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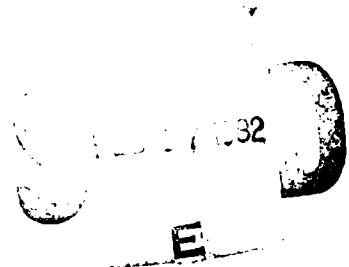
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# LASER CANDIDATE REACTIONS OF O<sub>2</sub>F

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Final Report



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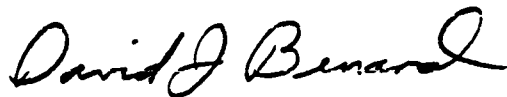
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Gas phase O <sub>2</sub> F radicals have been shown to be produced by the thermal decomposition of solid O <sub>2</sub> <sup>+</sup> AsF <sub>6</sub> <sup>-</sup> . O <sub>2</sub> F generated in this manner exhibits a second order decay governed by a rate constant $k=1.4\pm 0.4\times 10^{11}$ cm <sup>3</sup> mole <sup>-1</sup> sec <sup>-1</sup> . Chemiluminescent reactions of O <sub>2</sub> F with several added gases were observed. Electronically excited halogen monofluorides in the A( <sup>3</sup> Π <sub>1</sub> ) and B( <sup>3</sup> Π <sub>0</sub> <sup>+</sup> ) states were produced by reactions of molecular halides with O <sub>2</sub> F or by reactions of halogen atoms with O <sub>2</sub> F in the presence of singlet molecular (over)		

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20. ABSTRACT (Continued)

oxygen. The reactions of magnesium and calcium atoms with  $O_2F$  produced electronically excited MgF and CaF, respectively, in several accessible excited states. The measurement of photon yields for a number of these reactions indicated that direct production of excited electronic states is not a favored mechanism. On the contrary, the dominant mechanism in the reactions studied appears to be the production of vibrationally excited diatomic fluorides. The electronically excited species responsible for the visible-UV chemiluminescence are most likely formed either by resonant interactions with highly vibrationally excited ground state molecules or by collisional V-E energy transfer. ✓

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## TABLE OF CONTENTS

	Page
I. INTRODUCTION.....	5
II. GENERATION AND TIME DECAY OF GAS PHASE $O_2F$ .....	13
III. REACTION SURVEY.....	23
1. Reactions Producing Excited $BrF$ .....	23
2. Reactions Producing Excited $IF$ .....	35
3. $O_2F$ Reactions with $Mg(^1S)$ and $Mg^*(^3P)$ .....	44
4. The Reaction of Calcium with $O_2F$ .....	65
IV. CONCLUSIONS.....	73
V. REFERENCES.....	76

## LIST OF ILLUSTRATIONS

1. $O_2F$ ultraviolet absorption spectrum.....	14
2. Apparatus used for measurement of the time decay of $O_2F$ .....	18
3. Second order plot for $O_2F$ decay.....	20
4. Modified apparatus used for observation of reactions of $O_2F$ with added gases.....	24
5. $BrF B(^3\Pi_0^+) \rightarrow X(^1\Sigma^+)$ emission spectrum.....	27
6. $BrF B \rightarrow X$ photon yield vs the flowrate of bromine atoms.....	34
7. $IF_2$ emission spectrum showing $A(^3\Pi_1) \rightarrow X(^1\Sigma^+)$ and $B(^3\Pi_0^+) \rightarrow X(^1\Sigma^+)$ transitions.....	39
8. Apparatus used for generation of magnesium vapor.....	47
9. Apparatus used for observing the reaction of $O_2F$ with magnesium.....	48
10. Calibration of the flowrate of magnesium vs temperature.....	50
11. Broadband emission observed from the $Mg + O_2F$ reaction.....	53
12. Spectrum of $MgF A(^2\Pi) \rightarrow X(^2\Sigma^+)$ emission.....	55
13. Photon yield of the broadband emission vs the flowrate of magnesium.....	58

LIST OF ILLUSTRATIONS (Continued)

	Page
14. Photon yield of the MgF A + X emission vs the flowrate of magnesium.....	59
15. Cells used for observation of the reaction of Mg* (3P) with O <sub>2</sub> F.....	62
16. Spectra of emissions from the reaction of O <sub>2</sub> F with Mg( <sup>1</sup> S)/Mg*( <sup>3</sup> P).....	64
17. Calibration of the flowrate of calcium vs temperature.....	67
18. Spectrum of Ca + O <sub>2</sub> F chemiluminescence in the visible region.....	69
19. Spectrum of Ca + O <sub>2</sub> F chemiluminescence in the ultraviolet region.....	71

LIST OF TABLES

I. Results of O <sub>2</sub> F Time Decay Measurements.....	21
II. <sup>79</sup> BrF - <sup>81</sup> BrF Isotope Splittings Observed for the B( <sup>3</sup> Π <sub>0</sub> <sup>+</sup> ) + X( <sup>1</sup> Σ <sup>+</sup> ) Transition.....	29
III. Deslandres Table for the A( <sup>3</sup> Π <sub>1</sub> ) + X( <sup>1</sup> Σ <sup>+</sup> ) Transition of IF.....	40

## I. INTRODUCTION

The development of lasers based upon direct chemical pumping of population inversions among electronically excited states requires that two broad groups of conditions be met. The first such group pertains to the reaction; i.e., formation of the inversion. Either the dynamic constraints on the reaction must be such that excited product states are preferentially populated, or the spectroscopy of the system must be such that populated upper levels are optically connected to unpopulated lower levels (e.g., by favorable Franck-Condon shifts). In addition, the speed of the reaction must allow the production of excited products to compete well with deactivation mechanisms. The second condition pertains to the nature of the excited species: it must be suitable for lasing. The radiative lifetime of the excited state formed must be short enough to allow reasonable gain but not so short as to preclude build-up of the inversion density. The density of states in the levels populated by the reaction should be as low as possible (such that "dilution" of the inversion density is minimized), and intramolecular and intermolecular deactivation processes must not be efficient.

It is clear that progress in this area requires a judicious choice of candidate lasing species, and a number of atoms and molecules have risen to the forefront of attention in this regard. Many of these are diatomic fluorides, e.g., interhalogens, group VA fluorides, and metal fluorides. The potential of the interhalogen systems stems in part from the metastability of the lowest lying excited electronic states,  $A^3\Pi_1$  and  $B^3\Pi_0^+$ , which are

connected to the ground  $1\Sigma^+$  state by forbidden singlet-triplet transitions. The radiative lifetimes of the B states of these species have been found to be on the order of  $10^{-5}$  seconds (Ref. 1), with the lifetime of the A states being one to two orders of magnitude greater (Ref. 2, 3). Also, these excited triplet states exhibit strong Franck-Condon shifts. For IF,  $v' = 0$  of the B state is connected to  $v'' = 4$  and 5 of the ground state (Ref. 2). This displacement is even more pronounced for BrCl, for which transitions to  $v'' = 16-18$  are favored (Ref. 4). These attributes have led to an extended investigation of the chemical production of  $\text{BrCl}^*(3\Pi_0^+)$  at the AFWL (Ref. 5) and to the demonstration of a number of optically pumped molecular halogen lasers (Ref. 6, 7).

The chemical production of excited Group VA fluorides has been investigated (with quite promising results) in this laboratory (Ref. 8) as well as others (Ref. 9). The potential of these systems is based upon the preferential production of metastable triplet states by strongly spin-constrained reactions (Ref. 10), with the subsequent emission occurring in very narrow bandwidths. Numerous reactions producing excited metal fluorides have been investigated (Ref. 11, 12). These systems are of interest because of the highly energetic nature of  $M+F_2$  (or  $RF$ ) reactions, typically accessing many excited product states. Owing to the ionic nature of metal fluorides, production of excited species in these reactions generally occurs by curve-crossing mechanisms.

The work described herein was directed toward assessing the utility of gas phase  $O_2F$  radicals as a reagent for the production of electronically excited diatomic fluorides. The  $O_2F$  molecule is one in which the fluorine atom is very weakly bound to the  $O_2$  moiety. The strength of the O-F bond in this

species has been estimated to be on the order of 15 kcal/mole (Ref. 13, 14). The O-O bond strength is ~110 kcal/mole (Ref. 14) (i.e., only slightly weaker than in a free O<sub>2</sub> molecule). Owing to the lability of the fluorine atom, the reactions of O<sub>2</sub>F may liberate a very large amount of energy (~22 kcal/mole more than analogous processes involving F<sub>2</sub>). Such reactions may in fact be similar to three-body recombinations (with the O<sub>2</sub> acting as the third body) in their ability to form excited states, but should proceed with the speed of rapid bimolecular processes.

The O<sub>2</sub>F radical is unusually stable and has been well characterized in liquid solutions (Ref. 15) and solid matrices (Ref. 16) at cryogenic temperatures. It has been observed in the gas phase from flash photolysis of O<sub>2</sub> - RF mixtures at high pressures (hundreds of torr) (Ref. 17, 18). In such an environment, fluorine atoms produced by the flash combine with oxygen at a rate about two orders of magnitude greater than F+F+M recombination. Based on this kinetic situation, the formation of O<sub>2</sub>F has been used to monitor the quantum yields for F atom production by the photolysis of RI compounds (Ref. 18). The EPR and IR spectra of the radical are known from the condensed phase experiments mentioned above. The UV spectrum in the gas phase, dominated by a strong absorption in the vicinity of 210 nm, was measured in the F<sub>2</sub>-O<sub>2</sub> flash photolysis experiments.

In the experiments performed in our laboratory, gaseous O<sub>2</sub>F was produced by the thermal decomposition of solid O<sub>2</sub><sup>+</sup>AsF<sub>6</sub><sup>-</sup>:

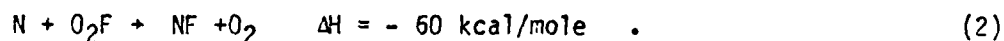


This material was synthesized for these experiments at the Rocketdyne Division of Rockwell International by the photolysis of mixtures of  $\text{O}_2$ ,  $\text{AsF}_5$ , and  $\text{F}_2$  contained in a quartz vessel. In this procedure the dioxygenyl salt forms as a precipitate on the vessel walls. Some of the material used early in the program was prepared by applying heat to gas mixtures contained in stainless steel vessels; this procedure was abandoned in favor of the photolysis since the solid precipitate clogged the valve of the metal vessel. Subsequent handling of the  $\text{O}_2^+\text{AsF}_6^-$  salt was done either under vacuum or in a dry box, since it reacts vigorously with water vapor present in the air.

The final decomposition products of  $\text{O}_2^+\text{AsF}_6^-$  have been shown to be  $\text{O}_2$ ,  $\text{F}_2$ , and  $\text{AsF}_5$  (Ref. 19). In their study of the decomposition of the similar salt  $\text{O}_2^+\text{BF}_4^-$ , however, Kieth and co-workers inferred an initial equilibrium involving gaseous  $\text{O}_2\text{F}$  and  $\text{BF}_3$  (Ref. 20). One would expect similar behavior from the arsenic salt and indeed the data presented below confirm this hypothesis. In our experiments, the presence of  $\text{O}_2\text{F}$  downstream of the decomposing solid was monitored using its strong UV absorption near 210 nm. Chegodaev, et. al., have reported an  $\epsilon_{\text{max}}(\text{O}_2\text{F})$  of  $\sim 10^4 \text{ l mole}^{-1}\text{cm}^{-1}$  at  $\sim 206 \text{ nm}$  (Ref. 17). Among the gas phase species possibly produced by decomposition of the salt ( $\text{AsF}_5$ ,  $\text{O}_2\text{F}$ ,  $\text{O}_2$ ,  $\text{F}_2$ , and less probably  $\text{F}$  and  $\text{O}_2\text{F}_2$ ), only  $\text{O}_2\text{F}$  and  $\text{O}_2\text{F}_2$  have appreciable absorptions at the wavelength. Since  $\epsilon(\text{O}_2\text{F}) \gg \epsilon(\text{O}_2\text{F}_2)$  in this region (Ref. 17), only absorptions due to  $\text{O}_2\text{F}$  were observed in our experiments. The strength of the absorptions observed (for a given pressure increase

caused by decomposition of the salt) were roughly commensurate with the reported magnitude of the  $O_2F$  extinction coefficient.

Techniques for the generation of  $O_2F$  from  $O_2^+AsF_6^-$  and for the observation of its reactions with added species were developed in experiments performed prior to the beginning of this contract. The first such experiments involved the reaction of active nitrogen with  $O_2F$  (Ref. 21). One would expect the production of NF in this system via a highly exothermic process:

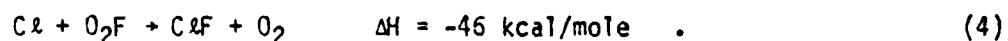


The most striking result of these experiments, however, was a dramatic enhancement (by a factor of 50 or more) of the  $N_2^*$  first positive ( $B^3\Pi_g \rightarrow A^3\Sigma_u^+$ ) emission when  $O_2F$  was present. The intensity distribution of the enhanced  $N_2^*$  emission was strongly shifted to the red relative to the normal Lewis-Rayleigh afterglow. Only very weak  $NF^*$  ( $b^1\Sigma^+ \rightarrow X^3\Sigma^-$ ) emission was observed. Deconvolution of the data to yield the steady state vibrational populations of the  $N_2^*$   $B^3\Pi_g$  state showed the results to be consistent with a mechanism in which reaction (2) above forms excited NF in the  $^1\Delta$  or  $b^1\Sigma^+$  states, which subsequently react with another nitrogen atom to form excited  $N_2$ :



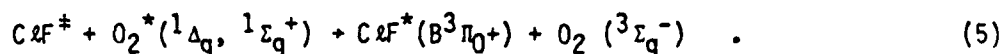
The weakness of the  $NF^*$  emission in this system argues that  $k_3 \gg k_2$ .

More detailed observations were made of the reaction of chlorine atoms with  $O_2F$  (Ref. 22). The initial reaction between these two species is insufficiently exothermic for direct production of the lowest lying excited electronic states ( $A^3\Pi_1$  or  $B^3\Pi_0^+$ ) of  $C\&F$ :



Although the energy of the  $C\&F$  A state is unknown, comparison to other interhalogens suggests that it would not be accessible by reaction (4). Indeed, no emission was evident in the experimental observation of the system, unless excited singlet molecular oxygen ( $O_2^* \ ^1\Delta_g, \ ^1\Sigma_g^+$ ) produced from a microwave discharge was also admitted to the flow. In this case, a bright orange flame was generated, the emission spectrum of which indicated the predominance of  $C\&F$   $B \rightarrow X$  transitions. These experiments represent the first observation of  $B \rightarrow X$  emission from the  $C\&F$  molecule. Due to the weakness of this transition, the only previous such data had been obtained from absorption studies using high pressures (hundreds of torr) and pathlengths up to 4 m (Ref. 23, 24). Analysis of the emission spectrum obtained in our experiments resulted in calculation of the most precise values of the molecular constants of the B and X states of  $C\&F$  currently available.

From the behavior of the system with respect to the added singlet oxygen, it was inferred that the excited  $C\&F$  was produced by a two step mechanism as follows:



Energy transfer processes analogous to reaction (5) have been previously suggested for other halogen and interhalogen systems (Ref. 2, 28). The identity of the intermediate  $\text{ClF}^\ddagger$  is unknown at present; it may be either a highly vibrationally excited ground state molecule or an electronically excited species in one of the metastable states of the  $^3\Pi$  manifold. The issue of the identity of this intermediate is addressed further by the data presented below.

The utility of  $\text{O}_2\text{F}$  in a potential laser system is a function of both the efficient production of excited species and the ability to generate sizable concentrations of the  $\text{O}_2\text{F}$  reagent. Hence, the program described below was divided into two basic tasks as follows:

1.  $\text{O}_2\text{F}$  Generation and Diagnostics. The goal of this task was the development of a calibrated and standardized source of  $\text{O}_2\text{F}$  to be used in reaction studies, and the determination of the lifetime of  $\text{O}_2\text{F}$  in the gas phase.
2. Reaction Survey. This task involved the analysis of chemiluminescence spectra and measurement of photon yields for the reactions of  $\text{O}_2\text{F}$  with atomic and molecular halogen and metal atoms.

After a number of iterations, a standardized  $O_2F$  cell was developed and the temporal behavior of the radical in the cell was determined. This apparatus was subsequently used for the observation of  $O_2F$  reactions producing electronically excited BrF and IF. A separate apparatus was constructed for metal +  $O_2F$  systems and it was subsequently used to observe reactions producing excited MgF and CaF. Chemiluminescence spectra and photon yields were measured for these reactions, and a number of new and unexpected results were obtained.

## II. $O_2F$ GENERATION AND DIAGNOSTICS

In the experiments noted above, the presence of gaseous  $O_2F$  downstream of the decomposing  $O_2^+AsF_6^-$  was inferred from the strong absorption by the radical of light in the vicinity of 210 nm. In the first part of our effort on this task, we obtained additional support for this inference by measurement of the UV absorption spectrum of the gas phase decomposition products of the salt. The cell used for these measurements was that previously used in the C&F experiments (described in detail in Reference 22), since it provides an absorption pathlength of ~20 cm.  $O_2F$  was generated at either end of the cell with the vacuum connection in the center. For the pressures used in the experiments, the residence time in the cell was less than 2 msec. The light source used was an Oriel deuterium lamp. An iris was placed in front of the lamp such that only a thin pencil of the relatively high intensity beam was admitted to the cell. The lamp transmission was measured using a 0.12 m Oriel monochromator with 500  $\mu$ m slits and an RCA IP28 photomultiplier tube whose response was monitored by a Kiethley 610B electrometer. The spectrum was obtained from comparison of the transmission with no heat applied to the  $O_2^+AsF_6^-$  reservoirs vs the transmission through a steady flow of decomposition products.

Five independent measurements of the spectrum were made, and all showed a broadband absorption peaking near 210 nm. No evidence of structure was observed within the resolution of the monochromator (~3.2 nm). Figure 1 shows a typical result as a plot of  $\log(I_0/I)$  vs wavelength. Also shown is

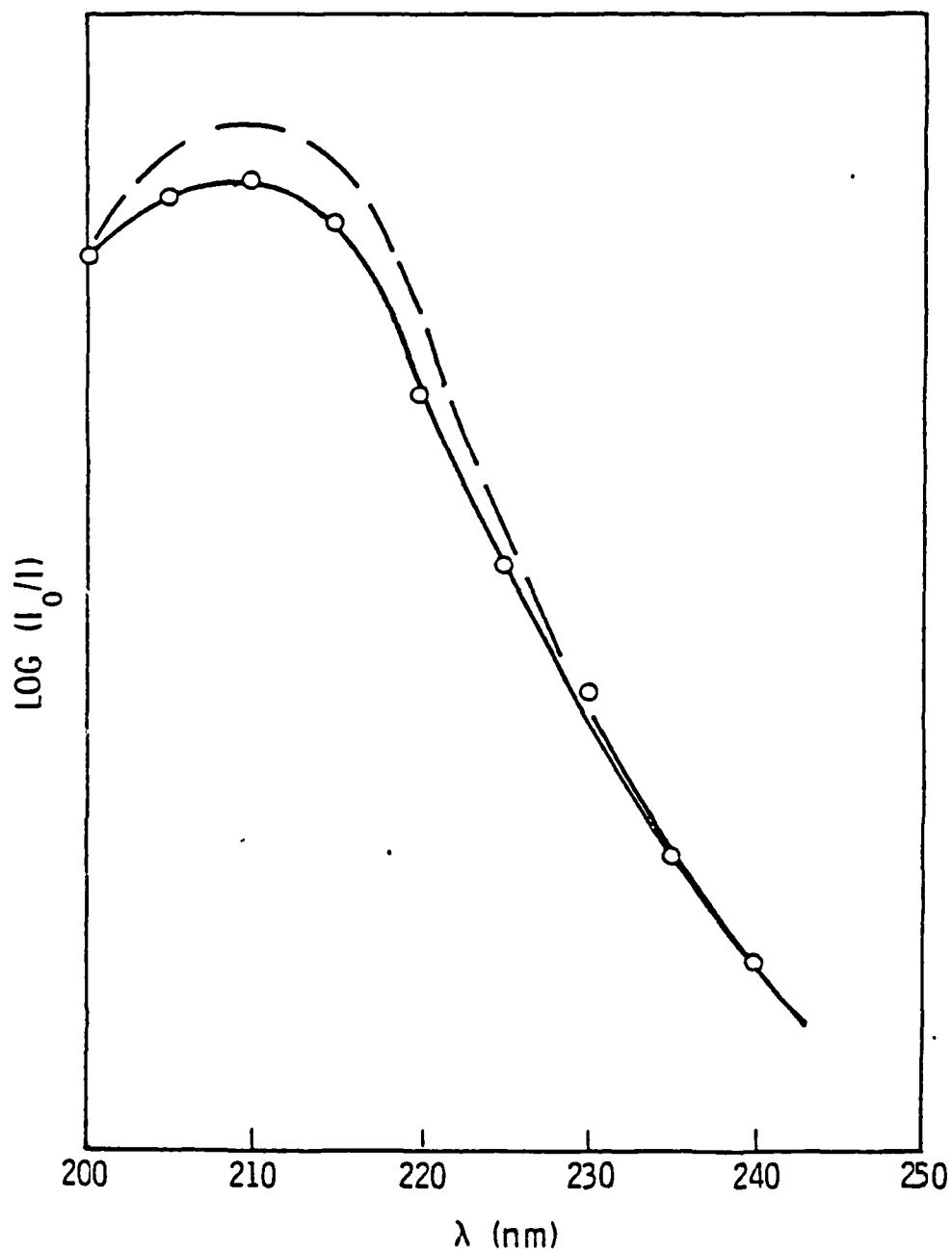


Figure 1. UV absorption spectrum of the gas phase products of the thermal decomposition of  $\text{O}_2^+\text{AsF}_6^-$  (solid line). The  $\text{O}_2\text{F}$  absorption spectrum reported in reference 17 is shown as a broken line.

the  $O_2F$  absorption spectrum obtained by Chegodaev, et. al., from the flash photolysis of  $RF + O_2$  mixtures (Ref. 17, 18). The two spectra, which have been normalized in the figure at 200 nm, clearly agree with one another. This is strong evidence that  $O_2F$  is in fact the species responsible for the absorption.

Accurate values of extinction coefficients could not be determined from our experiments due to the inexact pathlength and uncertainty in the  $O_2F$  concentration (some fraction of the radicals were undoubtedly removed on the walls of the 10 mm diameter vessel during transit). Assuming, however, an upper limit on the  $O_2F$  concentration equal to half the pressure rise caused by  $O_2^+AsF_6^-$  decomposition, the extinction coefficient at the maximum absorption (206 nm) is greater than  $5 \times 10^3 \text{ } \mu\text{mole}^{-1}\text{cm}^{-1}$ . The extinction coefficient reported from the  $RF + O_2$  photolysis experiments was  $\epsilon_{\text{max}} = 1 \times 10^4 \text{ } \mu\text{mole}^{-1}\text{cm}^{-1}$  (Ref. 17).

The authors of the flash photolysis studies reported that in their experiments the decay of  $O_2F$  could be described by a second order rate equation (Ref. 17, 26). A decay mechanism involving five elementary processes was proposed. Termolecular reactions were included since the experiments were carried out at pressures greater than 250 torr. The mechanism suggests that the second order behavior is brought about by a combination of first order effects rather than by an  $O_2F + O_2F$  elementary reaction, and the authors rule out the participation of a direct second order process. Consideration of the conditions of our experiments (pressures less than 1 torr and small  $O_2$  concentrations) reduces the mechanism to a two step decay as follows:





Hence, for a steady-state fluorine atom concentration, the mechanism would predict a simple first order decay dependent on the total pressure.

An alternative point of view is presented by Kieth, et. al. (Ref. 20), in their investigation of the thermal decomposition of dioxygenyl fluoroborate ( $O_2^+BF_4^-$ ), a species similar to the  $O_2^+AsF_6^-$  salt used in the present experiments. These authors' results suggest that this salt decomposes via an equilibrium with  $O_2F$  and  $BF_3$ , in accord with the present experiments:



An analysis of the kinetics of the formation of  $BF_3$  in the system was shown to be consistent with removal of  $O_2F$  from the equilibrium by a second order ( $O_2F + O_2F$ ) elementary process.

Measurement of the time decay of  $O_2F$  produced in our experiments requires that the concentration of the radical be measured simultaneously at individual points along the length of a flow tube. This requirement severely constrains the experimental apparatus, since the  $O_2F$  concentration and/or the absorption pathlength must be large enough to yield significant absorptions while the flow tube cross-sectional area must be small enough to maintain appropriate linear flow velocities. The apparatus developed for these experi-

ments is shown in Figure 2. The rectangular cell has internal dimensions 5.1 x 1.3 cm. The  $O_2^+AsF_6^-$  salt rests on two coarse fritted discs of ~1 cm diameter which are positioned in 1 cm tubes about 2.5 cm below (upstream of) the rectangular section of the cell. In the experiments,  $N_2$  was passed through the frits to carry the decomposition products of the  $O_2^+AsF_6^-$  into the flow stream.  $N_2$  was also added to the flow above the frits to increase the total pressure and linear velocity in the cell (see below). The entire cell, frit area, and  $N_2$  flow lines were heated using conventional heating tapes to cause decomposition of the salt and hence generation of  $O_2F$ . The walls of the rectangular cell were heated to prevent fogging.

$O_2F$  concentrations were monitored by measuring the absorption across the long dimension of the cell. For these experiments, the collimated output of an electrodeless  $I_2$  lamp (206.2 nm line) was split into three beams which were passed through the cell at positions spaced 3.8 cm apart. The intensities of the three beams were individually monitored by an array of IP28 photomultiplier tubes. The open aperture to each PMT was covered by a narrow band interference filter (Acton Research Corp.) centered at 210 nm. The responses of the detectors were simultaneously monitored by three electrometers and recorded on strip chart recorders.

The linear velocity of the flowing gases in the cell was calibrated vs pressure by passing  $N_2$  through the system via a Tylan FM-400 mass flowmeter. Pressures were monitored at either end of the rectangular cell using an MKS Baratron capacitance manometer (see Fig. 2). The measurements showed that

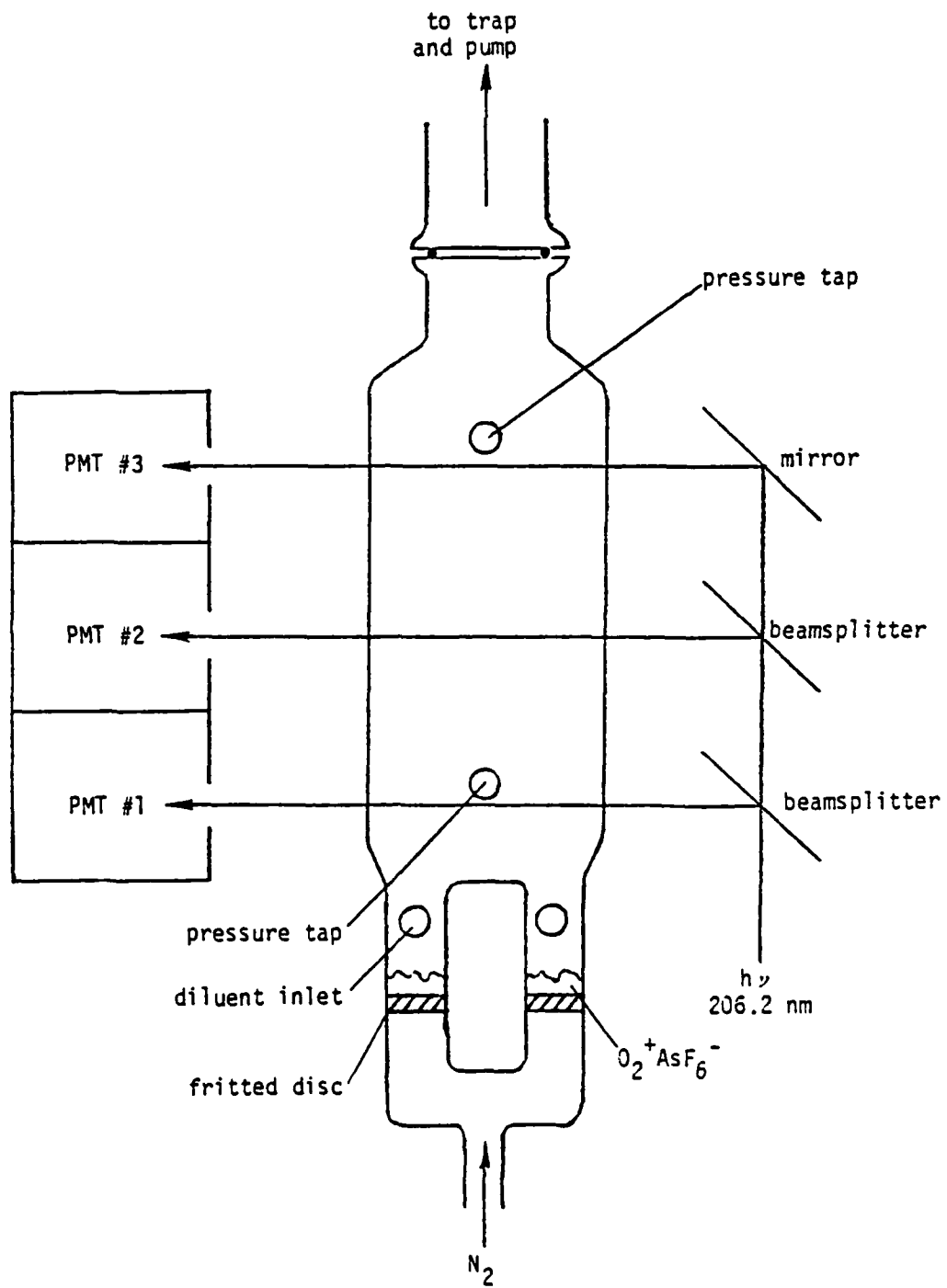


Figure 2. Apparatus used for measurement of the time decay of gas phase  $O_2F$ .

the pressure drop down the rectangular section was negligible. There was, however, a considerable variation of the linear velocity with pressure and hence the time between the points of the absorption measurement could be controlled by the amount of diluent added to the flow. For typical pressures used in the experiments, the time between each of the measurement points was 6 to 10 msec.

The  $O_2F$  concentration at each point was calculated from the measured absorption and the extinction coefficient reported in Reference 17,  $\epsilon_{206} = 1 \times 10^4 \text{ l mole}^{-1}\text{cm}^{-1}$ . The exact time separation of the measurements was determined from the total pressure. Since absorptions at all three points were continuously monitored in time, calculations were made for several times during a given experiment. Five such experiments were performed. There was some scatter in the data, resulting in a degree of uncertainty with regard to the order of the decay of  $O_2F$ . Many measurements were made, however, and in general the best agreement was obtained assuming a second order decay mechanism. Also, variations in the total pressure in the cell (by as much as 30%) were not reflected in the decay rates. Figure 3 shows a second order plot ( $[O_2F]^{-1}$  vs  $t$ ) for a typical experiment. In each case it was noted that measurements made during the rise of the absorption resulted in anomalously large slopes; more consistent results were obtained for the larger absorptions occurring later in the run.

Table I shows a compilation of all the values of  $k$  (23 results) for runs which gave measurable absorptions. In determining an average, 3 of the 23 values were rejected since their deviation from the mean of the remaining 20

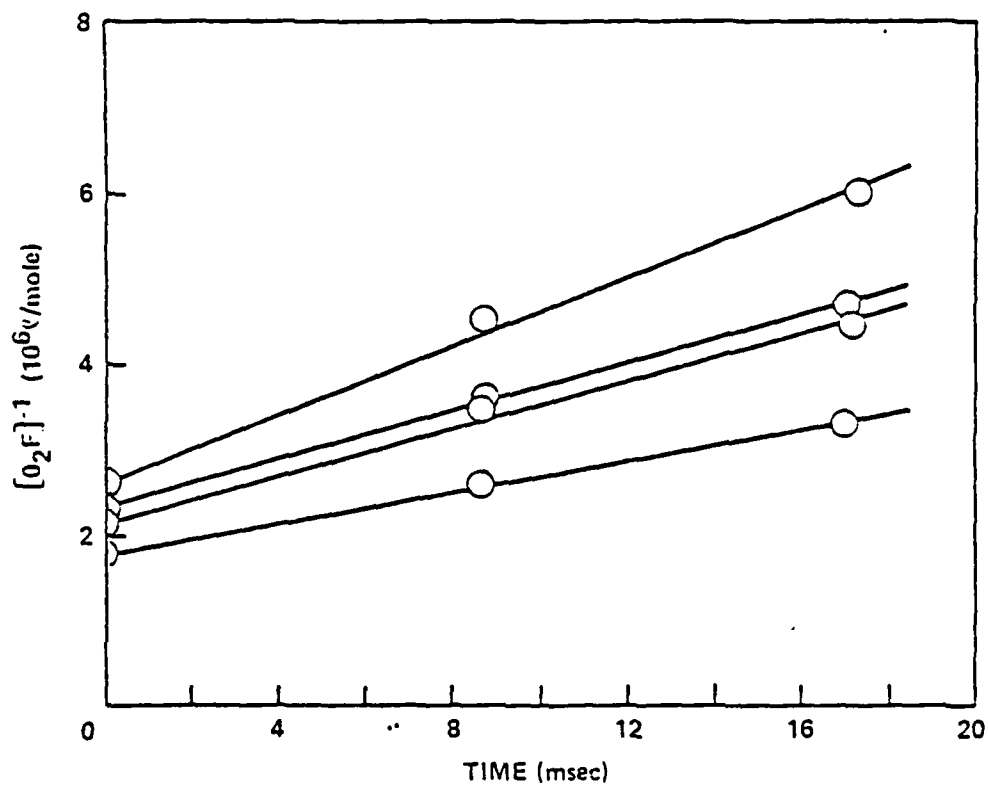


Figure 3. Second order plot of the time decay of  $O_2F$  for a particular run. Each of the lines represents data taken at a different time during the run.

TABLE I  
RATE CONSTANT FOR O<sub>2</sub>F SECOND ORDER REMOVAL

Run No.	T <sub>x</sub> (b)	k (cm <sup>3</sup> mole <sup>-1</sup> sec <sup>-1</sup> )
1B	T <sub>1</sub>	2.72 x 10 <sup>11</sup> (a)
	T <sub>2</sub>	2.00 x 10 <sup>11</sup>
	T <sub>3</sub>	1.43 x 10 <sup>11</sup>
	T <sub>4</sub>	1.38 x 10 <sup>11</sup>
	T <sub>5</sub>	0.94 x 10 <sup>11</sup>
2B	T <sub>2</sub>	1.25 x 10 <sup>11</sup>
	T <sub>3</sub>	0.94 x 10 <sup>11</sup>
	T <sub>4</sub>	0.99 x 10 <sup>11</sup>
	T <sub>5</sub>	0.88 x 10 <sup>11</sup>
5B	T <sub>2</sub>	2.50 x 10 <sup>11</sup> (a)
	T <sub>3</sub>	1.77 x 10 <sup>11</sup>
	T <sub>4</sub>	1.40 x 10 <sup>11</sup>
	T <sub>5</sub>	1.70 x 10 <sup>11</sup>
5D	T <sub>1</sub>	1.63 x 10 <sup>11</sup>
	T <sub>2</sub>	1.34 x 10 <sup>11</sup>
	T <sub>3</sub>	1.00 x 10 <sup>11</sup>
	T <sub>4</sub>	1.44 x 10 <sup>11</sup>
	T <sub>5</sub>	2.00 x 10 <sup>11</sup>
	T <sub>6</sub>	2.75 x 10 <sup>11</sup> (a)
5E	T <sub>1</sub>	1.31 x 10 <sup>11</sup>
	T <sub>2</sub>	1.19 x 10 <sup>11</sup>
	T <sub>3</sub>	1.13 x 10 <sup>11</sup>
	T <sub>4</sub>	1.25 x 10 <sup>11</sup>

$\langle k \rangle = 1.4 \pm 0.4 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$

- a. Values not included in final average (see text).
- b. T<sub>x</sub> indicate measurements made at different times during a given run.

points was greater than 4 times the average deviation of those points. The resultant value of  $k$  is  $1.4 \pm 0.4 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ .

The observed second order decay could result from an  $O_2F + O_2F$  reaction, or from the removal of  $O_2F$  by  $AsF_5$  via an equilibrium analogous to process (8) above:



This latter possibility seems unlikely, however, since the entire cell was heated well beyond the observation zone and there was no evidence of re-deposited  $O_2^+AsF_6^-$  solid downstream of the reservoirs. Hence, the present results suggest that either some discrepancy exists between the flash photolysis and thermal decomposition results, or that the decay mechanisms in these experiments are fundamentally different from one another.

Since the half-time of a second order process is given by  $t_{1/2} = (kC_0)^{-1}$ , an initial concentration of  $\sim 150$  mtorr of  $O_2F$  would decay to half its value in  $\sim 1$  msec. Hence,  $O_2F$  would appear to be a suitable reagent for use in moderate to high gain laser systems. It is likely not to be useful, however, for low gain systems requiring concentrations of excited species greater than  $10^{16}$  molecules/cm<sup>3</sup>.

### III. REACTION SURVEY

#### 1. Reactions Producing Excited BrF

As noted in the discussion above, halogen monofluorides are among the most promising of all diatomic fluorides with respect to their potential for sustaining lasing in the visible and near IR regions of the spectrum. Hence, the reactions of  $O_2F$  with halogen atoms were among the first that we chose to study.

In contrast to the  $CF$  case discussed above, a wealth of spectroscopic data exists concerning the  $B \rightarrow X$  transitions in  $BrF$  and  $IF$ . Detailed studies of these transitions involving chemiluminescence (Ref. 25, 27), absorption (Ref. 28, 29), and laser induced fluorescence (Ref. 30, 31) techniques have been published by a number of authors. In addition, observations of the  $A(^3\Pi_1) \rightarrow X(^1\Sigma^+)$  transition have been reported for both  $BrF$  (Ref. 29) and  $IF$ , (Ref. 2) although the  $BrF$  measurement has been the subject of some controversy (Ref. 32) and has not been reproduced. In view of the existence of this large body of spectroscopic information, the primary thrust of the present experiments was directed toward the nature and efficiency of the mechanisms producing the excited species. The results obtained, however, clearly demonstrated the potential of the  $O_2F$  reactions for producing detailed spectroscopic information.

Observations of  $O_2F$  reactions using the cell developed for absorption measurements (Fig. 2) required modifications to be made for rapid mixing of the reagents. The modified cell is shown in Figure 4. Reagents were added to

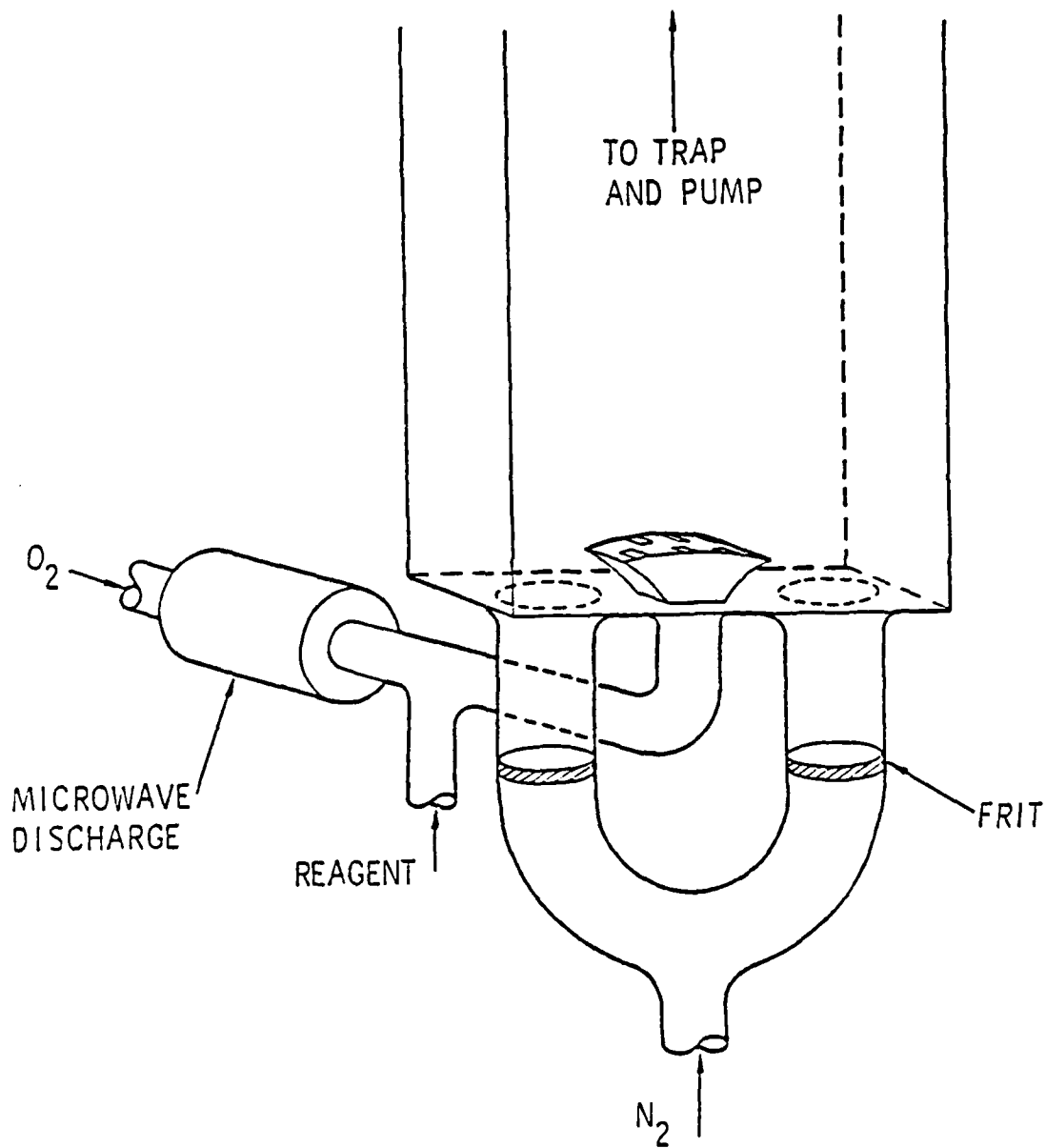


Figure 4. Modified apparatus (see Figure 2) used for observation of the reactions of  $O_2F$  with added gases.

the cell through a wedge shaped injector positioned between the two  $O_2F$  entry ports. The injector incorporated an array of slots through which reagents passed into the stream. Visual inspection of flames produced in the cell indicated that this arrangement resulted in rapid mixing. Emissions from within the cell were dispersed by a McKee-Pederson 0.5 m monochromator and detected by a photon counting apparatus consisting of a cooled RCA C31034 photomultiplier tube, a PAR-1120 amplifier-discriminator, and an SSR-1110 counting unit. The entrance slit of the monochromator was positioned such that the cone of sight passed through the short (1.3 cm) dimension of the cell directly over the reagent injector. The time duration of flames produced in the cell was monitored by an array of three RCA IP28 photomultiplier tubes positioned along the length of the cell.

BrF experiments were performed by adding a mixture of  $Br_2$  in Argon ( $\sim 10$  mtorr) to a stream of diluent oxygen ( $\sim 250$  mtorr) just upstream of the cell, as shown in Figure 4. Liquid  $Br_2$  was purified by multiple freeze-pump-thaw cycles at 196 K and the mixture with argon (Matheson U.H.P., 99.999%) was prepared in a 35 l vessel prior to use in the experiments. The mixture contained  $\sim 19\%$   $Br_2$ . Addition of these gases to  $O_2F$  generated in the cell ( $< 15$  mtorr) produced a very faint luminescence which was barely visible to the eye. The spectrum of this emission (recorded at the detection limits of our apparatus) showed it to be due to  $B(3\Pi_0^+) \rightarrow X(1\Sigma^+)$  transitions in BrF. Experiments were also performed in which the  $O_2$  was passed through an 80 W microwave discharge prior to mixing with the  $Br_2$ . In this case, bromine atoms are produced quantitatively by the rapid reactions (Ref. 33)



These experiments produced an extremely intense yellow emission which was clearly visible in the lighted room. A low resolution scan of the yellow emission, shown in Figure 5, indicated that it was also due to BrF B  $\rightarrow$  X transitions.

The yellow flame was well-defined and decayed within 3 cm of the injector, corresponding to a decay time  $\tau < 5$  msec. For a typical flow velocity of  $\sim 600$  cm sec<sup>-1</sup>, the time frame of B(<sup>3</sup> $\pi_0^+$ ) spontaneous emission ( $< 40$  usec)<sup>1</sup> is such that the average excited molecule travels less than 0.3 mm before radiating. Hence the observed decay time ( $\sim 3$  cm) must be due to the processes which limit formation of the excited species (e.g., mixing and the finite reaction rate). Given that the O<sub>2</sub>F concentration in these experiments was less than  $5 \times 10^{14}$  molecules cm<sup>-3</sup>, the decay time sets a lower limit on the formation rate of  $k > 2 \times 10^{11}$  cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup>. Hence the data indicate that excited BrF is produced by rapid bimolecular processes rather than by three-body recombination. Recombination processes occurring in our cell at comparable pressure were observed to yield flames lasting for many msec (extending well beyond the cell and into the trap). The BrF flame exhibited a sharp intensity peak with respect to the Br<sub>2</sub>/Ar flowrate. The peak intensity was many times (two or three orders of magnitude) greater than that produced by the similar C<sub>2</sub>-O<sub>2</sub>F-O<sub>2</sub>\* reaction. The BrF flame was completely quenched at Br<sub>2</sub>

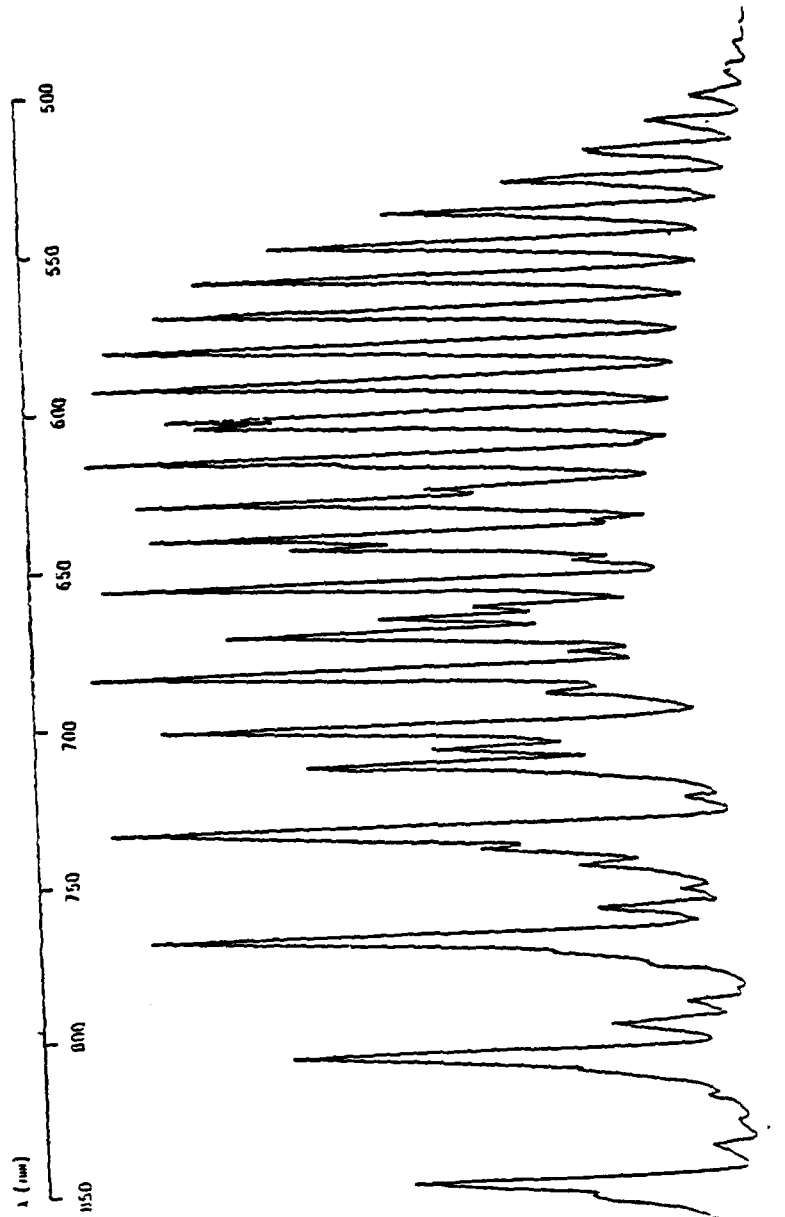


Figure 5.  $\text{BrF } B(3\pi_0^+) \rightarrow X(1\Sigma^+)$  emission spectrum.

flowrates only slightly greater than that which yielded the brightest flame. This behavior is consistent with the observations by Clyne and McDermid that BrF  $B(3\Pi_0^+)$  is quenched efficiently by collisions with either  $Br_2$  or ground state BrF (Ref. 34).

The BrF emission spectrum was recorded using the photon counting apparatus described above. Scans of the spectrum were made at 5 nm per minute with a counting interval usually less than 0.1 sec and a slitwidth of 100  $\mu$ m. Eight scans were made, covering the region 450 nm to 900 nm. The spectrum consisted of 63 red-degraded bands, all of which could be assigned to  $B(3\Pi_0^+) \rightarrow X(1\Sigma^+)$  transitions in BrF. Well resolved rotational structure was observed in many of the bands, and the  $^{79}BrF$ - $^{81}BrF$  isotope splitting was resolved for 22 bands of the long wavelength side of the spectrum. No previously unreported bands were observed, however, and no bands corresponding to possible  $A(3\Pi_1) \rightarrow X(1\Sigma^+)$  transitions were present in the spectrum. In general, the data agree well with the spectrum reported by Clyne and co-workers for BrF produced by recombination in the presence of excited singlet oxygen (Ref. 25). There were, however, some notable differences in the frequencies of bands occurring at longer wavelengths. Clyne et al., did not resolve the isotope splitting for these bands, and suggested that the measured frequencies probably corresponded most closely to transitions in  $^{79}BrF$ . Our data show that a number of the frequencies reported by these authors actually correspond to  $^{81}BrF$  bands. Since the isotope splittings for the longer wavelength bands have not been previously reported, we have compiled these frequencies in Table II. Also shown are calculated values for the splittings ( $\Delta\nu$ ) using the theoretical value of

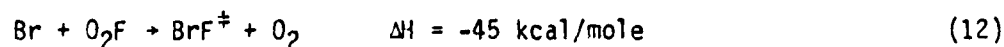
TABLE II  
OBSERVED ISOTOPE SPLITTINGS IN THE  
BrF B( $^3\Pi_0^+$ )  $\rightarrow$  X( $^1\Sigma^+$ ) EMISSION SPECTRUM<sup>a</sup>

Band	$^{79}\text{BrF}$	$^{81}\text{BrF}$	$\Delta\nu$	$\Delta\nu_{\text{calc}}^b$
0,4	15517 $\pm$ 2	15522 $\pm$ 2	5 $\pm$ 2	6.6
1,5	15252 $\pm$ 2	15259 $\pm$ 2	7 $\pm$ 2	7.3
4,7	15052 $\pm$ 2	15063 $\pm$ 2	9 $\pm$ 2	7.7
0,5	14883 $\pm$ 2	14893 $\pm$ 2	10 $\pm$ 2	8.1
1,6	14629 $\pm$ 2	14636 $\pm$ 2	7 $\pm$ 2	8.7
0,6	14259 $\pm$ 2	14269 $\pm$ 2	10 $\pm$ 2	9.6
1,7	14013 $\pm$ 2	14021 $\pm$ 2	9 $\pm$ 2	10.2
0,7	13642 $\pm$ 2	13654 $\pm$ 2	12 $\pm$ 2	10.2
3,9	13510 $\pm$ 4	13521 $\pm$ 4	11 $\pm$ 4	11.4
1,8	13408 $\pm$ 4	13417 $\pm$ 4	9 $\pm$ 4	11.7
2,9	13157 $\pm$ 2	13170 $\pm$ 2	13 $\pm$ 2	12.2
0,8	13032 $\pm$ 2	13044 $\pm$ 2	12 $\pm$ 2	12.5
4,11	12666 $\pm$ 2	12680 $\pm$ 2	14 $\pm$ 2	13.4
2,10	12568 $\pm$ 2	12581 $\pm$ 2	13 $\pm$ 2	13.7
0,9	12435 $\pm$ 2	12448 $\pm$ 2	13 $\pm$ 2	14.0
1,10	12212 $\pm$ 3	12227 $\pm$ 3	15 $\pm$ 3	14.5
4,12	12094 $\pm$ 3	12106 $\pm$ 3	12 $\pm$ 3	14.8
2,11	11986 $\pm$ 2	12000 $\pm$ 2	14 $\pm$ 2	15.1
0,10	11844 $\pm$ 2	11858 $\pm$ 2	14 $\pm$ 2	15.4
3,12	11760 $\pm$ 3	11774 $\pm$ 3	14 $\pm$ 2	15.6
1,11	11629 $\pm$ 3	11644 $\pm$ 3	15 $\pm$ 2	16.0
0,11	11260 $\pm$ 2	11275 $\pm$ 2	15 $\pm$ 2	16.8

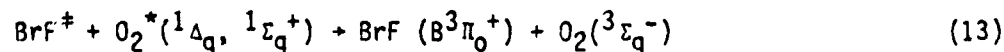
a. Frequencies reported in vacuum wavenumbers.  
b. Splittings calculated using  $\rho = 0.9976$ .

$\rho = [\mu(^{79}\text{BrF})/\mu(^{81}\text{BrF})] = 0.9976$ . The agreement is generally good (note that systematic contributions to the uncertainties of the transition frequencies do not apply to the splittings). Calculation of  $\rho$  from the sum of the data as in Reference 22 yields  $\rho = 0.9977$ , in good agreement with the theoretical value.

It seems likely that the mechanism responsible for production of excited BrF in the Br-O<sub>2</sub>F-O<sub>2</sub><sup>\*</sup> system is the same as that which has been proposed for ClF (B<sup>3</sup>π<sub>0</sub><sup>+</sup>) formation in the Cl-O<sub>2</sub>F-O<sub>2</sub><sup>\*</sup> system (Ref. 22). As in the ClF case, the initial reaction between bromine atoms and O<sub>2</sub>F is insufficiently exothermic for direct production of either the A(<sup>3</sup>π<sub>1</sub>) or B(<sup>3</sup>π<sub>0</sub><sup>+</sup>) states of BrF:



Here we have assumed the O-F bond strength in O<sub>2</sub>F to be about 15 kcal/mole (Ref. 13, 14). We postulate that reaction (12) forms an excited intermediate BrF<sup>‡</sup> which is subsequently pumped to the B state by collisions with singlet oxygen:



The efficiency with which the B state is formed may be a strong function of the nature of BrF<sup>‡</sup>. If it is a vibrationally excited species, the fraction pumped to the B state will be determined to some extent by the initial distribution among vibrational levels and the speed at which these excited levels

relax. It seems likely that in this case the fractional production of the B state will be low. If, on the other hand, the intermediate is an excited electronic state formed preferentially because of some dynamic constraint on the reaction, the efficiency for production of the B state may be quite high. One such state might be the metastable  $^3\Pi_2$  state.

We have probed this possibility by measuring the photon yield of the  $\text{Br-O}_2\text{F-O}_2^*$  reaction. For these measurements, calibrations of the light collection efficiency of our apparatus were made using the well known  $\text{O} + \text{NO}$  reaction as a chemical actinometer. For this system, the absolute rate constant for production of photons is known from the work of Fontijn and co-workers (Ref. 35) (as well as a number of other authors (Ref. 36)). Hence, we may define a parameter  $\alpha$  which when multiplied by the measured intensity (counts/time) equals this rate:

$$\alpha I = kf[\text{O}][\text{NO}] \quad (14)$$

Here  $k$  is the constant determined by Fontijn, et. al., and  $f$  is the fraction of the total  $\text{NO}_2^*$  spectral output that is monitored. For example, if the monochromator were set at a particular wavelength with a particular bandpass,  $f$  would be the fraction of the  $\text{NO}_2^*$  emission passed by the slit. Since the absolute intensity distribution of the  $\text{NO}_2^*$  emission is known,  $f$  can be calculated easily. In our experiments, emissions were observed from scans over a large wavelength region. This procedure is the same, however, as collecting light through a bandpass equal to the region scanned for a time

equal to that necessary to scan one actual bandpass. Hence, equation (14) can still be applied.

For the measurement of  $\alpha$ , the concentrations of O and NO were determined using calibrated mass flowmeters and standard titration techniques (Ref. 37), NO<sub>2</sub> photons were counted for scans from 450 nm to 850 nm (the wavelength region of the BrF flame), at 50 nm/minute with 250  $\mu$ m slits. Since in this case the bandpass is  $\sim$ 0.8 nm, this is the same as counting for 0.96 seconds with a 400 nm bandpass. Determinations of  $\alpha$  were made for different O and NO concentrations, yielding an average value  $\alpha = 1.0 \pm 0.1 \times 10^7$  photons  $\text{cm}^{-3}\text{sec}^{-1} \div$  counts  $\text{sec}^{-1}$ .

The BrF B  $\rightarrow$  X flame was generated as described above and the intensity scanned for conditions identical to those employed in the NO<sub>2</sub> calibrations. The absolute flowrate of the Br<sub>2</sub>/Ar mixture was measured using a calibrated mass flowmeter. The partial pressure of O<sub>2</sub>F generated in the cell was known from absorption measurements, and the flowrates of Br<sub>2</sub> used were such that O<sub>2</sub>F was in large excess. The measured photon yield ( $\phi$ ) is defined as the ratio of the rate of production of photons by the reaction to the flowrate of the limiting reagent (in this case, bromine atoms). Hence,

$$\phi = \frac{\alpha \int_{\nu} I(\nu) d\nu}{F} \quad (15)$$

where  $F$  is the bromine atom flowrate and the integral represents the intensity integrated over the flame volume. The value of the integral was estimated from the measured intensity and the shape and time duration of the flame.

The results of the measurements are presented in Figure 6 as a plot of  $\phi$  vs the bromine atom flowrate. We have assumed that the atom flowrate is twice that of  $\text{Br}_2$ , i.e., that all the  $\text{Br}_2$  is dissociated by reactions (10) and (11). The data show that the yield decreases with increasing bromine flow. This result agrees with the quenching behavior observed in our experiments and in Reference 34. The limiting photon yield (extrapolated to zero bromine flow) is  $\sim 2 \times 10^{-3}$ . We note that this is probably an underestimation of the true yield given the assumptions that all the  $\text{Br}_2$  is dissociated (and remains so) and all Br atoms are removed only by  $\text{O}_2\text{F}$ .

These results suggest that the  $\text{Br-O}_2\text{F-O}_2^*$  system is probably not a viable laser candidate. The 0.2% photon yield suggests that the system is not strongly constrained to form electronically excited states, in qualitative agreement with the suggestion that the initial reaction ( $\text{Br} + \text{O}_2\text{F}$ ) produces vibrationally excited ground state molecules. In this case a broad range of vibrational states would probably be formed, only a small percentage of which would have sufficient energy to be pumped to the B state by collisions with  $\text{O}_2^*$ .

It is difficult to explain the production of  $\text{BrF B}(^3\Pi_0^+)$  by the reaction of molecular bromine with  $\text{O}_2\text{F}$ . It is possible that the dim flame observed results from reaction between  $\text{Br}_2$  and  $\text{F}_2$  produced by the decay of  $\text{O}_2\text{F}$ .  $\text{BrF B} + \text{X}$  emission has been observed from flames of  $\text{Br}_2$  burning in  $\text{F}_2$  (Ref. 38). Our

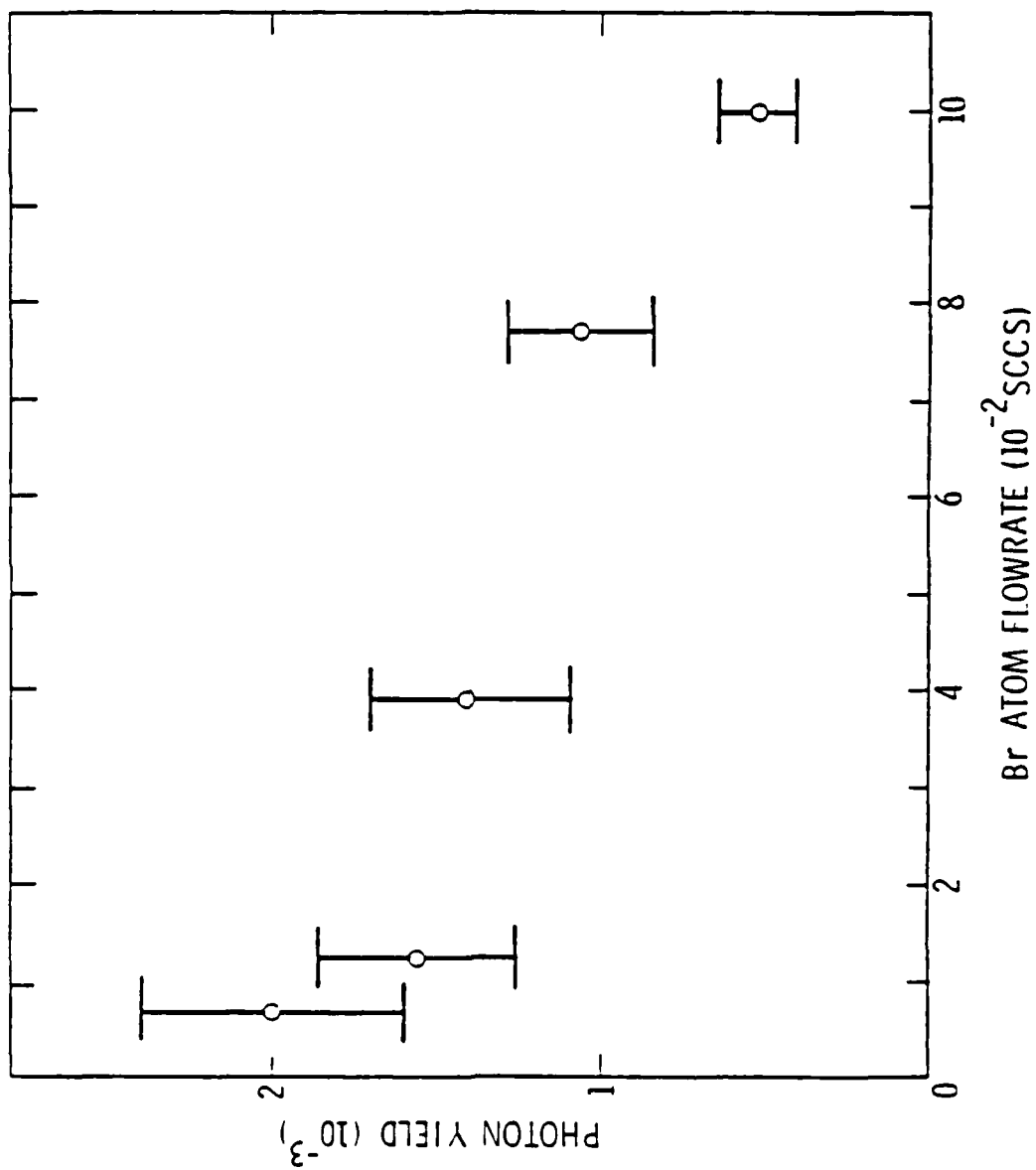


Figure 6.  $\text{BrF Br}(\text{}^3\text{I}_{1,+}) \rightarrow \text{X}(\text{}^1\Sigma^+)$  photon yield vs. Br atom flowrate for the  $\text{Br} + \text{O}_2\text{F} + \text{O}_2^*$  reaction.

observations of analogous reactions producing excited IF offer some further insight regarding this point (see below).

## 2. Reactions Producing Excited IF

Lasers based on electronic transitions in IF would have inherently higher gains than those based on BrF, since the transition probabilities for the IF  $A \rightarrow X$  and  $B \rightarrow X$  transitions should be significantly greater than those for BrF. In addition, the density of rotational and vibrational states is lower for IF. IF is particularly interesting with regard to  $O_2F$  reactions since the  $A(^3\Pi_1)$  state can be produced directly by the  $I + O_2F$  reaction:



The energy of the  $A(^3\Pi_1)$  state (48 kcal above the ground state) has been well established in this case by the chemiluminescence experiments of Birks, et al. (Ref. 2). Clyne and co-workers have suggested that IF  $A(^3\Pi_1)$  molecules formed by atom recombination may be pumped to the B state by singlet molecular oxygen (among other possible explanations for their results) (Ref. 25). The pumping mechanism of the  $I-O_2F-O_2^*$  reaction may therefore be fundamentally different from the mechanism of the analogous bromine reaction, possibly resulting in a higher photon yield for the  $B \rightarrow X$  transition.

ICl<sub>2</sub> was chosen as the source of iodine atoms for our initial experiments on the  $I + O_2F$  reaction. The apparatus used and the procedures followed were similar to those employed in the BrF experiments. The ICl<sub>2</sub> (PCR) was

purified by degassing at 77K followed by distillation into a trap at 196K. As with  $\text{Br}_2$ , a mixture with argon was prepared in a 35 l vessel (3%  $\text{ICl}_2$ ). The  $\text{ICl}_2/\text{Ar}$  mixture was added to a stream of microwaved oxygen such that I and Cl atoms were both produced (Ref. 25, 39). Hence the reaction mixture included I, Cl,  $\text{O}_2^*$ ,  $\text{O}_2\text{F}$  and probably  $\text{I}^*(5^2\text{P}_{1/2})$  produced by resonant energy transfer from  $\text{O}_2^*(1^1\Delta_g)$  (Ref. 40). The reaction produced a yellow-green flame consisting primarily of IF B  $\rightarrow$  X transitions, with a broadband peak intensity about an order of magnitude less than that obtainable from the BrF system. The weakness of the flame suggested that only a small fraction of the iodine atoms actually reached the reaction zone. Iodine atoms are known to recombine rapidly on surfaces (Ref. 41), and reactions producing iodine oxides have been observed to generate solid wall coatings (Ref. 42). In fact, considerable coating of the vessel walls was noted in these experiments. Hence a photon yield was not measured for this flame since the flowrate of iodine atoms that actually react with  $\text{O}_2\text{F}$  was unknown.

As in the BrF case, the reaction was observed to produce a flame without the assistance of a microwave discharge through  $\text{O}_2$ . The flame produced by mixing molecular  $\text{ICl}_2$  with  $\text{O}_2\text{F}$  was considerably weaker (perhaps by an order of magnitude) than the emission described above but it was still easily visible and many times more intense than its  $\text{Br}_2 + \text{O}_2\text{F}$  counterpart. As in the  $\text{Br}_2$  case, such emission might be produced by an  $\text{ICl}_2\text{-F}_2$  interaction ( $\text{F}_2$  being generated by the decay of  $\text{O}_2\text{F}$ ) analogous to the well known  $\text{I}_2 - \text{F}_2$  flame. This hypothesis was disproven, however, by an experiment in which  $\text{O}_2\text{F}$  was replaced by a stream of  $\text{F}_2:\text{N}_2 = 1:1$ . For  $\text{ICl}_2$  pressures comparable to those used in the

$O_2F$  experiments, the  $F_2$  partial pressure was varied between 10 and 65  $\mu$ torr. A very dim flame resulted, with an intensity no greater than 2% of that produced by  $ICl + O_2F$ . Hence the  $ICl - O_2F$  flame is in fact due to interactions between these two species.

Similar results were obtained from reactions of  $O_2F$  with  $I_2$  and  $HI$ . A stream of gaseous  $I_2$  was obtained from a saturator in which  $N_2$  (Airco, 99.999%) was passed through a bed of solid  $I_2$  (Malinckrodt). The pressure in the saturator was held at  $\sim 92$  torr. Hence, at the normal ambient temperature (293K) the stream contained  $\sim 0.3\%$   $I_2$ .  $HI$  (Matheson) was purified by fractional condensation at 273K and 77K. A mixture in argon ( $HI \approx 12\%$ ) was prepared in a 3L vessel. The reaction of  $I_2$  with  $O_2F$  produced a flame whose intensity was approximately eight times greater than that produced by an equivalent amount of  $ICl$ . The peak intensity of the  $HI + O_2F$  flame was comparable to that produced by  $I_2 + O_2F$ . The flame duration was short ( $\tau < 5$  msec) in each case, again indicating production rates greater than  $10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ . For the  $ICl$  and  $I_2$  systems, comparisons were made with the analogous flames produced by reactions with  $F_2$ . The  $ICl-F_2$  flame was very weak as noted above. The  $I_2 - F_2$  flame was brighter and extended through the entire body of the cell, having the visual appearance of a recombination reaction. The  $I_2 - O_2F$  flame was approximately ten times more intense in the observation zone than was the  $I_2 - F_2$  flame at comparable pressures. These findings indicate that the rates of production of excited species by the  $O_2F$  reactions are much more rapid than in the  $F_2$  analogues.

Spectra of the emissions produced by the reactions of  $O_2F$  with the three iodides were recorded as described above. Each of the systems was observed to yield virtually the same emission spectrum, consisting of a combination of  $A(^3\Pi_1) \rightarrow X(^1\Sigma^+)$  and  $B(^3\Pi_0^+) \rightarrow X(^1\Sigma^+)$  transitions in IF. Although the relative proportions of  $A \rightarrow X$  and  $B \rightarrow X$  emissions varied somewhat between the different reactions, the bands present and their relative intensities were unchanged. This result suggests that excited IF is produced by some process common to all three systems. Normally the most intense  $A \rightarrow X$  bands were about half the strength of the  $B \rightarrow X$  features. A portion of the spectrum showing bands of both transitions is shown in Figure 7. In view of the probable difference between the radiative lifetimes of the two states (the A state should have a longer lifetime by perhaps as much as two orders of magnitude (Ref. 2)), it would seem that the large majority of the electronically excited IF is produced in the  $A(^3\Pi_1)$  state. Emission from this state has been reported only once, from the experiments of Birks, et. al., on the  $I_2 - F_2$  flame at low pressure (Ref. 2). Our spectrum of the  $I_2 - O_2F$  reaction contained most of the  $A \rightarrow X$  bands observed by Birks and nine additional bands which have not been previously reported. The frequencies of bands observed in our experiments are presented in the form of a Deslandres table shown in Table III. The data were fitted directly using a multiple regression analysis as described in Reference 22, yielding the following values for the constants of the  $A(^3\Pi_1)$  state:  $\nu_e = 15696 \pm 6 \text{ cm}^{-1}$ ,  $\omega_e = 378.6 \pm 2.6 \text{ cm}^{-1}$ ,  $\omega_e x_e = 3.4 \pm 0.6 \text{ cm}^{-1}$ ,  $\omega_e y_e = -0.02 \pm 0.03 \text{ cm}^{-1}$ . These values are in reasonable agreement with those calculated in Reference 2.

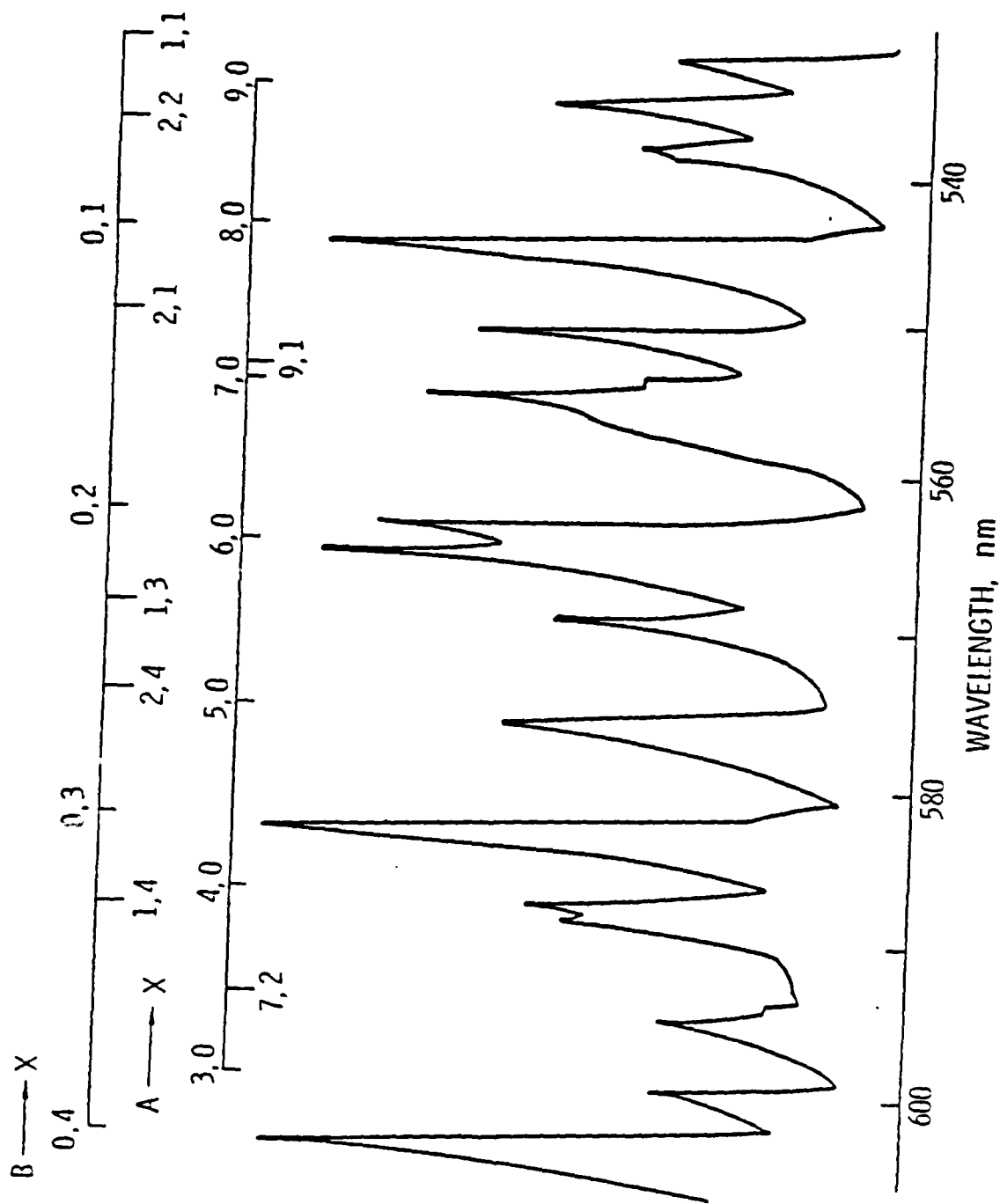


Figure 7. A portion of the emission spectrum obtained from the  $I_2+O_2F$  reaction showing bands of both the  $B(3/2g^+) \rightarrow X(1/2g^+)$  and  $A(3/2g^+) \rightarrow X(1/2g^+)$  transitions.

TABLE III

DES LANDRES TABLE FOR IF  $A(^3\Pi_1) \rightarrow X(^1\Sigma^+)^a$ 

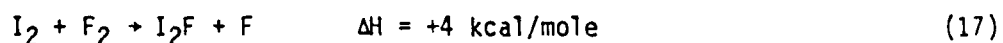
$v, v''$	0	1	2	3
0	[15582] (603)	14979 $\pm$ 3 (597) (371)	14382 $\pm$ 2 (370)	
1	b	15350 $\pm$ 5 (598) (364)	14752 $\pm$ 4	
2	16317 $\pm$ 6 (603) (356)	15714 $\pm$ 5 (364)		
3	16673 $\pm$ 3 (595) (352)	16078 $\pm$ 3 (348)		14881 $\pm$ 6
4	17025 $\pm$ 3 (599) (346)	16426 $\pm$ 6		
5	17371 $\pm$ 3 (336)		16167 $\pm$ 3 (585) (336)	[15582]
6	17707 $\pm$ 3 (326)		16503 $\pm$ 7 (333)	
7	18033 $\pm$ 6		16836 $\pm$ 6	
8	b	b		
9	18666 $\pm$ 4 (604) (304)	18062 $\pm$ 3		
10	18970 $\pm$ 4 (300)	b		
11	19270 $\pm$ 8			

a. Frequencies reported in vacuum wavenumbers.

b. Obscured by  $B(^3\Pi_0^+) \rightarrow X(^1\Sigma^+)$  bands.

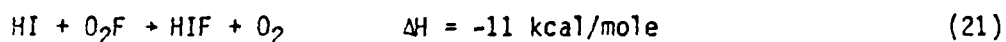
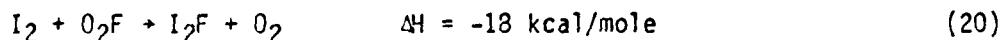
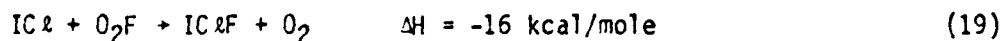
Photon yields were measured as described above for the reactions of  $O_2F$  with  $I_2$  and  $HI$ . The yields for these reactions were found to be more than an order of magnitude lower than for the  $Br-O_2F-O_2^*$  system for comparable limiting flowrates. In both cases the yields exhibited a very strong dependence on the iodide flowrate, indicating quenching by these species or by a reaction product. The yields rose so rapidly with decreasing reagent flowrates that it proved impossible to define a zero pressure limit with any certainty. The data suggested that this limit could be as high as  $\phi = 10^{-3}$ , however. This behavior is consistent with generation of the  $A(^3\Pi_1)$  state as the primary excited emitter in these reactions. The longer radiative lifetime of this state should make it much more susceptible to quenching than the  $B(^3\Pi_0^+)$  state.

The reactions of  $O_2F$  with  $ICl$ ,  $I_2$ , and  $HI$  can be understood to some extent by consideration of the mechanism currently accepted for the  $I_2 - F_2$  reaction. This reaction is thought to proceed as follows: (Ref. 43, Ref. 31).



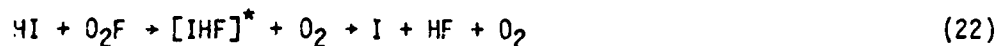
The stable  $I_2F$  intermediate has been observed in molecular beam studies of the reaction by Coggiola and co-workers (Ref. 43). Similar triatomic complexes were found for the reactions of  $F_2$  with  $ICl$  and  $HI$ . In all three cases, formation of the complex is substantially endothermic and hence should be slow (limiting the rate of production of excited  $IF$ ). The analogous processes

involving  $O_2F$  are all exothermic:



Hence these reactions may be expected to be much more rapid than their  $F_2$  counterparts, in accord with the results of our experiments.

Although the formation of triatomic complexes by the  $RI + O_2F$  reactions is consistent with the rapidity of these processes, subsequent reaction of any of the three complexes with  $O_2F$  (analogous to reaction 18 above) is not sufficiently energetic to produce the excited states of  $IF$  observed in our experiments. The reaction of  $O_2F$  with the  $IClF$  complex should not liberate enough energy to populate even the lowest levels of the  $A(^3\Pi_1)$  state of  $IF$ . Excited  $IF$  could be produced by a reaction of the complexes with fluorine atoms as in reaction (18), but the existence of free fluorine atoms in our system is unlikely given the large excess of  $O_2F$  and other scavengers. Also, we noted above that the three reactions produced essentially the same emission spectrum, suggesting a common pumping step. These observations are consistent with a mechanism in which the complexes formed by reactions with  $O_2F$  are produced with sufficient energy for dissociation into a diatomic and a free iodine atom. The iodine atom thus produced might then react with  $O_2F$  to form excited  $IF$ . For example,



The existence of channels analogous to process (22) for the  $I_2 - F_2$  reaction were reported in the molecular beam study (Ref. 43), and the authors indicated that these channels open at energies only slightly greater than that required for formation of the complex. Given the substantial exothermicities of reactions (19), (20), and (21), it seems plausible that such processes participate in the  $O_2F$  reactions. We note, however, that decay of the  $IClF$  complex to  $I + ClF$  is endothermic by  $\sim 4$  kcal/mole. In this case the complex may also decay to  $Cl + IF$  with an exothermicity of  $\sim 2$  kcal/mole. Chlorine atoms thus produced might react with  $ICl$  to generate free iodine atoms or they may be scavenged by excess  $O_2F$ . The existence of these other channels may account for the reduced intensity of the  $ICl + O_2F$  flame relative to the  $I_2$  and  $HI$  analogues.

Assuming the bond strength of  $O_2F$  to be about 15 kcal/mole (Ref. 13, 14) process (16) liberates  $\sim 52$  kcal/mole. This is sufficient for population of the  $A(^3\Pi_1)$  state of  $IF$  up to  $v' \sim 7$ . The observation of emission from higher levels of the  $A$  state suggests that either the  $O_2F$  bond strength is less than 15 kcal/mole or that the free iodine atom formed in reaction (22) carries with it some of the energy present in the excited complex. Process (16) might populate the  $A$  state directly or it might populate high vibrational levels of the ground state from which the  $A$  state may be produced by resonant interactions. The latter process seems more likely in view of the small photon yields measured and

by comparison to the BrF and ClF systems. In these cases, the  $A(^3\Pi_1)$  state cannot be produced by the reactions analogous to process (16), yet strong  $B \rightarrow X$  emission is still seen when the reactions proceed in the presence of singlet oxygen. We note that the mechanism discussed above (Reactions 22 and 16) may also apply to the  $Br_2 + O_2F$  reaction. In this case, however, very little emission is seen since the BrF A state cannot be produced by the second step and no  $O_2^*$  is present to generate the B state. The weak  $B \rightarrow X$  emission observed may be the result of energy pooling processes between vibrationally excited BrF molecules.

### 3. $O_2F$ Reactions with $Mg(^1S)$ and $Mg^*(^3P)$

Reactions of magnesium atoms with numerous oxidizers have been widely studied, primarily owing to the volatility of this metal at temperatures of a few hundred degrees centigrade. Magnesium reactions are also of interest because the lowest lying metastable excited state of this atom ( $Mg^* ^3P$ ,  $E = 63$  kcal/mole) can be produced chemically (Ref. 44).

The reaction of magnesium with  $F_2$  has been studied by Eckstrom and co-workers (Ref. 45) using standard chemiluminescence techniques and more recently by Engelke (Ref. 46) using a crossed beam apparatus. The reaction to form MgF liberates 68.5 kcal/mole:



This exothermicity is insufficient for population of the lowest lying state in the excited doublet manifold, the  $A(^2\Pi)$  state lying at  $\sim 79.5$  kcal/mole. Eckstrom, et. al., measured the photon yield for the production of this state by reaction (23) to be  $\sim 10^{-4}$ , in keeping with the generation of  $MgF^*$  by recombination of magnesium with F atoms formed in the reaction (Ref. 45). Under the single collision conditions of the crossed beam experiment, the reaction was observed to produce no  $A + X$  emission (Ref. 46). In contrast, the analogous reaction of Mg with  $O_2F$  would liberate  $\sim 90.5$  kcal/mole, more than enough for direct population of the  $A(^2\Pi)$  state. Hence we might expect a considerable enhancement of the  $A + X$  photon yield relative to the  $Mg + F_2$  case.

Spectroscopic studies of the Group IIA-halides have indicated that transitions between the ground states and lowest lying excited states of these molecules correspond to promotion of a non-bonding electron in the metal atom to orbitals corresponding to excited states of this atom (Ref. 46). Hence, it might be expected that the reactions of excited metastable Mg atoms with RF species would have enhanced  $MgF A + X$  photon yields, and this has been borne out by experiments using  $F_2$ . In the crossed beam experiments noted above, it was found that for the  $M^* + F_2$  reaction ( $M = Mg, Ca, Sr$  or  $Ba$ ), the cross-section for formation of excited MF was at least an order of magnitude greater than for formation of the ground state (Ref. 46).

In view of these facts, the objectives of the present experiments were to observe the reactions of  $O_2F$  radicals with Mg and  $Mg^*$ , to measure the spectrum of the emissions and to determine the photon yields for the states

produced. The experiments required a calibrated source of Mg atoms compatible with the technology developed for the generation of  $O_2F$ . The method chosen was the direct evaporation of Mg metal in the presence of a carrier gas. The apparatus constructed for this purpose is shown in Figure 8. It consists basically of a closed quartz tube with a small reservoir at the top which holds the powdered metal (50 mesh Mg powder was used in the experiments). Holes in the wall of the reservoir permit flow of a carrier gas (argon) from the tube into the reservoir. Heat is supplied from a resistively heated coil of tungsten wire as shown. Both commercial coils (R.D. Mathis Co.) and hand-made coils were used. The hand-made coils were thinner and hence required less current. Power was supplied to the coil by either a 20 amp "Variac" or by a 15 amp regulated DC power supply. The "oven" temperature was measured using an iron-constantan thermocouple positioned below the metal reservoir as shown in Figure 8.

The metal generator was designed to fit inside a 1.0" i.d. tube, coupled by a 1.0" by 0.75" "ultra-torr" reducing union. The reaction cell designed to accommodate both the metal oven and  $O_2F$  generation from  $O_2^+AsF_6^-$  is shown in Figure 9. This arrangement, which was arrived at after some iteration, incorporates two frit assemblies for production of  $O_2F$  as shown. The  $O_2F$  is admitted to the flow tube just downstream of the Mg oven orifice, with the observation window just downstream of the  $O_2F$  inlets. Under vacuum conditions, the heat generated by the Mg oven was found to have only a minor effect on the dissociation of the  $O_2^+AsF_6^-$  salt relative to the heat applied directly to the frits.

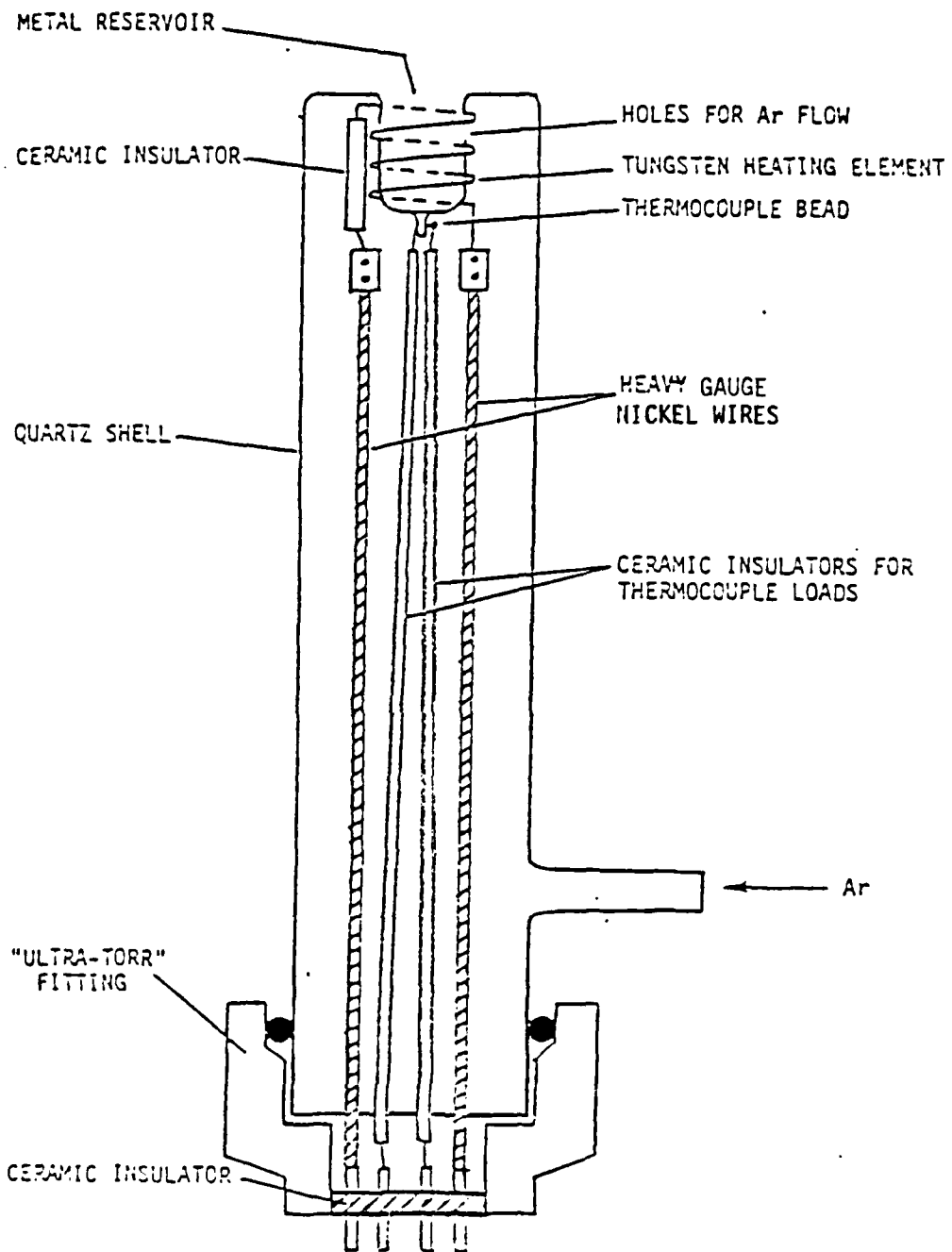


Figure 3. Apparatus used for generation of magnesium vapor.

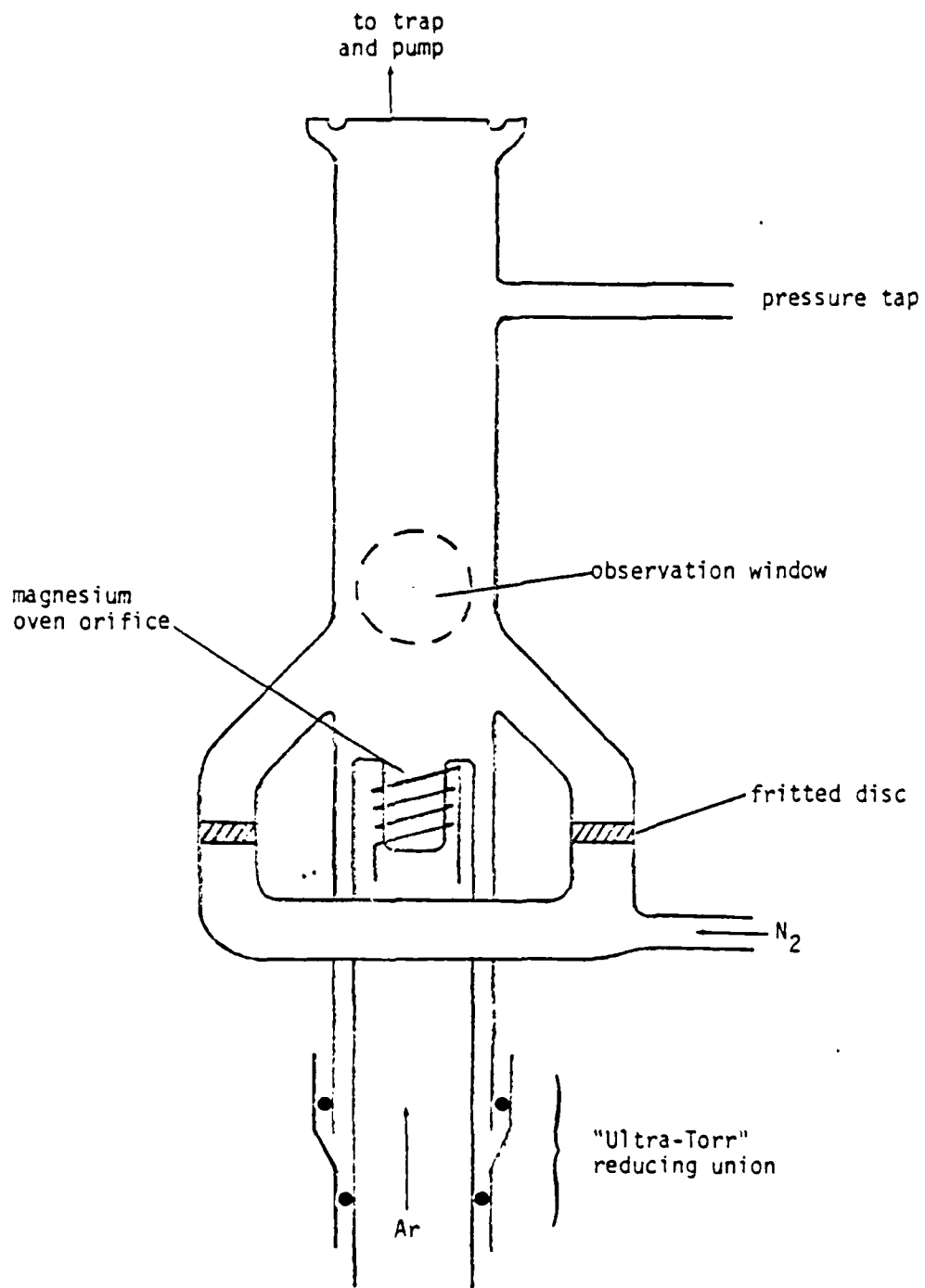


Figure 9. Apparatus used for observation of the reaction of  $O_2F$  with magnesium vapor.

In order to measure photon yields for the  $\text{Mg} + \text{O}_2\text{F}$  reaction, the flowrate of the metal atoms (the limiting reagent in the system) must be known. Calibrations of the Mg flowrate vs the measured temperature were made by allowing the Mg flow to condense on a removable surface, followed by measurements of the additional weight accumulated on the surface for a given run time. The calibrations were performed using both the cell described above and a separate 1.0" tube used exclusively for this purpose. The surface used for the condensation was an aluminum foil cylinder which lined the inner wall of the tube. The length of the foil liner (extending well above and below the oven orifice) was such that condensation of nearly all the oven effluent was assured. The weight of the foil before and after the runs was measured using a Mettler A30 balance; the minimum weight difference considered to be real was 0.3 mg. The carrier gas used in both the calibrations and the experiments was argon. The argon flowrate was typically 0.67 sccs (sccs = standard  $\text{cm}^3 \text{ s}^{-1}$ ) variations in the argon flowrate by as much as a factor of two were observed to have a relatively minor effect on the Mg flowrate. The calibration run times (up to two hours) were such that a stable equilibrium temperature existed for the major portion of any given run.

Calibration data obtained in this fashion for magnesium are shown in Figure 10. Data are shown for three separate groups of experiments which were separated by a period of months. The calibrations were performed using both homemade and commercial tungsten coils, and both AC and DC power supplies. The agreement between the three groups of runs demonstrates the reproducibility of the Mg flowrates over more than three orders of magnitude. The "gliche"

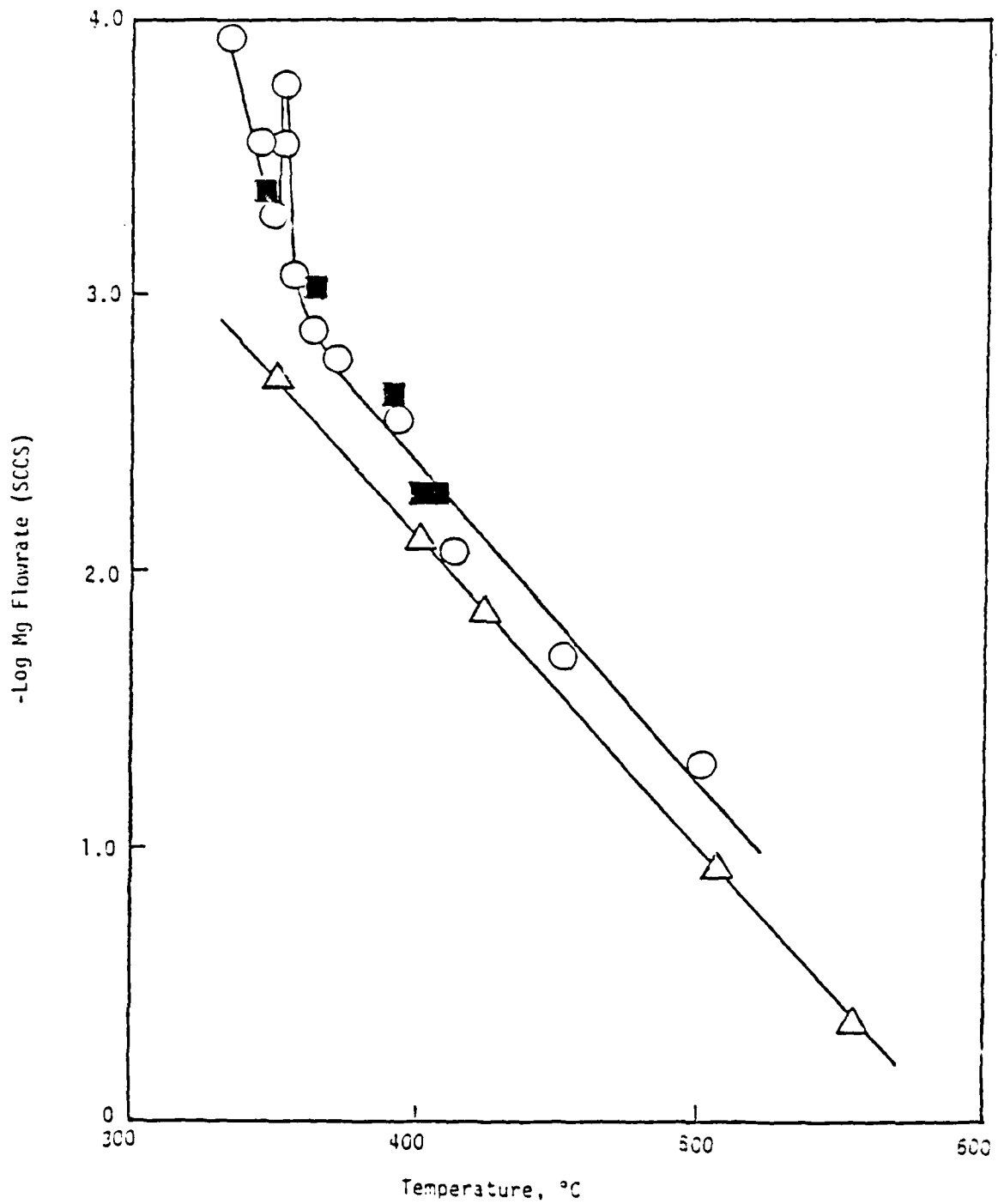


Figure 10. Calibration of the magnesium vapor flowrate vs. temperature measured in the evaporation apparatus (see Figure 8). The triangles, circles, and squares represent data obtained at different times over a period of several months.

shown in the data at  $\sim 350^\circ\text{C}$  was quite reproducible and appears to be real. The flowrate data shown, when deconvoluted with the tube area and linear velocity of the flowing gases, yield magnesium densities much greater than the vapor pressures at the temperatures indicated by the thermocouple. Hence the equilibrated temperature in the metal must be higher than in the vicinity of the thermocouple. The temperature recorded thus serves only as a convenient measure of the flowrate.

The results of the initial  $\text{Mg} + \text{O}_2\text{F}$  experiments were quite unexpected. The experiments were begun by generating a small ( $<10$  mtorr) concentration of  $\text{O}_2\text{F}$  in the cell with Ar and  $\text{N}_2$  carrier gases flowing to give a total pressure of  $\sim 250$  mtorr. Upon application of heat to the magnesium reservoir, a blue flame appeared almost immediately in the mixing zone of the cell. The intensity of the flame increased as the flowrate of Mg increased, becoming quite bright for flowrates as low as  $10^{-3}$  sccs. The flame died out when the  $\text{O}_2^+\text{AsF}_6^-$  was consumed or the frit heaters were turned off (in the latter case some emission remained as the heat generated by the Mg oven was sufficient to cause some decomposition by the salt). When the Mg powder was removed from the oven, the intensity of the flame was greatly reduced, although not completely eliminated. It was originally thought that this residual emission was due to magnesium deposits in the oven; later experiments, however, showed the emission to occur even with an apparatus completely uncontaminated with Mg. We attribute the residual emission to an interaction between the "hot" argon passed over the tungsten coils with either of the  $\text{O}_2^+\text{AsF}_6^-$  decomposition products ( $\text{O}_2\text{F}$  or  $\text{AsF}_5$ ). In any case, the intensity was

greatly enhanced by the presence of Mg, and can be attributed primarily to an Mg + O<sub>2</sub>F interaction.

The full emission spectrum of the flame was recorded using a combination of two gratings (blazed at 300 and 500 nm) in a McPherson model 218 0.3 m monochromator. A GaAs photomultiplier tube and photon counting apparatus were used as in previous experiments. For the UV grating, the response of the entire detection system vs wavelength was calibrated using a deuterium lamp with a known spectral output.

At low Mg flowrates (less than  $10^{-4}$  sccs) and relatively high O<sub>2</sub>F concentrations (>10 mtorr), the emission spectrum consists solely of a broad "continuous" emission which is responsible for the blue-white color of the flame. The spectrum of this broadband emission is shown in Figure 11a. Structure could not be resolved within the resolution of our apparatus (~2 nm), although the emission was not smooth and exhibited many irregularities. The emission begins at ~300 nm, reaching a peak at ~370 nm as shown in the figure. The intensity decays gradually with increasing wavelength, and is still quite evident beyond 750 nm. The emission intensity was found to be sensitive to the flowrate of both Mg and O<sub>2</sub>F, rising with increased flow of each species; it was much more sensitive to the Mg flow rate, however.

The shoulder shown on the rise of the emission near 310 nm is real, and under some conditions was observed to be a strong banded feature. Further experiments showed that this feature and a portion of the "continuous" emission at longer wavelengths could be attributed to the residual emission noted

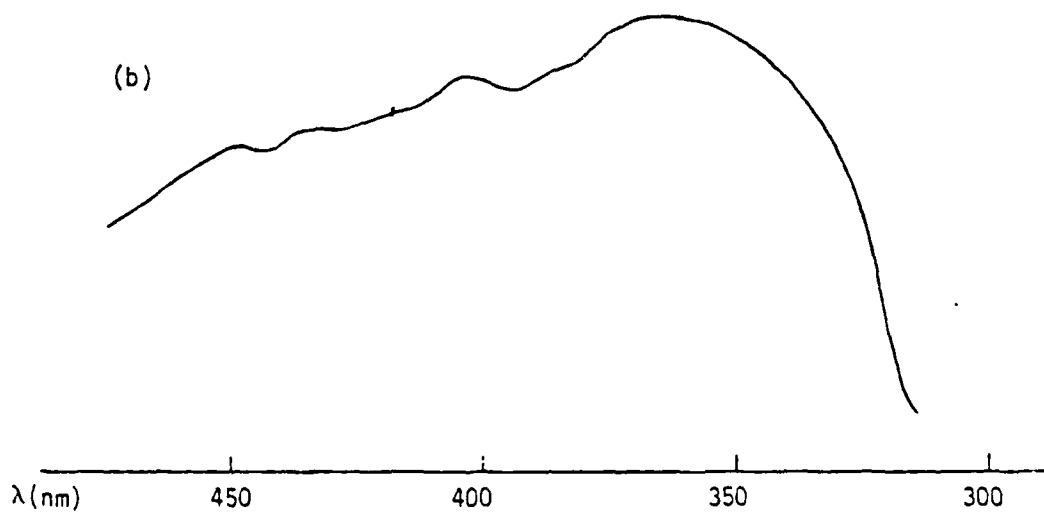
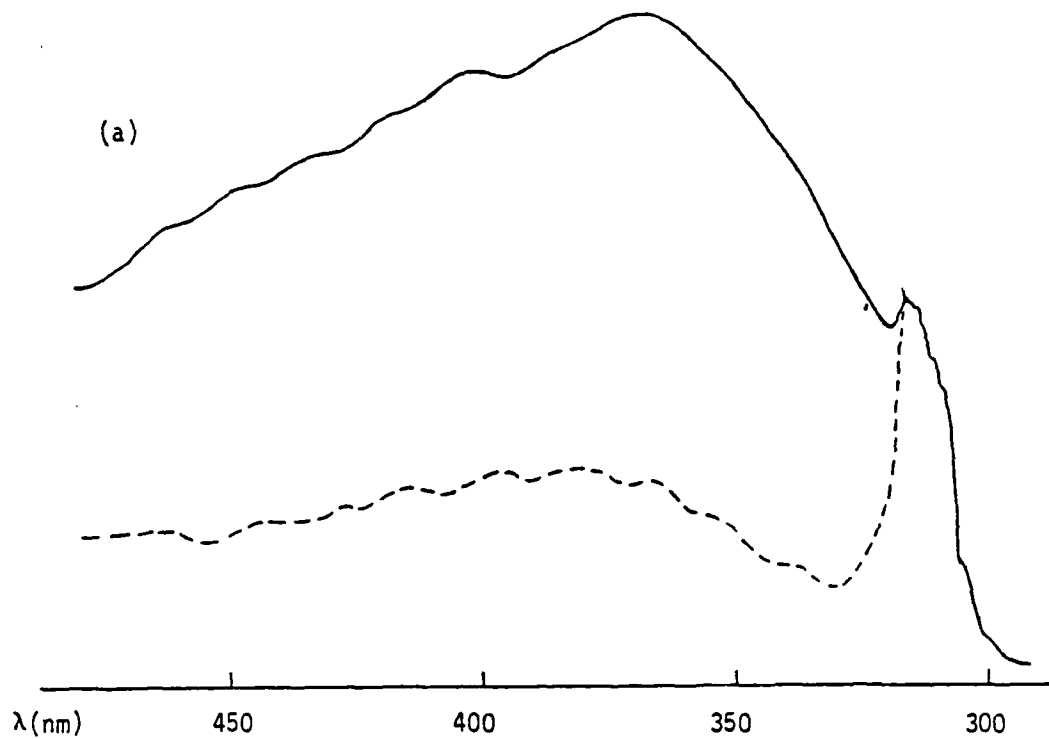


Figure 11. Spectra of broadband emission observed from the  $Mg+O_2F$  reaction. (a) total emission (solid line) and contribution from "residual" emission (broken line); (b) "difference" spectrum possibly attributable to excited  $MgF_2$ .

above (thought to be due to interaction between the hot argon and  $O_2F/AsF_5$ ). The spectrum of this emission, shown as a broken line in Figure 11a, was obtained using a new oven totally uncontaminated with Mg. A number of such comparison spectra were taken at different Mg flowrates in order to firmly identify the portion of the emission caused by the Mg +  $O_2F$  reaction. The results of the experiments were all similar to the data shown in Figure 11a. Figure 11b shows the difference between the total and residual emissions, attributable to Mg +  $O_2F$ .

For relatively low  $O_2F$  concentrations (<5 mtorr), a number of new features appeared in the spectrum as the Mg flowrate was increased. Three very intense bands were observed in the vicinity of 360 nm, and these were easily identified as the  $\Delta v = 1, 0,$  and  $-1$  sequences of the MgF  $A(^2\Pi) \rightarrow X(^2\Sigma^+)$  transition. These features are shown in Figure 12. For a fixed  $O_2F$  concentration, the intensity of the A  $\rightarrow$  X bands increased sharply with increasing Mg flowrate. For a fixed Mg concentration, the A  $\rightarrow$  X intensity diminished as the  $O_2F$  concentration increased (and the broadband intensity increased). These results suggest that the broadband emission is produced by reaction of  $O_2F$  with  $MgF^*(A^2\Pi)$ , or more likely with its precursor since the short radiative lifetime of the A state (perhaps 10 nsec) would preclude collisions. Such a long lived precursor might be, for example, vibrationally excited MgF ground state molecules which could mix with the A state by resonant interactions. This inference is consistent with production of excited  $MgF_2$  as the "continuum" emitter:

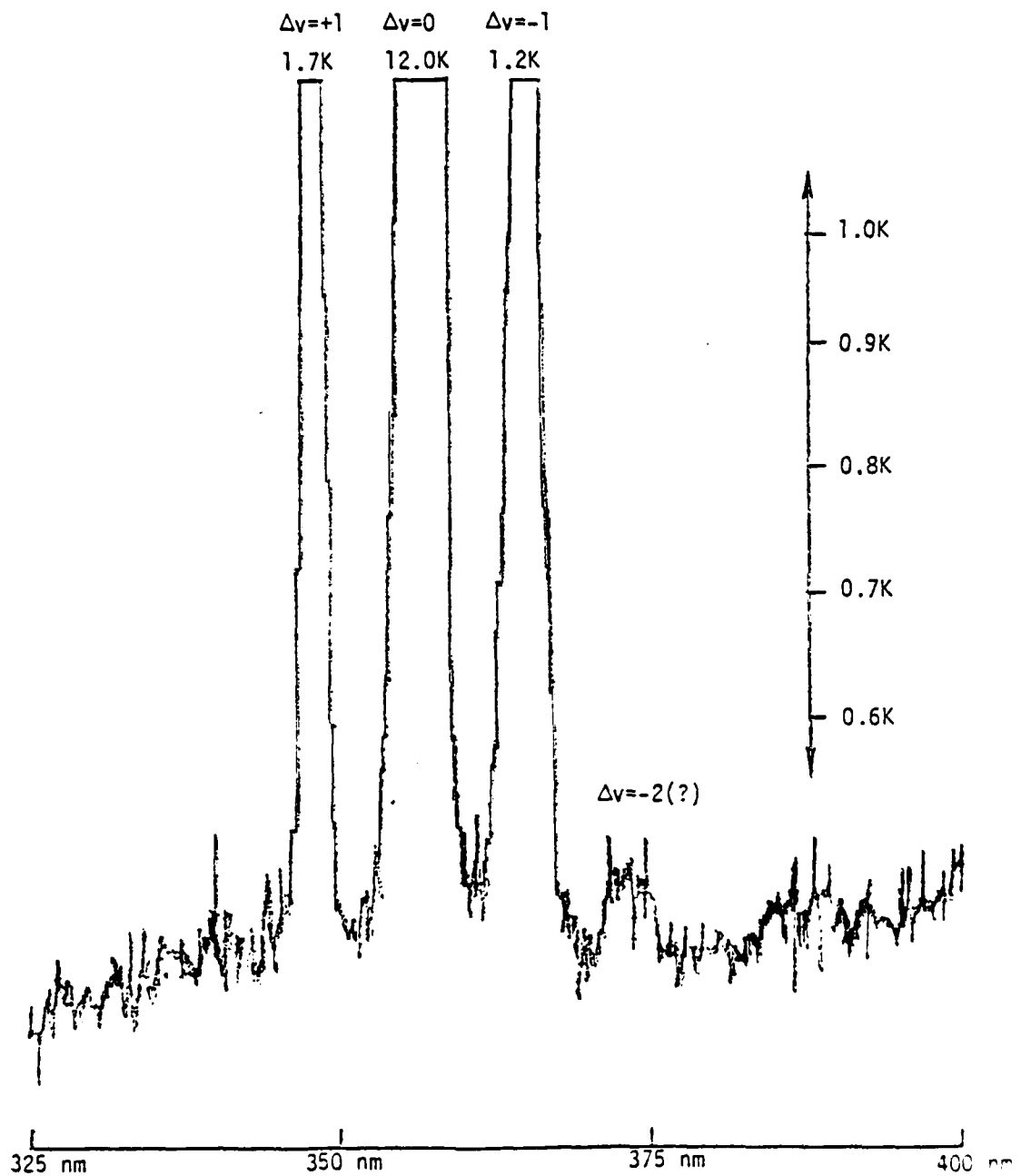


Figure 12. Spectrum showing the  $A(^2\Pi) \rightarrow X(^2\Sigma^+)$  transitions of MgF produced by the  $Mg+O_2F$  reaction. Scale to the right indicates intensity.



MgF<sub>2</sub> emission has been previously reported only once, from the recent molecular beam study by Engelke (Ref. 46). The data suggested that the source of the emission in this case was a novel Mg<sub>2</sub> - F<sub>2</sub> four center reaction. The spectrum reported is in fact in fairly good qualitative agreement with that obtained from the present experiments (Fig. 11b).

As the Mg flowrate was increased to still higher values (>10<sup>-2.5</sup> sccs), emissions from excited states of Mg atoms appeared in the spectrum. The strongest such feature was the Mg\* 3S → 3P transition in the vicinity of 518 nm. Considerably less intense emission from the well known 3P → 1S transition at 457.1 nm was also observed, as was 1P → 1S emission at 285.2 nm. Presumably these excited states are pumped by collisional energy transfer from the excited molecular species present in the reaction mixture.

Photon yields for the emissions produced by the Mg + O<sub>2</sub>F reaction were measured using the techniques described above. The light collection efficiency of the detection system was calibrated using the O + NO reaction as a chemical actinometer. Several calibrations were performed for scans from 350 to 500 nm at 50 nm/minute, yielding a calibration factor α = 1.5 × 10<sup>6</sup>. This value is in reasonable agreement with those measured previously, given the lower f number of the McPherson monochromator.

Measurements of the yield for the broadband emission were made by scanning from 300 to 500 nm. Hence the assumption was made that the value of  $\alpha$  between 300 and 500 nm is essentially the same as from 350 to 500 nm; i.e., that the system has an essentially flat response over this region. Many measurements of the broadband yield were made since the intensity in this case exhibited considerable scatter. The results are shown in Figure 13. The data exhibit a very rapid decline with increasing Mg flowrate, with the limiting yield at zero flowrate being approximately 2%. It should be noted that the data shown were not corrected for the "residual" contribution to the emission discussed earlier. This contribution may be a significant part of the total intensity for the data at lower Mg flowrates, hence clouding the true value of the limiting yield.

The  $\alpha$  parameter for the yield of the MgF A + X emission cannot be determined directly since the NO<sub>2</sub> emission is very weak in this region and its intensity distribution is not documented. Hence  $\alpha$  in this case was taken to be the value measured for the 350 to 500 nm region, corrected for the different spectral slitwidth used in the measurements, the different scan speed, and the spectral response of the system at 360 nm vs the average over the 350 to 500 nm range. These calculations yielded a value  $\alpha = 2.4 \times 10^5$ . MgF A + X yields were measured for scans from 340 to 370 nm at 10 nm per minute. The data obtained are shown in Figure 14. The zero flowrate yield in this case is much smaller, on the order of  $10^{-5}$ , but the yield was observed to increase with increasing Mg flowrate as shown. This behavior is in accord with the mechanism postulated above. Increasing the Mg flowrate should

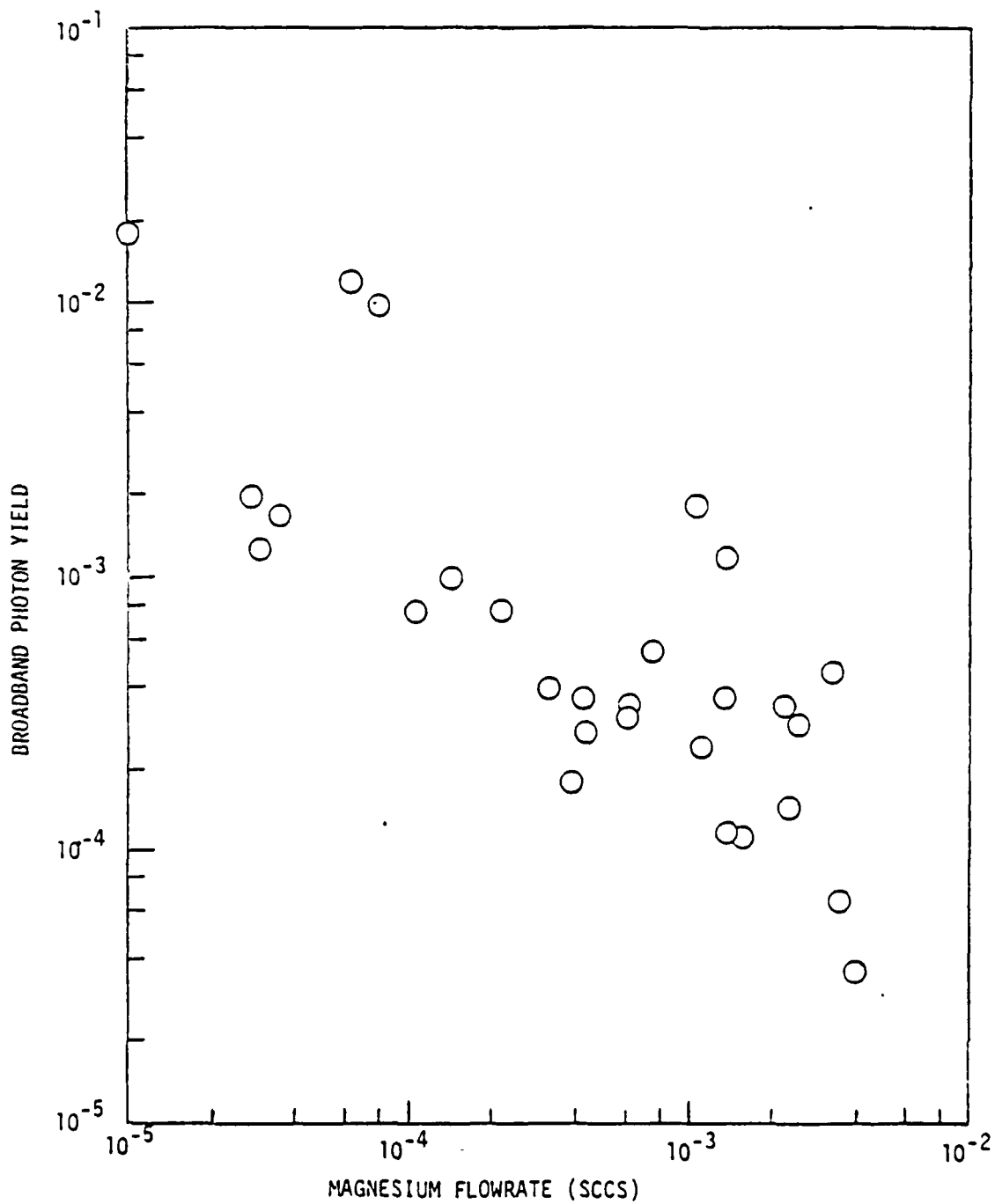


Figure 13. Photon yield of the broadband emission from the  $\text{Mg}+\text{O}_2\text{F}$  reaction vs. magnesium flowrate.

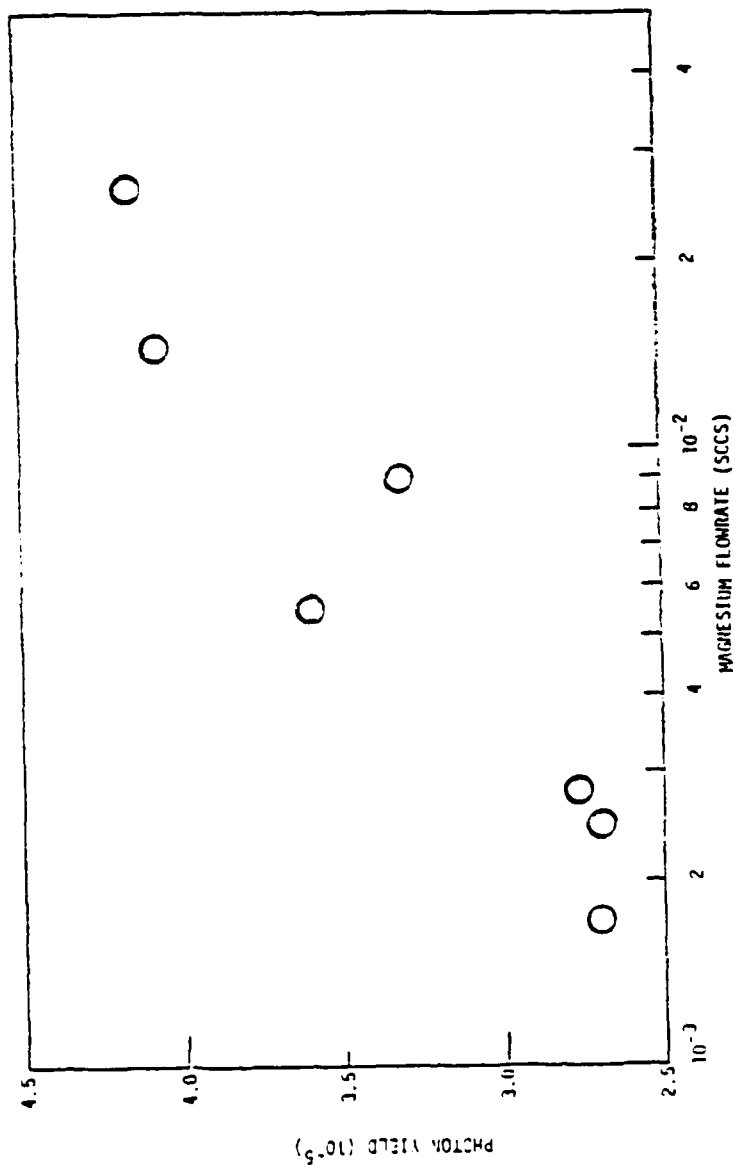


Figure 14. Photon yield of the  $\text{MgF } A(2\pi) \rightarrow X(2\Sigma^+)$  transition vs. magnesium flowrate for the  $\text{Mg} + \text{O}_2\text{F}$  reaction.

increase the rate of production of  $\text{MgF}^\ddagger$  (Eq. 24) relative to its removal by  $\text{O}_2\text{F}$  (Eq. 26). The steady state concentration of this species (and hence of  $\text{MgF}(A^2\Pi)$  by Eq. 25) should therefore increase. Owing to its short radiative lifetime, the  $\text{MgF}(A)$  state is not likely to be quenched before radiating. Hence the photon yield also increases.

We note that the measured  $A \rightarrow X$  photon yield is even lower than that reported for the  $\text{Mg} + \text{F}_2$  reaction, where  $\text{MgF}(A)$  can be formed only by recombination (Ref. 45). The fact that the yield for  $\text{Mg} + \text{O}_2\text{F}$  is lower supports the hypothesis that free fluorine atoms are not abundant in the system. Apparently, the conversion from  $\text{MgF}^\ddagger$  to  $\text{MgF}(A)$  (Eq. 25) is not efficient relative to other relaxation or reaction processes. If this conversion is a collision induced process, as suggested by Eq. 25, the  $A \rightarrow X$  photon yield should increase with increasing pressure. To test this hypothesis, an experiment was performed in which the intensity of the  $A \rightarrow X \Delta v = 0$  sequence was monitored as the total pressure in the system was increased by adding argon. The intensity was observed to rise by 165% for a 26% pressure rise. Although some of this effect may be due to an increase in the linear flow velocity with the pressure rise (i.e., shortening the observation time with respect to the time decay of the  $A \rightarrow X$  signal), the result is certainly in accord with the model.

A number of experiments were performed in an attempt to observe the effect of the presence of  $\text{Mg}^*(^3\text{P})$  in the system.  $\text{Mg}^*$  can be produced either chemically (Ref. 44) or by discharge techniques. We chose the latter method since it appeared to be the simplest for our apparatus. Modification of the cell design was required to incorporate the discharge, and two basic

arrangements were used as shown in Figure 15. In both cells, argon was passed through the discharge to produce excited metastable atoms capable of transferring their energy to magnesium. Magnesium vapor was admitted to the Ar/Ar\* flow ~10 cm downstream of the discharge for cell a and ~5 cm downstream for cell b. In both cases, addition of Mg to the excited argon produced very bright green luminescence due to Mg\* 3S → 3P transitions. For high Mg flowrates the blue Mg\* 3P → 1S emission at 457.1 nm could also be seen as a long diffuse tail to the bright green plasma zone.

In the first cell used ("a" in Fig. 15) O<sub>2</sub>F was admitted to the flow just downstream from the Mg/Ar\* mixing zone (i.e., in the plasma region). Argon was used as the carrier of O<sub>2</sub>F in these experiments since N<sub>2</sub> quenched the Ar\* metastables. The observation window was just downstream of the O<sub>2</sub>F inlet (~3 cm from the oven orifice), and it viewed a portion of the plasma zone. The spectrum recorded for this arrangement included many features attributable to excited Mg and Ar atoms. With no O<sub>2</sub>F present, the dominant feature was the Mg\* 1P → 1S transition at 285.2 nm. Mg\* 3S → 3P and 3P → 1S transitions were also evident, and it was observed that their intensity could be dramatically increased by increasing the Ar flowrate to give a total cell pressure of 800 to 900 mtorr.

The emission spectrum produced by the Mg\* + O<sub>2</sub>F interaction was strongly dependent on the O<sub>2</sub>F and Mg flowrates. For O<sub>2</sub>F pressures less than 5 mtorr and large Mg flowrates, the spectrum consisted of many Mg and Ar atomic transitions, plus some banded features which appeared to be MgF A → X and B → X transitions. Positive identification was difficult due to interference

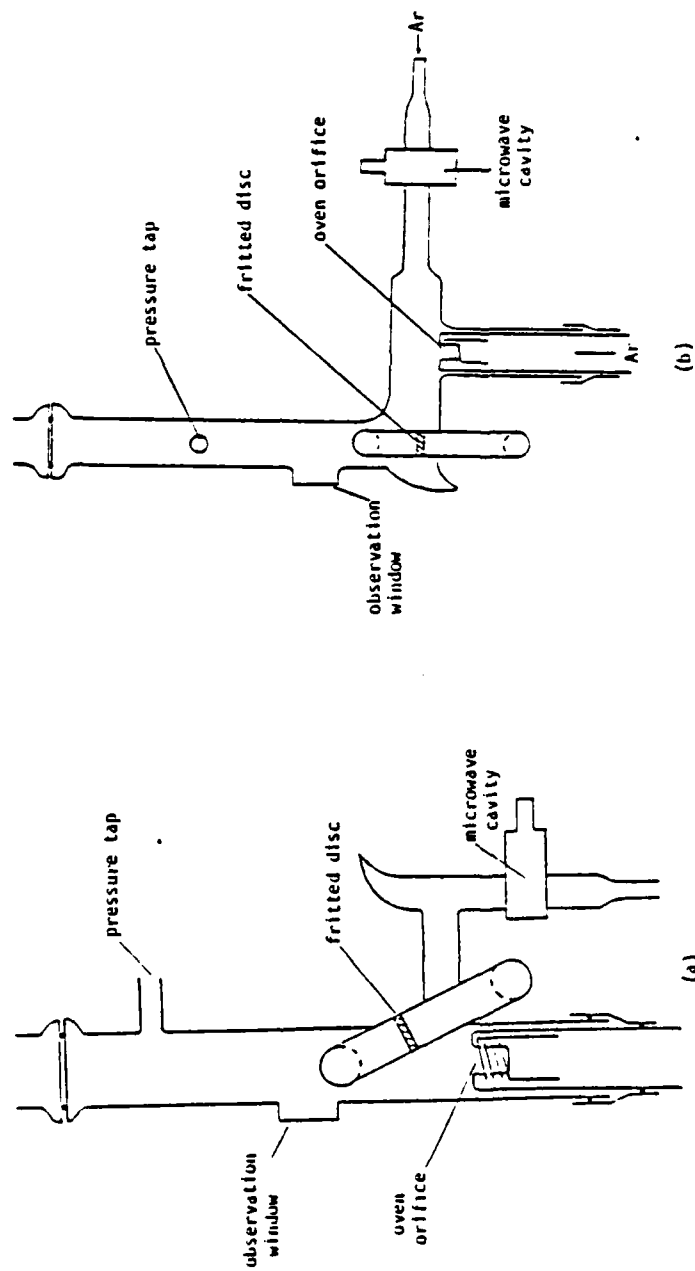


Figure 15. Cells used for observation of the reaction between  $Mg^*(^3P)$  and  $O_2F$ .

from the atomic lines. The lines and bands rose from what appeared to be two broad continua, one peaked at  $\sim 400$  nm (apparently the same feature seen in the  $\text{Mg(X)} + \text{O}_2\text{F}$  spectrum) and the other peaked near 270 nm. This spectrum is shown in Figure 16a. Increasing the  $\text{O}_2\text{F}$  concentration to partial pressures approaching 10 mtorr almost totally eliminated the green  $\text{Mg}^*$  emissions. Most of the line and banded features were eliminated from the spectrum, which reduced to the two continua as shown in Figure 16b. It was not possible to determine whether these broadband features increased in intensity with the increase in  $\text{O}_2\text{F}$  pressure. In any case, the B  $\rightarrow$  X bands and the second (270 nm) continuum are new features which were not present in the  $\text{Mg(X)} + \text{O}_2\text{F}$  spectrum. These features may be attributed to the  $\text{Mg}^* + \text{O}_2\text{F}$  reaction, or to excitation of  $\text{MgF}$  or  $\text{MgF}_2$  ground state molecules by metastables present in the flow. The  $\text{Mg}^*(^3\text{D}) + \text{O}_2\text{F}$  reaction liberates about 153 kcal/mole, sufficient for population of the  $\text{MgF A}(^2\pi)$ ,  $\text{B}(^2\Sigma^+)$ , and  $\text{C}(^2\Sigma^+)$  excited states. No C  $\rightarrow$  X bands were observed in the spectrum, however.

It was obvious from the experiments that a number of improvements in the spectrum could be realized by moving the observation port well downstream of its present position. Such a change should greatly reduce the interference from short-lived  $\text{Mg}^*$  and  $\text{Ar}^*$  atoms created in the plasma, and allow a more definitive characterization of the spectrum and its source. To this end, a new cell was constructed as shown in Figure 15b. The observation window in this cell is approximately 10 cm downstream of the Mg oven, such that it should be looking at only the blue ( $\text{Mg}^* 3\text{P} \rightarrow 1\text{S}$ ) "tail" of the emission from the discharge/mixing zone. The cell worked well in the sense that the emission spectrum in the

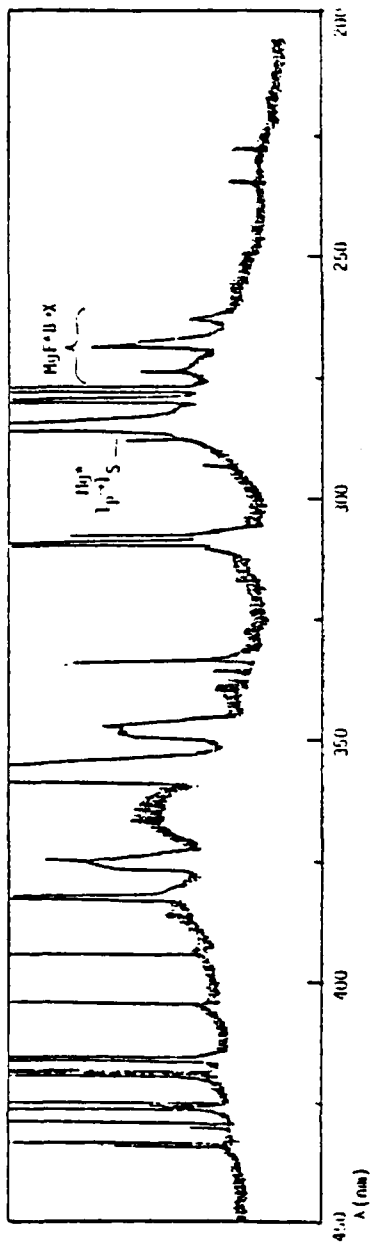


Figure 16a.  $Mg^{+}O_2F$  emission spectrum for  $P_{O_2F} < 5$  mtorr.

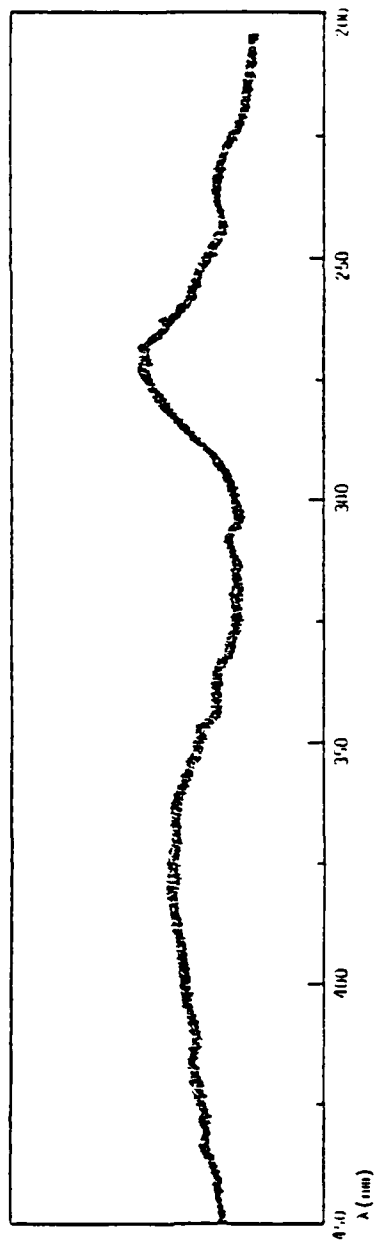


Figure 16b.  $Mg^{+}O_2F$  emission spectrum for  $P_{O_2F} \geq 10$  mtorr.

observation zone exhibited only the  $\text{Mg}^*$  ( $3p + 1s$ ) transition at 457.1 nm, with no evidence of excited argon or other Mg states. When  $\text{O}_2\text{F}$  was added to the  $\text{Mg}^*$  stream just below the window, the spectrum showed the "continuum" ( $\lambda > 300$  nm) previously seen from the  $\text{Mg} + \text{O}_2\text{F}$  system, but none of the new features found in  $\text{Mg}^* + \text{O}_2\text{F}$  experiments in which spectra were taken just downstream of the plasma. Hence we conclude that these features were not caused by the  $\text{Mg}^* + \text{O}_2\text{F}$  reaction, but by excitation of species present in the flow by metastables in the plasma.

#### 4. The Reaction of Calcium with $\text{O}_2\text{F}$

One would expect the reaction of calcium atoms with  $\text{O}_2\text{F}$  to behave much in the same way the  $\text{Mg} + \text{O}_2\text{F}$  reaction does. The dynamics of the two systems should be essentially the same and the arguments noted above concerning the correlation of  $\text{Mg}$  ( $1s$ ) and  $\text{Mg}^*$  ( $3p$ ) with  $\text{MgF}$  ( $X^2\Sigma^+$ ) and  $\text{MgF}$  ( $A^2\Pi$ ), respectively, should hold true for the  $\text{CaF}$  case. The primary differences lie in the much greater exothermicity of the  $\text{Ca} + \text{O}_2\text{F}$  reaction relative to  $\text{Mg} + \text{O}_2\text{F}$ , and in the fact that the excited electronic states of  $\text{CaF}$  lie at lower energies. Hence, many more of the excited states of  $\text{CaF}$  are accessible to the reaction. The  $\text{Ca} + \text{O}_2\text{F}$  reaction liberates  $\sim 113$  kcal/mole, sufficient for direct population of the  $A(2\Pi)$ ,  $B(2\Sigma^+)$ ,  $C(2\Pi)$ ,  $D(2\Sigma^+)$ ,  $E(2\Sigma^+)$ , and  $F(2\Pi)$  states of  $\text{CaF}$ .

The reaction of calcium atoms with molecular fluorine is also highly exothermic and can populate the A, B, C, and D states of  $\text{CaF}$ . The chemiluminescence produced by this reaction has been studied by Menzinger (Ref. 11) and by Eckstrom and co-workers (Ref. 45). The photon yields measured by Eckstrom,

et.al., are somewhat greater than for MgF; for the CaF case these authors found yields of  $\sim 10^{-3}$ ,  $10^{-4}$ , and  $10^{-5}$  for emissions from the A, B, and C excited states, respectively (Ref. 45). In studies of the reactions of Ca, Sr, and Ba with  $F_2$ , Menzinger noted the production of "continuum" emission in addition to the well known banded features (Ref. 11). The broadband emission was attributed to excited  $MF_2$  molecules, possibly produced by two body recombination ( $M + F_2 \rightarrow MF_2^*$ ) analogous to the mechanism proposed by Jonah and Zare for the  $Ba + O_2$  case (Ref. 47).

Hence, on the basis of the energetics of the  $Ca + F_2$  and  $Ca + O_2F$  systems we would expect little difference between the emissions produced by the two reactions. Higher lying CaF states (D, E, and F) may be produced by the  $O_2F$  reaction. Also, broadband  $CaF_2$  emission might be enhanced in the  $O_2F$  cases owing to a mechanism analogous to reactions (24) and (26) above.

The techniques used for the generation of calcium vapor and observation of its reaction with  $O_2F$  radicals were nearly identical to those described above for the Mg case. A new oven assembly was constructed and calibrations of the Ca flowrate were performed using the weight difference technique. The calibration data are shown in Figure 17. The two points labeled with triangles were obtained using a single large calcium turning in the oven reservoir; the other data were measured using several small turnings. The flowrates measured were somewhat higher for the latter case, possibly attributable to the greater metal surface area. The reproducibility of the measurements was good, as indicated by the plot. The temperatures required were much higher than in the Mg case, as expected, but calcium flowrates comparable to those used in the Mg +  $O_2F$  experiments were generated easily.

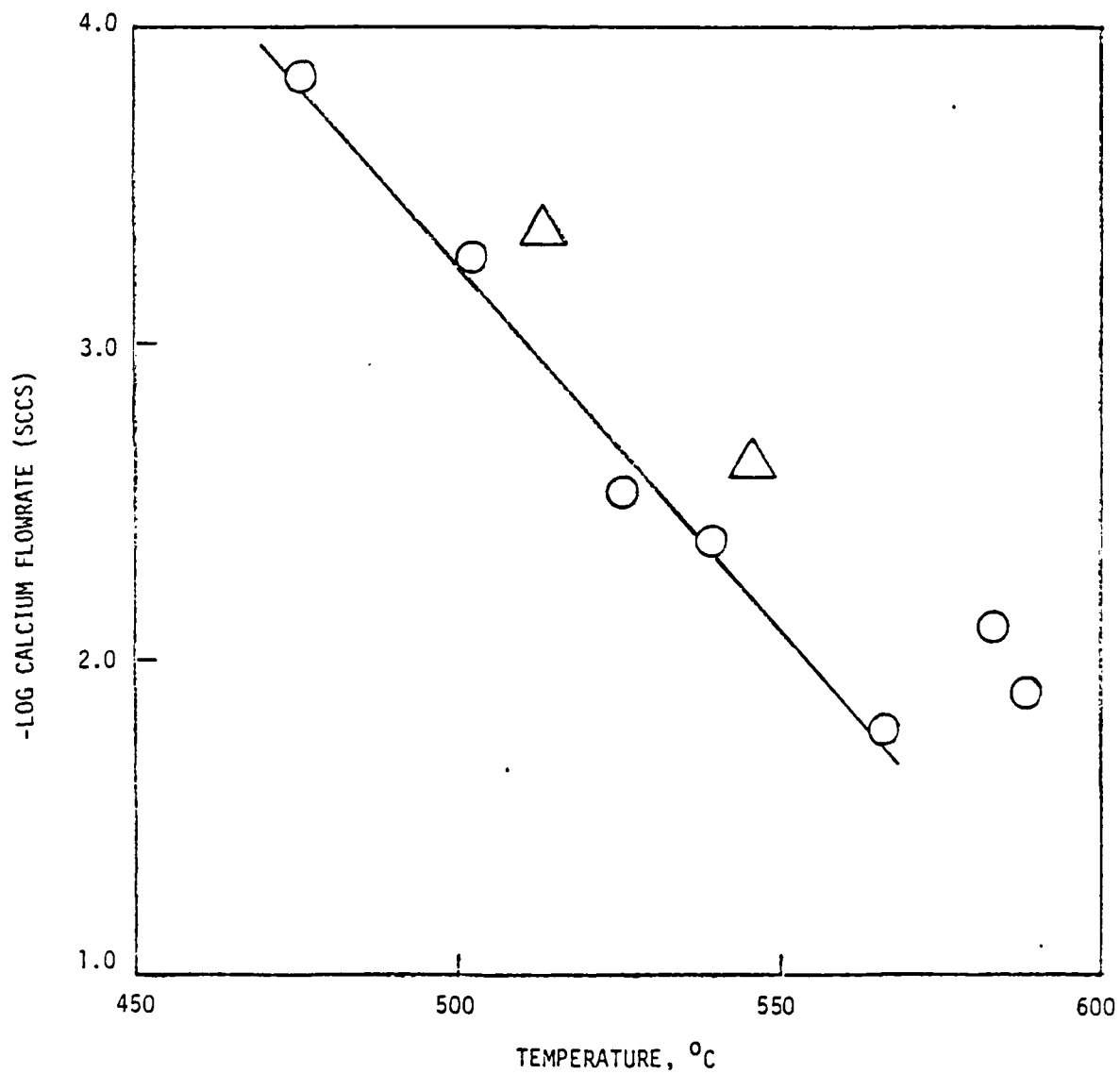


Figure 17. Calibration of the calcium vapor flowrate vs. temperature measured in the evaporation apparatus. The triangles represent data taken using a single large calcium turning; the circles represent data taken using several smaller turnings.

The procedures and apparatus used for the Ca + O<sub>2</sub>F experiments were the same as those described above. For a moderate O<sub>2</sub>F flowrate, application of current to the oven coils resulted in a blue-white luminescence like that previously observed in the magnesium experiments, apparently due to the "residual" emission noted above. As the oven temperature was increased (still at an extremely low Ca flowrate), the blue flame intensified and appeared to persist throughout the cell and into the pumping line. The color of the flame was not a pure blue as before but seemed to have a yellow-white hue. As the measured oven temperature reached ~540°C (corresponding to a calcium flowrate of ~ 3 x 10<sup>-3</sup> sccs) a yellow flame appeared in the reservoir area. The yellow flame became extremely intense with further increases in the calcium flowrate. For a flowrate of ~10<sup>-2</sup> sccs, the intensity of the flame (identified as A + X CaF emissions) was about ten times the intensity of the analogous MgF A + X emission for a comparable Mg flowrate.

The spectrum of the Ca + O<sub>2</sub>F flame in the visible region was measured using a grating blazed at 500 nm in the McPherson 0.3 m monochromator. The data obtained are shown in Figure 18. The spectrum exhibits the  $\Delta v = +1, 0, -1,$  and  $-2$  sequences of the CaF A + X transition, the  $\Delta v = 0$  sequence being nearly ten times the strength of any other feature present in the spectrum. The structure at the top of the bands is due to the  $^2\Pi_{3/2} - ^2\Pi_{1/2}$  splitting in the A state. The spectrum also exhibits emission from the  $\Delta v = +1, 0,$  and  $-1$  sequences of the B( $^2\Sigma^+$ ) + X( $^2\Sigma^+$ ) transition as shown. In general, the visible portion of the spectrum is nearly identical to that reported for the Ca + F<sub>2</sub> reaction (Ref. 11).

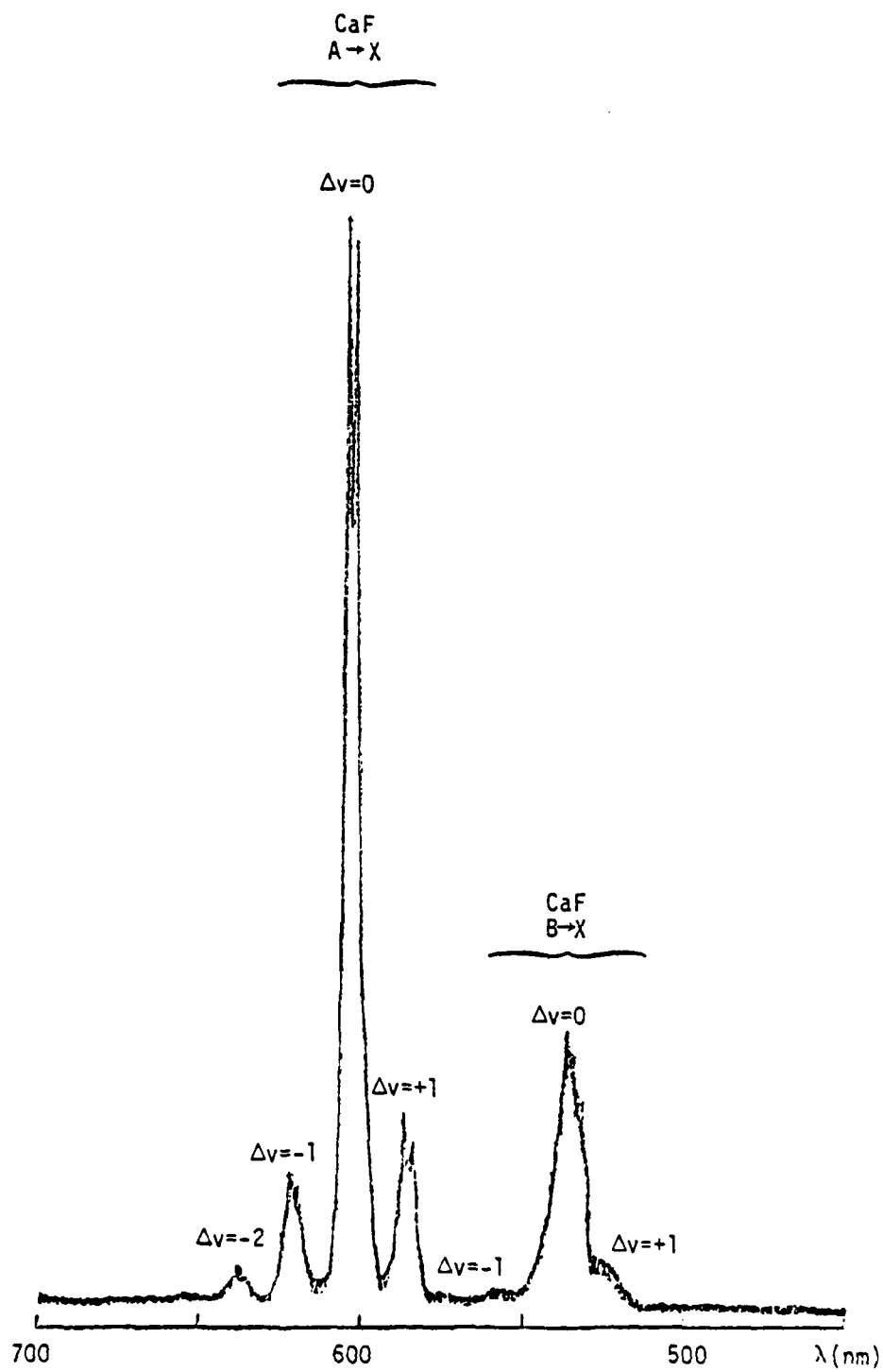


Figure 18. Spectrum obtained in the visible region from the  $\text{Ca} + \text{O}_2\text{F}$  reaction, showing the  $\text{A}(^2\Pi) \rightarrow \text{X}(^1\Sigma^+)$  and  $\text{B}(^1\Sigma^+)$  transitions of CaF.

The spectrum of emission produced by the  $\text{Ca} + \text{O}_2\text{F}$  reaction in the ultraviolet region was recorded using a grating blazed at 300 nm in the McPherson monochromator. The spectrum obtained is shown in Figure 19. The dominant features are the sharp banded sequences ( $\Delta v = +2, +1, 0, -1, \text{ and } -2$ ) of the  $\text{CaF C} \rightarrow \text{X}$  transition. The intensity of these features was roughly equivalent to that of the  $\text{B} \rightarrow \text{X}$  transition shown in Figure 18. The weaker structure at lower wavelengths may be a continuation of the  $\text{C} \rightarrow \text{X}$  emission or may possibly be due to  $\text{CaF D} \rightarrow \text{X}$  emission; a positive identification was not possible. The  $\text{C} \rightarrow \text{X}$  features rest on a strong continuum which appears to rise to a peak in the vicinity of 350 nm. The "pointed" nature of the maximum actually results from the presence of the  $\text{C} \rightarrow \text{X } \Delta v = -2$  sequence at this wavelength, which was resolved in a number of spectra.

The sharp band at ~358 nm is not part of the  $\text{C} \rightarrow \text{X}$  emission, and in fact does not appear to be due to  $\text{CaF}$  at all. Reduction of the calcium flowrate to a level just below that required for appearance of the  $\text{CaF A} \rightarrow \text{X}$  emission did not appreciably diminish the intensity of this feature. For this reduced calcium flowrate and an increased  $\text{O}_2\text{F}$  flowrate ( $P_{\text{O}_2\text{F}} > 10$  mtorr), the spectrum reduced to a continuum emission with the 358 nm feature still present. Small satellite bands were evident on either side of the 358 nm band. In fact, the spectrum obtained for these conditions was almost identical to that produced by the  $\text{Mg} + \text{O}_2\text{F}$  reaction, with the bands corresponding to the  $\text{MgF A} \rightarrow \text{X}$  transition (see Fig. 12). This result is highly suggestive of a magnesium impurity in the calcium sample. We note that the oven temperatures used in the calcium experiments were much higher than those necessary to produce strong  $\text{MgF}$

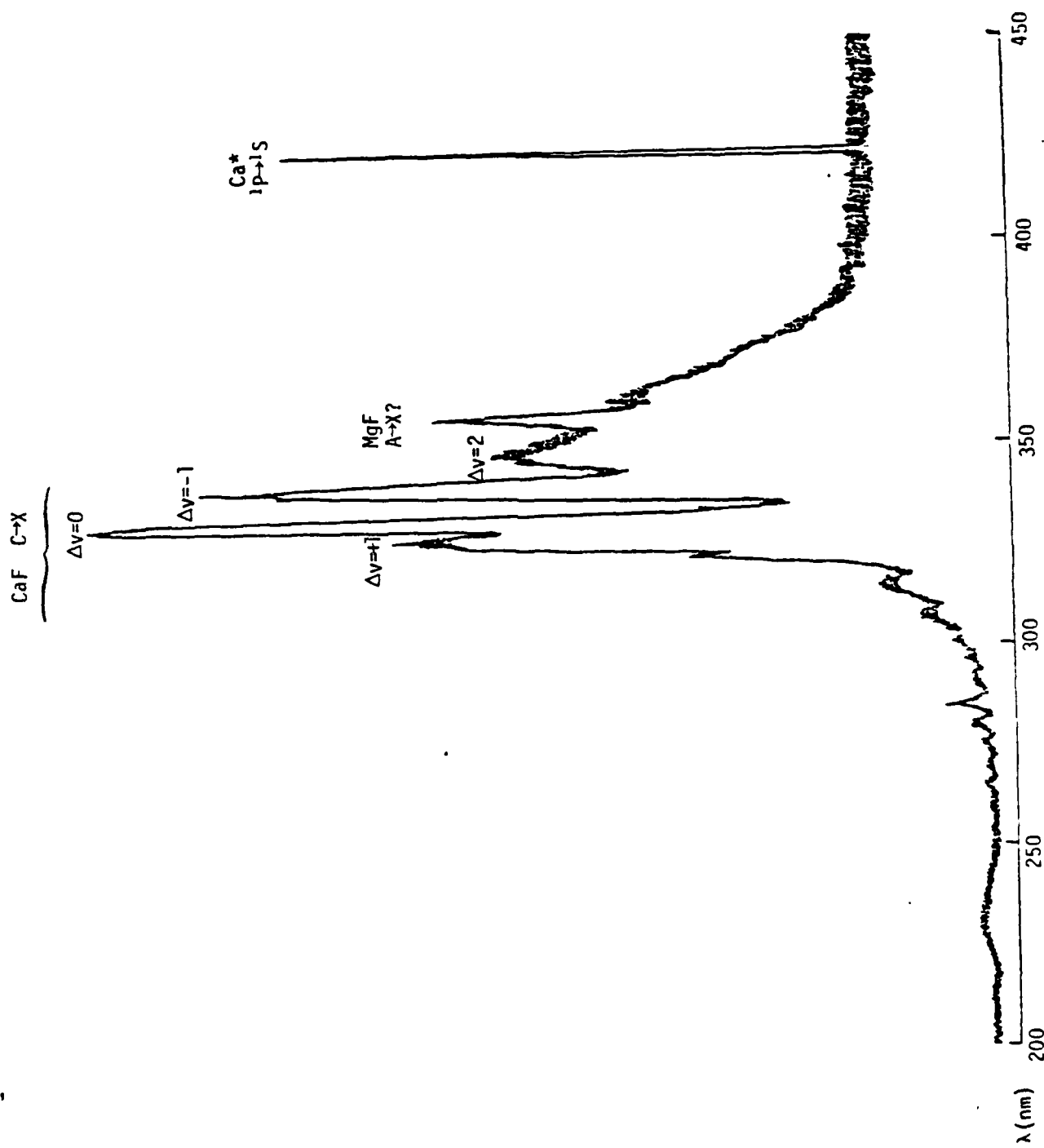


Figure 19. Spectrum of ultraviolet emission obtained from the  $\text{Ca} + \text{O}_2\text{F}$  reaction.

emissions in the Mg + O<sub>2</sub>F experiments. This possibility has the further result of leaving the source of the continuum emission in the Ca + O<sub>2</sub>F experiments in doubt, since it too might be caused by a magnesium impurity.

Additional features present in the Ca + O<sub>2</sub>F UV spectrum include the Ca (<sup>1</sup>P → <sup>1</sup>S) atomic line at 422.7 nm and a weak continuum peaking near 230 nm. The atomic line was also reported to appear in the spectrum produced by Ca + F<sub>2</sub> (Ref. 11), and probably results from energy transfer to calcium atoms from an excited molecular species (e.g., CaF\* C(<sup>2</sup>Σ<sup>+</sup>)). The identity or source of the small continuum is unknown; we note, however, that CaF absorption in this region has been reported by Fowler (Ref. 48).

Photon yields were not explicitly measured for the calcium system. It is clear, however, from intensity comparisons at comparable flowrates that the yield of CaF A → X emission is about ten times that of MgF A → X emission, or on the order of 10<sup>-4</sup>. Again, this is lower than reported for the Ca + F<sub>2</sub> reaction. In any case it is clear that the production of electronically excited states is not a major route for this system.

#### IV. CONCLUSIONS

The results described above have demonstrated the production of a number of electronically excited diatomic fluorides by chemical reactions of  $O_2F$  radicals. On the whole, the processes studied are quite different from the analogous reactions involving molecular fluorine. These differences were particularly evident in regard to the nature of the states produced (in some cases inaccessible by direct reactions with  $F_2$ ) and the rapidity of the processes involved (e.g., the reactions of molecular halides with  $O_2F$ ). The data obtained consequently yielded new spectroscopic information regarding the  $A \rightarrow X$  and  $B \rightarrow X$  transitions of  $BrF$  and  $IF$  (as well as  $C\&F$  in previous experiments), and the visible-UV emission from excited  $MgF_2$ .

It is apparent from the measured photon yields, however, that the reactions studied are not strongly constrained to produce electronically excited product molecules. The predominant mechanisms in these reactions would appear to channel the energy liberated into vibrational modes of the products. The visible and UV emissions observed probably stem from mixing of the populated vibrational levels with near resonant levels of the excited electronic states in question, or from V-E collisional energy transfer. The results of both the halogen +  $O_2F$  and metal +  $O_2F$  experiments suggested mechanisms involving such long-lived precursor states, with the radiating species being produced indirectly.

The fact that in most cases emissions were observed from states near the thermodynamic limit for the energy liberated by the reactions suggests that

a fair proportion of the exothermicity enters product vibrational modes. In order for this to occur, only a small amount of the energy gained by formation of the R-F bond must be channeled into product translation. During the collision the  $O_2$  must not recede from the fluorine during the formation of the R-F bond ("repulsive energy release"(Ref. 49)), but rather it must be relatively uninvolved in the collision until most of the energy has been gained from R-F bond formation ("attractive energy release"(Ref. 49)). This latter case is more like a normal recombination reaction. The results of our experiments in fact reinforce the idea that  $O_2F$  reactions are dynamically similar to three body recombinations. Of course the reactions with the metals Mg and Ca are somewhat more complex, since it seems likely that in these cases an electron jump at long range takes place to form the ionic ground states of the MgF and CaF molecules.

Given this scenario, it is clear that the reactions of  $O_2F$  with ground state atoms are not viable candidates for chemical laser systems, other than in special cases where ground state reagents may correlate directly with excited products. It would seem more likely that direct production of electronically excited species would result from reactions of  $O_2F$  with electronically excited atoms, which normally correlate with excited RF products. A case in point would be the reactions of metastable excited alkaline earth atoms ( $^3P$ ) with  $O_2F$  as discussed above. The experiments performed, using a microwave discharge for production of the excited atoms, did not bear out this hypothesis. These results are contradictory to similar studies involving  $F_2$ , and at the present time we consider this issue to be open to further investigation. Experiments

using alternative sources of  $Mg^*$  and  $Ca^*$ , e.g., chemical methods, should be performed before a final conclusion can be drawn. Similar circumstances apply to the reactions of  $I^*(^2P_{1/2})$  and  $Br^*(^2P_{1/2})$  with  $O_2F$ , which should correlate with product halogen monofluorides in the  $B(^3\Pi_0^+)$  states.

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### ABBREVIATIONS AND SYMBOLS (CONTINUED)

$\dot{N}_H$	Molar flux of atomic hydrogen at the nozzle surface
$D_{H-M}$	Diffusion coefficient for hydrogen atoms in argon within the gaseous plenum
$V_5$	Mean flow velocity of gas moving toward the nozzle inlet
$A^*$	Surface area of subsonic portion of nozzle
$\eta_x$	Molar flux of species x into reaction zone
$\theta$	A ratio of molar fluxes flowing into the reaction zone

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