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RESEARCH NOTE 21

THE ABSORPTION SPECTRA OF SHOCK-HEATED  
TEFLON/ARGON AND TEFLON/NITROGEN MIXTURES

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## ABSTRACT

Absorption spectra have been obtained for the equilibrium products of shock-heated teflon/argon and teflon/nitrogen mixtures. The ultraviolet  $\text{CF}_2$  band system has been identified, and its absorption coefficient has been measured as a function of wavelength in the spectral interval 2300 - 2800 Å. The spectral distribution of the  $\text{CF}_2$  absorption coefficient has been found to be independent of temperature at 1370 and 2320°K.  $\text{CF}_2$  is the only band system observed in absorption for teflon/argon mixtures in the spectral interval 2200 - 4400 Å. By contrast, only the CN violet system is observed for teflon/nitrogen mixtures in the same spectral interval.

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## 1. INTRODUCTION

The prediction of the intensities and spectral distribution of radiation from the boundary layers and wakes of ablating re-entry bodies requires detailed information on the flow field properties and concentrations of important radiating species. In addition, the reaction paths leading to the formation of the dominant radiating species, and the emissivities and absorptivities of the observed spectral transitions, must be known. In Reference 1, a brief review is given of the facilities and techniques that have been used to measure the chemical and spectroscopic properties of complex ablation product/air mixtures, and of the interpretive problems associated with each of these experimental techniques.

In References 1 to 4, are given analyses and reports of progress on the development of a shock tube facility for simulating real ablation product/air chemistry under controlled shock tube conditions for chemical kinetic and spectroscopic studies. The facility described consists of a conventional shock tube into which finely divided powders of selected ablation materials are injected. The passage of a shock wave through the gas and ablation powder mixtures produces rapid heating and vaporization of the ablation materials, and reaction between the products of vaporization and the shock heated gas. This approach to the study of ablation product air mixtures has the advantage of preserving the desired ablation material/air chemistry and at the same time, providing a one-dimensional flow field for simplified data interpretation. The development and performance of the shock tube facility for these studies has been well documented in References 1, 5, and 6. The development of techniques for producing, handling, and uniformly injecting submicron size particles into the driven section of the shock tube has been described in References 5 and 7. The

measurement of the burnup rates of teflon powders in an inert argon diluent is discussed in Reference 6.

The results of these studies may be summarized by stating that feasibility of producing submicron size particles, injecting them uniformly into a shock tube, and vaporizing them in a time short compared to the available testing time, has been proven. While the feasibility of using such a facility for studying the chemical kinetics of reaction between the vaporization products of injected powders and the shocked flow has not been proven as yet, it can be stated that this technique does provide a uniform one-dimensional mixture of selected ablation materials mixed in the desired gas at equilibrium. The equilibrium mixture then is suitable for the study of the emissivity and absorptivity of the important chemical constituents of the mixture. We have made absorption measurements on dilute mixtures of teflon and argon, and teflon and nitrogen. The results of these experiments are reported in the next section.

## 2. EXPERIMENTAL MEASUREMENTS

Since the work of Modica<sup>3</sup> shows that gaseous  $C_2F_4$  decomposes rapidly to  $CF_2$  over the temperature interval, 1700 to 3700°K, in an inert diluent of argon, our initial measurements were aimed at identifying the principal features of the  $CF_2$  spectrum. Laird et al.<sup>9</sup>, have studied the emission and absorption spectrum of  $CF_2$  produced by a discharge in a stream of fluorocarbon vapor at a reduced pressure of a few mm Hg. Some of the results of their studies are shown in Fig. 1. The regular behavior of the many-headed band system is clearly seen.

The spectrograph system used by us in making absorption measurements is shown in Fig. 2. The basic elements of the system are shown in the schematic of Fig. 2. The development of a suitable flash source for these measurements is described in the Appendix. The plate recording spectrograph is a Jarrell-Ash F/6.3, 3/4 meter grating instrument. The grating used was blazed at 5,000 Å, with 600 lines/mm. Due to the relatively high blaze angle, the efficiency of the grating fell off quite rapidly in the spectral region 2400 - 2800 Å where the absorption measurements were made. Nonetheless, the grating still dispersed sufficient energy into this interval to be useable.

The absorption spectrum produced by the equilibrium products of a shock-heated teflon/argon mixture behind the shock wave is shown in Fig. 3. The  $CF_2$  band spectrum is clearly seen from the record of Fig. 3. By comparing the  $CF_2$  absorption record with the Xenon flashlamp reference, it is possible to obtain the ratio of the transmitted intensity to the incident intensity. For the optical path length used, and the  $CF_2$  concentration present, the absorption coefficient may thereby be deduced.

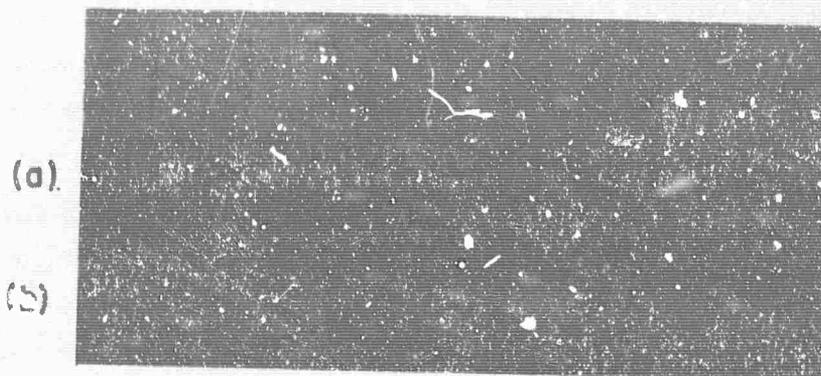


Fig. 1 Emission (a) and absorption (b) spectra of  $\text{CF}_2$  from Laird et al<sup>9</sup>, with an iron arc comparison spectra.

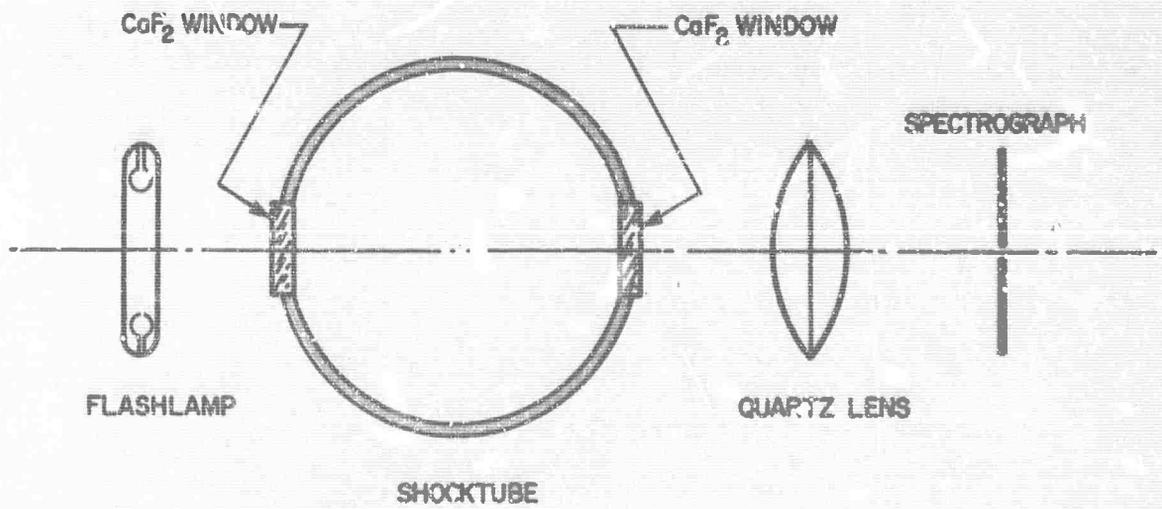


Fig. 2 Photograph of the shock tube test section showing the Xe flashlamp (left) and the  $f/6.3, 1/4$  meter grating spectrograph (right). The schematic identifies the components.

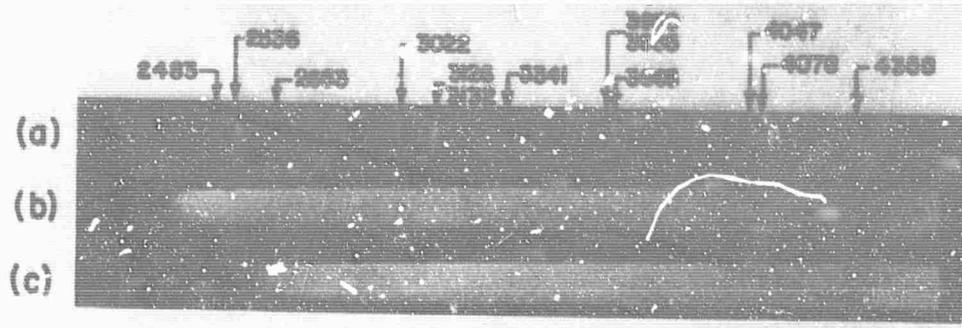


Fig. 3 Spectrograph record showing Hg reference spectrum (a), X<sub>2</sub> flashlamp reference (b), and CF<sub>2</sub> absorption spectrum (c). The absorption spectrum was obtained for a shock-heated teflon/argon mixture.

For each of the plate spectra obtained, we have determined the  $\text{CF}_2$  concentration by a measurement of the absorption at 2536 Å using the published  $\text{CF}_2$  absorption coefficient at that wavelength from Modica.<sup>8</sup> With the concentration thus determined, the transmission as a function of wavelength, determined from the plate records, then directly yields the absorption coefficient for the entire band system.

We have selected two plates for data reduction from among the tests we have conducted so far. These two tests were selected because the equilibrium temperatures differed by approximately 1,000°K, and at the same time, the  $\text{CF}_2$  concentration was nearly the same for both. We wished to cover as wide a temperature interval as possible in order to see the influence of temperature on the spectral distribution of the absorption coefficient; however, the highest temperature had to be restricted to a value for which  $\text{CF}_2$  was stable during the period of the experiment. The spectra for both of these experiments was recorded on the same plate, and the plate calibration curve is shown in Fig. 4. The plate calibration was made at a wavelength of 3700 Å for which the film gradient is similar to that at 2500 Å. The intensity of the flashlamp used to make the absorption measurements was adjusted to place the film exposure in the linear portion of its curve.

For each test, the xenon flashlamp reference spectrum, and the  $\text{CF}_2$  absorption spectrum, were densitometered to yield transmission values at selected wavelengths. The transmission at 2536 Å was monitored independently with a monochromator to check consistency. Using the transmission at 2536 Å, the  $\text{CF}_2$  concentration was deduced from the absorption coefficient measurements of Modica. With this concentration, and the measured transmission from the plate spectra at other wavelengths, the spectral absorption coefficient was deduced. The results of these measurements are shown in Fig. 5.

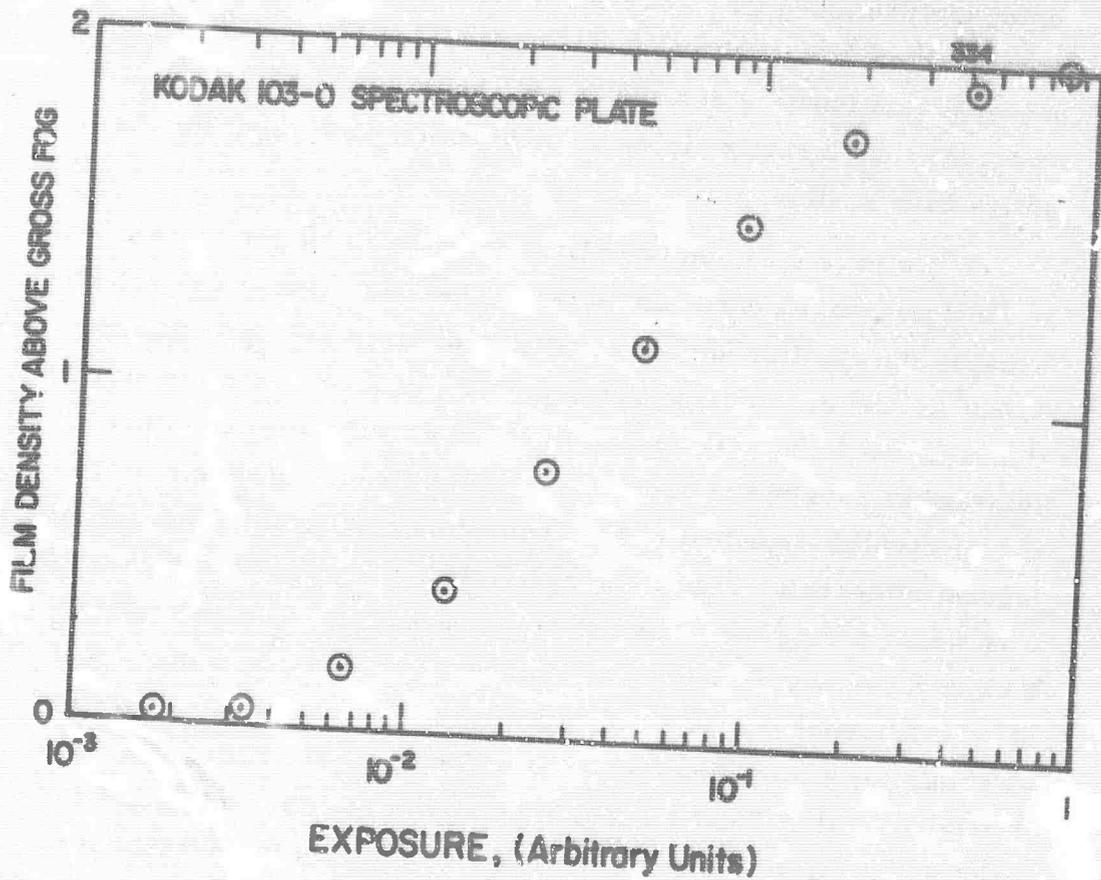


Fig. 4 Plate calibration for the absorption spectra measurements. A calibrated filter with a variable density of 0-3 was used to vary the exposure.

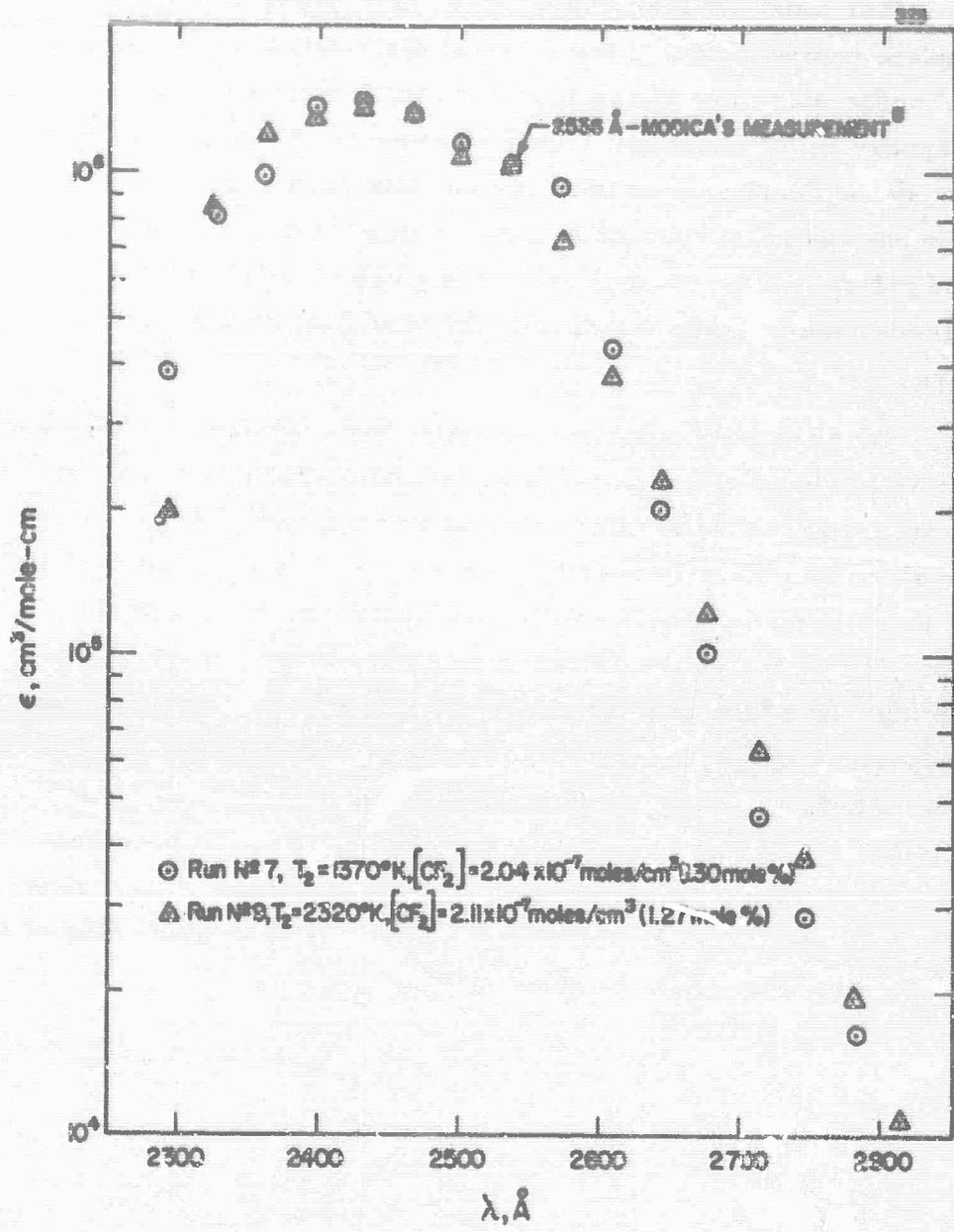


Fig. 5  $\text{CF}_2$  absorption coefficient versus wavelength

The most striking aspect of the data shown in Fig. 5 is the complete independence of the spectral distribution on temperature. The banded structure shown in the absorption record of Fig. 3 does not appear in the absorption coefficient curve shown in Fig. 5, because the densitometer used for the data reduction did not have sufficient spatial resolution to resolve this structure. Although these plates will be re-analyzed when a better densitometer is available, the average features of the band system will not be altered.

An absorption spectrum has also been obtained for the equilibrium products of a shock-heated teflon/nitrogen mixture. A spectrograph record for this experiment is shown in Fig. 6. Two things are immediately seen by reference to Fig. 6. The first is that there is no discernible  $CF_2$  band system present, and the second is that the entire CN violet system appears in strong absorption. The silicon lines shown are present due to absorption by vaporized materials from the quartz envelope of the xenon flash-lamp. There is no explanation available at present to show why CN is formed, rather than  $CF_2$ , and insufficient tests have been run to see if this is true over a wide range of temperature. However, it is clear that the nitrogen does not act as an inert diluent to help pyrolyze the teflon, as does argon.

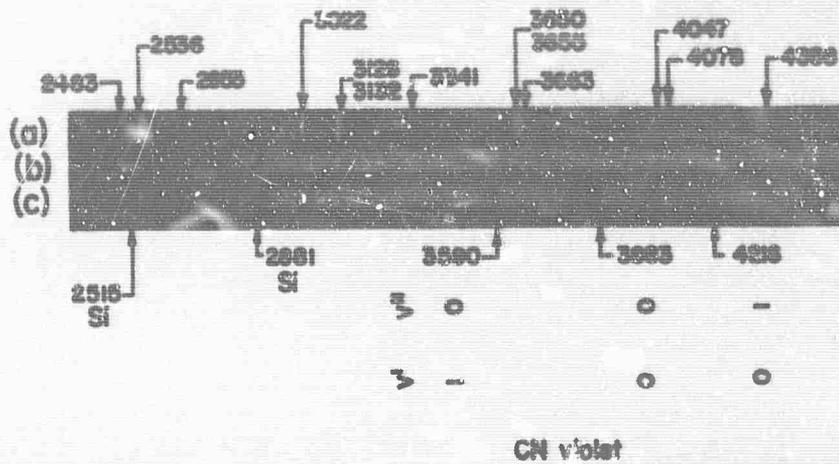


Fig. 6 Spectrograph record showing Hg reference spectrum (a), Xe flashlamp reference (b), and CN absorption spectrum (c). The absorption spectrum was obtained for a shock-heated teflon/nitrogen mixture.

### 3. CONCLUSIONS

The powder injection shock tube facility with which these tests were made has been shown to be a powerful tool for producing a gaseous mixture of the products of decomposition of the injected powders and the shock-heated gas. In the experiments quoted in this Note, the ultra-violet band system of  $CF_2$  has been identified, and the absorption coefficient as a function of wavelength for this band system has been measured at two different temperatures. This band system appears to be temperature-independent over the range of approximately 1300 - 2300°K. In the teflon/argon experiments, only the  $CF_2$  band system appears in absorption. However, in the teflon/nitrogen experiment, no  $CF_2$  appears but the CN violet system appears strongly. Whether  $CF_2$  is initially present immediately behind the shock wave in the teflon/nitrogen mixture is not known, since the time resolution of the present spectrograph equipment is not short enough to resolve the vaporization zone behind the shock wave. However, this matter will be investigated further in the future. In addition,  $CF_2$  absorption coefficient measurements will be made over a wider temperature range, and for different concentrations of  $CF_2$ .

## APPENDIX A

### THE GENERATION OF A FLASHLAMP CONTINUUM

In order to perform time resolved absorption spectroscopy measurements in a shock tube, it is necessary to have a high intensity, short duration, continuum source. This source must be able to operate in a pulse mode with low-time jitter. The flashlamps required are of the linear tube type, so that the image is rectangular when incident on the spectrograph slit. Since the first test exposures obtained by us showed the presence of many strong emission lines, and very little continuum, an experimental investigation was carried out in order to find a satisfactory system. The characteristics of the present system are presented in the following.

Fig. 2 is a photograph of the flashlamp installation, with a schematic of the optics. Construction of the lamp holder was to be coaxial, but since the capacitor available did not adapt readily to a true coaxial configuration, the holder was designed to reduce the inductance as much as possible. Brass and Teflon are the materials used in the lamp holder. Construction of the lamp assembly is shown in Fig. 7. Adjustments are included to permit using various flashlamps in the holder.

The electronics were designed to use as much of the existing instrumentation as possible. A schematic for the flashlamp trigger circuitry is illustrated in Fig. 8. The shock passage over the thin film heat transfer gage generates a signal which is amplified and sent on to the trigger input of sweep A of a Tektronix Model 545 Oscilloscope. A delay is introduced between the A sweep and the start of the B sweep to permit synchronization of the shock front and the triggering of the flashlamp. Gate pulse B provides the trigger for the 2D21W thyratron of the trigger driver. The pulse is increased to 15 kv by the 40:1 step-up ratio of the trigger



Fig. 7 Flashlamp with Holder Assembly

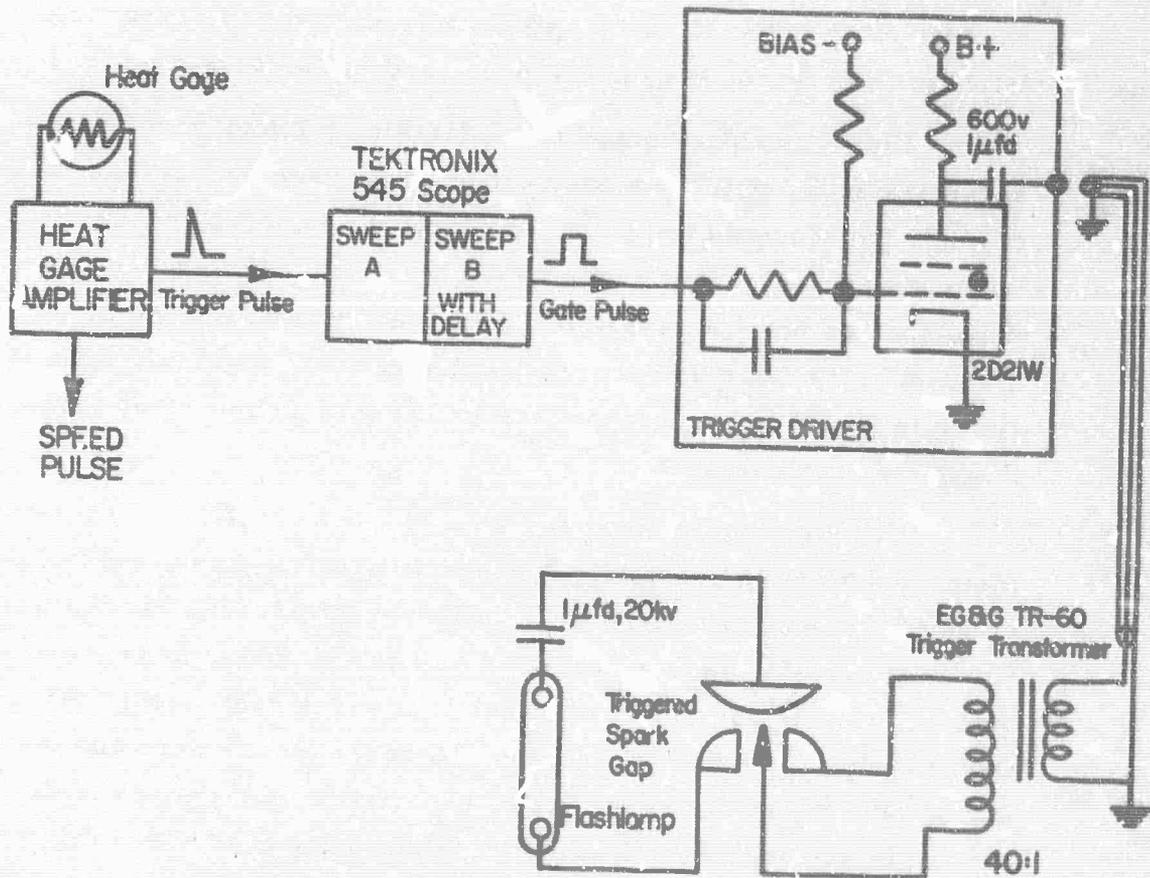


Fig. 8 Flashlamp Trigger Block Diagram

transformer. The triggered spark gap is ionized by the 15 kv pulse and discharges the energy from the capacitor into the lamp.

It has been shown<sup>10</sup> that it is necessary to have a current density in excess of 30,000 amps/cm<sup>2</sup> to produce a continuum. A series of exposures were made by us to study the influence of capacitor discharge energy on the flash spectrum. Shown in Fig. 9 are a sequence of exposures where the discharge voltage was varied with a fixed capacitance. These exposures were obtained using the optical setup shown in Fig. 2. The aperture referred to in the legend for Fig. 9 was placed over the lens of Fig. 2, and was used to reduce the flash intensity. At the higher discharge energies, strong silicon absorption lines are seen (produced by the flashlamp quartz envelope), but otherwise, the continuum is quite acceptable.

After viewing the pulse width of the light source discharge flash, it was decided to reduce the capacitance to obtain a shorter pulse width. Increasing the voltage, lowering the capacitance, and keeping the energy approximately constant, the current density would increase while the pulse width would decrease. A value of one  $\mu$ f rated for 20 kvdc was selected.

Additional spectrograms were taken from 10 kv to 20 kv to determine the best continuum produced. It was found that 20 kv produced the most satisfactory continuum.

The solutions leading to an acceptable continuum source, however, have caused secondary problems. The small size of the flashlamps (bore 4 mm, O.D. 6 mm, 38 mm arc length) make them physically weak, which has caused several failures. In addition, the light source pulse width has been most difficult to reduce. A study with Pek Laboratories<sup>11</sup> was conducted to produce a lamp geometry that would minimize the deionization time. The use of very pure quartz to reduce internal reflection and absorption of

LEGEND TO Fig. 9

<u>Line</u>	<u>Voltage, kv</u>	<u>Lens Aperture</u>
1	Hg reference	1"
2	Hg reference	1"
3	1	1"
4	1.5	1"
5	2	1"
6	2.5	1"
7	3	1"
8	3.3	1"
9	3.5	1"
10	blank	--
11	1	1"
12	1.5	1"
13	2	1"
14	2.5	1"
15	3	1"
16	3	3/4"
17	3	1/2"
18	3	1/4"
19	3	1/10"
20	3.5	1/10"
21	3.5	1/4"

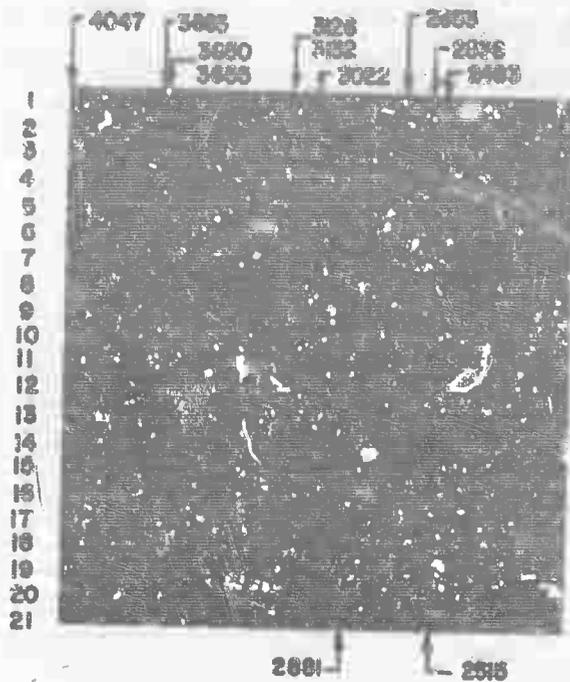


Fig. 9 Spectrophotograph record of Xenon flashlamp emission. A 15  $\mu$ f capacitor was discharged through an EG&G FX-33 lamp at selected voltages.

the ultra-violet radiation was utilized in the construction. Tests of the lamps in a special capacitor bank and holder developed by P-k Laboratories did show very short pulse widths for the lamp, but the discharge energy was not large enough to produce a continuum. When these lamps were tried in our system, the pulse width was very long. The system inductance was believed to be large enough to prevent a short rise time and to cause an under-damped system and, therefore, a test was conducted to determine the system inductance and resistance.

The flash lamp was replaced by a brass rod which has much less resistance than the lamp, and a loop probe was used to obtain an oscilloscope recording of the capacitor discharge. The waveform obtained was a damped sine wave, with the envelope a damped exponential,  $e^{-\alpha t}$ . Using the response functions of the RLC system as described by Scott<sup>12</sup> and Guillemin<sup>13</sup>, we get

$$\frac{1}{\alpha} = \frac{L_s}{R_s} = \text{time in seconds for the initial amplitude of the sinusoidal oscillation to decay to the value } 1/e \quad (A-1)$$

$$= 6.4 \times 10^{-6} \text{ sec from oscilloscope records.}$$

where

$L_s$  = system inductance, henrys

$R_s$  = system resistance, ohms

Therefore,

$$\alpha = .123 \times 10^6, \text{ sec}^{-1} \quad (A-2)$$

From the equation for the damped natural frequency,  $\omega_d$  (rad/sec) we have

$$\omega_d = \sqrt{\omega_o^2 - \alpha^2} = 2\pi/\tau_d, \quad (A-3)$$

where

$\omega_o$  = undamped natural frequency, rad/sec

and

$\tau_d$  = damped period, sec

=  $4.8 \times 10^{-6}$  sec from oscilloscope records.

Therefore,

$$\omega_d = 1.31 \times 10^6, \text{ sec}^{-1}. \quad (A-4)$$

Solving Eqs. (A-2), (A-3) and (A-4) for  $\omega_o$  yields

$$\omega_o = 1.315 \times 10^6, \text{ sec}^{-1} \quad (A-5)$$

Since  $\alpha < \omega_o$ , the system is underdamped.

From the relation

$$\omega_o^2 = 1/L_s C_s, \quad (A-6)$$

and noting that our system capacitance,  $C_s$ , is  $1 \mu\text{f}$ , we get the system inductance to be

$$L_s = .575 \times 10^{-6} \text{ henrys.} \quad (\text{A-7})$$

Combining Eqs. (A-1), (A-2) and (A-7), we get the system resistance

$$R_s = .07 \text{ ohm.} \quad (\text{A-8})$$

Since it was assumed that the brass rod contributed a negligible amount to the system resistance and inductance, the system parameters are

$$R_s = .07 \text{ ohms, } L_s = .575 \times 10^{-6} \text{ henrys, } C_s = 1 \mu \text{ farad.} \quad (\text{A-9})$$

If the flashlamp resistivity is calculated from Marshak<sup>14</sup>, we get

$$\rho = 0.1/\sqrt{V}, \text{ ohm - cm} \quad (\text{A-10})$$

where  $V$  is given in volts.

For the flashlamp used (4 mm base x 38 mm length), the lamp resistance at 20 kv is

$$R_L = \rho l/A = .02 \text{ ohm.} \quad (\text{A-11})$$

Adding the lamp resistance to the system resistance gives a combined resistance of 0.09 ohms, leading to a new damping constant

$$\alpha_L = .155 \times 10^6, \text{ sec}^{-1}, \quad (\text{A-12})$$

and a new time constant

$$\tau_{d,L} = 6.45 \times 10^{-6}, \text{ sec.} \quad (\text{A-13})$$

In order to reduce the continuum source pulse width, the time constant should be decreased. This can be done by reduction of the system inductance, which will permit a faster energy transfer into the lamp. Furthermore, a lower inductance will not store as much of the energy, thereby increasing the efficiency of the system. Since most of the inductance is contained in the capacitor, an improved version is required. Capacitors with an inductance of 40 nanohenrys or less are available commercially.

Based on the 40 nanohenrys value, the new system parameters are:

$R_s = .02$  ohms, the lowest value obtainable due to flashlamp limitation.

$L_s = .04 \times 10^{-6}$  henrys inductance of the capacitor.

$$\tau_d = \frac{L_s}{R_s} = 2 \times 10^{-6} \text{ sec}$$

$$\alpha = .5 \times 10^6, \text{ sec}^{-1}$$

These values are the optimum possible, but in actual practice the  $\tau_d$  will be larger and the  $\alpha$  smaller. This will be caused by an inductance and resistance contribution of the flashlamp holder assembly.

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Hallodyne Corporation, Los Angeles, California 90044  
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Unclassified Report

Absorption spectra have been obtained for the equilibrium mixtures of shock-heated teflon/argon and teflon/nitrogen mixtures. The ultraviolet  $CF_2$  band system has been identified, and its absorption coefficient has been measured as a function of wavelength in the spectral interval 2300 - 2800 Å. The spectral distribution of the  $CF_2$  absorption coefficient has been found to be independent of temperature at 1170 and 2320°K.  $CF_2$  is the only band system observed in absorption for teflon/argon mixtures in the spectral interval 2200 - 4400 Å. By contrast, only the CN violet system is observed for teflon/nitrogen mixtures in the same spectral interval.

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1. Absorption Spectra
  2. Absorption Products
  3. Shock Tube
  4. Title
  5. Hoener, W. J. and Sellers, R. P., Jr.
- Heliodyne Corporation  
Research Note 21  
Contract No. DA 04-493-  
AMC-614(Z)



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Heliodyne Corporation, Los Angeles, California 90064  
 THE ABSORPTION SPECTRA OF SHOCK-HEATED  
 TEFLON/ARGON AND TEFLON/NITROGEN MIXTURES,  
 by W. J. Hoobar and E. J. Sellers, Jr., June 1965,  
 23 p. incl. illus. (ARPA Order No. 360; Project  
 DEFENDER) (Heliodyne Corporation Research Note 21)  
 (Contract No. DA-04-495-AMC-448(2))

Unclassified Report

Absorption spectra have been obtained for the equilibrium products of shock-heated tetrafluoroethane/argon and tetrafluoroethane/nitrogen mixtures. The ultraviolet CF<sub>2</sub> band system has been identified, and its absorption coefficient has been measured as a function of wavelength in the spectral interval 2300 - 2860 Å. The spectral distribution of the CF<sub>2</sub> absorption coefficient has been found to be independent of temperature at 1370 and 2320°K. CF<sub>2</sub> is the only band system observed in absorption for tetrafluoroethane mixtures in the spectral interval 2800 - 4400 Å. By contrast, only the CN violet system is observed for tetrafluoroethane/nitrogen mixtures in the same spectral interval.

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 II. Hallidays Corporation  
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