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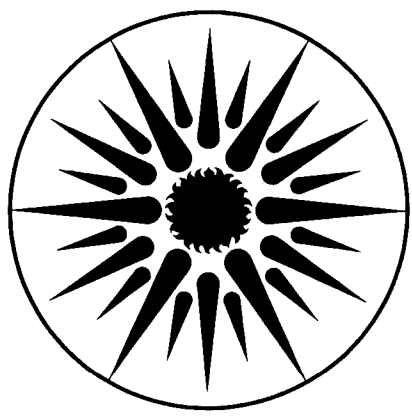
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D. Lucas, R. Peterson, N.J. Brown,
and A.K. Oppenheim

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Molecular Beam Mass Spectrometer Sampling of Flash Ignited Combustion

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Abstract

Mass signals from a transient combustion event have been measured using a molecular beam mass spectrometer with a time resolution of approximately 100 microseconds. The signals are normalized to signals of inert components to compensate for changes in beam intensity caused by rapidly changing source conditions. Pressure traces recorded simultaneously were used to correlate mass signals to significantly reduce variations in time dependent signals caused by experimental fluctuations. Temperature measurements of the sampled gas using a time-of-flight analysis show that there are no significant perturbations caused by cell walls or the sampling orifice. The measured temperature profile is used to predict the extent of beam overrun present during various phases of the combustion event, which is necessary to determine the validity of the recorded data. Mass signals from reactants and stable products in the flash ignited combustion of methane/oxygen/nitrogen dioxide/argon mixtures are presented and discussed, and provide insight regarding the mechanism of this complex system.

Introduction

The enormous value of direct sampling molecular beam mass spectrometers in the study of a wide range of combustion systems is well established¹⁻⁴. However, the use of this technique to interpret transient events is still a relatively unexplored field due to significant problems associated with sampling and interpretation of results. Researchers who have contributed to the solution of these difficult problems include Young et al.⁵ with their internal combustion engine investigation, Milne et al.⁶ who studied rapid pyrolysis, Sloane and Ratcliffe^{7,8} with their spark ignited methane flame studies, and Smith⁹ in his theoretical analysis of sampling and detection.

We have constructed a direct sampling molecular beam system to study transient combustion processes, especially those associated with ignition of lean homogeneous gas mixtures. A wide range of perturbations affect the sampling process, including the reproducibility of experimental conditions and the effects of rapidly changing temperature, pressure, and chemical composition on the formation of the molecular beam. We have previously reported on some of these problems, especially one of beam overrun during periods of rapidly increasing source temperature^{10,11}. In this paper we present mass spectra and temperatures recorded during flash ignited combustion, and show how molecular beam mass spectrometer systems can be used successfully to monitor a variety of chemical species and provide qualitative data with good temporal resolution in the study of transient combustion systems.

Experiment

The direct sampling molecular beam mass spectrometer used in this investigation has been described previously^{1,2}. Three stages of differential pumping are used to isolate the detector from the sampling region. First stage pumping is provided by a 10" NRC oil diffusion pump, and the second and third stages are pumped by individual Varian 6" oil diffusion pumps. The third stage also contains a water baffle to minimize backstreaming. Pressures in the three stages are approximately 4×10^{-4} , 5×10^{-5} , and $< 2 \times 10^{-7}$ torr, respectively, during experiments.

The reaction cell is situated in a flash chamber as depicted in Fig. 1. The cell was made from 2.5 cm O.D. thick-walled quartz tubing. It is provided with a window on the bottom for laser alignment, and is equipped with two access conduits, one for filling and purging and the other for mounting a Kistler 211B piezotron for pressure measurements. Situated at the top of the cell is a sampling probe tip with a 160 micrometer dia. orifice at the tip of a 120 degree included angle quartz cone.

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, initiated by a high voltage trigger pulse of variable delay, typically lasts 120 microseconds.

Flash photolysis of two chemical systems was studied. One consisted of a binary mixture of 0.915 Ar and 0.085 NO₂. The other was a mixture of 0.822 Ar, 0.047 CH₄, 0.052 O₂, and 0.069 NO₂. Initial pressure in the reaction chamber for both mixtures was 150 torr. Ignition consistently occurred in the combustible mixture for flash energies above 400 joules.

A Pyrex skimmer is located 1.15 cm from the sampling orifice, or 72

x/d (skimmer distance to orifice diameter). It has an included angle of 60 degrees and an orifice of 0.76 mm. 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 is used for time-of flight measurements, and one with two 90 degree sectors is installed when making concentration measurements.

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. An ionizing energy of 60 eV is used for all species in this study.

Previous studies¹⁰ have characterized the molecular beam for a wide range of source conditions. Room temperature argon beams had a Mach number of ~ 15 , and high temperature beams formed during combustion had Mach numbers above 5.

Signals are processed by a Lecroy model #8210 10-bit, 4-channel analog-to-digital converter with internal buffer memory. A DEC LSI-11/2 computer controls the experimental sequence and the data acquisition. A typical one shot run involves digitizing 500 points for each channel with a sampling rate of 200 Khz.

Results

1. Single Event Argon Data

The mass 40 signal obtained during a single combustion event is shown in Fig. 2. 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 microseconds¹³.

A significant increase in the signal is then observed, reaching a maximum at point B. This is caused by beam overrun resulting from the fact that the hotter, and thus faster, parts of the beam are formed later than its colder, and thus slower, portions. Severe overrun is observed only during photolysis. After the overrun period the signal changes gradually until point C, where the slope of the curve again changes. This point (~ 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.

2. Signal Averaging

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 upper half of Fig. 3 shows the argon traces from two experiments performed under identical experimental conditions. 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. The lower half of the figure shows the pressure traces recorded simultaneously with the argon signals. It is observed that the time of the maximum in the pressure trace is correlated with the induction time. The shape of the pressure curve is distorted by the flash discharge, which affects the transducer by flash heating in addition to electrical noise, and by cooling of the gas near the walls of the cell.

Averaged signals are obtained by recording and saving a mass signal and pressure trace for each event. After the desired number 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.

3. Normalization of Mass Data

In the course of the transient combustion there are rapid and significant changes in the stagnation conditions at the sampling orifice of the molecular beam system. These changes affect the resulting molecular beam in a manner that is difficult to predict a priori. Averaged mass signals are therefore 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 above 10^3 and by sampling at Knudsen numbers < 0.01 .⁹

4. Mass Signals

Averaged and normalized mass signals for many of the species known to be present during photolysis of an NO_2/Ar mixture and in the combustion of an $\text{NO}_2/\text{O}_2/\text{CH}_4/\text{Ar}$ mixture are shown in Figures 4 through 7. 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_4), 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.

A. Simple Photolysis

The data from the photolysis of NO_2 in argon, shown in Fig. 4, reveals that only a fraction of the NO_2 is photolyzed, and that both NO and O_2 appear as products.

B. Combustion

Mass signals from the flash ignited combustion mixture are shown in Fig. 5, 6, and 7. The masses measured, followed in parenthesis by the most likely chemical species producing the signal, were: 16 (CH_4 , O), 18 (H_2O), 28 (CO, N_2), 30 (NO, CH_2O), 32 (O_2), 44 (CO_2), and 46 (NO_2).

5. Temperature Profile

The temperature of the sampled gas is determined by the time-of-flight

technique described previously¹⁰. Briefly, a slotted chopper wheel produces pulses of gas 625 microseconds apart. The peak arrival times of these pulses are used to calculate the temperature of the actual gas that has produced the molecular beam. Experiments were performed with different timing between the chopper openings and the flash discharge to allow measurements during different periods in the combustion process. The same shifting procedure used for averaging the mass signals is employed for the temperature determination. Figure 8 is the temperature profile measured for the flash ignited combustion experiments. The initial temperature rise to ~ 1100 K is attributed to the absorption of light by NO_2 , and is confirmed in a series of experiments in which NO_2 and argon mixtures are photolyzed. Uncertainties in the temperatures, ± 150 K at the highest values, are primarily due to digitizing errors and not variations in the state of the molecular beam. The profile exhibits no unusual behavior, another indication that the averaging technique is reasonable.

Discussion

The experimental temperature profile shown in Fig. 8 has been used to determine the extent of the beam overrun encountered. A modeling technique, described in detail previously¹¹, divides the beam leaving the source into small packets of molecules which are allowed to evolve independently until they reach the detector plane. Results of the modeling are most clearly interpreted by expressing them in the form of an orthographic projection, as shown in Fig. 9. The abscissa and ordinate of the horizontal plane represent, respectively, the detector and source times. The vertical coordinate expresses the relative number of molecules arriving at the detector. The source temperature profile is shown on the left vertical plane. The right vertical plane is a plot of peak arrival

times for each time-of-flight curve as a function of detector time. Changes in the slope of this curve with respect to the diagonal is an indication of the degree of the overrun. These calculations confirm that severe overrun occurs during photolysis when the temperature of the sampled gas increases by a factor of four in <150 microseconds, leading to increased signal strength and loss of temporal information during this time period. Beam overrun does not significantly affect later results, when most of the chemistry of combustion takes place. The data also show no loss of time resolution at the detector due to spreading of the beam as the source temperature increases, as evidenced by the half-width of the individual curves.

Temperatures measured during photolysis and combustion indicate that the source cone samples gas representative of the homogeneous mixture. The temperatures are reasonable, based on calculations using the flash lamp output, absorption coefficient of NO_2 , and the thermodynamic properties of the systems studied.

The soundness of the averaging and normalization procedures used in this study is affirmed by the mass signals. Results from Fig. 4 show 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.

The $\text{NO}_2/\text{O}_2/\text{CH}_4/\text{Ar}$ system has been studied in shock tubes by a number of researchers, including Dorko¹⁴, Slack and Grillo¹⁵, and Dabora¹⁶.

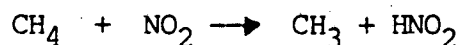
Initial temperatures for these systems ranged from 1200 to 1800 K. They measured a few of the product and reactant concentrations and found the addition of NO₂ caused a significant decrease in the induction time as compared to the O₂/CH₄/Ar system¹⁷.

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. In the following discussion, when we refer to chemical species instead of mass numbers, it is with the caveat that we have not conclusively identified all the sources of the mass signals.

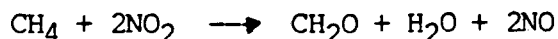
The photolysis experiments are interpreted by assuming that the NO₂ molecules that absorb photons at wavelengths below 404 nm dissociate into NO + O, followed by the rapid reaction $O + NO_2 \rightarrow NO + O_2$.¹⁸ These two reactions can account for the observed increases in the mass 32 and 30 signals, and the corresponding decrease in the mass 46 (NO₂) signal. While beam overrun prevents determination of reaction times and composition profiles, it can be stated that these reactions are complete within 1000 microseconds after the flash discharge (<600 microseconds when corrected for beam flight time). Thermal dissociation of NO₂ at these temperatures is not expected for these conditions¹⁹, and no significant changes in the NO₂ signal are observed after photolysis.

Nitrogen dioxide is again the only absorbing species in the combustion mixture, so the initial concentration of NO₂ after photolysis should be the same as in the photolysis experiments. 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_2 . Dorko et.al.¹⁴ postulate the decomposition of nitrogen dioxide as the important reaction in promoting ignition. Decomposition is not important in our system, as evidenced both by the mass 46 signal and the temperature measured following photolysis. Slack and Grillo¹⁵ suggest the initiation steps



followed by a fast linear chain with the net reaction stoichiometry



as the primary NO_2 sensitization mechanism. The stoichiometry implies that in our system, with an NO_2/CH_4 ratio of 1.47, most of the methane would be consumed in reaction with NO_2 , and that significant quantities of water would be produced as the NO_2 reacts. We do not observe significant growth of the mass 18 peak until after the NO_2 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 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_2O . The observation that there are no large changes in the mass 30 signal after photolysis suggests that CH_2O 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.

Comparisons of our experimentally determined induction times with those calculated from the expressions given in references 14 and 15 are not meaningful since there are large differences in temperatures (~ 250 K) and experimental conditions. We observe a gradual temperature rise during the entire induction period, with no abrupt change during the time period in which methane and oxygen decrease sharply. The temperature tends to follow the water signal, which has a much more gradual slope than the carbon dioxide curve. Thus the induction time in our system reflects the point at which the remaining reactants are consumed rather than an abrupt increase in temperature.

Conclusions

We have shown that it is possible to measure and interpret signals from a transient combustion event using a molecular beam mass spectrometer with a time resolution of approximately 100 microseconds. Mass signals are normalized to signals of inert components to compensate for changes in beam intensity caused by rapidly changing source conditions. Pressure traces recorded simultaneously can be used to correlate mass signals to significantly reduce variations in time dependent signals caused by experimental fluctuations. Temperature measurements of the sampled gas using a time-of-flight analysis show that there are no significant perturbations caused by cell walls or the sampling orifice. The measured temperature profile is used to predict the extent of beam overrun present during various phases of the combustion event, which is necessary to determine the validity of the recorded data. Mass signals from reactants

and stable products in the flash ignited combustion of methane/oxygen/nitrogen dioxide/argon mixtures are presented and discussed, and provide insight regarding the mechanism of this complex system. Modifications to the experimental system will be undertaken to increase signal strengths to permit measurement of radical species, which are necessary to understand flash ignited combustion.

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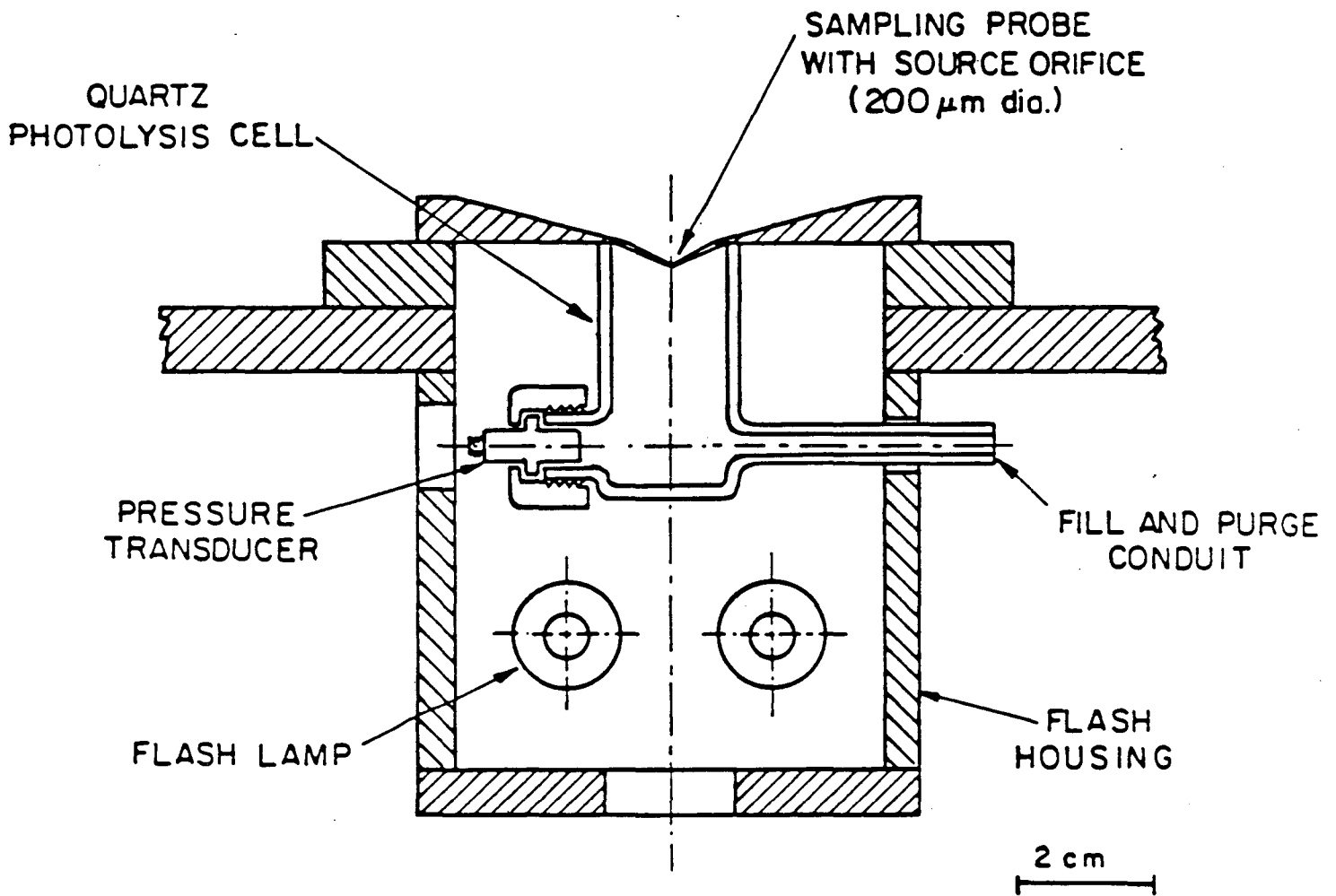
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Figure Captions

- Figure 1. Schematic diagram of the reaction cell and sampling probe.
- Figure 2. Mass 40 signal measured during combustion of an $\text{NO}_2/\text{CH}_4/\text{O}_2/\text{Ar}$ mixture. A denotes the time of the flash discharge, B marks time of maximum beam overrun, and C defines the induction time.
- Figure 3. Mass 40 signals and pressure traces recorded for two different combustion events showing variations due to experimental uncertainties.
- Figure 4. Mass 46, 30, and 32 signals recorded during photolysis of an NO_2/Ar mixture.
- Figure 5. Mass 46 and 30 signals recorded during flash ignited combustion of an $\text{NO}_2/\text{CH}_4/\text{O}_2/\text{Ar}$ mixture.
- Figure 6. Mass 16 and 32 signals recorded during flash ignited combustion of an $\text{NO}_2/\text{CH}_4/\text{O}_2/\text{Ar}$ mixture.
- Figure 7. Mass 18, 28, and 44 signals recorded during flash ignited combustion of an $\text{NO}_2/\text{CH}_4/\text{O}_2/\text{Ar}$ mixture.
- Figure 8. Experimental temperature profile determined for the combustion event.
- Figure 9. Beam overrun calculated using the temperature profile determined in Fig. 8.



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Fig. 1

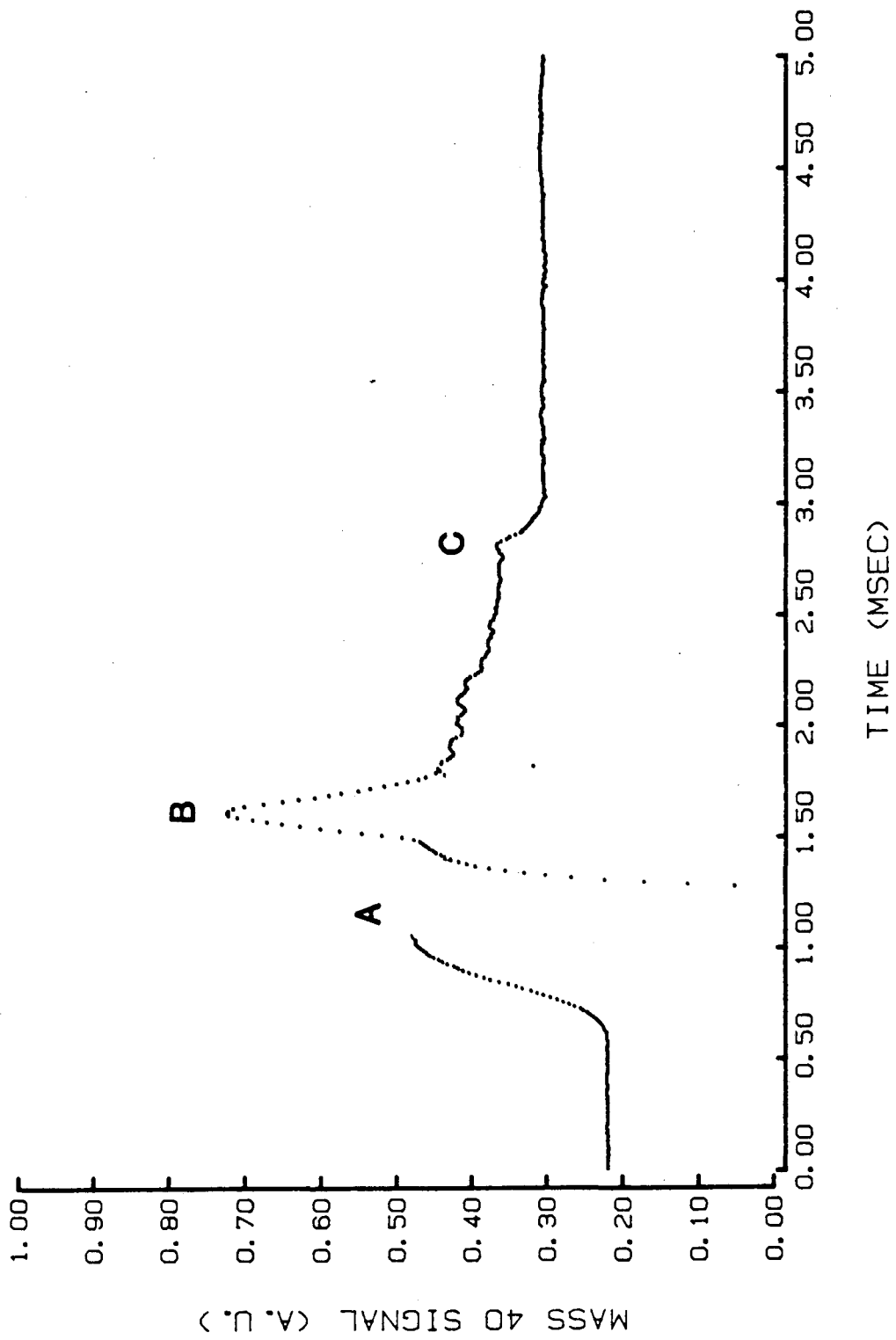


Fig. 2

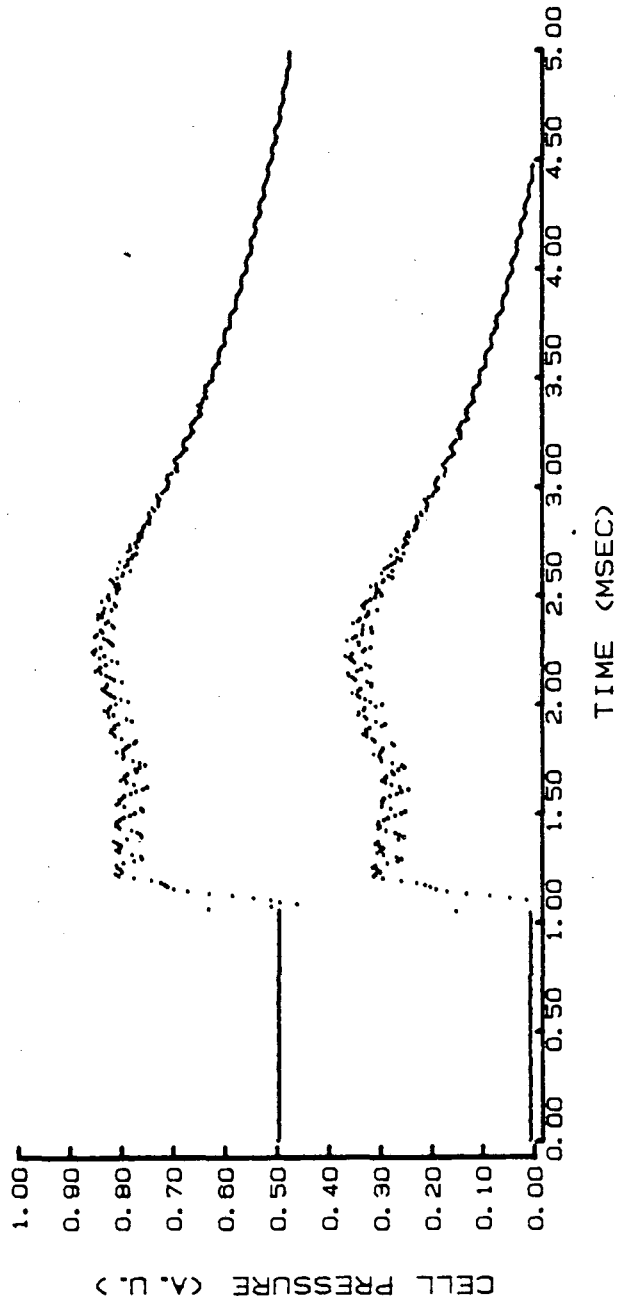
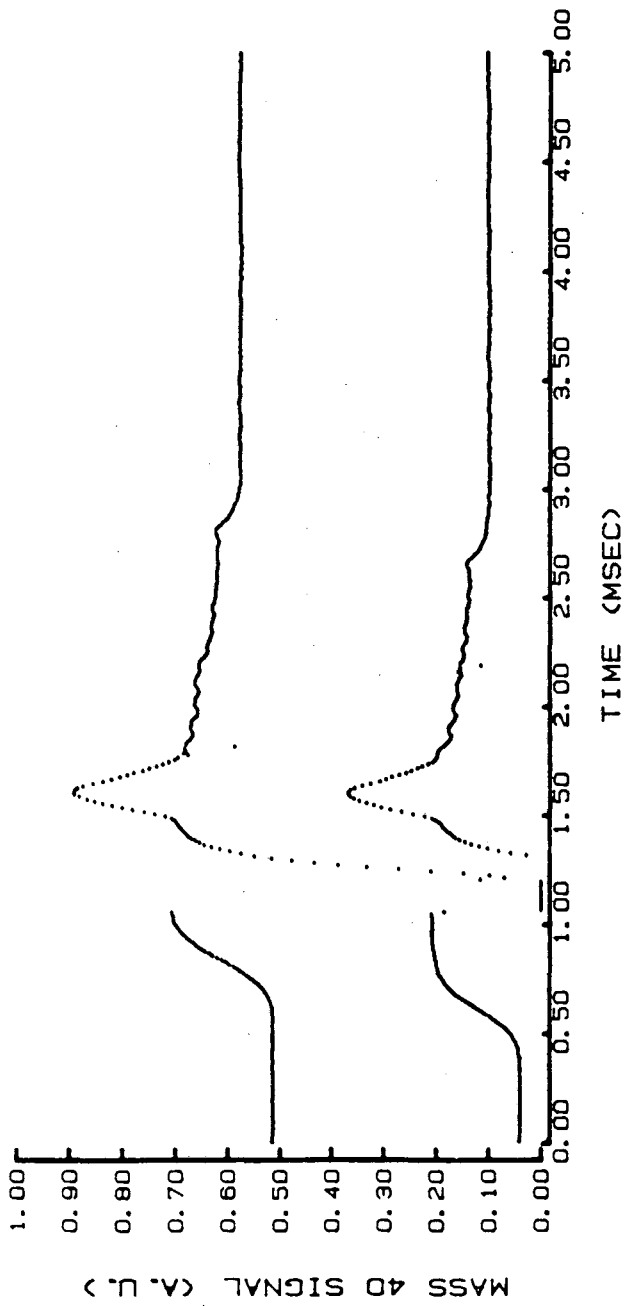


Fig. 3

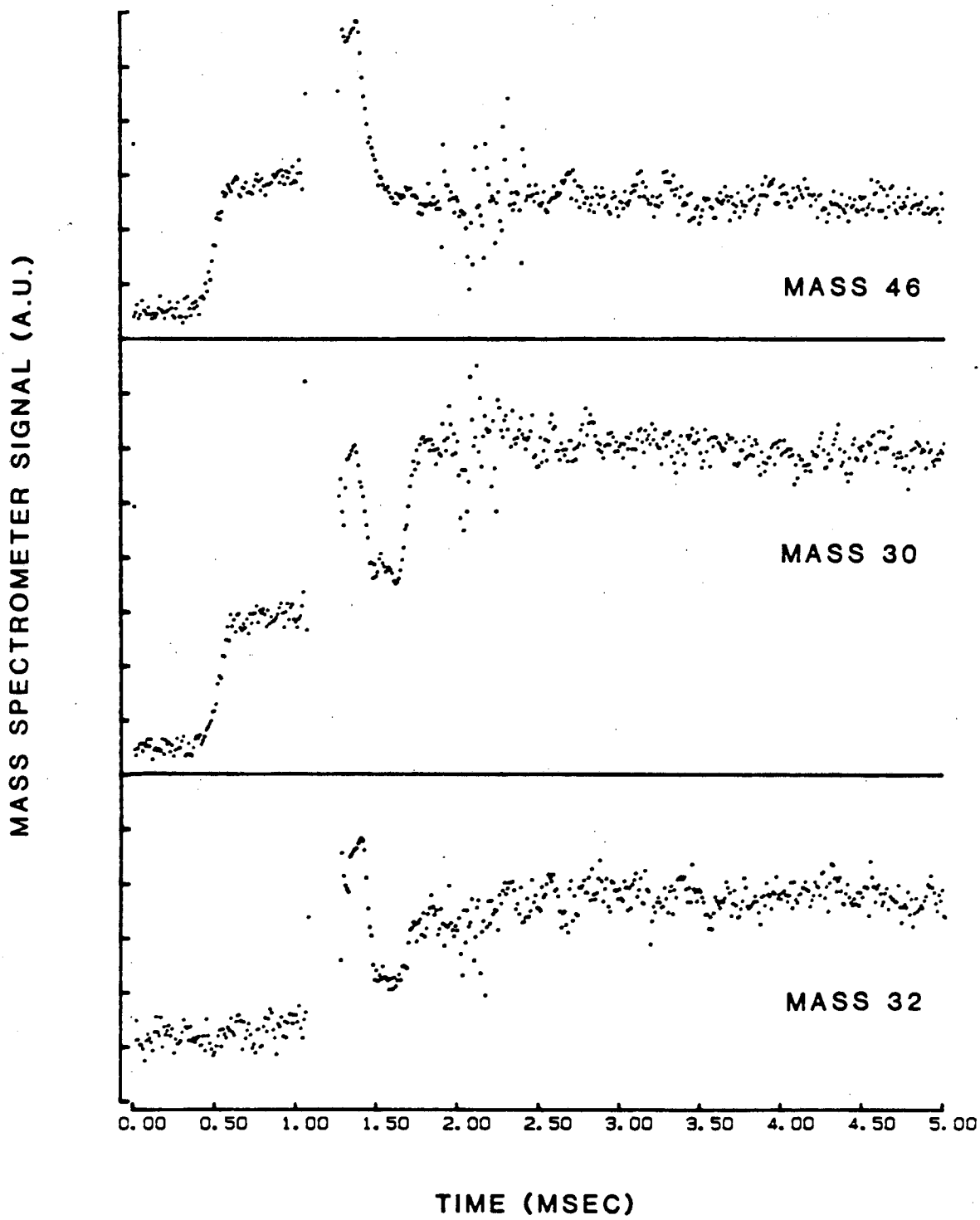


Fig. 4

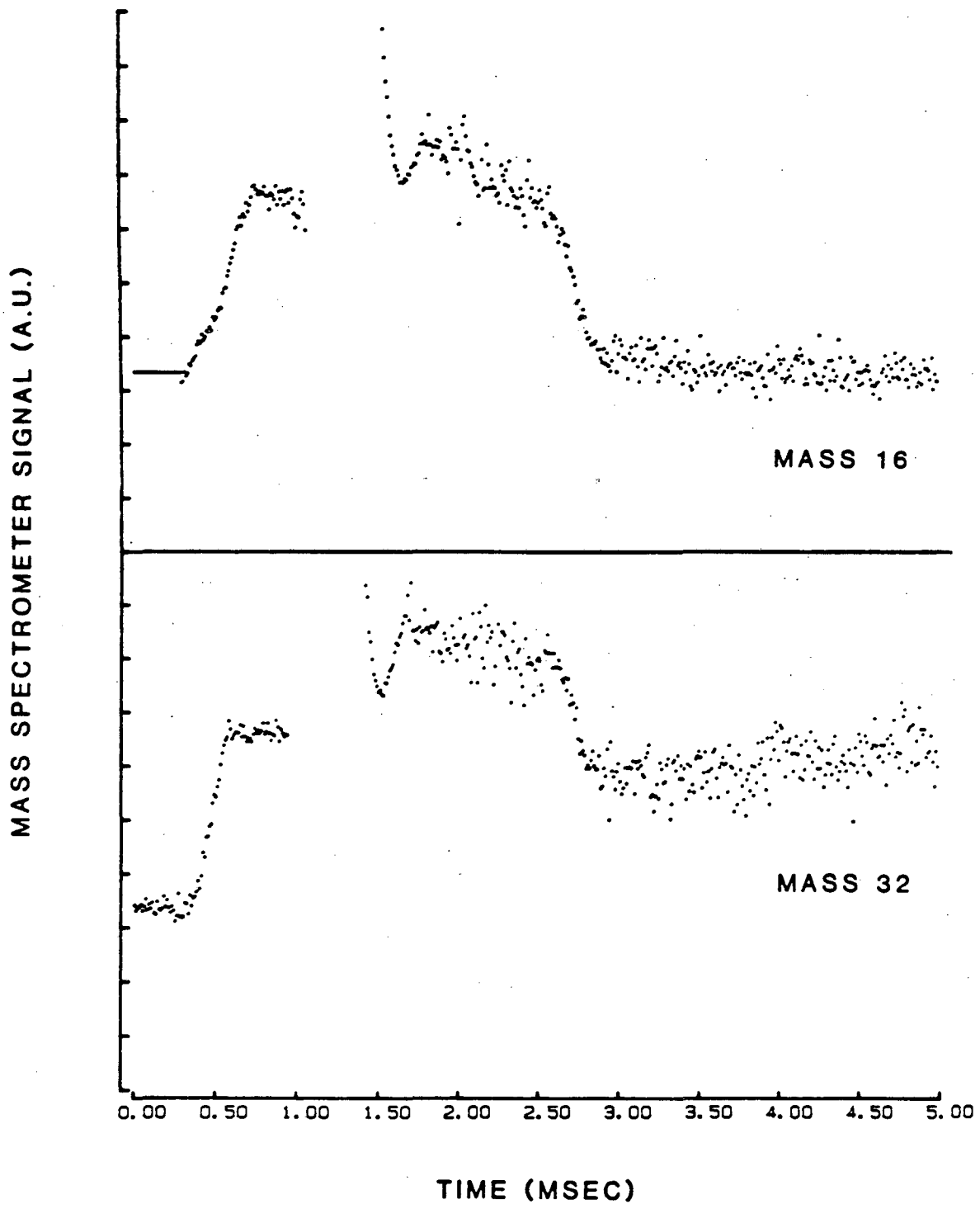


Fig. 5

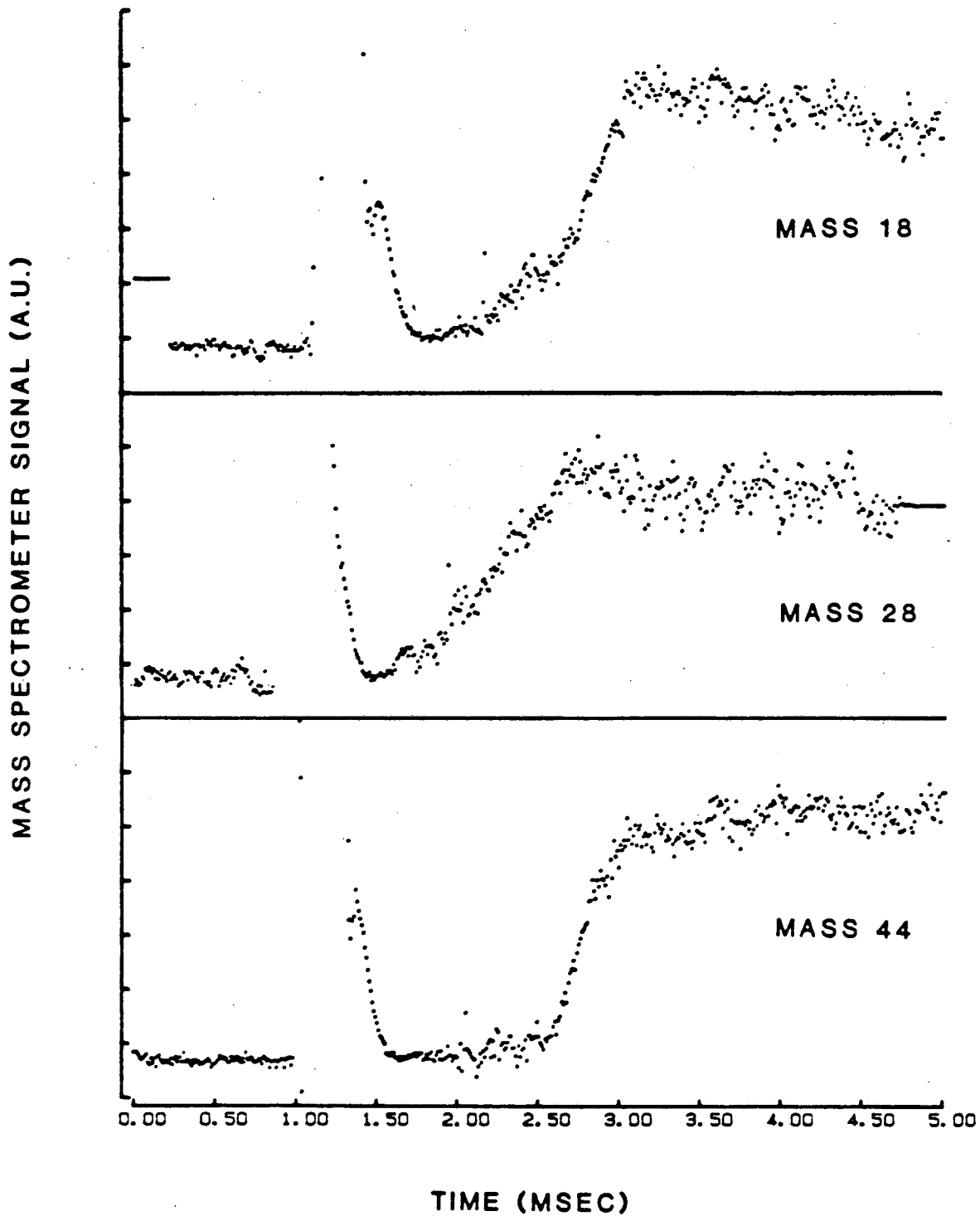


Fig. 6

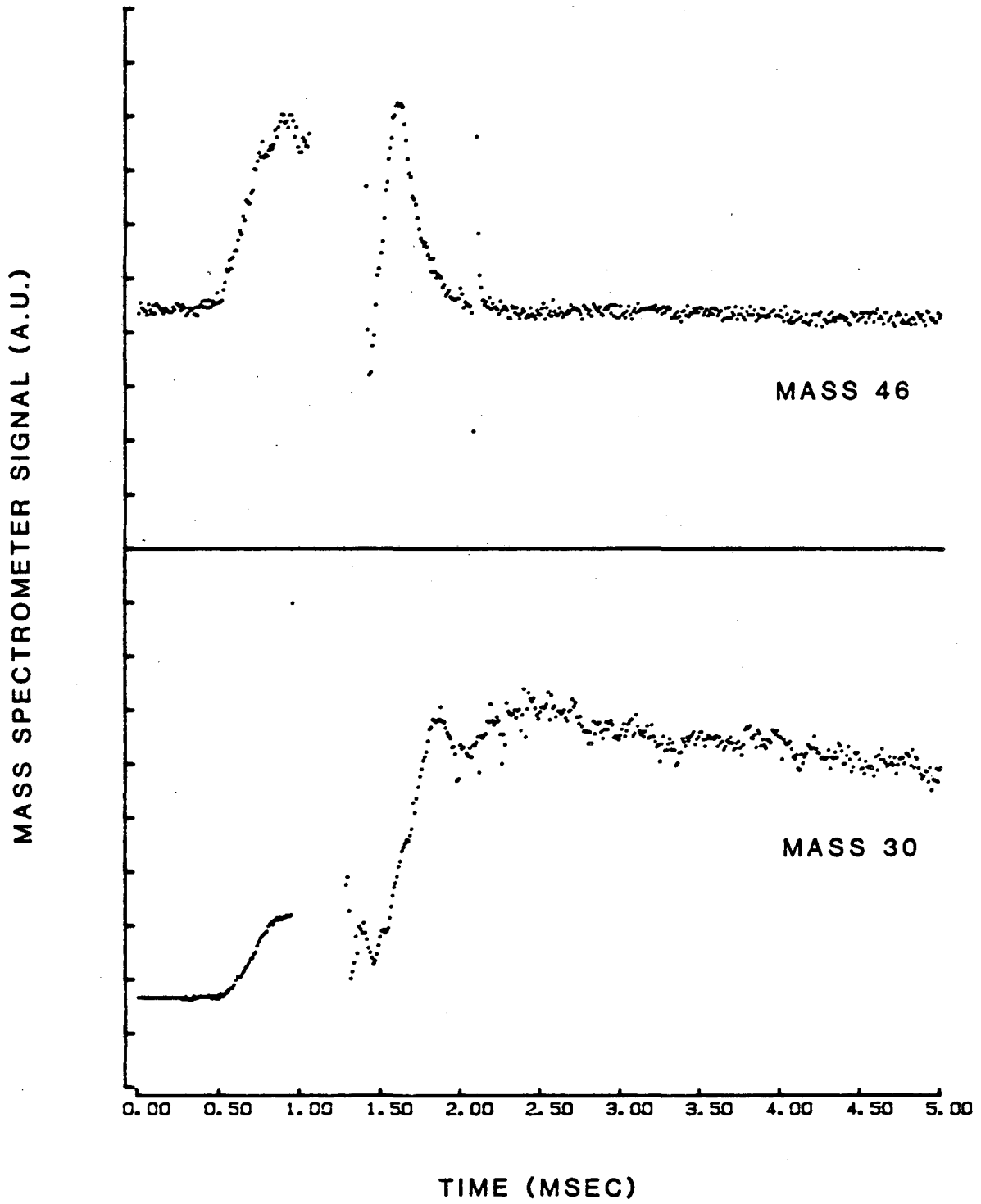


Fig. 7

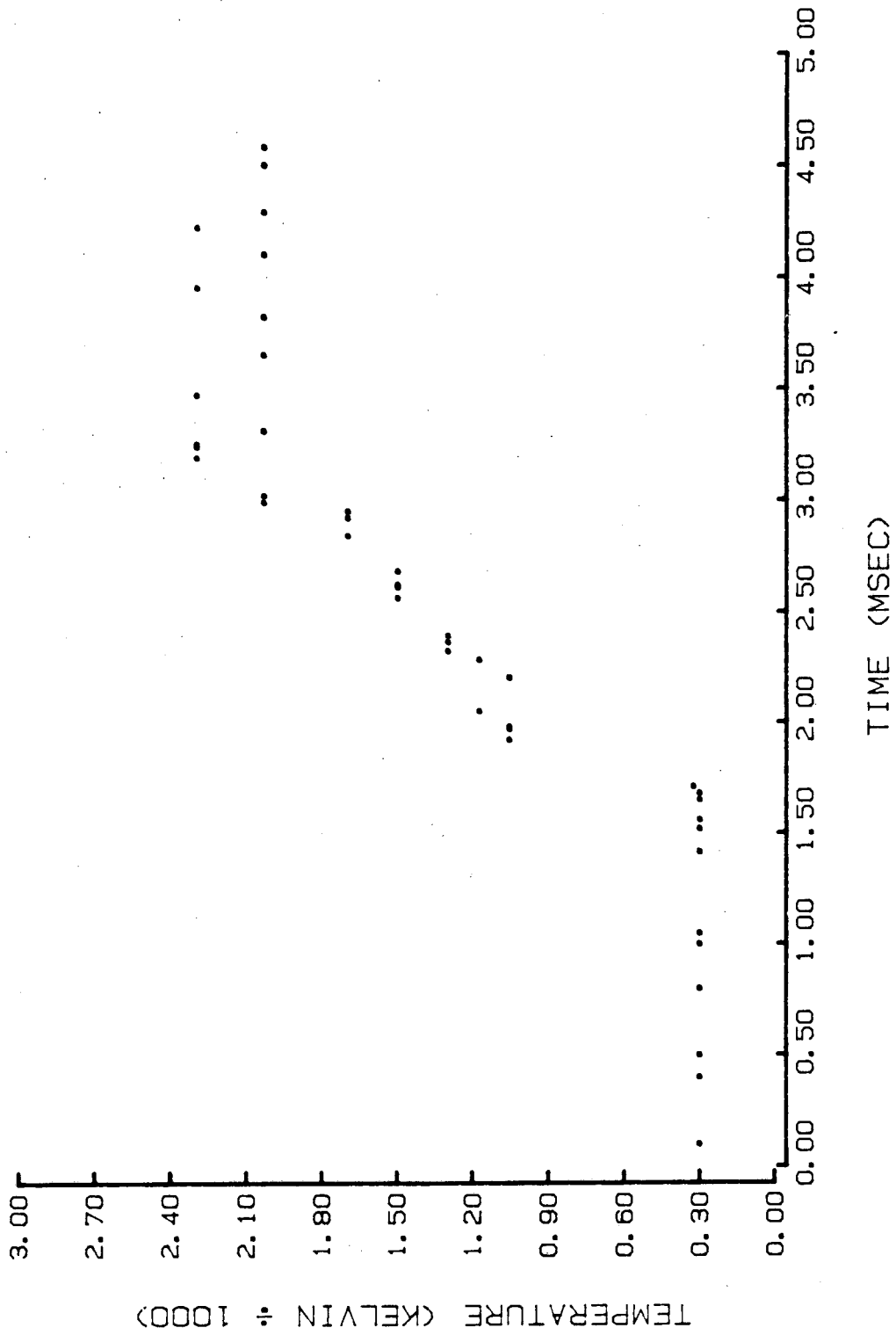


Fig. 8

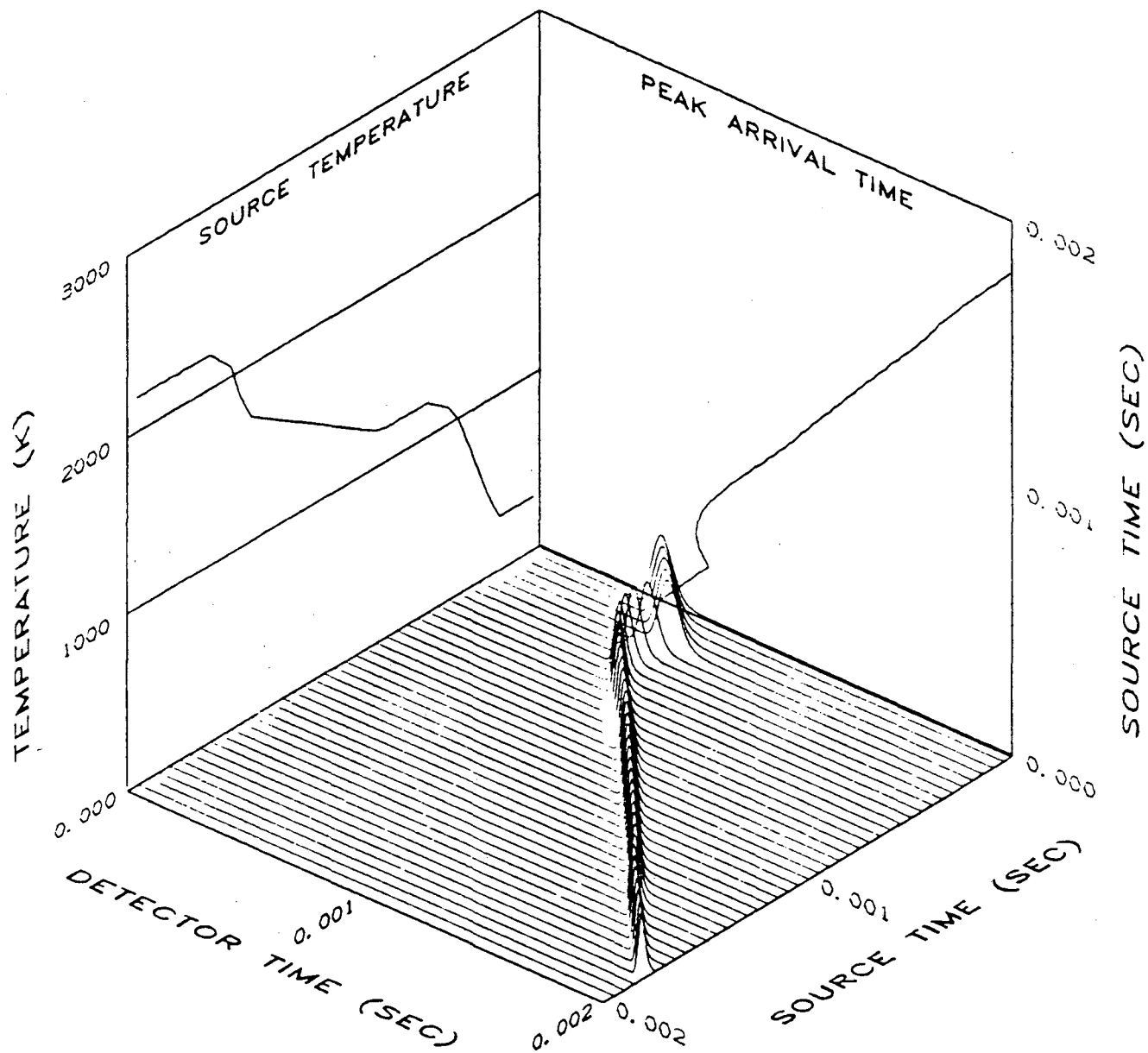


Fig. 9

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