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PROPAGATION OF SOUND IN VIBRATIONALLY EXCITED NITROGEN AND HYDROGEN GAS MIXTURES

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Measurements of the resonant reverberation of sound in a tube containing N_2/H_2, N_2/He, N_2/CH_4, and N_2/H_2O mixtures have shown an amplification of the sound following a rapid excitation of the gas by an electric discharge. [F. Douglas Shields and L. Dwynn Lafleur, J. Acoust. Soc. Am. 83, 2186 (1988)]. This effect has been named SACER (Sound Amplification from Controlled Excitation Reactions). This paper reports similar measurements in N_2/CO and in $CO/H_2/He$ mixtures. It has been possible in the past to determine vibrational relaxation times and relaxation times for the conduction of translational and vibrational energy to the tube wall from the changes in the translational temperature in the gas following the electric discharge. In the work reported here, these rates have been confirmed by direct measurement of the decay times of the CO infrared emission.

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ABSTRACT

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Measurements of the resonant reverberation of sound in a tube containing N_2/H_2, N_2/He, N_2/CH_4, and N_2/H_2O mixtures have shown an amplification of the sound following a rapid excitation of the gas by an electric discharge [F. Douglas Shields and L. Dwynn Lafleur, J. Acoust. Soc. Am. **83**, 2186 (1988)]. This effect has been named SACER (Sound Amplification from Controlled Excitation Reactions). This paper reports similar measurements in N_2/CO and in $CO/H_2/He$ mixtures. It has been possible in the past to determine vibrational relaxation times and relaxation times for *the conduction of translational and vibrational energy to the tube wall from the changes in* the translational temperature in the gas following the electric discharge. In the work reported here, these rates have been confirmed by direct measurement of the decay times of the CO infrared emission.

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Chapter I: Introduction

Excitation of a single vibrational mode of a gas often results in a rapid distribution of the energy pumped into this mode into the other vibrational modes of the gas, thus quickly producing a Boltzmann distribution of energy, allowing for the assignment of a vibrational temperature to the gas. However, distribution of this energy into the translational motion of the gas molecules may take much longer, allowing for a metastable state to be developed in which the vibrational temperature of the gas can be thousands of degrees greater than its translational temperature.

The peculiar nature of this metastable state can in principle be used to produce sound amplification. The pressure-dependence of the vibration-to-translation (vt) relaxation rate may lead, under appropriate conditions, to a selective dumping of vibrational energy into the compressional parts of a sound wave propagating through the excited gas, producing a sound amplification. This mechanism has been called SACER (Sound Amplification from Controlled Excitation Reactions) by Bauer and Bass. [1] The nature of this phenomenon was further investigated by Shields. [2]

Attempts to observe SACER have been made by pumping the vibrational states chemically [3] or

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[1] H.J. Bauer and H.E. Bass, Phys. Fluids **16**, 988 (1973).

[2] F.D. Shields, J. Acoust. Soc. Am. **76**, 1749-54 (1984).

[3] R.M. Detsch and H.E. Bass, J. Acoust. Soc. Am. **77**, 512 (1985).

optically. [4] However, these pumping techniques also add energy preferentially to the compressional part of the sound wave, making it difficult to separate the effect of the pumping from that of SACER.

In this thesis, an attempt was made to observe SACER under conditions where the vibrational modes have been pumped by an electric discharge. This technique was recently used to measure sound propagation in N_2/H_2 mixtures [5] and in N_2/He, N_2/CH_4 and N_2/H_2O mixtures. [6] These observations have shown acoustical gains much larger than those predicted by theory.

In the past the vibrational relaxation times and the relaxation times for conduction of translational and vibrational energy to the tube wall were inferred from observed changes in the translational temperature in the gas following the electric discharge. However, the vibrational temperatures of the gases under study were never directly observed. In the present experiment a small amount of infrared-active CO was added to the gas under study to act as a trace of the vibrational energy, allowing for measurement of this energy by direct observation of the infrared emission of the gas.

This paper will attempt to verify the wall de-excitation model used by Shields and Lafleur in the papers mentioned above, and also attempt to apply the techniques thereby developed to the measurement of vibrational relaxation in a H_2/He system, whose interest lies principally in the unique vibrational coupling between H_2 and CO (see Section IV.B).

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[4] E.P. DePlomb, Phys. Fluids **14**, 488 (1971).

[5] F.D. Shields, J. Acoust. Soc. Am. **81**, 87 (1987).

[6] F.D. Shields and L.D. Lafleur, J. Acoust. Soc. Am. **83**, 2186 (1988).

Chapter II: Experimental Procedure

The apparatus used in performing this experiment is outlined in Figure II.1. The reader will note that there are five principle experimental sections:

- The discharge tube
- The firing circuit
- The acoustic circuit (containing the microphone and filter)
- The infrared detection circuit, and
- The data analysis center

These sections will be discussed in detail below, as well as the manner in which they were used to achieve our result.

II.A The Discharge Tube

The discharge tube is a glass tube, 1.27 cm in radius and about a meter long, with a movable electrode at one end and a grounded screen attached to a brass chamber near the other. The

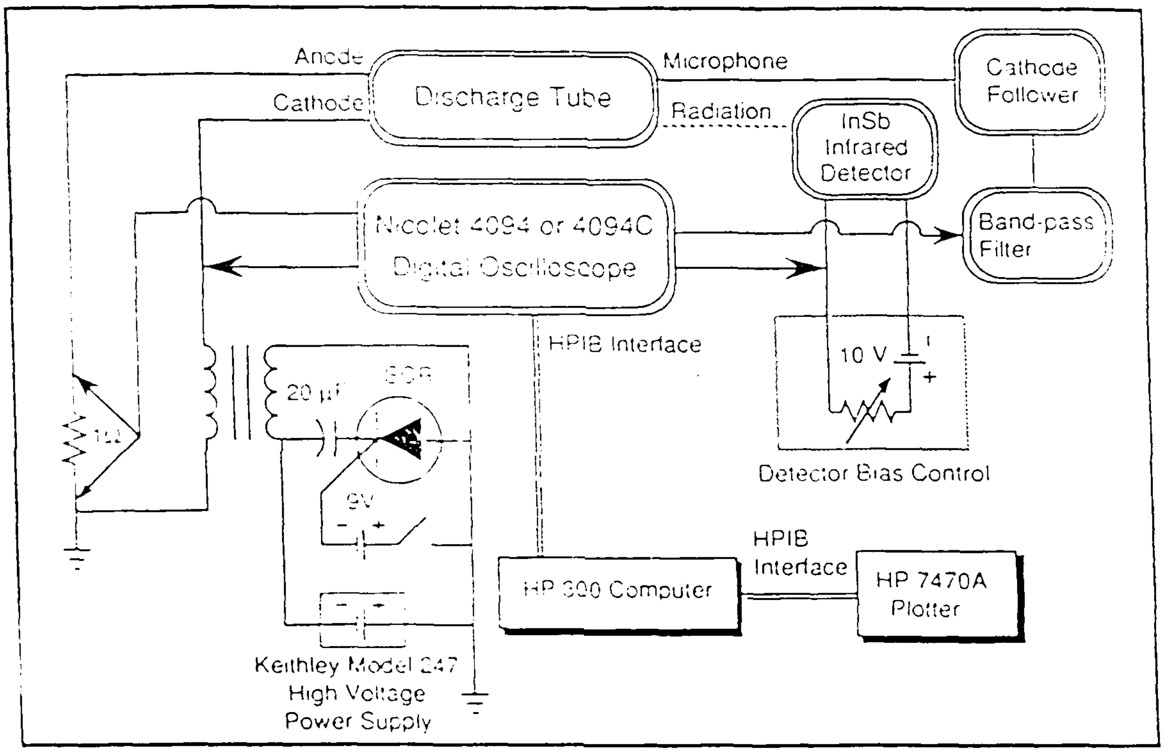

Figure II.1: Experimental Apparatus

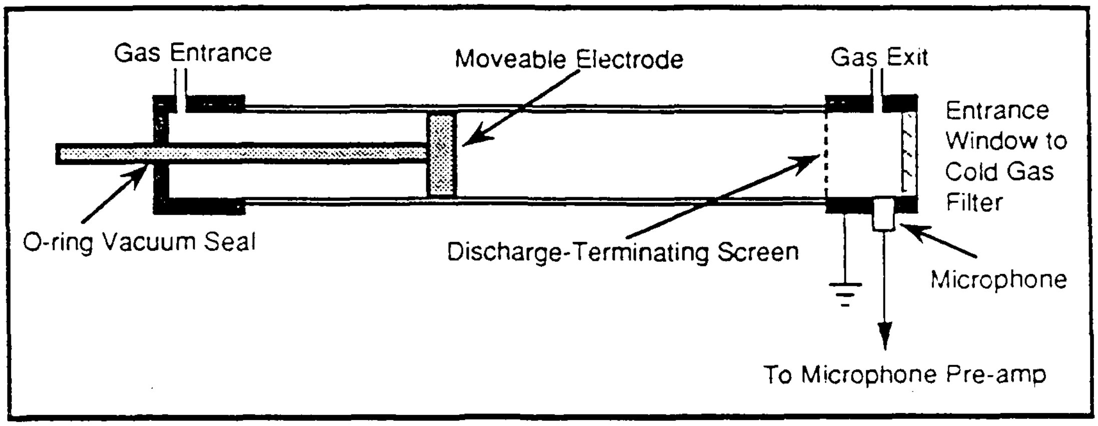

Figure II.2: The Discharge Tube

electrode is a steel slug at the end of a stainless steel rod passing through an O-ring seal at the end of the tube. The brass chamber extends from the grounded screen to the entrance window of the cold gas filter (discussed in section II.D). The window and the movable electrode form acoustic mirrors at the ends of the tube. Thus, the effective length of the tube could be changed.

II.B The Firing Circuit

The circuit used to produce the electric discharge is similar to that of Loy and Roland.[7] A Keithley Model 247 High Voltage Power Supply was used to charge a 10 μF or 20 μF capacitor. Triggering a silicon controlled rectifier (IR 250RA160) by means of a standard 9 volt battery caused these capacitors to discharge through the primary of a Delco D530 automobile ignition transformer. The transformer was immersed in mineral oil to prevent arcing. The voltage across the tube was

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[7] M.M.T. Loy and P.A. Roland, Rev.Sci.Instrum. 48, 554 (1977).

measured with a Tektronix P6015 high voltage probe connected to a voltage divider. The signal from the probe was then sent into one plug-in of a Nicolet 4094 or 4094C digital oscilloscope. Also fed into the oscilloscope was the voltage across a 1 Ω resistor in series with the discharge tube in order to measure the current through the tube. These values could then be multiplied together to determine the power pumped into the tube.

II.C The Acoustic Circuit

A sound pulse is produced when the gas heated by the electric discharge expands into unheated gas contained in the 4 cm brass end section bounded by the discharge termination screen and the cold gas filter entrance window. Mounted in the side of this end section is a standard Brüel and Kjær 1/2" microphone, whose output was fed through a Brüel and Kjær 2613 cathode follower and a Rockland 852 48 dB/octave filter into another plug-in of the Nicolet scope. No amplification of the .1-.7 V (unfiltered) microphone signal was performed.

II.D The Infrared Detection Circuit

The infrared detection equipment consisted of a cold gas filter, an InSb nitrogen-cooled detector and a Hewlett-Packard 6218A DC power supply. The power supply was used to reverse bias the detector to eliminate non-varying background signals.

The cold gas filter (see Figure II.3) is a brass cell 7.91 cm long which can be filled or evacuated through a gas intake line. It is terminated on one end with a CaF_2 window, and on the other by a CaF_2 lens (focal length: 75mm). The filter is attached to the discharge tube with the window side

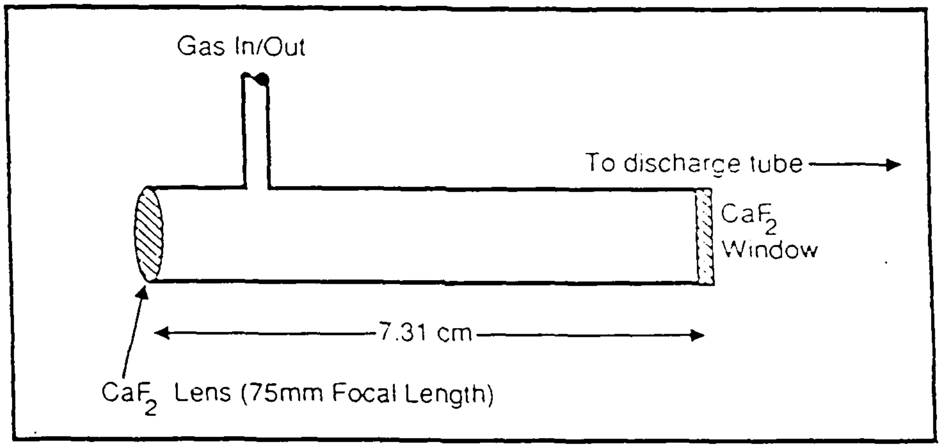

Figure II.3: The Cold Gas Filter

facing the discharge. Infrared light leaving the lens side is reflected by a gold mirror onto the InSb detector.

When the cell is filled with an atmosphere of room-temperature CO, it serves as a very effective filter of the infrared light produced by a 1 → 0 vibrational transition of the CO gas contained in the discharge tube. Thus, by observing a discharge with the CGF filled and with it evacuated, and assuming a Boltzmann distribution of vibrational states, one can determine the vibrational temperature of the gas. The details will be discussed below.

II.E The Data Analysis Center

The data analysis was conducted with a Hewlett-Packard 300-series computer with programs written in HP Basic 4.0. The computer was connected to the Nicolet scope by means of an HPIB (IEEE 488) parallel interface which allowed for the data collected by the scope to be downloaded into the computer. Also connected to the HPIB was a Hewlett-Packard 7470A plotter, a ThinkJet printer and a 9153 mass storage unit (containing a hard disk and one 3-1/2" floppy drive).

The Nicolet 4094 was configured with 4562 and 4851 plug-ins and an XF-44/1 5-1/4" floppy drive. The 4094C was configured with 4570 and 4180 plug-ins and an XF-44/2 dual 5-1/4" floppy drive. The plug-ins act as separate information storage devices for the scope, each with two channels and a time base independent of that of the other.

Chapter III: Theoretical Predictions

The experimental system has six characteristic times:

- The sound period τ;
- The vibrational relaxation time τ_v;
- The translational wall de-excitation time τ_{tc};
- The vibrational wall de-excitation time τ_{vc};
- The time required for the vibrating gas to achieve a Boltzmann distribution among its vibrational modes, τ_B;
- The vibration-vibration coupling time between the gas under study and the carbon monoxide trace τ_{CO}.

The translational and vibrational wall de-excitation times are the thermal diffusion times for conducting translational or vibrational energy to the tube walls. The sound period τ is controlled by varying the tube length.

III.A The Time-Dependence of the Specific Heat

The rate of change of vibrational energy at some vibrational temperature T_v is seen to be proportional to the difference between the current vibrational energy $E_v(T_v)$ and the vibrational energy when the system is in equilibrium at a translational temperature T: [8]

$$\dot{E}_v(T_v) = -\frac{E_v(T_v) - E_v(T)}{\tau_v}, \tag{III.1}$$

where τ_v, known as the relaxation time, is a constant of proportionality. Expressing τ_v in terms of transition rates $k_{10} = [p\tau_v\chi(T)]^{-1}$, where $\chi(T) = 1 - e^{\hbar\omega/k_BT} = 1 - e^{\Theta/T}$ and p is the pressure gives

$$\dot{E}_v(T_v) = -pk_{10}\chi(T)[E_v(T_v) - E_v(T)].$$

The quantity k_{10} is the frequency of collisions of one excited molecule in an atmosphere of the gas responsible for de-excitation, and ω is the fundamental vibrational frequency of the relaxing mode in radians per second.

The energy at a given temperature is given by

$$E(T) = Nk_B\Theta e^{-\Theta/T}/\chi(T),$$

where N is the number of excited gas molecules and k_B is the Boltzmann constant.

The change in energy due to a sound wave propagating through a slowly relaxing gas is then obtained by differentiating Equation III.1:

$$\Delta\dot{E}_v = \dot{E}_v^0\left[\left(\frac{1}{p}\frac{dp}{dT} + \frac{d(\ln k_{10})}{dT} - \frac{\Theta e^{\Theta/T}}{T^2\chi(T)}\right)\Delta T - \frac{\Delta E_v(T_v) - \Delta E_v(T)}{\tau_v\dot{E}_v^0}\right],$$

where it has been assumed that the transition rate depends only on translational temperature. Introducing a harmonic time dependence and using Equation III.1, as well as introducing specific

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[8] Ref. 2.

heats such that $\Delta E_v(T_v) = C_v(T_v)\Delta T_v$ and $\Delta E_v(T) = C_v(T)\Delta T$ leads to a heat capacity at constant volume

$$C_v = C_\infty + C_{\mathrm{vib}}\Delta T_v/\Delta T = C_\infty + \frac{C_{\mathrm{vib}}}{1 + i\omega\tau_v},$$

where C_∞ is the time-independent part of the specific heat (in our case due to translational and rotational modes) and C_{vib} is the time-dependent (vibrational) part of the specific heat given by

$$C_{\mathrm{vib}} = -(E_v(T_v) - E_v(T))\left[\frac{1}{T} + \frac{d(\ln k_{10})}{dT} - \frac{\Theta e^{-\Theta/T}}{T^2\chi(T)}\right] + C_{\mathrm{vib}}(T).$$

In the above calculations, the value of $1/T$ comes from assuming an ideal gas in determining $(1/p)(dp/dT)$. The value of $C_{\mathrm{vib}}(T)$ is given by the Planck-Einstein equation

$$C_{\mathrm{vib}}(T) = \left(\frac{\Theta}{T}\right)^2 \frac{e^{\Theta/T}}{\left(e^{\Theta/T} - 1\right)^2}.$$

Since the $1/T$ term does not appear in the heat capacity at constant pressure, otherwise given by $C_p = C_v + R$, we have

$$C_p = C_v + R + \frac{(E_v(T_v) - E_v(T))}{T(1 + i\omega\tau_v)}.$$

Hence, we have determined time-dependent and complex specific heats with which to describe the systems under study. It still remains to calculate the relaxation times: τ_v, τ_{tc} and τ_{vc}.

III.B Wall De-excitation Times

Margottin-Maclou, Doyennette, and Henry [9] give the wall de-excitation rate for a gas in a cylinder whose radius r is much less than its length.

$$\tau_{tc} = \frac{r^2\rho C_v}{K(\pi\beta_{mn})^2}, \tag{III.2}$$

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[9] M. Margottin-Maclou, L. Doyennete and L. Henry, Appl. Opt. 10, 1768 (1971).

where ρ is the gas density, K is the thermal conductivity of the gas, and $\pi\beta_{mn}$ is the nth zero of the mth-order Bessel function, which under the assumption of a temperature profile characterized by a single zero-order Bessel function, takes on a value of 2.4. Using the Eucken correction [10]

$$\frac{K}{C_v\eta} = \frac{1}{4}(9\gamma - 5)$$

produces

$$\tau_{tc} = \frac{4r^2\rho}{(2.4)^2(9\gamma - 5)\eta},$$

where η is the gas viscosity, determined by the procedure found in Hirschfelder, Curtiss and Bird, [11] and γ is the ratio of the specific heats.

Shields and Lafleur [12] have developed a relationship between τ_{vc} and τ_{tc}. The energy flux vector for the mixture may be written [13]

$$\begin{aligned} \mathbf{q} &= -\left[\frac{15K\eta}{4m} + \rho D \sum_j \hat{U}_j^{(\text{int})} \cdot \frac{d}{dT}\left(\frac{n_j}{n}\right)\right] \frac{\partial T}{\partial \mathbf{r}} \\ &= -K\frac{\partial T}{\partial \mathbf{r}} \\ &= -(K_{\text{tr}} + K_{\text{vib}})\frac{\partial T}{\partial \mathbf{r}}, \end{aligned}$$

where $\mathbf{q}$ is the energy flux vector for the mixture, D is the coefficient of self-diffusion, $\hat{U}_j^{(\text{int})}$ is the energy per unit mass in the internal degrees of freedom of the molecule in state j, n_j/n is the fraction of molecules in quantum state j, T is, of course, temperature, and K_{tr} and K_{vib} are the translational/rotational and vibrational parts of the thermal conductivity. Noting, as Hirschfelder,

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[10] J.D. Hirschfelder, C.F. Curtiss and R.B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1967), pp. 500-1.

[11] Ref. 10, pp. 528-31.

[12] Ref. 5.

[13] Ref. 10, pp. 500-1.

et al do, that

$$C_v^{(\text{int})} = C_{\text{vib}} = \sum_j \hat{U}_j^{(\text{int})} \frac{d}{dT}\left(\frac{n_j}{n}\right)$$

gives the following equations:

$$\begin{aligned} \frac{K_{\text{tr}}}{C_\infty} &= \eta\left(1 + \frac{9R}{4C_\infty}\right), \\ \frac{K_{\text{vib}}}{C_{\text{vib}}} &= \eta, \end{aligned}$$

where it is assumed that $\rho D/\eta = 1$ and where R is the gas constant. Therefore,

$$\frac{\tau_{vc}}{\tau_{tc}} = \left(\frac{C_{\text{vib}}}{K_{\text{vib}}}\right)\left(\frac{K_{\text{tr}}}{C_\infty}\right) = 1 + 2.25\frac{R}{C_\infty}. \qquad \text{(III.3)}$$

This equation has been shown by Shields and Lafleur to produce values which are near to those determined from previous measurements. It was also pointed out that while the Eucken correction does not strictly hold for gas mixtures, its accuracy in predicting the above ratio should be good.

III.C Vibrational and Translational Temperatures

While a rigorous analysis of this far-from-equilibrium system would be beyond the scope of this paper, a simple model proposed by Shields [14] has proven effective in predicting the translational temperature of a wide range of pressures, frequencies, and gas compositions. Testing the vibrational temperatures predicted by this model has been a chief goal in the present research.

In Shields's model, the translational and vibrational temperatures are assumed to be constant throughout the tube, variations coming only from the acoustical signal. The electrical discharge is assumed to instantaneously raise the gas's vibrational temperature by $(\Delta T_v)_0$ and the translational

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[14] Ref. 5.

temperature by $(\Delta T)_0$. The carbon monoxide and the gas under study are assumed to be in vibrational and translational equilibrium, and the vibrational energy is assumed to relax to the wall both directly and through translational energy.

It is noted that the vibrational specific heat C_{vib} and the various relaxation times τ_v,τ_{vc}, and τ_{tc} depend upon temperature and therefore vary with time. However, at each instant, the system obeys the coupled equations

$$\begin{aligned} C_\infty \frac{d}{dt}(T - T_w) &= \frac{C_{\mathrm{vib}}(T_v - T)}{\tau_v} - \frac{C_\infty (T - T_w)}{\tau_{tc}} \\ C_{\mathrm{vib}} \frac{d}{dt}(T_v - T_w) &= \frac{-C_{\mathrm{vib}}(T_v - T)}{\tau_v} - \frac{C_{\mathrm{vib}}(T_v - T_w)}{\tau_{vc}}, \end{aligned}$$

where T_w is the temperature of the tube walls. For all diatomic gasses under study, C_∞ was assumed to be 5/2 times the gas constant, and for He, C_∞ was assumed equal to 3/2 times the gas constant. The quantity T_w was assumed to be room temperature.

Defining $\Delta T = T - T_w$ and $\Delta T_v = T_v - T_w$ gives

$$C_\infty \frac{d}{dt}\Delta T = \frac{C_{\mathrm{vib}}}{\tau_v}(\Delta T_v - \Delta T) - \frac{C_\infty}{\tau_{tc}}\Delta T \qquad \text{(III.4)}$$

$$C_{\mathrm{vib}} \frac{d}{dt}\Delta T_v = \frac{C_{\mathrm{vib}}}{\tau_v}(\Delta T - \Delta T_v) - \frac{C_{\mathrm{vib}}}{\tau_{vc}}\Delta T_v . \qquad \text{(III.5)}$$

Taking the time derivative of equation III.4 gives

$$\frac{d^2}{dt^2}\Delta T + \left[\frac{C_{\mathrm{vib}}}{C_\infty \tau_v} + \frac{1}{\tau_{tc}}\right] \frac{d}{dt}\Delta T - \frac{C_{\mathrm{vib}}}{C_\infty \tau_v}\frac{d}{dt}\Delta T_v = 0.$$

Substituting in equation III.5 gives

$$\frac{d^2}{dt^2}\Delta T + \left[\frac{C_{\mathrm{vib}}}{C_\infty \tau_v} + \frac{1}{\tau_{tc}}\right] \frac{d}{dt}\Delta T - \frac{C_{\mathrm{vib}}}{C_\infty \tau_v^2}\Delta T + \left(\frac{1}{\tau_v} + \frac{1}{\tau_{vc}}\right)\frac{C_{\mathrm{vib}}\Delta T_v}{C_\infty \tau_v} = 0,$$

and from equation III.4

$$\frac{C_{\mathrm{vib}}\Delta T_v}{\tau_v} = C_\infty \frac{d}{dt}\Delta T + \left(\frac{C_{\mathrm{vib}}}{\tau_v} + \frac{C_\infty}{\tau_{tc}}\right);$$

so that

$$\frac{d^2}{dt^2}\Delta T + b\frac{d}{dt}\Delta T + c\Delta T = 0,$$

where

$$\begin{aligned} b &= \frac{C_{\text{vib}}}{C_\infty \tau_v} + \frac{1}{\tau_v} + \frac{1}{\tau_{tc}} + \frac{1}{\tau_{vc}} \\ c &= \left(\frac{1}{\tau_v} + \frac{1}{\tau_{vc}}\right)\left(\frac{C_{\text{vib}}}{C_\infty \tau_v} + \frac{1}{\tau_{tc}}\right) - \frac{C_{\text{vib}}}{C_\infty \tau_v^2}. \end{aligned}$$

The solutions to this equation have the form

$$\begin{aligned} \Delta T &= Ae^{-\lambda_1 t} + Be^{-\lambda_2 t} \\ \Delta T_v &= Ce^{-\lambda_1 t} + De^{-\lambda_2 t}, \end{aligned}$$

where the time constants may be expressed as

$$\begin{aligned} \lambda_1 &= \frac{1}{2}\left(b - \sqrt{b^2 - 4c}\right) \\ \lambda_2 &= \frac{1}{2}\left(b + \sqrt{b^2 - 4c}\right). \end{aligned}$$

Solving for the ratios C/A and D/B gives

$$\frac{C}{A} = \frac{C_\infty \tau_v}{C_{\text{vib}}}\left(\frac{C_v}{C_\infty \tau_v} + \frac{1}{\tau_{tc}} - \lambda_1\right)$$

$$\frac{D}{B} = \frac{C_\infty \tau_v}{C_{\text{vib}}}\left(\frac{C_{\text{vib}}}{C_\infty \tau_v} + \frac{1}{\tau_{tc}} - \lambda_2\right)$$

The values of A and B may be deduced from initial conditions.

The process for solving these time-dependent equations goes as follows: First, the initial values for ΔT, ΔT_v, τ_v, and τ_{tc} are provided (recalling that τ_{vc} may be calculated by Equation III.3). Then, the results of Section III.A provide a value for C_{vib}. Values of ΔT and ΔT_v are then calculated for a time interval small compared to the sound period (2 ms for nitrogen and .1 ms for hydrogen). These values are in turn used to calculate C_{vib} and the τ's, and the process is then repeated.

In order to proceed with the calculations, several assumptions must be made concerning initial conditions. These are:

- The percentage of the discharge energy initially dumped into vibration.

- The vibrational relaxation time τ_{v0} of the system under study at room temperature.

- The constant B in the temperature dependence of the relaxation time, given by

$$\tau_v = \tau_{v0} \exp[B(T^{-1/3} - T_w^{-1/3})](T_w/T).$$

  The final factor T_w/T is to account for temperature-dependent pressure changes in the tube.

- Calculation of τ_{tc} is given by Equation III.2, with $\pi\beta_{mn} = 2.4$.

Here, it becomes necessary to discuss the two systems separately. The assumptions used for each of these systems studied are detailed in the sections describing their experimental results (Section IV.A for N_2 and Section IV.B for H_2).

III.D Measuring Vibrational Temperature

Determination of the vibrational temperature of the carbon monoxide was achieved using the cold gas filter technique developed by McNair, *et al.* [15] If the energy levels in a gas are populated according to a Boltzmann distribution, then vibrational temperature T_v may be calculated from the ratio between the radiation emitted due to transitions from the first vibrationally-excited state to that emitted from all states. The cold gas filter allows us to determine this ratio.

In this technique, the infrared radiation from the CO is measured twice with a broad-band infrared detector, once with the filter evacuated and once with it filled to one atmosphere with pure CO gas. The cell is kept "cold," that is, at room temperature. The cold CO gas becomes a very narrow-band filter of the radiation given off by the 1 → 0 transition of the gas involved in the discharge. Even the slightest anharmonicity will prevent absorption from other energy levels. Assuming only a Boltzmann distribution of vibrational energy, and a harmonic oscillator 1 → 0 transition, gives

$$I_{10}/I_{\text{empty}} = \frac{1}{(1+\epsilon)^2},$$

where $I_{10} \equiv I_{\text{empty}} - I_{\text{full}}$ and

$$\epsilon = [\exp(\hbar\omega/k_B T_v) - 1]^{-1}.$$

Thus, only ratios of intensities are required, so that a fully calibrated intensity measurement is unnecessary.

The method (essentially detailed balancing) discussed by Weitz and Flynn [16] was used to determine the vibrational temperature of the gas under study, when the vibrational temperature of

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[15] R.E. McNair, S.F. Fulghum, G.W. Flynn, M.S. Feld and B.J. Feldman, Chem.Phys.Letters **48**, 241 (1977).

[16] E. Weitz and G. Flynn. *Advances in Chemical Physics*, 1981, pp. 185-235.

the CO was known.

The definition of a vibrational temperature T_i for the ith vibrational state is

$$\frac{N_i}{N_0} = g_i \exp\left(\frac{-E_i}{kT_i}\right),$$

where N_i is the population of the ith level, g_i is the degeneracy of level i and N_0 is that of the ground state. If $k_{i\to j}$ is the probability that a collision will result in a change from state i to state j, then at equilibrium $k_{i\to j}N_i = k_{j\to i}N_j$ or,

$$\frac{k_{i\to j}}{k_{j\to i}} = \frac{N_j}{N_i}. \tag{III.6}$$

The probabilities of collision depend only on the translational energy of the particles (and hence, the translational temperature T) and not their vibrational energy (or vibrational temperature T_i). Evaluating Equation III.6 at vibrational temperature $T_i = T_j = T$ gives

$$\frac{k_{i\to j}}{k_{j\to i}} = \exp\left(\frac{-(E_j - E_i)}{kT}\right).$$

Substituting this into Equation III.6 gives us the general form

$$\exp\left(\frac{E_i - E_j}{kT}\right) = \frac{\exp(-E_i/kT)}{\exp(E_j/kT)},$$

which becomes

$$\frac{E_i - E_j}{T} = \frac{E_i}{T_i} - \frac{E_j}{T_j}.$$

If the energies in question are those of harmonic oscillators, with $E_i = h\nu_i$ and $E_j = h\nu_j$, then we have

$$\frac{\nu_i - \nu_j}{T} = \frac{\nu_i}{T_i} - \frac{\nu_j}{T_j}.$$

If we use the vibrational frequencies of N_2 (2331 cm^{-1}) and CO (2143 cm^{-1}) we have

$$T_{N_2\mathrm{vib}} = 2331\left[\frac{188}{T} + \frac{2143}{T_{CO\mathrm{vib}}}\right]^{-1}.$$

In order for this technique to provide reliable temperatures, however, we must have a rapid τ_B and τ_{CO}, with $\tau_B \ll \tau_{CO}$, since both gases must retain a Boltzmann distribution, and the gases must remain in equilibrium with each other.

Chapter IV: Experimental Results

The experimental results can be readily divided into two parts: those involving the relaxation of a N_2/CO system and those involving the relaxation of a H_2/He/CO system. Nitrogen was chosen for its long relaxation time and strong vibrational coupling with CO (their vibrational frequencies differ only by about 8%). Hydrogen, however, was chosen for its short relaxation time and strong coupling of its 1 → 0 vibrational transition with carbon monoxide's 2 → 0 vibrational transition. The speed of vibrational relaxation in hydrogen was so fast, however, that helium was added to the mixture to slow the process.

Obviously, it would have been preferable to conduct this experiment in pure CO so that the complications of vibrational coupling may be avoided. However, it has proved difficult to produce an energetic discharge in pure carbon monoxide. Figure IV.1 below demonstrates the difficulty. The voltage tends to reach a certain maximum value then collapse to near zero very quickly. The discharge, furthermore, is not reproducible except in general shape. By comparison, Figure IV.2 shows a discharge in the nitrogen/carbon monoxide mixture. The difference between these discharges is probably due to the fact that carbon monoxide has a larger electron cross-section and smaller ionization energy than nitrogen, causing an increase in the number of free electrons in the gas.

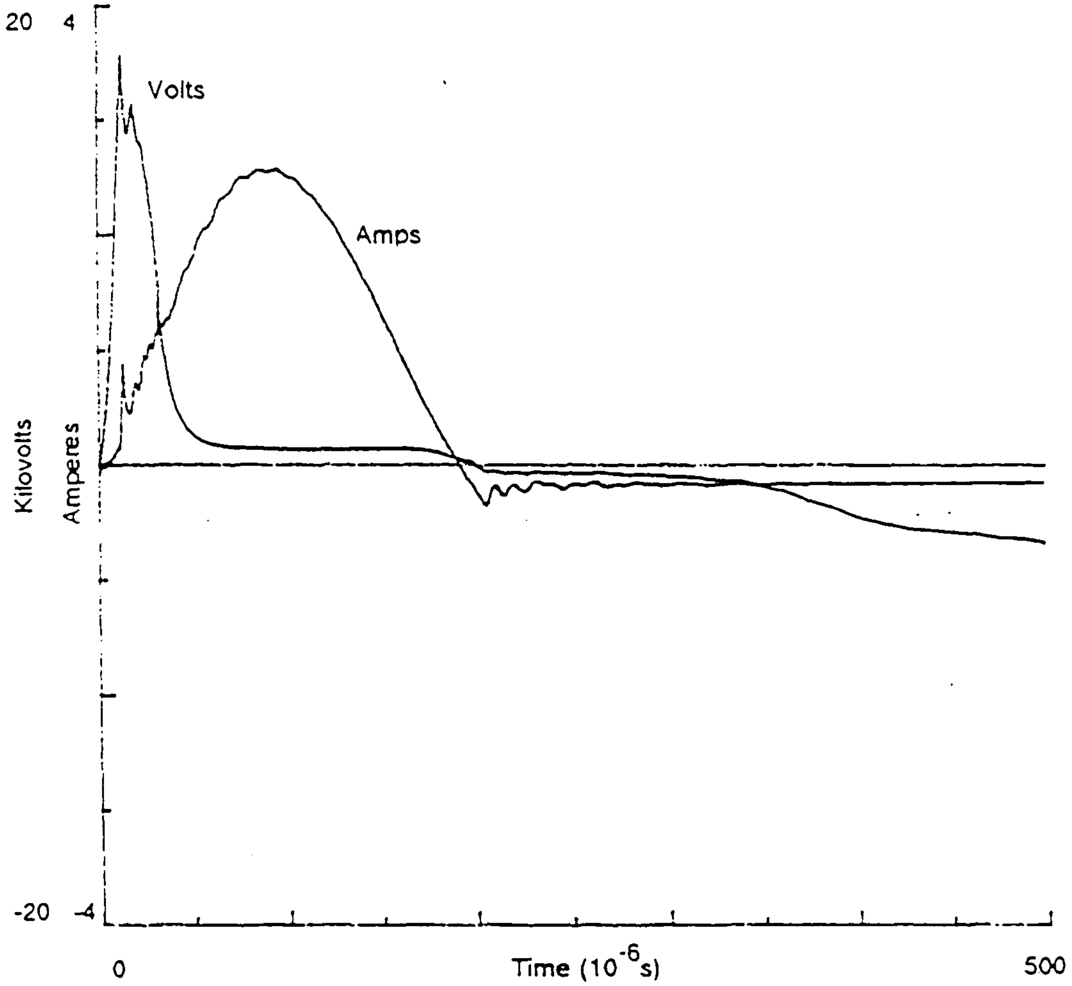

Figure IV.1: Voltage and current of a discharge in pure CO

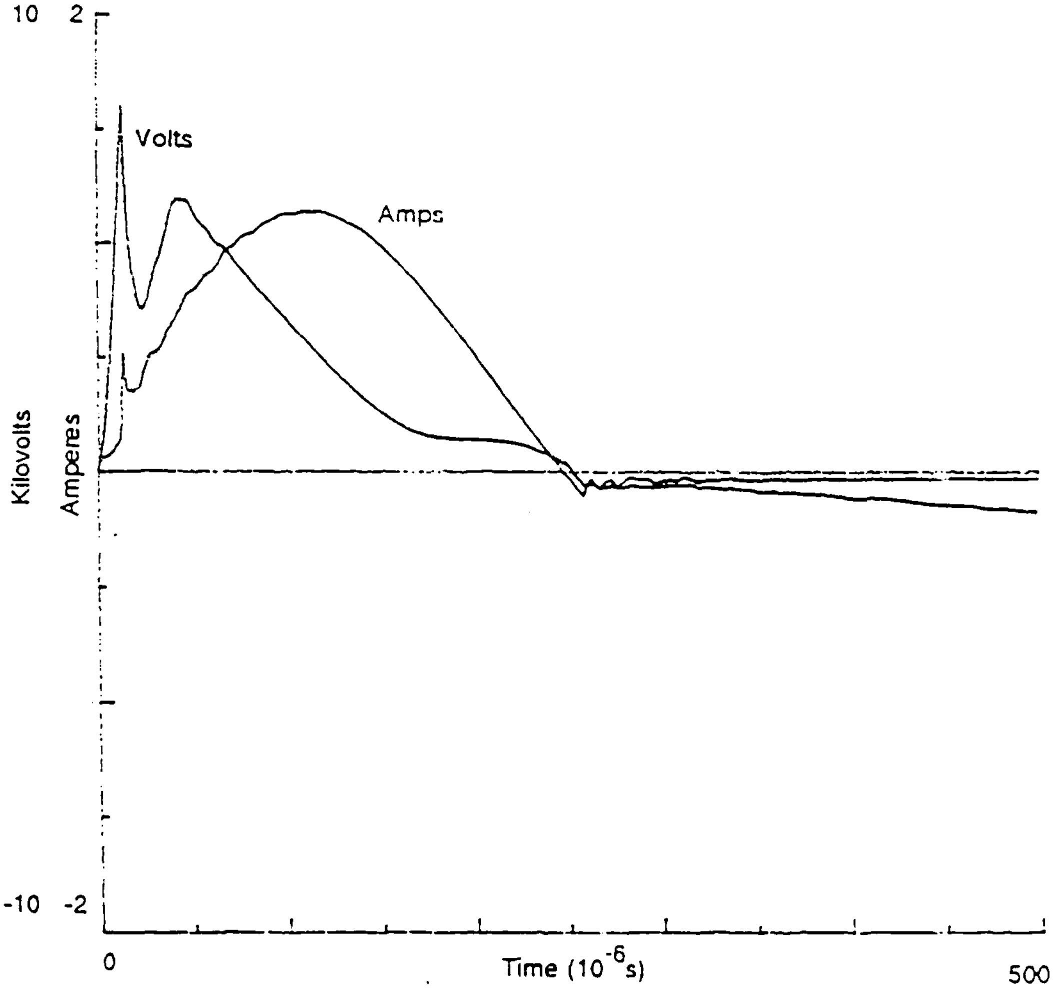

Figure IV.2: Voltage and current of a discharge in pure N_2

Another special factor to consider is the vibrational energy lost from the mixture by vibrational coupling, and then radiation, from the carbon monoxide. Margottin-Maclou, Doyennette, and Henry have shown [17] that the radiation relaxation constant of CO (i.e., the inverse of its relaxation time by this process) can be on the order of 10% of the relaxation constant for wall de-excitation in pure CO. However, since only a small amount of CO was used in any of the data we consider, such losses can, in our case, be neglected.

IV.A The Nitrogen/Carbon Monoxide System

Figure IV.3 shows the decay of the filtered acoustical signal after a discharge in a mixture of .25% CO in nitrogen. Since the vibrational relaxation time of pure nitrogen or pure carbon monoxide is on the order of seconds at the pressures used, one would expect the translational temperature to be virtually unaffected by the vibrational energy of the system, and these expectations are born out by the figure, with the sound wave displaying no gain. This measurement is used to check the calculated wall losses.

The sound velocity was calculated by multiplying the sound wavelength (assumed to be twice the tube length) by the sound frequency (assumed to be the reciprocal of the time between successive peaks in the scope trace). This velocity is compared with sound velocities calculated as a function of temperature, [18] resulting in a determination of the translational temperature.

Figure IV.4 shows the infrared decay following discharges of near identical energy (4875 J/mole of N_2 ±.3%) with the CGF filled and evacuated. The large difference in these curves indicates that

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[17] Ref. 9.

[18] F.D. Shields, J. Acoust. Soc. Am. **37**, 724 (1965).

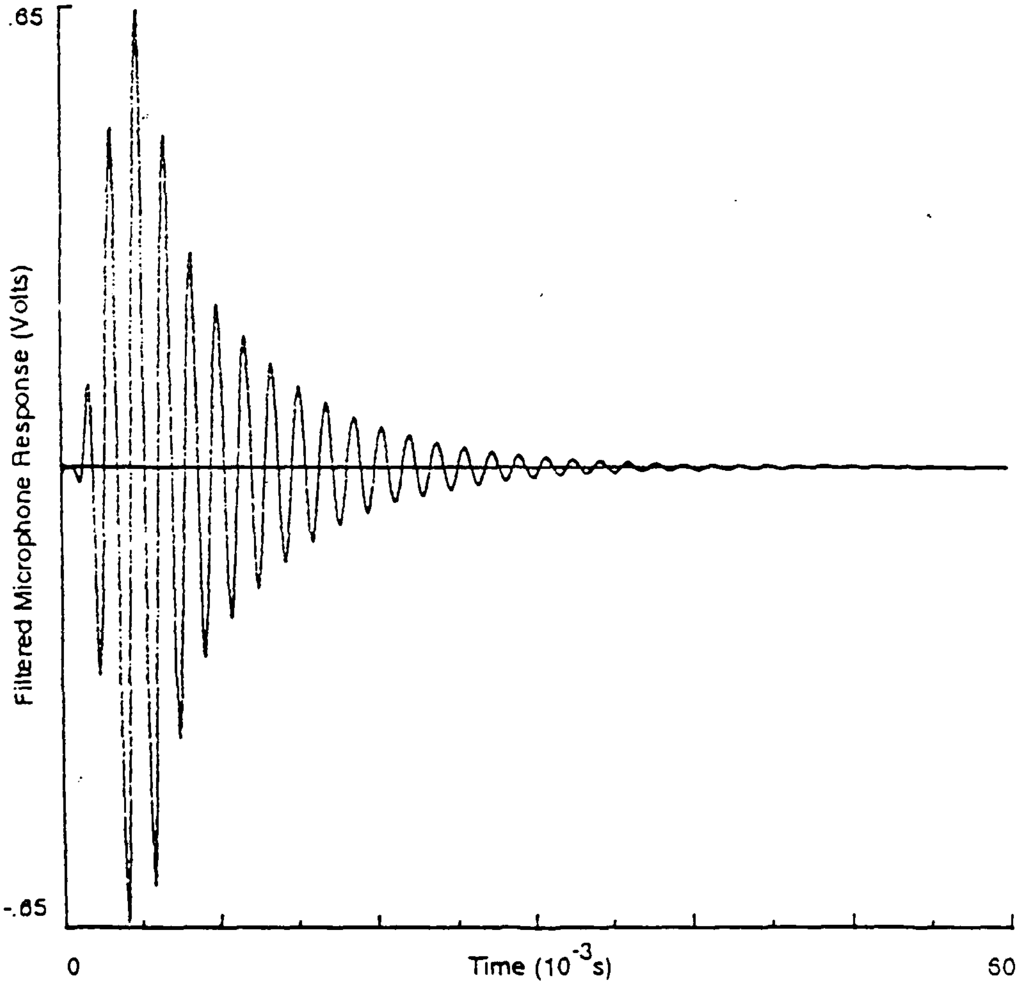

Figure IV.3: Filtered microphone responses of a discharge in N_2/CO the pressure in the filled CGF is sufficient to filter out the 1 → 0 transition of the CO.

The effect known as "ladder-climbing" (where the anharmonicity of the vibrating gas causes, by the same mechanism described in Section III.C, the boosting of energy into higher levels, producing a non-Boltzmann distribution) has been found to be negligible under the present experimental conditions. To begin with, the small anharmonicity of CO makes such an effect unlikely. Also, Stephenson [19] has shown that the intermode transition times in CO proceed very quickly (on the order of microseconds) in both directions. Finally, the filled CGF is seen to absorb very large amounts of radiation, so that CO vibrational levels greater than the first, which should be transmitted through the filled CGF, were not excited to any significant degree. [20]

These infrared decay curves were also transferred to the computer for analysis according to Section III.D. The result was the experimentally determined vibrational temperatures for the nitrogen and the carbon monoxide. These temperatures, together with the results predicted by the method of Section III.C are shown below in Figure IV.5.

The assumptions used in the prediction are the following:

- All of the discharge energy is initially dumped into vibration.

- The relaxation time τ_v is essentially infinite.

- The temperature coefficient B is irrelevant.

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[19] I.C. Stephenson, Appl. Phys. Lett. **22**, 576 (1973).

[20] W.H. Green and J.K. Hancock, J. Chem. Phys. **59**, 4326 (1973).

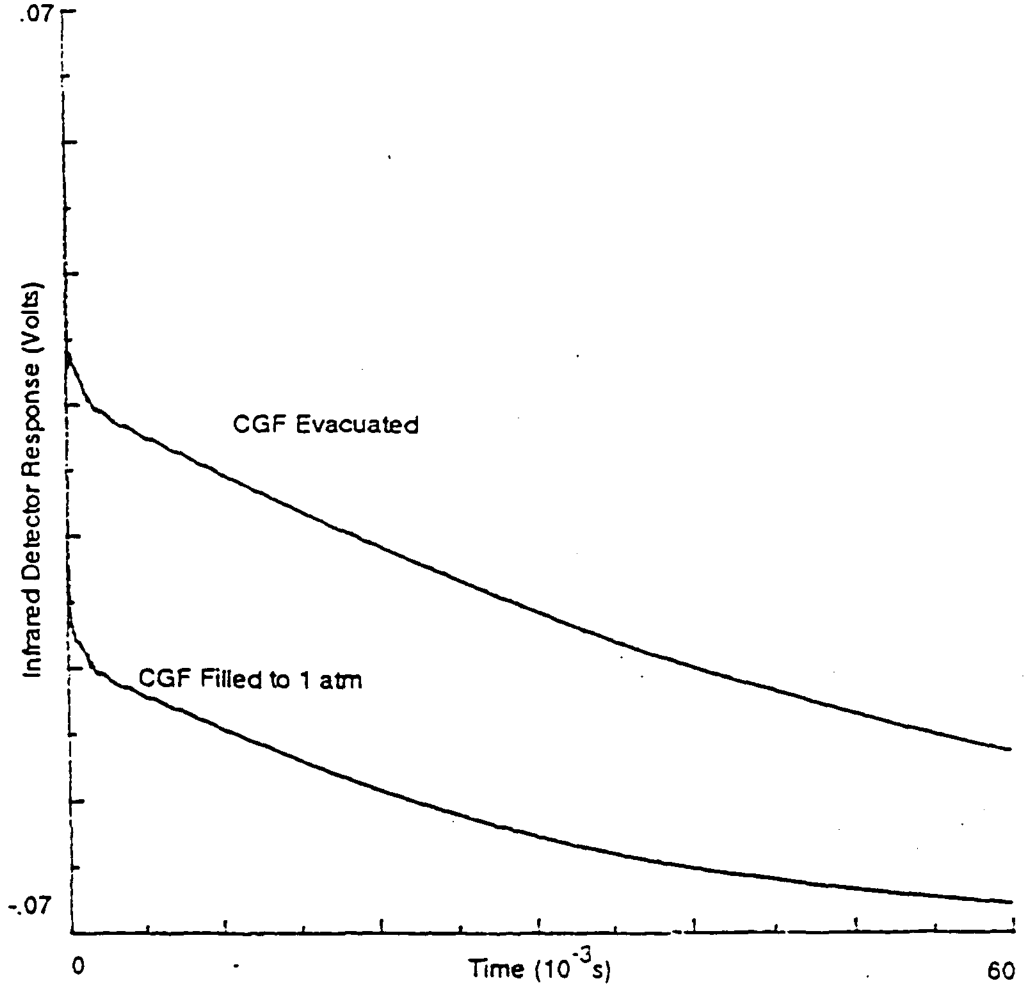

Figure IV.4: Infrared response of N_2/CO system with CGF filled to 1 atm and evacuated

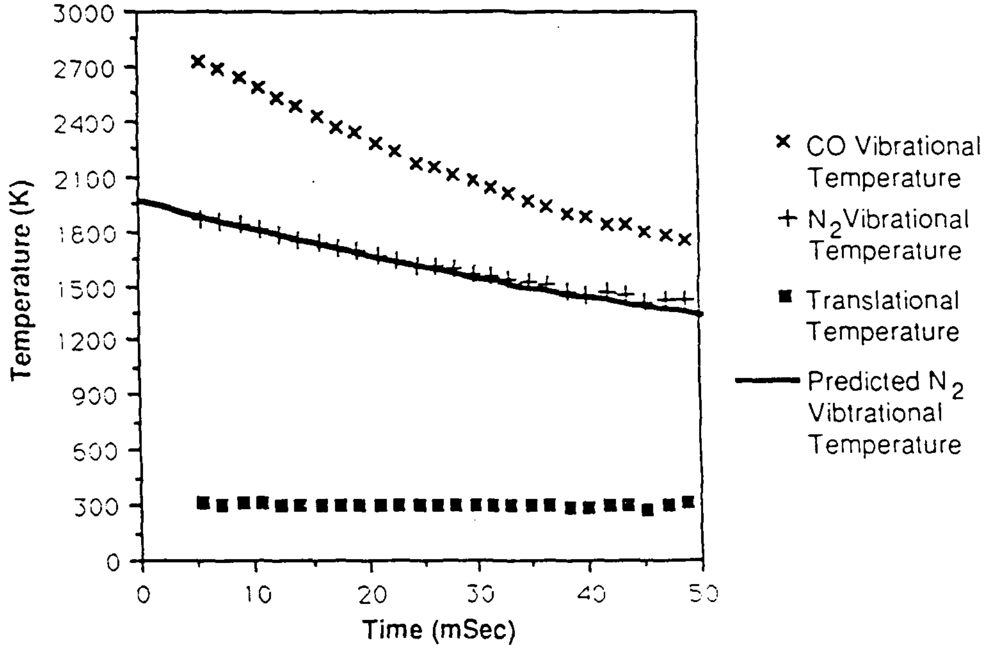

Figure IV.5: Predicted and Observed Translational and Vibrational Temperatures of N_2 and CO

- Calculation of τ_{tc} is given by Equation III.2 with $\pi\beta_{mn} = 2.4 \times \sqrt{1.67}$.

The assumption that $\pi\beta_{mn} = 2.4$ describes a radial dependence of temperature given by a single zero-order Bessel function. However, the discharge does not fill the tube, so that such a simple profile cannot be expected.

These assumptions are in complete agreement to those used by Shields. [21]

IV.B The Hydrogen/Helium/Carbon Monoxide System

One of the primary motivations for including a H_2/CO system in the present study is hydrogen's unusual vibrational coupling with carbon monoxide. The first excited vibrational state of hydrogen has nearly the same frequency as the second excited vibrational state of carbon monoxide. It was at first expected that this phenomenon would greatly facilitate the use of the "cold gas filter/carbon monoxide trace" method of determining vibrational temperature.

However, it was soon found that the relaxation time of H_2 was so rapid that system noise dominated the infrared detector signal after only a few milliseconds (see Figure IV.6) even with the cold gas filter evacuated so that measurements of intensity ratios, and hence vibrational temperatures, became impossible. Furthermore, it is suspected that, since hydrogen dumps energy into the second excited mode of carbon monoxide and not the first, that a non-Boltzmann distribution was temporarily produced in the CO. This is likely why the plot of the predicted vibrational temperatures does not strictly conform to the decay of the infrared radiation.

In order to slow the relaxation, a mixture of 46.7% helium, 52.6% hydrogen, and .65% carbon

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[21] Ref. 5.

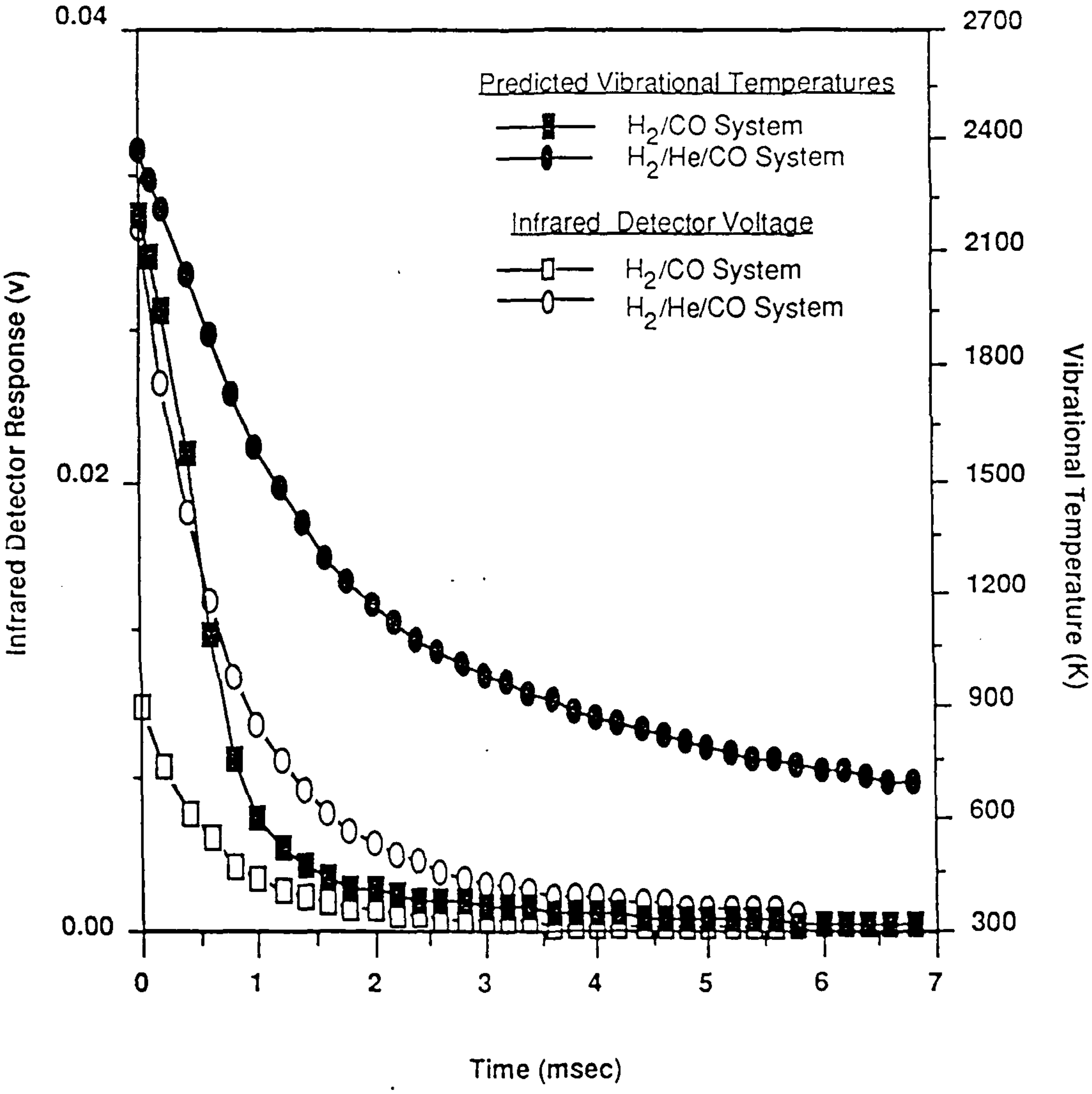

Figure IV.6: Infrared response and predicted vibrational temperature of discharges in hydrogen gas mixtures monoxide was tested. Even this mixture relaxed too quickly for vibrational temperature measurements to be made. However, by applying the procedures for predicting temperatures discussed above, and in the papers by Shields [22] and Shields and Lafleur [23] a vibrational relaxation time τ_{mix} and temperature dependence B_{mix} were obtained. A first attempt was also made to determine a relaxation time and temperature dependence for the H_2/CO mixture.

Figure IV.7 shows samples of the filtered acoustic pulses for the various mixtures, pressures and energies under study. As with the various mixtures reported by Shields and Lafleur the low-frequency rise in pressure caused by the rise in translational temperature following the discharge has been filtered out. Since the sound was seen to rapidly attenuate, the tube length was adjusted to 20 cm in order to increase the number of sound oscillations observable, while maintaining the condition that the microphone size is small compared to the tube length. Also, it was assumed that the gas took approximately a millisecond to achieve a metastable state, and data points were shifted by this amount.

Figures IV.8 and IV.9 display a plot of some measured values of the vibrational relaxation times (as a function of temperature) gathered from the literature. The relaxation times shown on Figure IV.8 (henceforth called $\tau_{H_2-H_2}$) are those of one molecule of excited H_2 in an atmosphere of ground state H_2, while the relaxation times shown in Figure IV.9 (henceforth called $\tau_{H_2-\text{He}}$) is that for one molecule of excited H_2 in an atmosphere of He.

There are two high-temperature shock-wave measurements [24], [25] and three room-temperature

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[22] Ref. 5

[23] Ref. 6

[24] J.E. Dove and H. Teitelbaum, Chem. Phys. 6, 431 (1974).

[25] J.H. Keifer and R.W. Lutz, J. Chem. Phys. 44, 668 (1966).

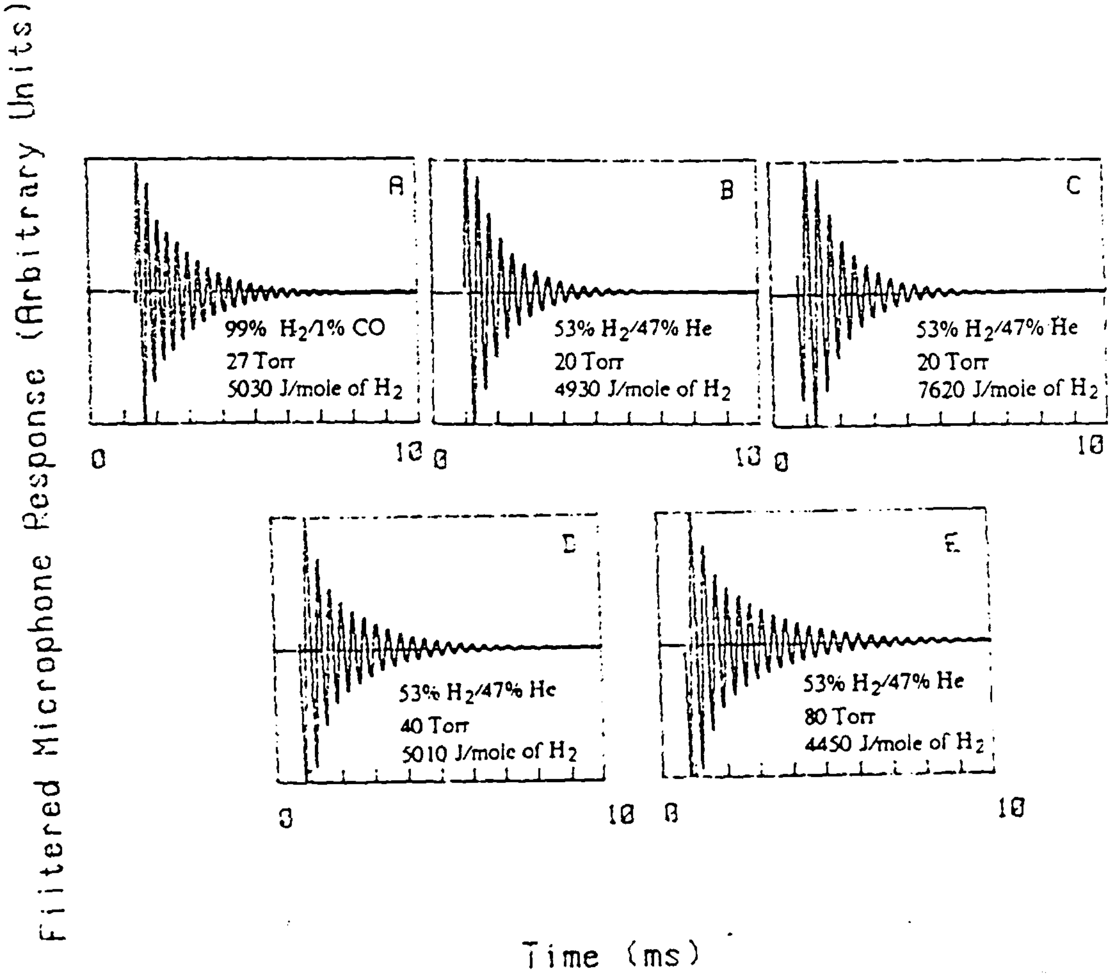

Figure IV.7: Filtered microphone responses of discharges in hydrogen gas mixtures or low-temperature measurements [26], [27], [28] plotted in Figure IV.8. Figure IV.9 shows a high-temperature measurement [29] and a room-temperature measurement. [30]

The predicted and measured temperatures are plotted in Figure IV.10. The fits were achieved using the model detailed above with the following assumptions:

- In the 20 torr samples, roughly 5% of the discharge energy went to electronic excitation and 5–10% into translational modes. In the higher pressure samples, the amount of energy into electronic excitation increased drastically, to as much as nearly 80%. The large amounts of He in the gas mixture makes these observations reasonable. Furthermore, Shields and Lafleur have reported a similar, though less drastic, loss of energy to non-vibrational modes in N_2/He mixtures.[31]

- The vibrational relaxation time τ_v at room temperature and atmospheric pressure for the H_2/He mixture is .09 ms, and that of the "pure" H_2 mixture is .05 ms.

- The temperature coefficient B for both the H_2/He mixture and the "pure" H_2 mixture is 120.

- Calculation of τ_{tc} is given by Equation III.2 with $\pi\beta_{mn} = 2.4 \times \sqrt{2.22}$. The difference between

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[26] M.-M. Audibert, C. Joffrin and J. Ducuing, Chem. Phys. Lett **25**, 158 (1974).

[27] M.A. Kovacs and M.E. Mack, Appl. Phys. Lett. **20**, 487 (1972).

[28] H. Matsui, E.L. Resler,Jr. and S.H. Bauer J. Chem. Phys. **63**, 4171 (1975).

[29] Ref. 24.

[30] M.- M. Audibert, C. Joffrin and J. Ducuing, Chem. Phys. Lett. **19**, 26 (1973).

[31] Ref. 6.

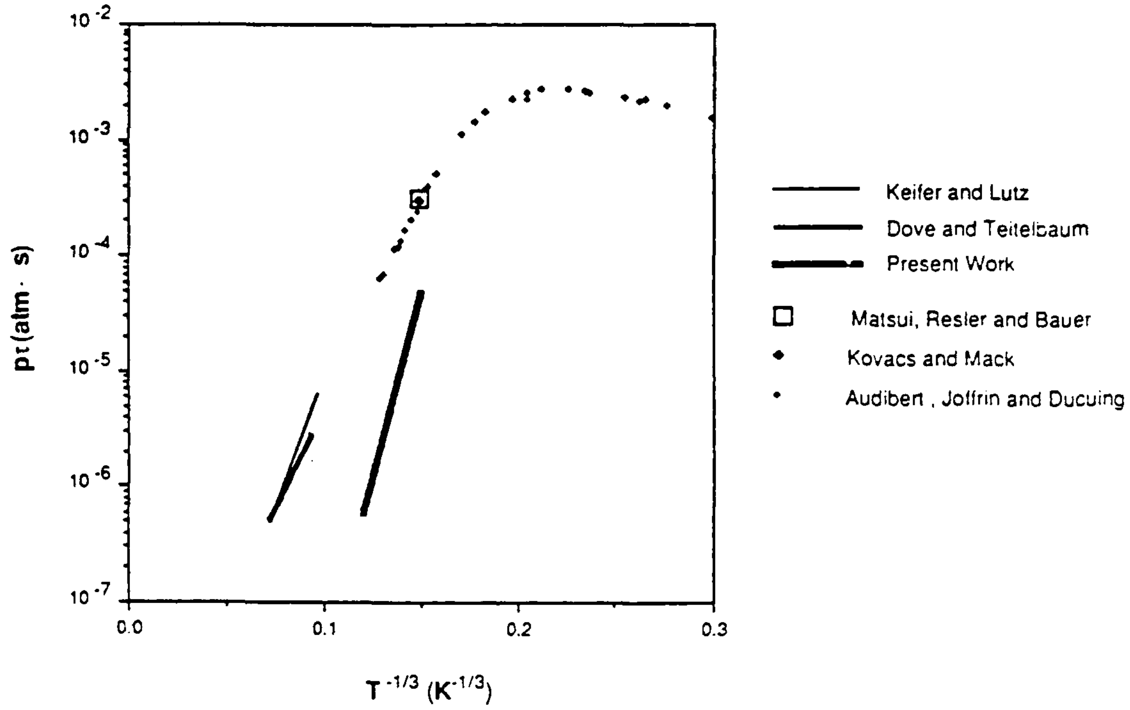

Figure IV.8: H_2-H_2 relaxation times as a function of temperature, as found in this and some previous experiments.

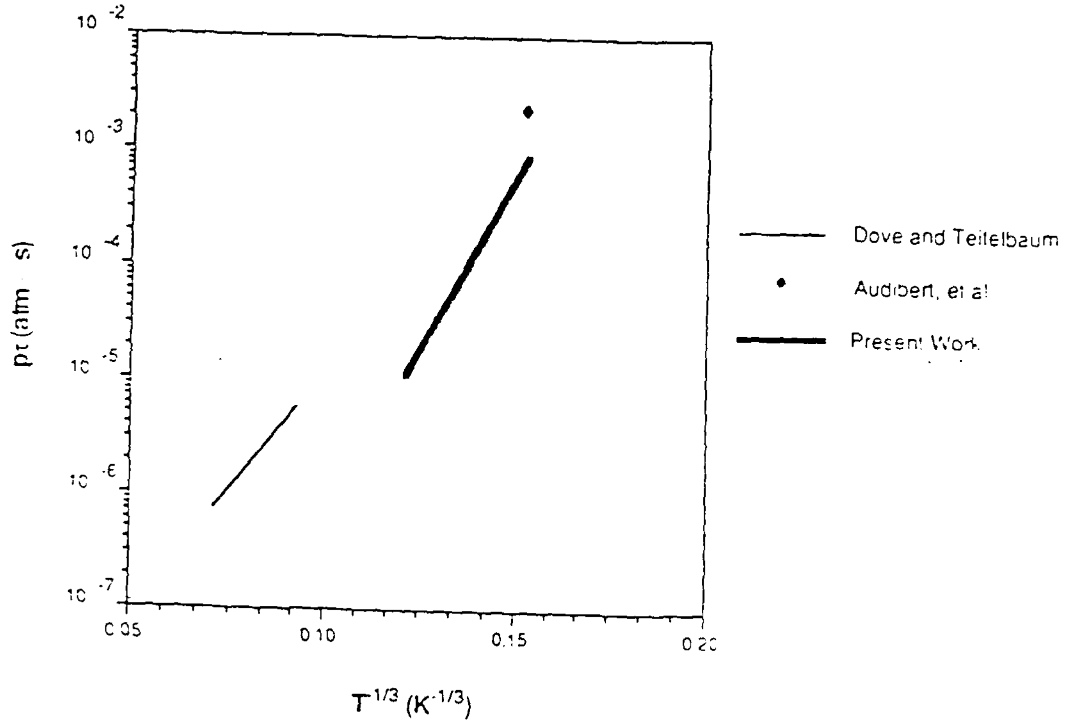

Figure IV.9: H_2-He relaxation times as a function of temperature, as found in this and some previous experiments.

this value and that reported for nitrogen (see Section IV.A) is likely due to differences in the precise character of the electric discharge in the two gasses.

It is now possible to determine both $\tau_{H_2-H_2}$ and $\tau_{H_2-\mathrm{He}}$ by making use of the equation [32]

$$\frac{1}{\tau_{\mathrm{mix}}} = \frac{X_{H_2}}{\tau_{H_2-H_2}} + \frac{X_{He}}{\tau_{H_2-\mathrm{He}}}$$

where X_{H_2} and X_{He} are the molar concentrations of the two gases. By this equation, we obtain a value of $\tau_{H_2-\mathrm{He}}$ of .93 ms and a temperature dependence $B = 120$. These results are also plotted in Figures IV.8 and IV.9 as thick solid lines.

It is noted that the relaxation times determined here are far shorter than those reported from others. Yet, the rapid decline of the infrared emission confirms, at least qualitatively, the present determinations. It is submitted that the disparity with previous findings is a result of the presence of CO in the H_2/He mixture, and the disturbances in the vibrational energy distribution thereby caused. The exact nature of these disturbances is not yet understood; further research is required.

IV.C Sound Amplification

Figure IV.11 shows the acoustical gain as a function of time for the H_2/He/CO and the H_2/CO mixtures. These curves were corrected for viscous, thermal and end losses. End losses were calculated to adjust the 80 torr curve (plot E) to zero. Shields [33] explains how the rest of these corrections were made. The amplification coefficients obtained in this manner and averaged over six time periods are plotted as points in the figure. Theoretical curves for the H_2/CO and for the high-H_2/He/CO

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[32] Ref. 30.

[33] Ref. 5.

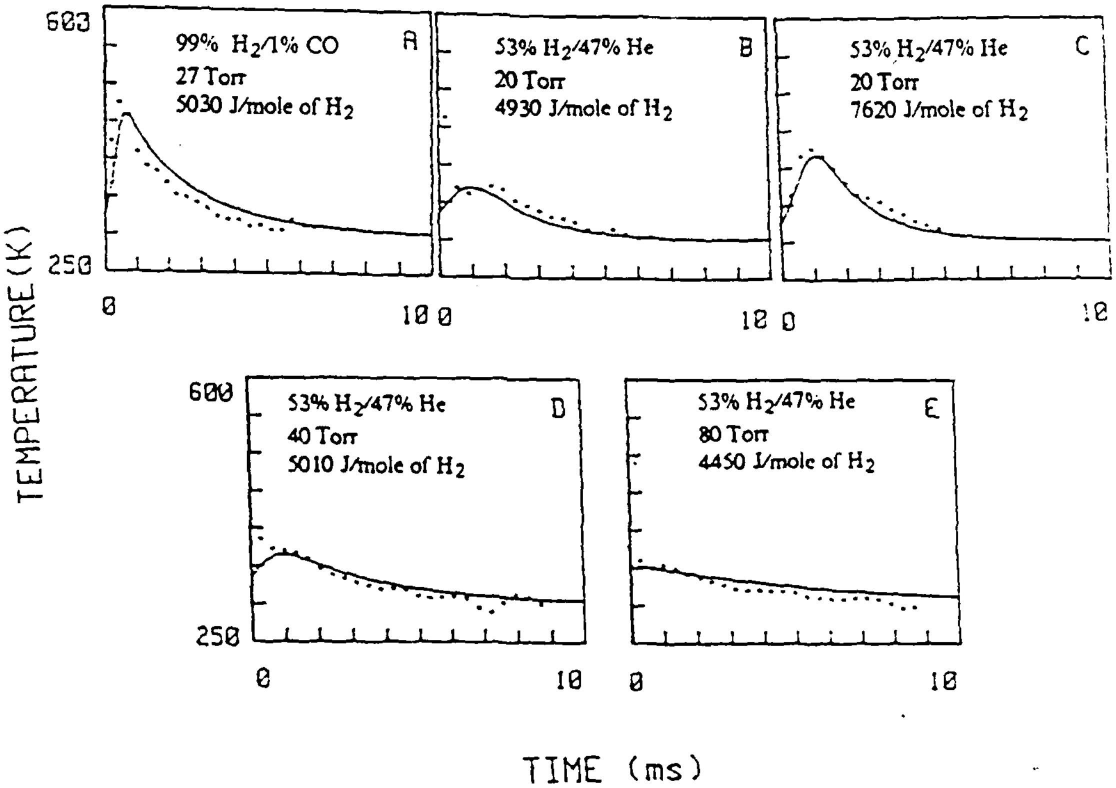

Figure IV.10: Predicted and Observed Translational Temperatures of H_2/He mixtures curves are not shown since the calculated relaxation times become comparable to the sound period, so that no metastable state is established and the theory developed by Shields for predicting these gains cannot be applied. It is notable that what curves can be fitted comply with the theoretical predictions fairly well.

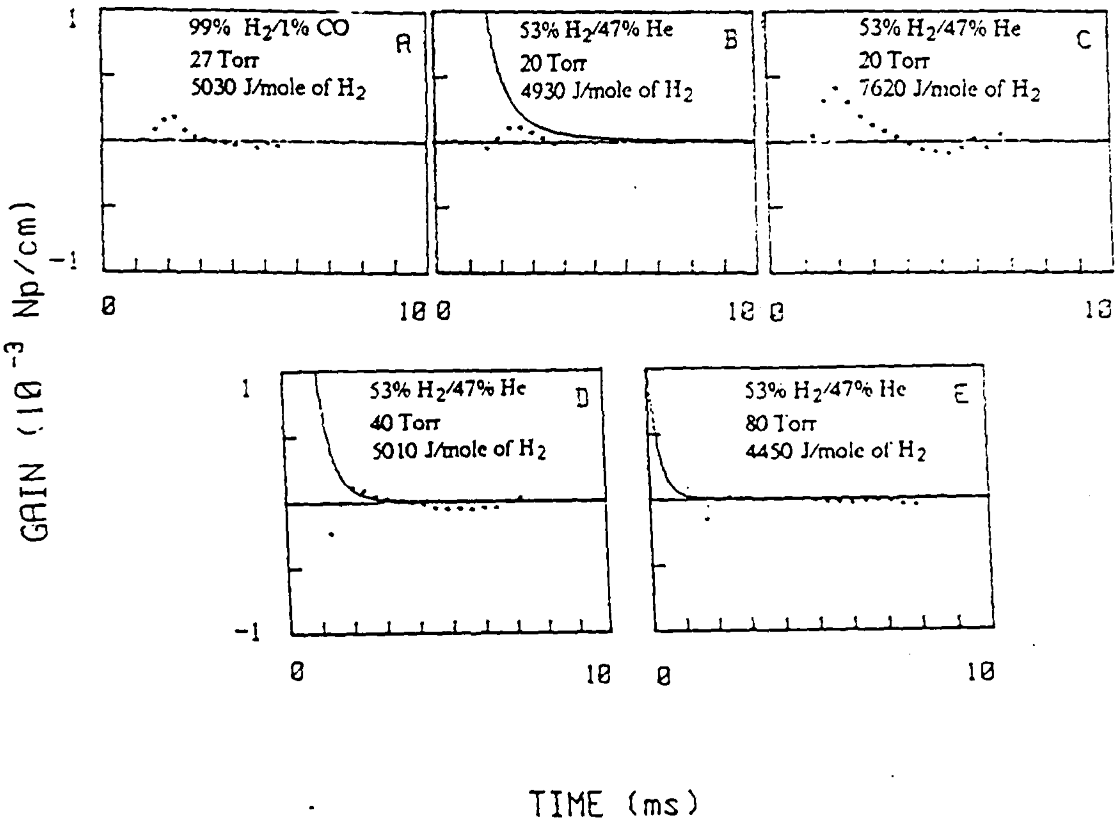

Figure IV.11: Predicted and Observed Acoustical Gain in H_2/He/COmixtures

Chapter V: Conclusion

The measurements in the hydrogen gas mixture show that the unusual nature of the hydrogen-carbon monoxide vibrational coupling (i.e., the coupling of hydrogen's $1 \rightarrow 0$ mode with carbon monoxide's $2 \rightarrow 0$ mode) tends to make accurate vibrational temperature measurements using the CGF method difficult. However, the predicted relaxation times in the hydrogen- helium mixtures and the measured amplification due to SACER are of the right order of magnitude, though the relaxation times are shorter than those previously measured.

The confirmation of the predicted nitrogen vibrational temperatures is intriguing in that it confirms the values of τ_{vc}/τ_{tc} and the relaxation times previously reported.[34] This is the first experimental verification of Equation III.2. However, as has been noted, the predicted gains are well below those which have been observed in these papers when the relaxation time is shortened by the addition of other gasses (most notably hydrogen). By applying variations of the methods discussed in this paper, the relaxation model may be more stringently tested, and the nature of this gain may be more fully understood.

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[34] Refs. 5 and 6.

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Appendix: Physical Properties of the Gasses Under Study

Gas	Molecular Mass	Vibrational Wavenumber
CO	28.01	2143 cm^{-1}
H_2	2.0158	4159
He	4.0026	—
N_2	28.01	2331

Mixture	Mass	Viscosity	Viscosity Temperature Coefficient
99.75% N_2/.25% CO	28.01	2.1995×10^{-4} g/cm-K	$3.89 \times 10^{-7} K^{-1}$
99% H_2/1% CO	2.276	1.07×10^{-4}	1.71×10^{-7}
52.6% H_2/46.7% He/.65% CO	3.112	1.65×10^{-4}	2.7×10^{-7}

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