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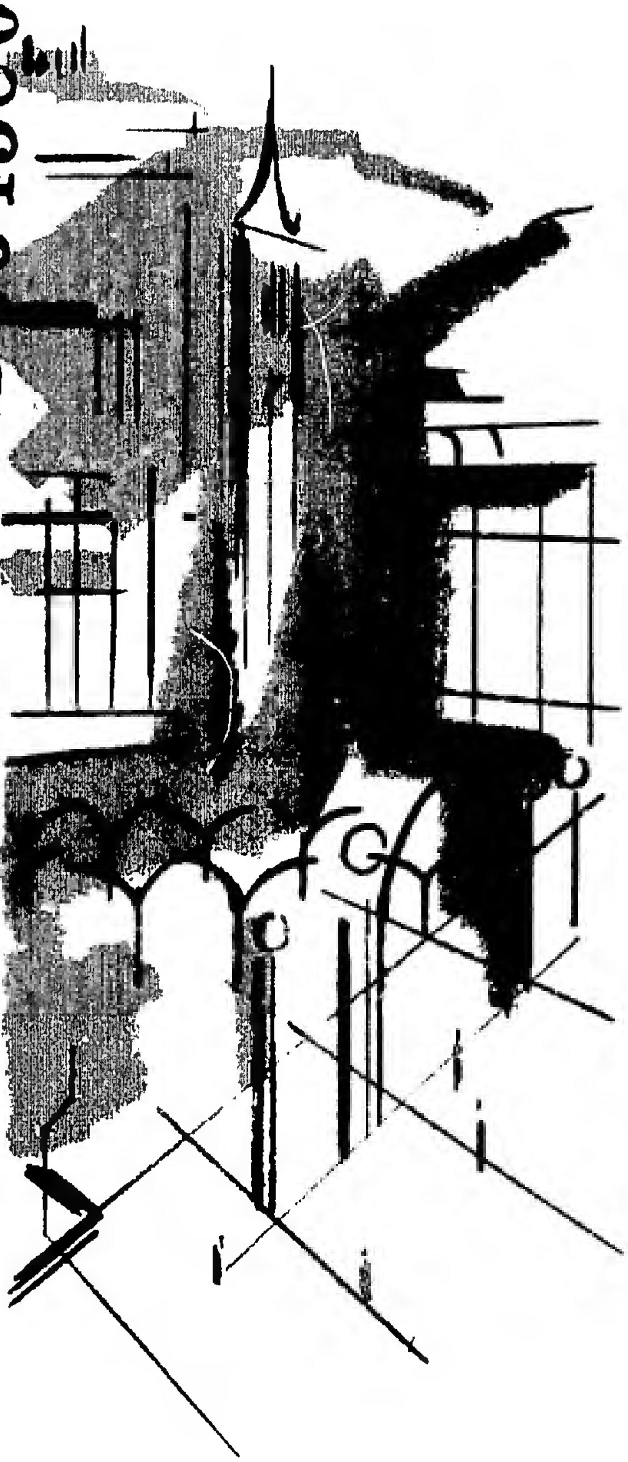

MASS SPECTROSCOPIC OBSERVATION OF IGNITION PHENOMENA IN A SMALL ROCKET COMBUSTION CHAMBER*

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The ignition of rocket propellants most commonly has been studied by measurement of ignition delay through observation of chamber pressure, light emission, or chamber temperature rise. Such observations are useful in establishing the effects of initial chamber pressure, propellant temperature, and injection timing upon ignition delay time but yield little information on the chemical mechanism of the ignition process. The possibility of studying ignition through determination of the chemical species in the combustion chamber before, during, and after ignition was suggested by measurements of combustion product composition reported by Summers and McMullen (1).

EXPERIMENTAL TECHNIQUE

The experimental technique and apparatus used in this study were developed for the Air Force Rocket Propulsion Laboratory by Rocketdyne and are described in references (1) and (2). A small water cooled rocket combustor with a characteristic length, L^*, of about 100 inches and thrust level of about 10 pounds was employed. The important feature of the apparatus is the sampling system, located at the nozzle end of the combustion chamber, see Figure 1. The sampling system is designed to deliver a representative combustion product sample to a time of flight mass spectrometer for qualitative and quantative analysis. A molecular beam of sample gas is created in a differentially pumped, two skimmer system as described schematically in Figure 2. Rapid initial cooling of the sample at the rate of about 5×10^7 °K/sec is obtained in the inlet of the sampling probe to reduce the sample temperature to an estimated

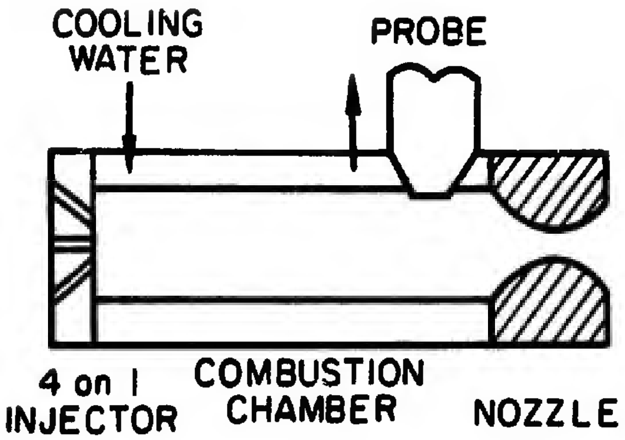

FIGURE 1 LABORATORY COMBUSTOR
$L^* = 100$ in, $F = 10$ lbs

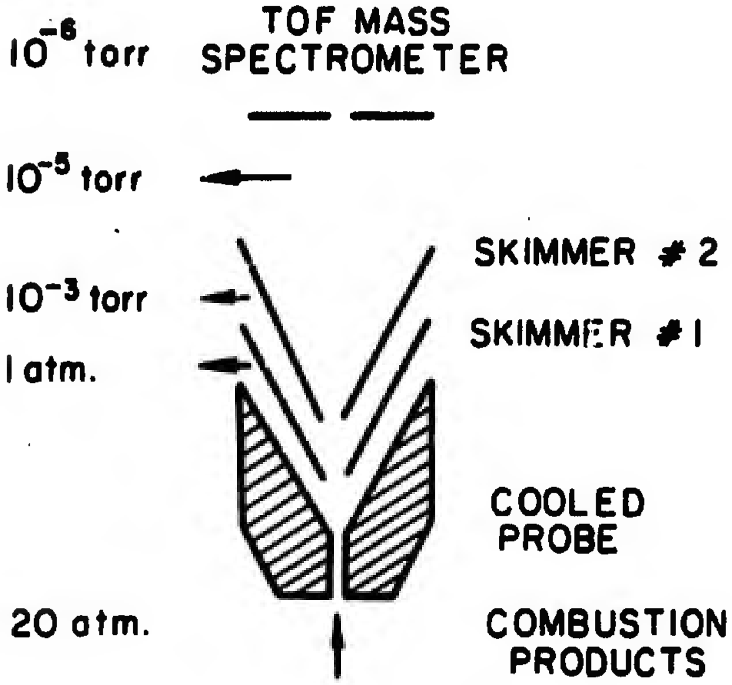

FIGURE 2 SAMPLING SYSTEM

$540^{\circ}K$ in about 40 microseconds (2). This rapid quenching should freeze the sample composition, at least in terms of the more stable (non-radical) species.

Data collected in studies of steady state combustion and propellant performance were made available by Captain E. T. McMullen of the Air Force Rocket Propulsion Laboratory. Mass spectra were recorded photographically from an oscilloscope display. The frequency of data collection was limited by the recording technique and in all cases was less than the 10 kilocycle scan frequency of the Bendix Model 14 time of flight mass spectometer. Data from early studies of the hydrazine/nitrogen propellant combination were recorded at approximately 150 msec time intervals. Data from more recent studies of the hydrazine/chlorine pentafluoride propellant combination were recorded at 22 msec time intervals. Since the time scale of ignition phenomena is likely to be of the order of 5 msec or less, utilization of the mass spectrometer at its full capacity of 100 microsecond sample analysis (or 10 microsecond for newer models) would be desirable. The alternate possibility of observing a few, selected mass numbers might reduce data recording problems.

The time response of the sampling system -- mass spectrometer combination is important to interpretation of observed spectra. The sample transit time through the sampling system is comparable to the mass spectrometer scanning time of 100 microseconds. The sampling system, however, introduces relatively large "background" concentrations which appear to reduce the effective system response time. Species appear in the mass spectra at least within the data recording time period, 22 msec, following introduction into the combustor. Species disappear, for example the helium purge gas, however, from the mass spectra rather slowly and may persist for as long as one second following termination of flow into the combustor. For a characteristic chamber length of $L^* = 100$ inches, the stay time, τ, can be estimated from the relation

$$\tau = 2.38 \frac{L^*}{c^*}$$

to be about 3 msec. The persistence of species in the mass spectra following termination of introduction into the combustion chamber is thought to result from retention in the sampling system introduced "background." The use of a chopped beam in the sampling system should allow compensation for this effect. As a result of the apparently more rapid response to the introduction of a specie than its termination, the appearance of a specie is to be given more significance than its disappearance or failure to disappear.

HYDRAZINE/NITROGEN TETROXIDE IGNITION

Although data were recorded at the relatively slow rate of approximately every 150 msec, interesting information is contained in the mass spectra from the ignition of hydrazine and nitrogen tetroxide. Interpretation of the spectra is limited to qualitative identification of the species present. Quantitative analyses have been made (1) but the spectra studied in the present investigation were not judged to be of adequate clarity for quantitative analysis. The injector configuration was 4 oxidizer on one fuel.

A sequence of mass spectra are presented in Figures 3a, 3b, and 3c for an oxidizer rich mixture at an equivalence ratio (fuel to oxidizer) of $\phi = .65$. Propellants were injected simultaneously and preceded by a helium purge. The first spectrum shows the "background" which for this apparatus includes the gases introduced in the sampling system in addition to the usual mass spectrometer residuals and inleaking gases. The species N_2, O_2, CO_2 Ar, H_2O, and He can be identified. At 150 msec following the first spectra, the presence of nitrogen tetroxide, as indicated by the appearance of mass number 46 (NO_2) and 30 (NO) peaks, is noted. The following spectrum, at 300 msec, (not shown) has the same general features as Figure 3b. At one second following the first spectrum, combustion is well established and the presence of the species N_2, O_2, CO_2, Ar, NO, and H_2O and disappearance of NO_2 and He are noted. Of particular interest is the long duration during which the NO_2 peak is observed, at least 300 msec. It is not expected that the relatively reactive and unstable NO_2 would survive as long as He in the form of a "system residual." The source of this peak, in addition to N_2O_4 or NO_2, could be a nitrate compound, such as ammonium of hydrazinium nitrate.

Similar spectra are presented for the ignition of a near stoichiometric, $\phi = .93$, mixture of hydrazine and nitrogen tetroxide. The background spectrum appears in Figure 4a. In contrast to the previous example, at 150 msec later, Figure 4b, the mass spectrum contains only N_2, O_2, Ar, CO_2 and H_2O. Missing are the NO and NO_2 observed in the previous case. A rather speculative interpretation is that an excess of nitrogen tetroxide favors deposition of a condensed phase nitrate or nitrogen tetroxide on the wall and that this condensed phase survives for a relatively long period, i.e., in excess of 300 msec.

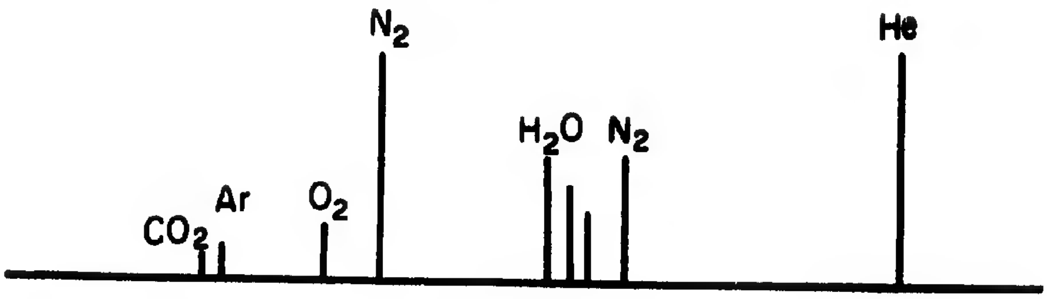

FIGURE 3a. N_2H_4/N_2O_4, PRE - IGNITION, t = 0 sec.
$\phi = 0.65$, 4 ox on 1 fuel

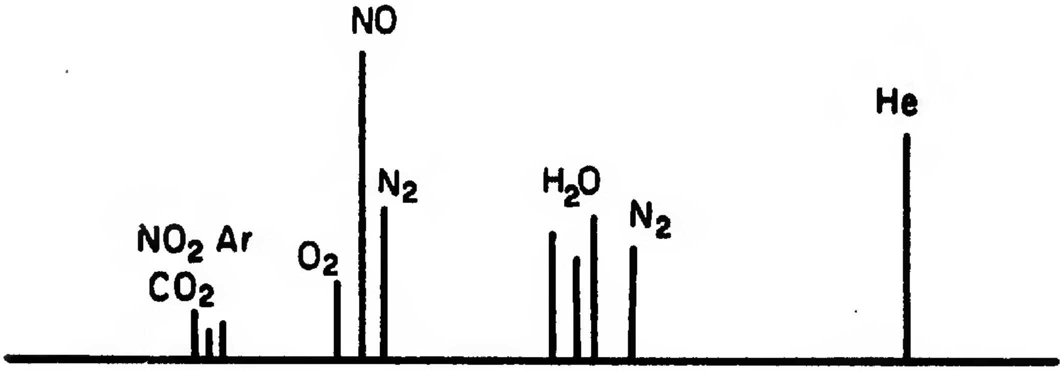

FIGURE 3b. N_2H_4/N_2O_4, POST - IGNITION, t = 0.150 sec.
$\phi = 0.65$, 4 ox on 1 fuel

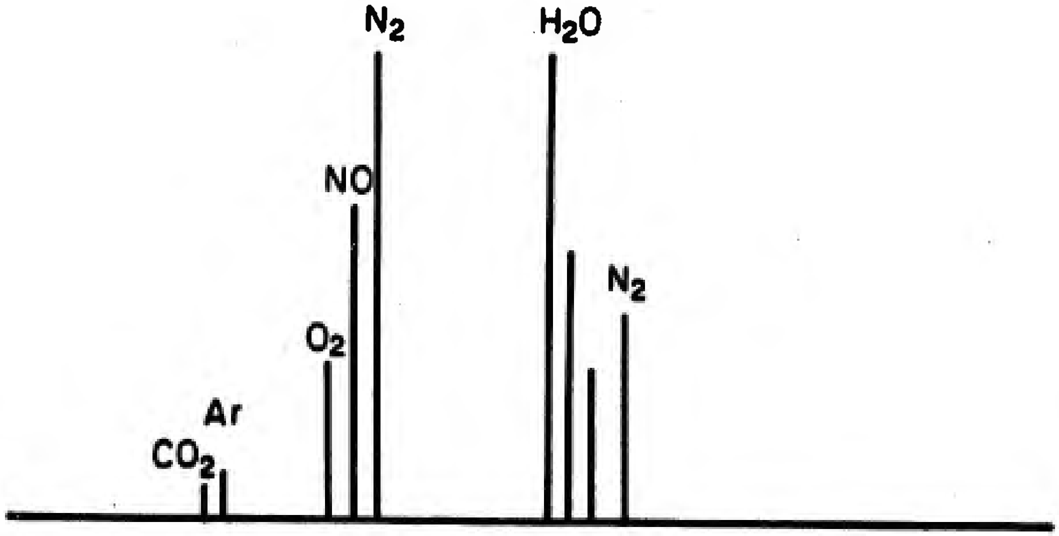

FIGURE 3c. N_2H_4/N_2O_4, POST - IGNITION, t = 1.000 sec.
$\phi = 0.65$, 4 ox on 1 fuel

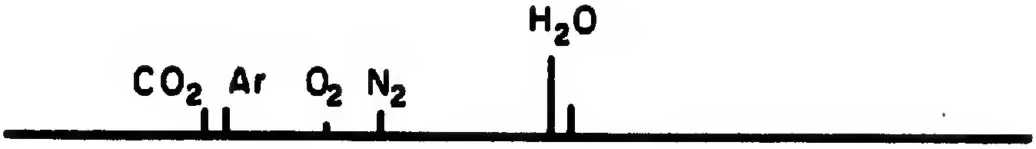

FIGURE 4a. N_2H_4/N_2O_4, PRE-IGNITION, t = 0 sec.
$\phi = 0.93$ 4 ox. on 1 fuel

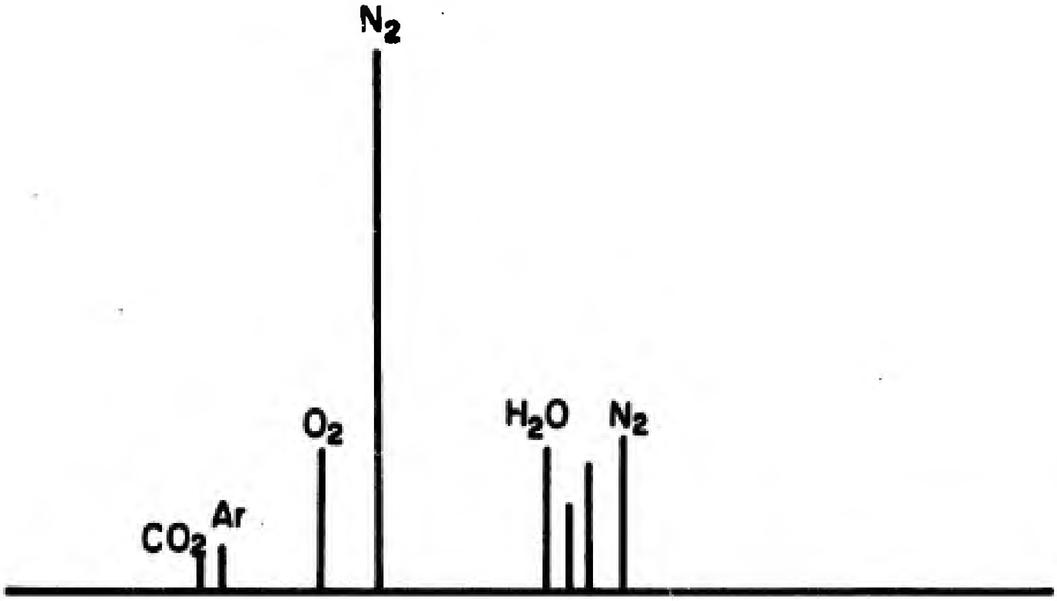

FIGURE 4b. N_2H_4/N_2O_4, POST-IGNITION, t = 0.150 sec.
$\phi = 0.93$, 4 ox on 1 fuel

No data were collected at fuel rich mixture ratios becuase of plugging of the sampling system under such conditions.

HYDRAZINE/CHLORINE PENTAFLUORIDE IGNITION

Two sets of data were available from hydrazine/chlorine pentafluoride propellant performance studies which contained sufficient information during the ignition process to be of interest. Once again the poor quality of the spectra obtained, largely due to low sample to background ratios, prevented quantitative analysis.

The first case is for a fuel rich mixture, $\phi = 1.21$. The injector configuration was reversed from the previous studies, now being 4 fuel on one oxidizer. The sample spectra have been located in time on a chamber pressure -- time history of the combustion process, as shown in Figure 5. Also changed from the previous studies, an oxidizer lead of about 200 msec was employed. The mass spectra, as presented in Figures 6a, 6b, 6c, and 6d may be summarized according to the species identified.

spectrum	time	species
a	"background"	N_2, O_2, Ar, H_2O, He
b	oxidizer, pre-ignition	N_2, O_2, Ar, ClF, F, H_2O, He
c	near-ignition	N_2, O_2, ClF, F, HF, H_2O, He
d	post-ignition	N_2, O_2, Ar, HCl, HF, H_2O, H_2

The pressure of the oxidizer is clearly indicated by the mass fragments ClF and F. Ignition is indicated by the appearance of the product specie HF. The time delay between the appearance of the CPF fragments, ClF and F,

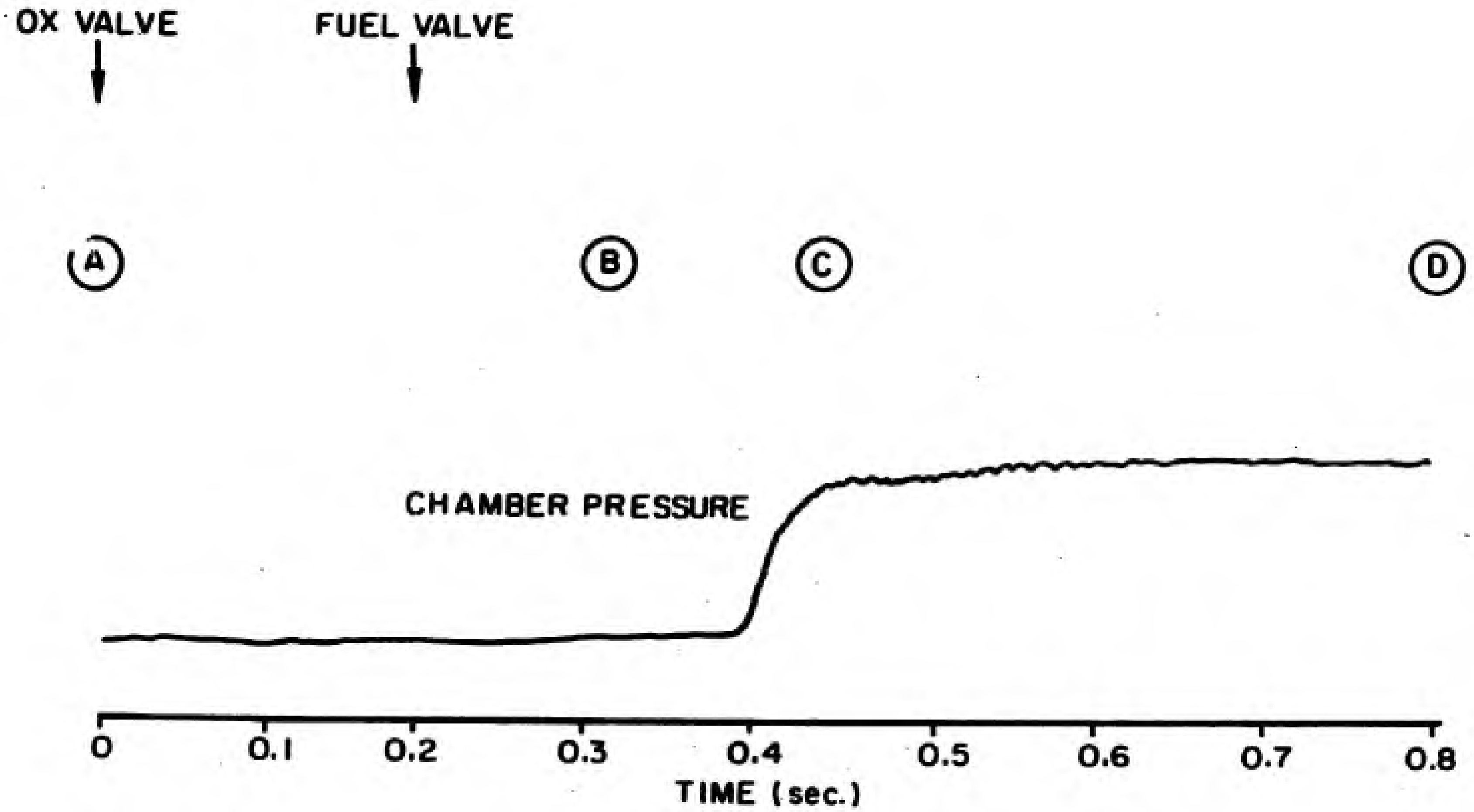

FIGURE 5 HYDRAZINE/CPF IGNITION, $\phi = 1.21$
4 fuel on 1 ox

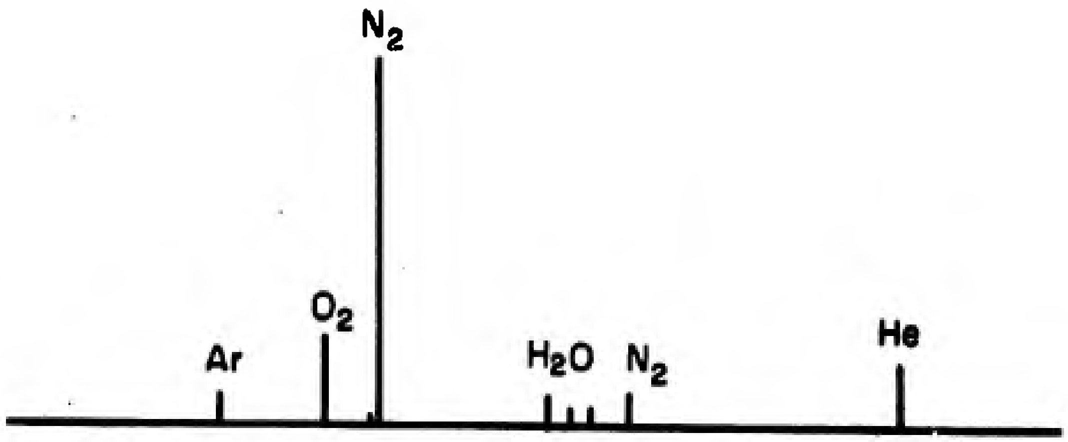

FIGURE 6a. N_2H_4/CPF PRE-IGNITION BACKGROUND
$\phi = 1.21$, 4 fuel on 1 ox, TIME A

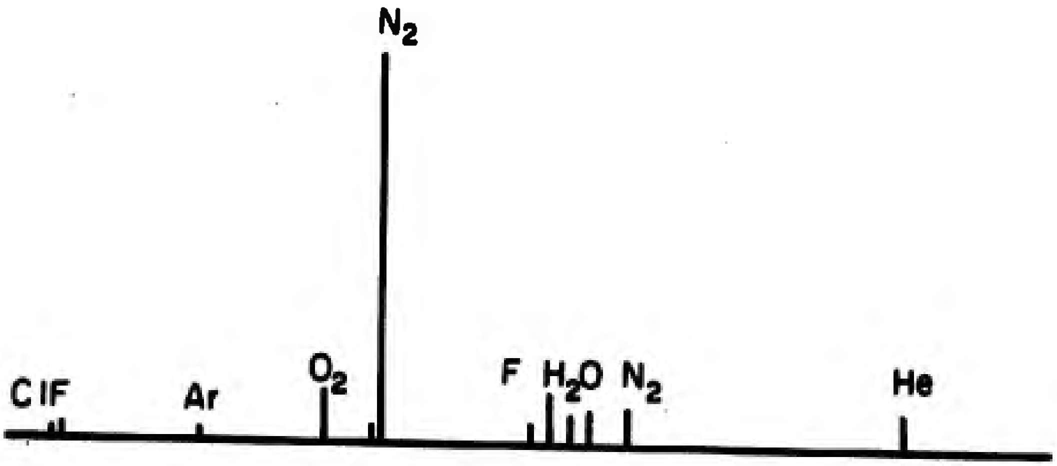

FIGURE 6b. N_2H_4/CPF PRE-IGNITION, CPF LEAD
$\phi = 1.21$, 4 fuel on 1 ox, TIME B

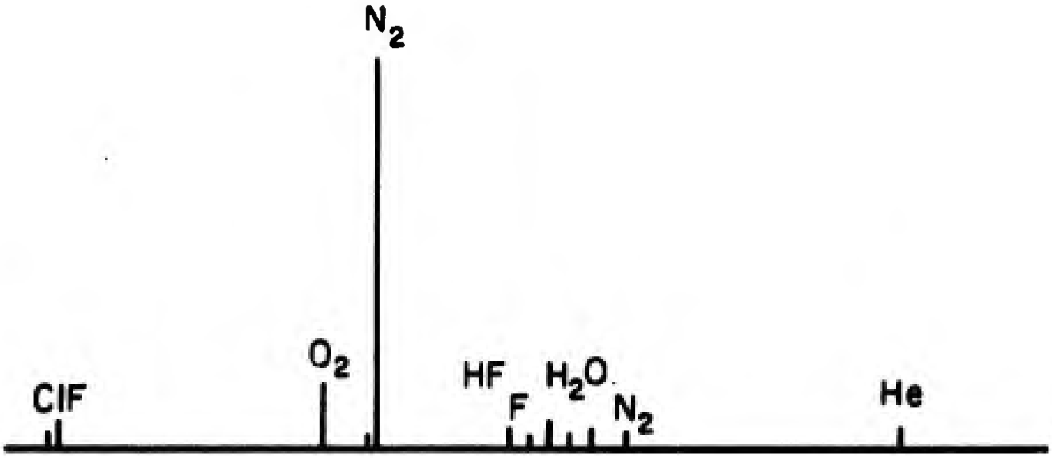

FIGURE 6c. N_2H_4/CPF, IGNITION
ϕ = 1.21, 4 fuel on 1 ox, TIME C

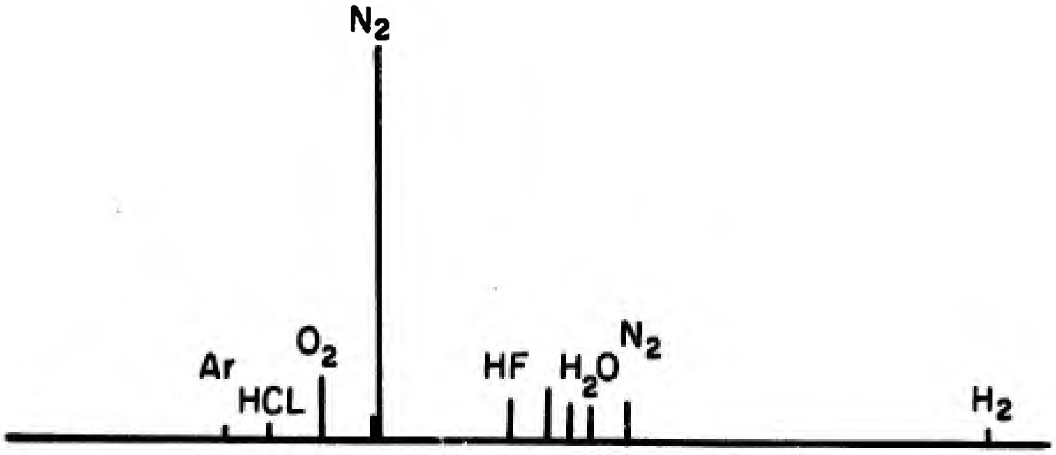

FIGURE 6d. N_2H_4/CPF, PRE-IGNITION
ϕ = 1.21, 4 fuel on 1 ox, TIME D

and the product specie, HF, agrees within one time interval (or 22 msec) with the oxidizer lead time. The post-ignition phase is characterized by the appearance of HCl and H_2 and disappearance of ClF, F, and He. The O_2, Ar, and H_2O are background species and not combustion products.

The second case is for a near stoichiometric mixture, $\phi = 1.08$. Once again an oxidizer lead was used by the injector configuration was reversed to 4 oxidizer on one fuel. Mass spectra are presented for the times as indicated on the pressure -- time record for this particular run, Figure 7. The spectra are presented as Figures 8a, 8c, and 8d, and, also, are summarized as follows.

spectrum	time	species
a	"background"	O_2, N_2, Ar, CO_2, H_2O, He
b	oxidizer, pre-ignition	O_2, N_2, Ar, CO_2, ClF, H_2O, He
c	near-ignition	O_2, N_2, Ar, CO_2, ClF, HF, H_2O, He
d	post-ignition	O_2, N_2, Ar, CO_2, ClF, HCl, HF, He, H_2

The results are quite similar to the fuel rich case, with the notable difference that ClF presists as a product specie in the near stoichiometric case whereas it had disappeared in the preceding fuel rich case. The injector configuration plays no apparent role in determining the product species detected.

Determination of the presence of ammonia was sought, both in the ignition and post-ignition spectra. Because of the masking effect of the background water and oxygen spectra, identification of ammonia was questionable.

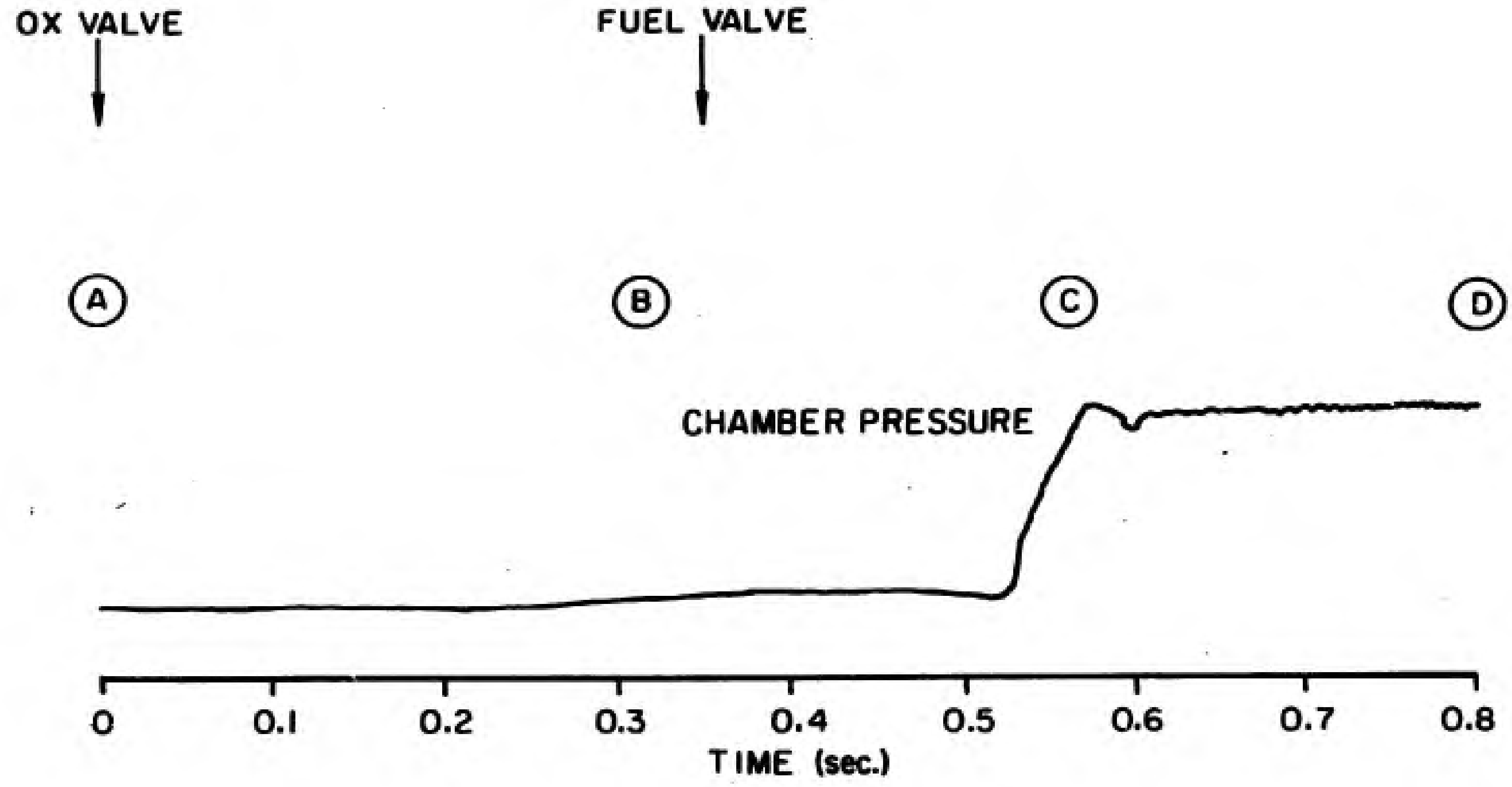

FIGURE 7 HYDRAZINE/CPF IGNITION, $\phi = 1.08$
4 ox on I fuel

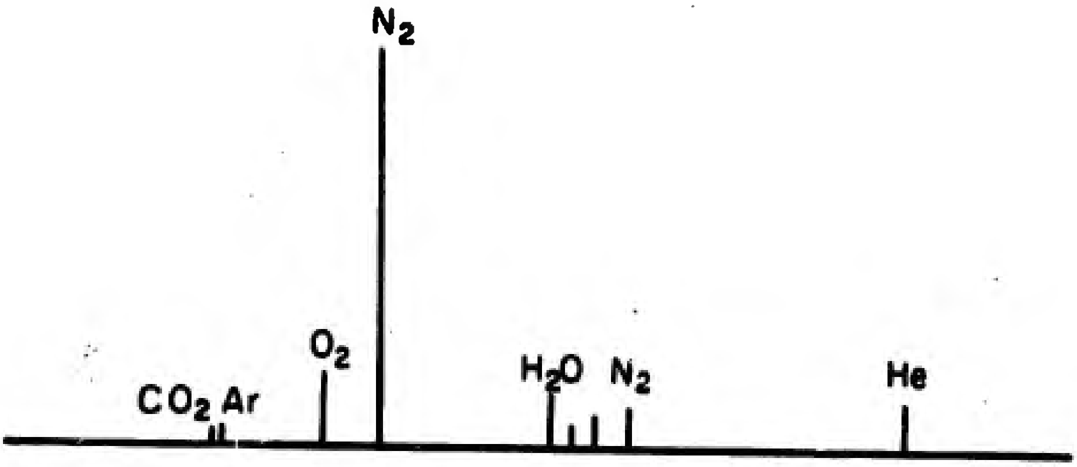

FIGURE 8a. N_2H_4/CPF, PRE-IGNITION BACKGROUND
ϕ = 1.08, 4 ox on 1 fuel, TIME A

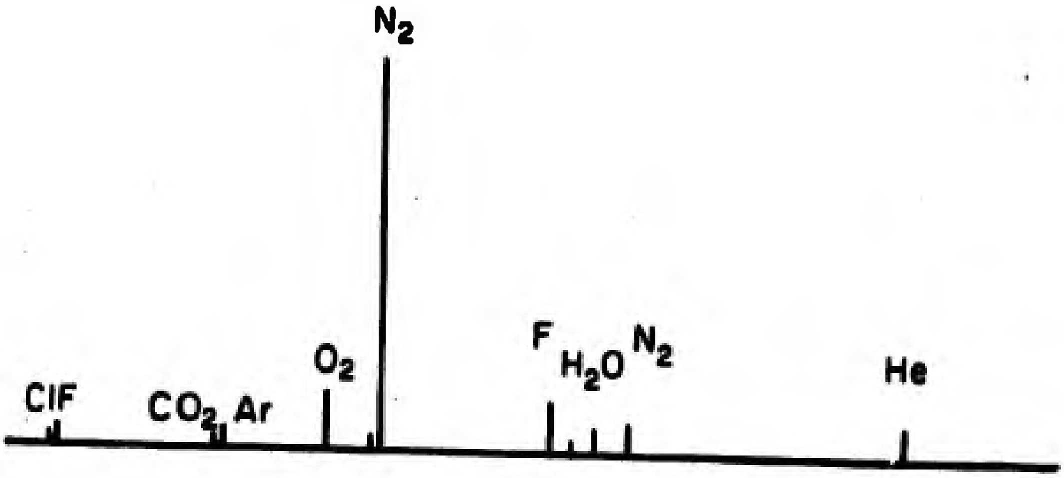

FIGURE 8b. N_2H_4 /CPF, PRE-IGNITION, CPF LEAD
ϕ = 1.08, 4 ox on 1 fuel, TIME B

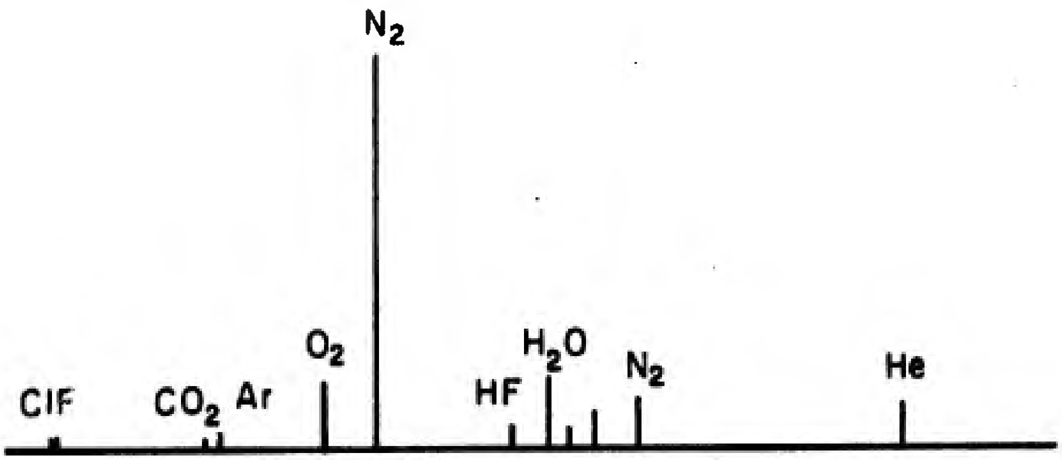

FIGURE 8c. N_2H_4/CPF, IGNITION
ϕ = 1.08, 4 ox on 1 fuel, TIME C

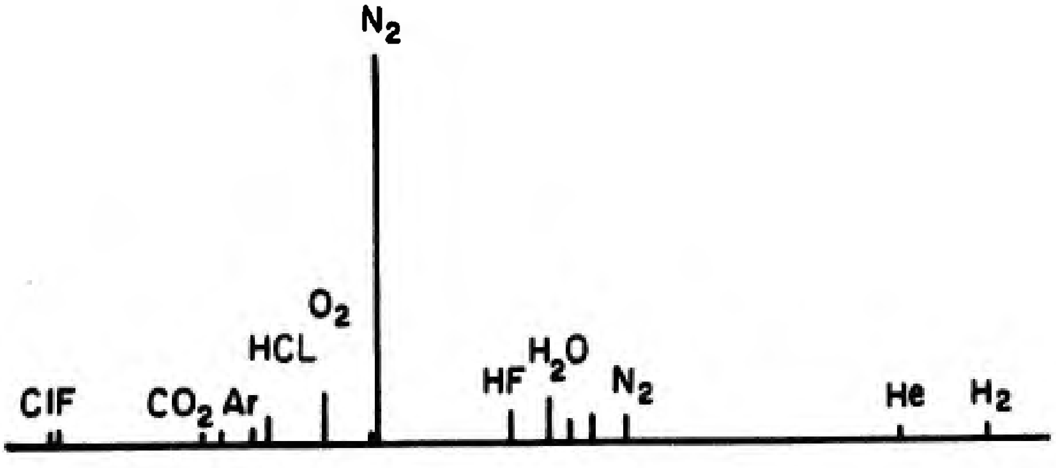

FIGURE 8d. N_2H_4/CPF POST-IGNITION
ϕ = 1.08, 4 ox on 1 fuel, TIME D

COMMENTS ON OBSERVATIONS AND TECHNIQUE

The sequential change from oxidizer species to product species during the ignition phase of hydrazine/chlorine pentafluoride is consistent with the expected behavior of ignition with an oxidizer lead. The ignition process commences at an equivalence ratio of $\phi = 0$ and concludes at an equivalence ratio $\phi > 0$.

The observed presence of ClF without the presence of F or F_2 plus the late appearance of HCl indicates a preferential reaction of fluorine in the reduction of the interhalogen. The observations of the hydrazine/nitrogen reaction confirm the suggested (3) preferential reduction of nitrogen dioxide to nitric oxide and disappearance of the nitric oxide only through reaction with hydrazine or hydrazine decomposition products. It is noted that nitric oxide, contrary to equilibrium predictions, survives in oxidizer rich combustion.

As a means of studying ignition, the technique of direct sampling and analysis provides information not available from other approaches. Since the data analyzed were not collected with the study of ignition in mind, it is expected that the technique could be refined to yield more fruitful results than herein presented. In particular, more rapid data recording and reduction of the background to sample ratio are required to yield quantitative information on combustor gas compositon. The potential response time of the sample system and time of flight mass spectrometer are well suited to the study of ignition phenomena.

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13. ABSTRACT

Observations of small rocket firings were examined for evidence of ignition phenomena. Qualitative analysis of product gas composition was made through molecular beam sampling from the combustor wall and direct mass spectrometer analysis. The combustion of hydrazine/nitrogen tetroxide and of hydrazine/chlorine pentafluoride were observed. The technique allows following the sequence of species present in the chamber during the ignition phase. Time resolution was limited by data recording techniques to 22 msec.

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