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Title A SPECTROPHONE STUDY OF VIBRATIONAL RELAXATION
IN METHANE

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The spectrophone method for the study of vibrational relaxation has been claimed to possess a distinct advantage over the more commonly used ultrasonic techniques in that it permits the relaxation of the various infrared-active vibrational modes in a polyatomic molecule to be studied separately. A discussion of the rate equations governing the exchange of energy between several degrees of freedom in polyatomic gases is given which shows that the characteristic relaxation frequencies for such a system are completely independent of the method of excitation, indicating that the information which can be obtained using the spectrophone is essentially the same as that to be found from ultrasonic measurements. An expression is derived for the spectrophone frequency response to be expected from a polyatomic gas which predicts that at sufficiently high light-chopping frequencies an increased loss in the spectrophone signal due to relaxation phenomena should be observed. A study of the spectrophone response in the

frequency range where this increased signal loss occurs should thus afford a means for determining the effective vibrational relaxation time of the gas in the spectrophone cell.

An apparatus is described which was used to measure spectrophone signal amplitudes over a range of chopping frequencies from 200 to 1600 cps, at gas pressures from one atmosphere down to a few millimeters. Response curves obtained for methane gas at pressures of one atmosphere and one-half atmosphere exhibit the behavior predicted by the theory, but show no increased signal loss at the higher chopping frequencies. However, the response curves for methane at pressures of 5 mm, 10 mm, and 20 mm do exhibit such a high frequency loss; from these response data a vibrational relaxation time of $\tau = 1.1$ microseconds at one atmosphere has been assigned to methane. This value agrees within a factor of two with all similar results reported by other workers.

Studies of the spectrophone frequency response obtained for mixtures of methane and carbon dioxide, with carbon dioxide concentrations of one percent and five percent, indicate that the presence of carbon dioxide serves to decrease the vibrational relaxation time in methane.

Studies of the spectrophone frequency response obtained for three deuterated methanes, CH_3D , CH_2D_2 , and CHD_3 , yield values of $\tau = 0.87$ microseconds for CH_3D , $\tau = 0.99$ microseconds for

CH_2D_2 , and $\tau = 1.45$ microseconds for CHD_3 , all at one atmosphere pressure. The longer time for CHD_3 is interpreted in terms of the decreased rotational velocity of the deuterium atoms in this molecule, which reduces the probability of vibrational-rotational energy transfer during molecular collisions.

A SPECTROPHONE STUDY OF VIBRATIONAL
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A SPECTROPHONE STUDY OF VIBRATIONAL RELAXATION IN METHANE

INTRODUCTION

Molecules in the gas phase possess energy due to translation, rotation, vibration, and electronic motion. If a collection of gas molecules is at equilibrium at a given temperature the total energy of the system is distributed among the various degrees of freedom in a definite manner, as described by statistical mechanical considerations. If a given amount of energy is added to a particular degree of freedom the total energy of the system assumes a new distribution consistent with the new equilibrium temperature. During the equilibration process energy must be exchanged between the various degrees of freedom. In general the rate of change of energy in a specific degree of freedom is proportional to the difference between the instantaneous value of that energy and the equilibrium value towards which it tends. The reciprocal of the rate constant for this process, with units of time, is known as the relaxation time for the specific degree of freedom concerned.

If a gas undergoes a rapid adiabatic compression or expansion, an equilibrium distribution of the vibrational energy is reached only after a finite lapse of time. In 1904 Jeans (16, p. 374) predicted that adiabatic compressions of a gas in a high frequency sound field would

occur so rapidly that equilibrium between translational and vibrational energy could not be maintained. With the vibrational degrees of freedom unavailable for energy uptake, a decrease in the heat capacity and a consequent increase in the velocity of sound in the gas would be expected. Pierce (27) in 1925 first observed such an increase or dispersion of the velocity of sound in carbon dioxide. Turrell (33, p. 1-8) has given a historical account of the subsequent development of the theory and experimental methods of vibrational relaxation, while Herzfeld and Litovitz (13) and Cottrell and McCoubrey (6) have given detailed descriptions of the most common measuring techniques and summaries of the basic theoretical considerations. In addition Cottrell and McCoubrey give an excellent summary of experimental results through mid-1960.

A large majority of the experimental results reported to date in the field of vibrational relaxation have been obtained from measurements of the velocity or absorption of sound in gases. In these methods, as in all methods except the spectrophone, translational energy is fed into the gas and the resulting change in the vibrational energy is deduced from a measurement of some property of the gas, such as sound velocity. In the spectrophone, energy is added to one or more vibrational degrees of freedom by illumination of the gas with radiation of appropriate wavelength, and the behavior of the translational energy is studied.

When molecules absorb infrared radiation the energy appears directly as quanta of vibrational energy. A molecule which has absorbed a quantum of vibrational energy may lose it by spontaneous emission of radiation, by induced emission, or by transfer of energy to another molecule during a collision. In this last process the energy usually appears as translational motion, although it may be transferred to one or more vibrational degrees of freedom in the collision partner. Thus when an absorbing gas is illuminated by radiation of appropriate wavelength, it warms up to a new average translational temperature, which is determined by the intensity of the incident radiation and the rate of heat loss from the system. If the intensity of the radiation is modulated periodically, the gas will alternately heat and cool, and a periodic pressure variation will be exhibited by a constant volume system.

The spectrophone basically consists of a gas cell, fitted with infrared-transparent windows, which contains a transducer for conversion of the pressure variations into an electrical signal, together with a source of infrared radiation and a device for modulating its intensity. Since a finite period of time elapses between the absorption of energy by the gas and the subsequent increase in its pressure, the signal produced at the transducer will exhibit a phase lag relative to the modulation of the incident radiation. In general this effect is not a simple one, due to heat conduction and other effects in the cell,

but in principle the measurement of this phase lag should afford a means for determination of the vibrational relaxation time of the gas. Most applications of the spectrophone to the study of vibrational relaxation have been based on the phase shift principle.

In theoretical studies of the absorption and redistribution of energy in the spectrophone cell Jones (18, p. 15-29) and Montan (24, p. 35-61) have shown that the signal produced at the microphone should be related to the light modulation frequency and the relaxation time of the gas in the cell according to the expression

$$E_{\text{mic}} \propto \frac{1}{\omega [1 + \omega^2 \tau^2]^{\frac{1}{2}}} ,$$

where ω is the angular modulation frequency, and τ is the vibrational relaxation time. In the frequency range where $\omega\tau$ is small compared to unity the signal should be inversely proportional to ω , while at frequencies for which $\omega\tau$ is much greater than unity the signal should be inversely proportional to ω^2 . Thus, a study of the frequency response of the spectrophone in the region where increased signal loss occurs should also afford a means for determining the vibrational relaxation time of the gas. To date Woodmansee (37) has been the only worker to employ this method.

The spectrophone method for the study of vibrational relaxation has been claimed to possess one distinct advantage over the more

commonly used techniques (33, p. 7; 18, p. 14; 24, p. 6; 37, p. 8). Theoretical treatments of vibrational relaxation (13, p. 260-350) predict that the probability of energy transfer during a molecular collision will depend exponentially on the amount of energy to be transferred to or from translation. Thus, a polyatomic molecule might be expected to exhibit a separate relaxation time for each different frequency of vibration. With the spectrophone it is possible, by the use of filtered radiation, to selectively excite the different infrared-active vibrational modes in a polyatomic molecule, and thus to possibly observe separately the various relaxation processes which may occur. However, further consideration indicates that the situation is somewhat more complicated, as will be shown in a later section of this thesis.

Several studies of vibrational relaxation in methane have been reported; the results of these are summarized in Table 1. As indicated, the value reported by Cottrell, Hunter, and Read was obtained from spectrophone measurements in which the 3.3 micron vibrational band was excited. Most of the other results were obtained from ultrasonic dispersion and absorption measurements, and pertain primarily to the lowest frequency band in methane, at 7.7 microns. The different values obtained for the vibrational relaxation time from the two types of experiments appears to be significant, and was considered to merit further investigation. The research to be described

here was undertaken in an attempt to study vibrational relaxation in methane by the frequency response spectrophone method first used by Woodmansee.

Table 1. Reported Vibrational Relaxation Times for Methane

Method	Temperature (°K)	τ (μ sec-atm)	Author
Velocity of sound	382	0.84	Eucken, Aybar 1940 (10)
	477	0.65	
	574	0.58	
	595	0.51	
	626	0.49	
Impact tube	289	0.48	Griffith 1950 (11)
Velocity of sound	303	1.68	Cottrell, Martin 1957 (4)
	333	1.72	
Absorption of sound	298	1.86	Edmonds, Lamb 1958 (9)
Velocity of sound	298	2.0	Cottrell, Matheson 1962 (5)
	348	1.1	
Absorption of sound	244	1.60	Madigosky 1963 (22)
	259	1.38	
	273	1.26	
	303	1.03	
Spectrophone	298	100 (3.3 μ band)	Cottrell, Hunter, Read 1963 (3)

SUMMARY OF SPECTROPHONE STUDIES

Woodmansee (37, p. 7-14) has given a detailed account of spectrophone studies conducted by Slobodskaya (30) in 1948, Turrell (33) in 1954, Jacox and Bauer (15) in 1957, Jones (18) and Slobodskaya (31) in 1958, and Montan (24) in 1959, all of whom employed the phase shift method to determine vibrational relaxation times. Of these, Slobodskaya, Jacox and Bauer, and Montan attempted to measure separate times for different modes of vibration in polyatomic molecules. Slobodskaya and Jacox and Bauer reported slightly different relaxation times for different bands in carbon dioxide, while Montan was unable to detect any significant differences for the four bands in nitrous oxide which he studied.

In 1959 Delaney (7) employed the phase shift method in his spectrophone studies of carbon dioxide and carbon monoxide. He used a measuring cell containing two microphones opposite each other which were calibrated for each experimental condition by the reciprocity technique. It is claimed that this procedure eliminated difficulties due to phase shifts occurring in the measuring system. Delaney reported a relaxation time of 11 microseconds for carbon dioxide, in good agreement with the results of Slobodskaya (30) and other workers. However, his time of 13 microseconds for carbon monoxide appears to be far too small. Work by Millikan (23) on infrared fluorescence in carbon monoxide indicates that the relaxation time is at least as long as 0.2 seconds.

Woodmansee (37) used the spectrophone to investigate vibrational relaxation in carbon monoxide by studying the frequency behavior of the microphone signal rather than its phase shift relative to a reference signal. The response curves which he obtained over a light-chopping frequency range of 200 to 2000 cycles per second did not follow the theoretical form

$$E_{\text{mic}} \propto \frac{1}{\omega [1 + \omega^2 \tau^2]^{\frac{1}{2}}} ,$$

presumably because of acoustical resonances of an undetermined nature occurring in the cell. Nevertheless Woodmansee concluded that a gas for which the product $\omega\tau$ approaches unity in the range of chopping frequencies used should exhibit a loss of signal relative to a gas for which $\omega\tau$ remains negligible compared to unity in the same frequency range. Comparisons of response curves for carbon monoxide and carbon dioxide at pressures from 0.5 to 4 atmospheres showed that the former gas exhibited such a signal loss relative to the latter. From such comparisons Woodmansee estimated the relaxation time for carbon monoxide to be two milliseconds. A measurement of the phase of the spectrophone signal relative to a reference signal showed a change of nearly 180 degrees over a small frequency range centered about the resonance point. Since Woodmansee's data indicated that the resonant frequency was a function of

both pressure and gas composition, he concluded that previous results obtained by the phase shift method should be viewed with some suspicion.

Although Millikan's results indicate that Woodmansee's value is also too small, the discrepancy can probably be attributed to impurities in the carbon monoxide samples used by Woodmansee.

Millikan found that a few parts per million of an impurity such as water was sufficient to quench the fluorescence in carbon monoxide.

In 1963 Cottrell, Hunter, and Read (3) used two modifications of the spectrophone to study vibrational relaxation of the 3.3 micron band in methane. The first involved measurement of the energy absorbed by the gas in the spectrophone cell at reduced pressures under steady state conditions, while the second was a conventional phase shift measurement. In each case the results were compared with those obtained from similar measurements on CClF_3 , a gas which is expected to have a very short relaxation time. From such comparisons a relaxation time of 1×10^{-4} seconds was assigned to the 3.3 micron band in methane. This value is in contrast with a time of 2.0 microseconds obtained by Cottrell and Matheson (5) from sound velocity measurements.

THEORY OF SPECTROPHONE FREQUENCY RESPONSE

Jones (18, p. 15-29) and Montan (24, p. 35-61) have treated the theory of spectrophone response in considerable detail, including such effects as heat conduction, diffusion, and variations in energy absorption within the cell. Their results indicate that these effects, while possibly making significant contributions to the phase shift, should not have a marked influence on the frequency response. Each treatment however, was restricted to consideration of energy exchange between a single vibrational mode and translation, while in general the response from a polyatomic gas may be complicated by exchange of energy between the various vibrational modes. In the following discussion the simple case involving a single vibration will be treated first. The exchange of energy between several degrees of freedom will then be considered, and the equations describing the general form of the spectrophone response to be expected from a polyatomic gas will be developed. In light of the results of Jones and Montan, effects such as diffusion and heat conduction within the cell will not be considered.

Schwartz, Slawsky, and Herzfeld (28) have shown that the direct exchange of energy between a single vibrational mode and translation is described by the equation

$$-\frac{dE_v}{dt} = \frac{1}{\tau} [E_v - E_v(T_{tr})] ,$$

where E_v is the instantaneous vibrational energy, $E_v(T_{tr})$ is the equilibrium vibrational energy at the translational temperature, T_{tr} , and τ is the relaxation time. If vibrational energy is being added to the gas at a rate D , the total rate of change of the vibrational energy is given by

$$\frac{dE_v}{dt} = D - \frac{1}{\tau} [E_v - E_v(T_{tr})] . \quad (1)$$

The rate of production of translational energy, E_{tr} , is given by

$$\frac{dE_{tr}}{dt} = \frac{1}{\tau} [E_v - E_v(T_{tr})] . \quad (2)$$

In equation (2) exchange of energy between translational and rotational degrees of freedom has been neglected. However, it has been shown (13, p. 90) that equilibration between translation and rotation generally takes place much more rapidly than between translation and vibration, so that translation and rotation may effectively be lumped together as "external" degrees of freedom. In this discussion the term "translation" will be understood to include all external degrees of freedom, i. e., translation and rotation.

For temperature variations which are small with respect to the equilibrium temperature T_0 the energies in equations (1) and

(2) may be approximated by the relations

$$E_v = E_v^0 + C_v(T_v - T_0)$$

$$E_v(T_{tr}) = E_v^0 + C_v(T_{tr} - T_0) \quad (3)$$

$$E_{tr} = E_{tr}^0 + C_{tr}(T_{tr} - T_0),$$

where E_v^0 and E_{tr}^0 are the equilibrium vibrational and translational energies, respectively, at temperature T_0 , C_v and C_{tr} are the vibrational and translational heat capacities at T_0 , and T_v and T_{tr} are the instantaneous vibrational and translational temperatures. Equations (1) and (2) then take the form

$$C_v \frac{dT_v}{dt} = D - \frac{C_v}{\tau} (T_v - T_{tr})$$

$$C_{tr} \frac{dT_{tr}}{dt} = \frac{C_v}{\tau} (T_v - T_{tr}),$$

or

$$C_v \frac{d}{dt} (T_v - T_0) = D - \frac{C_v}{\tau} [(T_v - T_0) - (T_{tr} - T_0)] \quad (4)$$

$$C_{tr} \frac{d}{dt} (T_{tr} - T_0) = \frac{C_v}{\tau} [(T_v - T_0) - (T_{tr} - T_0)] \quad (5)$$

If D is a periodic function, given by

$$D = D_0 \exp(i\omega t),$$

then it may be assumed that the temperature variations are also periodic, i. e. ,

$$T_v - T_0 = T'_v \exp (i\omega t)$$

$$T_{tr} - T_0 = T'_{tr} \exp (i\omega t).$$

Equations (4) and (5) then become

$$i\omega C_v T'_v = D_0 - \frac{C_v}{\tau} (T'_v - T'_{tr}) \quad (6)$$

$$i\omega C_{tr} T'_{tr} = \frac{C_v}{\tau} (T'_v - T'_{tr}) . \quad (7)$$

Simultaneous solution of equations (6) and (7) for T'_{tr} gives

$$T'_{tr} = \frac{D_0}{i\omega (C_v + C_{tr}) - \omega^2 C_{tr} \tau} . \quad (8)$$

Since the spectrophone cell is a constant-volume system, the oscillatory part of the translational temperature, T'_{tr} , should be directly proportional to the oscillatory pressure, and consequently to the voltage produced at the microphone in the spectrophone cell. The magnitude of equation (8) should then describe the frequency behavior of the spectrophone signal. This is given by

$$|T'_{tr}| = \frac{|D_0|}{\omega (C_v + C_{tr}) \{1 + \omega^2 [C_{tr}/(C_{tr} + C_v)]^2 \tau^2\}^{\frac{1}{2}}} .$$

Thus, when a single vibrational mode is involved, the spectrophone signal should decrease as ω^{-1} at low frequencies, becoming proportional to ω^{-2} at high frequencies.

In polyatomic gases, where more than one vibrational degree of freedom exists, the relaxation process may be quite complicated. Theoretically, two limiting situations may be described. In the first, often referred to as relaxation in parallel, each vibrational mode exchanges energy with translation only, independently of other modes. In such a case the relaxation equations for a gas with n vibrational modes, where energy is being added to the i -th mode at a rate D_i , are

$$\frac{dE_i}{dt} = D_i - \frac{1}{\tau_i} [E_i - E_i(T_{tr})], \quad i = 1, 2, \dots, n \quad (9)$$

$$\frac{dE_{tr}}{dt} = \sum_{i=1}^n \frac{1}{\tau_i} [E_i - E_i(T_{tr})] \quad (10)$$

Here E_i is the instantaneous vibrational energy of mode i , $E_i(T_{tr})$ is the equilibrium vibrational energy of mode i at the translational temperature T_{tr} , and τ_i is the relaxation time of mode i . Using approximations analogous to equations (3), equations (9) and (10) become

$$C_i \frac{d}{dt} (T_i - T_0) = D_i - \frac{C_i}{\tau_i} [(T_i - T_0) - (T_{tr} - T_0)] \quad (11)$$

$$i = 1, 2, \dots, n$$

$$C_{tr} \frac{d}{dt}(T_{tr} - T_0) = \sum_{i=1}^n \frac{C_i}{\tau_i} [(T_i - T_0) - (T_{tr} - T_0)], \quad (12)$$

where C_i is the heat capacity of the i -th vibrational mode at temperature T_0 . If the driving functions, D_i , are periodic, the set of equations (11) and (12) can, in theory, be solved for the oscillatory part of the translational temperature, as in the simple case above.

According to the theory of Schwartz, Slawsky, and Herzfeld (28) the probability of a vibrational transition occurring during a collision decreases rapidly with an increase in the amount of energy to be transferred to or from translational motion. Thus, in the case of parallel relaxation a separate relaxation time will be associated with each frequency of vibration, and equilibration between high-frequency modes and translation may take place very slowly. Consequently, complex collisions, in which the energy exchanged with translation is decreased by increasing the number of vibrational quanta involved, may play an important role in vibrational relaxation in polyatomic molecules. In a complex collision a quantum of vibrational energy is transferred from one vibrational mode to another, with only the energy difference being absorbed or supplied by the translational motion. The second limiting case, then, is that in which only the lowest-frequency vibrational mode exchanges energy directly with

translation, while other modes exchange with this one and with each other by complex collisions. Such a process is called relaxation in series.

Herzfeld and Litovitz (13, p. 117) have shown that the equations describing series relaxation in a polyatomic gas with n vibrational degrees of freedom are

$$- C_1 \frac{dT_1}{dt} = \frac{C_1}{\tau_1} (T_1 - T_{tr}) + \sum_{j=2}^n \frac{C_1}{\tau_{1j}} \sqrt{\frac{C_j}{C_1}} \left[\frac{\nu_1}{\nu_j} (T_1 - T_{tr}) - (T_j - T_{tr}) \right] \quad (13)$$

$$- C_s \frac{dT_s}{dt} = \sum_{j \neq s}^n \frac{C_s}{\tau_{sj}} \sqrt{\frac{C_j}{C_s}} \left[\frac{\nu_s}{\nu_j} (T_s - T_{tr}) - (T_j - T_{tr}) \right] \quad (14)$$

$$s = 2, 3, \dots, n.$$

Here ν_i is the vibration frequency of mode i , τ_{ij} is the relaxation time for exchange of energy between mode i and mode j , and all other symbols are defined as before. Since conservation of energy requires that in an isolated system

$$C_{tr} \frac{dT_{tr}}{dt} + \sum_{i=1}^n C_i \frac{dT_i}{dt} = 0,$$

the rate of change of translational energy is given by

$$C_{tr} \frac{dT_{tr}}{dt} = \frac{C_1}{\tau_1} (T_1 - T_{tr}) + \sum_{i=1}^n \sum_{j \neq i}^n \frac{C_i}{\tau_{ij}} \sqrt{\frac{C_j}{C_i}} \left[\frac{\nu_i}{\nu_j} (T_i - T_{tr}) - (T_j - T_{tr}) \right]. \quad (15)$$

The set of equations (13), (14), and (15), with a set of external driving functions, can be reduced to a particularly convenient and symmetric form, which in matrix notation is

$$-\dot{y} = Ky - d. \quad (16)$$

y is a vector whose components are given by

$$y_i = \sqrt{\frac{C_i}{C}} T_i' = \sqrt{f_i} T_i',$$

where C_i is the heat capacity of the i -th degree of freedom (including translation) at the equilibrium temperature T_0 , and C is the total heat capacity of the system. f_i is thus the fractional heat capacity associated with the i -th degree of freedom. T_i' is the deviation of the instantaneous temperature of the i -th degree of freedom from the equilibrium temperature, i. e. ,

$$T_i' = T_i - T_0.$$

K is the rate matrix for the relaxation process, and d is a vector whose components d_i are the driving functions for the various degrees of freedom. \dot{y} indicates differentiation of the vector y with respect to the time. It can be shown that when the set of equations (13), (14), and (15) is reduced to the form of equation (16) the matrix K is symmetric, i. e. , $K_{ij} = K_{ji}$.

If the driving functions d_i are periodic, and are given by

$$d_i = d_i^0 \exp(i\omega t), \quad (17)$$

it can be assumed that the y_i 's are also periodic with the same frequency, and have the form

$$y_i = y_i^0 \exp(i\omega t). \quad (18)$$

Substitution of equations (17) and (18) in equation (16) gives

$$-i\omega y = Ky - d,$$

where the superscript zero has been dropped. Thus,

$$y = (K + i\omega E)^{-1} d, \quad (19)$$

where E is the unit matrix. Since K is a symmetric matrix it can be diagonalized by the transformation

$$L^{-1}KL = \text{diag } k, \quad (20)$$

in which the matrix L is orthogonal, i. e., $L^{-1} = L'$. The matrix $\text{diag } k$ is diagonal with elements $(\text{diag } k)_{ii} = k_i$, where the k_i 's are eigenvalues of the matrix K . The columns of the matrix L are the eigenvectors of K .

It should be noted that conservation of energy requires that

$$\sum_i \frac{C_i}{C} \dot{T}_i' = \sum_i (f_i)^{\frac{1}{2}} \dot{y}_i = \sum_i (f_i)^{\frac{1}{2}} d_i,$$

which is equivalent to stating that the rows of the K matrix are linearly dependent. Thus at least one eigenvalue of K vanishes; its corresponding eigenvector has components $(f_i)^{\frac{1}{2}}$.

From equation (20),

$$K = L(\text{diag } k)L^{-1}.$$

Substitution for K in equation (19) yields

$$y = [L(\text{diag } k)L^{-1} + i\omega E]^{-1}d$$

or

$$y = L[(\text{diag } k) + i\omega E]^{-1}L^{-1}d.$$

Thus, by the rules of matrix multiplication and the orthogonality of L ,

$$y_i = \sum_j \sum_k L_{ij} (k_j + i\omega)^{-1} L_{kj} d_k = \sum_j \frac{A_{ij}}{k_j + i\omega},$$

where

$$A_{ij} = \sum_k L_{ij} L_{kj} d_k.$$

It is important to note at this point that the eigenvalues or characteristic frequencies, k_j , of the system are determined

entirely by the elements of the K matrix, and are independent of the method of excitation of the system, specifically, the magnitudes of the driving functions, d_i . However, the amplitudes, A_{ij} , associated with the eigenvalues do depend upon the method of excitation, so that although the characteristic relaxation frequencies should be the same in both the spectrophone and ultrasonic dispersion experiments, the amplitudes corresponding to a given relaxation frequency may well be different in the two types of experiments.

For a molecule with n degrees of freedom ($n - 1$ vibrations plus translation) the oscillatory part of the translational temperature is given by

$$y_n = \sum_{j=1}^n \frac{A_{nj}}{k_j + i\omega},$$

where the subscript n refers to the translational degree of freedom.

If a single vibrational mode, k' , is excited, $d_{k'}$ is the only non-zero component of the vector d , and the amplitudes A_{nj} are given by

$$A_{nj} = L_{nj} L_{k'j} d_{k'}.$$

From the orthogonality of the matrix L ,

$$\sum_{j=1}^n A_{nj} = 0. \quad (22)$$

If k_1 denotes the vanishing eigenvalue of the matrix K , substitution from equation (22) for A_{n1} in equation (21) yields

$$y_n = \sum_{j=2}^n A_{nj} \left(\frac{1}{k_j + i\omega} - \frac{1}{i\omega} \right),$$

or

$$y_n = \frac{-1}{i\omega} \sum_{j=2}^n \frac{A_{nj}}{(1 + i\omega/k_j)} . \quad (23)$$

If one eigenvalue, k_2 , is much smaller than all others (except, of course k_1 , which is zero), the approximate behavior of y_n in the frequency range for which $\omega \ll k_j$, $j \neq 1$ or 2 , is described by

$$y_n \approx \frac{-1}{i\omega} \left[\frac{A_{n2}}{1 + i\omega/k_2} + \sum_{j=3}^n A_{nj} \right],$$

or

$$y_n \approx \frac{-1}{i\omega} \left[\frac{A_{n2}}{1 + i\omega/k_2} + B \right],$$

where $B = \sum_{j=3}^n A_{nj}$, a constant.

As an example of the method outlined above for the solution of the equations describing relaxation in series, the specific case of a gas with two vibrational degrees of freedom will be discussed. Indicating the translational degree of freedom by the subscript three,

and collecting coefficients of the T_i 's, equations (13), (14), and (15)

become for such a case

$$-C_1 \frac{d}{dt}(T_1 - T_0) = \left[\frac{C_1}{\tau_1} + \frac{\sqrt{C_1 C_2}}{\tau_{12}} \quad \frac{\nu_1}{\nu_2} \right] (T_1 - T_0) - \frac{\sqrt{C_1 C_2}}{\tau_{12}} (T_2 - T_0) \\ + \left[-\frac{C_1}{\tau_1} + \frac{\sqrt{C_1 C_2}}{\tau_{12}} \quad \frac{\nu_3}{\nu_2} \right] (T_3 - T_0) - C_1 D_1$$

$$-C_2 \frac{d}{dt}(T_2 - T_0) = -\frac{\sqrt{C_1 C_2}}{\tau_{12}} (T_1 - T_0) + \frac{\sqrt{C_1 C_2}}{\tau_{12}} \frac{\nu_2}{\nu_1} (T_2 - T_0)$$

$$-\frac{\sqrt{C_1 C_2}}{\tau_{12}} \frac{\nu_3}{\nu_1} (T_3 - T_0) - C_2 D_2$$

$$-C_3 \frac{d}{dt}(T_3 - T_0) = \left[-\frac{C_1}{\tau_1} + \frac{\sqrt{C_1 C_2}}{\tau_{12}} \quad \frac{\nu_3}{\nu_2} \right] (T_1 - T_0)$$

$$-\frac{\sqrt{C_1 C_2}}{\tau_{12}} \frac{\nu_3}{\nu_1} (T_2 - T_0)$$

$$+ \left[\frac{C_1}{\tau_1} + \frac{\sqrt{C_1 C_2}}{\tau_{12}} \frac{\nu_3^2}{\nu_1 \nu_2} \right] (T_3 - T_0) - C_3 D_3 ,$$

where $\nu_3 = \nu_2 - \nu_1$, and the driving functions D_i are included. Introducing the change of variable

$$y_i = (f_i)^{\frac{1}{2}} T_i' = (f_i)^{\frac{1}{2}} (T_i - T_0)$$

and the relation

$$d_i = (f_i)^{\frac{1}{2}} D_i,$$

a straightforward calculation shows that the matrix K has the following form, in which

$$k_1 = \frac{f_1}{\tau_1}, \quad k_{12} = \frac{\sqrt{f_1 f_2}}{\nu_1 \nu_2 \tau_{12}}.$$

$$K = \begin{bmatrix} \frac{k_1 + k_{12}^{\nu_1^2}}{f_1} & \frac{-k_{12}^{\nu_1 \nu_2}}{\sqrt{f_1 f_2}} & \frac{-k_1 + k_{12}^{\nu_1 \nu_3}}{\sqrt{f_1 f_3}} \\ \frac{-k_{12}^{\nu_1 \nu_2}}{\sqrt{f_1 f_2}} & \frac{k_{12}^{\nu_2^2}}{f_2} & \frac{-k_{12}^{\nu_2 \nu_3}}{\sqrt{f_2 f_3}} \\ \frac{-k_1 + k_{12}^{\nu_1 \nu_3}}{\sqrt{f_1 f_3}} & \frac{-k_{12}^{\nu_2 \nu_3}}{\sqrt{f_2 f_3}} & \frac{k_1 + k_{12}^{\nu_3^2}}{f_3} \end{bmatrix}$$

For the spectrophone response, y_3 (the oscillatory part of the translational temperature) is the variable of interest. If energy is being added only to vibrational mode two, d_2 is the only non-zero component of the vector d , and the amplitudes of interest are

$$A_{3j} = L_{3j} L_{2j} d_2.$$

If k_1 again denotes the vanishing eigenvalue of the matrix K, the

form of the solution for y_3 is, from equation (23),

$$y_3 = \frac{-1}{i\omega} \left[\frac{A_{32}}{1 + i\omega/k_2} + \frac{A_{33}}{1 + i\omega/k_3} \right] .$$

Assuming that k_2 and k_3 are well separated, with $k_3 \gg k_2$, it is interesting to consider the behavior of y_3 in the frequency range $\omega \ll k_3$. In this range y_3 has the approximate form

$$y_3 \approx \frac{-1}{i\omega} \left[\frac{A_{32}}{1 + i\omega/k_2} + A_{33} \right] ,$$

and the magnitude of y_3 is given by

$$|y_3| \approx \frac{1}{\omega} \left[\frac{A_{32}^2 + 2A_{32}A_{33}}{1 + \omega^2/k_2^2} + A_{33}^2 \right]^{\frac{1}{2}} .$$

At frequencies for which $\omega \ll k_2$ the product $\omega |y_3|$ should be constant, and equal to $(A_{32}^2 + A_{33}^2)$, while as ω approaches k_2 this product decreases, becoming equal to A_{33} in the range $k_2 \ll \omega \ll k_3$.

EXPERIMENTAL PROCEDURE

The experimental data for this research was obtained from measurements of the amplitude of the spectrophone signal produced when a periodically interrupted beam of infrared radiation was passed through the cell containing an infrared-active gas. The behavior of this amplitude was studied as the light-chopping frequency was varied.

Apparatus

The apparatus employed in this work is essentially the same as that used by Woodmansee (37), and is shown in block form in Figure 1. The basic components are a source of radiation (A), a mechanical chopping device for modulating the radiation (C), the spectrophone cell, and a means for amplification and measurement of the signal produced at the microphone in the cell.

In a number of preliminary measurements a Perkin-Elmer Nernst glower served as the infrared source. This glower is of the type used in modern infrared spectrometers, and was operated in the manner described by Woodmansee (37, p. 26) at a current of 0.3 amperes. In later work a Sylvania Type DWY "Sun Gun" movie lamp was used. This lamp consists of a tungsten filament enclosed in a glass envelope which is filled with iodine vapor. It is designed to operate at 118 volts with a black body temperature of 3400°K. Due

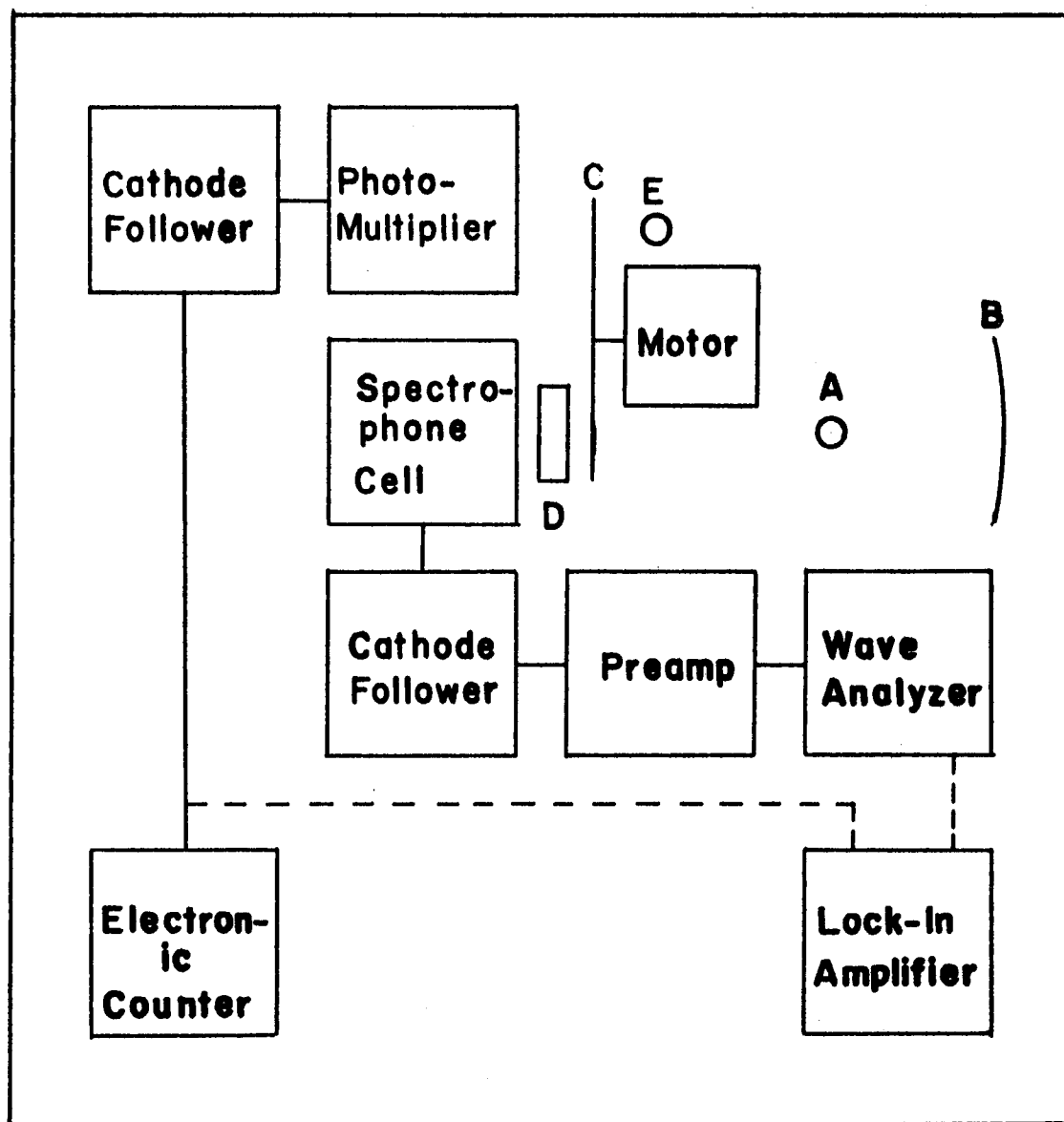


Figure 1. Block Diagram of Spectrophone Apparatus.

to the transmission properties of the glass envelope this lamp is restricted to use at wavelengths less than about 3.5 microns. A similar lamp, Sylvania Type DXL, was also used. This lamp has a slightly higher black body temperature than the Type DWY, and employs a quartz envelope, permitting its use at wavelengths up to about 4.5 microns. In their regions of usefulness both Sylvania lamps gave a substantial gain in intensity over the Nernst glower, resulting in a significant increase in the magnitude of the spectrophone signal.

Light from the infrared source was focused by a 20 cm spherical front surface mirror (B) to form an image of the source in the plane of the light chopper. An iris diaphragm located between the source and the chopper was used to mask the beam to approximately the size of the holes in the chopping disk.

A chopping disk of 1/16 inch aluminum sheet, seven inches in diameter, with 20 1/2 inch diameter holes uniformly spaced along its periphery was mounted on a Globe fractional horse-power synchronous motor. This motor was driven by a Hewlett-Packard audio oscillator through a Dynakit 50 watt audio amplifier. The phase of the amplifier output was split by means of a capacitance substitution box containing capacitors of 4, 10, 16, 25, 30, 40, 50, and 60 microfarads. An ammeter was placed between the audio amplifier and the motor so that the motor current could be maintained at its specified value of 0.32 amperes by adjustment of the audio oscillator output

voltage. With this arrangement the motor could be driven at shaft revolution rates from 5 to 160 rps, corresponding to chopping frequencies from 50 to 1600 cps. At frequencies beyond this range the motor speed tended to drift significantly. A shield of 1/4 inch fibre board was placed between the light chopper and the cell to absorb sound which was generated by the chopping disk at frequencies above 1000 cps. In addition, the cell was placed on a 1-1/2 inch thick rubber sponge pad in order to uncouple it from vibrations in the mounting bench produced by the chopper.

For many of the signal amplitude measurements a light filter (D) was used to permit excitation of a single vibrational band in the gas being studied. For studies of the 3.3 micron band in methane this filter consisted of a glass microscope slide whose infrared spectrum showed 55 percent transmission at 3.3 microns, and zero percent at wavelengths greater than 5 microns. For studies of the 7.7 micron band in methane an Eastman Kodak Type 250S far infrared filter was employed. The transmittance of this filter is about 50 percent at 7.7 microns, and zero percent at wavelengths less than 4.5 microns.

The spectrophone cell used by Woodmansee in his high pressure studies (37, p. 33) was employed in this work, and is shown in Figure 2. Preliminary measurements were made with the same Turner No. 11 moving-coil microphone used by Woodmansee, which

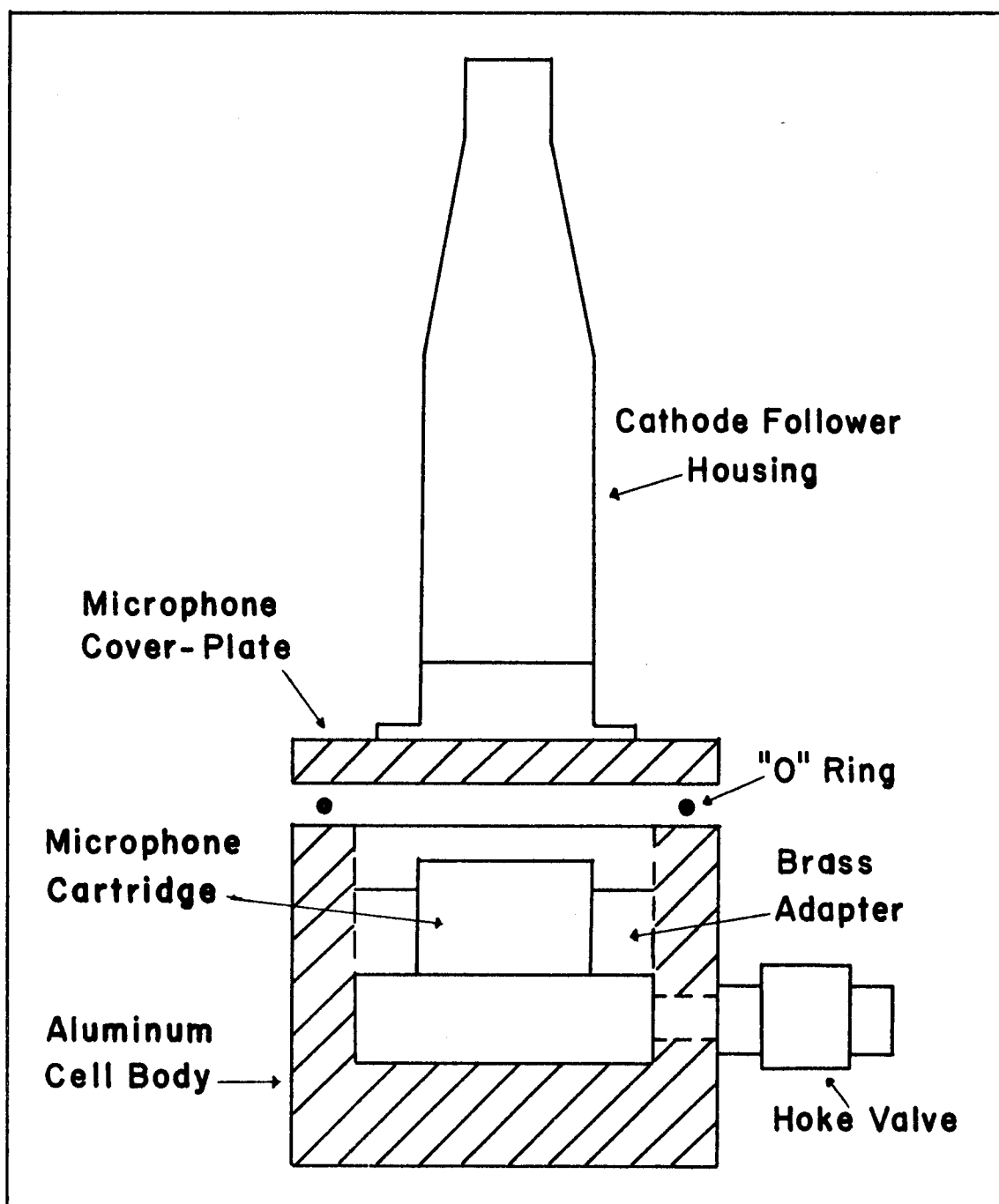


Figure 2. Spectrophone Cell.

has a sensitivity of 54 db below 1 volt/dyne/sq cm and a frequency response of ± 2.5 db between 50 and 10,000 cps. The microphone leads were connected to the 200 ohm primary tap of a Turner TR-2 matching transformer, which amplified the microphone voltage by a factor of ten. The high-impedance secondary of the transformer was connected to the preamplifier input.

In later measurements a Brüel and Kjaer Type 4132 one inch condenser microphone cartridge was used in the spectrophone cell. This cartridge was mounted in a brass adapter of the same diameter as the Turner No. 11 microphone so that its installation required no modification of the cell interior. Details of the installation are illustrated in Figure 2. The microphone cartridge leads were connected to a Brüel and Kjaer Type 2613 cathode follower, which was specifically designed for use with this cartridge, and which was mounted directly on the microphone cover plate outside the cell. The manufacturer's specifications for the combined cartridge and cathode follower include a sensitivity at 250 cps of 48.1 db below 1 volt/dyne/sq cm and a frequency response of ± 1 db between 20 and 8000 cps, both measured with a polarization voltage of 200 volts applied to the cartridge. The cathode follower has an input impedance of 270 megohms in parallel with 3 micromicrofarads, an output impedance of 750 ohms, and a gain of -0.8 ± 0.2 db. The self-generated noise level is approximately 20 microvolts in the frequency range 20 to 20,000

cps, corresponding to approximately 0.14 microvolts per unit bandwidth. The 200 volt polarization voltage for the microphone cartridge and the 150 volt plate supply for the cathode follower were provided by a Lambda Model 28 regulated power supply, while the cathode follower filament was powered by a storage battery.

The cathode follower output was connected through shielded cable to the input of a Tektronix Type 122 low level preamplifier which has gain settings of 100 or 1000. The high-frequency cutoff of this preamplifier can be adjusted to give three-decibel points at 50 cps, 250 cps, 1000 cps, 10 kc, or 40 kc. The low-frequency cutoff can similarly be varied to give three-decibel points at 0.2, 0.8, 8, or 80 cps. Amplifier linearity is within five percent with output levels below 20 volts peak-to-peak at high gain setting and below ten volts peak-to-peak at low gain setting. The self-generated noise level is four microvolts, expressed as equivalent input, for a 40 kc bandwidth, corresponding to 0.02 microvolts per unit bandwidth. The necessary high voltages for the preamplifier were obtained from a Lambda Model 28 power supply in the manner described by Woodmansee (37, p. 36), while the filaments were powered by storage batteries.

The output of the preamplifier was taken to a Hewlett-Packard Model 302A harmonic wave analyzer (26). This instrument is a tunable, narrow passband AC voltmeter, and can be used to measure

voltages in the frequency range 20 cps to 50 kc with an accuracy of five percent. The accuracy of the dial for frequency determinations is $\pm (1 \text{ percent} + 5 \text{ cps})$. Full scale voltage readings are available from 30 millivolts to 300 volts in 15 ranges in a 30, 100, 300 sequence. The selectivity of the wave analyzer is such that a signal $\pm 3.5 \text{ cps}$ from the band center is reduced by three decibels; at $\pm 25 \text{ cps}$ a signal is down 50 db, and at $\pm 70 \text{ cps}$ 80 db reduction takes place. Due to the high selectivity of this instrument, an automatic frequency control circuit is provided, which tracks a signal of slowly varying frequency over a range of $\pm 100 \text{ cps}$ from the band center before control is lost. The automatic frequency control may be locked out by operation of the instrument in the Normal mode. The wave analyzer provides a restored frequency output signal, whose frequency is that of the input signal, and whose amplitude is proportional to the needle deflection of the voltage meter, up to a maximum of one volt. A variable attenuator is provided to decrease the amplitude of the output signal.

In order to obtain more accurate frequency determination than is possible with the wave analyzer, the photomultiplier arrangement shown in Figure 1 was used. Light from a dry cell flashlight (E) was focused through the chopper onto the light-sensitive cathode of an RCA-931A photomultiplier tube. This photomultiplier and its associated cathode follower were used by Woodmansee to provide a

reference signal for his phase shift measurements (37, p. 43). The necessary high voltage for the photomultiplier tube was supplied by a Baird-Atomic Model 312A super-stable power supply, while the plate and filament voltages for the cathode follower were provided by a Lambda Model 28 power supply. The cathode follower output was taken to a Hewlett-Packard Model 5232A electronic counter, which can be used to measure frequencies in the range 2 cps to 1.2 Mc. The maximum accuracy obtainable with this counter at 1000 cps is one part in 10^4 .

With the Nernst glower serving as the infrared source the spectrophone signal at gas pressures lower than about 50 mm Hg was too weak to be adequately measured with the harmonic wave analyzer. In such cases a Model JB-5 lock-in amplifier (25) manufactured by the Princeton Applied Research Corporation was employed, as shown in the block diagram in Figure 1. The lock-in amplifier is a narrow band detection system in which a signal is beat with a reference signal of the same frequency, giving a d-c output. The basic component of the lock-in amplifier is a phase-sensitive or synchronous detector, essentially a balanced mixer. The lower side band (d-c) derived from the mixer is passed by a low-pass filter, the bandwidth of which determines the bandwidth of the amplifier. The lock-in amplifier derives its name from the fact that the center frequency of the pass-band is determined by the reference frequency; thus, if the input and

reference signals are derived from the same frequency source, the center of the passband is always locked to the signal frequency. In the Model JB-5 the input signal is first passed through a narrow band tuned amplifier; this initial stage reduces noise signals that could overdrive the phase-sensitive detector, thus allowing a larger output before non-linearity is encountered. In the reference channel a variable phase-shifter controls the phase between reference and signal. Since the waveform applied to the input of the phase-shifter must be nearly sinusoidal, a tuned amplifier is also provided in the reference channel. When a nearly sinusoidal reference signal is available externally, the tuned amplifier may be switched out of the reference circuit. In addition, the tuned amplifier can be used with a positive feedback loop as an oscillator, thus providing an internal reference, as well as an external sinusoidal output. The output of the low-pass filter, after passing through a d-c amplifier, can be read from a meter on the front panel of the instrument, and is also available to drive a strip chart recorder. The tuned amplifiers in the signal and reference channels are gang-tuned over the full operating range of the instrument, which is 1.5 cps to 150 kc, in five ranges. The minimum equivalent bandwidth obtainable with this instrument is 0.025 cps, although provision is made for the use of external capacitors to achieve even narrower bandwidths as desired.

For measurements of spectrophone signals the input to the

lock-in amplifier was taken from the restored frequency output of the harmonic wave analyzer. In this application the wave analyzer essentially served as tunable, narrow passband filter, with a bandwidth of a few cps, and was very effective in reducing noise signals reaching the input of the lock-in amplifier. It was necessary to first tune the wave analyzer to the proper frequency by applying the photo-multiplier output to the wave analyzer input, after which the photo-multiplier output was connected to the reference input of the lock-in amplifier.

The limiting factor for signal detection with the amplification and measuring system employed in this research is the noise level of 0.14 microvolts per unit bandwidth generated by the microphone cathode follower. It is of interest to compare this figure with the noise level due to random pressure fluctuations in the gas, which is 110 db below 1 dyne/sq cm at one atmosphere pressure (35, p. 24); with the microphone sensitivity of 48.1 db below 1 volt/dyne/sq cm this level is 0.013 microvolts per unit bandwidth. Assuming the effective bandwidth of the harmonic wave analyzer to be 10 cps, and with a 1000-fold gain provided by the Tektronix preamplifier, the noise voltage at the wave analyzer meter should be approximately 0.5 millivolts. Experimentally, the measured noise level at a frequency of 400 cps was approximately one millivolt, in fair agreement with the predicted value. The practical lower limit, then, for

measurement of spectrophone signals with the harmonic wave analyzer was a signal level of one millivolt. The lowest signal level measured with the lock-in amplifier during the course of this work was approximately 0.5 millivolts, and at this level the signal was recovered with good stability. Theoretically, the lock-in amplifier should permit measurement of considerably weaker signals. The manufacturer specifies that with this instrument a signal 47 db below ambient white noise in a one kilocycle bandwidth centered about the signal frequency can be recovered with a signal-to-noise ratio of one. For a 10 cps bandwidth this level is equivalent to 27 db below ambient white noise, and for a noise level of one millivolt in this bandwidth the minimum detectable signal should be approximately 0.05 millivolts. With the 1000-fold gain of the preamplifier and the microphone sensitivity of 48.1 db below 1 volt/dyne/sq cm, this signal level is equivalent to a pressure variation in the gas of approximately 1.3×10^{-4} dyne/sq cm.

Procedure

The vacuum system illustrated in block form in Figure 3 was used to prepare gas samples for study and to evacuate and fill the spectrophone cell. Prior to filling, the cell was evacuated and pumped down for at least two hours; after flushing with the gas to be studied, the cell was again evacuated, and gas was admitted to the

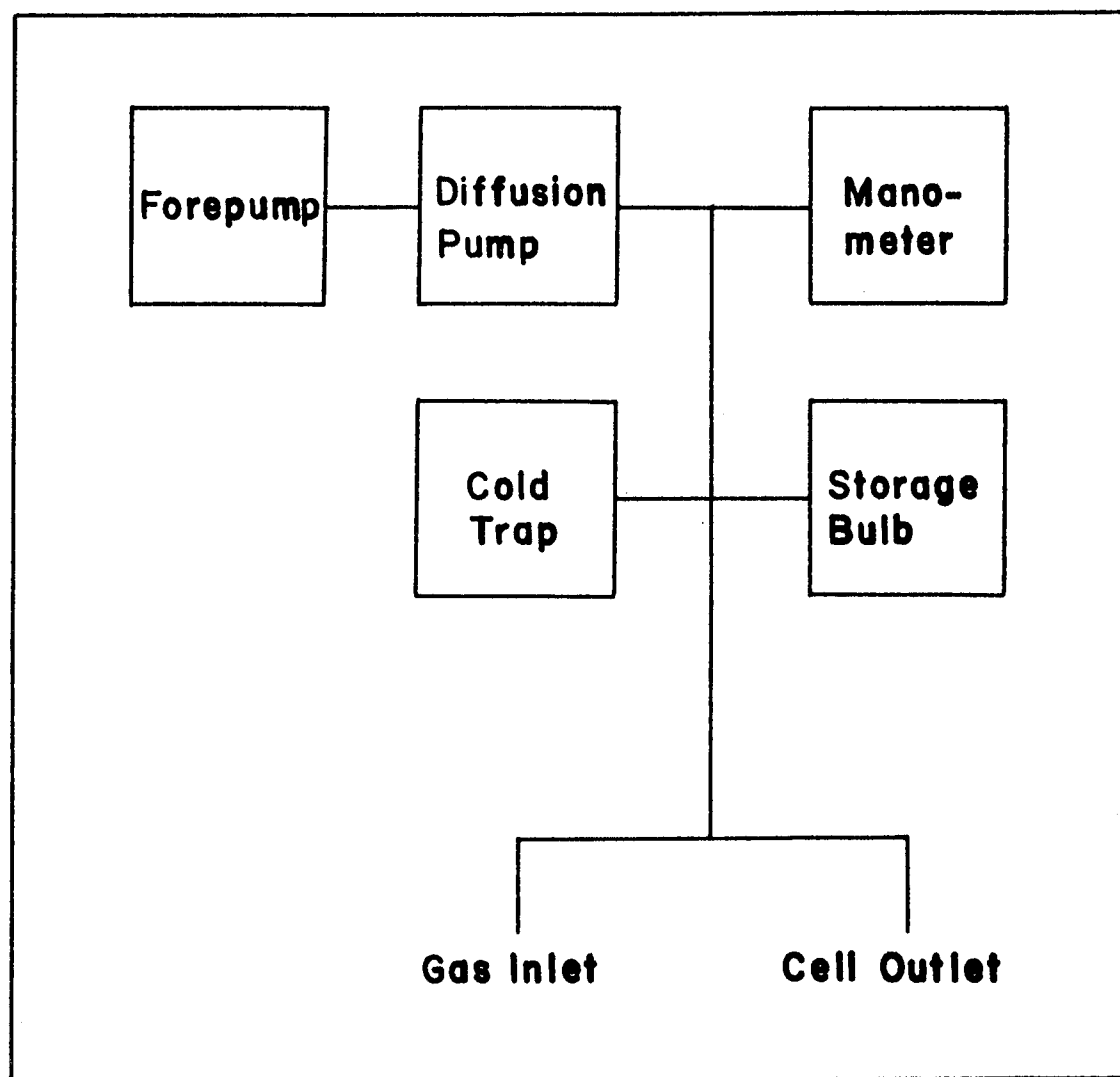


Figure 3. Block Diagram of Vacuum System.

desired final pressure. It was necessary to evacuate and fill the cell slowly in order to avoid rupturing the diaphragm of the microphone cartridge; typically, pumping and filling rates were held to less than 100 mm Hg per minute.

After the cell was filled to the desired gas pressure it was removed from the vacuum system and placed behind the light chopper in the path of the infrared beam. The infrared source and all electronic components in the amplification and measuring system were turned on and allowed to warm up for a period of at least 30 minutes before any measurements were made. After the warm-up period the frequency and voltage of the audio oscillator output and the value of the phasing capacitor were adjusted to give the desired chopping frequency, as read from the electronic counter. The frequency dial of the harmonic wave analyzer was then adjusted to give the maximum voltage on the wave analyzer meter. In this manner the signal amplitude was measured at frequency intervals sufficient to determine its behavior over the range of chopping frequencies available with this apparatus.

Sample Preparation

Most of the gas samples studied in this work were taken from a cylinder of research grade methane supplied by the Phillips Petroleum Company, who specified the purity to be 99.58 mole percent, as

determined by mass spectrometric analysis. The most probable impurities were stated to be carbon dioxide, nitrogen, and ethane. The infrared spectrum of a sample taken directly from the cylinder was measured using a Beckman Model IR-7 spectrometer, and showed an absorption peak due to carbon dioxide at 2350 cm^{-1} . The height of this peak corresponded to a carbon dioxide concentration roughly equivalent to that in air, about 0.03 percent. No absorption was observed at 321 cm^{-1} , the center of a fairly intense band in ethane.

In order to further purify the methane prior to its admission to the spectrophone cell, one atmosphere of the gas from the cylinder was admitted to the storage bulb shown in Figure 3, and was allowed to stand over potassium hydroxide pellets for a period of at least 24 hours. Infrared analysis showed that this procedure reduced the carbon dioxide absorption at 2350 cm^{-1} to a level which was undetectable with the Beckman IR-7 spectrometer. It was estimated that this decrease in absorption corresponded to a reduction in the carbon dioxide concentration of at least two orders of magnitude.

After removal of carbon dioxide in this manner, the methane was withdrawn from the storage bulb by freezing the gas at liquid nitrogen temperature in the cold trap shown in Figure 3. The stopcock to the cold trap was then closed while the remainder of the system was evacuated, after which the cold trap was again opened to the system, and any highly-volatile impurities which may have been present were pumped off. The spectrophone cell was then opened to the

system, and the liquid nitrogen bath surrounding the cold trap was partially removed until the pressure in the system rose to the desired level. At this point the stopcock to the coldtrap was closed and the nitrogen bath was replaced. The spectrophone cell was then closed and removed from the vacuum system.

Gas mixtures of methane diluted with carbon dioxide were prepared by admitting carbon dioxide to the storage bulb until the desired partial pressure was attained. Methane was then admitted directly from the cylinder to bring the total pressure to one atmosphere. The storage bulb was closed and allowed to stand for several hours to insure adequate mixing of the gases, after which the spectrophone cell was filled to the desired total pressure directly from the storage bulb. The carbon dioxide used in these mixtures was taken from a cylinder supplied by the National Cylinder Gas Company.

The deuterated methanes studied in this research, CH_3D , CH_2D_2 , and CHD_3 , were obtained from the Volk Radiochemical Company, and were specified to be at least 98 percent enriched in deuterium. Prior to their study these compounds were purified in the manner described above for methane.

EXPERIMENTAL RESULTS

Initial Frequency Response Measurements

The spectrophone response data obtained by excitation of the 3.3 micron band in methane at pressures of 755 mm and 380 mm are listed in Table 2, and are illustrated graphically in Figure 4. The significant feature of these curves is their $1/\omega$ dependence, predicted by the theory, with no evidence of increased signal loss at higher frequencies due to relaxation phenomena. If a vibrational relaxation time of 100 microseconds were associated with the 3.3 micron band, as reported by Cottrell, Hunter, and Read (3), the response curves should show a significant increased signal loss in this frequency range, provided the amplitude associated with this relaxation time were not negligibly small relative to the amplitudes associated with other characteristic relaxation times for the gas. In order to investigate this point more fully, signal amplitude measurements were made using the light filters previously described to selectively excite both the 3.3 micron and 7.7 micron vibrational bands. The response data for these measurements, at 760 mm of methane, are listed in Table 3, and are illustrated in Figure 5. Aside from the signal magnitudes, no apparent differences exist between the two curves.

Table 2. Spectrophone Signal Measurements. Methane, 3.3 μ Band.

f(cps)	380 mm E(volts)	755 mm E(volts)
200	1.02	1.72
250	0.82	1.38
280	0.75	1.22
320	0.65	1.08
350	0.60	0.98
400	0.52	0.87
450	0.47	0.79
500	0.42	0.70
550	0.38	0.64
650	0.32	0.53
700	0.30	0.50
750	0.28	0.47
800	0.26	0.44
850	0.25	0.41
950	0.22	0.37
1000	0.21	0.35
1050	0.20	0.33
1100	0.19	0.31
1150	0.185	0.30
1200	0.18	0.29
1250	0.17	0.28
1300	0.16	0.27
1350	0.155	0.26
1400	0.15	0.25
1450	0.145	0.24
1500	0.14	0.23
1550	0.13	0.22
1600	0.13	0.21

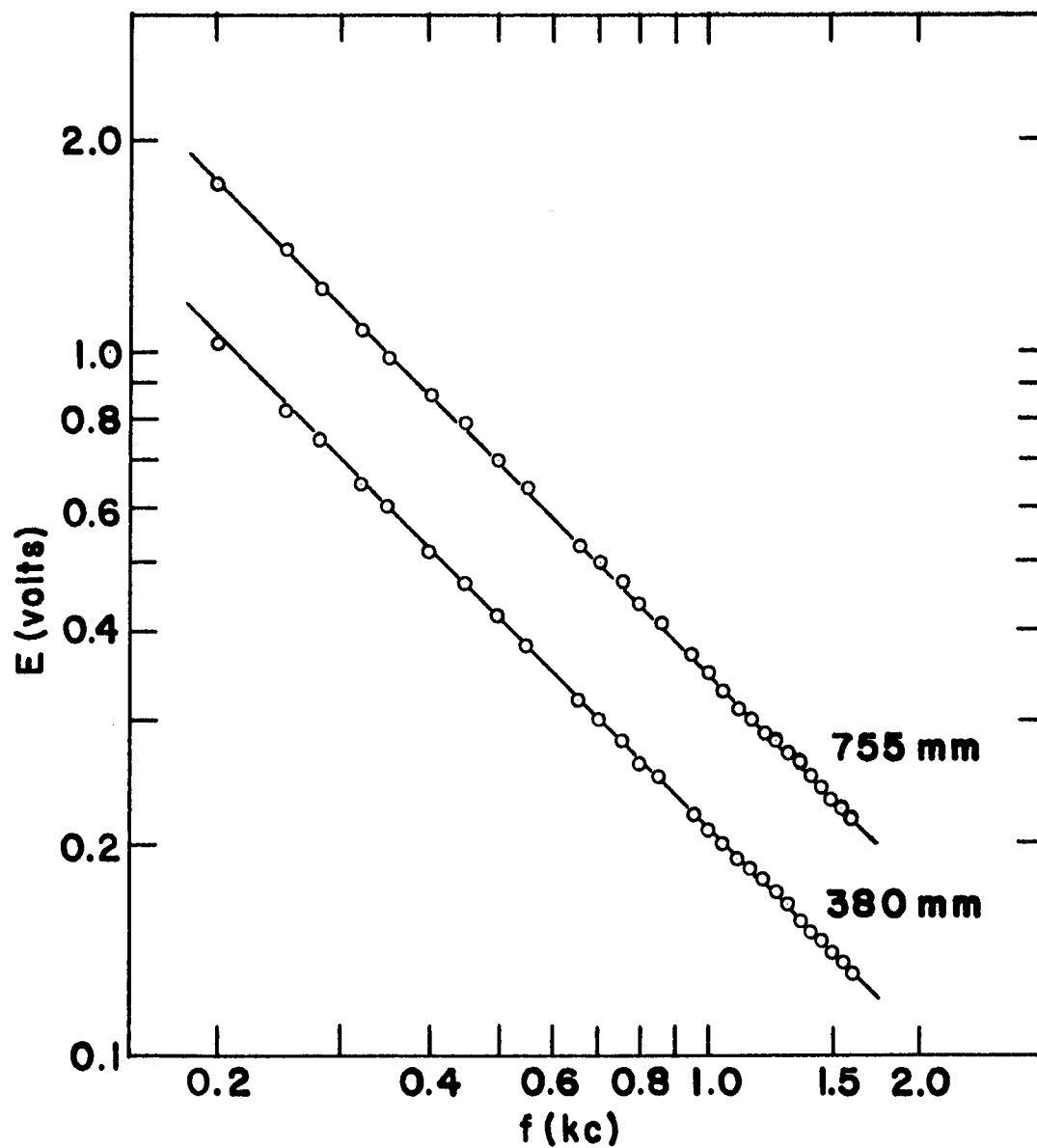


Figure 4. Spectrophone Signal vs Chopping Frequency. Methane, 3.3 μ Band.

Table 3. Spectrophone Signal Measurements. Methane, 760 mm.

f(cps)	3. 3 μ Band E(volts)	7. 7 μ Band E(volts)
100	0. 285	0. 215
110	0. 265	0. 20
130	0. 23	0. 17
140	0. 21	0. 155
150	0. 195	0. 145
160	0. 185	0. 135
170	0. 175	0. 13
190	0. 16	0. 115
200	0. 15	0. 11
220	0. 135	0. 10
260	0. 115	0. 089
280	0. 105	0. 083
320	0. 095	0. 073
340	0. 090	0. 069
380	0. 081	0. 061
400	0. 077	0. 058
450	0. 069	0. 051
500	0. 062	0. 046
550	0. 055	0. 042
600	0. 051	0. 038
650	0. 046	0. 035
700	0. 043	0. 032
750	0. 041	0. 030
800	0. 038	0. 029
850	0. 036	0. 027
900	0. 034	0. 025
950	0. 032	0. 024
1000	0. 029	0. 022
1050	0. 028	0. 021
1100	0. 026	0. 020
1150	0. 025	0. 019
1200	0. 024	0. 019
1250	0. 023	0. 018
1300	0. 022	0. 017
1350	0. 021	0. 016
1400	0. 021	0. 015
1450	0. 020	0. 015
1500	0. 019	0. 014
1600	0. 018	0. 013

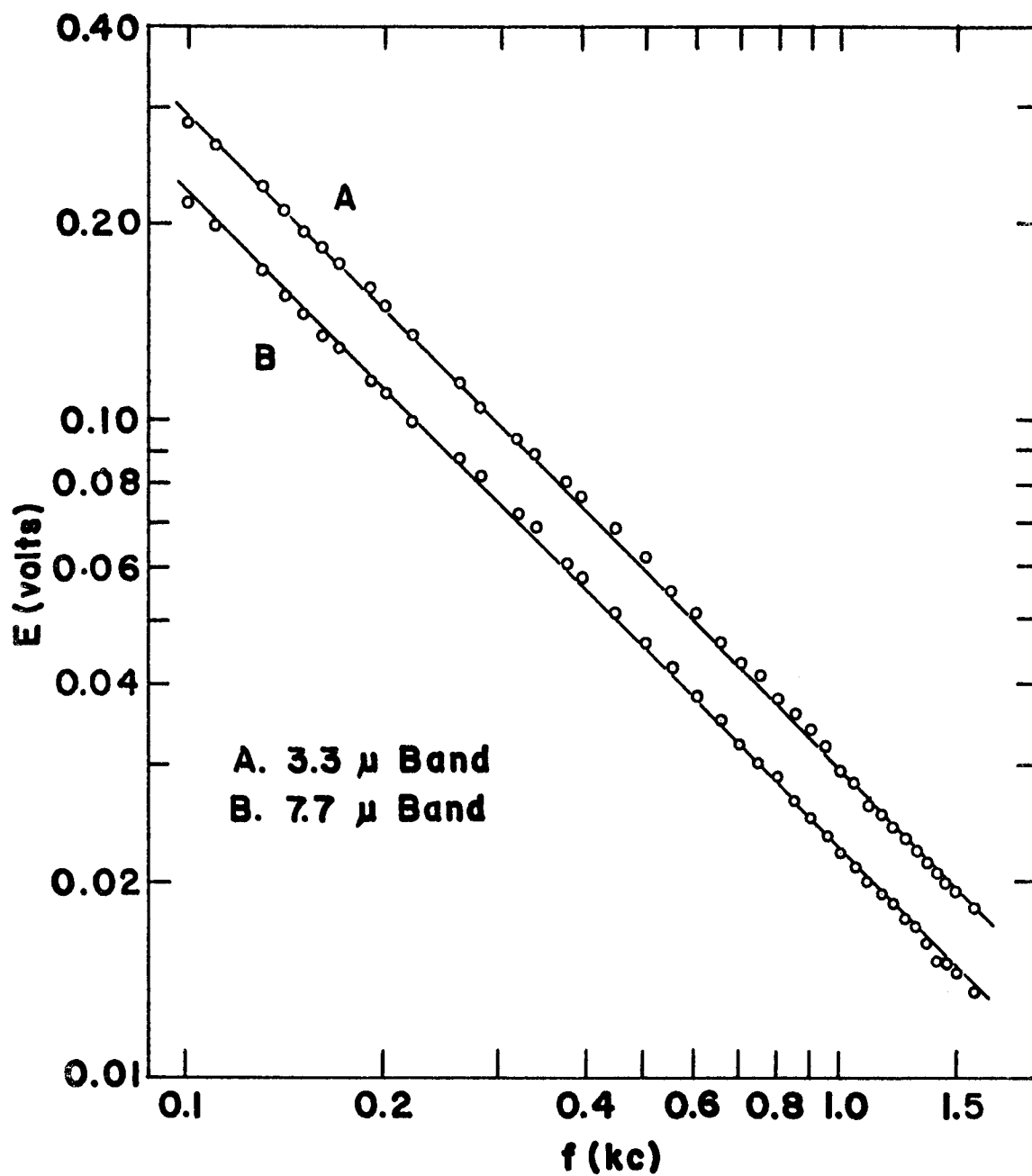


Figure 5. Spectrophone Signal vs Chopping Frequency. Methane, 760 mm.

None of the response curves described previously for methane show any of the acoustic resonance phenomena encountered by Woodmansee in his spectrophone studies (37, p. 51-56). In order to investigate the possible occurrence of acoustic resonances in gases other than methane, signal amplitude measurements were made with ethane in the spectrophone cell. The response data for these measurements, at pressures of 760 mm and 380 mm, are listed in Table 4 and illustrated in Figure 6. The response curves exhibit a resonance maximum at a chopping frequency of 1400 cps. Woodmansee demonstrated that the positions of the resonance maxima in the gases which he studied were directly proportional to the sound velocity in the gas (37, p. 65-68). Since the sound velocity in methane exceeds that in ethane by a factor of 1.43 (37, p. 69), the resonance maximum in methane would be expected to occur at approximately 2000 cps, well beyond the range of chopping frequencies covered in this work.

Response Studies of Methane at Low Pressures

On the assumption that the process of vibrational relaxation occurs by the mechanism of binary collisions, the effective relaxation time of a gas would be expected to be inversely proportional to the gas pressure. This behavior has been demonstrated for a number of gases by van Itterbeek and Mariens (36), who experimentally verified the relation

Table 4. Spectrophone Signal Measurements. Ethane.

f(cps)	380 mm E(volts)	760 mm E(volts)
200	1.40	2.12
250	1.12	1.70
280	1.00	1.52
320	0.87	1.34
350	0.80	1.22
400	0.71	1.05
450	0.64	0.95
500	0.56	0.87
550	0.51	0.80
650	0.43	0.67
700	0.40	0.61
750	0.37	0.57
800	0.35	0.53
850	0.33	0.50
950	0.30	0.45
1000	0.28	0.42
1050	0.26	0.40
1100	0.25	0.38
1150	0.23	0.35
1200	0.21	0.32
1250	0.185	0.28
1300	0.15	0.22
1350	0.10	0.15
1360	0.12	0.17
1370	0.18	0.26
1380	0.30	0.45
1390	0.41	0.67
1400	0.50	0.81
1410	0.49	0.79
1420	0.45	0.70
1430	0.42	0.64
1450	0.36	0.54
1470	0.32	0.49
1500	0.28	0.43
1550	0.25	0.38
1600	0.23	0.34

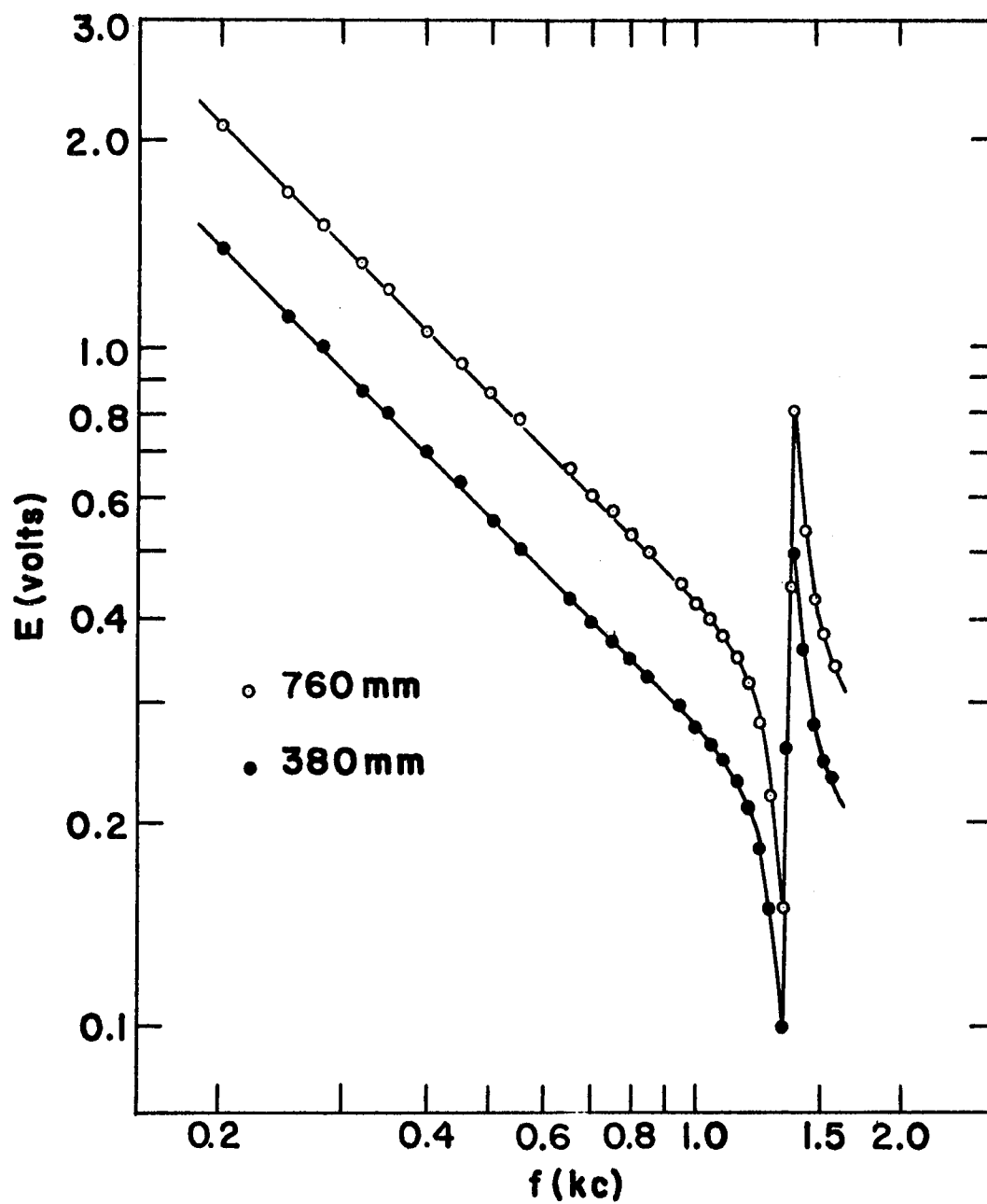


Figure 6. Spectrophone Signal vs Chopping Frequency. Ethane.

$$\tau = \tau_0/p,$$

where τ is the effective relaxation time, τ_0 is the relaxation time at one atmosphere pressure, and p is the gas pressure in atmospheres. Thus, if the pressure is reduced sufficiently, the vibrational relaxation time of a gas should increase to the point where a significant loss in the spectrophone signal would be observed in the range of chopping frequencies up to 1600 cps.

The response data for signal measurements obtained by excitation of the 3.3 micron band in methane at pressures of 5, 10, and 20 mm are listed in Table 5, and are illustrated graphically in Figure 7. Due to the high intensity of the Sylvania lamp source, a signal was also observed when the spectrophone cell was evacuated; the response curve for the empty cell is also shown in Figure 7. For each curve a 45 degree line has been drawn through the points at lower chopping frequencies, in order to illustrate any departure of the curves from $1/\omega$ behavior. As is evident from the figure, the response curve for five millimeters of methane shows a significant increased signal loss at higher frequencies, while this effect is exhibited to lesser degrees by the curves for 10 mm and 20 mm. The empty cell curve, on the other hand, shows no significant deviation from the 45 degree line.

As a check against any unexpected acoustic resonance

Table 5. Spectrophone Signal Measurements. Methane, 3.3 μ Band.

f(cps)	Empty Cell E(mv)	5 mm E(mv)	10 mm E(mv)	20 mm E(mv)
200	30	41	54	89
250	24	33	43	71
280	21.5	29	38	--
320	18.5	26	34	--
350	17	23	30	52
400	14.5	20	27	45
450	13	18	24.5	40
500	12	16	22	36
550	11	14.5	20	33
650	8.9	12	16.5	23
700	8.5	11	15	26
750	8.0	10	14	--
800	7.5	9.3	13.5	23
850	7.0	9.0	12.5	--
900	6.5	8.5	--	19
950	6.4	7.8	11	--
1000	6.0	7.5	10	17.5
1050	5.7	7.1	9.7	--
1100	5.4	6.6	9.5	16
1150	5.0	6.3	9.0	--
1200	4.7	6.0	8.7	14.5
1250	4.6	5.6	8.0	--
1300	4.4	5.3	7.8	13.5
1350	4.3	5.1	7.4	--
1400	4.3	5.0	7.1	12
1450	4.0	4.6	6.8	--
1500	3.8	4.5	6.5	10.5
1550	3.7	4.3	6.2	--
1600	3.6	4.0	6.0	10

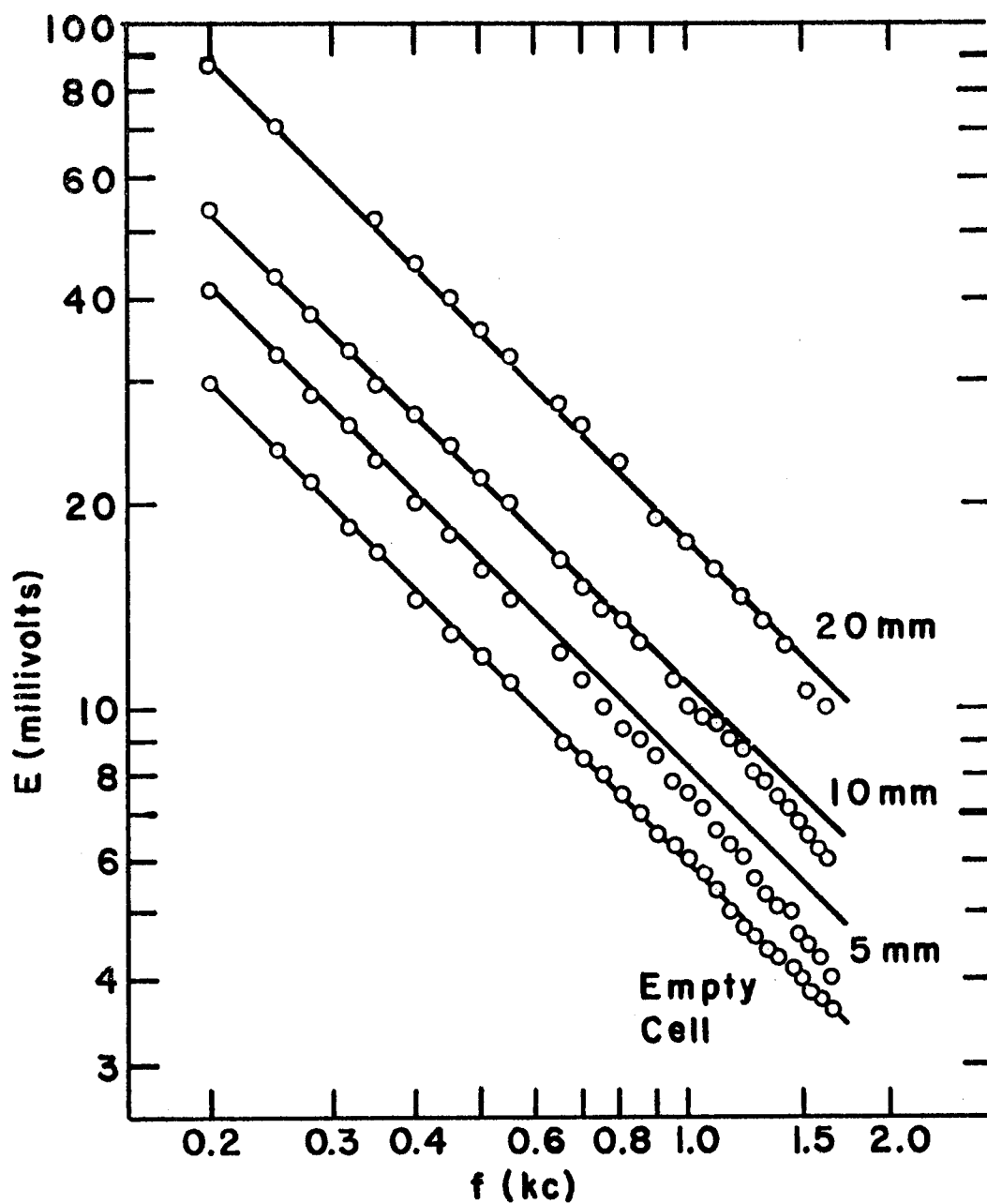


Figure 7. Spectrophone Signal vs Chopping Frequency. Methane, 3.3μ Band.

phenomena which could be responsible for the observed signal loss in methane at low pressures, Figure 8 illustrates the response curve obtained for ethane at 10 mm pressure. The position of the resonance maximum, at 1400 cps, is unchanged from the higher pressure curves, while the minimum is shifted to a slightly lower frequency. However, the curve appears to be completely free of resonance effects at frequencies up to at least 1000 cps; thus, any signal loss in methane due to acoustic resonance would be expected to occur only at frequencies above about 1450 cps. Since the observed signal loss in the response curve for five millimeters of methane begins at frequencies well below 1000 cps, it appears that this loss can hardly be attributed to resonance phenomena.

Table 6. Spectrophone Signal Measurements. Ethane, 10 mm.

f(cps)	E(mv)	f(cps)	E(mv)
200	158	1050	29
250	125	1100	27.5
280	112	1150	25.5
320	100	1200	24
350	91	1250	23
400	80	1300	24
450	72	1330	27
500	64	1350	29
550	59	1370	30
650	50	1400	31
700	45	1420	30
750	42	1450	29.5
800	40	1500	27
850	38	1550	25.5
950	34	1600	24
1000	31		

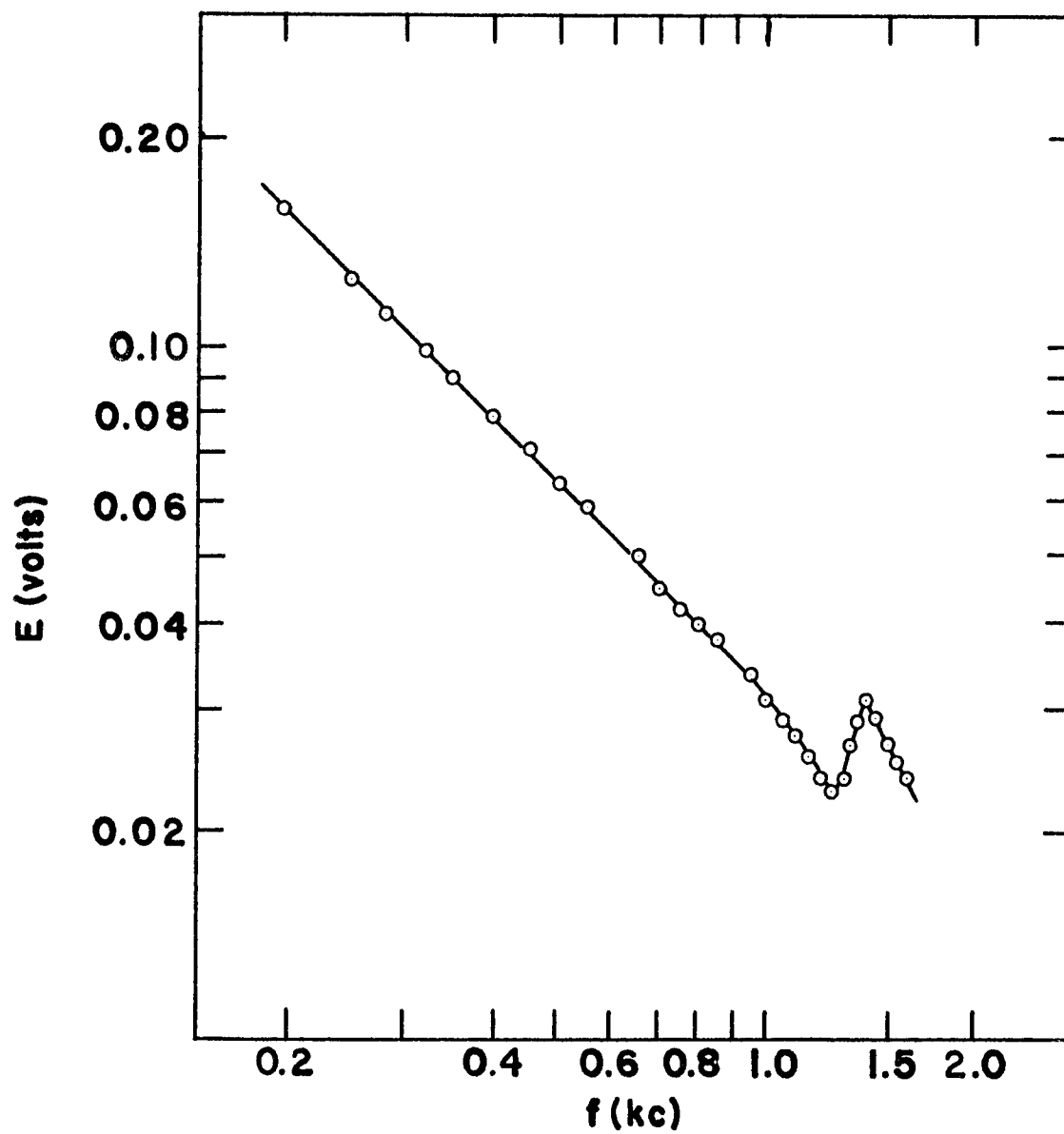


Figure 8. Spectrophone Signal vs Chopping Frequency. Ethane, 10 mm.

Due to the existence of the empty cell signal, the assignment of a vibrational relaxation time for methane based on the response curves shown in Figure 7 is somewhat complicated. In a previous section of this thesis the spectrophone response to be expected from a polyatomic gas with one eigenvalue, k_2 , small relative to other non-zero eigenvalues was shown to have the form

$$y_{tr} = \frac{-1}{i\omega} \left[\frac{A}{1 + i\omega/k_2} + B \right]$$

in the frequency range for which $\omega \ll k_j$, $j \neq 1$ or 2. The microphone signal produced by the gas will be proportional to y_{tr} , while the empty cell signal has been shown to behave as $1/\omega$. Thus, the overall spectrophone response may be described by

$$R = \frac{-1}{i\omega} \left[\frac{A}{1 + i\omega/k_2} + B + C \right],$$

where C is an "amplitude" associated with the empty cell. The observed spectrophone signal, E , is proportional to the magnitude of the response, and is given by

$$E^2 = \rho^2 |R|^2 = \frac{\rho^2}{\omega^2} \left[\frac{A^2 + 2A(B+C)}{1 + (\omega/k_2)^2} + B^2 + 2BC + C^2 \right],$$

where ρ is a proportionality constant. Collecting constants, E^2

takes the form

$$E^2 = \frac{\rho^2}{\omega^2} \left[\frac{A'}{1 + (\omega\tau')^2} + B' \right] + E_0^2 ,$$

in which $E_0 = \rho C/\omega$ is the observed empty cell signal, and $\tau' = 1/k_2$.

The above equation yields the relation

$$\omega^2(E^2 - E_0^2) = \rho^2 \left[\frac{A'}{1 + (\omega\tau')^2} + B' \right] . \quad (24)$$

Thus, a study of the quantity $\omega^2(E^2 - E_0^2)$ in the frequency range where the product $\omega\tau'$ is comparable to unity should afford a determination of the relaxation time τ' .

Figure 9 shows the behavior of the reduced spectrophone response, $f^2/f_L^2(E^2 - E_0^2)$, for the methane response curves illustrated in Figure 7. Here f is the cyclic chopping frequency ($f = \omega/2\pi$), and f_L is the lowest frequency at which signal amplitude measurements were made. For the curves shown in Figure 9 $f_L = 200$ cps. The solid curves shown in the figure are the results of fitting the experimental points to the function $F = M/[1 + (\omega\tau')^2]$ by the method of least squares, with M and τ' as parameters. In fitting the points to this function, the assumption has been made that the constant B' in equation (24) is small relative to A' . This assumption appears to be justified by the fairly close fit obtained.

Table 7. Reduced Spectrophone Response. Methane, 3.3 μ Band.

f(cps)	$\frac{f^2}{f_L^2} (E^2 - E_0^2) \quad (10^3 \text{ millivolts}^2)$		
	5 mm	10 mm	20 mm
200	0.810	2.05	7.05
250	0.826	2.02	7.00
280	0.777	1.96	--
320	0.859	2.09	--
350	0.745	1.89	7.41
400	0.729	2.05	7.23
450	0.769	2.17	7.23
500	0.729	2.15	7.23
550	0.721	2.15	7.37
650	0.650	2.00	7.41
700	0.611	1.88	7.41
750	0.535	1.88	--
800	0.513	2.05	7.59
850	0.588	1.95	--
900	0.588	--	6.44
950	0.505	1.85	--
1000	0.528	1.63	6.79
1050	0.520	1.72	--
1100	0.447	1.88	6.87
1150	0.439	1.80	--
1200	0.425	1.88	6.70
1250	0.354	1.63	--
1300	0.312	1.70	6.61
1350	0.312	1.62	--
1400	0.354	1.60	6.19
1450	0.245	1.60	--
1500	0.271	1.51	5.45
1550	0.238	1.43	--
1600	0.158	1.42	5.53

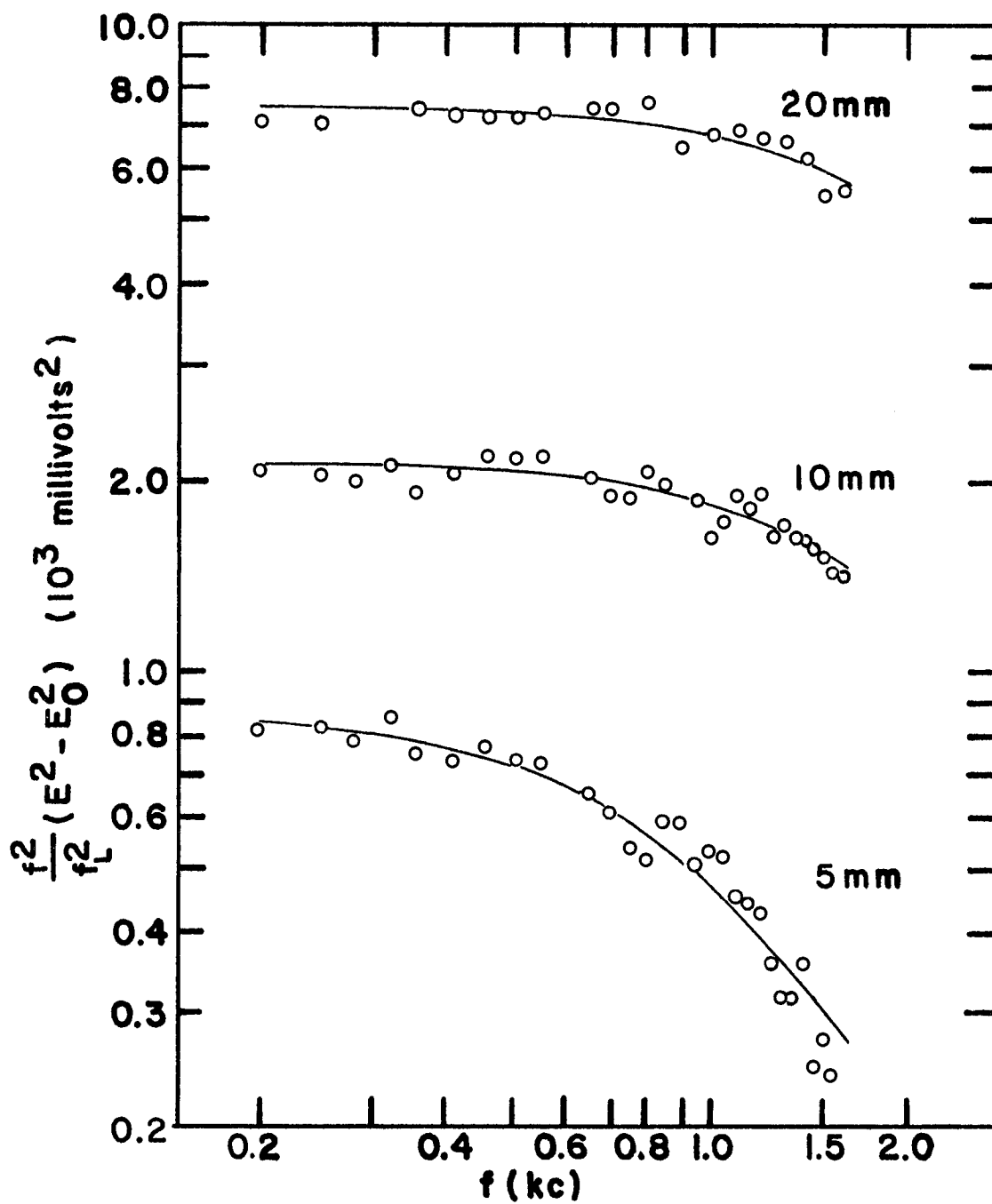


Figure 9. Reduced Spectrophone Response. Methane, 3.3 μ Band.

The least squares analysis of the data shown in Figure 9 yields values of $\tau' = 1.47 \times 10^{-4}$ sec for the five millimeter curve, $\tau' = 0.65 \times 10^{-4}$ sec for the 10 mm curve, and $\tau' = 0.53 \times 10^{-4}$ sec for the 20 mm curve. On the assumption that the relaxation time should vary inversely with the pressure, the agreement between the values for the two lower pressures is quite good. The apparent discrepancy between these two values and the 20 mm value may be due, at least in part, to the fact that the loss exhibited by the 20 mm curve is relatively small, particularly when the scatter in the experimental points is considered. Again assuming the inverse pressure dependence, the value for the five millimeter curve is equivalent to a relaxation time at one atmosphere pressure of $\tau' = 0.97$ microseconds. For comparison with results obtained from ultrasonic measurements this value must be adjusted according to the relation (13, p. 62)

$$\tau' = \frac{C - C_{\text{vib}}}{C} \tau ,$$

in which C is the total heat capacity of the gas, and C_{vib} is the contribution of all vibrational modes to the heat capacity. With a value for methane of $C_{\text{vib}} = 0.62$ cal/mole deg at 300°K (6, p. 101), the result $\tau = 1.07$ microseconds is obtained.

Discussion of Methane Results

Both the classical theory of Landau and Teller (21) and the quantum mechanical theory of Schwartz, Slawsky, and Herzfeld (28) predict a linear relationship between the logarithm of the vibrational relaxation time for a gas and the inverse cube root of the absolute temperature. For purposes of comparison, the value for methane obtained in this research and several of the results of other workers listed in Table 1 in the Introduction are shown in Figure 10 in a plot of $\log \tau$ vs $T^{-1/3}$. The value of $\tau = 0.48$ microseconds at 289°K obtained by Griffith (11) from impact tube measurements is open to question, since the gas sample he used was known to contain one percent ethane; consequently, this result is not shown in the figure. Eucken and Aybar (10) determined relaxation times from sound velocity and sound absorption measurements at several temperatures ranging from 382°K to 626°K . They used tank methane of unstated purity, which they passed through glass wool at -80°C , condensed at liquid air temperature, and distilled several times in vacuum. Madigosky's results (22) were obtained from sound absorption measurements at high pressures, and at temperatures ranging from 244°K to 303°K , using c-p grade methane with a stated minimum purity of 99.0 percent. Cottrell and Matheson (5) appear to have taken the greatest care regarding the purity of methane used. They purified

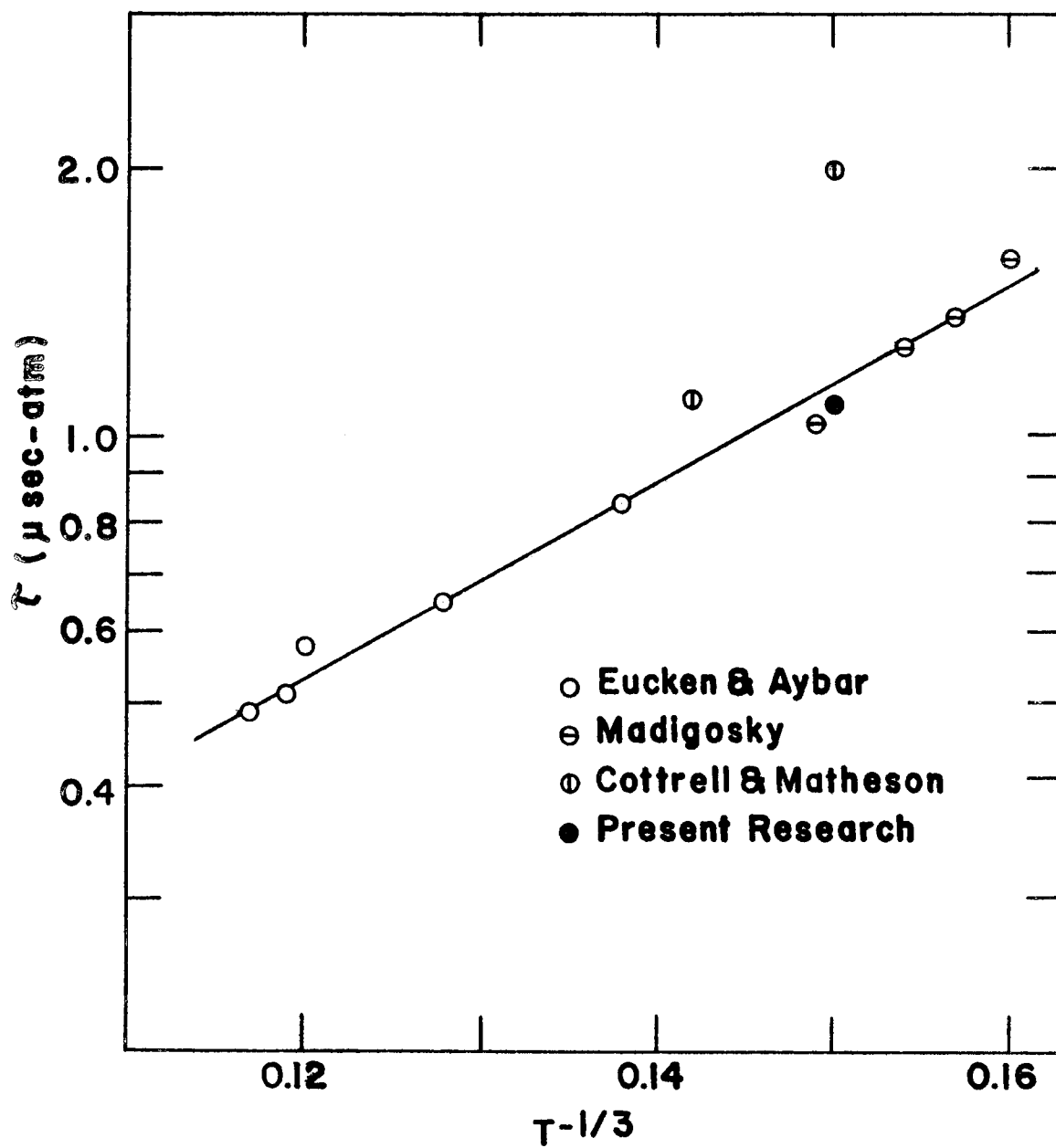


Figure 10. Relaxation Data for Methane.

samples from three different sources in a low-temperature fractionation column and obtained values of $\tau = 2.0$ microseconds at 298°K and $\tau = 1.1$ microseconds at 348°K for each sample from sound velocity measurements. The purified methane was shown to contain less than 0.01 percent ethane and less than 0.1 percent air.

Table 8. Vibrational Relaxation Data for Methane.

Author	T($^\circ\text{K}$)	$T^{-1/3}$	$\tau(\mu \text{ sec-atm})$
Eucken, Aybar (10)	382	0.138	0.84
	477	0.128	0.65
	574	0.120	0.58
	595	0.119	0.51
	626	0.117	0.49
Madigosky (22)	244	0.160	1.60
	259	0.157	1.38
	273	0.154	1.26
	303	0.149	1.03
Cottrell, Matheson (5)	298	0.150	2.0
	348	0.142	1.1
Present Research	298	0.150	1.07

The excellent agreement between the results of the present work and those of Eucken and Aybar and of Madigosky is illustrated by the straight line shown in Figure 10, and lends considerable support to a value of $\tau = 1.1$ microseconds at 300°K for the vibrational relaxation time of methane. However, due to the careful purification methods employed by Cottrell and Matheson, their results cannot be

overlooked. In addition, their lower temperature value is supported by the results of Cottrell and Martin ($\tau = 1.68$ microseconds at 303°K) (4) and of Edmonds and Lamb ($\tau = 1.86$ microseconds at 298°K) (9). The significance of the increased temperature dependence of Cottrell and Matheson's results over that found by other workers is not clear at present, although the effect is certainly worthy of note.

The disparities which exist among the various results discussed above seem to indicate a need for further investigation. In particular, a repetition of Cottrell and Matheson's experiments over a wider temperature range would be most valuable in helping to clarify the temperature dependence of the vibrational relaxation time in methane.

The apparent inconsistency of the results of this research with the spectrophone studies reported by Cottrell, Hunter, and Read (3) merits further clarification. Cottrell (2) has since encountered anomalous effects in the measurement of both the phase lag of the spectrophone signal and the energy absorption in the spectrophone cell; consequently the value of $\tau = 100$ microseconds reported by these workers for the 3.3 micron band in methane must be regarded as inconclusive.

The assumption of a single effective vibrational relaxation time for methane is supported by the results of all workers mentioned above except Cottrell, Hunter, and Read, and appears to be justified. Conclusive evidence of multiple relaxation has been found for a very

limited number of molecules, in particular for sulfur dioxide (19), methylene chloride (29), and ethane (14, 20, 34). In each of these molecules the lowest vibration frequency is well separated from all others, and is assumed to relax independently. On the other hand, for molecules in which the vibration frequencies are not widely separated, the theory of Schwartz, Slawsky, and Herzfeld (28) predicts that exchange of energy between the various vibrational modes by the mechanism of complex collisions may be highly probable. Bauer (1, p. 130) and Dickens and Linnett (8) have concluded from theoretical studies that in such a case practically the total vibrational energy of all modes relaxes in a single relaxation process. For methane the fundamental vibration frequencies are $\nu_1 = 2914 \text{ cm}^{-1}$, $\nu_2 = 1526 \text{ cm}^{-1}$, $\nu_3 = 3020 \text{ cm}^{-1}$ (3.3 microns), and $\nu_4 = 1306 \text{ cm}^{-1}$ (7.7 microns), with the overtone $2\nu_4 = 2600 \text{ cm}^{-1}$, and the combination $\nu_2 + \nu_4 = 2823 \text{ cm}^{-1}$ (12, p. 307-308). Due to the close spacing of the frequencies between 2600 cm^{-1} and 3020 cm^{-1} , transitions between these vibrational levels would be expected to be highly probable. Transitions between the levels 2600 cm^{-1} and 1306 cm^{-1} should also be highly probable, according to the "exact Resonance" theory of Schwartz, Slawsky, and Herzfeld (28). Finally, Tanczos (32) has shown that the two lowest frequency vibrations, $\nu_2 = 1526 \text{ cm}^{-1}$ and $\nu_4 = 1306 \text{ cm}^{-1}$, relax together to produce a single effective vibrational relaxation time.

Response Studies of Methane Diluted with Carbon Dioxide

In order to investigate the effect of small amounts of carbon dioxide on vibrational relaxation in methane, spectrophone signal amplitude measurements were made on methane-carbon dioxide mixtures with carbon dioxide concentrations of one percent and five percent. The reduced spectrophone response, $f^2/f_L^2(E^2 - E_0^2)$, obtained by excitation of the 3.3 micron band in methane at a total pressure of five millimeters is shown in Figure 11 for both concentrations. Here again, the solid curves are the result of a least squares fit of the data to the function $F = M/[1 + (\omega\tau')^2]$, with M and τ' as parameters. The least squares analysis yields values of $\tau' = 0.97 \times 10^{-4}$ sec for the one percent carbon dioxide curve, and $\tau' = 0.53 \times 10^{-4}$ sec for the five percent carbon dioxide data.

Assuming that vibrational relaxation occurs through the mechanism of binary collisions, the effective relaxation time for a mixture of gas B in gas A is given by (6, p. 32)

$$\frac{1}{\bar{\tau}} = \frac{X_A}{\tau_{AA}} + \frac{X_B}{\tau_{AB}},$$

if B is present in low concentrations, i. e., such that the number of BB collisions per second is negligibly small compared to the number of AB collisions per second. Here $\bar{\tau}$ is the effective relaxation time

Table 9. Reduced Spectrophone Response. Methane-Carbon Dioxide Mixtures, 5 mm.

f(cps)	$\frac{f^2}{f_L^2} (E^2 - E_0^2) \quad (10^3 \text{ millivolts}^2)$	
	1% CO ₂	5% CO ₂
200	2.15	2.27
250	2.15	2.29
280	2.19	2.27
320	2.27	2.45
350	2.27	2.27
400	2.27	2.27
450	2.29	2.29
500	2.15	2.29
550	2.15	2.30
650	2.18	2.36
700	2.08	2.27
750	2.08	2.29
800	2.05	2.27
850	1.96	2.18
900	--	2.05
950	1.88	2.38
1000	1.73	2.15
1050	1.72	2.17
1100	1.69	2.15
1150	1.63	2.12
1200	1.60	2.05
1250	1.51	2.01
1300	1.44	2.03
1350	1.36	2.05
1400	1.32	2.02
1450	1.28	1.71
1500	1.23	1.89
1550	1.08	1.75
1600	1.00	1.75

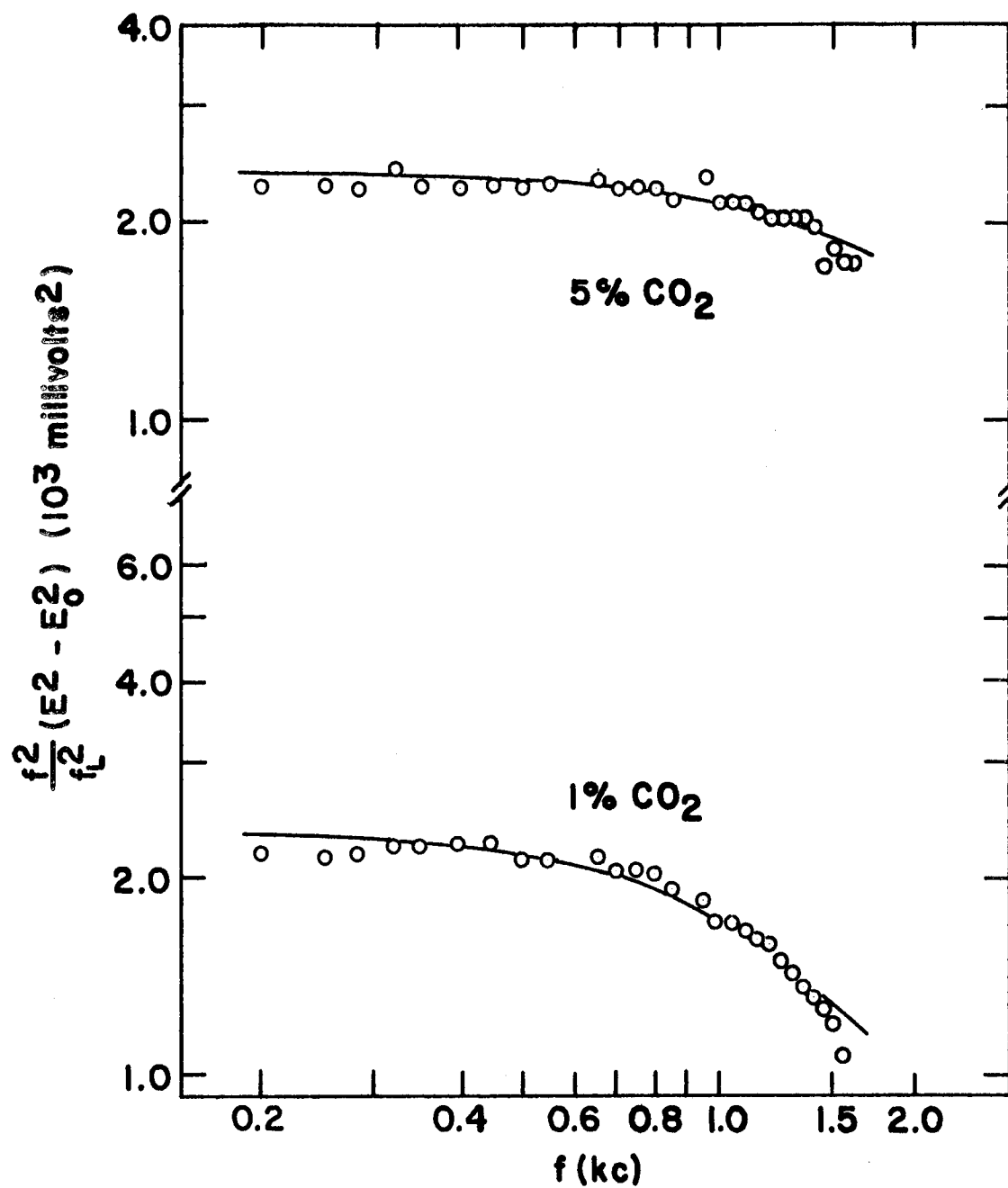


Figure 11. Reduced Spectrophone Response. Methane-Carbon Dioxide Mixtures, 5 mm.

of the mixture, τ_{AA} is the relaxation time of pure A at the total pressure of the mixture, and τ_{AB} is the relaxation time for A in a hypothetical mixture in which only AB collisions occur, again at the total pressure of the mixture. X_A and X_B are the mole fractions of A and B respectively. If $\tau_{AA} = 1.47 \times 10^{-4}$ sec, the value obtained for five millimeters of "pure" methane in an earlier section of this thesis, then for the one percent carbon dioxide mixture $\bar{\tau} = 0.67 \tau_{AA}$, and $\tau_{AA}/\tau_{AB} = 50$. For the five percent carbon dioxide mixture $\bar{\tau} = 0.36 \tau_{AA}$, and $\tau_{AA}/\tau_{AB} = 36$.

Eucken and Aybar (10) measured the effect of carbon dioxide at temperatures ranging from 382°K to 578°K. Their values show a linear dependence of $\log \tau_{AB}$ on $\bar{\tau}^{-1/3}$, and extrapolation of their results to 300°K yields $\tau_{AA}/\tau_{AB} = 13$. This value differs from the average of the two values obtained above by a factor of three. Although the agreement is only qualitative, the results seem to confirm the fact that the presence of carbon dioxide serves to decrease the vibrational relaxation time in methane.

Response Studies of Deuterated Methanes

Cottrell and Matheson (5) have studied vibrational relaxation in tetradeuteromethane, CD_4 , by means of sound velocity measurements, and have obtained the value $\tau = 3.9$ microseconds for the vibrational relaxation time at 298°K. This value is almost twice that

found by these workers for methane at 298°K. However, the theory of Schwartz, Slawsky, and Herzfeld (28) predicts that the effect of deuteration should be a decrease in the relaxation time, the effect of the lower vibration frequencies more than compensating for the increased mass of the molecule. Cottrell and Matheson have interpreted their results in terms of exchange of energy between vibrational and rotational degrees of freedom. Using a semi-classical treatment, they have shown that the higher probability of energy transfer in methane can be attributed to the greater rotational velocity of the hydrogen atoms in methane as compared to that of the deuterium atoms in tetradeuteromethane. Their experimental results yield a value of $\tau_{\text{CD}_4}/\tau_{\text{CH}_4} = 1.95$, in qualitative agreement with the value of 3.9 predicted by their calculations.

In order to investigate the effect of partial deuteration on vibrational relaxation in methane, spectrophone signal amplitude measurements were made on samples of monodeuteromethane, CH_3D , dideuteromethane, CH_2D_2 , and trideuteromethane, CHD_3 . Tetradeuteromethane, CD_4 , was not studied because its highest fundamental vibration frequency is below the low frequency cutoff of the output from the Sylvania lamp used as the infrared source. The reduced spectrophone response, $f^2/f_L^2 (E^2 - E_0^2)$, for each of the compounds studied, at five millimeters pressure, is shown graphically in Figure 12. Here again, the solid curves are the results of a

Table 10. Reduced Spectrophone Response. Deuterated Methanes, 5 mm.

f(cps)	$\frac{f^2}{f_L^2} (E^2 - E_0^2) \quad (10^3 \text{ millivolts}^2)$		
	CH ₃ D	CH ₂ D ₂	CHD ₃
200	1.83	1.53	0.729
250	1.89	1.63	0.729
280	1.81	1.53	0.777
320	1.92	1.59	0.729
350	1.89	1.53	0.753
400	1.83	1.63	0.729
450	2.05	1.69	0.681
500	1.89	1.63	0.535
550	1.86	1.58	0.611
650	1.67	1.51	0.528
700	1.70	1.53	0.483
750	1.70	1.33	0.483
800	1.63	1.25	0.483
850	1.52	1.32	0.403
950	1.39	1.16	0.396
1000	1.39	1.15	0.354
1050	1.36	1.12	0.333
1100	1.31	1.07	0.333
1150	1.25	1.04	0.278
1200	1.15	0.944	0.258
1250	1.05	0.885	0.271
1300	0.969	0.753	0.271
1350	1.05	0.713	0.265
1400	0.893	0.611	0.258
1450	0.835	0.666	0.244
1500	0.769	0.535	0.218
1550	0.876	0.513	0.185
1600	0.785	0.543	0.153

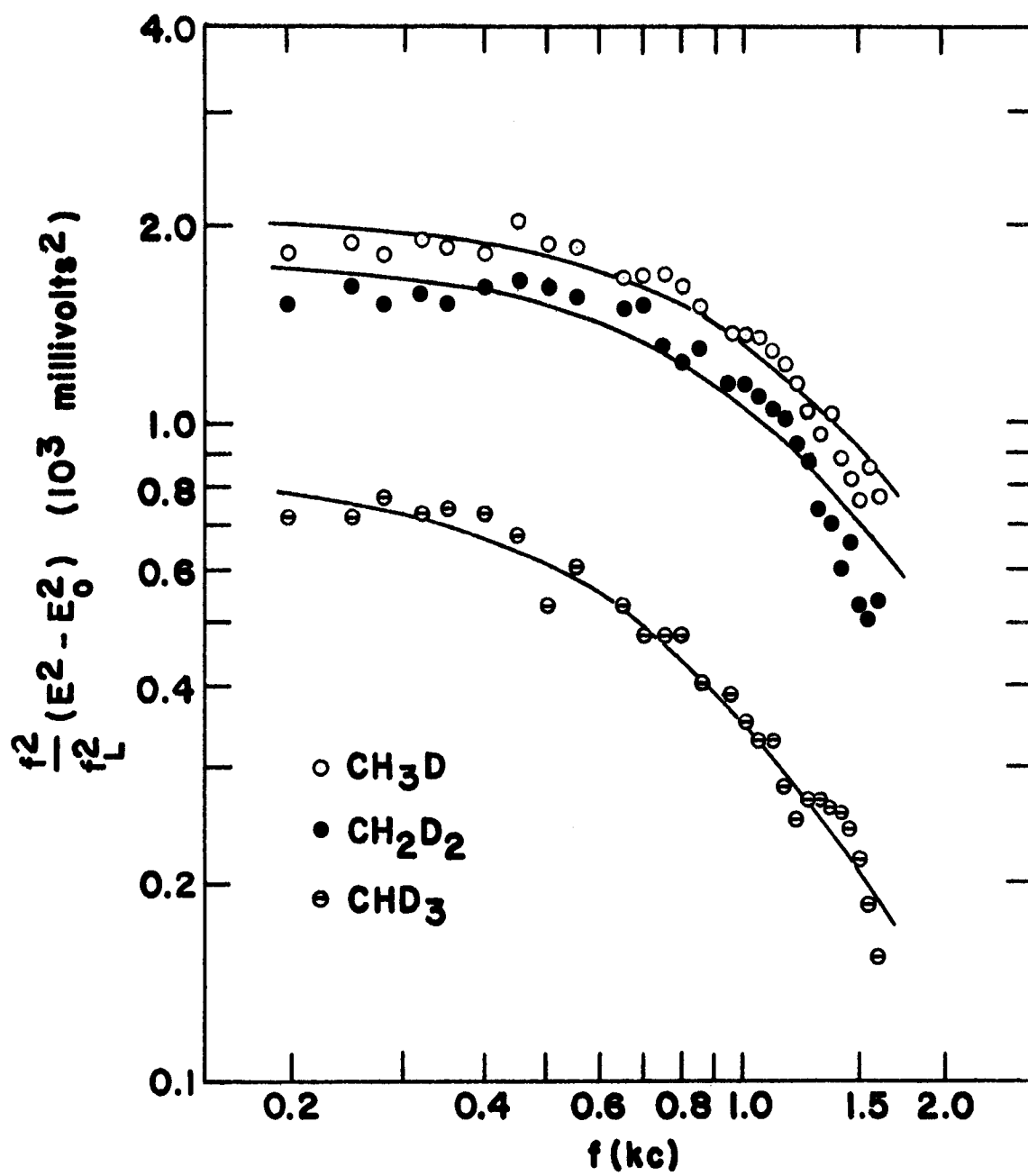


Figure 12. Reduced Spectrophone Response. Deuterated Methanes, 5 mm.

least squares fit of the experimental points to the function

$F = M/[1 + (\omega\tau')^2]$, with M and τ' as parameters. The least squares analysis yields the values $\tau' = 1.17 \times 10^{-4}$ sec for CH_3D , $\tau' = 1.29 \times 10^{-4}$ sec for CH_2D_2 , and $\tau' = 1.80 \times 10^{-4}$ sec for CHD_3 . Using heat capacities calculated by Jones and McDowell (17), the values for τ at one atmosphere pressure are $\tau = 0.87$ microseconds for CH_3D , $\tau = 0.99$ microseconds for CH_2D_2 , and $\tau = 1.45$ microseconds for CHD_3 .

The above results can be reasonably interpreted in terms of the theory proposed by Cottrell and Matheson. Presumably the effect of the decreased vibration frequencies in CH_3D and CH_2D_2 more than compensates for the reduced rotational velocities in these molecules, resulting in vibrational relaxation times which are shorter than that in methane. However, it appears that in CHD_3 the effect of the reduced rotational velocity is dominant, resulting in a relaxation time longer than that in methane.

CONCLUSIONS

The results obtained from this research indicate that the spectrophone can be a useful tool for the study of vibrational relaxation phenomena in gases. However, the discussion of the rate equations governing relaxation processes in polyatomic molecules which has been given shows that the information which can be obtained using the spectrophone method is essentially the same as that to be found from ultrasonic velocity and absorption measurements. Thus, the advantage heretofore claimed for the spectrophone, i. e., that it permits the determination of individual relaxation times for different vibration frequencies in polyatomic molecules, seems to be unfounded.

The value of $\tau = 1.1$ microseconds for the vibrational relaxation time in methane obtained by studies of the spectrophone frequency response has been shown to be in good agreement with the results of Eucken and Aybar (10) and Madigosky (22). However, as mentioned earlier, the disagreement with the results of Cottrell and Matheson (5) indicates a need for further investigation of the problem.

Finally, the studies of methane-carbon dioxide mixtures indicate that carbon dioxide serves to decrease the vibrational relaxation time in methane, as reported by Eucken and Aybar (10), while the studies of the deuterated methanes suggest that vibrational-rotational

energy transfer may play an important role in vibrational relaxation in molecules with high rotational velocities, as proposed by Cottrell and Matheson (5).

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