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Author

Peterson, R.

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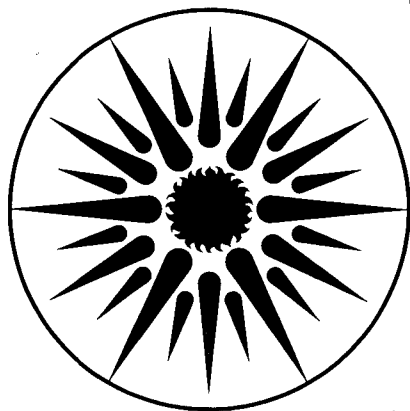
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MOLECULAR BEAM OVERRUN IN SAMPLING OF TRANSIENT COMBUSTION PROCESSES

R. Peterson*, D. Lucas, F.C. Hurlbut*, and A.K. Oppenheim*

Applied Science Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

*and
Department of Mechanical Engineering
University of California, Berkeley
Berkeley, CA 94720

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Abstract

Effects of combustion generated source temperature variations on direct sampling in a molecular beam mass spectrometer is examined. The problem of particular concern is the influence of beam overrun on the distribution of molecules arriving at the detector. The overrun is due to the fact that the hotter, and thus faster, constituents of the molecular beam are formed later than its colder, and thus slower, portions. Photolysis of NO_2 in Ar and flash ignited mixtures of Ar/ CH_4 / O_2 / NO_2 using a chopped molecular beam time-of-flight technique yields time resolved temperature measurements, while concomitant numerical analysis accurately predicts the observed beam overrun. Analysis of continuous sampling in representative transient combustion processes indicates that the molecular beam mass spectrometer is capable of measuring meaningful time-resolved concentration profiles.

Introduction

The use of direct sampling molecular beams to investigate steady state combustion phenomena is well established ¹⁻⁴. When applied to a transient process, however, this technique poses significant and relatively unexplored problems ⁵⁻⁷.

Our previous studies have been concerned with the time-of-flight measurement in steady state systems, pertaining in particular to the interpretation of data from flash photolysis initiated combustion ⁸. It was shown that the source temperature governs the peak arrival time without significantly affecting the beam half-width.

This paper reports on the investigation of the temporal distribution of molecules arriving at the detector of a molecular beam system from a source whose temperature is increasing rapidly. Of particular interest is the phenomenon of beam overrun - a feature caused by the fact that the hotter, and thus faster, constituents of the beam are formed later than its colder, and thus slower, portions.

Both chopped and unchopped molecular beams were investigated; the former was used to obtain the temperature profile during a transient event, while the latter was employed for continuous measurement of species. Data obtained by the chopped mode technique for simple photolysis as well as combustion were analyzed, yielding temperature profiles at the source. Using these results one can assess the influence of beam overrun upon a continuous sampling measurement during a transient event.

Experiment

The direct sampling molecular beam mass spectrometer used in this investigation has been described previously⁸. Chopping was accomplished by a thin 5.08 cm dia. disk with eight, 0.165 cm wide, equally spaced slots around the periphery, spun to produce pulses at a frequency of 1600 Hz. In these experiments source-to-chopper and chopper-to-detector distances were 8.7 and 20.5 cm, respectively.

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 quartz sampling probe tip with a 100 micrometer dia. orifice.

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 μ fd. capacitor charged to 3.0 kilovolts. The lamp discharge, initiated by a high voltage trigger pulse of variable delay, typically lasts 120 μ sec.

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 0.70 Ar, 0.08 CH₄, 0.15 O₂, and 0.07 NO₂. Initial pressure in the reaction chamber for both mixtures was 300 torr. Ignition consistently occurred in the combustible mixture for flash energies above 400 joules.

Background

Consider a molecular beam produced by skimming a flow in the post-translational freezing zone of an expanding free jet. Molecules in the beam have a velocity distribution

$$f(v,T) = A v^2 \text{EXP} \left\{ -B(v-U(T))^2 \right\} \quad (1)$$

where v is the molecular speed, T is the stagnation temperature, U is the mean macroscopic beam velocity, and A and B are constants. For a given beam intensity at the source, $C(t)$, the distribution of molecules at the detector is

$$N(t) = \int_0^t \frac{L C(\tau)}{(t-\tau)^2} f(L/t-\tau, T) d\tau \quad (2)$$

where f has the form specified in eq (1) while v is expressed in terms of $L/(t-T)$, L being the source-to-detector distance. Eq. (2) can be integrated numerically using standard techniques, as demonstrated by Alcay and Knuth⁹ and Hagena and Varma¹⁰.

Previously⁸ we have evaluated the molecular distribution $N(t)$, by using an indirect method. Briefly, this was done as follows. Molecules in the beam having a velocity in the interval v to $v+\Delta v$ arrive at the detector within the time interval t to $t+\Delta t$. By the use of eq. (1) to evaluate $f(v,T)$, the relative number of molecules in a particular velocity interval can be determined. By stepping through the domain of physically realizable velocities, $N(t)$ is obtained. In essence, one integrates eq. (2) by the use of a delta function to represent $C(t)$. For the next time step, the calculation is repeated using a new source temperature and the delta function of strength $C(t)$. Summing the results for each time step leads to

a complete solution describing $N(t)$ for any $C(t)$ and source temperature profile.

Results

Chopped Beam Mode

Inclusion of temperature variation into the chopped beam analysis requires the consideration of two regions. The first extends between the source and the chopper, and the second between the chopper and the detector. For the first region eq. (2), with the appropriate source-to-chopper distance, describes the process quite accurately. The resulting number density profile, $N(t)$, specifies the molecular distribution at the chopper. Of the molecules reaching the chopping plane, only those coincident with the opening of the chopper are transmitted. The distribution transmitted is thus

$$N'(t) = A(t) N(t)$$

where $A(t)$ is the area function of the chopper opening determined previously⁸. One can then calculate the final time-of-arrival (TOA) distribution at the detector using the velocities of molecules transmitted through the chopping plane. In this way we have been able to evaluate the effects of rapidly increasing source temperature on the TOA distribution.

We applied this analysis to the binary gas mixture using an average molecular weight of 39.67 and a specific heat ratio of 1.57. Results indicate that when the source gradient is below 1×10^6 K/sec, the use of one unique temperature in eq. 2 adequately characterizes the resulting TOA curve. For higher gradients, however, this is no longer possible. To demonstrate this, Fig. 2 was generated using a temperature profile that increases from 300 K to 1200 K at a rate of 6×10^6 K/sec. The double peaked

curve results from the hotter parts of the beam arriving at the detector earlier than the colder portions. However, even when beam overrun occurs, the temperature gradient can be estimated by fitting the general shape of the curve.

Experimental results of NO_2/Ar photolysis for a particular flash lamp trigger delay are presented in Fig. 3. The upper trace is the Ar signal recorded in the course of photolysis while the lower one is the signal obtained from the same mixture in the absence of photolysis, i.e. at room temperature. The shift in the peak arrival time is a measure of the temperature of the sampled gas. From the measured peak arrival times, we can assign initial and final temperatures to the gas of 300 and 1200 K, respectively. Figure 4 presents data from a similar experiment with the flash lamp discharging at a slightly different trigger delay. Analysis indicates that unless the temperature increase takes place in less than 200 usec, the double peak cannot occur. These results yield data on the temperature excursion for the photolysis event shown in Fig. 5.

Figure 6 presents the results for combustion. A mixture of $\text{Ar}/\text{CH}_4/\text{O}_2/\text{NO}_2$ was used in flash initiated experiments where the TOA and pressure data were recorded simultaneously. Various flash lamp trigger delays were used so that data at different times in the combustion process could be obtained. The TOA curves were correlated by aligning the simultaneously acquired pressure traces. The analysis proceeded in a manner similar to that used for photolysis, using $M=36.67$ and $\gamma=1.54$.

Continuous Beam Mode

To evaluate and visualize the analysis of the unchopped beam mode of operation, we have modified the algorithm by keeping separate the individual responses at each time step and expressing them in the form of

three-dimensional plots. Figure 7 presents the results calculated from the simple photolysis experiment whose temperature profile was previously shown in Fig. 5. The abscissa and ordinate of the floor of the plot in Fig. 7 represents, respectively, the detector and source times. Displayed by the vertical coordinate is the relative number of molecules arriving at the detector, evaluated by the use of eq. (2). It should be noted that, in order to obtain a clear representation of the overrun, each individual TOA curve is independently normalized. The source temperature profile used in generating the figure is shown on the left hand wall.

The right hand wall presents a plot of the peak arrival time of each individual TOA curve as a function of the detector time. The deviation of the slope of this curve with respect to the diagonal across the graph manifests the overrun. A critical situation arises when the slope approaches infinity. This occurs when adjacent portions of the beam arrive simultaneously at the detector. Negative slopes indicate that the signal at the detector is no longer a single valued function of the time the molecules leave the source.

The temperature gradient needed for the critical overrun has been discussed by Smith⁵. We have expressed it in terms of the source-to-detector distance, L, and the thermodynamic properties of the sampled gas, as follows

$$\frac{dT}{dt} = \frac{T^{3/2}}{L} \left(\frac{8\gamma}{\gamma-1} - \frac{R}{M} \right)^{1/2} \quad (3)$$

where γ is the specific heat ratio, R is the universal gas constant, and M the molecular weight. Graphic portrayal of this effect is evident in the photolysis results presented Fig. 7. It should be noted that overrun occurs soon after the start of the process, a consequence of the fact that

at lower temperatures the beam velocity is more sensitive to the source temperature.

Results for combustion are shown in Fig. 8. As in the previous case, the flash produces the initial rise in temperature and pressure. After a delay of ~ 500 usec, further increases in temperature and pressure, this time due to combustion, are observed (Fig. 6). Figure 8 demonstrates that beam overrun is present during both photolysis and combustion. However, overrun during combustion is not as severe as during photolysis. There are two reasons for this. First, as a consequence of photolysis, combustion occurs at an initially elevated temperature. This reduces the effect of the overrun due to the relative insensitivity of the beam velocity to temperature variation at higher source temperatures. Second, in contrast to photolysis, combustion generated source temperature variations are slower.

Discussion

It is obvious that overrun should be avoided since it can make experimental data nearly impossible to interpret. The degree of beam overrun occurring in the course of direct sampling is controlled by three factors. The first involves the characteristic physical dimensions of the sampling device, specifically the source-to-detector distance. As the source-to-detector distance is reduced, molecules leaving the source reach the detector in a shorter period of time, preventing faster portions of the beam from overtaking slower parts. The second factor concerns the rate of the temperature rise at the source. Slowing the reaction, either by the use of a diluent or by operating at lower pressures, improves direct sampling capability. The third factor is associated with the initial

temperature of the source, overrun being enhanced at lower temperatures. This factor is particularly relevant for our case since photolysis raises the reactant gas temperature to approximately 1000 K before combustion occurs. As evident from eq. (3), the critical rate of source temperature increase is proportional to $T^{3/2}$. Changing the initial temperature from 300 to 1000 K increases the critical temperature rise by a factor of six.

To quantify these observations, eq. (3) was used to generate a family of curves, shown in Fig. 6, relating the quantity, $T^{-3/2} \cdot dT/dt$, to the source-to-detector distance. The parameter

$$\eta = \left(\frac{8\gamma}{\gamma - 1} \frac{1}{M} \right)$$

varies from 0.5 to 5, covering the range applicable to most combustion studies.

For our case of a source-to-detector distance of 30 cm, an initial temperature of 300 K, a mean M of 39.67 and $\gamma = 1.57$, the critical rate of source temperature increase is 1.2×10^6 K/sec. The rate of temperature increase during photolysis far exceeds this value. In the case of combustion, at an initial reactant gas temperature of 1000 K, a mean M of 36.67, and a γ of 1.54, the critical rate in source temperature increase is 7.6×10^6 K/sec. This is a higher rate than achieved by combustion; hence this case is within the manageable realm for direct sampling measurements. Of course, there is still some loss of time resolution in any system where the source temperature changes. Whether this loss can be tolerated depends on the particular system under investigation.

The conditions for direct sampling of a propagating flame are estimated as follows. The rate of temperature increase at the source is $dT/dt = S \cdot dT/dz$ where dT/dz is the temperature gradient in the flame and S is the propagation velocity. In hydrocarbon-oxygen mixtures the flame thickness

is inversely proportional to pressure, while its speed is essentially independent of this parameter. Thus $dT/dt = S (\Delta T/\delta) (P/P_r)$ where δ is the flame thickness, P is the pressure, and subscript r denotes a reference condition. From the critical rate in source temperature increase deduced from Fig. 6, one can then determine the upper bound on the pressure during sampling measurement. For a mixture of 10% methane in oxygen at a pressure of 0.1 atm and room temperature, the flame thickness is of the order of 2 mm, and the flame propagation velocity is 55 cm/sec¹¹. For a source-to-detector distance of 30 cm, initial temperature of 300 K, $M=30.4$ and $\gamma = 1.36$, the critical condition is produced by a sampling pressure of 0.48 atmospheres. Thus direct sampling from propagating flames is possible if proper care is taken in the design of the system.

Conclusion

The problem of obtaining meaningful time-resolved measurements using a direct sampling molecular beam technique has been analyzed. A numerical technique has been developed which accurately predicts the beam overrun phenomena observed in experimental systems. Its application to the case of ignition by photolysis and flame propagation in 10% methane-oxygen mixture indicates that these systems can yield meaningful results.

ACKNOWLEDGEMENTS

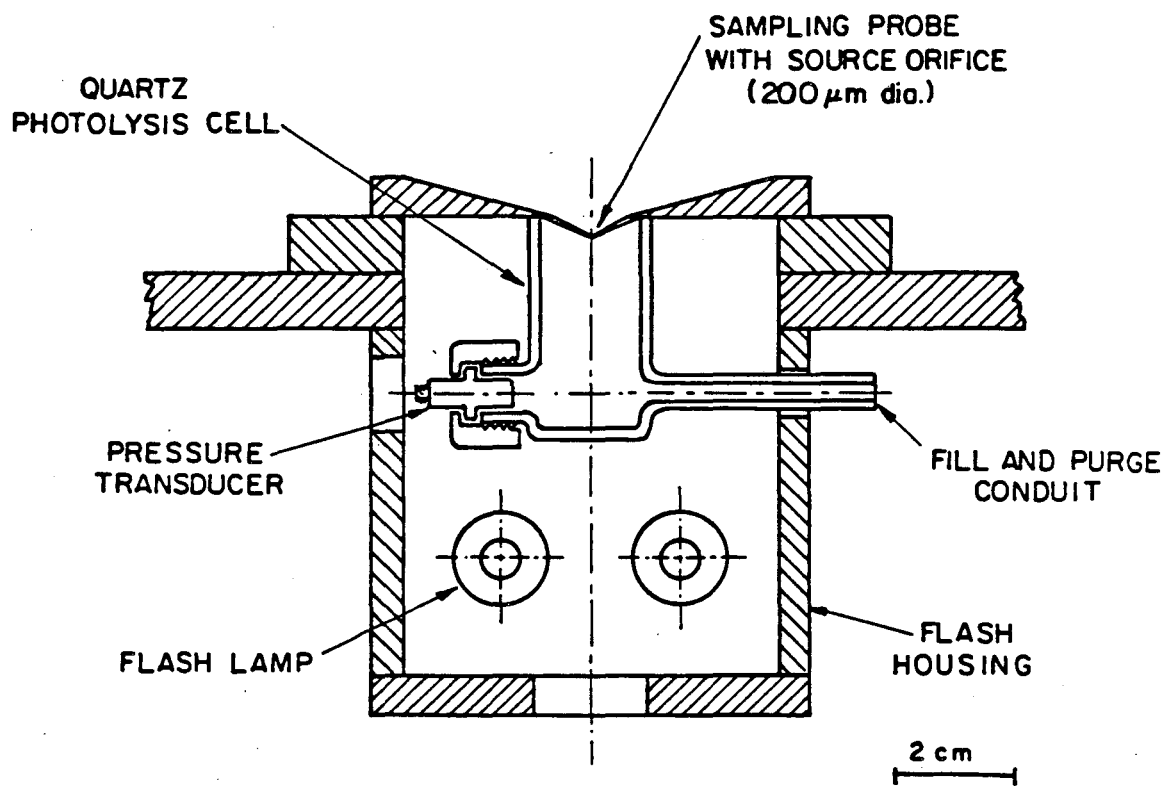
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Figure Captions

- Figure 1. Schematic diagram of the reaction cell.
- Figure 2. Calculated time-of-arrival curve generated with a temperature rise from 300 to 1200 K at a rate of 6×10^6 K/sec. The dashed line is the chopper function used in the computation.
- Figure 3. Argon signal measured during photolysis and under steady-state conditions. The arrow denotes flash lamp discharge.
- Figure 4. Argon signal measured during combustion and under steady-state conditions. The arrow denotes flash lamp discharge.
- Figure 5. Measured temperature profile for the photolysis event.
- Figure 6. a) Measured temperature profile for flash-ignited combustion.
b) Reaction cell pressure measured during combustion.
- Figure 7. Beam overrun calculated using the temperature excursion shown in Fig. 5.
- Figure 8. Beam overrun calculated using the temperature excursion shown in Fig. 6
- Figure 9. Critical temperature increase as a function of source-to-detector distance.



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Fig. 1

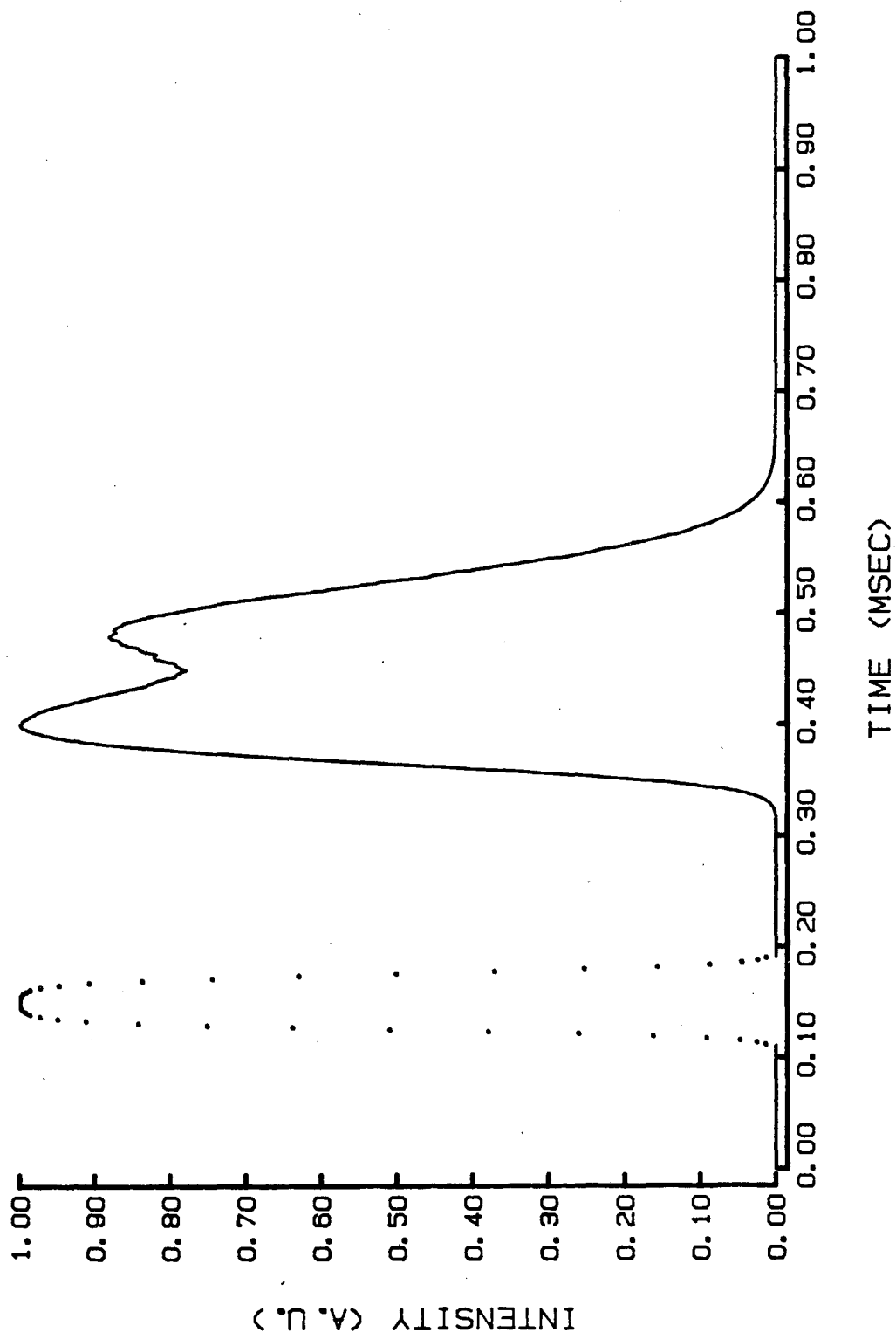


Fig. 2

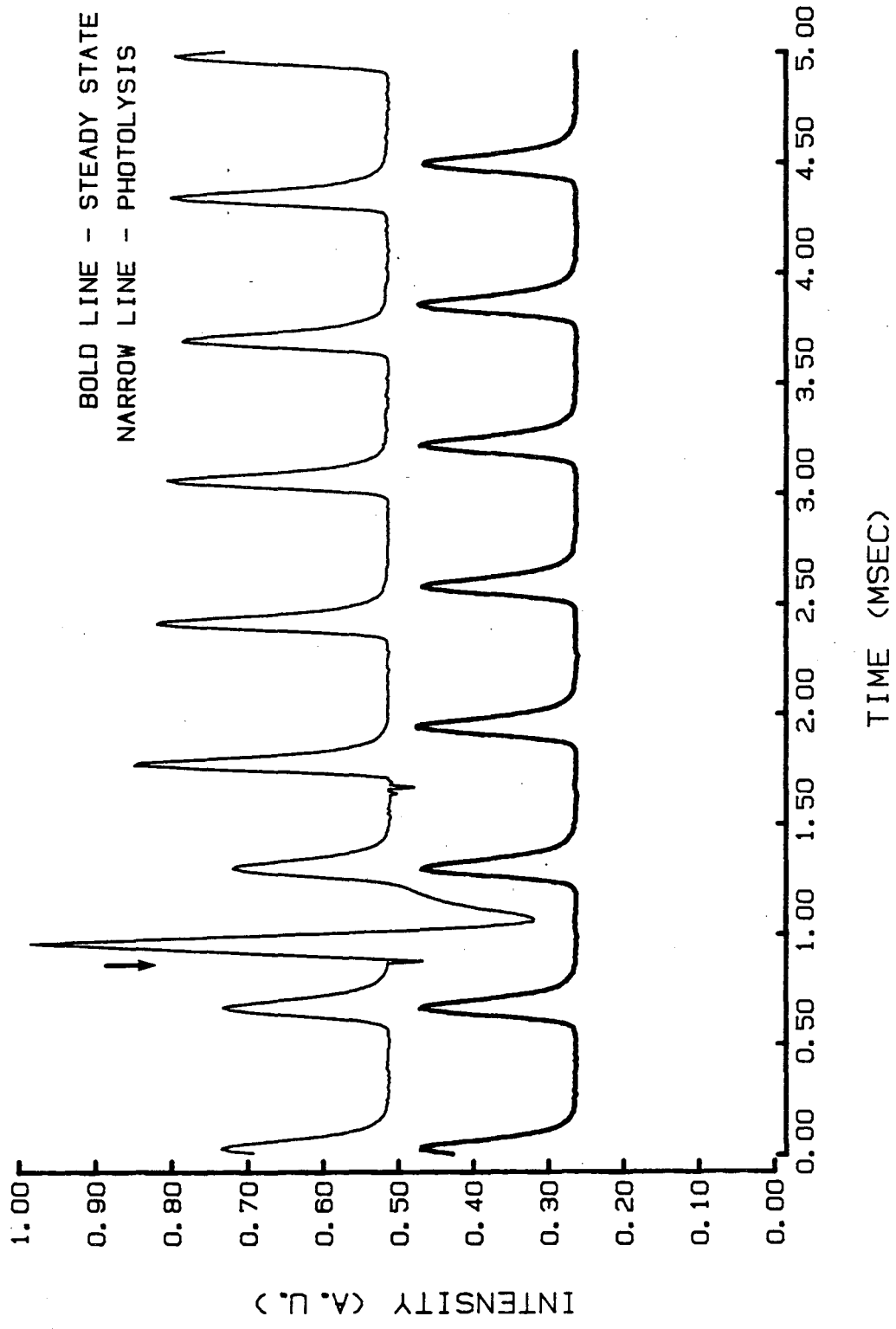


Fig. 3

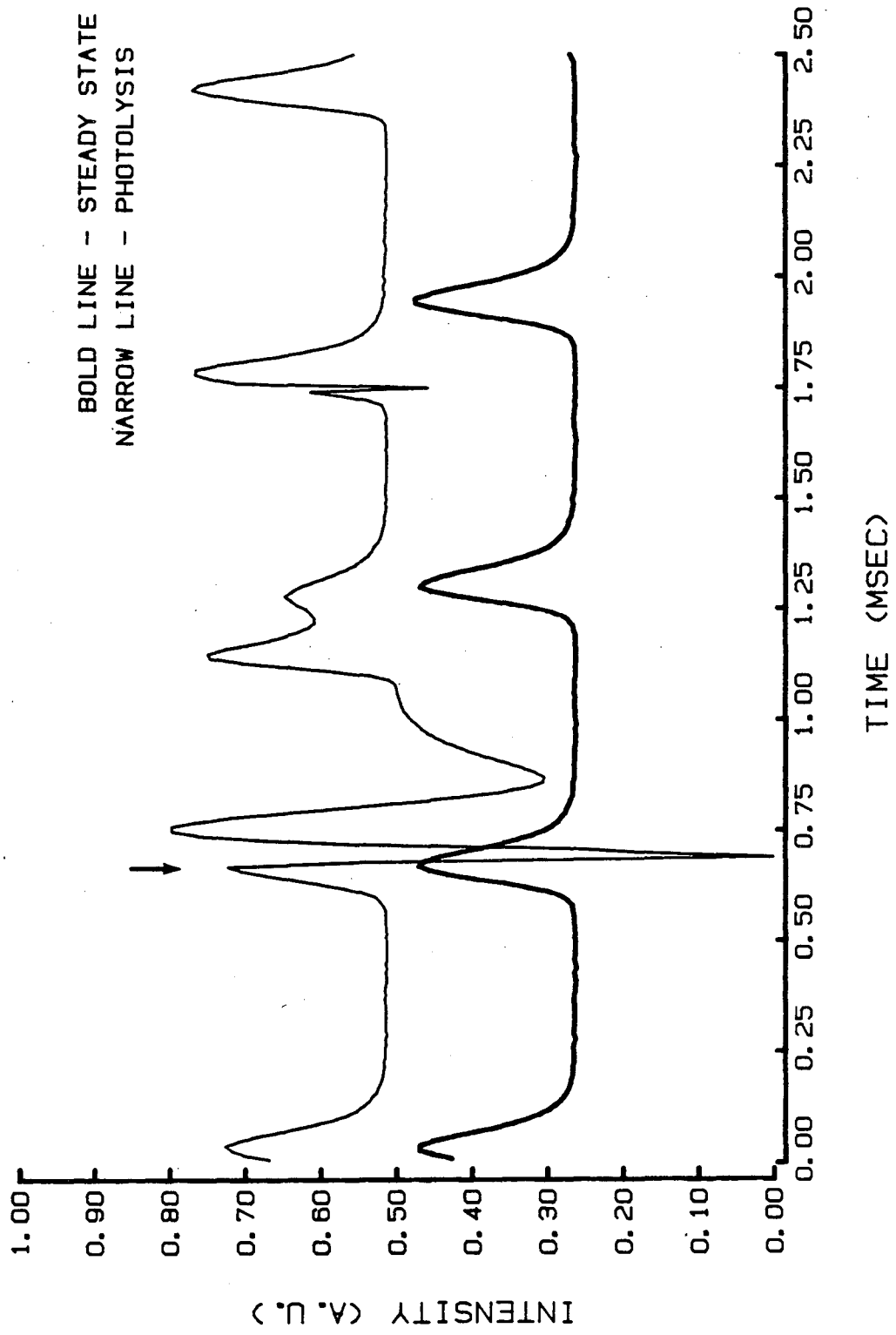


Fig. 4

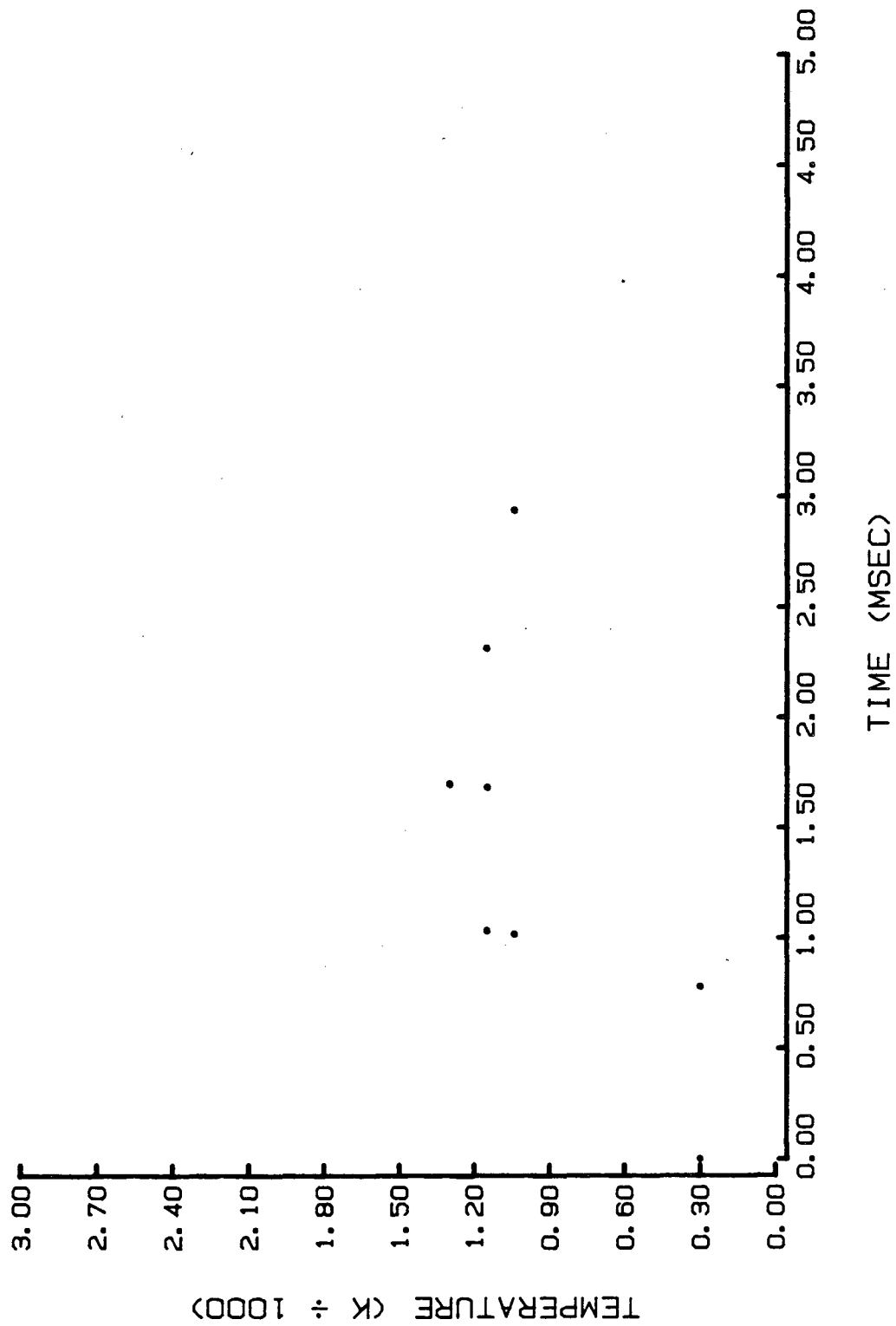


Fig. 5

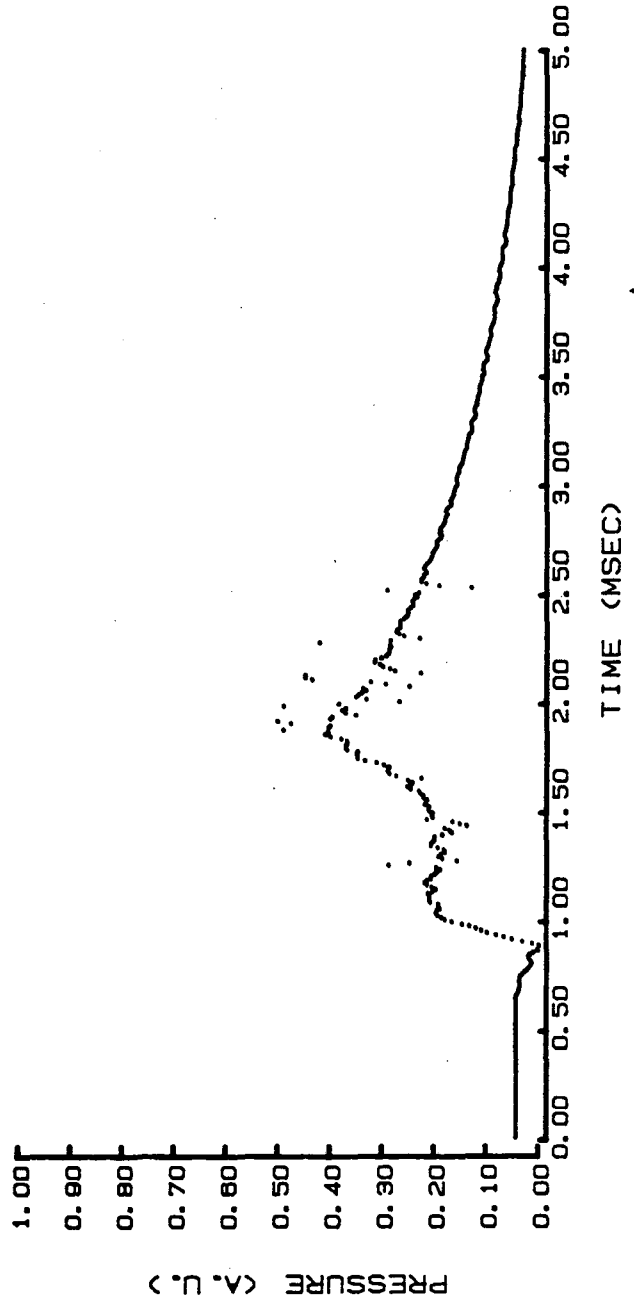
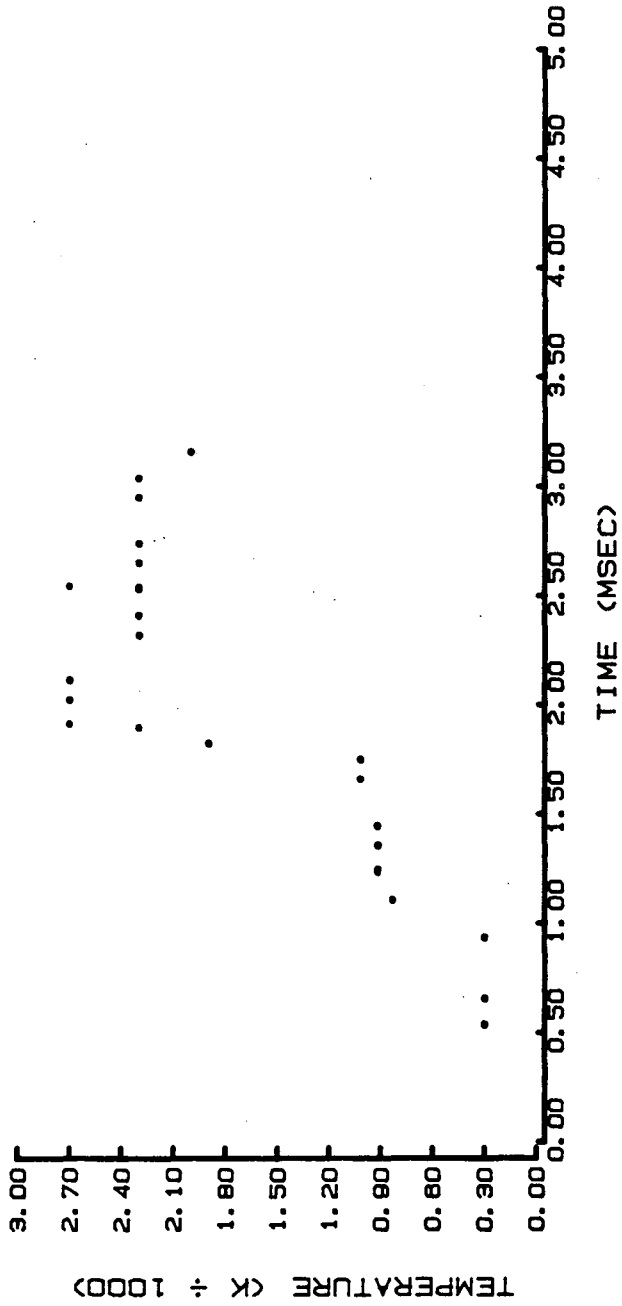


Fig. 6

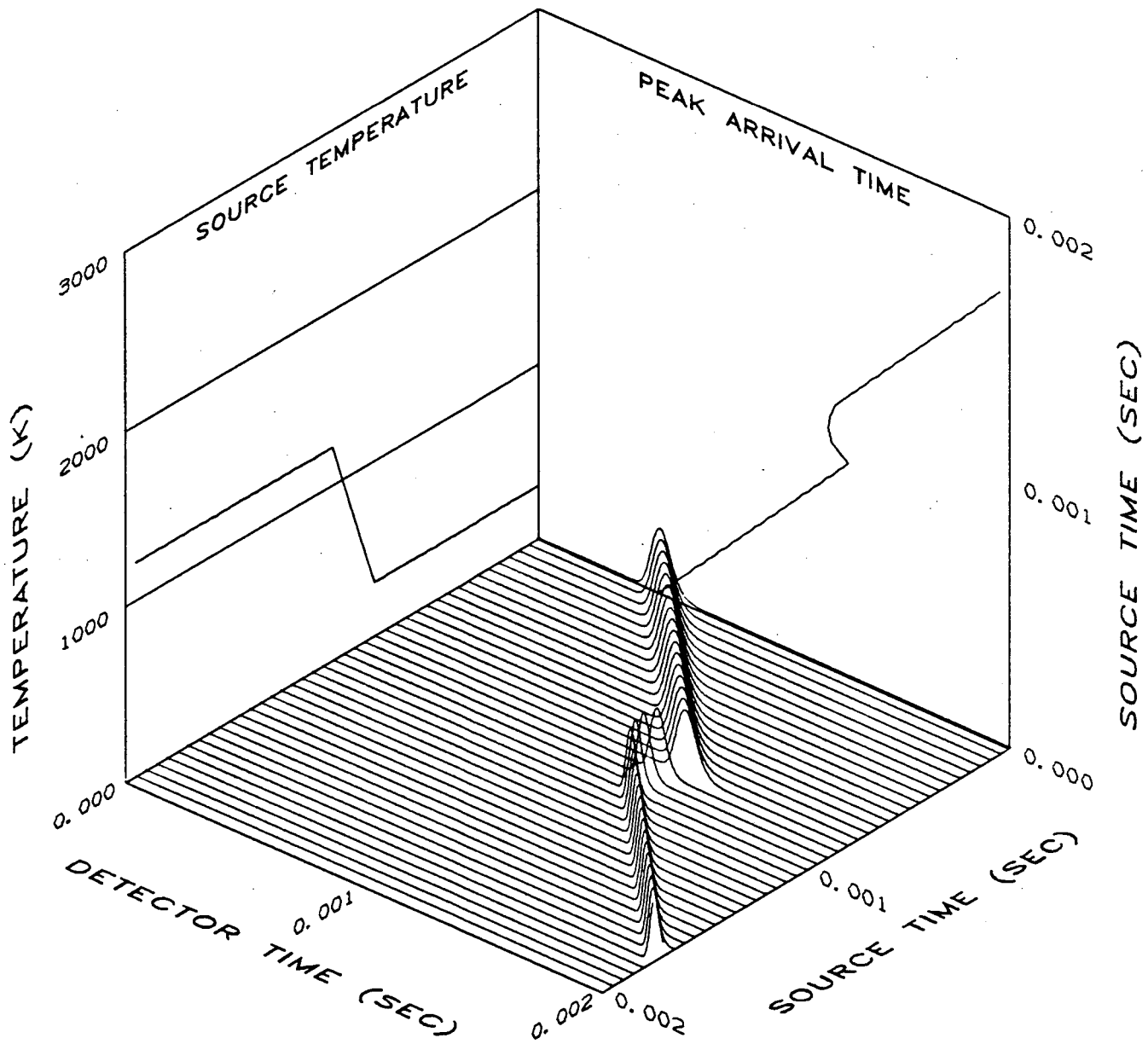


Fig. 7.

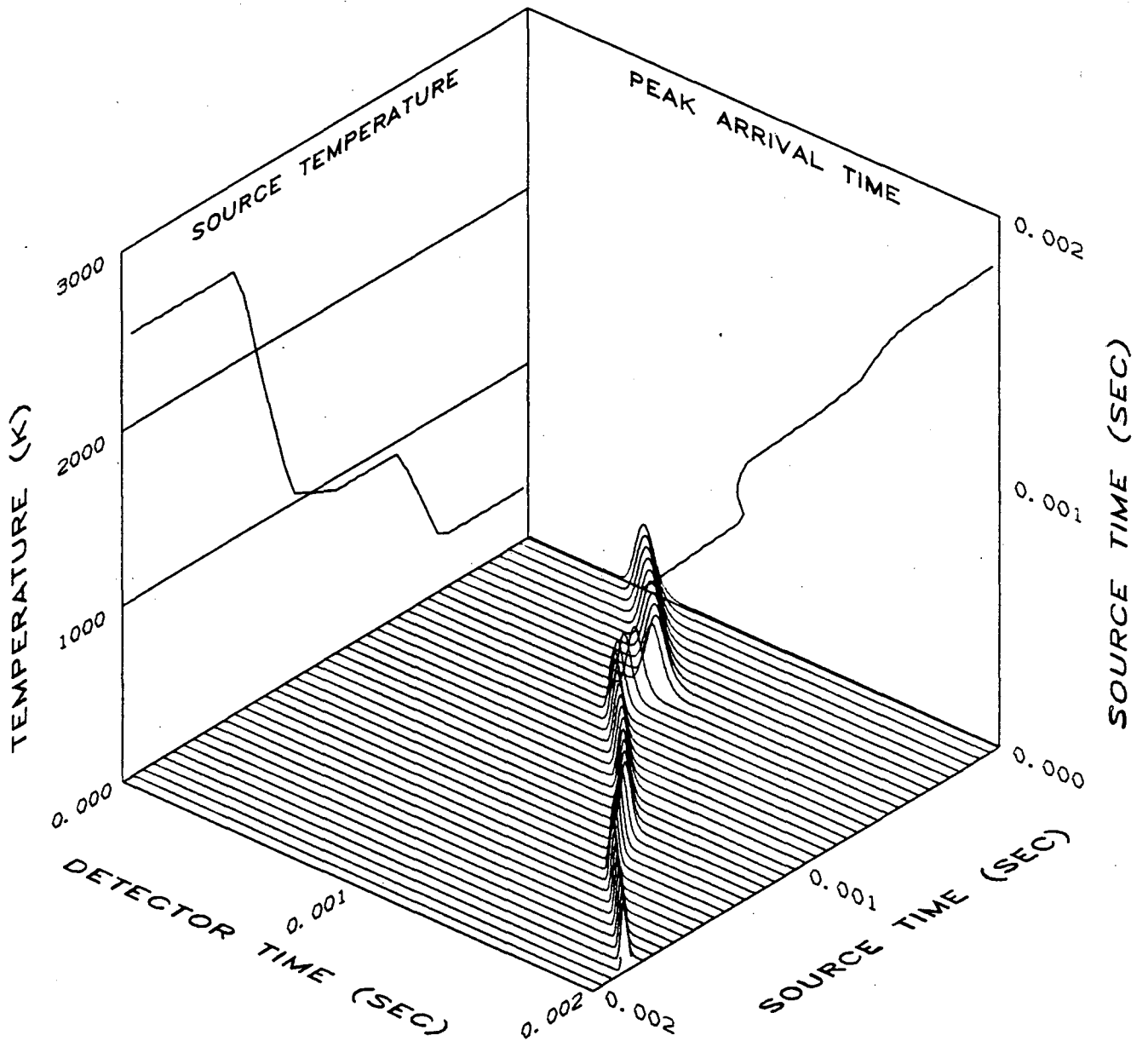


Fig. 8

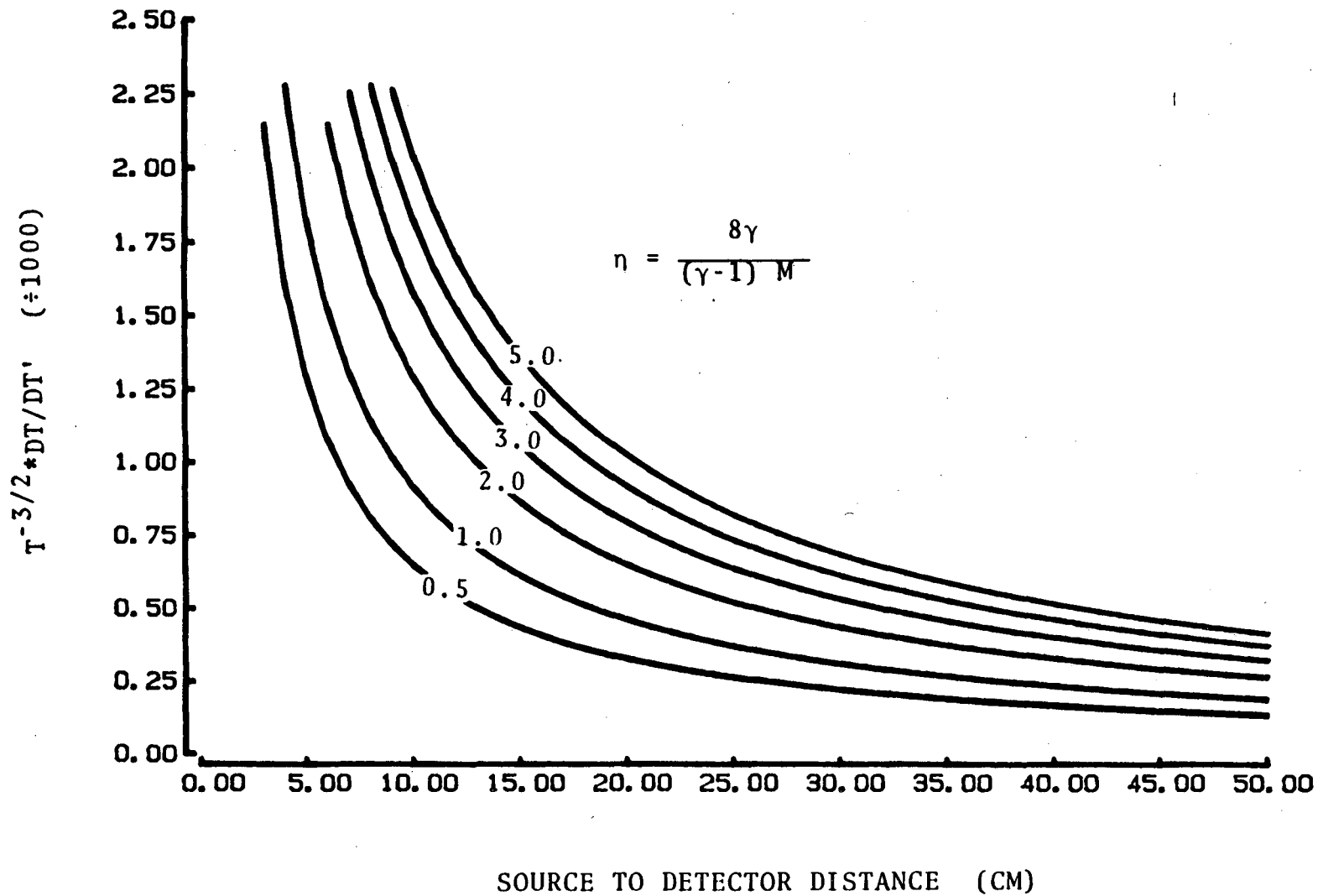


Fig. 9

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