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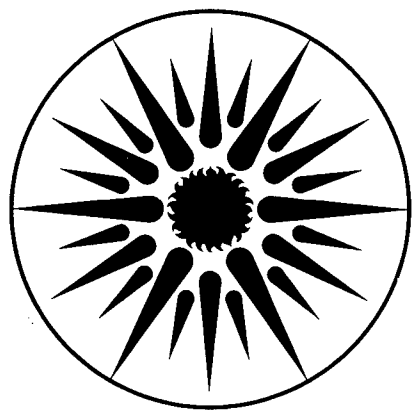
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and A.K. Oppenheim

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## MOLECULAR BEAM SAMPLING OF TRANSIENT COMBUSTION

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## ABSTRACT

Transient combustion has been studied with a molecular beam mass spectrometer. The molecular beam has been fully characterized using time-of-flight measurements for the entire range of temperatures and pressures encountered during combustion of flash-ignited mixtures of CH<sub>4</sub>/O<sub>2</sub>/NO<sub>2</sub>/Ar. Temperature profiles of reacting mixtures are measured, and indicate that there are no significant perturbations of a homogeneous gas mixture due to the sampling technique. Mass signals are recorded and presented with a time resolution of ~100 usec. Beam overrun, due to the hotter, and thus faster, constituents of the molecular beam formed later than the colder and slower portions, is quantified using a numerical technique developed for this purpose.

## INTRODUCTION

A wide range of combustion problems have been explored with molecular beam mass spectrometers[1]. Application of this technique to transient combustion events is not well established, due to the significant problems associated with sampling and data interpretation. Researchers previously have studied pyrolysis[2], spark ignition[3], internal combustion engines[4], and some of the theoretical problems of the technique[4,5].

We have constructed a direct sampling molecular beam system to study the chemical species important in the ignition process of lean homogeneous gas mixtures. The rapid and large changes in temperature, pressure, and chemical composition in transient combustion effect the formation of the molecular beam and influence the time resolution achievable in a system. A thorough understanding of these phenomena is necessary before any meaningful mass determinations are possible. We have previously reported on some of the significant perturbations in our system[6,7], and will use those results to show how mass signals can provide information on a variety of chemical species.

## EXPERIMENT

The Molecular Beam Mass Spectrometer (MBMS) apparatus used in this investigation is shown schematically in Fig. 1. Three stages of differential pumping are used to isolate the detection chamber from the sampling region. First stage pumping is provided by a 10" NRC oil diffusion pump (rated speed of 5300 l/s) backed by a Welch

Duo-Seal 7 1/s mechanical forline pump. The second and third stages are each pumped by individual Varian 6" oil diffusion pumps with a rated speed of 2400 1/s. Each diffusion pump is backed by a 5 1/s mechanical pump. The third stage also contains a water baffle to minimize back streaming into the detection chamber. Pressures in the three stages are approximately  $4 \times 10^{-4}$ ,  $5 \times 10^{-5}$ , and  $2 \times 10^{-7}$  torr, respectively, during experiments.

A 2.5 cm O.D. reaction cell is situated in a flash chamber below the first stage. The cell has two ports, one for filling and purging and the other for mounting a Kistler 211B piezotron for pressure measurements. The flash chamber consists of a highly polished aluminum housing containing two E.G.&G. FX-47C-3 xenon flash lamps, powered by a 140 ufd. capacitor charged to 3.0 kilovolts. The lamp discharge typically lasts 120 usec.

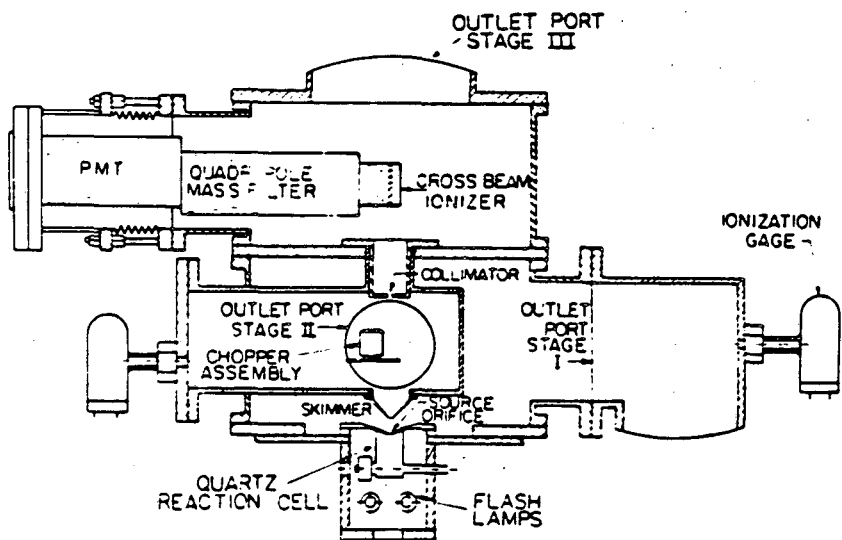


Fig. 1. Schematic diagram of the apparatus

Heated argon beams at atmospheric pressure were used to evaluate beam characteristics at temperatures below 1000 K. Flash ignited combustion of  $\text{CH}_4/\text{O}_2/\text{NO}_2/\text{Ar}$  mixtures were studied at initial source pressures between 150 and 300 torr. A typical mixture contained 0.82 Ar, 0.05  $\text{CH}_4$ , 0.06  $\text{O}_2$ , and 0.07  $\text{NO}_2$ .

The sampling orifice is circular with a hole diameter of 160 micrometers. The orifice is at the apex of a 120 degree included angle quartz cone which is made by a vacuum forming process followed by selective polishing. This procedure produces a sampling orifice with a small channel length with respect to the orifice diameter. A Pyrex skimmer is located 1.15 cm from the sampling orifice, or  $72 \times d$  (skimmer distance to orifice diameter). It has an included internal angle of 60 degrees and a skimmer orifice diameter of 762 micrometers.

A mechanical chopper, located in the second stage 8.7 cm from the source, is a thin aluminum disk 0.165 cm thick and 5.08 cm in diameter. A disk with eight 0.165 cm wide slots evenly spaced around its periphery was used for time-of-flight measurements, and one with two 90 degree sectors was installed when making concentration measurements. A timing aperture is placed inside the slots which allows a photodiode-detector assembly to signal each revolution. The chopper is spun by a synchronous motor (Globe Industries Model #53A1000-2) lubricated for vacuum service. The two phase drive circuitry allows operating speeds in excess 200 Hz. The distance from the chopper to the detector plane is 20.5 cm.

A 0.114 cm diameter collimating aperture is located between the second and third stage vacuum chambers. The detector is an Extra-Nuclear quadrupole mass filter, equipped with a cross beam electron impact ionizer. Filtered ions are detected by a 21 stage copper-beryllium particle multiplier tube (PMT). The current output from the PMT is dropped across a 100 K resistor to ground, and the resulting voltage is amplified by a Pacific Photometric amplifier (model #60A-2).

Signal acquisition is performed by a 10-bit, 4-channel, high speed analog-to-digital converter (ADC) with internal buffer memory (Lecroy model #8210). A DEC LSI 11/2 computer controls the data acquisition process by using the photodiode-detector signal from the beam chopper to initiate the ADC. Typical one shot data acquisition

runs included digitizing 500 points for each channel with a sampling rate of 200 Khz. The maximum digitizing rate is 1 Mhz.

The analysis of the experimental data requires extremely accurate temporal positioning of the shutter function. Detection of the position of the shutter function ideally would be concurrent with the detection of the TOF signal. This can be accomplished by directing a laser through the molecular beam path with detection by a photodetector. Thus both the shutter function position and the resulting TOF curve can be obtained simultaneously with little, if any, timing error. Measurements of the laser gate timing were taken throughout the experiments, and no variations were observed within the uncertainty of the digitizing error ( $\sim 2$  usec). The advantage of the optical technique is that it provides a reliable reference time for the shutter function for each slot in the chopper wheel, independent of mechanical imperfections and chopping rate. Also, since the shutter function is a purely geometric entity, it is valid at any chopping speed as long as its width is scaled properly. This scaling is accomplished by comparison with the chopped laser timing pulse obtained during the high speed TOF experiments.

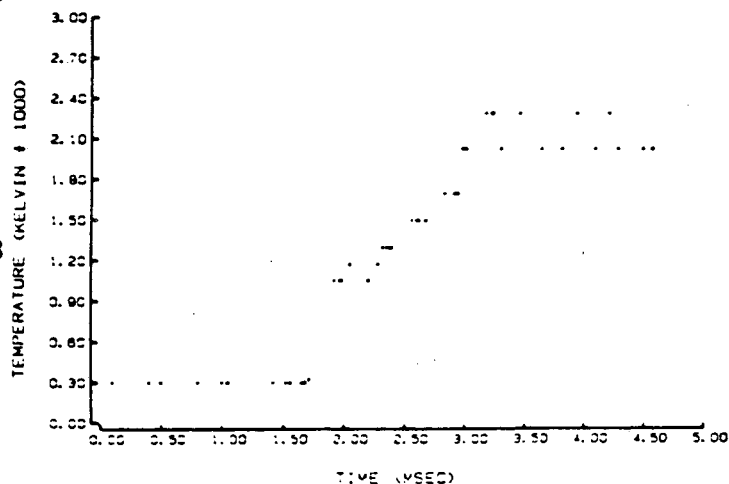
## RESULTS AND DISCUSSION

### 1. Theoretical Calculations

A modeling technique, described in detail previously [6,7], divides the beam leaving the source into small packets of molecules which are allowed to evolve independently until they reach the detector plane. These calculations can be performed for both the chopped and unchopped beam cases. The chopped beam results are used to determine effects of source conditions on beam spread at the detector. Calculations for argon beams at various source temperatures are shown in Table I. For temperatures expected during combustion the half-width of the signal is not a strong function of the source conditions, and the time of arrival of the signal peak can be used to determine the source temperature. At the higher temperatures the beam is indeed spreading more rapidly, but there is less time for spreading due to the increased velocity. The implication for continuous sampling is that the time resolution achievable during a transient event remains essentially constant at  $\sim 100$  usec. Calculations have been performed using mixture compositions representative of combustion mixtures, and for the case of continuous sampling.

### 2. Temperature Determination

The temperature of the sampled gas is determined by measuring the peak arrival time of the chopped beam in comparison with a room temperature beam of the same composition. Altering the flash lamp trigger delay allows different parts of the combustion process to be examined. A temperature profile determined for the flash ignited combustion of a 0.70 Ar/0.08 CH<sub>4</sub>/0.15 O<sub>2</sub>/0.07 NO<sub>2</sub> mixture initially at 300 torr is shown in Fig. 2. The initial temperature rise at  $\sim 1.7$  msec is due to flash heating of the gases, and is followed at  $\sim 2.3$  msec by another rise, this time due to combustion. The final temperature measured,  $\sim 2250$  K, is reasonable for this mixture and is further evidence that the sampling and beam formation does not significantly perturb the sample, and that the data collection and averaging techniques used are correct.



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Fig. 2. Temperature profile determined by time-of-flight analysis for flash ignited combustion.

TABLE I  
Calculated Argon Arrival Curves

SOURCE TEMPERATURE (K)	MACH NUMBER	BEAM VELOCITY (m/sec)	TIME OF PEAK ARRIVAL (usec)	HALF WIDTH (usec)
300	5.0	541	404	134
	10.0	566	400	76
	15.0	572	398	58
600	5.0	765	296	98
	10.0	801	296	60
	15.0	809	294	52
900	5.0	937	252	82
	10.0	982	248	54
	15.0	991	248	50
1500	5.0	1210	206	68
	10.0	1267	202	52
	15.0	1280	202	48
2100	5.0	1432	180	64
	10.0	1500	178	50
	15.0	1513	176	48

Chopper to detector plane = 20.5 cm. Gating function used is 80 usec long, and the time resolution is 2 usec. Experimental argon beams have a Mach number of 15.0 at 305 K, and 12.0 at 880 K.

### 3. Beam Overrun

When rapid temperature increases are present concern about molecular beam overrun arises. The overrun is due to fact that hotter molecules, forming a beam with higher velocity, are formed later in the combustion process than colder, and thus slower, molecules. Overrun degrades the ability to perform time-resolved measurements, and must be quantified for the particular process and system under investigation.

Knowing the temperature profile for a reaction allows one to calculate the degree of overrun present. We have adapted the algorithm described above to the case of continuous sampling and express the results in the form of an orthographic projection, shown in Fig. 3. The abscissa and ordinate of the horizontal plane represent, respectively, the detector and source times. The vertical coordinate is the relative number of molecules arriving at the detector. The source temperature profile measured for these experiments and used in the computation is shown on the left vertical plane.

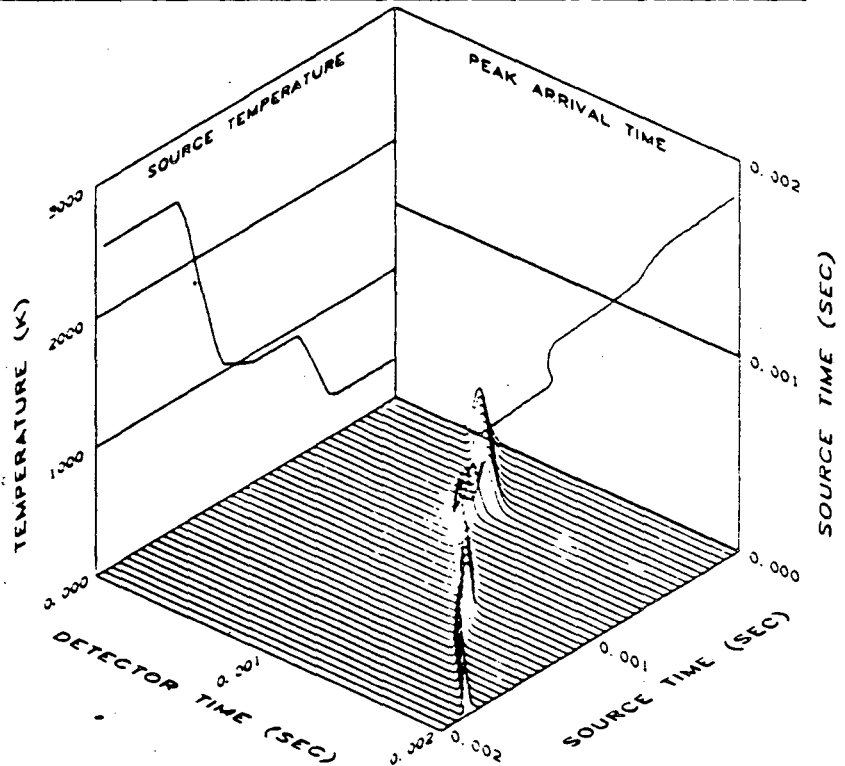


Fig. 3. Beam overrun calculated for combustion of a CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub>/Ar mixture.

The right hand vertical plane presents a plot of the peak arrival time for each individual TOA curve as a function of the detector time. The deviation of the slope of this curve from a diagonal across the graph manifests the overrun. As the slope approaches infinity adjacent portions of the beam begin to overlap at the detector. Negative slopes indicate that the signal at the detector is no longer a single valued function of the time molecules leave the source.

It is evident from Fig. 3 that beam overrun occurs both during photolysis and combustion. However, overrun is not as severe during combustion, because the reaction is slower than during photolysis, and combustion occurs at a higher initial temperature. Thus while meaningful mass measurements cannot be made during the photolysis part of the reaction, overrun does not significantly affect the measurements during combustion.

#### 4. Mass Measurements

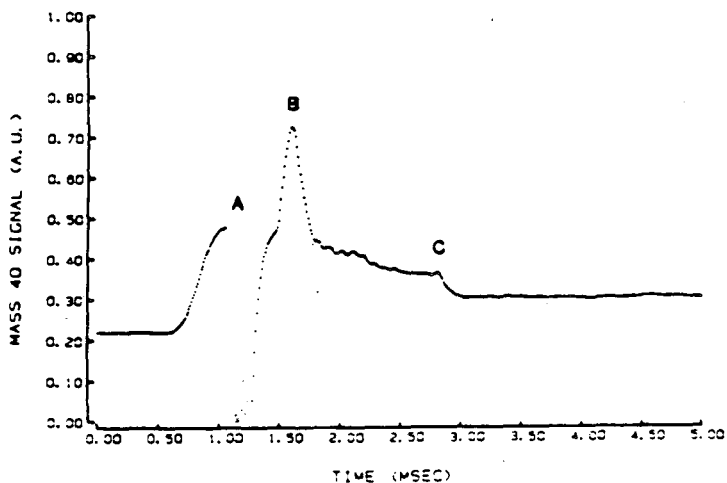
The mass 40 signal obtained during a single combustion event is shown in Fig. 4. The mole fraction of argon is essentially constant throughout the process, and no other chemical species are expected to yield a measurable signal at this mass. Various portions of the curve are labeled and will be described in more detail below.

Initially the chopper, located in the second stage, blocks the beam. This initial signal is the zero level for each species. The chopper then begins to open, reaching its full open position prior to point A, the time that the flash lamp discharge occurs. The signal intensity level obtained before the flash may be used as a room temperature calibration for the reactant species; however, care must be taken in using this data for transient combustion. For the next 250 microseconds electrical noise from the lamp discharge prevents any meaningful measurements. It is important to note that no information is lost due to the finite flight time of the molecules in the apparatus during this period. For example, argon at 300 K does not reach the detector plane for 400 microseconds, and molecules at temperatures near 2000 K require  $>180$  microseconds.

A significant increase in the signal is then observed, reaching a maximum at point B. This is caused by beam overrun as described previously. After the overrun period the signal changes gradually until point C, where the slope of the curve again changes. This point ( $\sim 2.7$  msec) is used to determine the induction time, in analogy with shock tube investigations of ignition. The signal then approaches an essentially constant value.

Single shot measurements for argon can yield meaningful results due to a high signal-to-noise ratio. For other species, signal averaging must be used. However, variations have been observed in the argon signals which preclude simple averaging techniques. These variations are manifested most in the induction times. The

differences in induction times, on the order of 10%, are assumed to be due to variations in the flash lamp output which alters the number of free radicals generated in the cell. It is observed that the time of the maximum in the pressure trace is correlated with the induction time. Averaged signals are thus obtained by recording and saving a mass signal and pressure trace for each event. After the desired number



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Fig. 4. Argon signal measured during a single combustion event.



of experiments have been performed, the pressure traces are shifted in time until the maxima coincide. Each mass signal is then shifted an identical amount. This method is validated by averaging the argon signals: there is no significant difference in the signal shape between a single event and the averaged events for times after the overrun period.

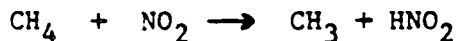
Averaged mass signals are also normalized with respect to the averaged argon signal. Because the argon mole fraction is constant, its signal reflects the variations in the molecular beam intensity. Other species will exhibit similar behavior providing there are no mass or concentration dependent perturbations. Care has been taken in this system to minimize such effects, and by keeping the Reynold's number in the source high and by sampling at Knudsen numbers  $< 0.01$ .

Averaged and normalized mass signals for many of the species known to be present during photolysis of an NO<sub>2</sub>/Ar mixture and in the combustion of an NO<sub>2</sub>/O<sub>2</sub>/CH<sub>4</sub>/Ar mixture are shown in Figures 5 through 8. These results are presented as mass rather than species signals since the high ionizing energy necessary for sufficient signal strength does not allow resolution of different species which have the same mass (such as O and CH<sub>4</sub>), and the cracking patterns for all parent species as a function of temperature and internal energy are not well known. It should also be noted that each mass signal is scaled independently, so that qualitative rather than quantitative information can be extracted from this data. The number of experiments averaged varies depending on the signal-to-noise ratio of each mass, and ranges from 1 to 45.

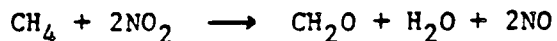
The soundness of the averaging and normalization procedures used in this study is affirmed by the mass signals. Results from simple photolysis experiments (not shown) indicate that after photolysis the mass 30, 32, and 46 signals remain constant, as would be expected in this system where no further reaction is anticipated at these times. Combustion results in mass signals that vary considerably, ranging from the slow growth of the mass 28 signal to the sharp decrease in the mass 32 signal at ~2.6 msec. The decrease, which occurs in ~130 microseconds, illustrates the time resolution possible in our system, and is close to our estimated theoretical resolution of 100 microseconds.

Flash ignited combustion is significantly different from shock tube combustion in that ignition is not a purely thermal process since oxygen atoms are produced during photolysis. There is also a much lower initial temperature than in experiments with shock heating. We have directly measured the temperature and the mass signals due to all major reactants and products, making it possible to derive qualitative ideas about the nature of the reaction mechanism from our results.

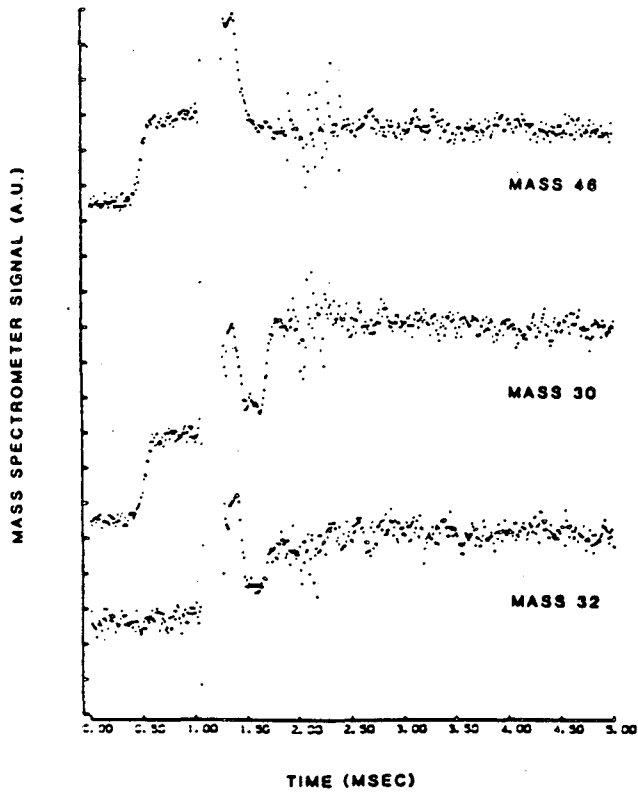
Nitrogen dioxide is the only absorbing species in the combustion mixture, so the initial concentration of NO<sub>2</sub> after photolysis should be the same as in the photolysis experiments, where only 17% of the NO<sub>2</sub> was dissociated. However, it can be seen that the mass 46 signal is at its background value (essentially zero) as soon as meaningful mass determinations can be made and before the temperature rises above 1100 K. This implies the existence of a fast reaction which consumes NO<sub>2</sub>. Decomposition is not significant at the temperature achieved by photolysis. Slack and Grillo[8] suggest the initiation steps



followed by a fast linear chain with the net reaction stoichiometry

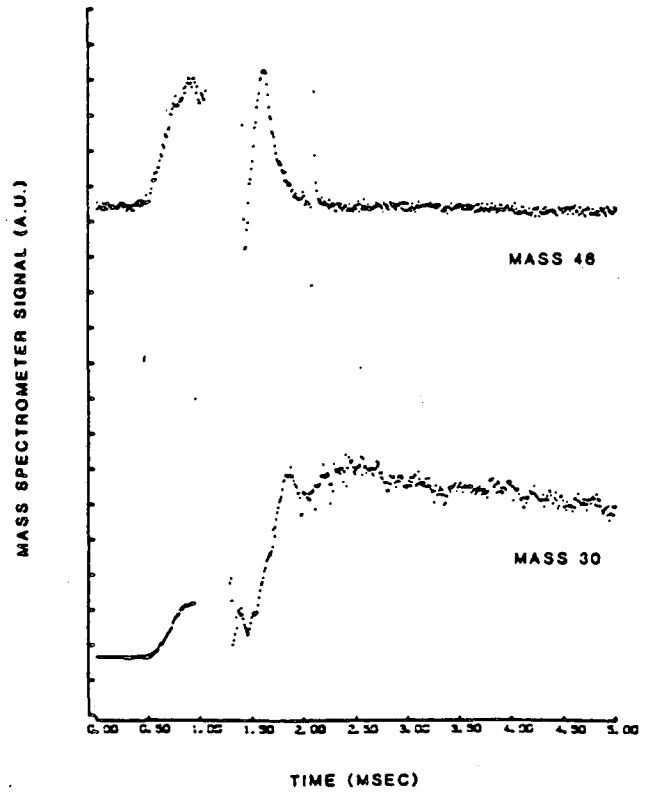


as the primary NO<sub>2</sub> sensitization mechanism. The stoichiometry implies that in our system, with an NO<sub>2</sub>/CH<sub>4</sub> ratio of 1.47, most of the methane would be consumed in reaction with NO<sub>2</sub>, and that significant quantities of water would be produced as the NO<sub>2</sub> reacts. We do not observe significant growth of the mass 18 peak until after the NO<sub>2</sub> signal drops. The mass 16 signal remains high and then drops to nearly zero after combustion. Although the mass 16 signal can result from other species, the most



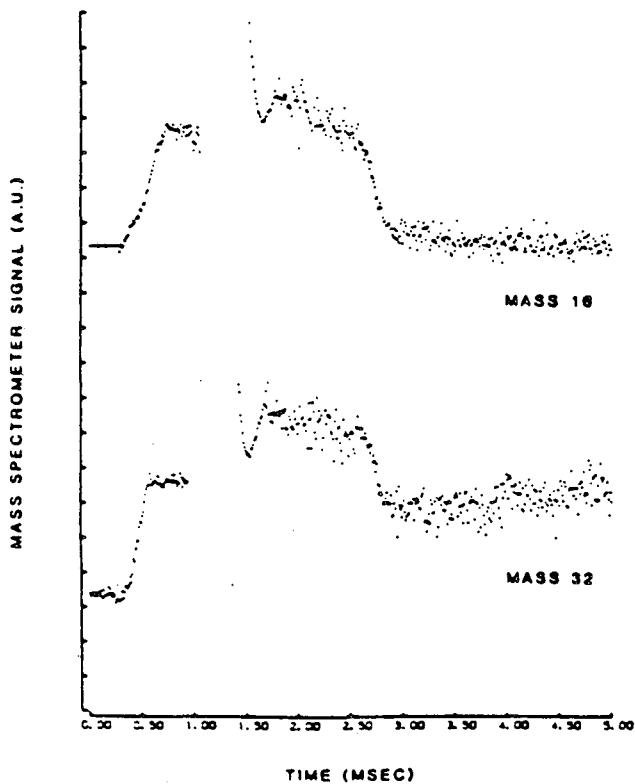
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Fig. 5. Mass signals measured during photolysis of an  $\text{NO}_2/\text{Ar}$  mixture.



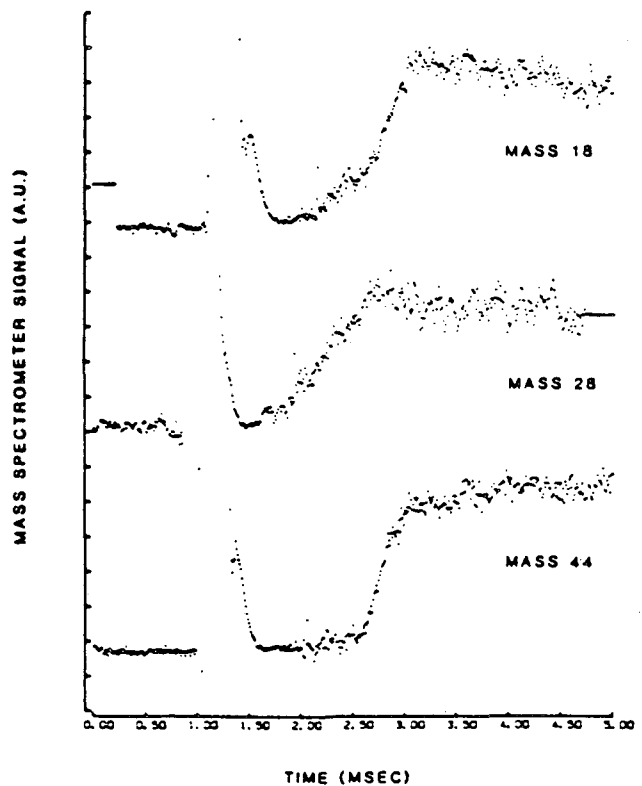
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Fig. 6. Mass signals measured during combustion: mass 46 and 30.



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Fig. 7. Mass signals measured during combustion: mass 16 and 32.



JPL 843-1158

Fig. 8. Mass signals measured during combustion: mass 18, 28, and 44.

probable assignment (based on measured cracking patterns) suggests that a large fraction of the signal is due to methane, and it does not appear to be consumed until after the induction period. The mass 30 signal is due to NO with possible contribution from CH<sub>2</sub>O. The observation that there are no large changes in the mass 30 signal after photolysis suggests that CH<sub>2</sub>O is not present in any appreciable concentration. The behavior of the mass signals thus indicates that a different mechanism is needed to explain our results. We can provide temporally resolved mass and temperature measurements at this time, but calibration procedures are needed to completely quantify species concentrations. These calibrations will be undertaken in future experiments.

#### ACKNOWLEDGEMENTS

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