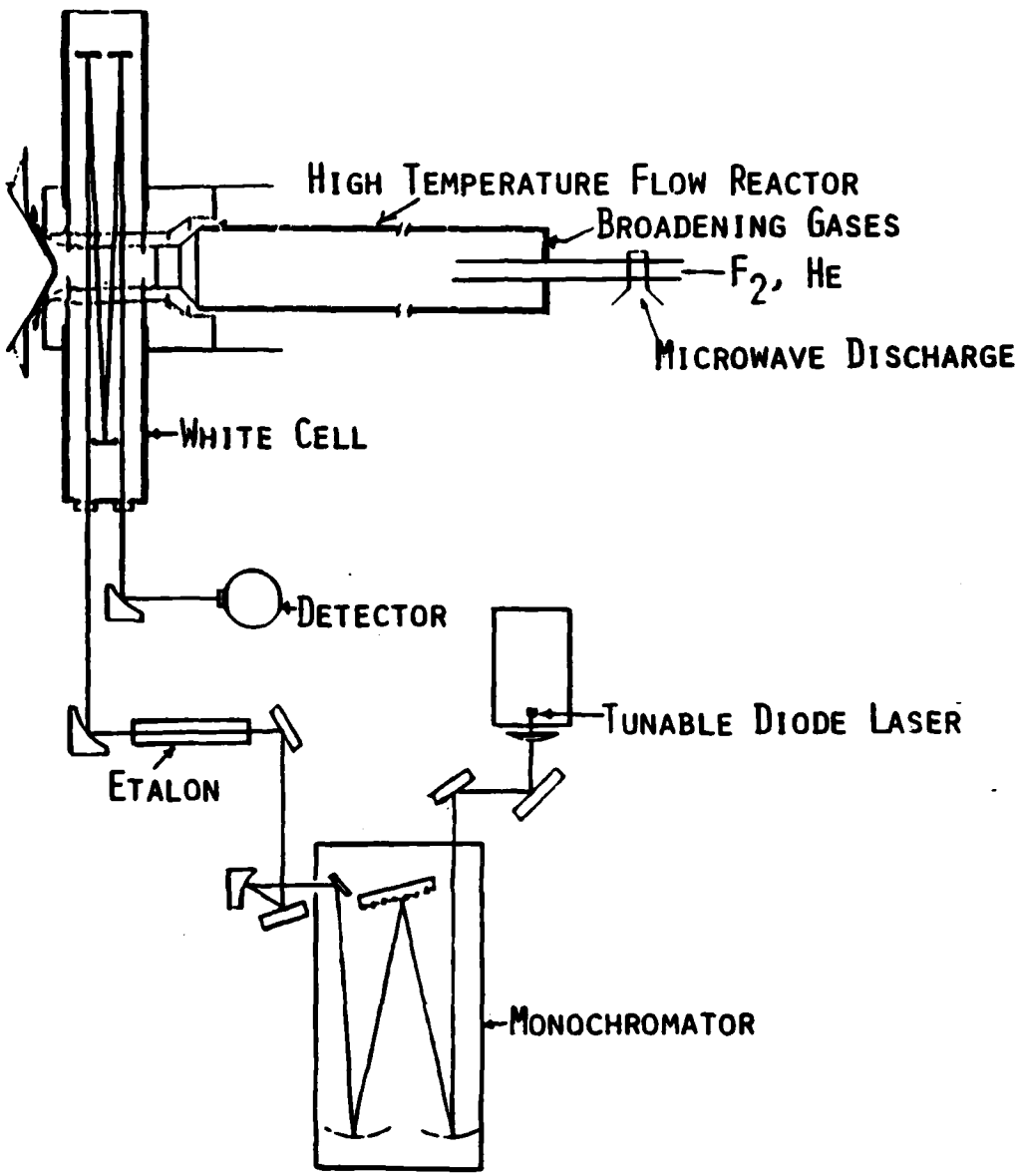

Figure 1. Schematic of Experimental Arrangement for Measurement of F Atom Collisional Line Broadening

For the He and Ar measurements, the discharge buffer gas was chosen to be the same as the perturbing gas introduced downstream. The flow tube pressure was measured with a capacitance manometer (MKS Industries). The temperature of the flow tube gases was determined from the temperature controller readings which had previously been calibrated against shielded thermocouple measurements in the flow (12).

The optical arrangement for the tunable diode laser measurements of the absorption line profiles is also shown in Figure 1. A single longitudinal mode from the multimode diode laser output is selected using a grating monochromator. The radiation in this mode is collimated with an off-axis paraboloidal mirror after exiting the monochromator. This collimated radiation is then passed through an air-spaced Fabry-Perot etalon with a free spectral range of 0.015 cm^{-1} (the etalon is removable from the beam). The collimated radiation is then refocused with a second off-axis paraboloid into a multiple pass White cell which constitutes the analysis region of the flow reactor. The radiation emerging from the White cell is focused onto a liquid helium-cooled Ge:Cu photoconductive detector. The laser emission is mechanically chopped, and the synchronously detected signal is displayed on an X-Y recorder. For these experiments, the White cell mirrors were adjusted for forty passes through the F atom flow, which is aerodynamically confined to the central region of the cell (approximately 4 cm absorption path length per pass). For these conditions, the line center absorption was typically in the range of 10 to 50%.

The measurements of the absorption line profiles were made by ramping the diode laser current to scan in wavelength across the line. For each measurement condition, the laser was scanned six times repetitively across the absorption line. The experimental line width (full width at half maximum) was taken as the average of the six scans. The calibration for the diode laser wavelength tuning rate was obtained from the current scans with the air-spaced etalon in the optical path. Also, interferences between consecutive passes in the White cell produced small-amplitude Fabry-Perot fringes in the laser

scans, with a spacing between fringes of 5.81×10^{-3} cm^{-1}. These fringes provided a convenient wavelength scale on the X-Y recorder which could be directly compared with the line profile scans.

Collisional contributions to the experimental line widths were analyzed by assuming a Voigt profile. The measured line width (FWHM) for the pressure and temperature range of the experiments ranged from approximately 1.5×10^{-3} cm^{-1} to 4.0×10^{-3} cm^{-1}. (The room temperature Doppler width is 1.15×10^{-3} cm^{-1}). The collisional component of the total line width was obtained from the Voigt profile analyses of Olivero and Longbothum (13), with a small correction for a finite instrumental line width ($\simeq 2 \times 10^{-4}$ cm^{-1}).

Experimental Results

Room temperature F atom collisional widths (FWHM) for argon and nitrogen broadening are plotted in Figure 2. The error bars shown represent two standard deviations for the six scans at each condition. The line broadening coefficients, taken as the slopes of linear least squares fits to the pressure-dependent data, are given in Table 1, for Ar, N_2, and He. The estimated uncertainty in these values is ±30%. The room temperature results for argon and helium are essentially equal, within the uncertainty of the experiments. The major uncertainty arises from small drifts in the correlation of wavelength with current, which are probably due to temperature instabilities in the laser.

Measurements of F atom collisional broadening by helium were also made at higher temperatures (T = 575 and 800 K). Limited data were also obtained at 1000 K for low helium pressures, however these data were not sufficient to derive a broadening coefficient at 1000 K. The 300, 575, and 800 K broadening coefficients are plotted in Figure 3. These data are fit by a temperature dependence of $\Delta\nu \propto T^{0.47}$.

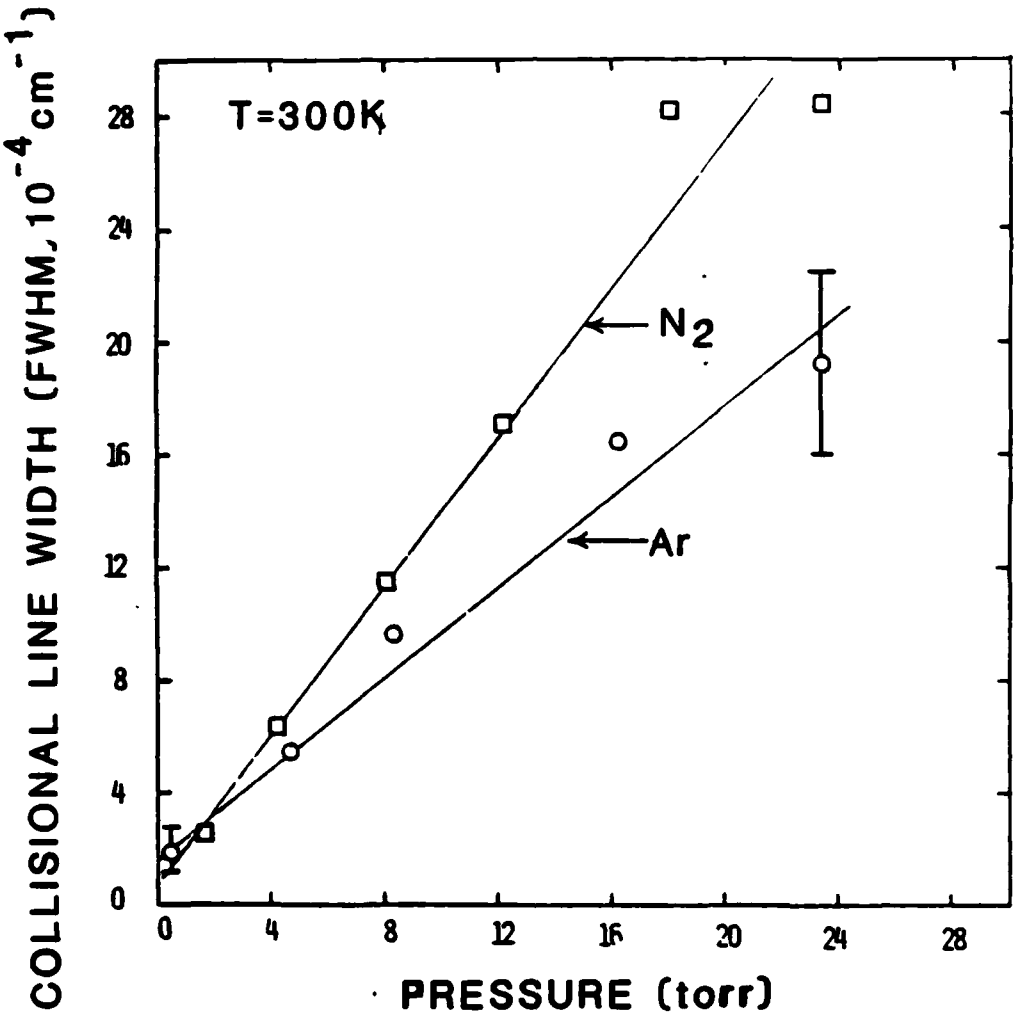

Figure 2. Measured F Atom Collisional Line Widths As a Function of Perturbing Gas Partial Pressure (T = 300K)

Table 1 - Measured Room Temperature Collisional Broadening Coefficients for the F Atom $^2P_{1/2}$ (F=1) + $^2P_{3/2}$ (F=2) Transition

Perturbing Gas	$\Delta\nu$ (cm^{-1})/amagat)
He	0.062
Ar	0.067
N_2	0.11

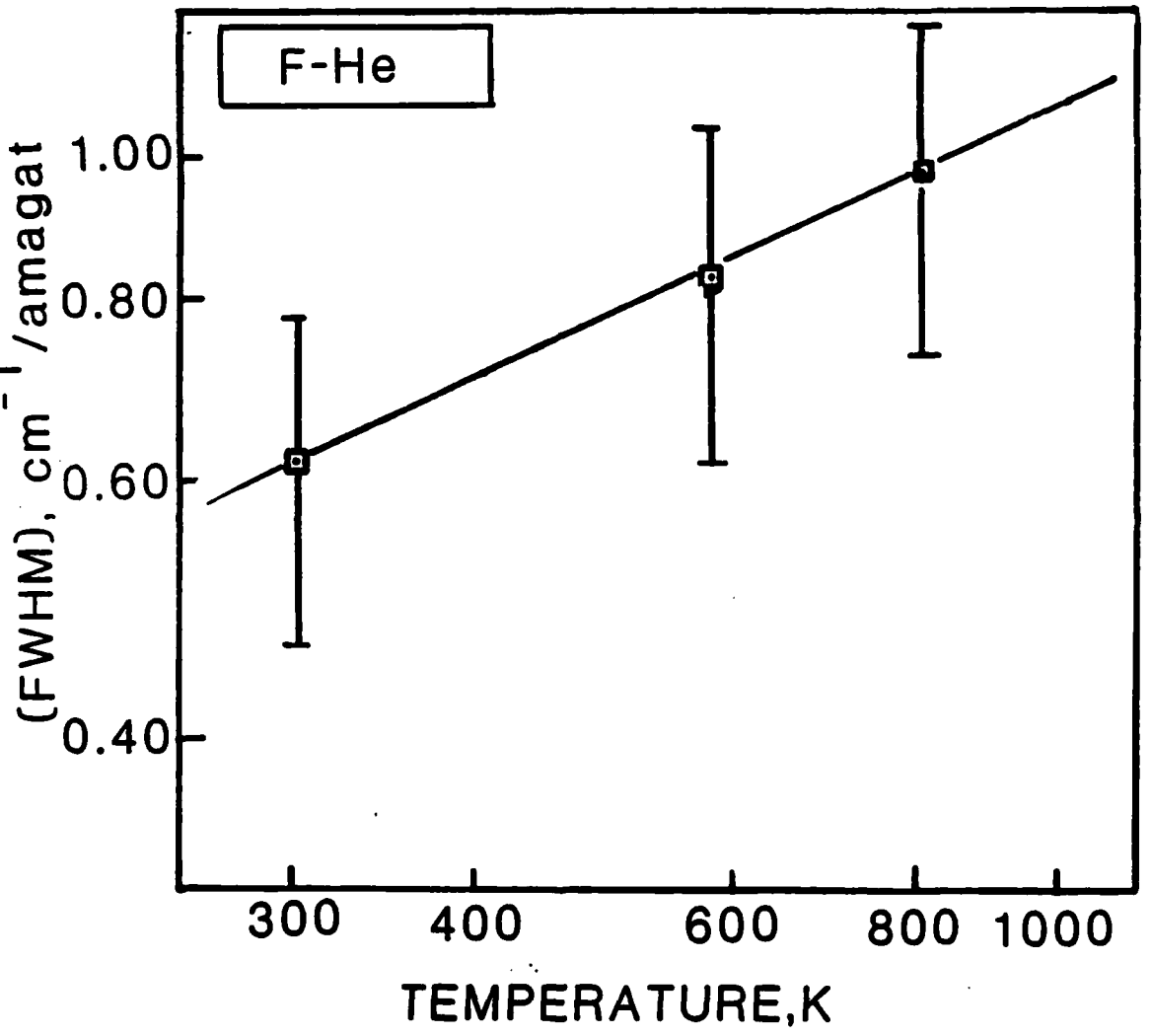

Figure 3. F Atom Collisional Line Broadening by Helium As a Function of Temperature

Comparison of Measurements to Predictions

To calculate linewidths, we used the classical phase shift theory of line broadening (11). For the Lennard-Jones (12,6) potential, the phase-shift integrals have been tabulated (12). To evaluate the theory for potentials of arbitrary form, we first numerically integrated the difference potential along a straight line trajectory to determine the phase shift. (This could just as easily be done along a curved path determined by the interatomic potential.) Then we averaged over impact parameters using a one-dimensional Monte Carlo integration. (This could also be extended to two dimensions, including the average over relative velocities, but here the average velocity was used in the expression for the straight line path.)

For the fluorine-argon system, we had the opportunity to compare predictions based on three models of the difference potential, a semiempirical one using correlations which could be applied to any system, an ab initio calculation of the potential curves (7), and one using information derived from molecular beam scattering (8, 9). These curves are shown in Figure 4 for the levels involved in one absorption line. It can be seen that the interaction with the perturbing atom splits the lower $^2P_{3/2}$ level of the radiative transition into two states, giving rise to two difference potentials, the $^2\Sigma_{1/2}$ and $^2\Pi_{3/2}$ states. At small interatomic distances, one state joins with that from the $^2P_{1/2}$ level (the $^2\Pi_{1/2}$ state) to become a π molecular state. In the semiempirical case, we estimated parameters for only one difference potential, and in the other cases we added lineshapes for two equally probable transitions to produce an effective width. Since these two transitions are shifted differently, and also by different amounts for each potential model, this introduces an additional uncertainty into this effective width for the observed line. Shifts are particularly sensitive to the details of the potential; however, those calculated here are small enough that the effective linewidth is less than 2% larger than a simple average.

All three potential models used have the same long range C_6/r^6 dispersion form. In Reference 8, the change in C_6 between the two states formed from the

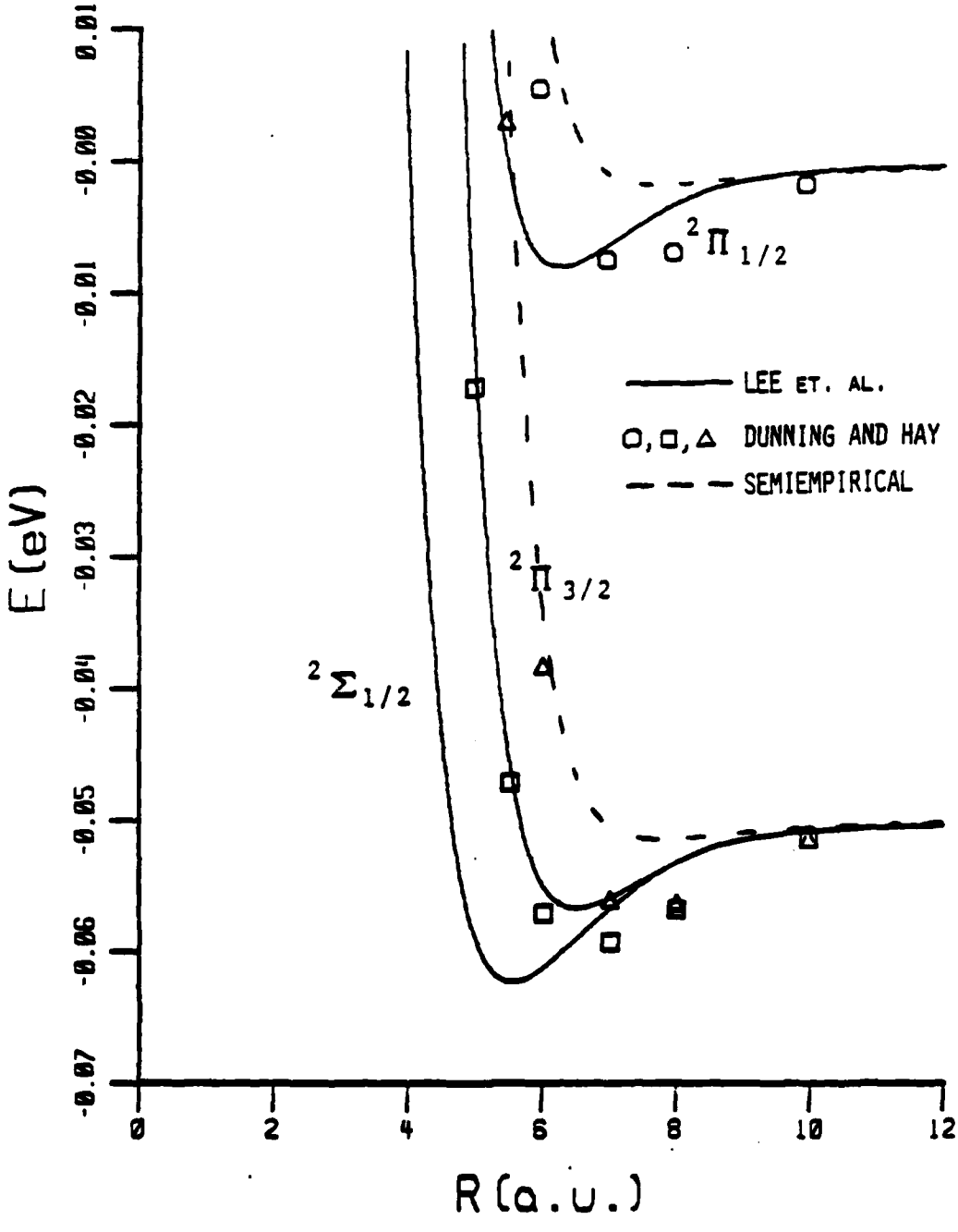

Figure 4. F-Ar Interatomic Potentials Used in Line Broadening Predictions

$^2P_{3/2}$ level was estimated from the change in calculated polarizability from Σ to π orientations. By diagonalizing a Hamiltonian written in terms of the Σ and Π potentials and the spin-orbit splitting 2Δ, one can obtain expressions for all three potentials (15, 16), for the $^2\Pi_{3/2}$ state,

$$V = V_\Pi - \Delta \tag{1}$$

and

$$V = \frac{1}{2}\left\{V_\Sigma + V_\Pi - \Delta \pm \left[(V_\Sigma - V_\Pi)^2 + \Delta^2 - \frac{2}{3}\Delta\,(V_\Sigma - V_\Pi)\right]^{1/2}\right\} \tag{2}$$

where the upper sign refers to the $^2\Pi_{1/2}$ state and the lower to the ground $^2\Sigma_{1/2}$ state. When $(V_\Sigma - V_\Pi)/\Delta \ll 1$, which applies at large interatomic distances, Eq. (2) reduces to:

$$V\,(^2\Pi_{1/2}) = 1/3\ V_\Sigma + 2/3\ V_\Pi + \Delta \tag{3}$$

and

$$V\,(^2\Sigma_{1/2}) = 2/3\ V_\Sigma + 1/3\ V_\Pi - \Delta \tag{4}$$

or

$$V\,(^2\Pi_{1/2}) - V\,(^2\Pi_{3/2}) = -\left[V\,(^2\Pi_{1/2}) - V\,(^2\Sigma_{1/2})\right] = 1/3\,(V_\Sigma - V_\Pi) \tag{5}$$

Thus the changes in C_6 for the two transitions are equal (and of opposite sign, but only the absolute magnitude appears in the expression for the

width), and are taken as half the change between $^2\Sigma_{1/2}$ and $^2\Pi_{3/2}$ states reported in Reference 8.

To compare this ΔC_6 with one obtained using information of the sort which might be available for less studied systems, we note that use of the 0.025 fractional change in polarizability or C_6 fit by Padrick and Palmer (1) to their linewidth data for the same transition in iodine, together with an asymmetrized Hartree calculation for the ground state F atom polarizability (17) and the London correlation (18) for C_6 in terms of polarizabilities α and ionization potentials I,

$$C_6 = 3/2 \frac{I_F I_{Ar}}{I_F + I_{Ar}} \alpha_F \alpha_{Ar} \qquad (6)$$

results in the same 7 $Å^6$ kcal/mole ΔC_6 for F-Ar as in Reference 8.

The repulsive part of the potential (and therefore the depth and position of the attractive well) was modeled in the three different ways mentioned above. To complete the semiempirical potential, we choose a pair of C_{12}'s using the Hindmarsh, et al. correlation (14),

$$C_{12} = 0.9 \times 10^{-16} \text{ erg } (R_F + R_{Ar})^{12}$$

where the R values for the rare gases were those chosen in Reference 14 and a ground state fluorine R of 2.4 Å was assigned using similar orbital size considerations. The fractional change in R of 0.10 fit to iodine width and shift data in Reference 1 was used to generate a ΔC_{12}.

In the other two models, the three ab initio curves of Dunning and Hay (7) (continued by the same C_6/r^6 outside 5 Å) and the Morse-Morse-switching function-Van der Waals functions fit to the scattering data (8) were used directly in the line broadening integrals. Since the scattering work only

determined two curves, the $^2\Sigma_{1/2}$ and $^2\Sigma_{3/2}$ states, the third curve was obtained using Eqs. (1) and (2).

Table 2 presents calculated linewidths for the F-Ar system from the three potential models, together with the experimentally observed linewidth. The trend to smaller linewidths with increasing accuracy of the potential is mirrored in the smaller interatomic distances at which the change in repulsive potentials becomes large, as seen in the plot of difference potentials in Figure 5.

Table 2 - Comparison of Measured and Calculated Broadening Coefficients

Calculations: Lindholm-Foley Classical Theory With:
(1) Experimental potentials
(2) Ab initio potentials
(3) Hindmarsh semiempirical correlations for C_{12} coefficient

Ar-F, T = 300 K:

	Potential Energy Curves			
	Exp	(1)	(2)	(3)
Broadening Coefficient (cm^{-1}/amagat)	0.067 ±0.02	0.076	0.[illegible]	0.[illegible]

All three models can be used for Ne, Ar, Kr, and Xe perturbers, but for helium only the semiempirical Lennard-Jones model was available to compare with the temperature dependent observations. The temperature exponent obtained is 0.41, similar to that observed. Both are significantly larger than the 0.3 expected for a pure $1/r^6$ interaction, showing the influence of the repulsive potential.

Summary

In summary, the results of the measurements reported here provide accurate information on line broadening cross sections and their dependence on

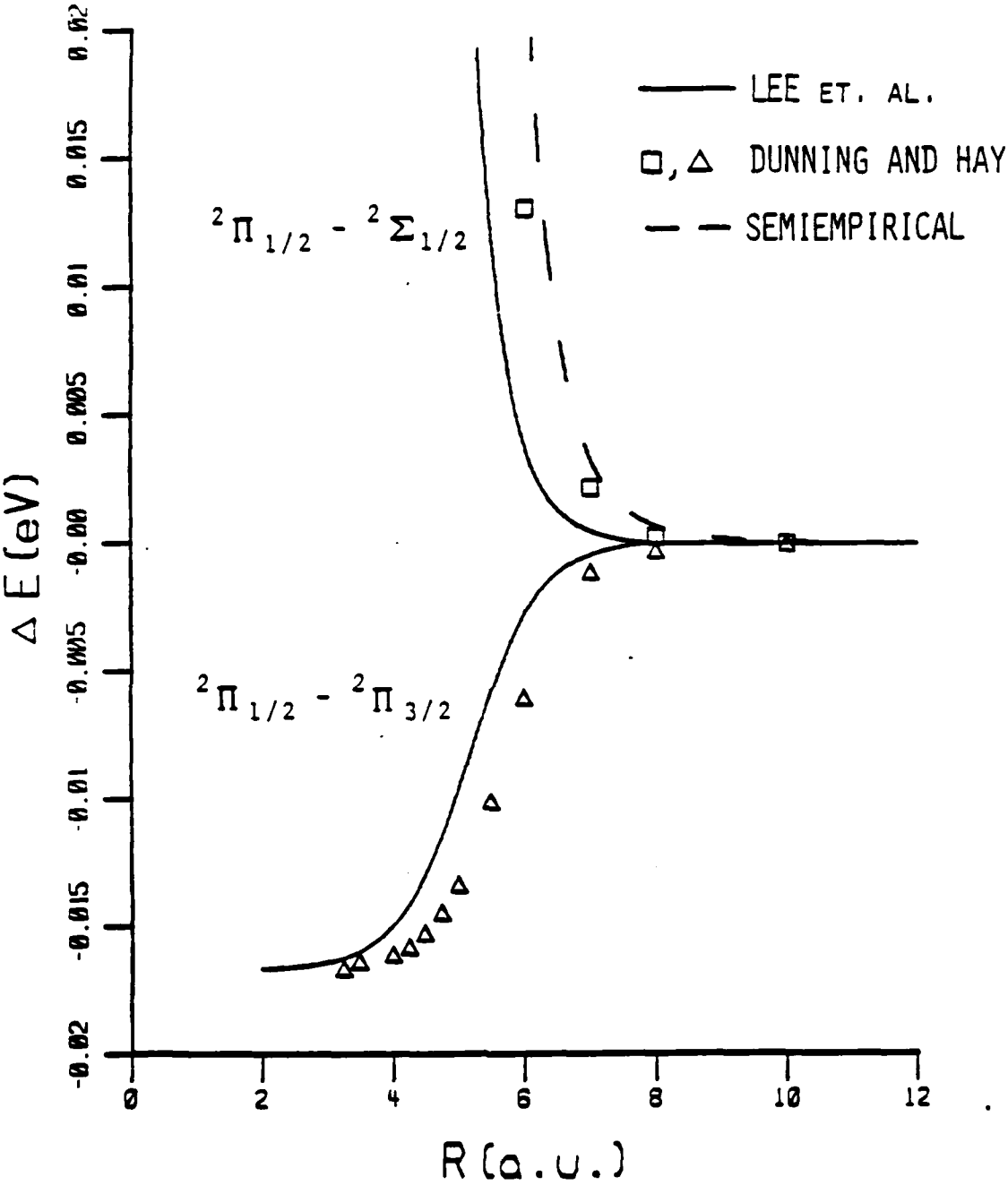

Figure 5. Ar-F Difference Potentials

perturbing gas and temperature. The transition is of theoretical interest due to its magnetic dipole nature and to the splitting of the lower state with collisional interaction, as well as being of practical interest as a fluorine atom concentration diagnostic. The agreement between the F-Ar linewidth and the prediction based on scattering data and calculated long range potentials is well within the combined uncertainties and gives the promise that further line broadening measurements can be used to add to the knowledge of interatomic potentials.

Acknowledgments

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3. PERSONNEL

The Principal Investigator for this work has been Dr. Alan Stanton, who is on the scientific staff of the Applied Sciences Division of Aerodyne Research, Inc. He has been assisted in the laboratory by Mr. Robert Brown and Mr. Warren Goodwin.

Dr. Joda Wormhoudt and Dr. James Duff, both members of the scientific staff of the Applied Sciences Division, developed the calculations of fluorine atom line broadening by rare gases.

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

1. 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).

2. A.C. Stanton, J.C. Wormhoudt, and J.W. Duff, "Collisional Broadening of the Atomic Fluorine $^2P_{1/2} \leftarrow {}^2P_{3/2}$ Spin Orbit Transition," to be published in the Proceedings of the 6th International Conference on Spectral Line Shapes (Walter de Gruyler and Son, Berlin).

3. An expanded version of the line broadening paper (No. 2 above) will be submitted to the Journal of Chemical Physics.

4.2 Presentations

Presentations of work performed under this contract have been made at the following meetings:

1. Conference on High Resolution Infrared Applications and Developments, National Bureau of Standards, Gaithersburg, MD, June 1980 (presentation by Dr. Stanton).

2. Symposium on Lasers in Chemistry, 28th Congress of the International Union of Pure and Applied Chemistry, Vancouver, BC, August 1981 (presentation by Dr. Stanton).

3. 6th International Conference on Spectral Line Shapes, Boulder, CO, July 1982 (presentation by Dr. Stanton).

4. Gordon Research Conference on High Temperature Chemistry, Tilton, NH, July 1982 (presentation by Dr. Kolb on "Kinetic and Spectroscopic Measurements on Reactive Species in a High Temperature Flow Facility").

5. A presentation will be made by Dr. Stanton at the 7th Tri-Service Chemical Laser Symposium, Air Force Weapons Laboratory, Kirtland AFB, NM, October 1982.

6. Dr. Stanton will present an invited paper on this work at Lasers '82, New Orleans, LA, December 1982.

4.3 Interactions

Captain Ralph Hill of the Chemical Lasers Branch, Air Force Weapons Laboratory, visited Aerodyne in April, 1982, to observe fluorine atom measurements using the diode laser technique and to discuss possible applications of the technique as an in-situ F atom diagnostic for chemical lasers.

In addition, the potential diagnostic applications of this method were discussed with other industrial contractors involved in chemical laser development.

5. DISCOVERIES AND APPLICATIONS

The measurements performed under this program, particularly measurements of fluorine atom absorption line positions, line strengths, and collisional broadening cross sections, provide all of the detailed spectroscopic information required in order to develop and implement a diode laser fluorine atom diagnostic for measurement of F atom concentrations in HF/DF chemical lasers.