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CHEMILUMINESCENT REACTION OF TELLURIUM WITH FLUORINE
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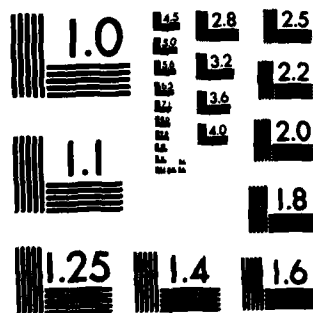
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→ spectrum revealed the presence of TeF , TeF_2 , TeF_3 , and TeF_5 in the flame. The apparently complex chemistry and the distribution of chemical energy over several vibrational levels in excited TeF suggest that this flame is not a promising candidate for chemical laser development. ←

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Chemiluminescent Reaction of Tellurium with Fluorine

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NOVEMBER 1982

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SUMMARY

Tellurium vapor reacts with gaseous fluorine to produce a chemiluminescent flame. The emission in the visible and near infrared part of the spectrum of the flame has been previously attributed to the $A^2\Pi - X^2\Pi$ system of TeF. Excited TeF produced in the flame was investigated as a possible candidate for chemical lasing. This work was intended to further characterize the TeF flame using computer controlled simultaneous optical and mass spectroscopy. Assignment of some band head wavelengths in the TeF (A-X) system were checked and a mass spectrum of the flame was obtained. The mass spectrum revealed the presence of TeF, TeF₂, TeF₃, and TeF₅ in the flame. The apparently complex chemistry and the distribution of chemical energy over several vibrational levels in excited TeF suggest that this flame is not a promising candidate for chemical laser development.

PREFACE

The work reported here represents the conclusion of a work unit whose objective was to investigate Group VI A fluorides formed in flames. The excited fluorides formed have potential as chemical laser active species. Part of the work was done as faculty research by Capt Moody who was on the Department of Chemistry faculty until being reassigned in June 1982. The programming and much of the experimental work was done as an Independent Study course project by CIC Joseph A. Menapace, who was commissioned in June 1982 and is now a Second Lieutenant on active duty at McClellan AFB, CA. We acknowledge the excellent work of Judy Cross in typing the manuscript. This is the final report on this work unit.

I. INTRODUCTION

Work previously done in this laboratory¹ investigated the chemiluminescent spectra of SeF and TeF flames to determine their feasibility as active media for chemical lasers. The flames were produced by reaction of Te and Se vapor or selenium hydride with F_2 in He diluent at total pressures of 1-10 torr. The work reported here included development of a computer-controlled system for observing the mass spectra and optical spectra of these flames simultaneously. We obtained parts of the optical spectrum of the TeF flame generated by reaction of Te vapor with F_2 for confirmation of the vibrational band wavelength assignments made in Ref. 1 and also obtained mass spectra of the Te and F_2 flame.

II. EXPERIMENTAL

A. Interface Scheme

The equipment used is as described previously.¹ The optical spectrometer is a 0.5 meter McPherson (Model 216.5) and the mass spectrometer is a UTI 100C. The computer used was a MINC 11 by Digital. It is a dual diskette computer with 512, 512 bytes/disk and digital and analog input/output capability. The operating system was MINC BASIC. The burner assembly was modified somewhat and is shown in Fig 1. The computer program controlling acquisition of both optical and mass spectra allows up to ten mass spectra to be obtained in a given emission spectrum scan. To accomplish this, the interface program subdivides the emission spectrum into a finite number of points, P_n , whose number depends upon the degree of spectral resolution desired (see Figure 2). The analysis begins at point P_0 ; which coincides with the starting wavelength, λ_0 , of the emission spectrum. Between the points P_0 and P_1 , a preset number of the spectrometer's stepping motor increment pulses, N , are counted indicating a finite wavelength increase,

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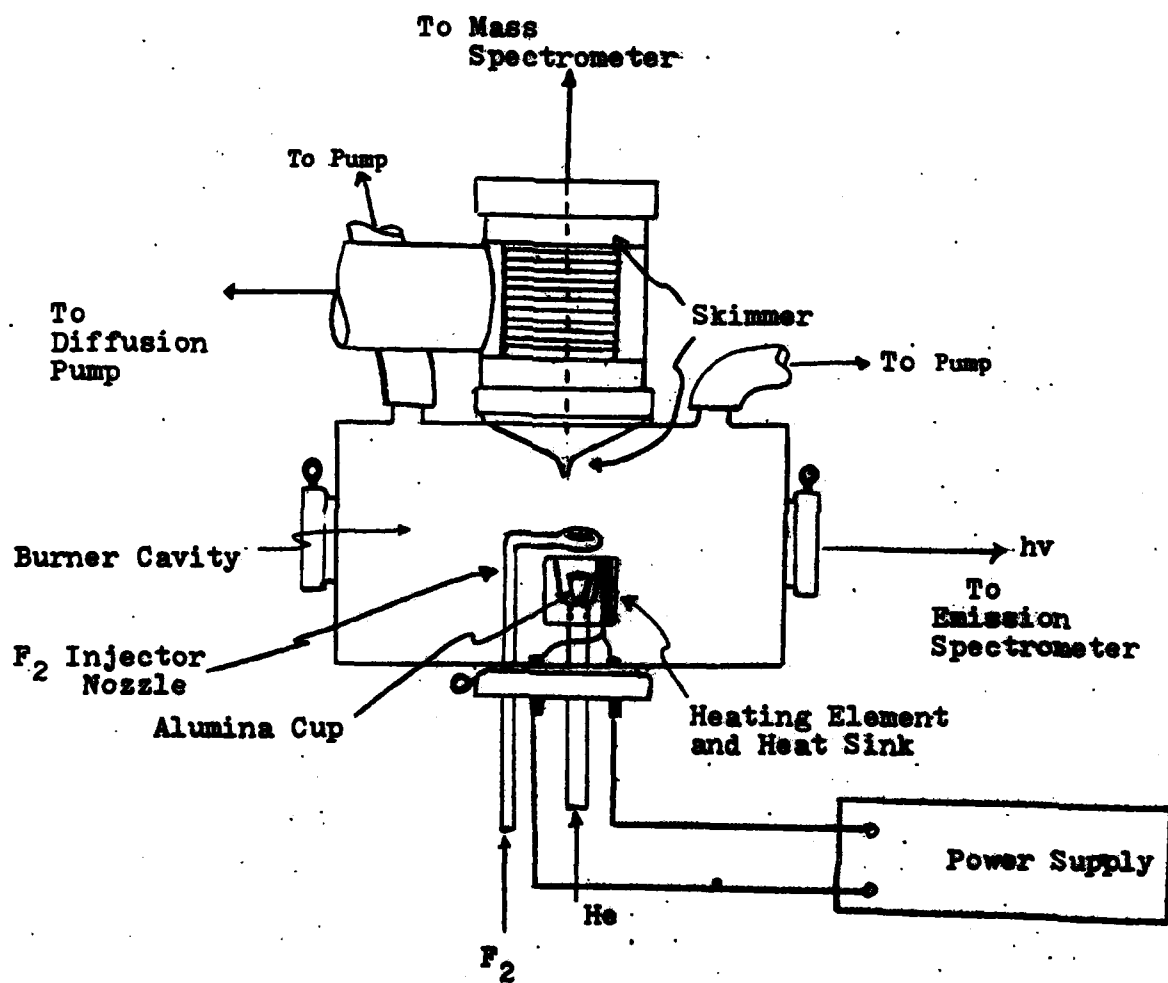


FIGURE 1 BURNER ASSEMBLY

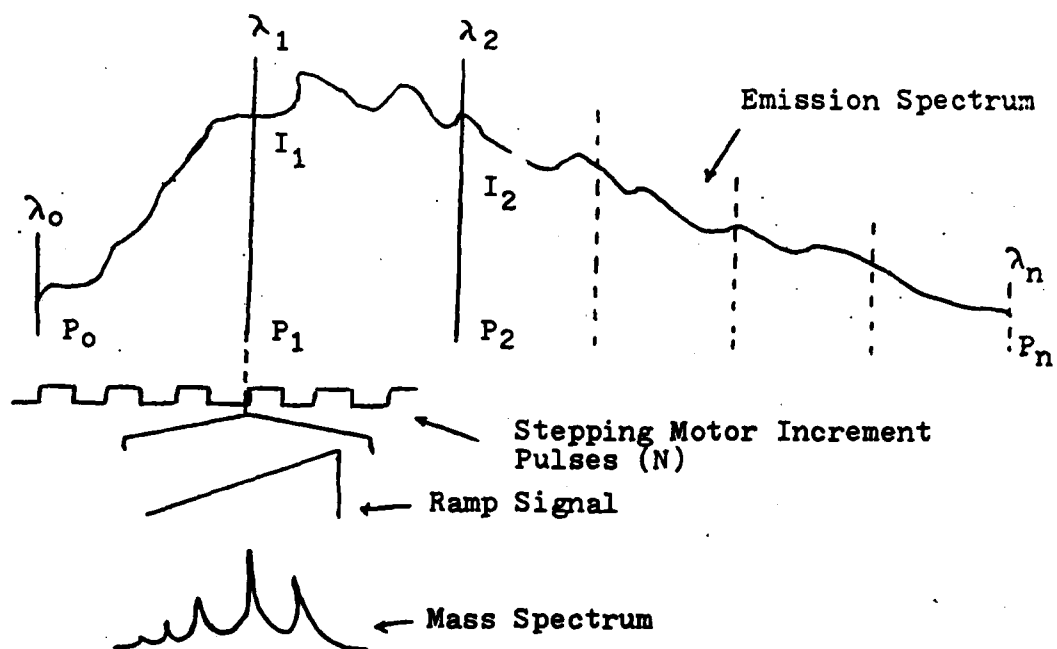


FIGURE 2 INTERFACE SCHEME

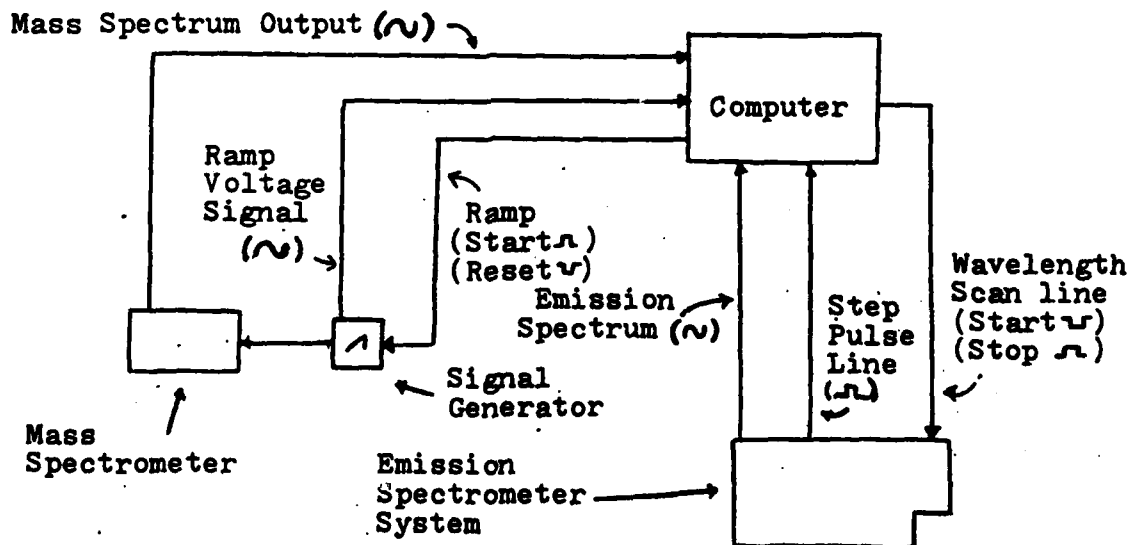


FIGURE 3 COMPUTER INPUT AND OUTPUT REQUIREMENTS

which brings the scan to wavelength λ_1 (at point P_1). The emission scan is stopped and the emission intensity, I_1 , is recorded. This process is repeated between points P_1 and P_2 , and so on. If the wavelength at a given point also corresponds to a point where a mass spectrum is to be taken, a ramp voltage signal is initiated to control the mass spectral scan and both its voltage and the mass spectrometer's output are recorded. The emission scan then continues until the terminating wavelength, λ_n , is reached.

B. Computer Input and Output Requirements

In the interface scheme discussed above, the computer controls the spectrometer's scanning and the operation of the signal generator which provides the ramp voltage signal (see Figure 3). The computer must output a digital logic 0 to start the spectrometer's wavelength scan and to reset the ramp voltage signal from the signal generator for subsequent use. It also outputs a digital logic 1 (5.0 Volts) to stop the wavelength scan and to initiate the ramp voltage signal from the signal generator.

During data acquisition, the computer must input both analog and digital signals. The spectrometer's stepping motor pulses must be input into the computer and counted for wavelength determination. The computer counts these pulses by advancing one clock pulse for every logic 1 signal entering its clock module. The data input into the computer from the two spectrometers and the signal generator are analog signals. The intensity data from the detector is in the range of -1 to +1 volts, and the data from both the mass spectrometer and the signal generator are in the range of 0 to +10 volts.

C. Interface Program

The interface program stores the emission and mass spectrometric data in disk memory and formats them to be compatible with other data processing

programs available for data analysis. It also offers a visual observation of the analyses during experimentation by graphically displaying the spectral and mass spectrometric data on the terminal screen.

Figure 4 contains the interface program. The first section of the program (lines 10-240) inputs the emission and mass spectrometric control parameters. It establishes the emission spectrometer's scanning range, monochromator pulse increase per data point, and disk storage file. It also establishes the optical wavelengths of the emission spectrum at which mass spectra are to be taken. Program line 370 initiates the emission scan by starting the monochromator's stepping motor. Line 380 samples and counts the stepping motor's pulses, and when the pulse number equals the selected monochromator pulse increase per data point, the scan stops. The computer then acquires the emission intensity from the detector (line 410). If a mass spectrum is to be taken, the signal generator's ramp voltage signal initiates (line 440), and a mass spectrometric analysis proceeds (lines 450 and 490). The computer then stores the mass spectrometric data in a virtual array disk storage file (lines 510-570). The emission scan resumes and repeats the above sequence until the emission scan is completed. At the end of the analysis, the computer stores the emission spectrometric data in a virtual array disk storage file (lines 580-650).

The optical spectrometer data acquisition system was calibrated using a mercury lamp. The Hg spectrum in the region 4300-5100Å acquired using the system is shown in Fig 5.

III. RESULTS

A. Emission Spectrum of TeF

A diffuse chemiluminescent flame was obtained by heating solid Te in the alumina cup and flowing He as a carrier gas at a pressure of 0.8 torr. Then

```

10 DIM V(1000),P(800),Z(500),W(20,3)
20 SET_GAIN(1,0,2)
30 SET_GAIN(2,10)
40 SET_LINE(0,1,0)
50 PRINT "THIS PROGRAM TAKES EMISSION SPEC AND MASS SPEC SCANS FOR AN INTERVAL
    <= 5000 ANG" \ PRINT
60 PRINT "CHOICES FOR EMISSION SCAN RATES FOLLOW (ANGSTROMS/SEC)" \ PRINT
70 PRINT "RATE-- 0.50 1.00 2.00 5.00 10.0 20.0 50.0"
80 PRINT "CHOICE-- 0 1 2 3 4 5 6" \ PRINT
90 PRINT "(SCAN RATES CAN BE MULTIPLIED BY 100)" \ PRINT
100 PRINT "ENTER YOUR SCAN SPEED CHOICE" \ INPUT P5
110 SET_LINE(P5,1,0) \ PRINT
120 PRINT "DO YOU WANT TO MULTIPLY RATE BY 100?" \ INPUT C5
130 IF C5="Y" THEN SET_LINE(7,1,0) \ PRINT
140 PRINT "ENTER START AND STOP WAVELENGTHS FOR EMISSION SCAN (ANGSTROMS)"
150 INPUT W5,W7
160 W5=100*(W5-W6) \ PRINT
170 PRINT "ENTER EMISSION SPEC FILE NAME" \ INPUT W6
180 PRINT "ENTER MASS SPEC FILE NAME" \ INPUT W5
190 PRINT "MINIMUM EMISSION SAMPLING IS":W5/100000.01139E-03;"ANGSTROMS"
200 PRINT "ENTER EMISSION SAMPLING DESIRED (ANGSTROMS)" \ INPUT W4
210 W4=W4/9.91139E-03
220 PRINT "ENTER # OF MASS SPEC'S TO BE TAKEN (1/WAVELENGTH)" \ INPUT M
230 IF M=0 GO TO 290
240 FOR C=0 TO M-1 \ PRINT "ENTER WAVELENGTH FOR MASS SPEC.":C+1 \ INPUT W(C,0)
250 PRINT "ENTER LOWER AND UPPER AMU FOR THIS MASS SPEC (MAX RANGE= 50 AMU)"
260 INPUT W(C,1),W(C,2)
270 W(C,1)=W(C,1)*0.0320114-.0313106 \ W(C,2)=W(C,2)*0.0320114-.0313106
280 W(C,0)=(W(C,0)-(W5-6.48354))/9.91139E-03 \ NEXT C
290 PRINT "SET WAVELENGTH AT STARTING WAVELENGTH" \ PRINT
300 PRINT "HIT RETURN TO PUT SPECTROMETER INTO REMOTE MODE" \ INPUT F5
310 SET_LINE(10,1,0)
320 AIM("D",1)
330 PRINT "HIT RETURN TO START" \ INPUT F5
340 J=-1
350 SET_LINE(11,1,0) \ J=J+1
360 START_TIME("E") \ IF J>0 THEN T1=Z(J-1)
370 SET_LINE(0,1,0)
380 GET_TIME(T0) \ IF T0>=W4 THEN SET_LINE(0,0,0) \ START_TIME \ GO TO 400
390 GO TO 380
400 Z(J)=T0-T1+S \ S=0
410 AIM("D",P(J),1,0,10) \ PRINT Z(J),J,Z(J)*9.91139E-03+W5-6.48354,P(J)
420 IF Z(J)>=W5/2+U GO TO 580 \ IF W(F,0)>Z(J) GO TO 350
430 IF W(F,0)=0 GO TO 350
440 SET_LINE(11,0,0)
450 FOR N=0 TO 999 STEP 2
460 AIM("D",V(N),2,.01,0,2)
470 IF V(N)<W(F,1) GO TO 460
480 K=K+1
490 IF V(N)>=W(F,2) GO TO 510
500 NEXT N
510 OPEN W5 AS FILE 1
520 DIM B1,A(10000)
530 FOR N=0 TO 2047 STEP 2
540 A(C)=V(N)*30.4763+.958330
550 A(C+1)=V(N+1) \ C=C+2
560 NEXT N
570 CLOSE B1 \ GO TO 670
580 OPEN W6 AS FILE 2
590 DIM B2,B(1000,2)
600 FOR N=0 TO J
610 B(N,0)=P(N)
620 B(N,1)=Z(N)*9.91139E-03+W5-6.48354
630 N=N+1
640 NEXT N
650 CLOSE B2
660 S=Z(J) \ U=W5/2 \ T1=0 \ IF Z(J)=0 GO TO 340
670 IF Z(J)=0 GO TO 700
680 K=0 \ F=F+1
690 IF Z(J)=0 GO TO 380
700 SET_LINE(10,0,0) \ DISPLAY_CLEAR \ END

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READY

FIGURE 4 - MONMAS INTERFACE PROGRAM

REPRODUCED ON D115P COMER

MERCURY LINE SPECTRUM (4300-5100 ANGSTROMS)

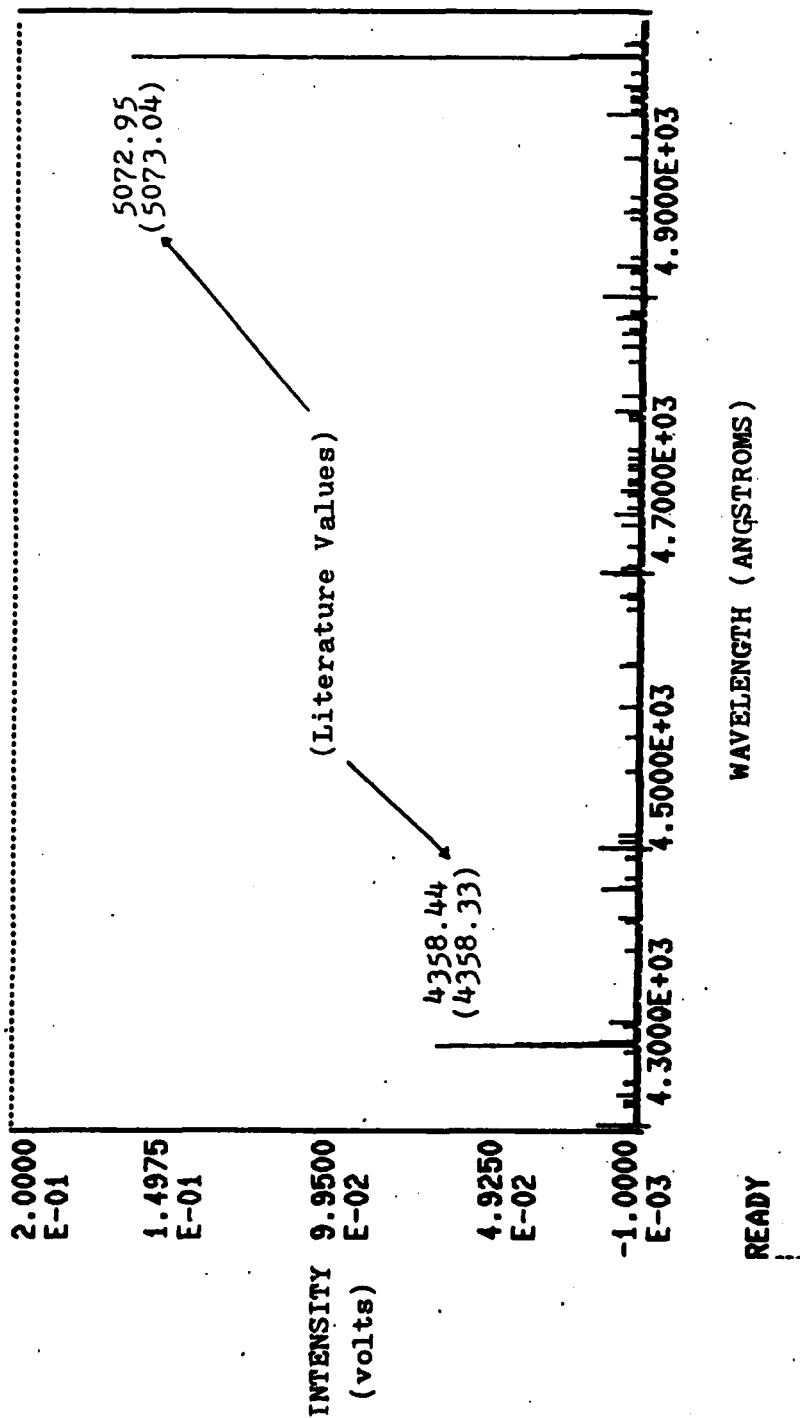


FIGURE 5 COMPUTER REGENERATED MERCURY EMISSION LINE SPECTRUM

F_2 was added to increase the total pressure to 1.2 torr. An example of the spectrum obtained is shown in Fig 6. Once the spectrum is stored it can be retrieved and shown at higher dispersion as shown in Figs 7 and 8. Comparison of the band head assignments obtained from these spectra with those reported by Thorpe ¹ and by Newlin ² who generated TeF flames using H_2Te and F_2 is given in Table 1. Band heads from Figs 7 and 8 were assigned the wavelengths at which the steepest increase in intensity occurred. For the six band heads shown, the average difference in wavelengths assigned compared to those by Thorpe is 3 λ . The scatter in the difference reflects the difficulty in establishing and using consistent criteria for assignment of band head wavelengths but may also reflect slight differences in the flames used to generate the two spectra. Unfortunately, experimental difficulties prevented our repeating these studies at higher resolution and for a wider range of the spectrum. The lower intensity in the region 6300-6700 $\text{\AA}$ compared to that obtained by Thorpe was due to a lowering of the Te pressure in our experiment.

Table I
Assignment of some Band Head Wavelengths ($\text{\AA}$)
in the TeF Spectrum ($\lambda^2 \pi_i - X^2 \pi_i$)

$v' - v''$	This work (λ_2)	Thorpe ¹ (λ_1)	Newlin ²	$\lambda_2 - \lambda_1$
1 - 0	6897	6892	6900 $\pm$ 2	+5
2 - 0	6698	6694	6701 $\pm$ 2	+4
4 - 0	6337	6333	6337 $\pm$ 2	+4
5 - 0	6169	6168	6174 $\pm$ 2	+1
2 - 1	6980	6979	6985 $\pm$ 2	+1
6 - 1	6248	6244	6246 $\pm$ 2	+4
				ave +3

REPRODUCED IN SPSS CORP.

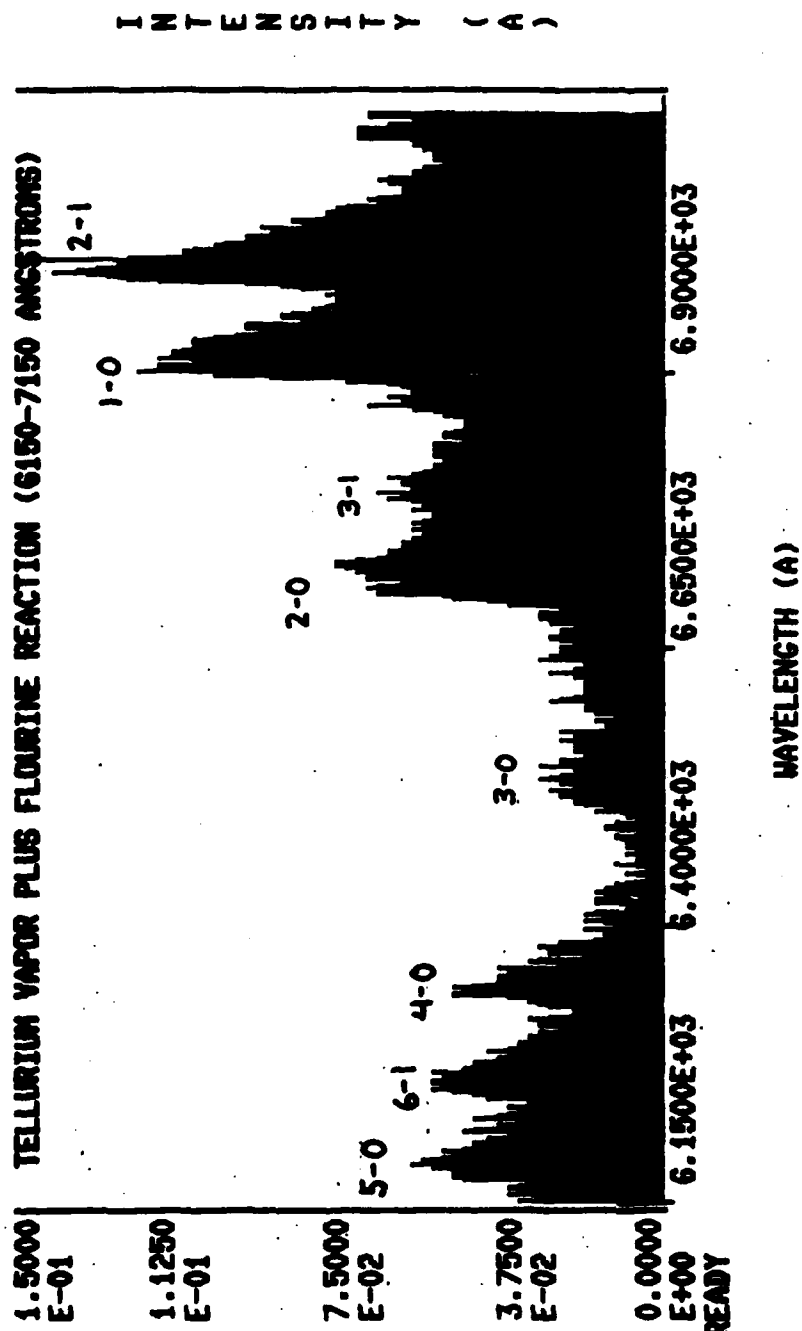


FIG 6 TeF FLAME SPECTRUM (6150 - 7100 Å)

REPRODUCED ON OPAS COMER

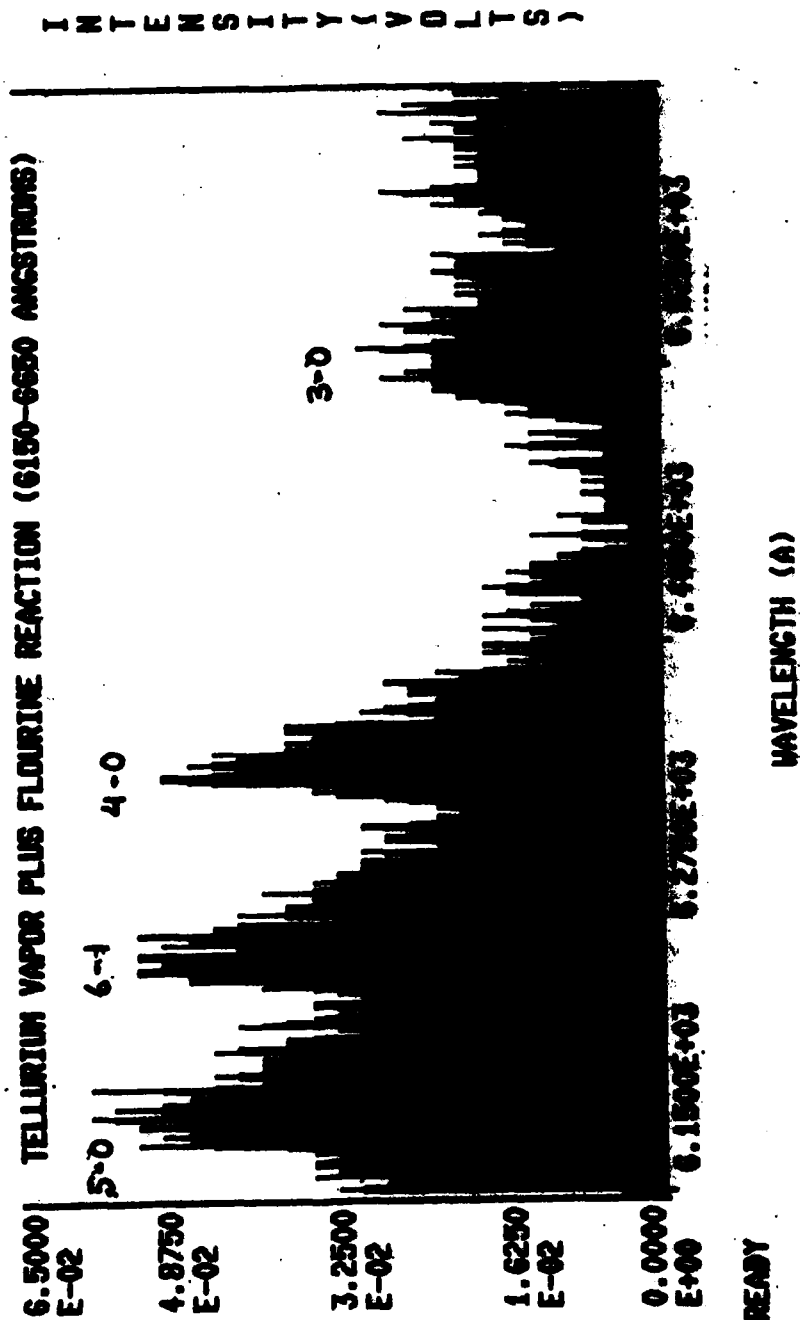


FIG 7 TeF FLAME SPECTRUM (6150 - 6650 Å)

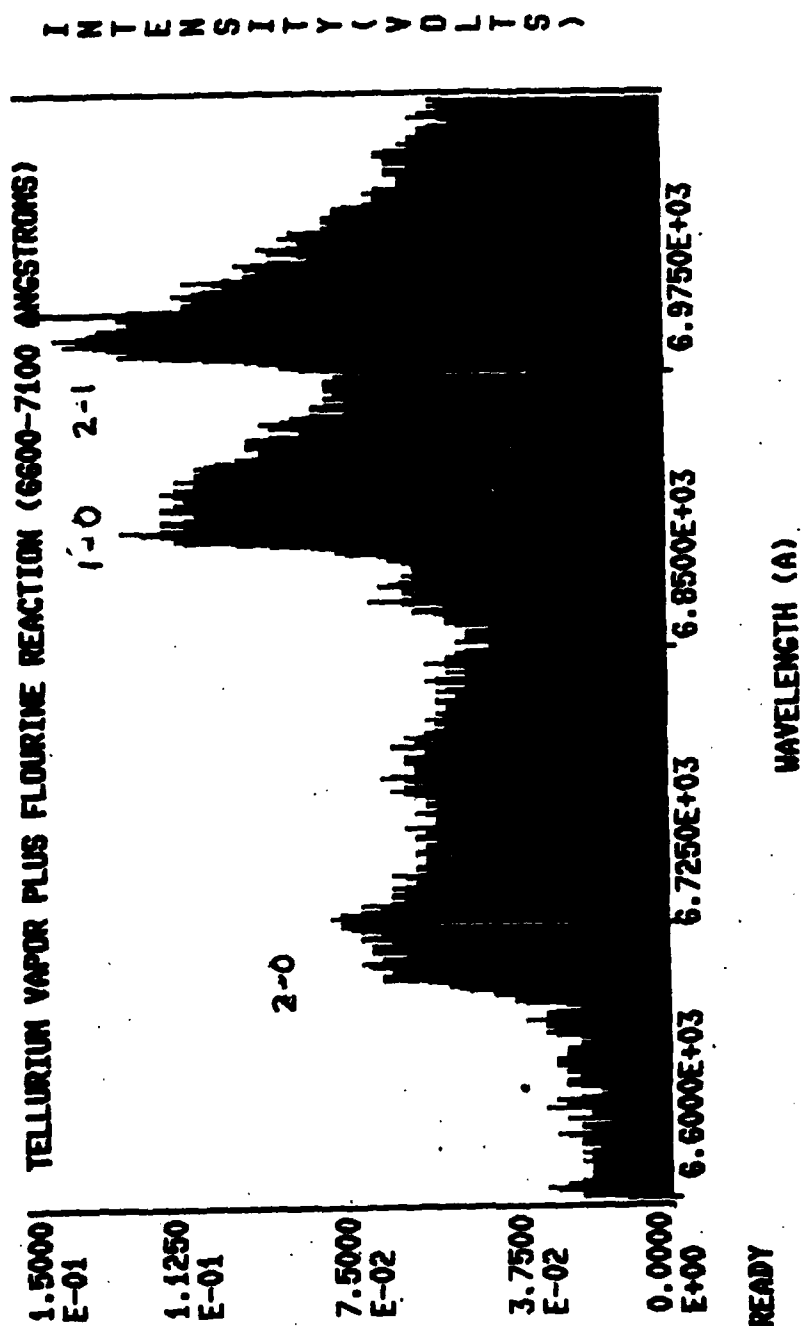


FIG 3 TeF PLAME SPECTRUM (6600 - 7100 A)

B. Mass Spectrum of TeF Flame

The mass spectrum of the flame generated by heating solid Te, using He as a carrier gas and adding F_2 through the injector above the burner was obtained in the system used by Thorpe.¹ Partial pressures were 0.3 torr F_2 and 0.87 torr He. The skimmer was at the outer edge of the flame. The spectrum was recorded on an X-Y recorder and then transcribed into a Hewlett-Packard 5985 GC/Mass Spectrometer where relative abundances were calculated and recorded and the data formatted as shown in Fig. 9.

When the apparatus shown in Fig 1 was used to generate the flame, the skimmer was above the outer edge of the flame and the mass spectra obtained did not show the species shown in Fig 9. Since the optical spectrum obtained indicated the presence of TeF, it appears that the flow characteristics in the apparatus and the flame kinetics are such that the skimmer must be in the visible part of the flame in order for the TeF and TeF_n species to be detected.

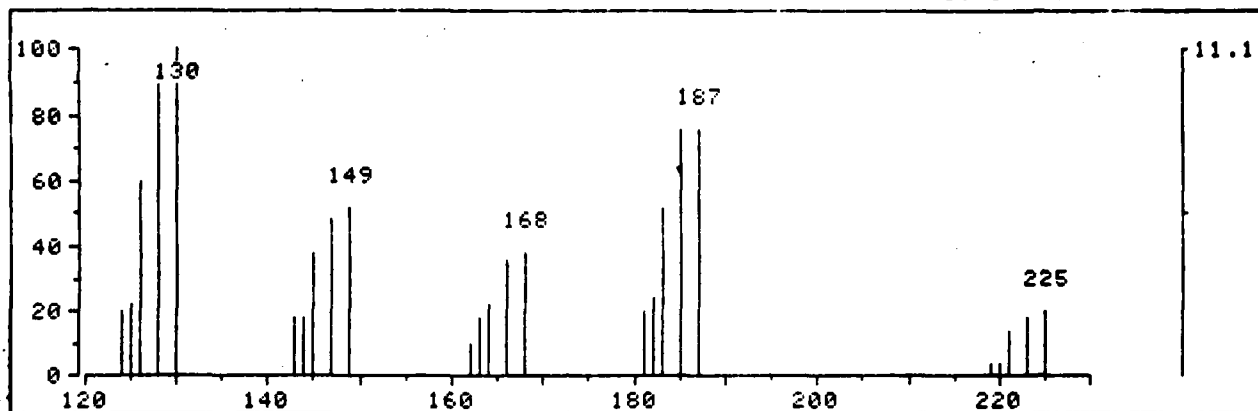
IV. CONCLUSIONS

While the computer-controlled acquisition of mass and optical spectra of the $Te + F_2$ flame did operate as planned, experimental difficulties in flame generation prevented a thorough study of the flame. Two conclusions may be drawn from the limited results obtained. First the mass spectrum indicates that several TeF_n species are generated and that TeF is by no means easily produced with high yield. The absence of TeF_4 from the products raises an interesting question and suggests that the chemistry of the flame may be quite complex. Since the energy generated in the flames we observed is distributed among many vibrational levels of electronically excited TeF and several products are generated in quantities greater than TeF, it is unlikely that this system will be readily developed as the basis of a chemical laser.

TE/F2 FLAME
 0.3 TORR F2; 0.87 TORR HE; 360-380 DEG C 1 SCANS (1 SCANS, 5040, 2
 x 1.0 MASS RANGE: 123.0, 225.0 TOTAL ABUND= 9880. .02 MINS)

SCAN *

* 1 RET. TIME: .00 TOT ABUND= 8982. BASE PK ABUND: 130.0 1000.



FRN 5040, SPECTRUM # 1 RET. TIME: .00, 25 PEAKS

M/Z	REL ABUND	M/Z	REL ABUND	M/Z	REL ABUND	M/Z	REL ABUND
124	20.0	145	38.0	168	38.0	220	4.0
125	22.0	147	48.0	181	20.0	221	14.0
126	60.0	149	52.0	182	24.0	223	18.0
128	92.0	162	10.0	183	52.0	225	20.0
130	100.0	163	18.0	185	76.0		
143	18.0	164	22.0	187	76.0		
144	18.0	166	36.0	219	4.0		

>PAUSE

FIG 9 MASS SPECTRUM OF TeF FLAME

The second result is that the band head wavelengths assigned by Thorpe¹ appear to be on the average 3Å lower than those obtained after thorough calibration of the spectrometer. This change in assignment would have negligible effect on his vibrational analysis.

REFERENCES

1. W. G. Thorpe, Chemiluminescent Reactions of Selenium and Tellurium with Fluorine, FJSRL-TR-80-0010, April 1980
2. D. E. Newlin, G. W. Stewart, and J. L. Gole, Canadian Journal of Physics, 59(3), 441, (1981)