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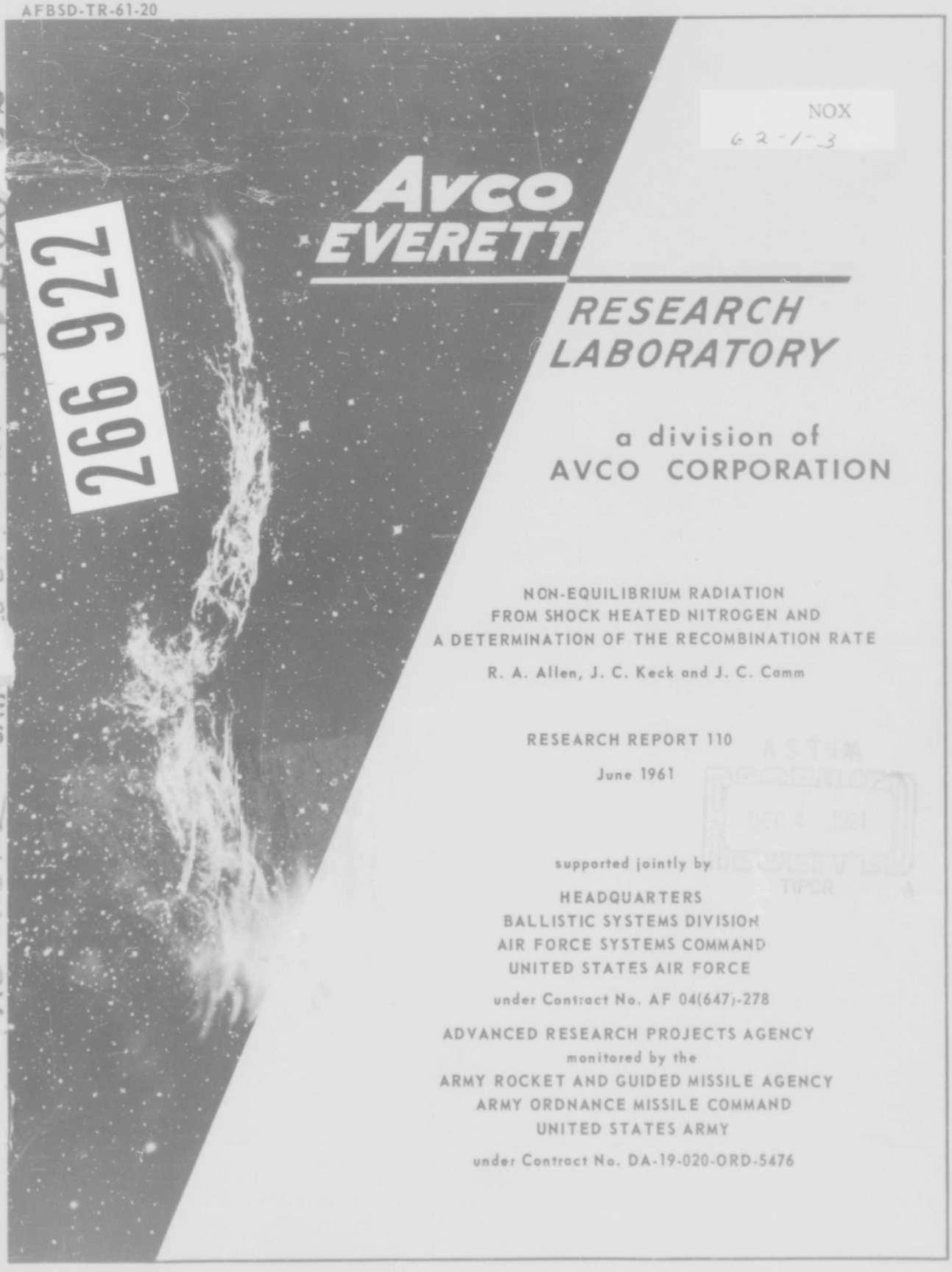

AVCO EVERETT RESEARCH LABORATORY

a division of
AVCO CORPORATION

NON-EQUILIBRIUM RADIATION FROM SHOCK HEATED NITROGEN AND A DETERMINATION OF THE RECOMBINATION RATE

R. A. Allen, J. C. Keck and J. C. Camm

RESEARCH REPORT 110

June 1961

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ABSTRACT

The radiation emitted by shock heated nitrogen is studied in the wavelength range 3300 to 7100Å at an equilibrium temperature from 6000 to 6800°K and densities from .01 to .20 atmospheres. The various radiating bands are identified by spectroscopic and photometric techniques. The radiation consists of bands from the N_2^+ (1-), N_2(1+) and N_2 (2+) systems. The radiation overshoot observed at the shock front relaxes very rapidly to an equilibrium level. The rate of decay of the N_2 (1+) radiation near equilibrium is studied at various densities and shock speeds and is used to determine the recombination rate constants, k_{RN} and k_{RN_2} for the reactions $N + N + N \rightarrow N_2 + N$ and $N + N + N_2 \rightarrow N_2 + N_2$, respectively. k_{RN} is found to be $1.8 \times 10^{-32} \pm .6$ cm^6/sec at 6400°K and k_{RN_2} to be at least 13 times smaller than k_{RN}. Using these rate constants, calculations of the N_2 (1+) non-equilibrium radiation we made using: (1) no coupling of the dissociation rates with the vibrational relaxation, and (2) a coupling which assumes that dissociation can take place equally well from any vibrational level of the ground state. Comparison is made between these calculations and observations. It is concluded that the coupling scheme of the second case mentioned above is a realistic approximation. The integral non-equilibrium radiation and the time of occurrence of peak radiation behind the shock front are also examined.

1. INTRODUCTION

The present interest in the field of high temperature gas dynamics, and in particular the study of chemical reaction rates in air and its components, stems from many problems important to our understanding of the physics of the upper atmosphere and the aerodynamics of hypersonic flight.

The shock tube provides a very direct simulation of a hypersonic object entering the earth's atmosphere. The radiative properties of high temperature air and its constituents have been intensively studied[1, 2] at thermodynamic equilibrium and are reasonably well understood. A study[3] associated with the work described in this paper was made of the equilibrium radiation from shock heated nitrogen. In this previous work, the various radiating species were clearly identified, and absolute intensity measurements were made. The effect of impurities on the equilibrium radiation was also examined.

This paper describes a study of the non-equilibrium radiation from shocks in nitrogen. The optical radiation from the $N_2(2+)$, $N_2(1+)$ and $N_2^+(1-)$ systems is observed to rise abruptly at the shock front to a peak value, then decay to an equilibrium value in a few microseconds. A simple explanation of this may be found in the following considerations:

When a diatomic gas such as nitrogen passes through a normal shock, the translational and rotational degrees of freedom relax to local equilibrium

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1. Kivel, B., Mayer, H. and Bethe, H., Annals of Physics 2, 57 (1957).
2. Keck, J., Camm, J., Kivel, B., and Wentink, T., Jr., Annals of Physics, 7, 1 (1959).
3. Allen, R.A., Camm, J.C., and Keck, J.C., Avco-Everett Research Laboratory RR 102, April 1961. Submitted to J. of Quantitative Spectroscopy, June 1961.

within a few mean free paths, and the resulting temperature and density may be computed from the usual Rankine-Hugoniot relations for a gas with a constant ratio of specific heats equal to 1.4. As time proceeds, energy is transferred into molecular vibration and dissociation, and the translational temperature falls. If we now assume that the rates of electronic excitation are sufficiently fast to keep the electronic temperature in local equilibrium with the translational temperature, then the number of molecules in excited electronic states may be very much in excess of the final equilibrium value and a large overshoot in the radiation intensity will result.

By studying the time dependence of this radiation overshoot one can obtain information not only about the chemical rates which control the temperature of the gas[4] but also about the rate of energy transfer in atoms and molecules from heavy particle degrees of freedom to electronic degrees of freedom. This latter process is one about which relatively little information exists, and it is of considerable importance not only in many practical problems, but also in that it is one manifestation of the breakdown of the Born-Oppenheimer approximation usually made in dealing with atomic and molecular collisions.

2. LINEARIZED THEORY OF RADIATION RELAXATION

The existence of an overshoot in the radiation intensity behind a shock wave in a diatomic gas implies that the electronic rate processes which control the population of radiating states are fast compared to rate processes which control the gas temperature. If this were not the case and the gas relaxed to equilibrium before the radiating states were populated,

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4. Hammerling, P., Teare, J.D., and Kivel, B., Physics of Fluids, 2, 422 (1959).

the radiation intensity would approach the final equilibrium value from below. Further it is known that, under the conditions of interest in the present experiment, translational, rotational and vibrational relaxation are fast compared to the rate of chemical adjustment in the gas. Therefore, during the approach to final equilibrium only the chemical state of the gas is changing and all other internal degrees of freedom, including electronic, will be in local thermodynamic equilibrium at the translational temperature of the gas.

Under the above conditions, the intensity, I, of the radiation from a shock-heated gas such as nitrogen may be regarded as a function only of the translational temperature, T, which is in turn a function of the degree of dissociation. Following Hammerling, Teare, and Kivel[5] we may then write

$$\frac{dI}{dt} = \frac{dI}{dT} \cdot \frac{dT}{d(N_2)} \cdot \frac{d(N_2)}{dt} \tag{1}$$

where $(N_2) = [N_2]/L_o\,(\rho/\rho_o)$, $[N_2]$ is the number of nitrogen molecules per unit volume, (ρ/ρ_o) is the ratio of the density to standard density, and L_o is Loschmitd's number.

Combining Eq. (1) with the chemical rate equation

$$\frac{d(N_2)}{dt} = K_R \left\{ K(N_2) - L_o\left(\rho/\rho_o\right)(N)^2 \right\} \tag{2}$$

and linearizing with respect to small departures from final equilibrium, we obtain

$$\frac{dI}{dt} = -\frac{I - I_e}{\tau} \tag{3}$$

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5. Hammerling, P., Teare, J.D., and Kivel, B., Avco-Everett Research Laboratory RR 49, April 1959.

where

$$\tau^{-1} = \frac{dT}{d(N_2)} K_R L_o \left(\rho/\rho_o\right)(N)^2 \left[\frac{1}{K}\frac{dK}{dT} + \left\{\frac{1}{(N_2)} + \frac{4}{(N)}\right\}\frac{d(N_2)}{dT} - \frac{1}{\rho}\frac{d\rho}{dT}\right] \quad (4)$$

In the above equations $K_R \equiv L_o\,(\rho/\rho_o) \times \left[k_{RN}\,(N) = k_{RN_2}\,(N_2)\right]$, $K = L_o\,(\rho/\rho_o)\,(N)^2/(N_2)$ is the equilibrium constant, and k_{RN} and k_{RN_2} are, respectively, the recombination rate constants for N and N_2 as catalysts. The right-hand side of Eq. (4) is to be evaluated at equilibrium with the derivatives $d(N_2)/dT$ and $d\rho/dT$ being obtained from the linearized Rankine-Hugoniot relations for a plane normal shock.

Eq. (4) may be expressed in a form more convenient for later analysis as follows:

$$\frac{F}{\tau} = k_{RN_2} + \frac{(N)}{(N_2)} k_{RN} \quad (5)$$

where

$$F^{-1} \equiv L_o^2 \left(\rho/\rho_o\right)^2 (N)^2 (N_2) \frac{dT}{d(N_2)} \left[\frac{1}{K}\frac{dK}{dT} + \left\{\frac{1}{N_2} + \frac{4}{(N)}\right\}\frac{d(N_2)}{dT} - \frac{1}{\rho}\frac{d\rho}{dT}\right] \quad (6)$$

The function F and the ratio $(N)/(N_2)$ have been evaluated for various shock conditions in nitrogen by Hammerling, Teare and Kivel and are shown in the graphs in Appendix A. If T can be determined from observations of the radiation decay for various equilibrium temperatures and densities, then Eq. (5) shows that a plot of F/τ vs $(N)/(N_2)$ for constant temperature should give a straight line with slope k_{RN} and intercept k_{RN_2}. This is a basic premise of the present experiment.

In concluding this discussion, we should like to point out that we have made the common assumption that the ratio of the rate constants for

dissociation and recombination is equal to the equilibrium constant.[6] Although this is not in general true in a gas which is out of equilibrium, it is true under the assumption made above that close to final equilibrium all internal degrees of freedom are in local equilibrium.

3. APPARATUS

The experimental work associated with this study was performed primarily in a 1.5" combustion driven shock tube in pure nitrogen with initial pressures of 1.0 to 10 mm Hg., and shock speeds up to Mach 20. A schematic diagram of the shock tube, recording equipment and optical arrangement, is shown in Fig. 1. The shock tube had a 15 foot pyrex test section of 1.5 inches inside diameter. The high pressure driver section was separated from the low pressure test section by a steel diaphragm. The driver section was of stainless steel 3 feet long and 1.5 inches inside diameter. The test section was evacuated by an oil diffusion pump prior to introducing the test gas. Pressures of less than 2.0 microns of Hg and virtual leak rates of less than 1.0 micron of Hg per minute were obtained. A flow system was used to minimize impurities due to out gassing of the apparatus. Also used was a cold trap to remove water vapor from the N_2.

The shock speeds were measured by observing with a single photomultiplier the radiation from the shock as it passed a series of six equally spaced slits arranged 10 inches apart along the last half of the shock tube. The output of the photomultiplier was doubly differentiated and displayed on a folded oscilloscope sweep which was normally read to the nearest 0.4 microsecond. A speed profile was constructed and the velocity at the test point was determined with a maximum error of about 1%. Initial pressure

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6. Gilmore, F.R., Rand Corp. Research Memorandum RM-1543, (1955).

in the test section was measured by a manometer with an estimated maximum error of 0.4%.

Measurements of the spectral intensity and radiation histories were made using a calibrated dual channel grating monochromator. The experimental apparatus is shown schematically in Fig. 1. The entrance slit of the monochromator was imaged perpendicular to the shock tube at the center of the test gas by an optical train consisting of two aluminized mirrors. The monochromator was equipped with three photomultipliers; two which measured the radiation intensity in two adjacent narrow wavelength bands selected by the monochromator and the third which monitored a fraction of the radiation passing through the entrance slit. The outputs of the photomultipliers were fed directly to Tektronix 545 oscilloscopes equipped with 53k/54K preamplifiers.

The optical resolving time was determined by the entrance slit width which was set at .50 mm. Therefore, for a shock speed of 5 mm/μ sec, the optical resolution was approximately .1 μ sec. The theoretical electronic rise time was evaluated to be approximately .03 μ sec. The oscilloscope traces were photographed by Land cameras and enlarged for evaluation.

4. MEASUREMENT OF EXPONENTIAL DECAY TIMES

A study[3] associated with the present work was made of the equilibrium radiation from shock heated nitrogen. The radiation species were identified, and the wavelength distribution and relative intensities are displayed in Fig. 2 versus wavelength.

For studying the radiative relaxation of the N_2 (1+) system a Dumont K1292 photomultiplier with a filter placed directly in front of it to cut off radiation below 5500Å was used as the monitor. The spectral sensitivity of this monitor is shown in Fig. 2 and some typical oscillograms of the radiation profile obtained with it are shown in Fig. 3. The oscillograms are shown for three

different shock speeds and an initial pressure of 2 mm Hg. The radiation is observed to overshoot, then decay to an equilibrium value in a few microseconds. Near equilibrium the decay is exponential and an experimental decay time, τ, can be determined for a given run. This was done by plotting the ratio $(I-I_e)/I_e$, where I is the radiation intensity and I_e is its final equilibrium value, as a function of laboratory time and making the best straight line fit to the data in the region $(I-I_e)/I_e < 1$. The procedure is illustrated in Fig. 4. The restriction $(I-I_e)/I_e < 1$ was imposed in an attempt to stay within the range of temperatures wherein an exponential approach to equilibrium would be valid. Since the radiation intensity varies as the tenth power of the temperature T in the range studied, $(I-I_e)/I_e < 1$ implies $(T-T_e)/T_e < 0.1$. The reading error of the decay time constant was determined by the largest and smallest τ which could reasonably fit the data points of the $(I-I_e)/I_e$ versus t graph.

Fig. 5 is a graph of the exponential decay times versus shock speed with initial pressures as a parameter. The superimposed grid is based on the recombination rates and will be discussed later.

In the examination of the equilibrium radiation reported in Ref. 3, the N_2 (1+), N_2 (2+) and N_2^+ (1-) were identified. Further the theory of P. Hammerling et al[4] predicts that the exponential decay times of the radiating systems near equilibrium should be independent of wavelength. To verify this point, decay time constants were obtained at approximately the same shock speeds for measurements taken at various wavelengths corresponding to the various radiating systems. The results are presented in Fig. 6a and b. The scatter of the points can be attributed to the inability to reproduce shocks of exactly 4.8 mm/μ sec and is also somewhat indicative of scatter to be expected from shock tube experiments. The results indicate

that the rate of decay of the radiation near equilibrium for shocks in pure nitrogen is independent of wavelength within the experimental scatter of ± 30 percent.

Since CN impurity radiation has always been troublesome in shock tube experiments, an investigation of the effect of CN contamination on the exponential decay times was made before choosing a wavelength region to study in determining the recombination rates. In this study, the nitrogen was purposely contaminated with known amounts of C_2H_2. The results are presented in Fig. 7 and Table 1. The conclusion drawn was that although the CN violet system can contribute appreciably to the radiation, it has no effect on the observed exponential decay time.

5. MEASUREMENT OF TOTAL DECAY TIMES

In this study, measurements of the total decay times were also made. The total decay times are not to be confused with the exponential decay times discussed in the previous section. The total decay time, $t_{0.1}$, is defined as the time starting from the shock front necessary for the radiation to fall within 10% of its equilibrium value. This corresponds to a temperature of approximately 1% above the equilibrium temperature. $t_{0.1}$ is shown in Fig. 8 versus shock speed, U_s, for various initial pressures. The times have been normalized to normal density by multiplying them by the initial pressure. The total decay time, $t_{0.1}$, should scale approximately as this factor if the chemical reactions and excitation mechanisms, without the radiation term, are initially binary. The two sets of theory lines shown as dashed and solid lines in the figure will be discussed in a later section.

6. MEASUREMENT OF ELECTRONIC EXCITATION TIME

The time for the observed radiation to rise to its maximum value measured from the shock front is designated t_M. Measurements, as before,

GAS P_1 = 1cm Hg	$U_s \frac{mm}{\mu sec}$	.38 < λ < .39 μ (CN Band Head)		.39 < λ < .40μ (N_2^+(1-) Band Head)		.55-1.1 μ (N_2(1+) System)	
		I/I, 100% N_2	τ μ sec	I/I, 100% N_2	τ μ sec	I/I, 100%N_2	τ μ sec
100% N_2	4.93	1	.35	1	.40	1	.38
2% C_2H_2	4.98	8.05	.37	1.01	.36	1	.38

Table I Effect of 2% C_2H_2 contamination on equilibrium intensity and radiation decay measurements - all results being normalized to the results for the pure nitrogen run. CN contamination produces no noticeable effect except in the CN violet region where the radiation is greatly enhanced.

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were made in the .55-1.0 μ wavelength region for normal shocks in pure nitrogen. Fig. 9a is a graph of t_M versus shock speed. The t_M's show saturation at a time which corresponds to the response time of the apparatus. For this reason the points falling below the dashed line in the graph were discarded in making up the graph in Fig. 9b. Fig. 9b is a graph with the t_M's normalized by multiplying them by the initial pressure as was also done in Fig. 8.

The integral non-equilibrium radiation of these radiation profiles was also evaluated. The ratio of the integrated non-equilibrium radiation up to the time $t_{0.1}$ divided by the integrated equilibrium radiation up to the same time is plotted in Fig. 10 versus shock speed.

7. DETERMINATION OF RECOMBINATION RATES

As shown in Section 2 of this paper the exponential decay time, τ, is related to the rate constants for the recombination of nitrogen by Eq. (5) in which F is a function dependent only on the final equilibrium conditions in the shock heated gas. As shown earlier the recombination rates k_{RN} and k_{RN_2} can be obtained by making a graph of F/τ versus $[N]/[N_2]$.

Fig. 11 shows a graph of F/τ vs $[N]/[N_2]$ with all the points extrapolated to 6400°K using a $T^{-1.5}$ dependence for the rate constants.[7] The temperature range of the measurements was from 6000°K to 6800°K, and the exponential decay times used were for the results obtained from observations of the N_2 (1+) radiation. The graphical relationship between all the pertinent parameters can be found in Appendix I. As was discussed in section 2 of this paper, all the points should fall along a straight line with the intercept at the F/τ axis determining the value for k_{RN_2} and the slope

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7. Bates, D.R., Physical Review, 78, 492 (1950).

determining k_{RN}. The best fit to the data gives a $k_{RN} = 1.8 \times 10^{-32}$ cm^6/sec with a deviation of $\pm$ .6 x 10^{-32} cm^6/sec and a k_{RN_2} of not measurably different from zero.

By referring the points which fall on the straight line fit to the data in this figure to corresponding F and U_s values, and also assuming a $T^{-1.5}$ dependence of the rate constants to extrapolate to higher and lower temperatures, a relationship between τ and U_s was established based on the experimental recombination rate constants. This relationship is the superimposed grid in Fig. 4 which is a graph of the decay time constants versus shock speed with initial pressure as a parameter. The general agreement between the superimposed grid and the experimental points makes evident the essential correctness of the theory since it predicts fairly well the decay time constant dependence on shock speed, a dependence which cannot be so easily demonstrated in the F/τ vs $[N]/[N_2]$ graph. A dashed curve in the grid in Fig. 4 was constructed using a T^{-1} dependence for the rate constants rather than a $T^{-1.5}$ dependence and indicates the relative insensitives of the experiment to this extrapolation factor.

The total decay time, $t_{0.1}$, was defined in connection with Fig. 8, and is the time necessary for the radiation to fall to 10% above the equilibrium level. Theoretical calculation of these decay times was made based on the experimentally determined recombination rate constants. The dissociation rates in the non-equilibrium region were based upon the equilibrium constant at the local translational temperature and also upon a $T^{-1.5}$ temperature dependence. Hammerling, Teare and Kivel in Ref. 4 discuss a possible coupling scheme between vibrational relaxation and the dissociation rates immediately behind normal shocks. Calculation of the decay times were made and plotted in Fig. 10 for: (1) no coupling between the vibrational

relaxation and the dissociation rates marked by D, and (2) the coupling which is outlined in Ref. 4 and marked CVD. The conclusion that can be drawn from this analysis is that the CVD scheme better fits the observations than a scheme which does not incorporate coupling; however, the difference is small.

Figure 12 shows an observed radiation profile along with theoretical predictions based on the CVD scheme previously mentioned. The fit near equilibrium is excellent with deviations becoming large near the shock front. The prediction of the radiation profile was accomplished by assuming that the excited electronic states were in equilibrium with the local translational temperature, an assumption which will predict an upper bound for the radiation immediately behind the shock front. An excitation process must be incorporated into the theory since there is some finite time involved in populating the upper electronic levels of the molecule starting immediately behind the shock front.

An alternative assumption which would provide for a finite excitation time is that the excited electronic states are in equilibrium with the local vibrational rather than local translational temperature. The time for vibrational equilibrium to be obtained, measured from the shock front, will very nearly be the time for peak vibrational temperature. The time for vibrational equilibrium of the ground electronic state of the molecule is plotted in Fig. 10b as a dashed line. The rate at which the vibration modes are excited is based on the adiabatic theory of Landau and Teller[8] and on the rates reported by V. Blackman[9]. The agreement

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8. Landau, L. and Teller, E., Physik. Z. Sonjetunion 11, 18 (1937).

9. Blackman, V., J. Fluid Mech. 1, 61 (1956).

between the times of maximum radiation and the vibrational relaxation times strongly suggests that the electronic states are excited by collisions in which energy is transferred from vibrational degrees of freedom rather than translational. This is in accord with observations made in gas discharges that radiation is quenched more effectively in molecules than atomic collisions.[10]

8. DISCUSSION OF RECOMBINATION RATES

k_{RN_2} and k_{RN} are the recombination rate constants for the reactions $N_2 + N + N \rightarrow N_2 + N_2$ and $N + N + N \rightarrow N_2 + N$, respectively. The value of $k_{RN} = 1.8 \pm .6 \times 10^{-32}$ cc^2/sec found in this experiment is in good agreement with the theoretical estimates of Keck[11] based on Camac's[12] observed dissociation rates for O_2. k_{RN_2} could not be determined, due to experimental scatter of the data, but is shown to be small compared to k_{RN}. This is also in accord with the O_2 results of Byron[13] where the ratio of (k_{RN_2}/k_{RN}) for O_2 was 1/7. For purposes of the nitrogen calculations (k_{RN_2}/k_{RN}) was taken as 1/100. A factor of up to 1/13 for (k_{RN_2}/k_{RN}) corresponding to the error in intercept in Fig. 11, made less than 1% difference in the predicted radiation profile compared with the calculation using a factor of 1/100 for (k_{RN_2}/k_{RN}).

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10. Massey, H.S.W. and Burhop, E.H.S., Electronic and Ionic Impact Phenomena, Oxford, London (1951) p. 422.

11. Keck, J.C. personal communication. See also Keck, J.C., J. Chem. Phys. 32, 1035 (1960).

12. Camac, M. and Vaughan, A., J. Chem. Phys. 34, 460 (1961).

13. Byron, S.R., J. Chem. Phys. 30, 1380 (1959).

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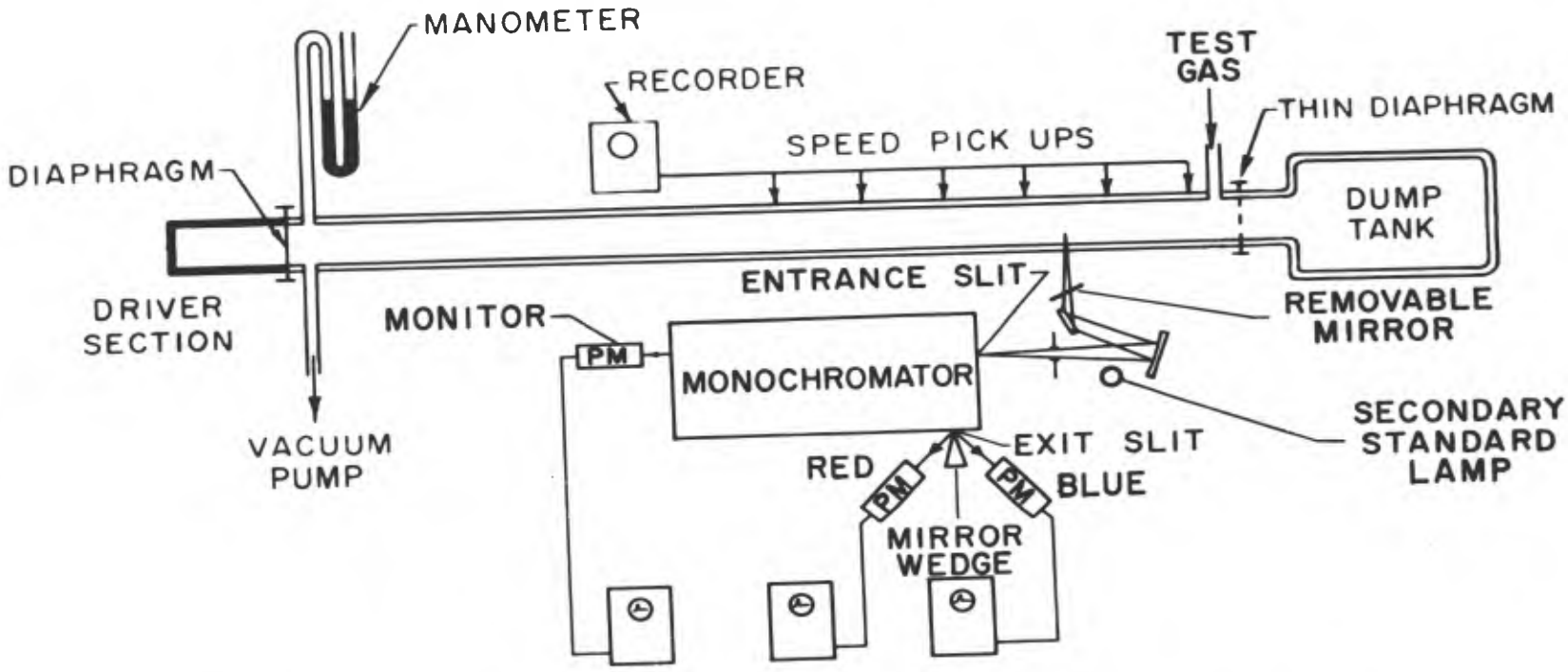

Fig. 1 Schematic diagram of 1.5 inch combustion driven shock tube.

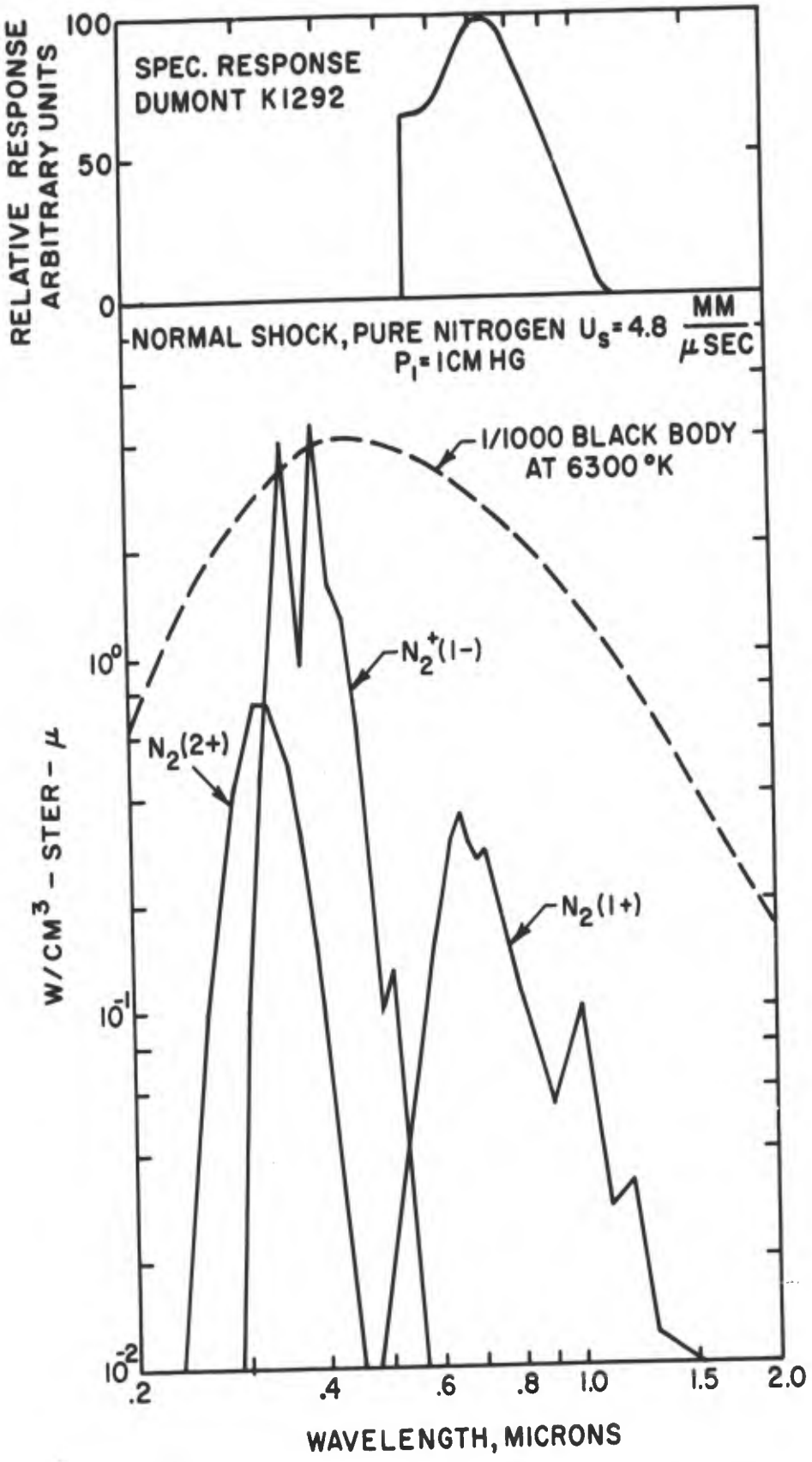

Fig. 2 Top: Spectral response curve of Dumont K1292 photomultiplier and filter used to monitor the $N_2(1+)$ radiation.
Bottom: Spectral intensity distribution of equilibrium radiation from normal shock in nitrogen. P_1 = 1.0 cm Hg, U_s = 4.8 $\frac{mm}{\mu sec}$.

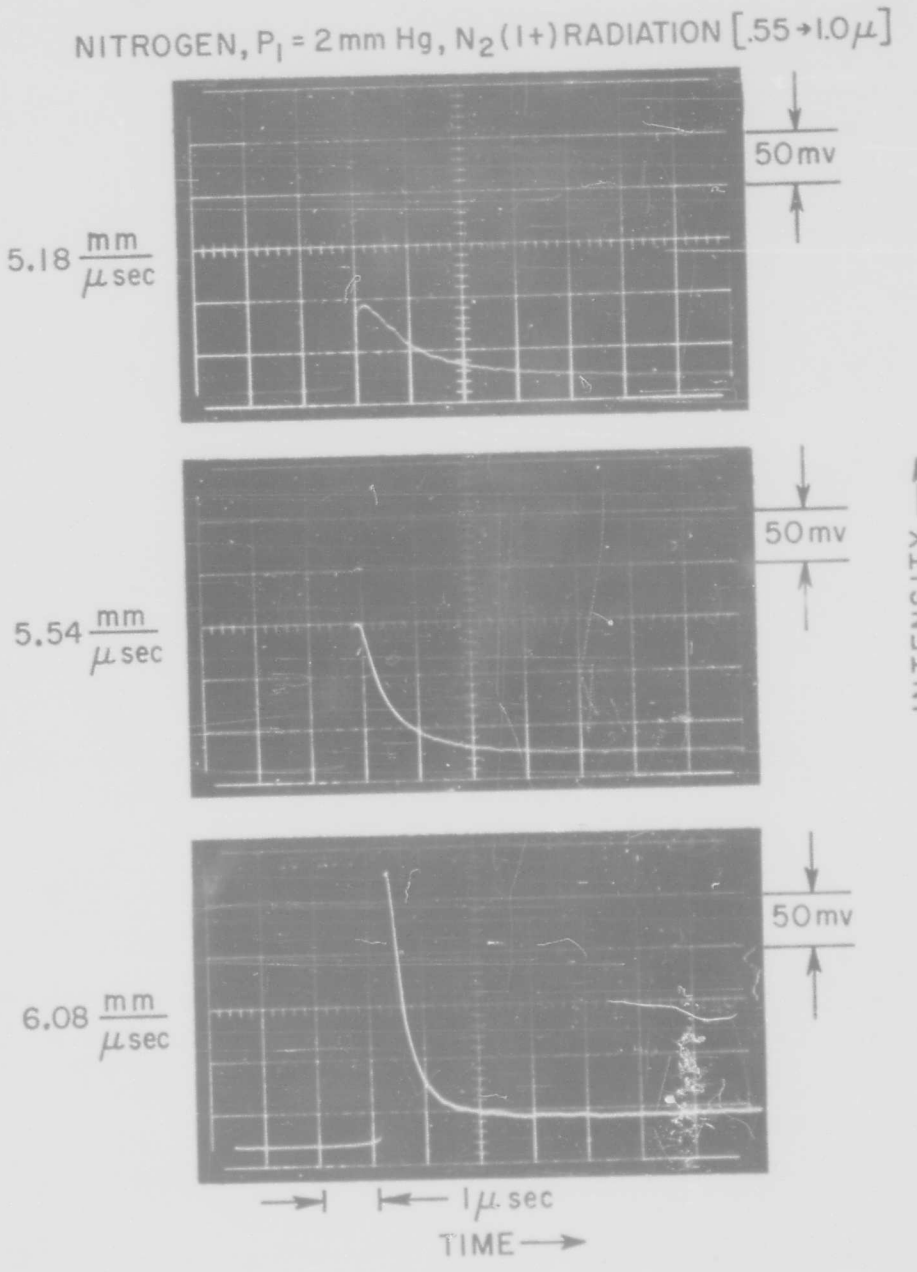

Fig. 3 Typical oscillograms of the N_2 (1+) radiation from shock waves in pure N_2 showing the radiation overshoot behind the shock front and subsequent relaxation to equilibrium for several shock speeds.

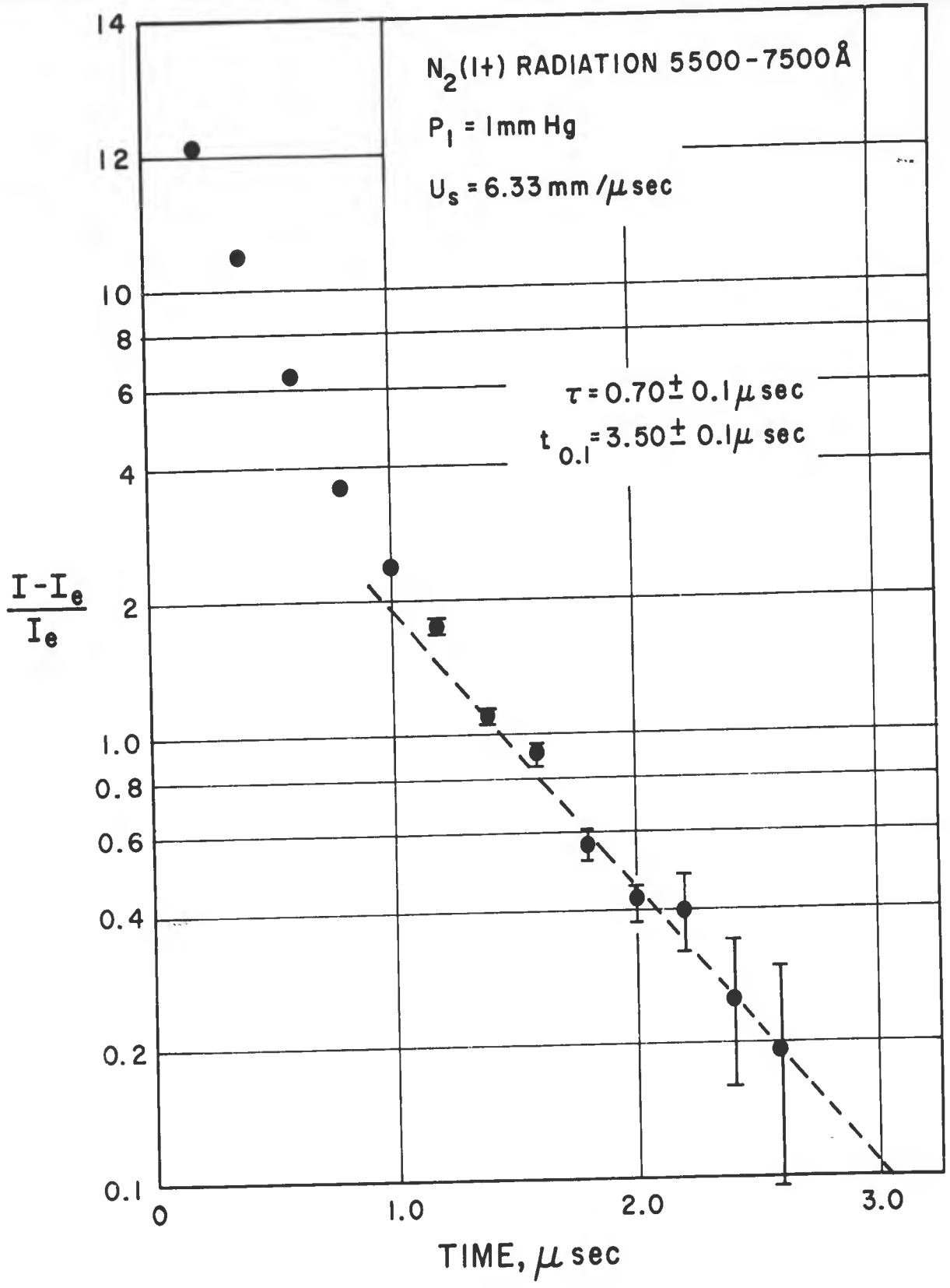

Fig. 4 Ratio of radiation overshoot to equilibrium level as a function of time for a 6.33 mm/μ sec shock in nitrogen at a P_1 of 0.1 cm Hg. The radiation decay constant, τ, is found by measuring the time required for the intensity to fall by a factor of 2.7 near the equilibrium intensity level.

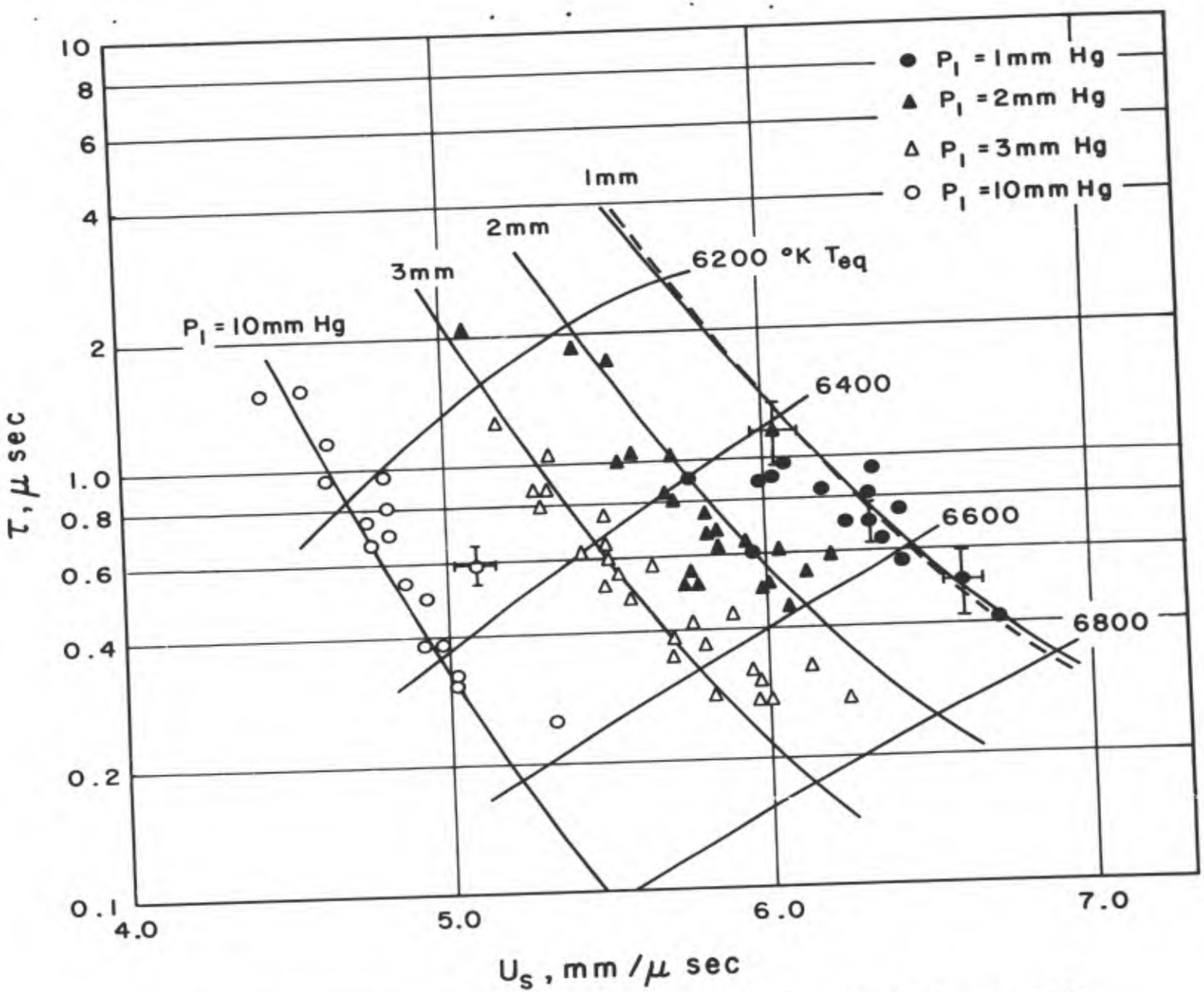

Fig. 5 Radiation decay constant, τ, versus shock speed for runs made at four different initial pressures. The superimposed grid is calculated from the recombination rates determined in Fig. 11.

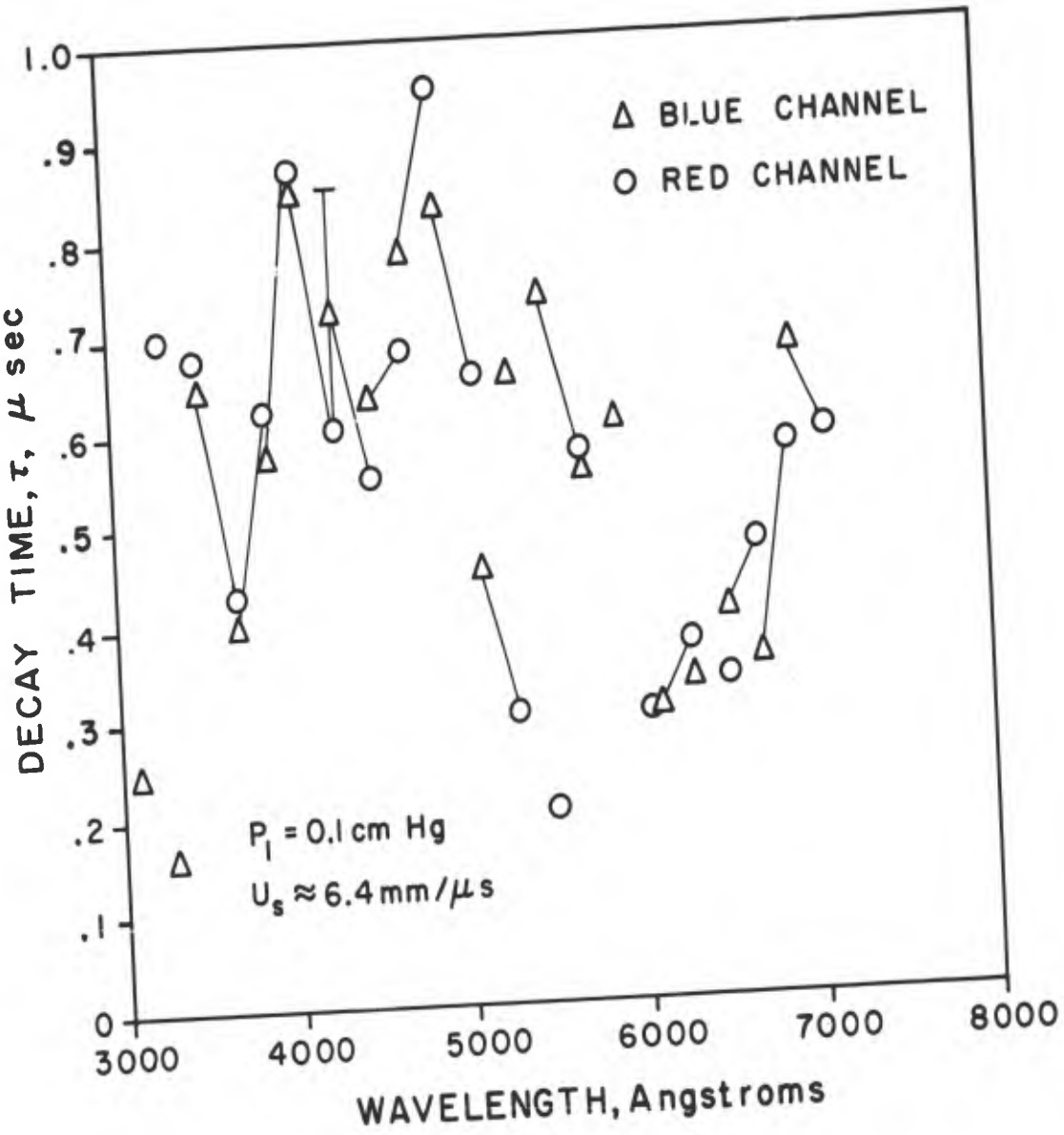

Fig. 6a Radiation exponential decay times versus wavelength for normal shocks in nitrogen (P_1 = 0.1 cm Hg).

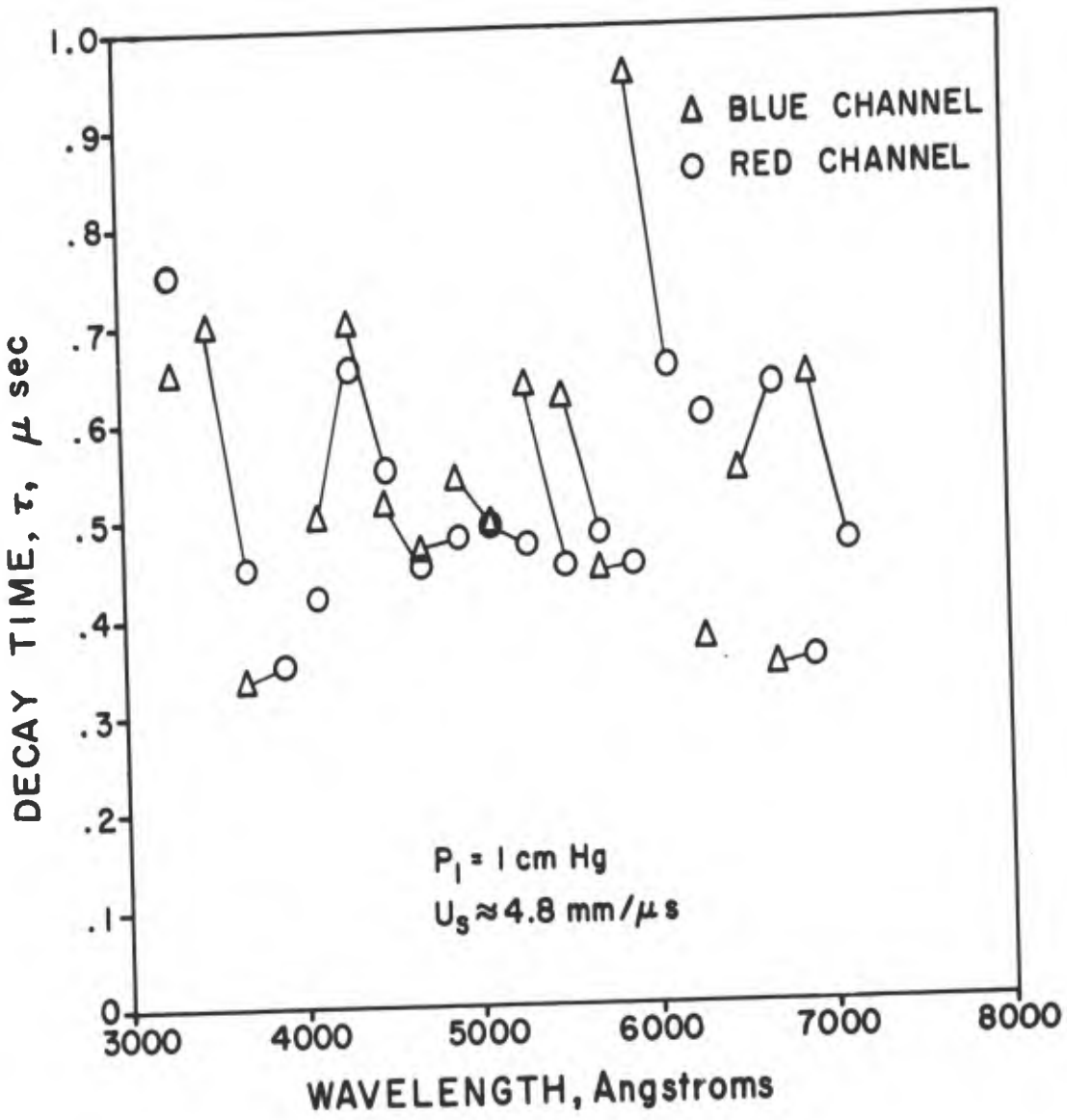

Fig. 6b Radiation exponential decay times versus wavelength for normal shocks in nitrogen (P_1 = 1.0 cm Hg).

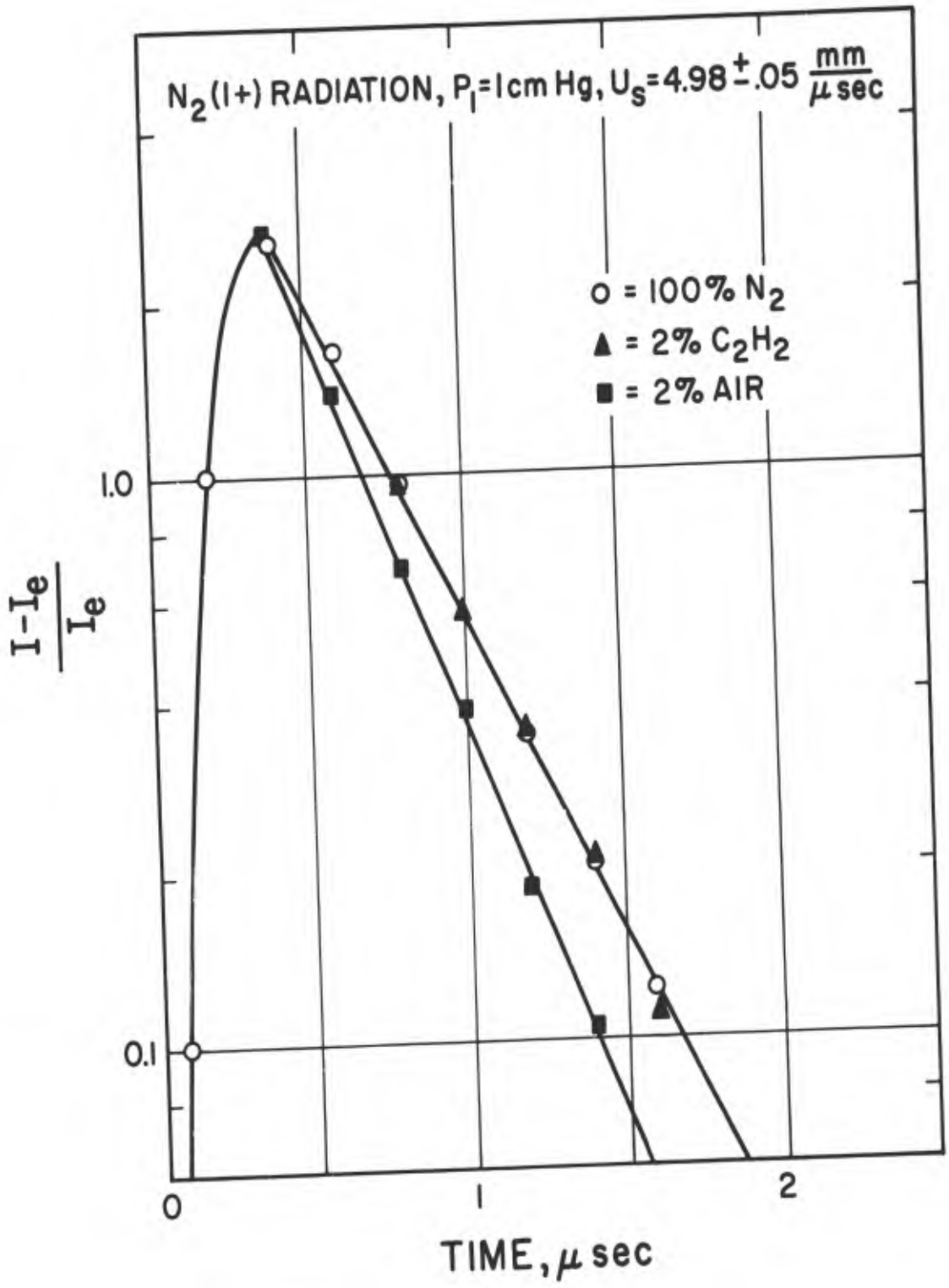

Fig. 7 Radiation profiles of N_2 (1+) radiation of contaminated runs showing how the decay time constant is relatively uneffected by air or C_2H_2 contamination.

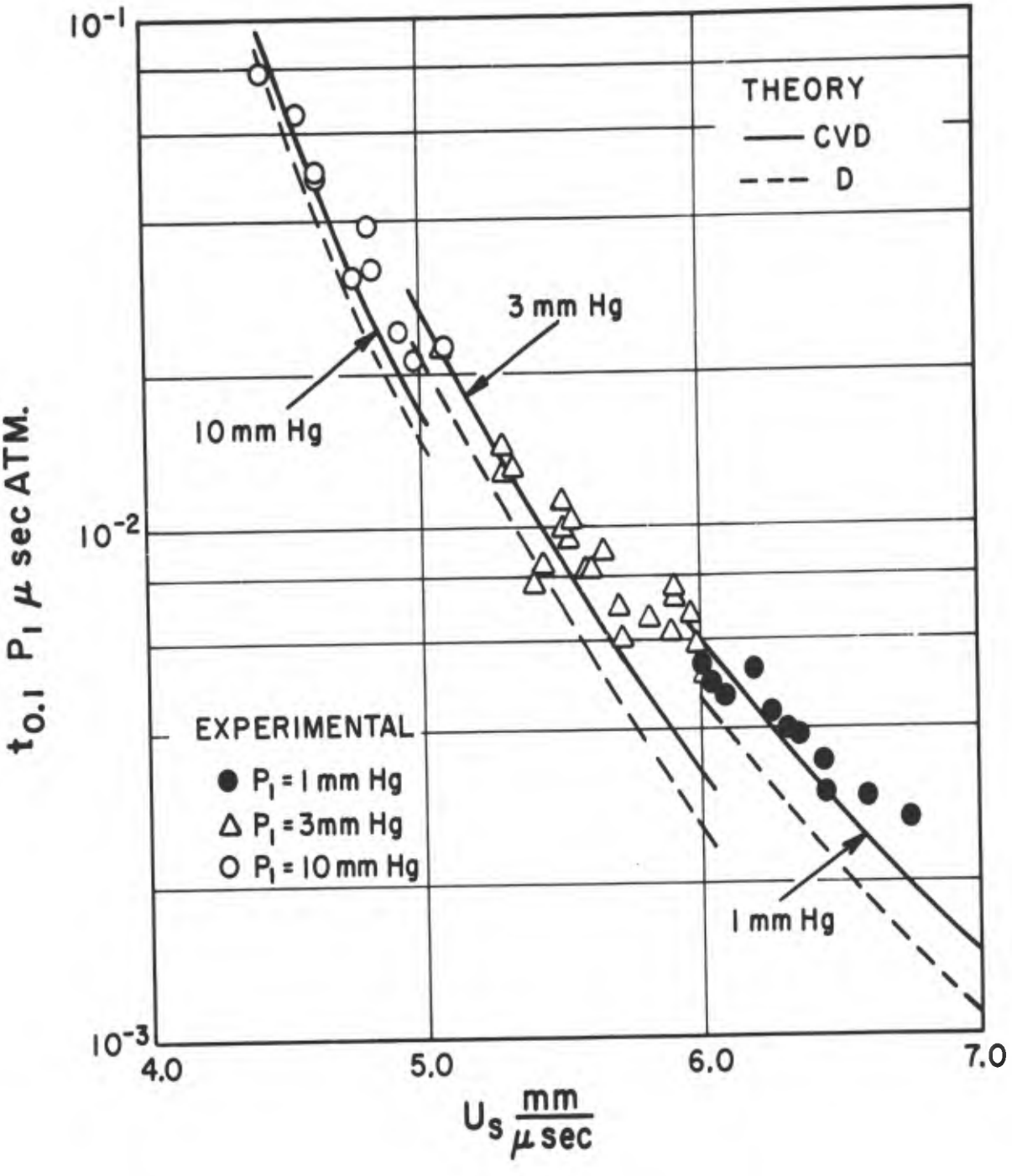

Fig. 8 Comparison of the experimentally observed times $t_{0.1}$ for relaxation of the N_2 (1+) radiation overshoot to 1.1 times its equilibrium value with theoretical estimates based on recombination rate constants in Fig. 11.

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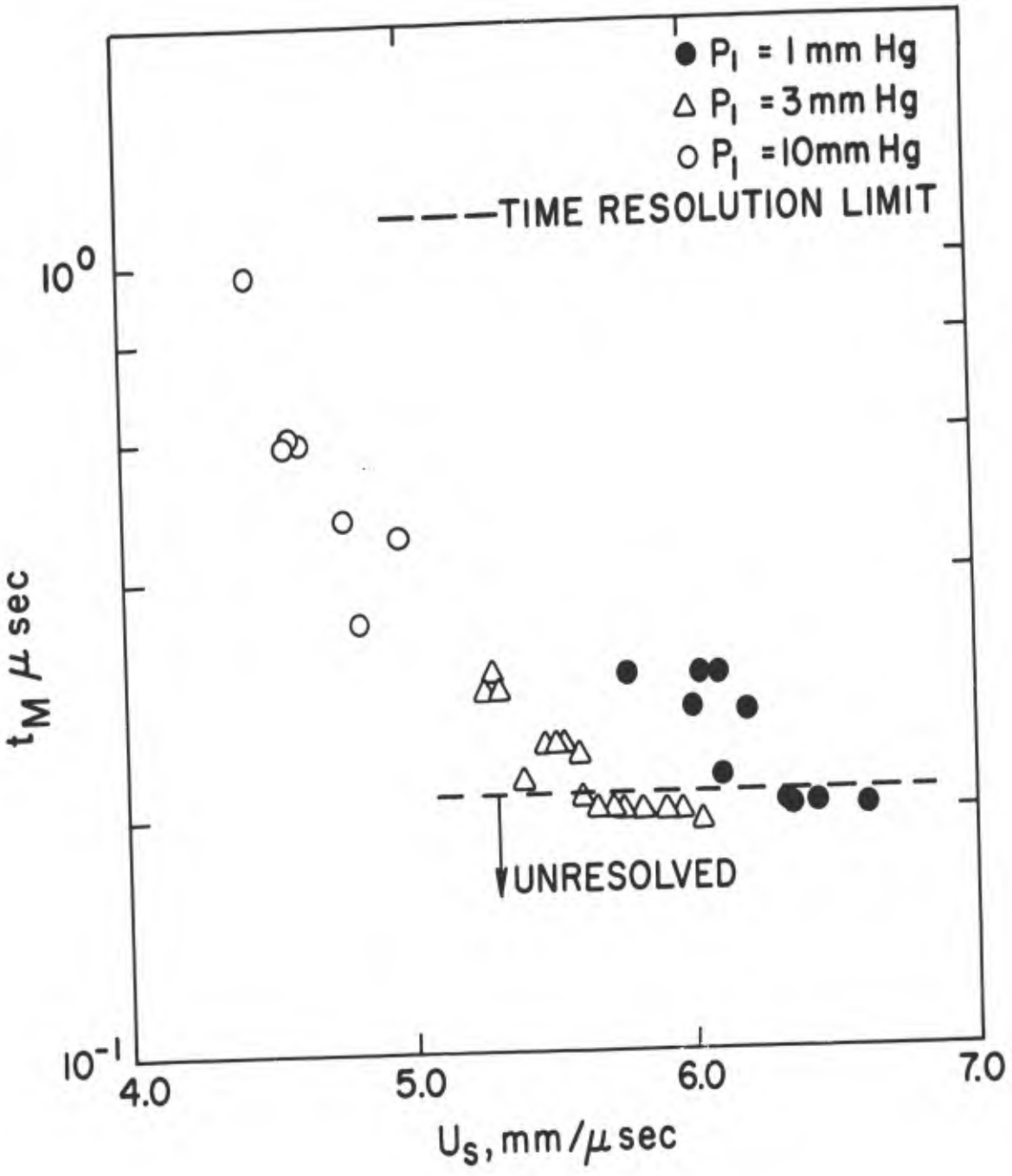

Fig. 9a Observed time of peak radiation of the N_2 (1+) radiation in nitrogen shocks versus shock speed for three different conditions of P_1.

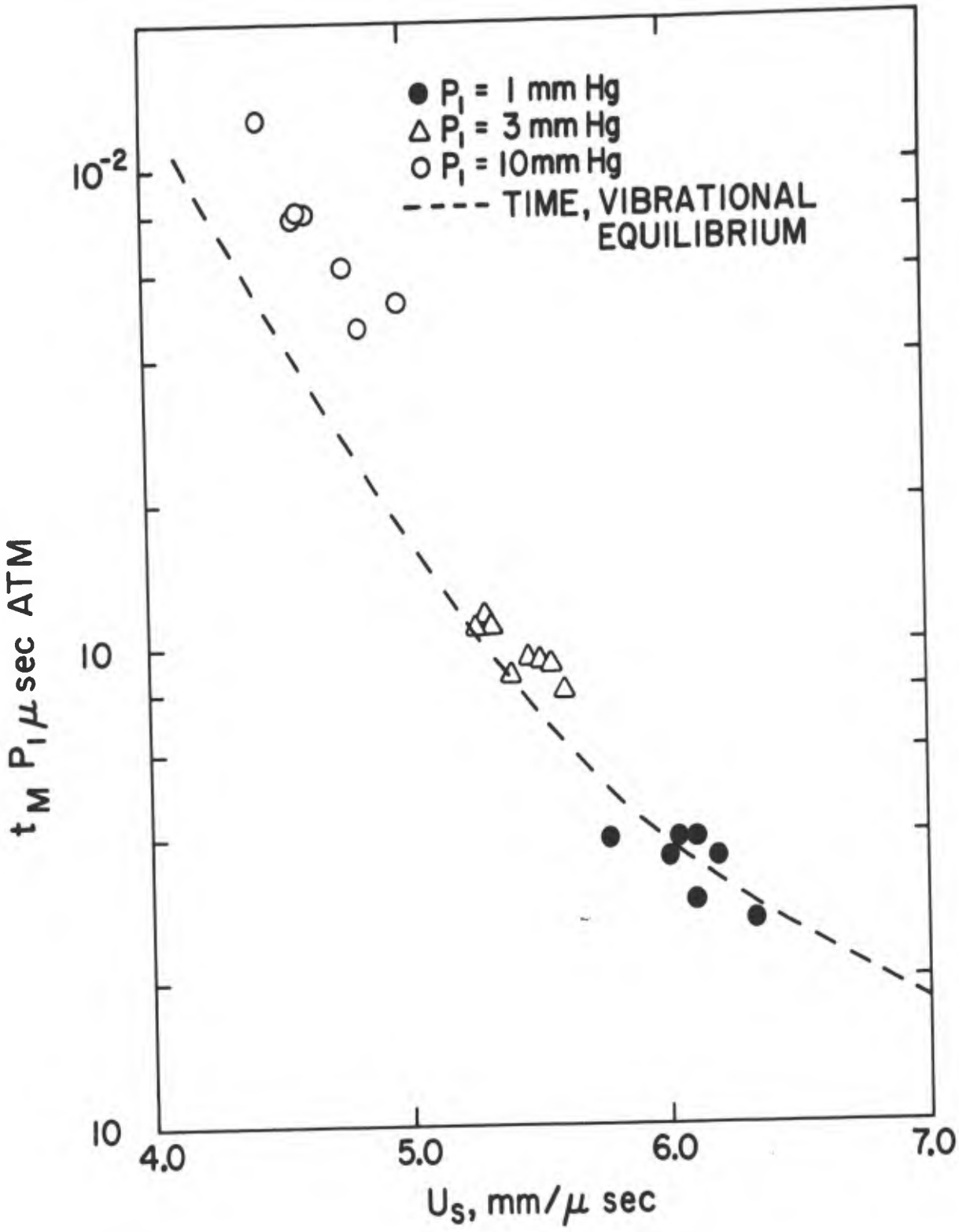

Fig. 9b Points from Figure 9a are replotted discarding points below the dashed line and using the initial pressure as a scaling factor. The time for vibrational equilibrium is also plotted.

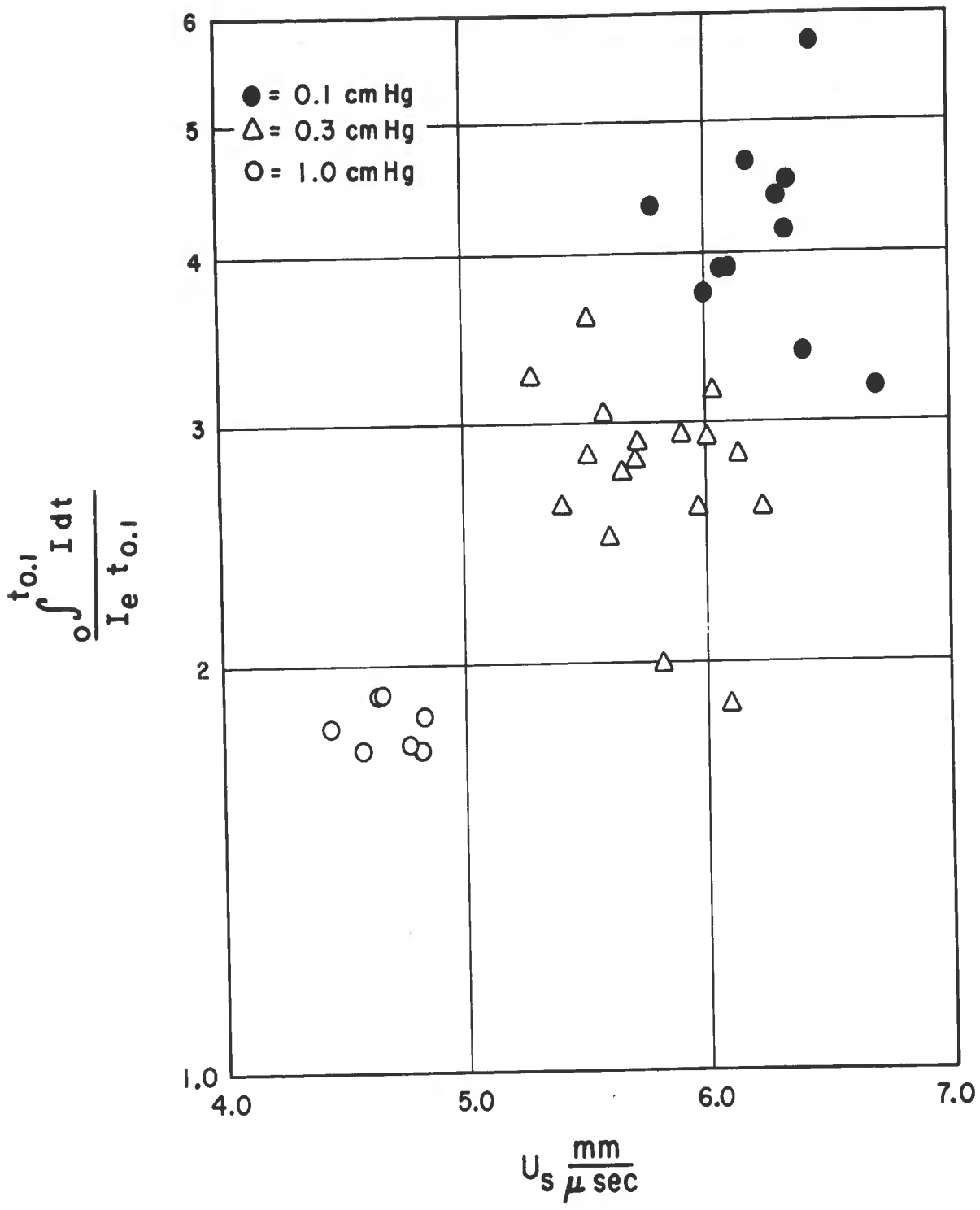

Fig. 10 Ratio of integral nonequilibrium to equilibrium radiation up to the time $t_{o.1}$ versus shock speed for three conditions of P_1.

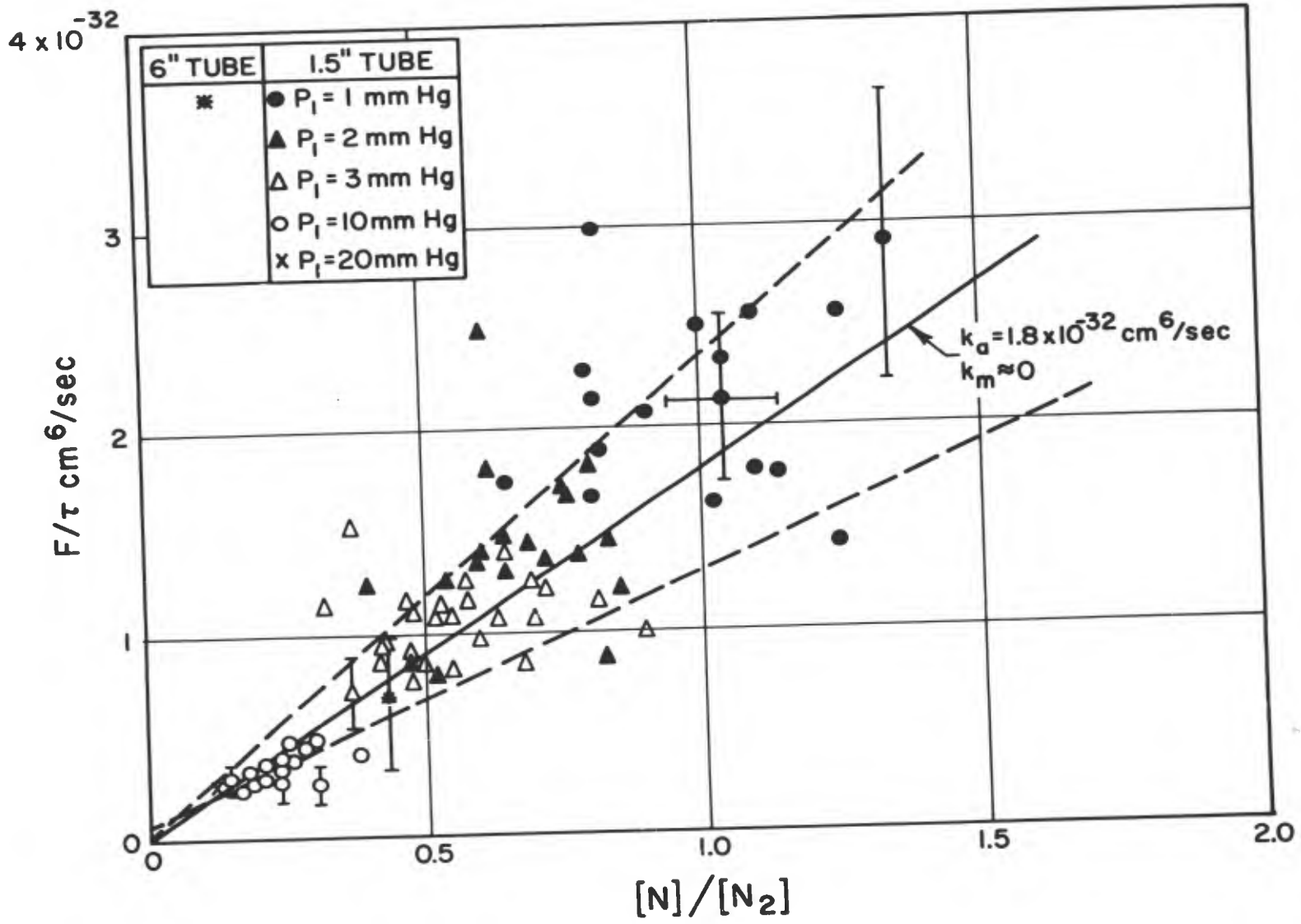

Fig. 11 F/τ vs $[N] / [N_2]$ for nitrogen at 6400°K, showing how k_{RN} (slope) and k_{RN_2} (ordinate intercept) are determined.

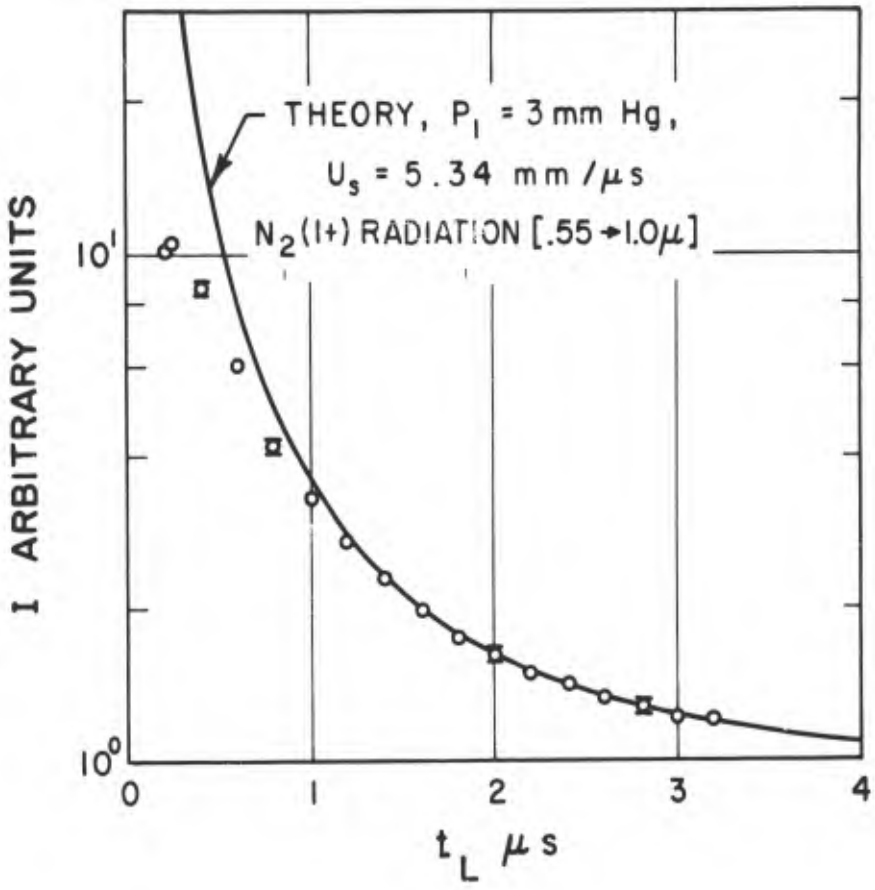

Fig. 12 Comparison of the experimentally observed N_2 (1+) radiation profile with theoretical calculations. The departure of the points from the theoretical curve at short times gives an indication of the finite time required to excite the radiating states in molecular collisions.

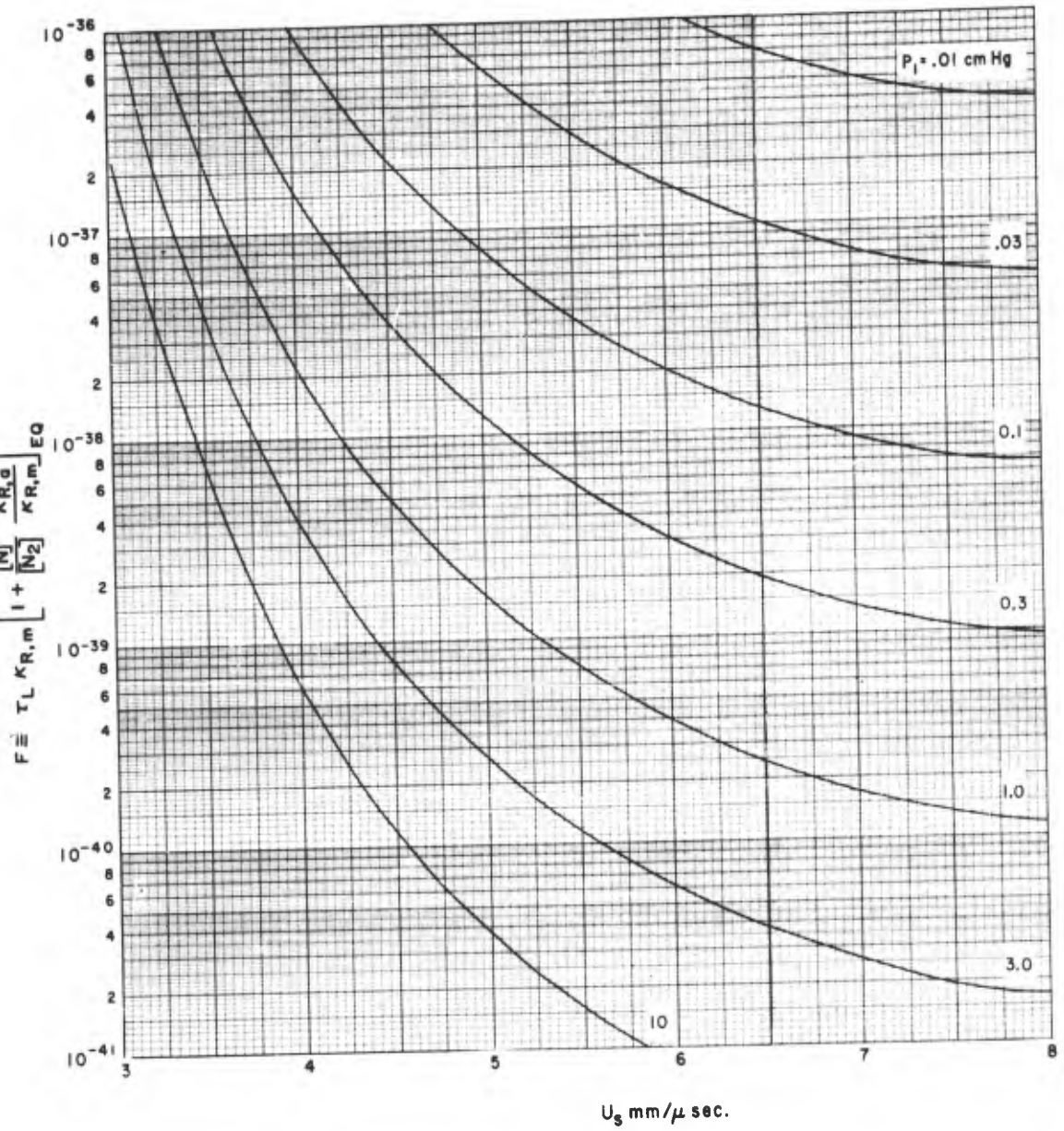

Fig. 13 Exponential decay time τ for the final approach to equilibrium behind normal shock waves in pure nitrogen. The function F is plotted against U_s for various various values of P_1 with $T_1 = 294^oK$.

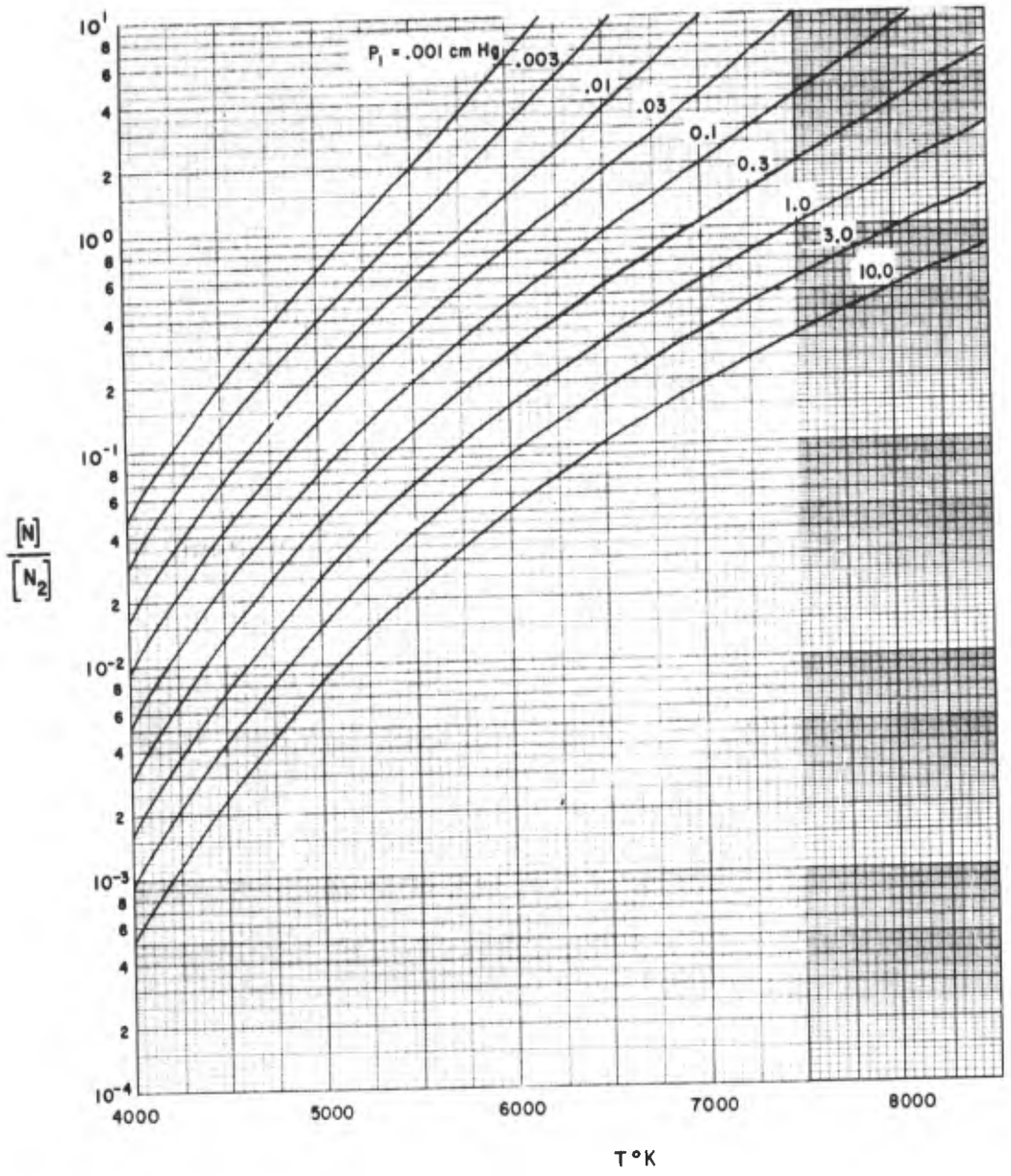

Fig. 14 Equilibrium concentration of N behind normal shock waves in pure nitrogen. The ratio $[N]/[N_2]$, which appears in F, is plotted as a function of equilibrium temperature with P_1 as a parameter, and with $T_1 = 294^{\circ}K$.

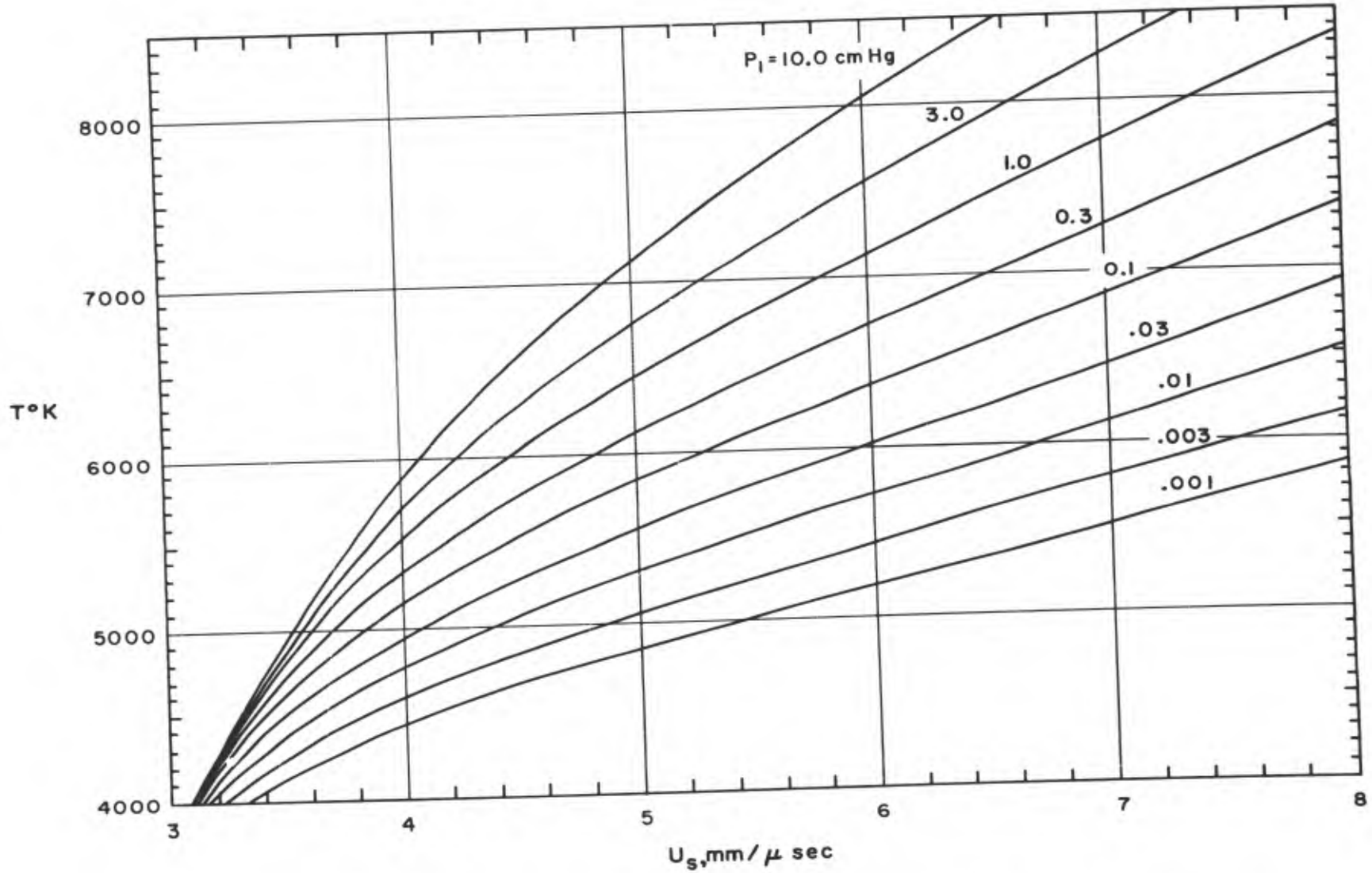

Fig. 15 Equilibrium temperature behind normal shock waves in pure nitrogen, plotted as a function of shock speed with P_1 as a parameter, and with $T_1 = 294^{\circ}K$.

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