THE INFLUENCE OF ROTATIONAL AND TRANSLATIONAL ENERGY EXCHANGE ON THE VIBRATIONAL RELAXATION OF CARBON DIOXIDE

By

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CHAPTER I

INTRODUCTION

The acoustic behavior of gases has been the subject of scientific investigation for over one hundred years, and while the behavior of the noble gases can be predicted with accuracy in the region where the wavelength of the sound wave is substantially greater than the mean free path of the molecules (see Figure 1), the microscopic phenomena and their influence on the macroscopic behavior is not so well understood. From purely classical considerations Stokes(1), Poisson(2), and Navier(3) were able to independently formulate the effect of internal "friction", the effect which in more modern (and less descriptive) terminology is attributed to viscosity. Twenty five years after Stokes published his work on the subject Kirchhoff(4) was able to formulate the effect of thermal conductivity on the propagation of a sound wave through a gas. It is interesting to note that Stokes was not specifically looking for a way to explain the absorption of sound in a gas, but was concerned with problems more relevant to his time. "Of what form must (an aqueduct) be, in order to ensure a given supply of water with the least expense of materials in the construction?"(1) The "classical" sound absorption postulated by the theory of these men, now called the Navier-Stokes theory, was a result of their postulates on the nature of gas and liquid materials, but as they did "not possess any means of measuring the intensity of sound the theory (could) not be tested, nor the numerical

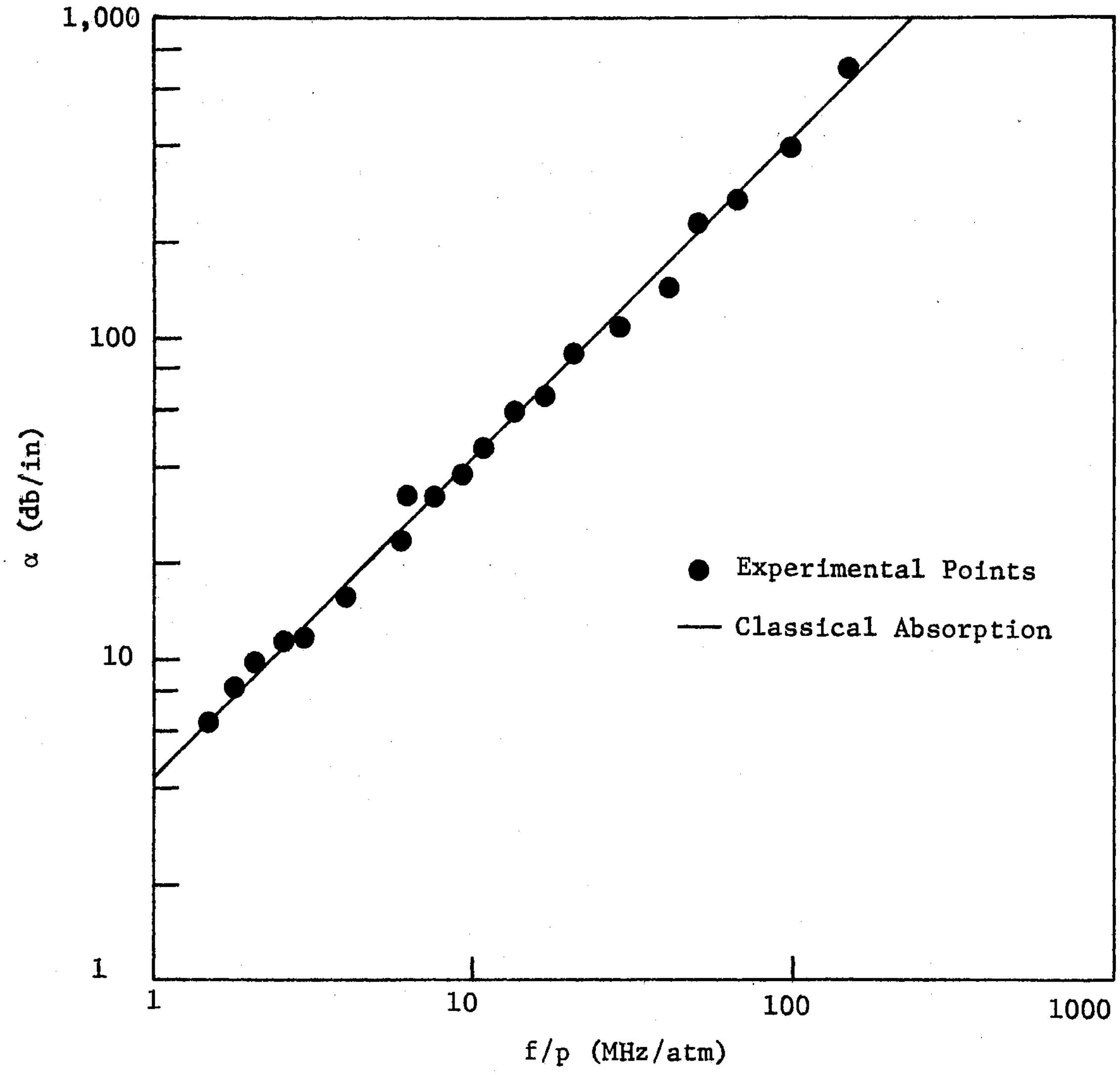

Figure 1. Sound Absorption in Argon at 298°K

value of u (the viscosity coefficient) determined in this way."(1)

The predictions of their theory were well accepted until Pierce(5) constructed a piezoelectric acoustic interferometer and was able to show conclusively in 1925 that the sound absorption of carbon dioxide gas was very much greater than that predicted by the Navier-Stokes theory. Until then researchers were not able to measure the high frequency sound absorption with much accuracy. Three years later Rice and Herzfeld(6) postulated that the excess absorption was due to the lack of equilibrium of the internal degrees of freedom of the gas molecules with respect to the translational degree of freedom. Using this postulate they were able to predict the behavior of relatively simple molecular systems. The result of their postulate is to introduce a relaxation time, tau, into the hydrodynamic equations. One assumes a relaxation equation of the form

$$-dE(t)_{\mathrm{int}}/dt = (1/\mathrm{tau})(E(t)_{\mathrm{int}} - E(tr)_{\mathrm{int}}) \tag{1}$$

where $E(t)_{\mathrm{int}}$ is the instantaneous value of the internal energy, and $E(tr)_{\mathrm{int}}$ is the value of the internal energy if it were in equilibrium with the translation energy. One can then deduce an effective specific heat:(7)

$$C_v^{\mathrm{eff}} = C_v^{\mathrm{inf}} + C_v^{\mathrm{int}}/(1 + jwt) \tag{2}$$

where w = the angular frequency of the sound, C_v^{inf} = specific heat at very high (infinite) frequency. Putting this into the equation of motion of a plane wave in a fluid one has:

$$(V_o/V) - j\ \alpha\ V_o/w)^2 = \mathrm{gam}_{st}/\mathrm{gam}_{eff} \tag{3}$$

where

V_o = velocity of the sound wave at zero frequency

V = velocity of the sound wave at frequency w

gam_{st} = static value of the specific heat ratio

gam_{eff} = effective specific heat ratio using Eq. 2

α = absorption coefficient of the sound wave

j = $\sqrt{-1}$

In Figure 2 the absorption per wavelength and the velocity dispersion is plotted versus the frequency.

The relaxation for a certain process can be connected with the reaction rate for that process. It can be shown(8) that for a gas with only two internal energy states separated by an energy hv the relaxation time and the reaction rate are related by:

$$1/\text{tau} = K_{21} (1 + g2/g1) \exp (-hv/KT)) \quad (4)$$

where K_{21} is the rate for a molecule going from state 2 to state 1 via a collision with another molecule. gi is the degeneracy of state i. The fact of the matter is that molecules usually have more than just two internal energy levels, and the relationship between a relaxation time (or times) and the rates for all of the possible reactions is not as straight forward. If one assumes that the molecules behave like quantum mechanical harmonic oscillators one can, by making several approximations, show that the relaxation time is related to the rate for energy transfer between the two lowest levels by:

$$1/\text{tau} = K_{10} (1 - \exp (-hv/KT)) \quad (5)$$

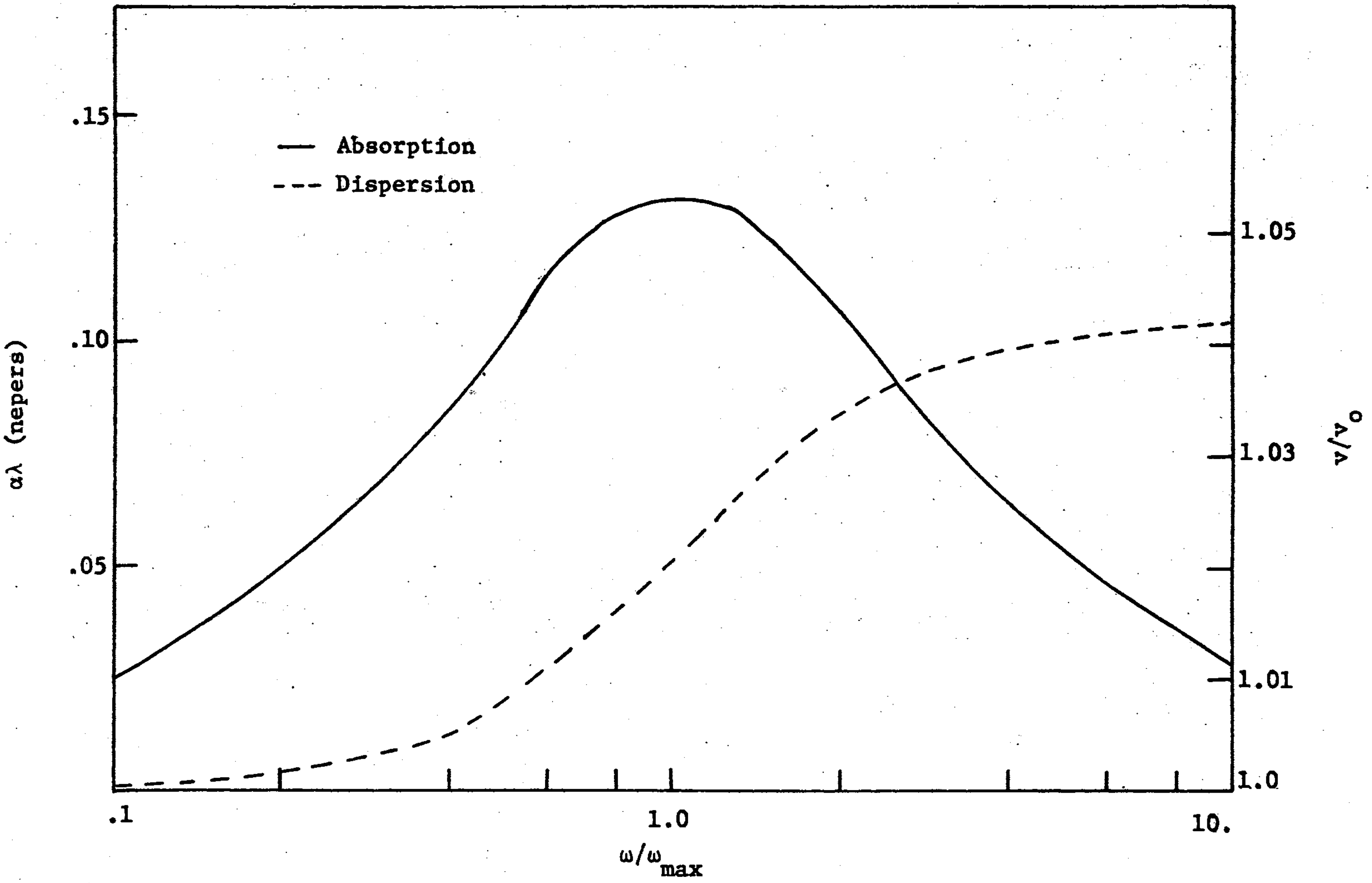

Figure 2. Absorption and Dispersion in a Gas With Molecular Relaxation

This result is from the work of Landau and Teller.(9) Using this approach several authors(10,11,12) have developed theories concerning multiple relaxation in gases composed of harmonic oscillator type molecules, but their theories are not applicable to other types of relaxation: e.g., rotational relaxation.

H. J. Bauer has developed a theory for the analysis of multiply relaxing systems based on the thermodynamics of irreversible processes. (13,14) His ideas have not been widely applied by researchers in this country although the theory was presented in English in 1965. The details of this approach will be presented in Chapter III. Briefly it is based on the linearity of the phenomenological laws of irreversible thermodynamics. It should be noted that Stokes' approach to the viscosity effects mentioned above is also based on a linear model. Its applicability to acoustic work follows from the fact that acoustic signals are usually small perturbations to the system. In cases of a large perturbation, such as a shock wave, the theory may not be useful, but this depends on the magnitude and width of the shock front.(15)

Bauer's approach reduces the problem to one similar to a normal mode analysis of small oscillations of a system of masses and springs. The problem is reduced to an eigenvalue problem, where one can identify the relaxation times with the eigenvalues. This procedure is a very powerful tool for understanding multiple relaxation processes, and will be used in this work.

Bauer's theory depends on a knowledge of the rates for all of the reactions in a system. One must set up a model for the system under consideration, calculate the rates involved, and then put these rates into the theory to see if the model predicts the experimental behavior.

It is only in this way that meaningful statements about the microscopic behavior of the system can be deduced from any macroscopic experimental results.

The calculation of these rates is a problem in scattering theory, and the state of the art is such that the cross sections for most reactions cannot be calculated exactly. The obvious correct answer would be that given by the solution of the quantum mechanical equations for the interaction of two molecules. Such a problem is formidable to say the least. For CO_2-$CO_2$2 collisions it would be a 50 body quantum mechanical calculation which is beyond the scope of this work. Instead various assumptions are made regarding the nature of the interacting systems.

A first choice could be to quantize nothing and treat the problem with a purely classical approach. Of course all quantum mechanical information would be lost in such a calculation, and one would still have a 50 body problem to solve. Another formulation is called the "classical approach" which usually implies that it is the equations of motion that are classical, but the substances are quantum mechanical. In other words, one quantizes the energy levels that a molecule may have but uses Hamilton's equations for the time evolution of the system rather than the Schrödinger equation. Of course this model seems to be physically unrealistic since the infinite channel nature of the classical approach seems to exclude the idea of discrete states to which a system can make transitions.

In solving the problem this way one must average the classical energy transferred over many collisions. Although this is very different from the quantum mechanical picture where a quantum of energy is either transferred or it isn't, the results with respect to the average energy transferred per unit time are identical.(16)

Another model which can be used is the semiclassical model. This model has almost as many variations as people who use it, depending on what is treated classically and what is treated quantum mechanically. The essence of the problem is to find the scattering amplitudes between a given ingoing and any outgoing channel using a form of first order perturbation theory. Extension of this approach to higher orders of the perturbation expansion have been presented by Rabitz and Gordon(17,18,19). The details of this approach will be outlined in Chapter III. The result is that the scattering amplitude between an initial state, i, and a final state, f, is given by:

$$\mathrm{amp}_{if} = -j \int (f{:}V_s(t){:}i) \exp(j\, w_{if}\, t)\, dt \qquad (6)$$

The differences in semiclassical approaches come in the analysis of $V_s(t)$, the potential of the interaction, which depends on time, t. The time dependence of the potential is gotten from assuming a potential of the form $V(\underline{R}(t))$ and postulating a form for $\underline{R}(t)$. In this work two different forms of V(r(t)) will be used:

$$\text{i.}\quad V(\underline{R}) = V_o \exp(-aR) = V_o\,(1 - aR + (aR)**2/2! - \ldots)^{(10)} \qquad (7)$$

$$\text{ii.}\quad V(\underline{R}) = \sum_i \frac{e_i}{|\vec{R}-\vec{r}_i|} = 4\pi \sum_i e_i \sum_{\ell,m} \frac{r_1{}^{\ell}\; Y_\ell^m(\vec{r}_i)\; Y_\ell^m(\vec{R})}{(2\ell+1)\, R^{\ell+1}}^{(17-22)} \qquad (8)$$

where approximations are made concerning the form of $\underline{R}(t)$.

Another approximation to the transition amplitude which will be used is that it is a constant between certain limits. This approximation is artificial, and it is simply an attempt to fit the observed result to a form that gives the correct experimental results in certain situations. Its usefulness lies with the fact that it can indeed give the correct temperature dependence of the observed macroscopic phenomena in hydrogen and nitrogen.(23)

Purpose and Scope

The reaction rates mentioned above are of interest not only to acousticians measuring sound absorption, but also to laser researchers where detailed understanding of the energy transfer processes is important in understanding how a given laser works, and how it can be made to work more efficiently. Using the above methods to calculate the reaction rates and Bauer's theory to calculate the acoustic behavior from the rates inferences can be made concerning, (i) the nature of the energy transfer processes for carbon dioxide and binary gases, (ii) the reason for the anomolous effect that hydrogen has on the absorption of sound in carbon dioxide-hydrogen mixtures, (iii) the regions of validity for the various rate calculation schemes giving some insight into which methods can be used for rate calculations of rates which cannot be measured or which have no acoustic effect. Hydrogen and nitrogen were chosen as the binary gases because of the insight they can give into the nature of the energy exchange processes in the carbon dioxide laser, as they are both present along with the carbon dioxide in many laser systems now in operation. Because of the large energy gaps in its rotational levels, hydrogen has been postulated(22) as being very efficient in exchanging energy with the vibrational levels of carbon dioxide. Nitrogen on the other hand has very small spacings in its rotational level spectrum, and should not exhibit any vibration-rotation effects.

Experimentally the temperature and frequency dependence of ultrasonic absorption in carbon dioxide - hydrogen mixtures over a frequency/pressure (f/p) range of 1 MHz to 100 MHz per atmosphere, and a temperature range of $300^{\circ}K$ to $1000^{\circ}K$ was observed. A model has been postulated which includes vibration to translation energy exchange, rotation to translation energy exchange and vibration to rotation energy exchange for carbon dioxide-hydrogen and carbon dioxide-nitrogen reactions.

Remainder of Thesis

In Chapter II the experimental procedure is discussed including the experimental apparatus, the data taking procedure, and the method and theory of the data reduction. The experimental results are presented for mixtures of carbon dioxide with hydrogen and carbon dioxide with nitrogen. Chapter III contains a detailed discussion of Bauer's theory and its use. Also included in Chapter III is a discussion of the method of rate calculation which makes use of multipole moments, Eq. 8 Chapter IV contains a comparison of the theory with experiment. Theoretical predictions of the following systems are presented:

1) pure CO_2 (using SSH rate calculation)$^{(10)}$

2) pure H_2 (using a modified calculation based on work of Raff and Winter)$^{(23)}$

3) CO_2 with H_2 (no vibration-rotation interactions)

4) CO_2 with H_2 (including vibration-rotation interactions)

5) CO_2 with N_2 (no vibration-rotation interactions)

Chapter V, the conclusion, will contain an analysis of Bauer's theory and of the various theories used to calculate the rates. The appendicies will outline the computer programs used, and they will include the programs for data reduction, and for using Bauer's theory to calculate relaxation times from a reaction scheme.

CHAPTER II

EXPERIMENTAL RESULTS

Apparatus Description

Measurements of sound absorption and velocity were made on carbon dioxide and on two carbon dioxide - hydrogen mixtures. Two instruments were used to make the measurements. A high pressure acoustic interferometer(24) was used to measure the absorption in carbon dioxide at room temperature. Because small amounts of impurities can cause a large shift in the relaxation time which would imply a shift in the observed frequency of maximum absorption the high pressure instrument was used to verify the purity of the carbon dioxide used. Since the instrument is capable of making measurements on the frequency/pressure range of 20 KHz/atm to 1 MHz/atm the peak in absorption occurring around 30 KHz/atm could be observed. The results of this measurement done at room temperature are shown in Figure 3. The procedure for obtaining absorption measurements with this instrument is adequately described elsewhere(25). A numerical analysis of this curve to determine a fit to a single relaxation equation is difficult because of the high pressures involved. Using a crystal frequency of 1 MHz the pressure at the maximum absorption point is approaching the point at which carbon dioxide liquifies. For this reason the shape of the curve becomes distorted and no analysis to fit a single relaxation time was made except to note that the frequency/pressure ratio at maximum absorption occurs at 30 KHz/atm agree-

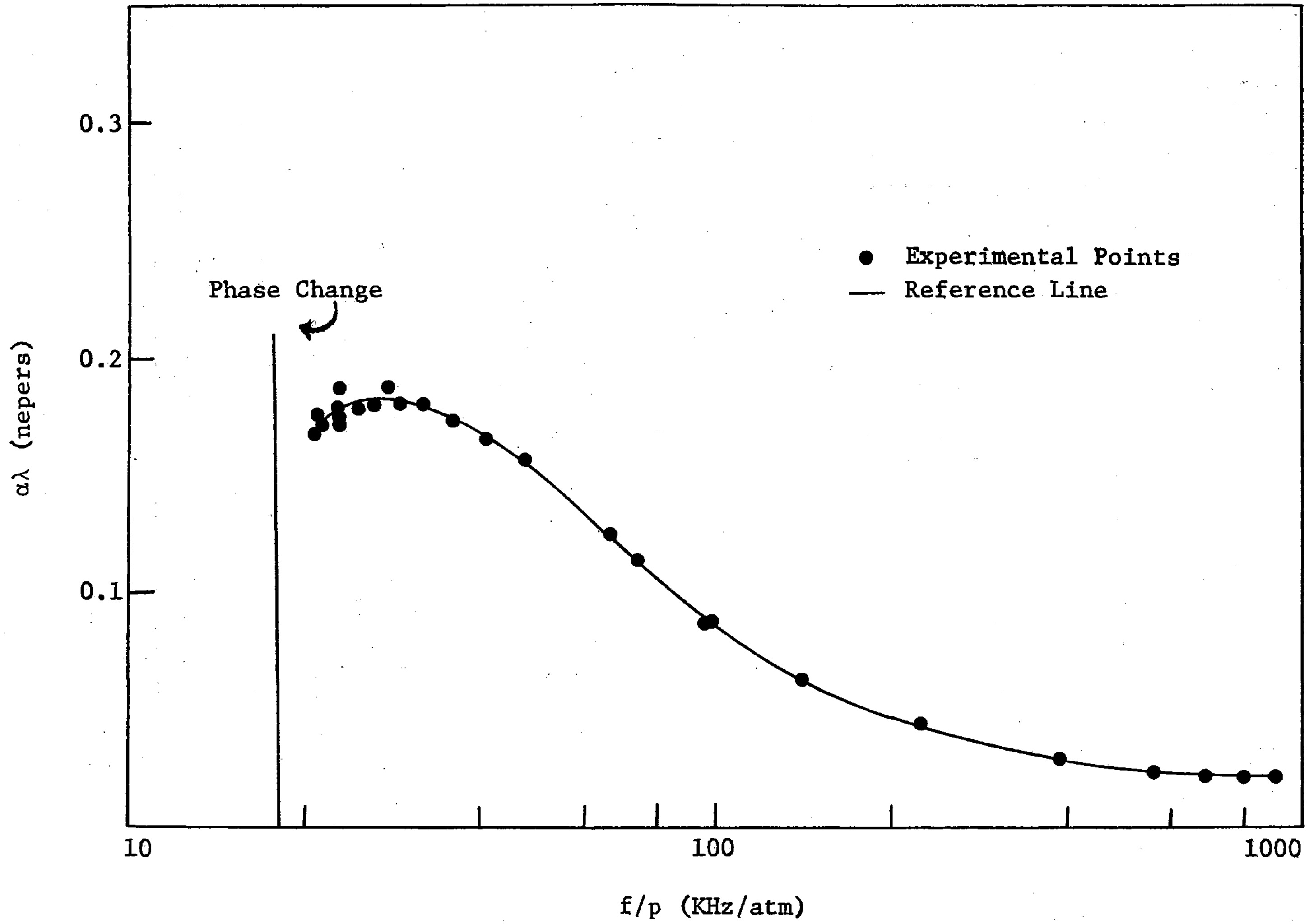

Figure 3. Sound Absorption in CO_2 at $298^{\circ}K$ Measured With High Pressure Interferometer

ing with the work of Shields(26) using a lower frequency instrument.

The second instrument, a pulsed ultrasonic interferometer(27), was used to determine the absorption at higher temperatures and higher frequency/pressure ratios, and this instrument was used to make the remaining measurements reported in this work. The instrument is capable of making measurements in the temperature range 300 degrees Kelvin to 1000 degrees Kelvin and within the frequency/pressure range of approximately 1 MHz/atm to about 100 MHz/atm, but measurements at the higher frequency/pressure ratios are difficult. The signal to noise ratio becomes poor and problems with sound being propagated through the walls of the stainless steel chamber become a problem when making measurements on carbon dioxide. The instrument is capable of making measurements at high frequency/pressure ratios and high absorptions as is indicated by Figure 1 in Chapter I where results for measurements on Argon indicate that measurements up to an absorption of 700 db/in at a pressure of 7×10^{-3} atmospheres are possible. There appears to be no systematic error and the random error appears to be small, less than 10%.

Pure Carbon Dioxide

After the gas was checked for purity measurements were done on pure carbon dioxide mainly to verify that the instrument was capable of predicting absorptions that agreed with those of other researchers(26,28). It was found necessary to dry the carbon dioxide over Dririte for at least 24 hours before measurements were taken. Even very small, 0.01%, of water vapor in the gas can cause a marked shift in the absorption curve(29). The results for dried carbon dioxide at room temperature taken with the pulsed instrument are shown in Figure 4. The data points

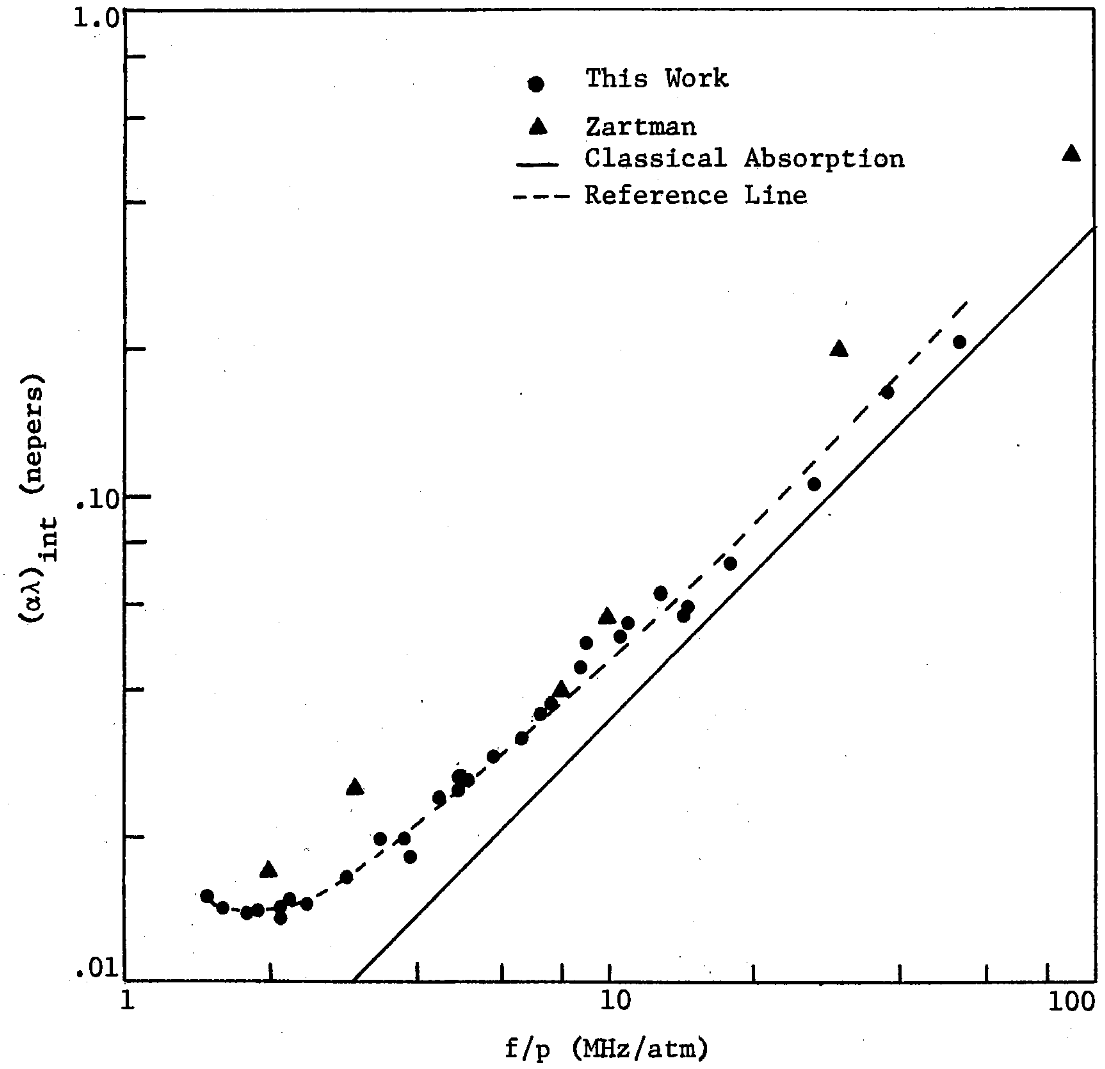

Figure 4. Total Measured Absorption in CO_2 at 298°K Using Pulsed Instrument

are compared with those of Zartman(30).

In order to extract relaxation times from this data it is necessary to determine the absorption due to internal effects and that due to the so called classical effects of viscosity and thermal conductivity. In order to calculate the classical absorption and hence determine the absorption due to internal effects accurately it is necessary to account for the frequency dependence of the transport coefficients(31). This poses somewhat of a problem. In order to determine the frequency dependence of the coefficients one must know the relaxation times, but the relaxation times cannot be determined until the internal absorption is determined which in turn cannot be determined until the classical absorption is known. The problem of extracting relaxation times from the data can be formally written as an attempt to invert an equation containing the relaxation time, τ, and the observed absorption per wavelength, $(\alpha\lambda)_{obs}$:

$$(\alpha\lambda)_{obs} = F(\tau)$$

Where the necessary parameters are defined by:

$$F(\tau) = (\alpha\lambda)_{int} + (\alpha\lambda)_{cl}$$

$$(V_o/V - j\,\frac{(\alpha\lambda)_{int}}{2\pi})^2 = \gamma_o/\gamma_{eff}$$

where:

V_o = velocity at zero frequency

γ_o = specific heat ratio at zero frequency

$$\gamma_{eff} = (C_p)_{eff}/(C_v)_{eff}$$

$$(C_p)_{eff} = R + (C_v)_{eff} = C_p^{\infty} + \sum_{i=1}^{2} \frac{C_i}{1 + j\, 2\pi f\, \tau_i}$$

C_i = "relaxing" internal specific heat

τ_i = relaxation time corresponding to C_i

$$(\alpha\lambda)_{cl} = \frac{8\pi}{3} \frac{f^2}{V^2\, \rho_o} \left[\eta + 3/4\ (\gamma_{eff} - 1) \frac{K(f)}{(C_p)_{eff}}\right]$$

η = viscosity; ρ_o = density; $K(f) = \eta/M\, [(C_p)_{eff} + 5/4\ R]$

The complex specific heat, $(C_p)_{eff}$, is obtained by assuming that the vibrational specific heat, C_1, relaxes with a single relaxation time, τ_1, and the rotational specific heat relaxes independently with a relaxation time, τ_2. The point of the measurements is to determine τ_1 and τ_2 as a function of temperature.

Several assumptions have been made about the nature of the system under consideration. In order to derive the equation for the classical absorption the wavelength of the sound wave must be much greater than the mean free path of the molecules, or equivalently the time between collisions must be much less than the frequency of the sound wave. This does not present difficulties until frequency/pressure ratios of the order of 10^{10} Hz/atm(32), well beyond the resolving power of the instrument. Further an assumption as to the nature of the relaxation process was made. There is no a priori reason for only two relaxation times being able to describe the absorption of the system. That the results from this assumption can be made to agree with experiment to within the experimental error is its justification. As the data indicates the theoretical curves can be made to generally fit the experiment the assumption of parallel relaxations appears to be a good one, but care must be taken not to attach too much physical significance to this fact. No inference about the microscopic process is implied, and the relaxation times should be viewed as adjustable parameters in the theory which fit the data. More accurate measurements of the absorption might require more than just two relaxation times, and it would be incorrect to connect the two relaxation times to the rate for a specific process.

Rather than attempting to invert the above equations to determine τ_1 and τ_2 a best fit procedure, suggested by Bass(27), is used. The data was analyzed using program AMD001 described in the Appendix. The program is not very subtle, as it depends on a brute force method to find a local minimum of

$$F(\tau_1, \tau_2) = \sum_{\substack{\text{all} \\ \text{observations, i}}} \left| (\alpha\lambda)_{\text{obs}} - (\alpha\lambda)_{\text{calc.}} \right|$$

as a function of τ_1 and τ_2. One makes an educated guess about the approximate values of the relaxation times and searches the τ_1, τ_2 plane for a minimum around this guess. Although the procedure is not mathematically rigorous and may not find a true minimum experience has shown that it is capable of giving an $(\alpha\lambda)$ that agrees with experiment. Even though the equations for the theoretical calculations of $(\alpha\lambda)$ appear complicated they are easily programmable, and the program makes up for its lack of finesse by its simplicity. The results of these calculations for pure carbon dioxide at different temperatures is plotted in Figures 5-9. The quantity plotted is $(\alpha\lambda)_{\text{int}} = (\alpha\lambda)_{\text{total}} - (\alpha\lambda)_{\text{cl}}$.

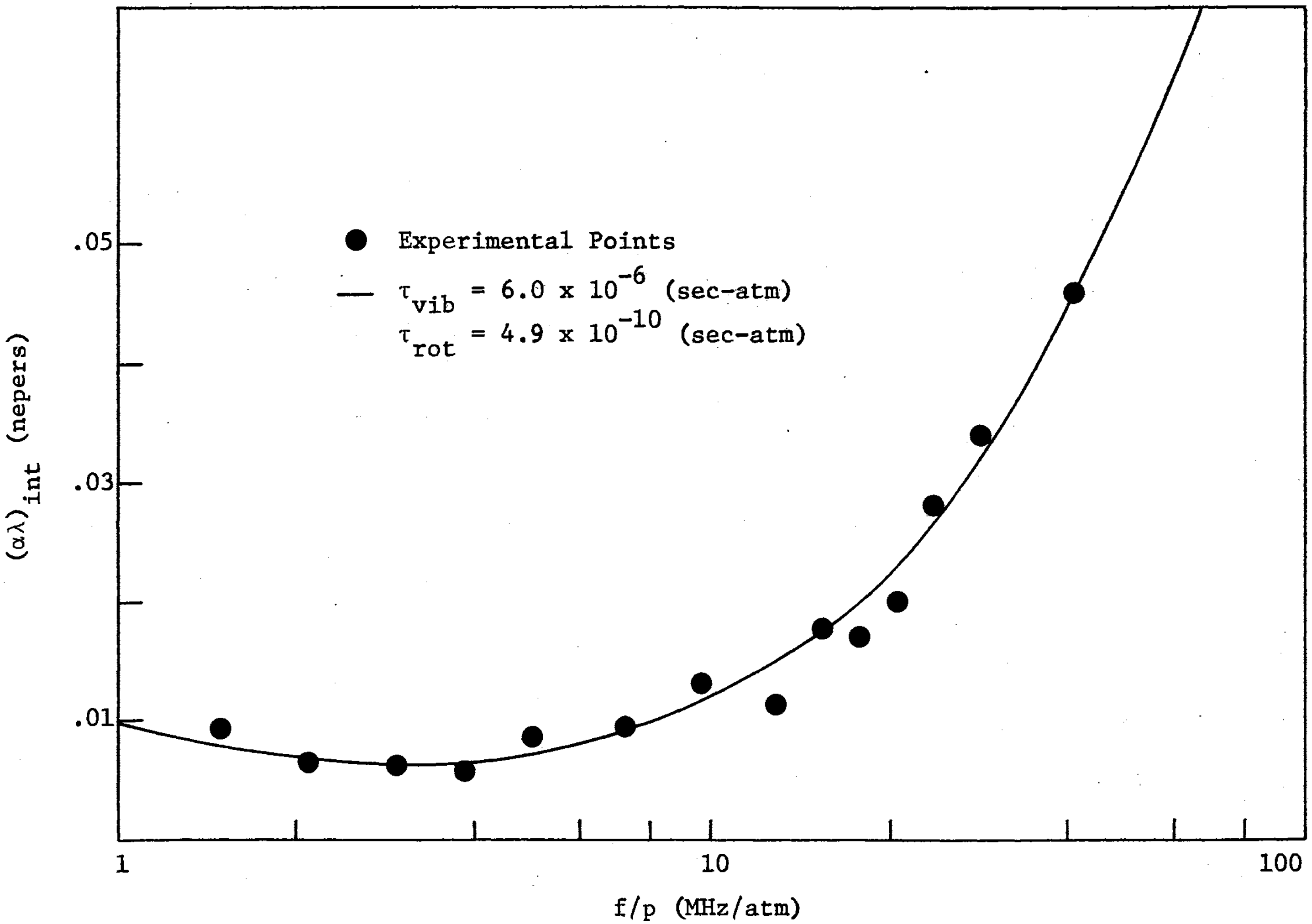

Figure 5. Absorption in CO_2 at 298°K

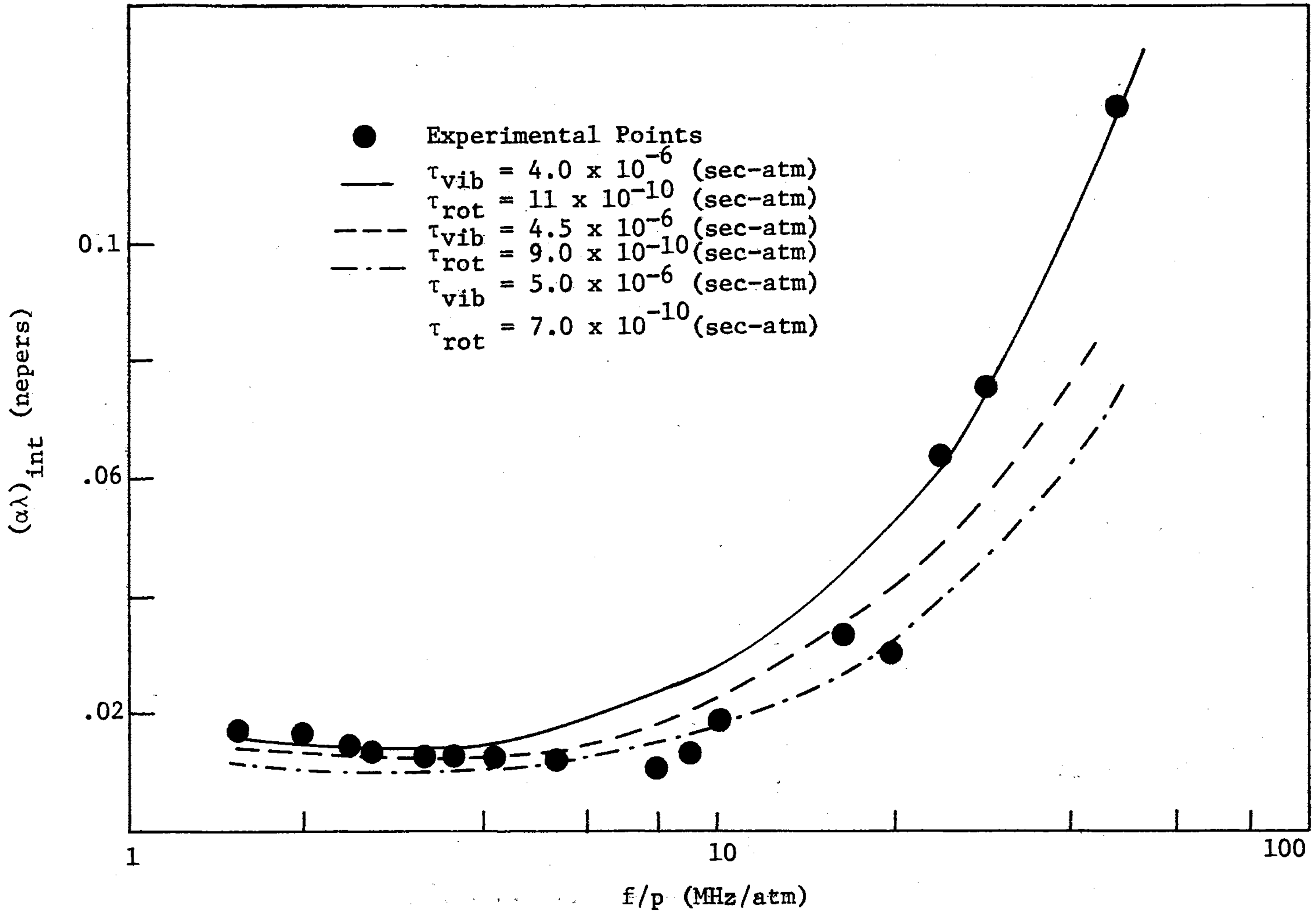

Figure 6. Absorption in CO_2 at 365°K

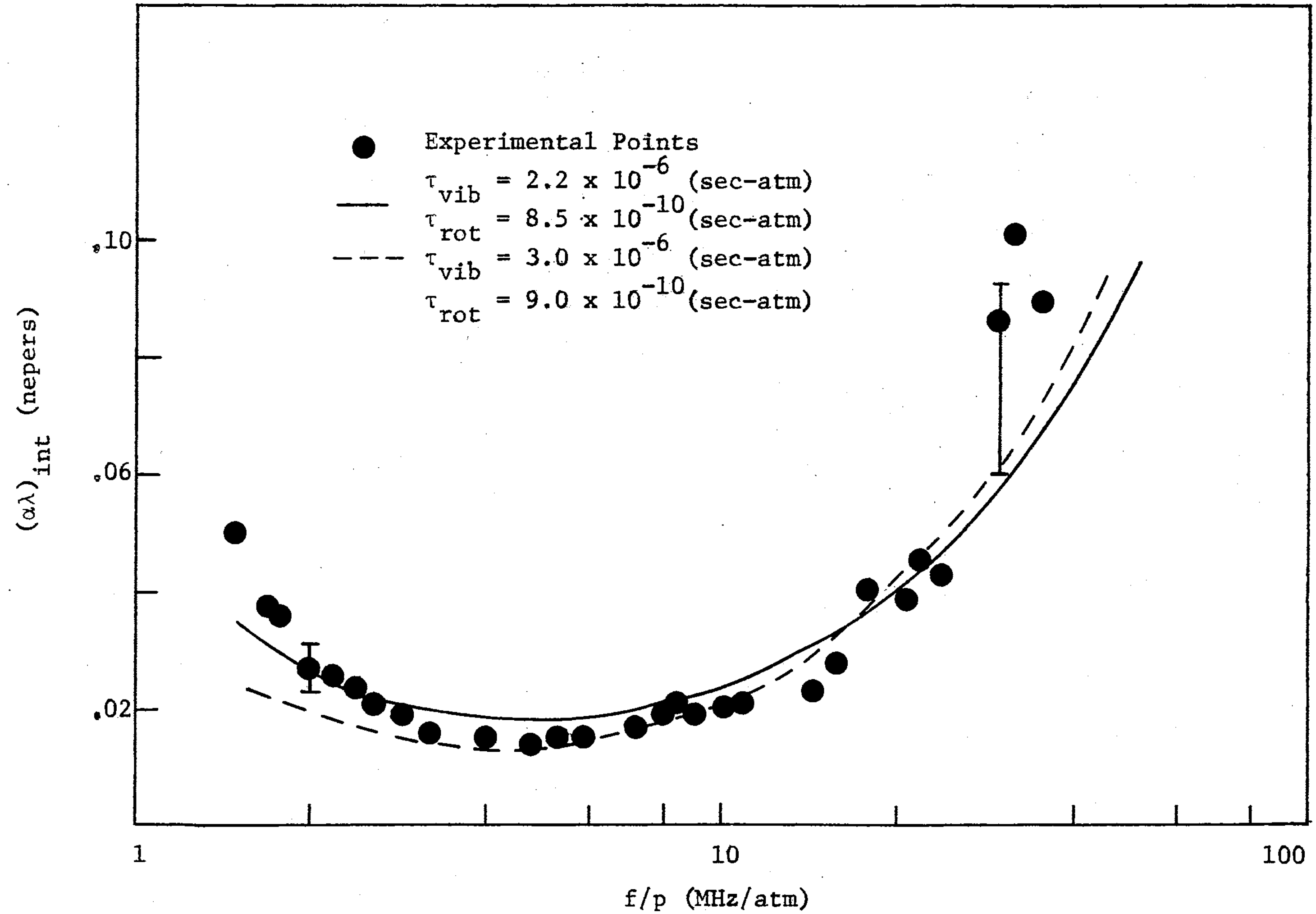

Figure 7. Absorption in CO_2 at 450°K

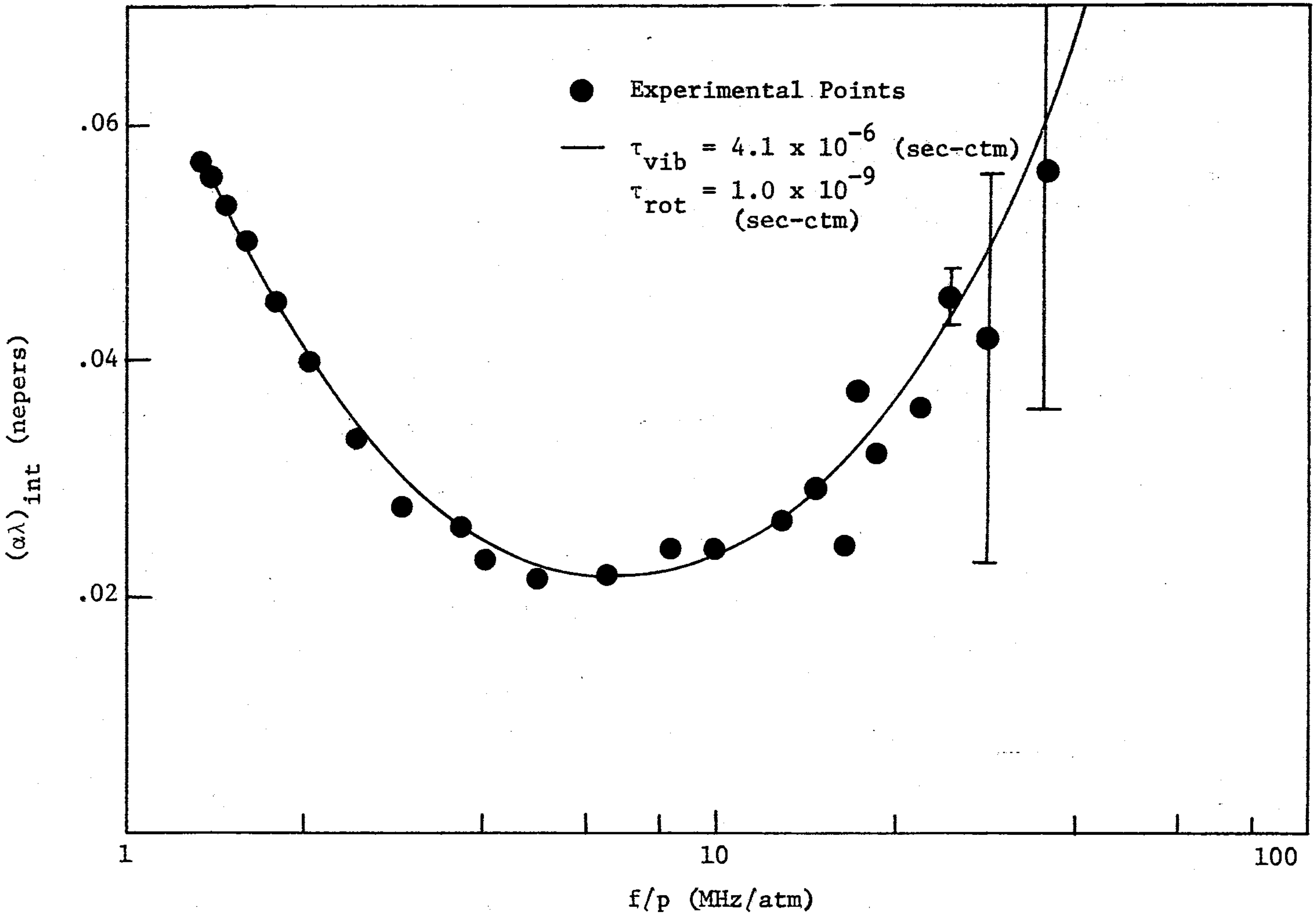

Figure 8. Absorption in CO_2 at 500°K

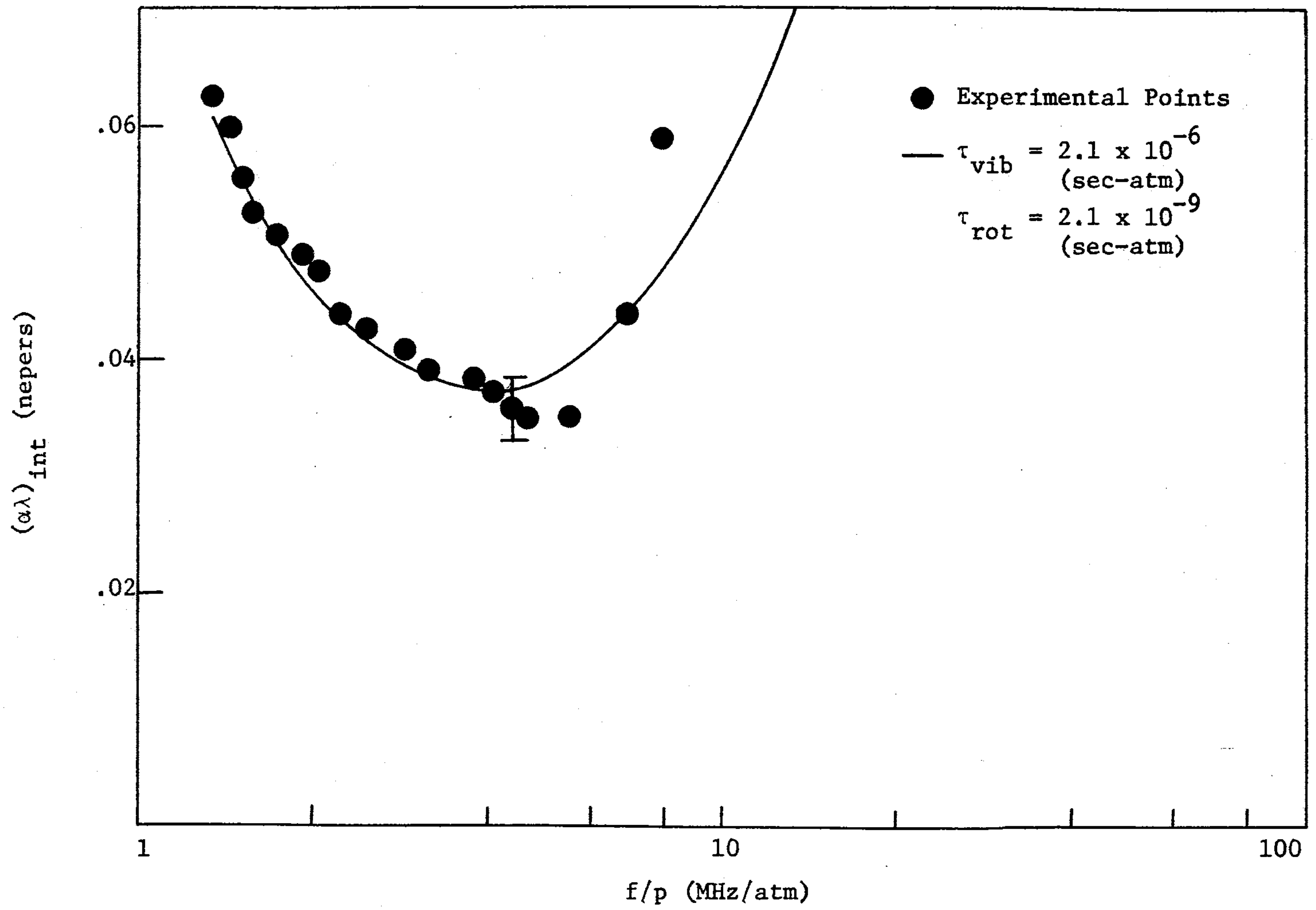

Figure 9. Absorption in CO_2 at 825°K

Mixtures

A mixture of 2% hydrogen and 98% carbon dioxide was prepared by using the law of partial pressures. A high pressure cylinder was evacuated and then filled to a pressure P_H with hydrogen. Carbon dioxide was then admitted until the total pressure, P_T, was such that $P_H/P_T = 0.02$. This method is straight forward and as long as the total pressure remains relatively low, 5 atmospheres or so, problems with the density not being directly proportional to the pressure can be ignored. Some care must be taken to allow the system to come to thermal equilibrium as the expanding gas cools as the mixing cylinder is filled from the compressed gas bottles.

An analysis was made using the above equations modified for a simple mixture, and the results are shown in Figures 10 to 15. The transport coefficients were calculated according to formulas for mixtures in _Molecular Theory of Gases and Liquids_(33). The program used was AMD002.

A mixture of 15% hydrogen and 85% carbon dioxide was prepared in a similar manner. There are several problems involved in using this high percentage of hydrogen in the pulsed instrument and in the analysis of the data. The acoustic chamber of the pulsed instrument is stainless steel and hydrogen is known to adsorb and diffuse into stainless steel. This did not appear to be a problem at moderate temperatures, but at higher temperatures so much hydrogen diffused that the pressure of the mixture inside the cylinder was seen to change. This problem can be somewhat alleviated by flowing the gas, but nevertheless it was discovered that measurements could be made to only 750 degrees Kelvin on the 15% mixture. It should be noted however that all of the measurements made on the 15% concentration may be in error because of this problem.

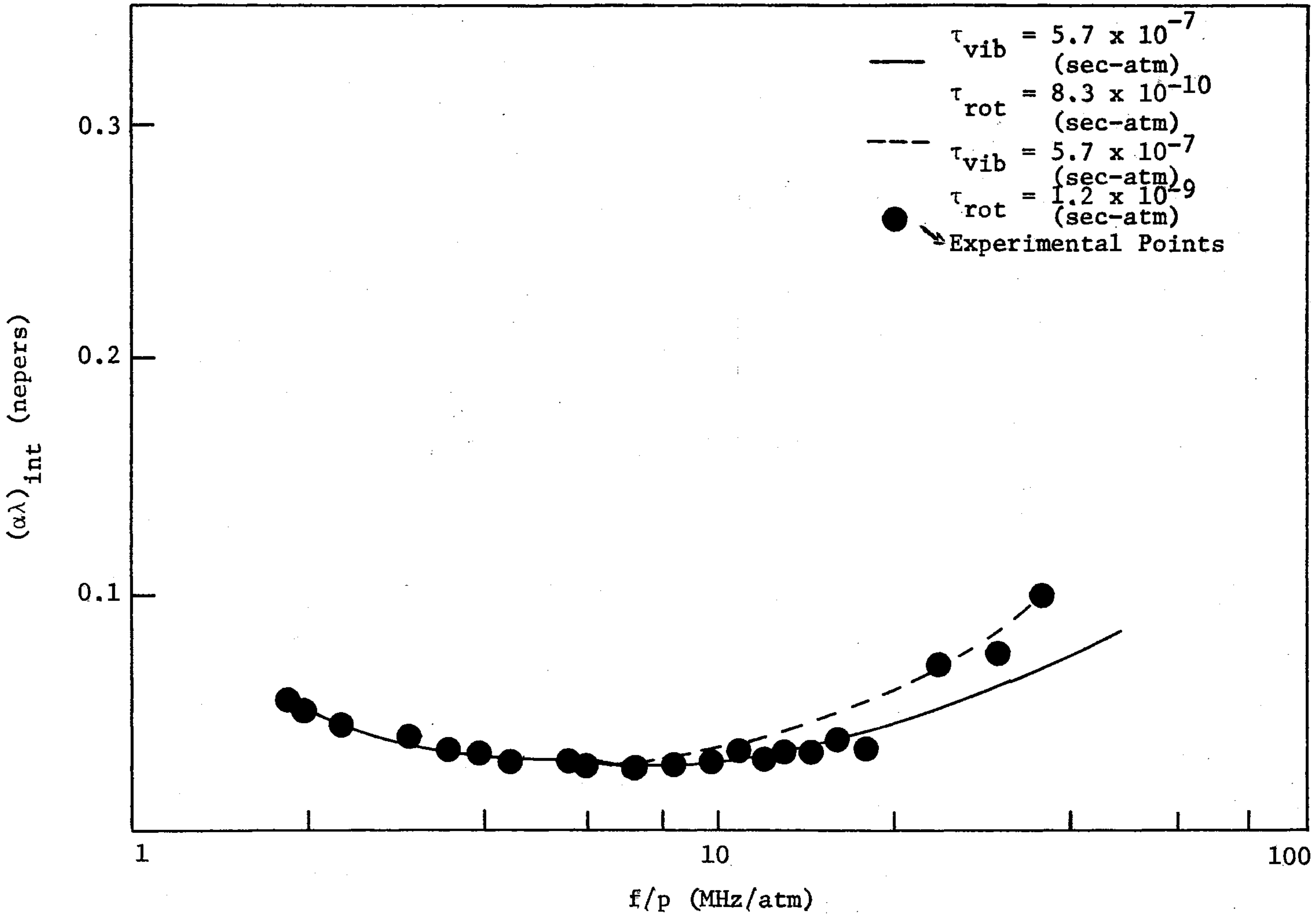

Figure 10. Absorption in 98% CO_2 + 2% H_2 at 300°K

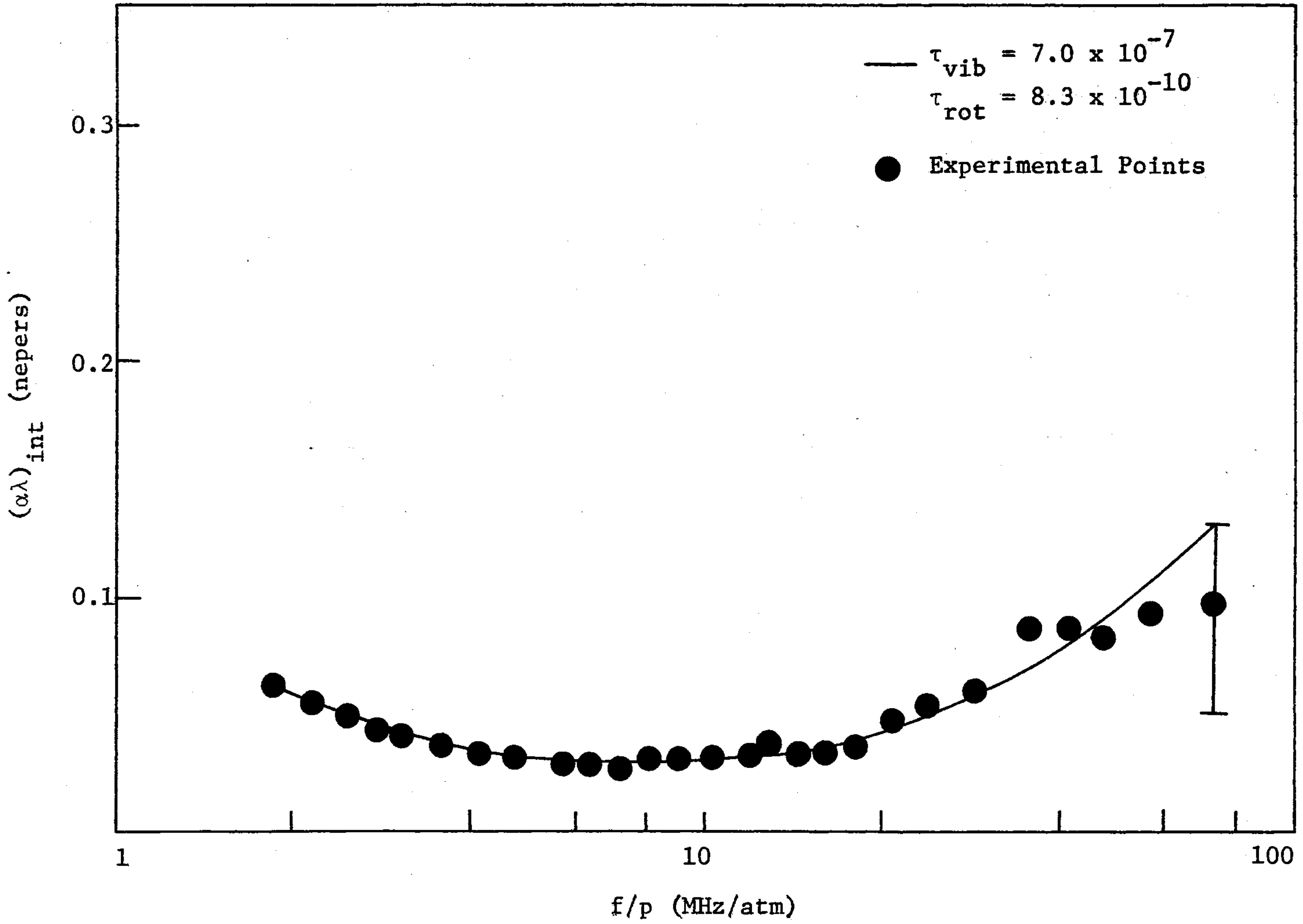

Figure 11. Absorption in 98% CO_2 + 2% H_2 at 384°K

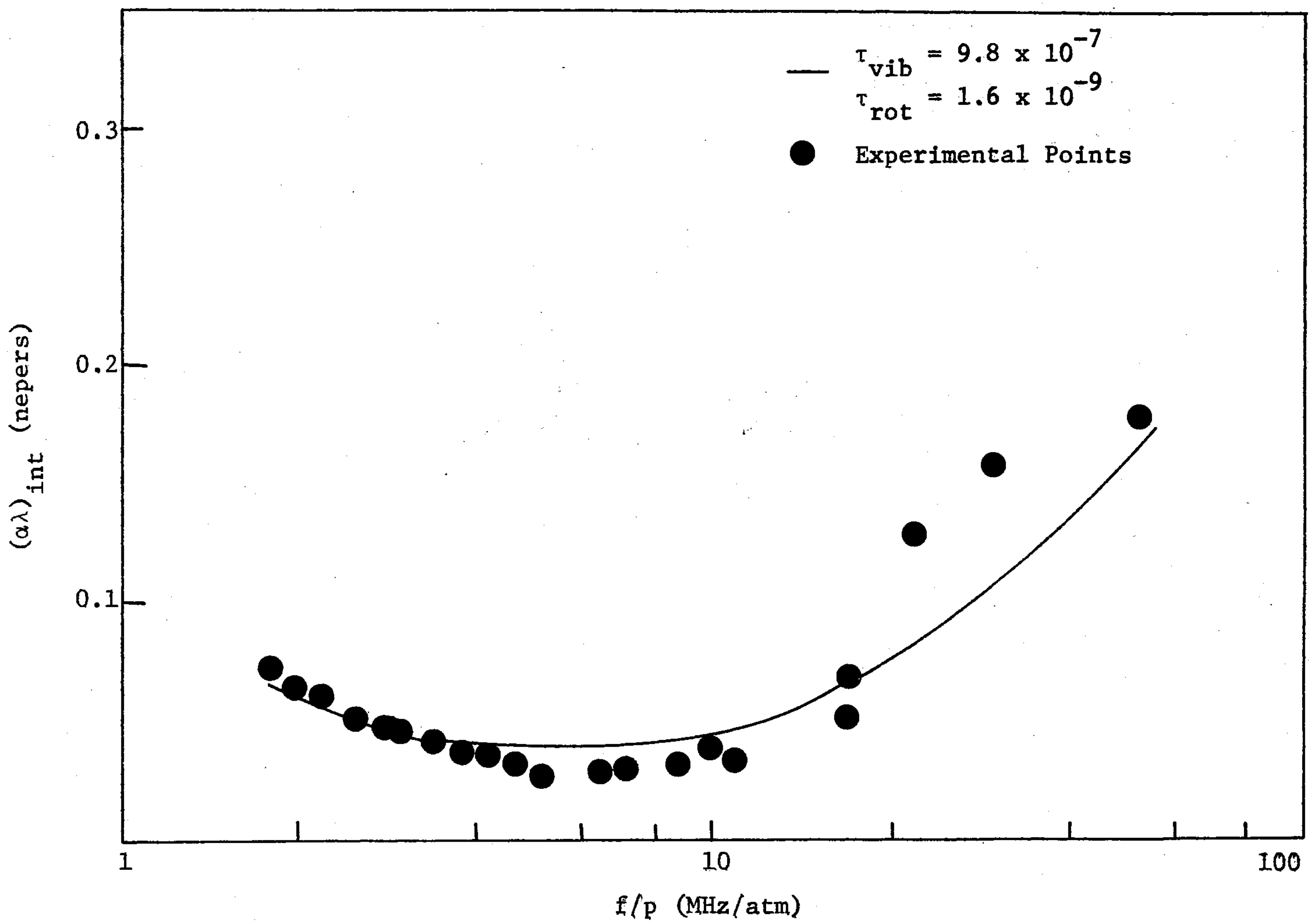

Figure 12. Absorption in 98% CO_2 + 2% H_2 at 509°K

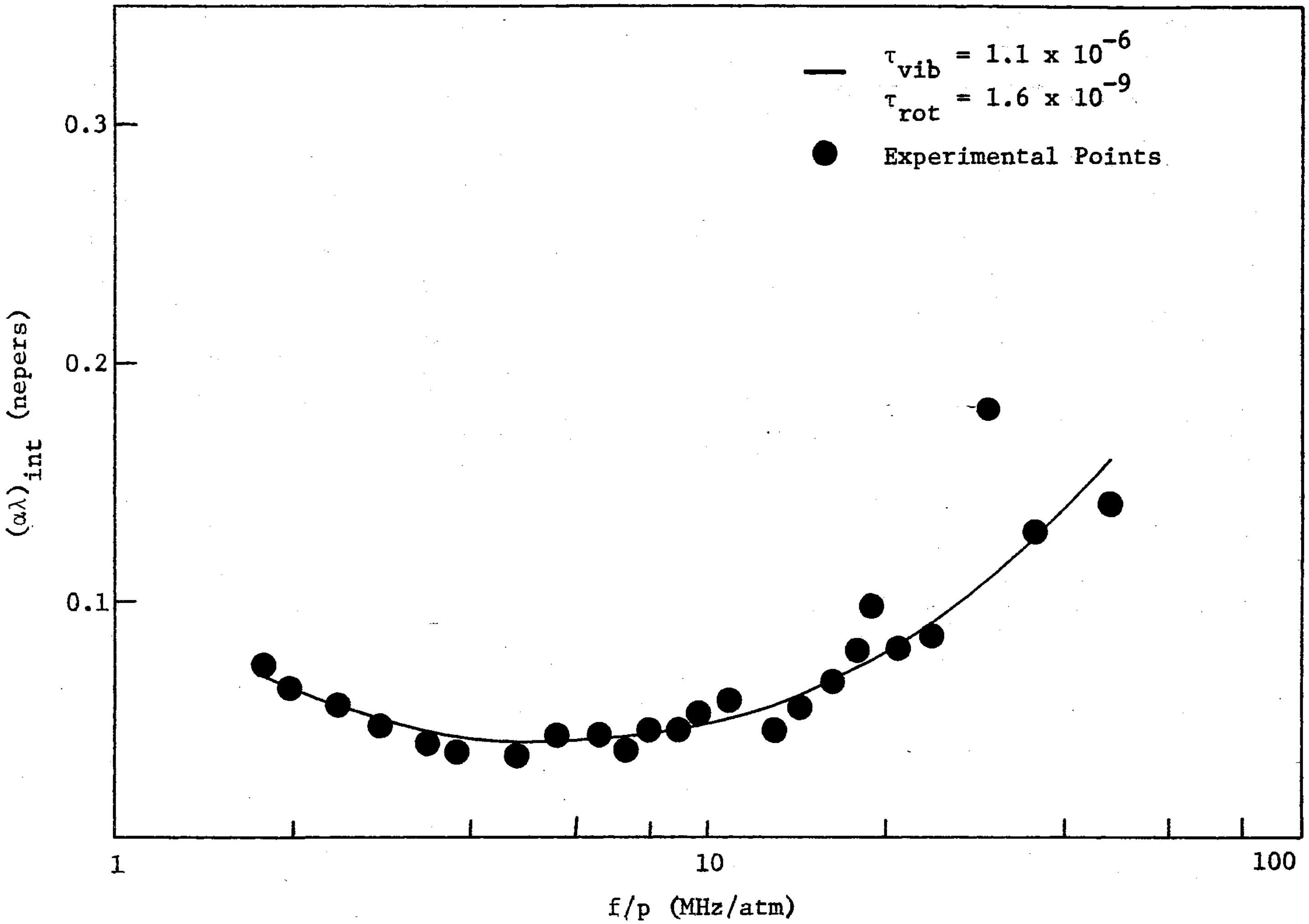

Figure 13. Absorption in 98% CO_2 + 2% H_2 at 607°K

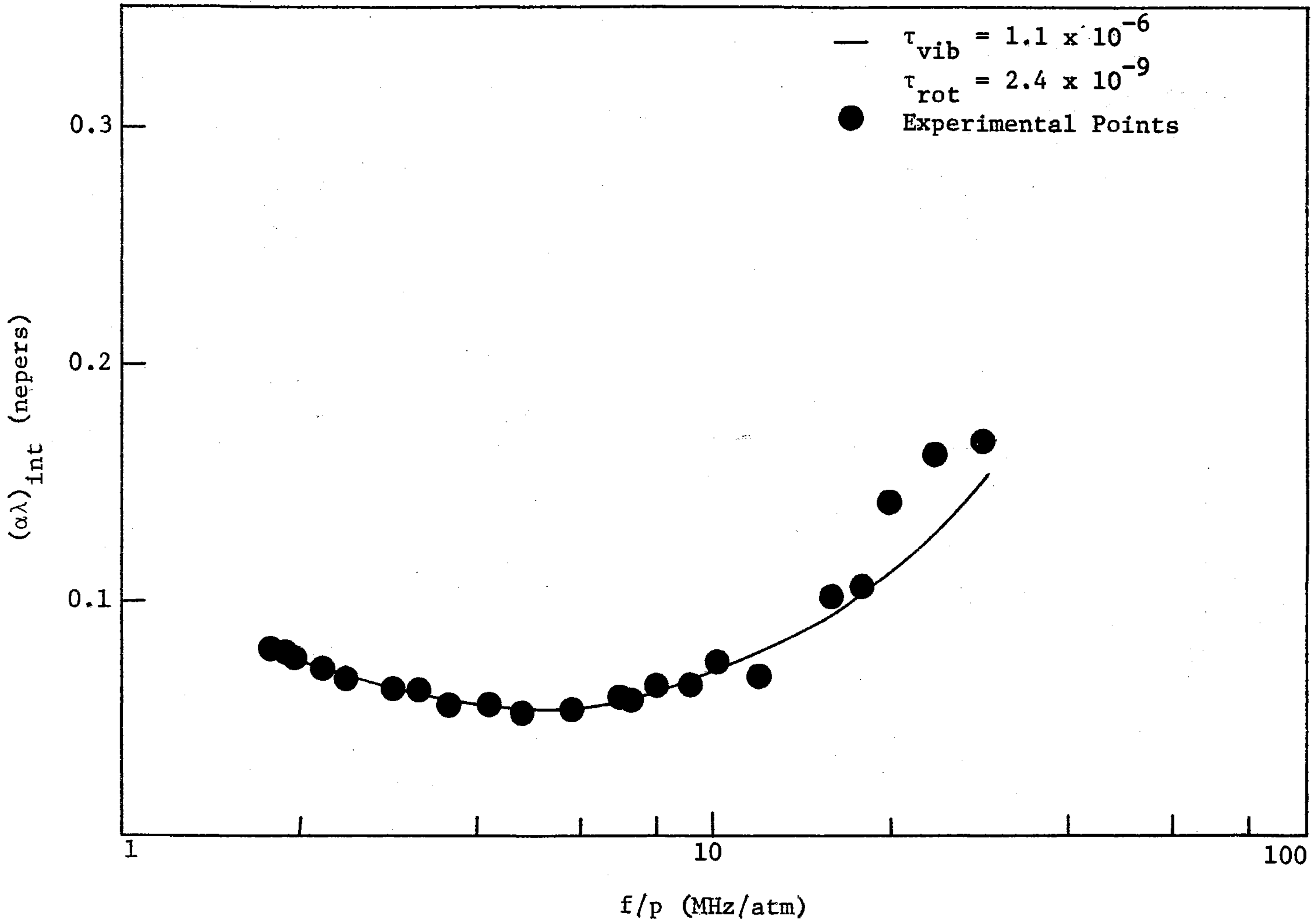

Figure 14. Absorption in 98% CO_2 + 2% H_2 at 722°K

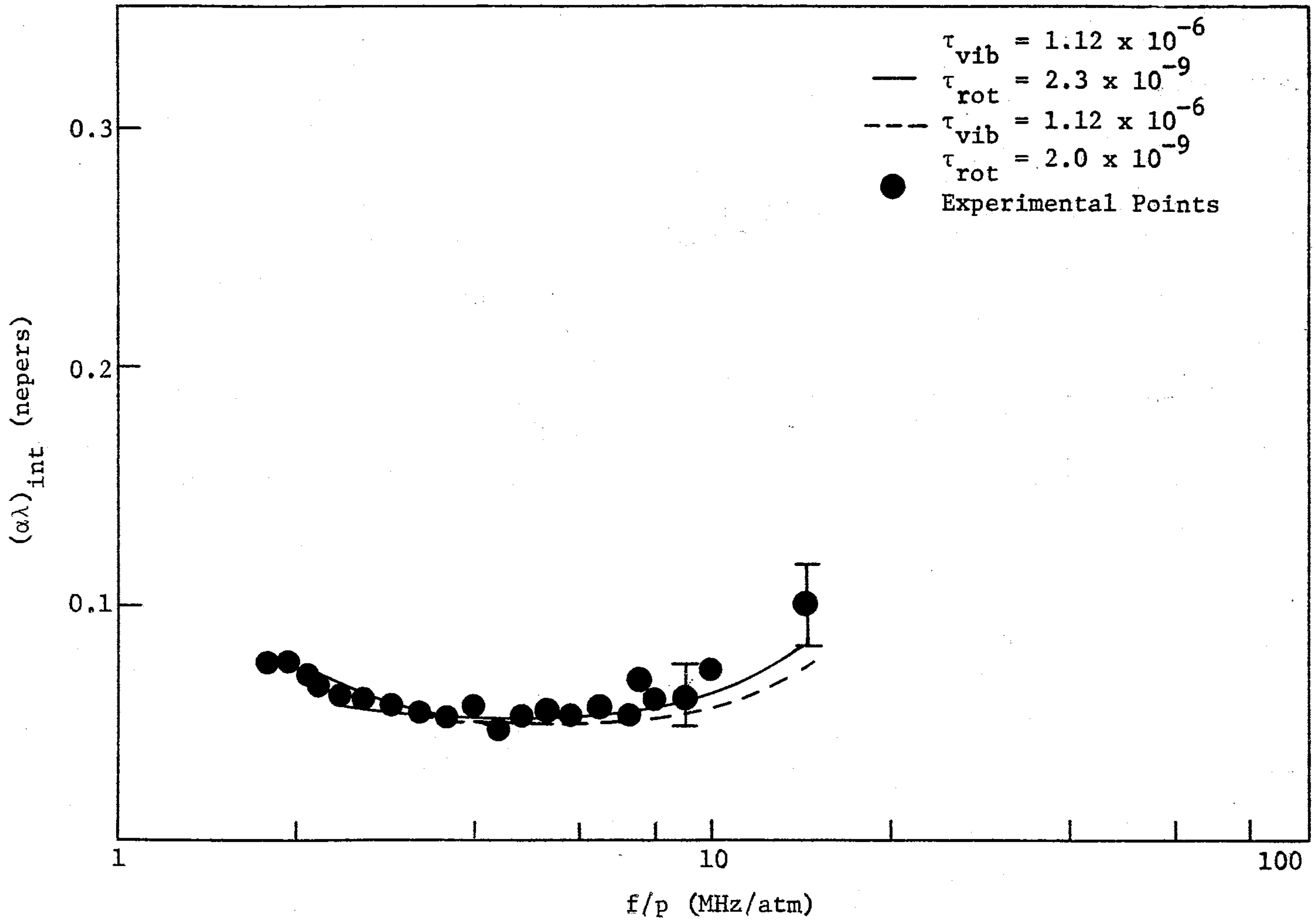

Figure 15. Absorption in 98% CO_2 + 2% H_2 at 984°K

Shortly after the high temperature measurements it was noted that the stainless steel chamber itself had developed cracks and would no longer hold a vacuum. This was probably due to hydrogen embrittlement of the stainless steel.

The analysis of the data is complicated by the fact that one must consider the effect of mass diffusion on the absorption of sound. Following Hunt$^{(34)}$ and Kohler$^{(35)}$ the following expression for $(\alpha\lambda)_{cl}$ is used:

$$(\alpha\lambda)_{cl} = f/p \; \frac{2\pi^2}{\gamma^*} \{\frac{4}{3}\eta^* + \frac{(\gamma^*-1)}{C_p^*} K^* + \gamma^* \frac{X_1X_2}{V^2} PD_{12} [\frac{M_2-M_1}{M^*} + \frac{\gamma^*-1}{\gamma^*} \frac{K_T}{X_1X_2}]^2 \}$$

where an asterik (*) indicates values of the quantity evaluated for the gas mixture, and:

X_i = concentration of species i

M_i = molecular weight of species i

PD_{12} = diffusion coefficient

K_T = thermal diffusion ratio

These quantities are completely described in Hunt's thesis$^{(34)}$ and in <u>Molecular Theory of Gases and Liquids</u>$^{(33)}$, but one modification was made. As noted above γ, C_p and K are frequency dependent quantities. Since K_T can be written in terms of K it too becomes frequency dependent$^{(33)}$. The calculation of K_T is straight forward but unfortunately the results agree with experiment only to within about 10% for carbon dioxide - hydrogen mixtures$^{(33)}$. At a concentration of 2% hydrogen the diffusion term makes a contribution of less than 10% to the total classical absorption whereas at a 15% concentration the contribution is about 50%. For this reason this more complicated expression was used to analyze only the 15% data. As noted below using this approach on the 2% data yielded no difference from the more straight forward approach described above.

It was also found that the analysis of the 15% hydrogen data required the use of an additional relaxation time corresponding to the rotational relaxation of the hydrogen in the mixture. A new computer program was written to handle these calculations for mixtures. When used with the 2% data no significant change was noticed in the calculated absorption or the relaxation times. The program, AMD003, is outlined in the Appendix, and the results of the analysis are shown in Figures 16 to 19. The program incorporates three relaxation times, vibrational relaxation of carbon dioxide, rotational relaxation of carbon dioxide and rotational relaxation of hydrogen. The method for finding the best fit to the data was modified. Instead of finding the minimum of $F(\tau_1, \tau_2)$ a different function $G(\tau_1, \tau_2, \tau_3) = \Sigma|(\alpha\lambda)_{obs} - (\alpha\lambda)_{calc.}|$ was minimized with respect to τ_1, τ_2, and τ_3. Even if this minimization only involved increasing the number of points searched from 100 (= 10 different τ_1 x 10 different τ_2) to 1000 (corresponding to an additional 10 τ_3's) the calculation would be 10 times longer, but because of the inclusion of the diffusion term in the calculation of $(\alpha\lambda)_{cl}$ the expression for G is more involved than that of F with a corresponding increase in computational time.

A minimum of G was found by finding minima on a surface gotten by

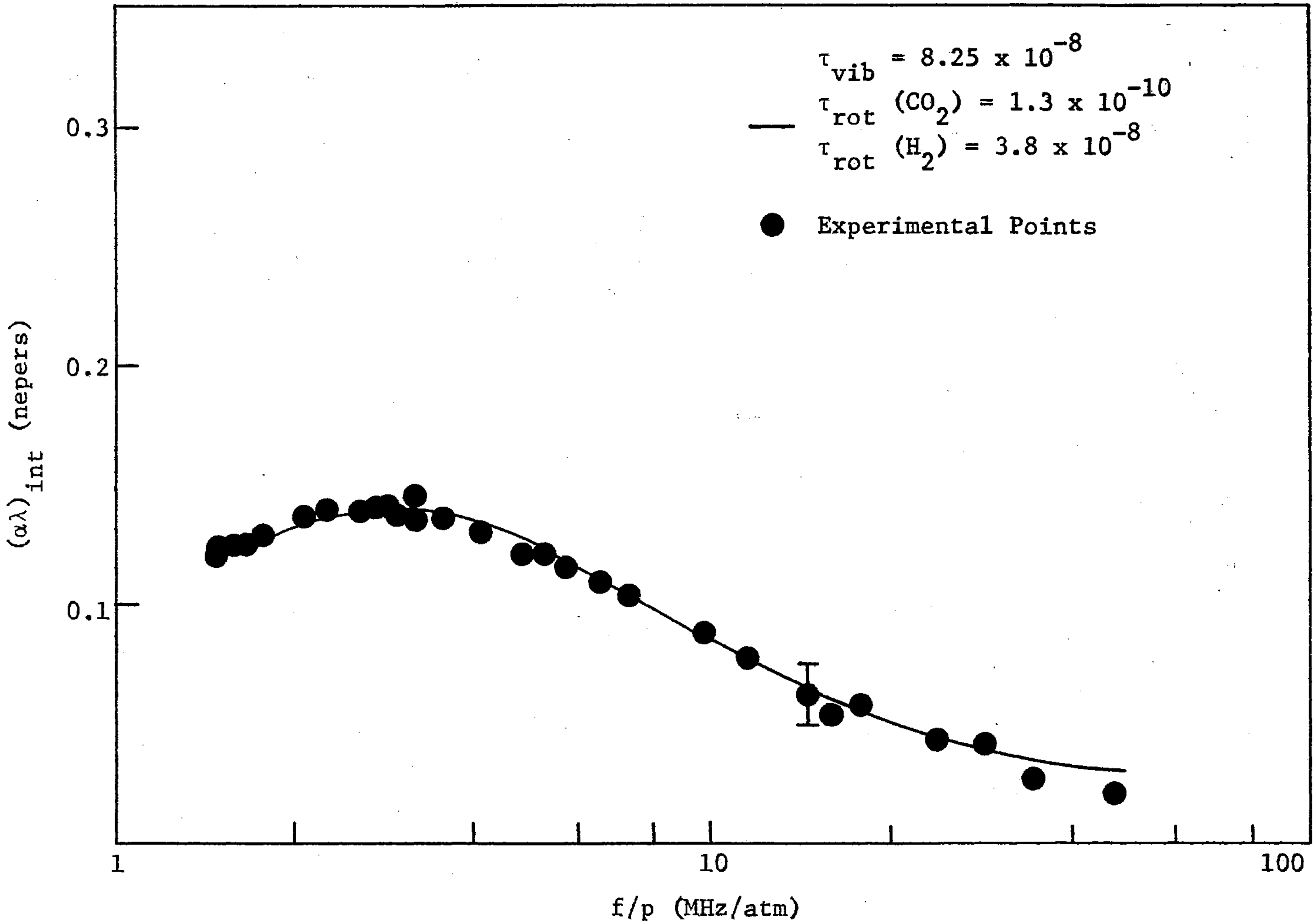

Figure 16. Absorption in 85% CO_2 + 15% H_2 at 300°K

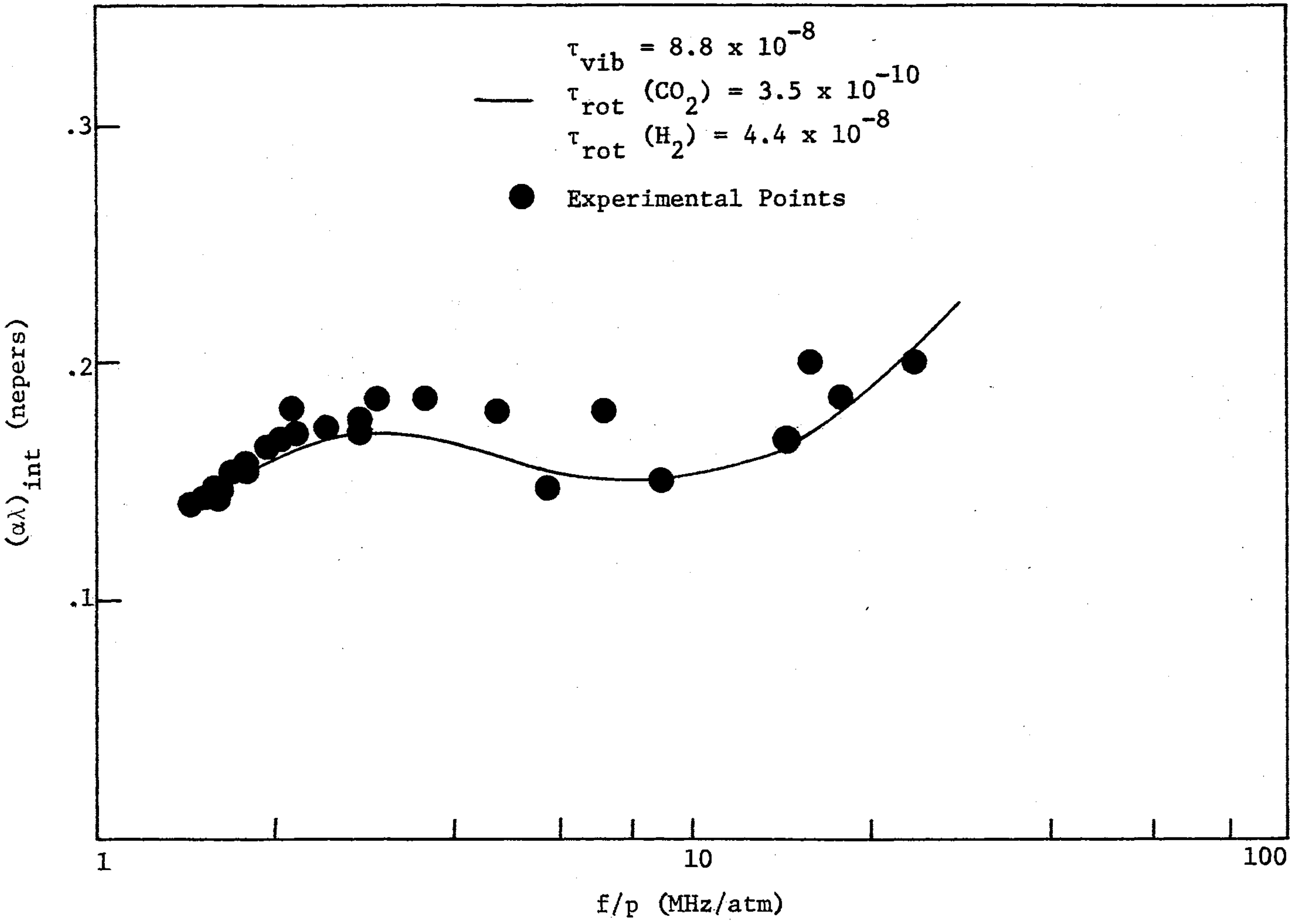

Figure 17. Absorption in 85% CO_2 + 15% H_2 at 388°K

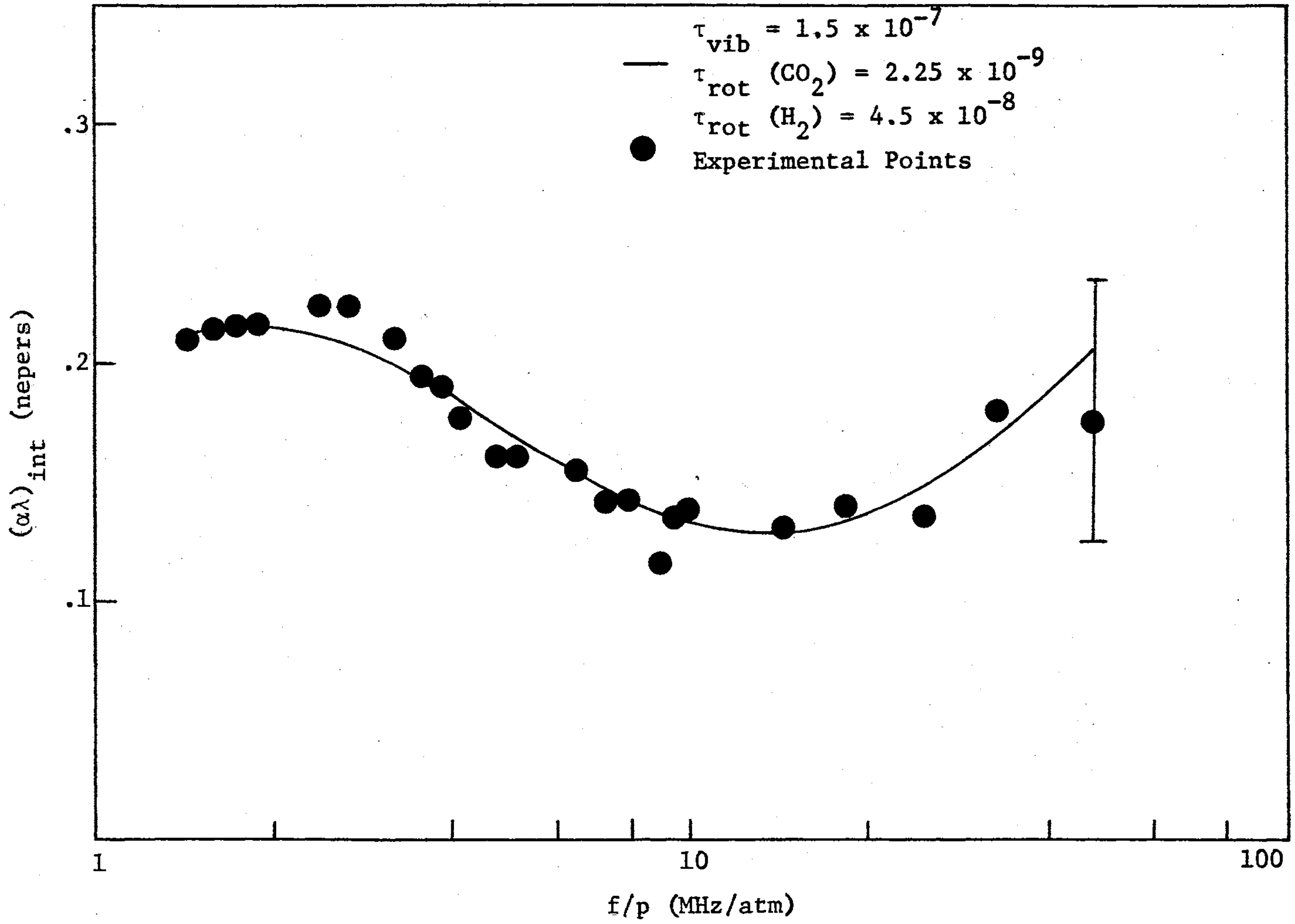

Figure 18. Absorption in 85% CO_2 + 15% H_2 at 543°K

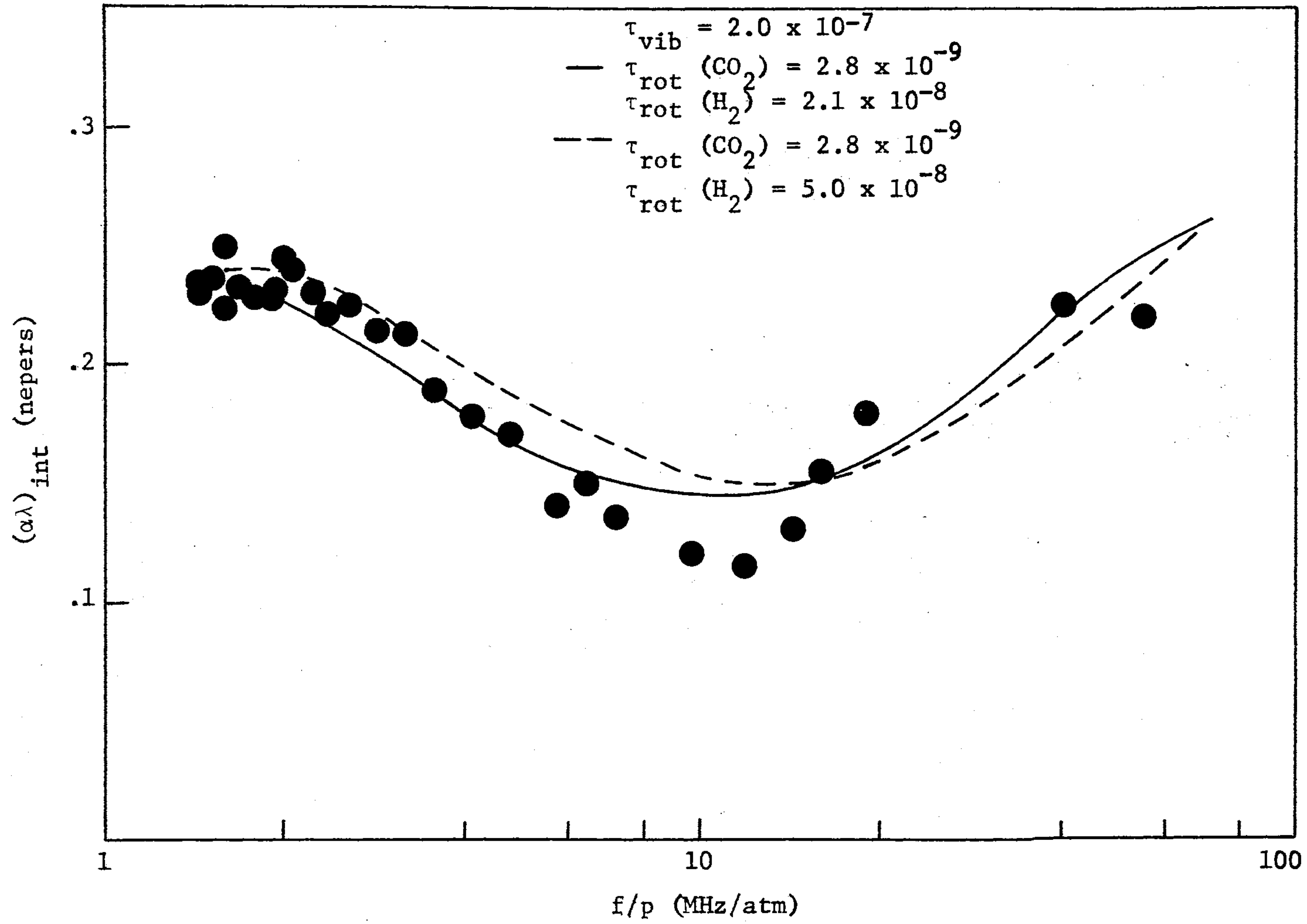

Figure 19. Absorption in 85% CO_2 + 15% H_2 at 750°K

keeping in turn one of the τ's constant. The surface was searched in the following manner. Three τ's are selected as being a first guess and on the surface with one of the τ's constant the value of G is computed for all values of the other two τ's that would be adjacent to the guess value:

$$\tau_1 = \tau_1^o, \tau_1^o + \Delta\tau_1, \tau_1^o - \Delta\tau_1$$

$$\tau_2 = \tau_2^o, \tau_2^o + \Delta\tau_2, \tau_2^o - \Delta\tau_2$$

Of these nine values for G the smallest is selected and the search is done again from that point on the surface. If the point in the center is the smallest point the range of the search is reduced until the change, $\Delta\tau/\tau$ becomes less than some parameter ε. The search is then repeated holding a different τ constant and varying the other two. This process can be repeated using different τ's until convergence is reached. Essentially from the point where the initial guess was made the direction of the true minimum is assumed to be given by the direction of the next nearest minimum, and although the searching procedure is not rigorous experience has shown that it seems to be able to predict absorptions that agree with experiment, and calculations on the 2% data in this manner gave the same results as searching the entire surface. Furthermore, the procedure seems to be insensitive to the choice of which τ would be kept initially constant. It is possible that a local rather than a true minimum of G would be found and care must be taken so that the initial increment of τ_i is large enough to keep this from happening. In the program a method is also established to keep from recalculating G for values of τ_1 and τ_2 already calculated. Although this increases the complexity of the program by giving it more bookkeeping to do it reduces the computational time as the greatest amount of time is spent calculating G rather than making decisions about the region to be searched.

Experimental Conclusions

It is believed that the relaxation times calculated are the best choice to fit the data to an accuracy of approximately 10%. This is indicated by Figure 20 where an expanded scale is used and calculations were made using a relaxation time for the vibrational specific heat that is different by 14% from that judged to be the best fit. It has been argued that some measure of the error in the best fit relaxation times can be inferred from assigning a random 10% error to a set of theoretically generated data points and then determining the best fit to this artificial data(27). This procedure is useful in determining the number of data points necessary to get a true best fit(27), but it is not believed that it is any measure of the accuracy of the inferred relaxation times. Rather it is a check on the accuracy of the best fitting procedure and the true randomness of the assignment of the 10% error. It was found that if a large enough set of data points were used the assignment of a truly random error made no difference in the best fit relaxation times. The conclusions of Bass(27) concerning the number of data points necessary to insure accurate results are valid however.

The vibration relaxation time for pure carbon dioxide decreases with temperature and a plot of the log (τ_{vib}) vs. $T^{-1/3}$ yields a straight line as shown in Figure 21 where the results are compared to those of Simpson and Chandler(36) obtained in a shock tube experiment. The addi-

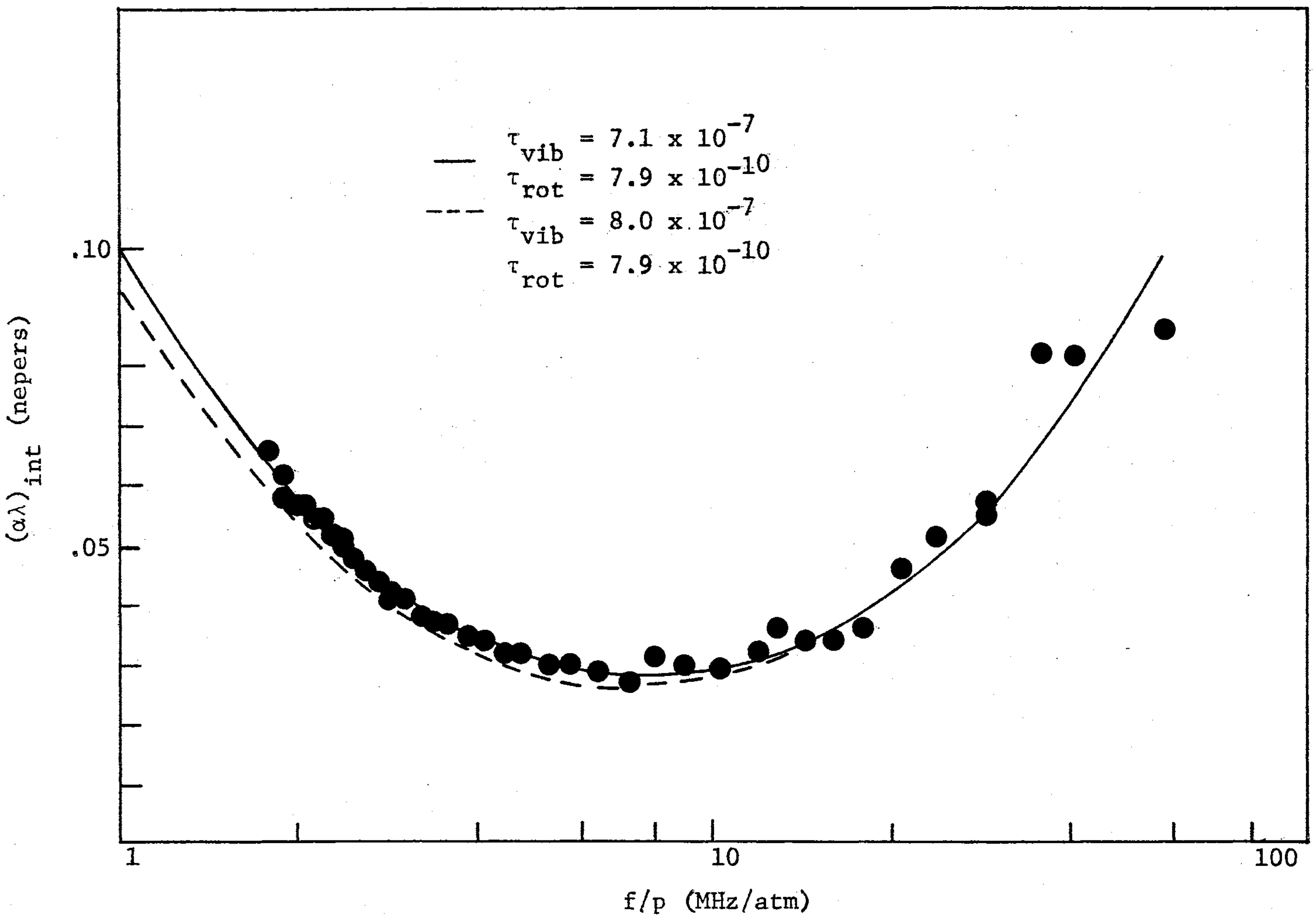

Figure 20. Absorption in 98% CO_2 + 2% H_2 at 384°K Showing Calculations for Two Vibrational Relaxation Times

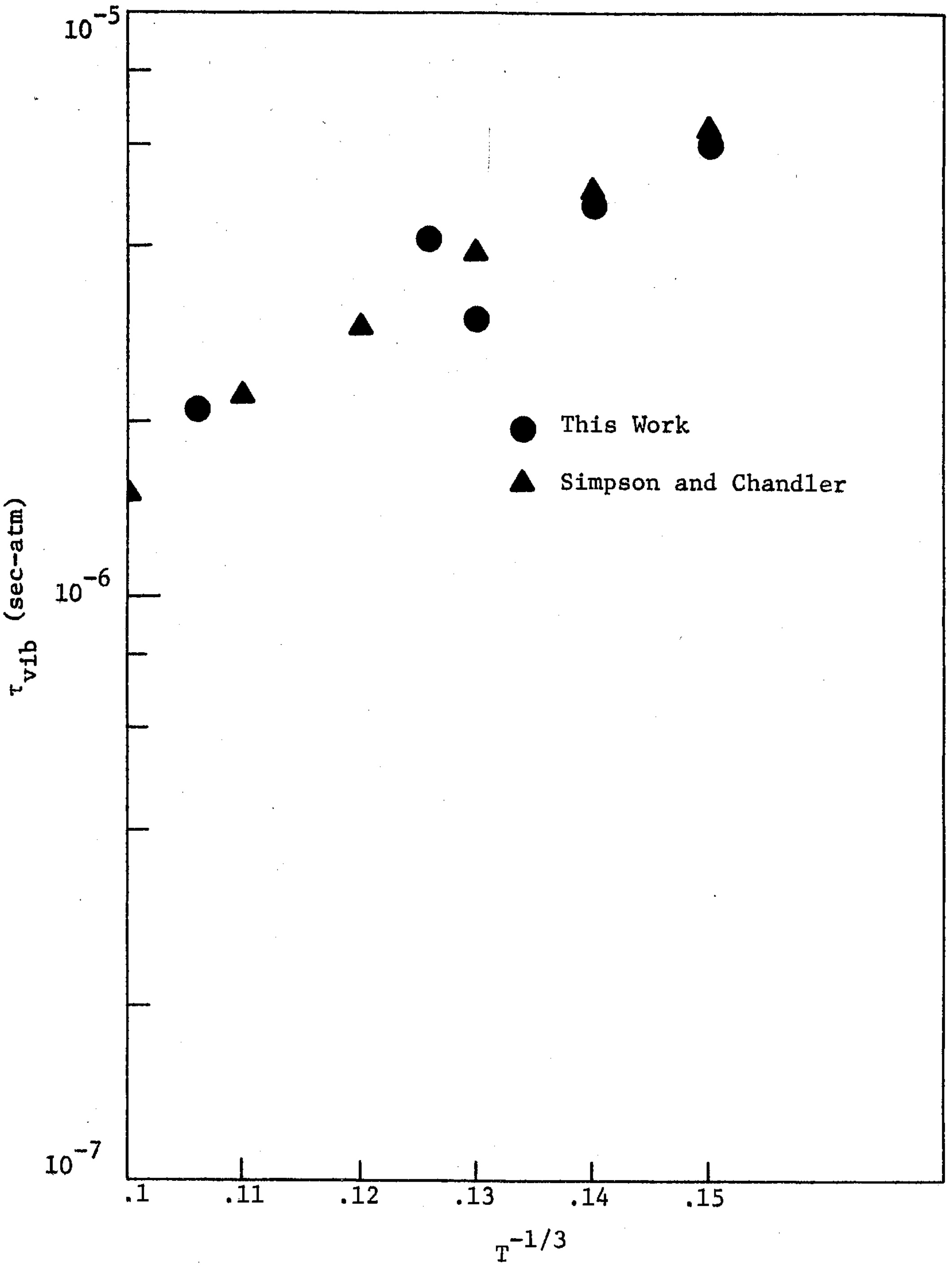

Figure 21. Vibrational Relaxation Time of 100% CO_2 Versus $T^{-1/3}$

tion of hydrogen to the carbon dioxide has a peculiar effect. At room temperature the relaxation time of the 2% mixture is lowered by an order of magnitude, but rather than decreasing with temperature the relaxation time rises slightly and then appears to be approximately constant with temperature as shown in Figure 22. Although there may be some error in the 15% data as noted above it appears that the vibrational relaxation increases with temperature at least to 750 degrees Kelvin, Figure 23.

The rotational relaxation of carbon dioxide generally increases with temperature, Figure 24, but there is considerable scatter in the data. In order to measure rotational relaxation times accurately it is necessary to have accurate measurements of the absorption at high frequency/pressure ratios. As noted above this was difficult with the available instrument because of sound being passed through the walls of the acoustic chamber. Although this effect is present at all gas pressures it becomes a problem only at low pressures where the signal going through the walls of the chamber becomes an appreciable part of the total signal. The problem, although not unique with carbon dioxide is not severe with measurements made on most other gases made with the instrument(27) as results of measurements on Argon indicate. The problem comes with the acoustic velocity of the sound wave in the gas. If the wave going through the gas and that going through the walls arrive at approximately the same time the problem will occur. Also if the sound wave in the gas is sufficiently strong the problem will not exist. It may be possible to modify the design of the instrument to alleviate this effect, and such an approach has been suggested by Bass(27).

The temperature dependence of the vibrational relaxation time of the carbon dioxide - hydrogen mixtures cannot be explained by existing

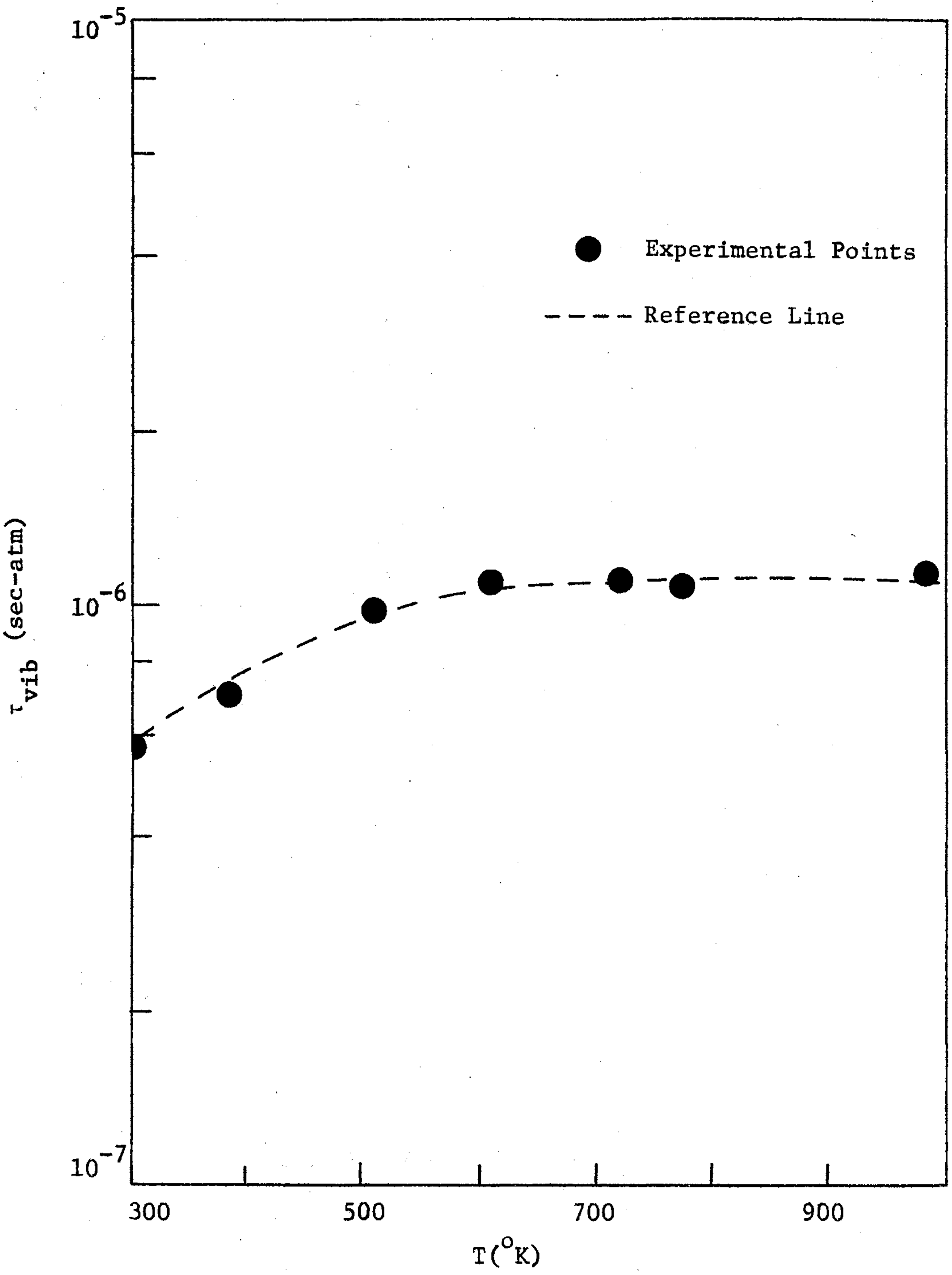

Figure 22. Vibrational Relaxation Time of 98% CO_2 + 2% H_2

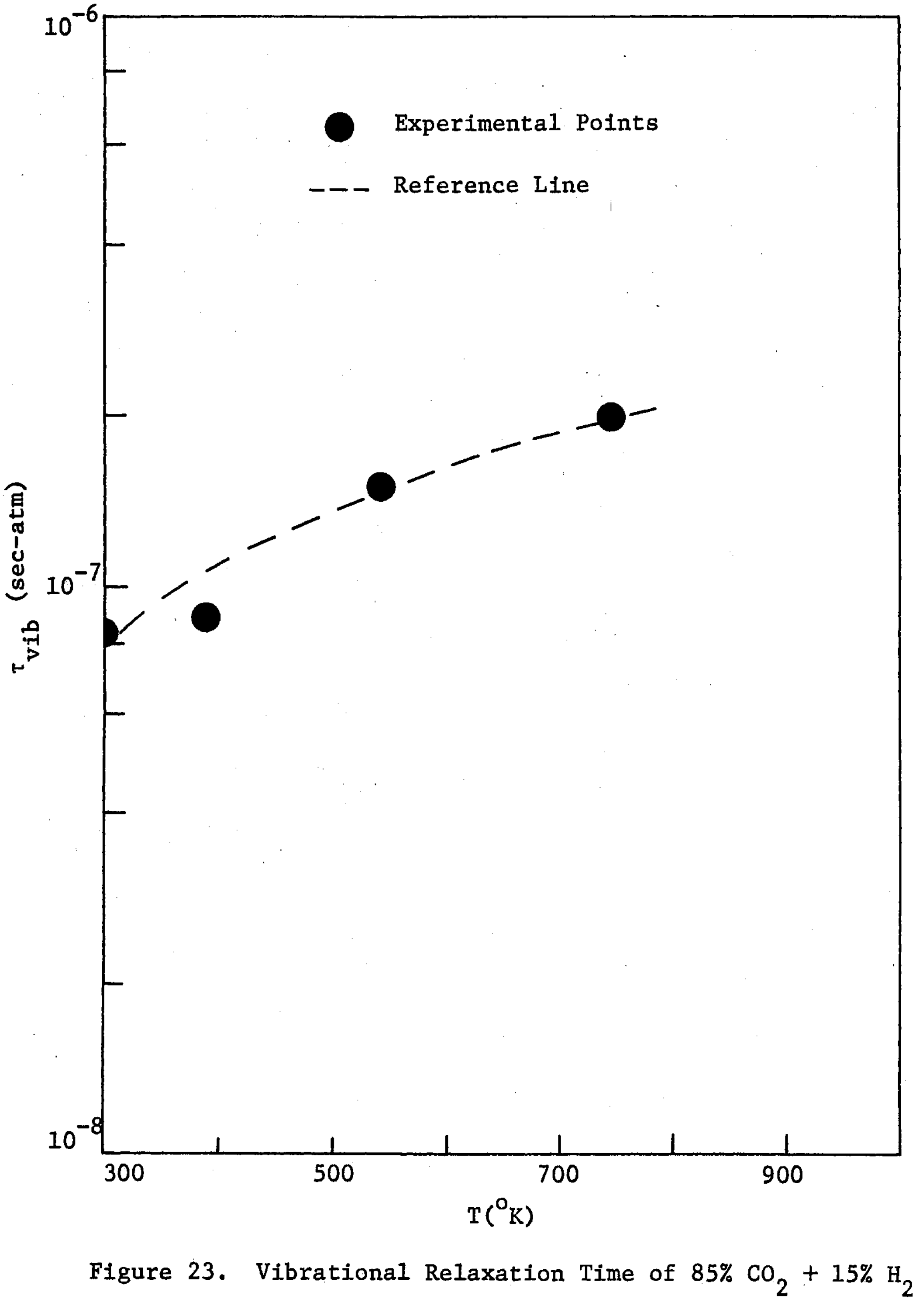

Figure 23. Vibrational Relaxation Time of 85% CO_2 + 15% H_2

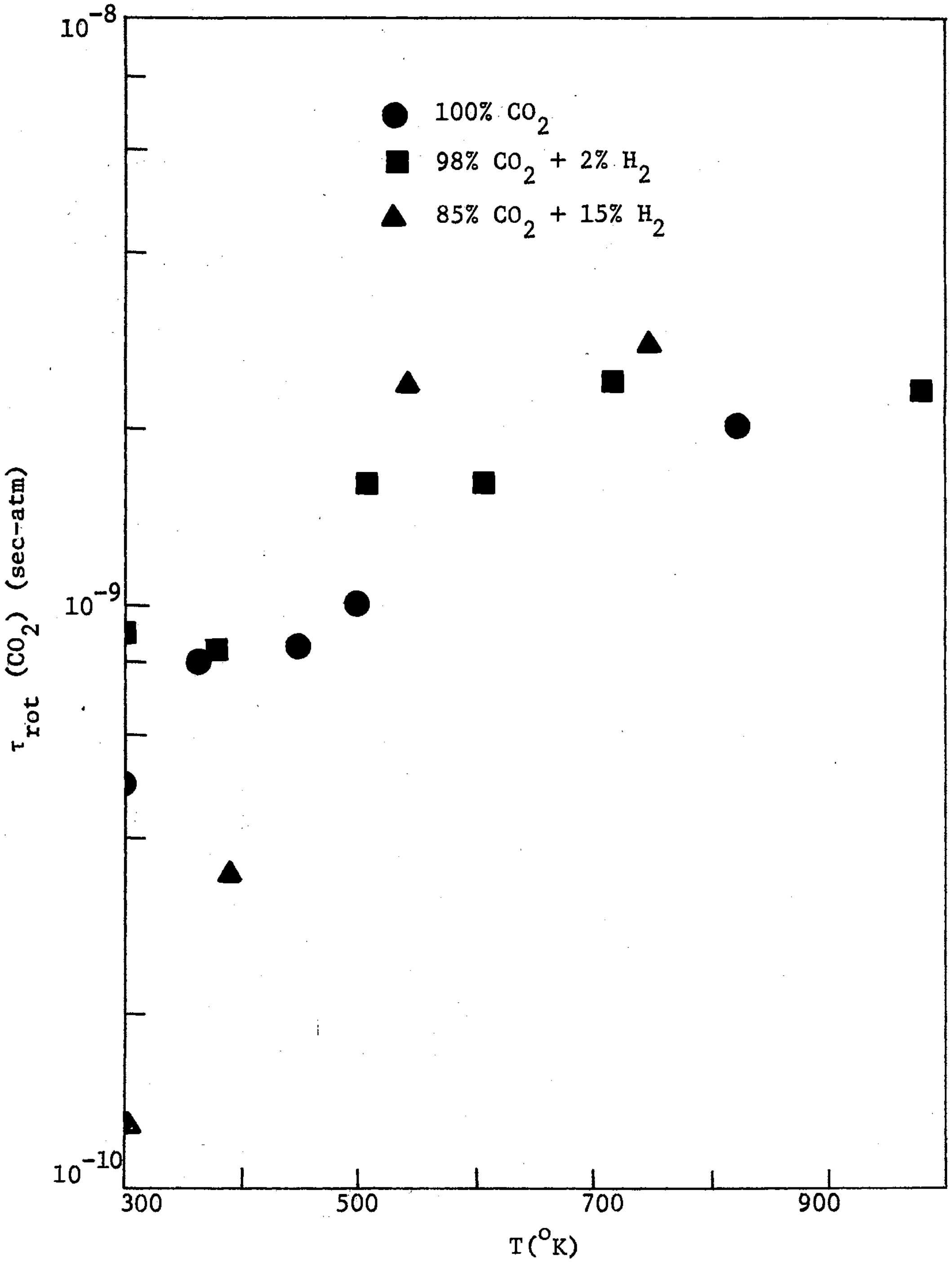

Figure 24. Rotational Relaxation Times

theories concerning vibration - translation (VT) energy transfer, and for this reason a model was developed that would calculate what effect a possible vibration - rotation (VR) energy exchange between carbon dioxide and hydrogen would have on the observed relaxation time.

CHAPTER III

THEORY

Multiple Relaxation

This section of Chapter III is based on the work done by H. J. Bauer on multiply relaxing systems; especially that part which deals with acoustical phenomena(13,14). A multiply relaxing system will be considered as one in which there are more than one means by which energy can be transferred into the internal degrees of freedom of a molecule, and each of these is governed by a specific reaction rate. The problem of deducing reaction rates from relaxation times is quite complicated, and a rigorous connection can only be made for simple models of the gas(7,37). Bauer's method effectively deals with any system, no matter how complicated, and it is a means of going from a reaction scheme and a set of reaction rates to the actual acoustic data. Because this method was used extensively in this work and because it has, in general, not been used to its potential by other researchers a reformulation of the procedure is presented. Since a complete rederivation of Bauer's work would be unwarranted only a brief outline of that part that deals with acoustical phenomena observed in multiply relaxing systems is presented. The notation used follows that of reference 14, but where feasible the notation has been changed so that the results would be in a form more recognizable to researchers in acoustics.

In a gas of molecules with internal degrees of freedom, vibration or rotation, the sound wave perturbation will cause a nonequilibrium situation, and chemical reactions which were at equilibrium before the introduction of the perturbation will no longer be so. A chemical reaction can be written in terms of the stochiometry of the reaction. Namely if there are N reactants reacting by R reactions the stochiometry can be written:

$$\sum_{i=1}^{N} \nu_{i\alpha} M_i \overset{R_\alpha}{\rightleftarrows} \sum_{i=1}^{N} \nu'_{i\alpha} M_i \qquad (9)$$

The $\nu_{i\alpha}$ are the stochiometric coefficients and are simple integers. The above equation is simply a mathematical formulation of what is taught to all students of freshman or high school chemistry; namely in the reaction:

$$A + B \rightleftarrows C$$

one mole of A and one mole of B will react to produce one mole of C. In the above reaction there is only one reaction implying $\alpha = 1$, and there are 3 substances implying $N = 3$. The terms in the stochiometric equation become:

M_1 = number of moles of A = 1
M_2 = number of moles of B = 1
M_3 = number of moles of C = 1
$\nu_{11} = 1$ $\qquad \nu'_{11} = 0$
$\nu_{21} = 1$ $\qquad \nu'_{21} = 0$
$\nu_{31} = 0$ $\qquad \nu'_{31} = 1$

The equation then implies that one mole of A and one mole of B react to form one mole of C; the usual result.

From the stochiometric coefficients, $\nu_{i\alpha}$, one can define a new variable, ξ_α, defined by:

$$dn_i^\alpha = \Delta\nu_{i\alpha}\, d\,\xi_\alpha \tag{10}$$

where: dn_i^α = differential number of moles of substance i produced by reaction α

$\Delta\nu_{i\alpha} = \nu_{i\alpha}' - \nu_{i\alpha}$

ξ_α is in some sense a progress variable for reaction α. In a reacting system one of the independent variables which describe the system could be the number of moles of substances produced by reactions in the system, dn_i^α; instead $d\xi_\alpha$ will be used as one of the independent variables. Later a transformation will be made to go from the variable ξ to the variable η, but for mathematical convenience ξ will be used to derive the final result.

The energy of a thermodynamic system can be written $U = U(V,S,\xi)$ and

$$dU(V,S,\xi) = \left(\frac{\partial U}{\partial S}\right)_{V,\xi} dS + \left(\frac{\partial U}{\partial V}\right)_{S,\xi} dV + \sum_\alpha \left(\frac{\partial U}{\partial \xi_\alpha}\right)_{\xi\neq\xi_\alpha,V,S} d\xi_\alpha \tag{11}$$

the so called Gibbs equation. The connection between the partial derivatives and the thermodynamic variables is made in most elementary books on thermodynamics whereby:

$$\left(\frac{\partial U}{\partial S}\right)_{V,\xi} = T \text{ (= temperature)}$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,\xi} = -P \text{ (= - pressure)}$$

$$\left(\frac{\partial U}{\partial \xi_\alpha}\right)_{\xi \neq \xi_\alpha, V, S} = -A \text{ (-affinity)}$$

Physicists most often learn this equation as:

$$dU = TdS - PdV$$

but removing the restraint of no chemical reactions gives Equation 11; a form probably more familiar to chemists. The affinity, A_α, can also be defined in terms of other thermodynamic variables: $H = U + PV$; $G = H - TS$; $F = U - TS$ (called A in some notations which could be a cause for some confusion). A useful choice would be to define the affinity in terms of F, the Helmholtz function or Helmholtz free energy:

$$A_\alpha = -\left(\frac{\partial F}{\partial \xi_\alpha}\right)_{V,T} = -\sum_{i=1}^{N} \left(\frac{\partial F}{\partial n_i}\right)_{V,T} \frac{\partial n_i}{\partial \xi_\alpha}$$

but from equation $\frac{\partial n_i}{\partial \xi_\alpha} = \Delta\nu_{i\alpha}$ and $\left(\frac{\partial F}{\partial n_i}\right)_{V,T} = \mu_i$ the chemical potential so that

$$A_\alpha = -\sum_i \mu_i \, \Delta\nu_{i\alpha} \tag{12}$$

μ_i is a measure of the effect on the Gibbs function of adding substance i to the system$^{(38)}$.

The above equations are commonly used to connect the effect of chemical reactions to the thermodynamic behavior of the system, but calculations are usually of the quantity $\frac{dn_i^\alpha}{dt}$ and not dn_i^α, and an equation for dn_i^α/dt in terms of the macroscopic variables must be formulated. In order to connect ξ_α and the rates to macroscopic thermodynamics it is convenient to introduce the concepts of forces and fluxes from the field of irreversible thermodynamics (14,33).

Two fundamental equations of thermodynamics are:

$$dU = dQ + dW$$

$$dS \geq dQ/T$$

where, as usual: dU = change in energy of a system

dW = work done on the system

dQ = change in heat of the system

dS = change in entropy of the system

T = temperature of the system

The equation for the entropy can be made exact by noting that for reversible process: $TdS_{rev} = dQ$. Therefore, an exact equation for dS would be:

$$dS = dQ/T + dS_{irreversible}$$

Then $dW = dU - TdS + TdS_{irr}$, but $dU - TdS$ is the reversible work done on the system so that:

$$dS_{irr} = (dW - dW_{rev})/T$$

The rate of entropy production, σ, due to irreversible processes is defined:

$$\sigma = dS_{irr}/dt = (dW - dW_{rev})/Tdt.$$

It is assumed that the entropy production rate, σ, can be written as $\sigma = \sum_i J_i X_i$, where J_i is a generalized flux, and X_i is a generalized force. At equilibrium both the forces and fluxes go to zero (14), and it is assumed that the fluxes are functions of the forces: $J_i = J_i(X_1, X_2, \ldots.)$. A Taylor expansion of J_i is then made about the equilibrium point, J_i^0, X_i^0:

$$J_i(X_1, X_2, \ldots.) = \frac{\partial J_i}{\partial X_i} X_i + \frac{\partial J_i}{\partial X_2} X_2 + \ldots.$$

Then for systems not too far removed from equilibrium σ can be written:

$$\sigma = \sum_i \left(\sum_J \frac{\partial J_i}{\partial X_j} X_j\right) X_i = \frac{1}{T} \sum_{i,j} L_{ij} X_i X_j \tag{13}$$

The coefficients, L_{ij} are symmetric for conditions not too far removed from equilibrium(39,40). This is the Onsager reciprocity theorem, and its proof lies beyond the scope of this work. The quantity 1/T is pulled out of the coefficient for simplicity since the L's can be a function of the equilibrium thermodynamic coordinates.

Combining the equation for σ with the equation for reversible work reformulates σ as:

$$\sigma = \frac{1}{T} \sum_\alpha A_\alpha \frac{d\xi_\alpha}{dt}$$

The above equation is similar to the equation for σ, (written earlier in terms of forces and fluxes) and the same sort of expansion as that done for the generalized flux, J_i, is made for $\frac{d\xi_\alpha}{dt}$:

$$\begin{aligned} \dot{\xi}_\alpha &= \frac{1}{T} \left\{\left(\frac{\partial \dot{\xi}_\alpha}{\partial A_1}\right) A_1 + \left(\frac{\partial \dot{\xi}_\alpha}{\partial A_2}\right) A_2 + \ldots.\right\} \\ &= \frac{1}{T} \sum_i L_{\alpha i} A_i \end{aligned} \tag{14}$$

$\dot{\xi}_\alpha$ is considered as a flux, while A_α is the corresponding force. That this expansion can be made and truncated in the manner shown is the basic assumption of Bauer's linear model. It is a specific case of a more general assumption often made in the field of irreversible thermodynamics$^{(33)}$. It is convenient to introduce a matrix notation at this time.

$\bar{\xi}$ = a vector with elements ξ_α

$\underline{L}$ = a matrix with elements L_{ij}

$\bar{A}$ = a vector with elements A_i

giving an equation for $\dot{\bar{\xi}}$:

$$\dot{\bar{\xi}} = \underline{L}\bar{A}/T$$

Since the force goes to zero at equilibrium a Taylor expansion of A_i is made about the equilibrium point A_i^0.

$$A_i = A_i(P,T,\xi) = \left(\frac{\partial A_i}{\partial T}\right)_{eq} \Delta T + \left(\frac{\partial A_i}{\partial P}\right)_{eq} \Delta P + \sum_{\alpha=1}^{R} \left(\frac{\partial A_i}{\partial \xi_\alpha}\right) (\xi_\alpha - \xi_\alpha^0)$$

or in matrix notation:

$$\bar{A} = \left(\frac{\partial \bar{A}}{\partial T}\right) \Delta T = \left(\frac{\partial \bar{A}}{\partial P}\right) \Delta P + \sum_{\alpha=1}^{R} \left(\frac{\partial \bar{A}}{\partial \xi_\alpha}\right) \xi_\alpha \qquad (15)$$

The last term of the above equation can be written: $-\underline{G}\,\bar{\xi}$

Where $(\underline{G})_{i\alpha} = -\frac{\partial A_i}{\partial \xi_\alpha}$, and $(\underline{G}\,\bar{\xi})$ is a vector with elements $(\underline{G}\,\bar{\xi})_i = \sum_\alpha G_{i\alpha}\,\xi_\alpha$. Combining with Equation (15):

$$\vec{\dot{\xi}} = \frac{1}{T}\,\underline{L}\,\bar{A} = \frac{1}{T}\,\underline{L}\,\{\frac{\partial\bar{A}}{\partial T}\,\Delta T + \frac{\partial\bar{A}}{\partial P}\,\Delta P - \underline{G}\,\bar{\xi}\} \tag{16}$$

Using the definition of A_α and the fact that the second partial derivatives of U or F with respect to any pair of variables is independent of the order of differentiation$^{(41)}$ two new variables are defined by:

$$\bar{S}_P \equiv (\frac{\partial S}{\partial\vec{\xi}})_{P,T} = (\frac{\partial\vec{A}}{\partial T})_{\bar{\xi},P} \tag{17}$$

$$-\bar{V} = -(\frac{\partial V}{\partial\xi})_{P,T} = (\frac{\partial\vec{A}}{\partial P})_{\vec{\xi},T} \tag{18}$$

Giving for $\bar{\dot{\xi}}$:

$$\begin{aligned}\bar{\dot{\xi}} = \frac{1}{T}\,\underline{L}\,\bar{A} &= \frac{1}{T}\,\underline{L}\,\bar{S}_P\,(T-T_o) - \frac{1}{T}\,\underline{L}\,\bar{V}\,(P-P_o)\\ &\quad - \frac{1}{T}\,\underline{L}\,\underline{G}\,\bar{\xi}\end{aligned} \tag{19}$$

Making an expansion of the entropy S(T,P,ξ) about the equilibrium value, S_0, and again keeping only the linear terms:

$$\begin{aligned}S-S_o &= (\frac{\partial S}{\partial T})_{\xi,P}\,\Delta T + (\frac{\partial S}{\partial P})_{T,\xi}\,\Delta P + \sum_{\alpha=1}^{R}(\frac{\partial S}{\partial\xi_\alpha})_{P,T,\xi\neq\xi_\alpha}\,\xi_\alpha\\ &= (\frac{\partial S}{\partial T})_{\xi,P}\,\Delta T + (\frac{\partial S}{\partial P})_{T,\xi}\,\Delta P + \bar{S}_P\cdot\bar{\xi}\end{aligned} \tag{20}$$

In the acoustic case the assumption is made that $\xi(t) = \xi^o \exp(j\omega t + \phi)$ after a steady state has been reached$^{(14)}$. This gives immediately that $\bar{\dot{\xi}}(t) = j\omega\bar{\xi}(t)$ and implies that the populations of various chemical species vary about an equilibrium value harmonically with time. This is the result of a sinusoidal force being applied to the system. Putting this result into Equation 19 and assuming an isobaric process, $P = P_0$, yields:

$$\frac{\Delta S}{\Delta T} = \left(\frac{\partial S}{\partial T}\right)_{\xi,P} + \bar{S}_P \cdot [j\omega \underline{\underline{1}} + \frac{1}{T} \underline{L}\, \underline{G}]^{-1} \frac{1}{T} \underline{L}\, \bar{S}_P \qquad (21)$$

But

$$\frac{\Delta S}{\Delta T}\Big|_{\Delta P=0} = C_p/T$$

And $(\partial S/\partial T)_{\xi,P} = \frac{1}{T} C_p^{\infty}$ since constant ξ implies that the system cannot "see" the reaction which would be the case if the sound frequency were very high, infinite, and the only contribution to the specific heat, C_p, would be from the translation motion of the molecules$^{(7)}$.

This gives an equation for the frequency dependence of the specific heat:

$$\frac{1}{T} C_p(\omega) = \frac{1}{T} C_p^{\infty} + \bar{S}_p \cdot [j\omega \underline{1} + \frac{1}{T} \underline{L}\, \underline{G}]^{-1} \frac{1}{T} \underline{L}\, \bar{S}_p \qquad (22)$$

and in formal terms the problem is solved, but as with most formal solutions it is useless for any manner of calculation. The connection between the terms in the above equation and the reaction must be established, and the equation will be put in a more useable form.

From the definition of the progress variable, ξ, it can be seen that $\dot{\xi}f_\alpha = (\text{Rate})_{\text{forward}_\alpha} \underset{i}{\pi}\, C_i^{\nu_{i\alpha}}$, where C_i's are the molar concentrations and the rate is the rate per unit volume. Similarly the reverse reaction leads to $\dot{\xi}r_\alpha = (\text{Rate})_{\text{reverse}_\alpha} \underset{i}{\pi}\, C_i^{\nu'_{i\alpha}}$. At equilibrium the forward and reverse reactions balance and $\dot{\xi}_f = \dot{\xi}_r$. Giving:

$$\dot{\xi}_{net} = \dot{\xi}_f \, (1 - \dot{\xi}_r/\dot{\xi}_f) = \dot{\xi}_f \, (1 - (\frac{R_r}{R_f}) \underset{i}{\pi}\, C_i^{\Delta\nu_i})$$

Defining $K_c = R_f/R_r$ = mass action constant of molar concentration gives:

$$\dot{\xi}_{net} = \dot{\xi}_F \left(1 - \frac{1}{K_c} \underset{i}{\pi}\, C_i^{\Delta\nu_i}\right) \qquad (23)$$

or:

$$\dot{\xi}_{net} = \dot{\xi}_F \left(1 - \frac{1}{K_x} \underset{i}{\pi}\, X_i^{\Delta\nu_i}\right) \qquad (24)$$

where X_i is the mole fraction of species i, and K_x is the mass action constant of mole fraction. By defining $Q_x^\alpha \equiv \underset{i}{\pi}\, X_i^{\Delta\nu_{i\alpha}}$. The connection with the other variables is made by noting:

$$A_\alpha = - \sum_i \mu_i \,\Delta\nu_{i\alpha}$$

but $\mu_i = \mu_i^o + RT \ln X_i$.(38) This gives an equation for A_α:

$$\begin{aligned} A_\alpha &= - \sum_i \mu_i^o \,\Delta\nu_{i\alpha} - RT \sum_i \Delta\nu_{i\alpha} \ln X_i \\ &= - \sum_i \mu_i^o \,\Delta\nu_{i\alpha} - RT \sum_i \ln X_i^{\Delta\nu_{i\alpha}} \\ &= - \sum_i \mu_i^o \,\Delta\nu_{i\alpha} - RT \ln \left[\underset{i}{\pi}\, X_i^{\Delta\nu_{i\alpha}}\right] \qquad (25) \\ &= - \sum_i \mu_i^o \,\Delta\nu_{i\alpha} - RT \ln Q_x^\alpha \end{aligned}$$

Because A_α vanishes at equilibrium where $K_x = Q_x$: and $- \sum_i \mu_i^o \,\Delta\nu_{i\alpha} =$ $RT \ln K_x$. And an equation for A becomes:

$$A_\alpha = RT \ln (K_x^\alpha / Q_x^\alpha) \qquad (26)$$

Combining with Equation 24 yields: $\dot{\xi}_{net_\alpha} = \dot{\xi}_\alpha = \dot{\xi}_{f_\alpha} \left[1 - \exp(-A_\alpha/RT)\right]$

Expanding the exponential and keeping the first two terms:

$$\dot{\xi}_\alpha = \dot{\xi}_{F_\alpha} A_\alpha/RT = R_f^\alpha (\pi_i C_i \Delta\nu_{i\alpha}) A_\alpha/RT$$

$$= \frac{1}{T} \{\frac{R_f^\alpha}{R} (\pi_i C_i^{\Delta\nu_{i\alpha}})\} A_\alpha \tag{27}$$

In keeping with the spirit of keeping only linear terms in the expansions it is noted that the term in brackets in Equation (27) is a constant at equilibrium which is not zero. Taking the value at equilibrium for this term the equation for $\dot{\xi}_\alpha$ is:

$$\dot{\xi}_\alpha = \text{constant x } A_\alpha$$

From Equation (14): $L\alpha\beta = \partial\dot{\xi}_\alpha/\partial A_\beta$

$$= \frac{1}{T} (\pi_i C_i^{\Delta\nu_{i\alpha}}) R_f^\alpha/R \qquad \alpha = \beta \tag{28}$$

$$= 0 \qquad \text{otherwise}$$

And the connection between $\underline{L}$ and the rate constants is established. Essentially $\underline{L}$ is a diagonal matrix of the rate constants.

From the definition of $\underline{G}$:

$$(\underline{G})_{\alpha\beta} = -(\partial A_\alpha/\partial\xi_\beta)_{P,T}$$

$$= RT \frac{\partial}{\partial\xi_\beta} \ln (K_x^\alpha/Q_x^\alpha) \tag{29}$$

But K_x^α is a constant with respect to ξ_β and:

$$(\underline{G})_{\alpha\beta} = -RT \frac{\partial \ln (Q_x{}^{\alpha})}{\partial \xi_\beta}$$

$$= -RT \frac{\partial}{\partial \xi_\beta} \ln \prod_i x_i^{\Delta\nu_{i\alpha}} = -RT \sum_i \Delta\nu_{i\alpha} \frac{\partial \ln x_i}{\partial \xi_\beta} = -RT \sum_i \frac{\Delta\nu_{i\alpha}}{x_i} \frac{\partial x_i}{\partial \xi_\beta} \qquad (30)$$

Evaluation of $\partial x_i/\partial \xi_\beta$ follows:

$$\partial x_i/\partial \xi_\beta = \frac{\partial}{\partial \xi_\beta} (n_i/n) = \frac{1}{n} \frac{\partial n_i}{\partial \xi_\beta} + n_i \frac{\partial}{\partial \xi_\beta} \frac{1}{n}$$

$$= \frac{1}{n} \Delta\nu_{i\beta} - \frac{n_i}{n^2} \frac{\partial n}{\partial \xi_\beta}$$

$$= \frac{1}{n} (\Delta\nu_{i\beta} - x_i \sum_j \Delta_{j\beta}) \qquad \text{since } n = \sum_j n_j \qquad (31)$$

$$\text{so that: } \frac{\partial A_\alpha}{\partial \xi_\beta} = -\frac{RT}{n} \{ (\sum_i \frac{\Delta\nu_{i\alpha}\ \Delta\nu_{i\beta}}{x_i}) - (\sum_i \sum_j \Delta\nu_{i\alpha}\ \Delta\nu_{j\beta}) \} \qquad (32)$$

This expression is very complicated and Bauer was able to simplify the notation by the introduction of matricies.

Let $\underline{\nu}$ be a matrix such that: $(\underline{\nu})_{i\alpha} = \Delta\nu_{i\alpha}$ (33)

and $\underline{X}$ be a matrix such that: $(\underline{X})_{ij} = x_i\ \delta_{ij}$ (34)

$\underline{X}$ is a diagonal matrix of mole fractions. The first term of Equation (32) can now be written:

$$\sum_i \frac{\Delta\nu_{i\alpha}\ \Delta\nu_{i\beta}}{x_i} = \sum_i (\underline{\nu})_{i\alpha}\ (x)^{-1}_{ii}\ (\underline{\nu})_{i\beta}$$

$$= \sum_i \sum_j (\tilde{\underline{\nu}})_{\alpha i}\ (x)^{-1}_{ij}\ (\nu)_{j\beta}$$

$$= (\underline{\tilde{\nu}}\ \underline{x}^{-1}\ \underline{\nu})_{\alpha\beta} \tag{35}$$

It is the (α,β) component of the matrix $(\underline{\tilde{\nu}}\ \underline{x}^{-1}\ \underline{\nu})$, where $\underline{\tilde{\nu}}$ indicates the transpose of $\underline{\nu}$. The second term of Equation (32) will always be zero for all cases considered here--the acoustic case. To show this one simply notes the physical meaning of $\sum_i \Delta\nu_{i\alpha}$. This is the change in the total number of moles in the system by reaction proceeding to completion. Assume reaction α was of the form: $A + B \rightarrow C$. Then: $\sum_i \Delta\nu_{i\alpha} = -1 + (-1) + 1 = -1$. But energy transfer reactions considered are always of the form: $A + B \rightarrow C + D$. Giving: $\sum_i \Delta\nu_{i\alpha} = -1 - 1 + 1 + 1 = 0$. In situations where a recombination reaction is considered the second term will be necessary, but no such cases are considered here. Formally:

$$\underline{G} = \frac{RT}{n} (\underline{\tilde{\nu}}\ \underline{x}^{-1}\ \underline{\nu}) \tag{36}$$

It remains to find a more familiar form for $\bar{S}_p$ defined as:

$$(\bar{S}_p)_\alpha = \left(\frac{\partial S}{\partial \xi_\alpha}\right)_{P,T}$$

Noting $dG = dH - TdS - SdT = 0$ at constant P and T:

$$\left(\frac{\partial S}{\partial \xi_\alpha}\right)_{P,T} = \frac{1}{T}\left(\frac{\partial H}{\partial \xi_\alpha}\right)_{P,T} = \frac{1}{T}\Delta H_\alpha \tag{37}$$

Where ΔH_α is known as the heat of reaction α. The equation for the specific heat becomes:

$$C_p(\omega) = C_p^{\infty} + T\,\bar{S}_p \cdot [j\omega\underline{1} + \frac{1}{T}\underline{L}\ \underline{G}]^{-1} \frac{1}{T}\underline{L}\ \bar{S}_p$$

Where all of the terms have been defined. This is not the form used, however. If $\underline{G}$ were a diagonal matrix then:

$$C_p = C_p^{\infty} + T \sum_{i=1}^{R} (\bar{S}_p)_i^{\,2} \frac{(L_{ii}/T)}{(j\omega + \frac{1}{T} L_{ii}\, G_{ii})}$$

$$= C_p^{\infty} + T \sum_i \frac{(\bar{S}_p)_i^{\,2}/G_{ii}}{(1 + j\omega\, (L_{ii}\, G_{ii}/T)^{-1})}$$

By making the identification of $L_{ii}\, G_{ii}/T$ with $(\tau_i)^{-1}$ and of $(\bar{S}_p)_i^{\,2}/G_{ii}$ with $\delta C_{p_i}/T$:

$$C_p(\omega) = C_p^{\infty} + \sum_i \frac{\delta C_{p_i}}{(1 + j\omega\tau_i)}$$

Which resembles the usual equation for relaxation in "series"$^{(7)}$. Before making a transformation in order to effect a diagonal matrix a change of variables is made:

$$\bar{n} = \underline{\nu}\, \bar{\xi} \tag{39}$$

and

$$\vec{A} = -\, \tilde{\underline{\nu}}\, \bar{\mu} \tag{40}$$

From Equations (15)(16) and (18):

$$\bar{A} = -\underline{G}\, \bar{\xi} + \bar{S}_p\, \Delta T - \bar{v}\Delta P = -\frac{RT}{n} (\tilde{\underline{\nu}}\, \underline{x}^{-1}\, \underline{\nu})\, \bar{\xi} + \bar{S}_p\, \Delta T \; (\bar{v} = 0) \tag{41}$$

and

$$\bar{S}_p = \frac{1}{T} \overline{\Delta H} = \frac{1}{T} \tilde{\underline{\nu}}\, \bar{E} \tag{42}$$

where $(\bar{E})_i \equiv (\frac{\partial u}{\partial n_i})_{P,T}$, the partial energies of each substance. This yields an equation for $\bar{\mu}$:

$$\bar{\mu} = \frac{RT}{n}\underline{x}^{-1}\,\bar{n} - \frac{1}{T}\,\bar{E}\,\Delta T \tag{43}$$

Following a development similar to the one above:

$$C_p = C_p^{\infty} + \frac{R}{n}\,\bar{E}\cdot\{[j\omega\underline{1} + \underline{\nu}\,\underline{L}'\,\underline{\tilde{\nu}}\,\underline{x}^{-1}]^{-1}\,\underline{\nu}\underline{L}\underline{\tilde{\nu}}\,\bar{E}\} \tag{44}$$

Where $\underline{L}' = (RT/n)\underline{L}$. As before this equation could be more easily used if $[j\omega\underline{1} + \underline{\nu}\,\underline{L}'\underline{\tilde{\nu}}\,\underline{x}^{-1}]$ were diagonal, and although this is not necessary and the equation for C_p has been used in the form shown there are often practical problems in inverting matricies, and the diagonal form is easier to understand in terms of familiar concepts. In order to effect a form of equation which is more amenable to calculation note the following three equations:

$$\bar{\mu} = \frac{RT}{n}\,\underline{x}^{-1}\,\bar{n} - \frac{1}{T}\,\bar{E}\,\Delta T \tag{45}$$

$$\bar{\dot{n}} = -\,\underline{\nu}\underline{L}\underline{\tilde{\nu}}\,\bar{\mu}\ \text{(From } \bar{\dot{\xi}} = \underline{L}\,\bar{A}\text{)} \tag{46}$$

$$S-S_o = \left(\frac{\partial S}{\partial T}\right)\Delta T + \frac{1}{T}\,\bar{E}\cdot\bar{n} + \text{(Terms in p)} \tag{47}$$

Equation (45) and (46) can be rewritten:

$$\underline{x}^{\frac{1}{2}}\,\bar{\mu} = \frac{RT}{n}\,\underline{x}^{-\frac{1}{2}}\,\bar{n} - \frac{1}{T}\,\underline{x}^{\frac{1}{2}}\,\bar{E}\,\Delta T \tag{48}$$

$$\underline{x}^{-\frac{1}{2}}\,\bar{\dot{n}} = -\,\underline{x}^{-\frac{1}{2}}\,\underline{\nu}\underline{L}\underline{\tilde{\nu}}\,\underline{x}^{-\frac{1}{2}}\,\underline{x}^{\frac{1}{2}}\,\mu \tag{49}$$

denote $\underline{x}^{-\frac{1}{2}}\,\underline{\nu}\underline{L}\underline{\tilde{\nu}}\,\underline{x}^{-\frac{1}{2}}$ by $\underline{M}$, and note that $\underline{M}$ is symmetric:

$$(M)_{ij} = \sum_{KLMN} x_{iK}^{-\frac{1}{2}}\,\nu_{KL}\,L_{LM}\,(\tilde{\nu})_{MN}\,x_{Nj}^{-\frac{1}{2}}$$

Since $\underline{L}$ and $\underline{x}$ are diagonal:

$$= \sum_{K,L,M,N} x_{iK}^{-\frac{1}{2}} \nu_{KL} L_{LM} (\tilde{\nu})_{MN} x_{Nj}^{-\frac{1}{2}} \delta_{Ki} \delta_{LM} \delta_{Nj}$$

$$= \sum_{M} x_{ii}^{-\frac{1}{2}} \nu_{im} L_{MM} (\tilde{\nu})_{Mj} x_{jj}^{-\frac{1}{2}}$$

$$= \sum_{M} x_{jj}^{-\frac{1}{2}} \nu_{jM} L_{MM} (\tilde{\nu})_{Mi} x_{ii}^{-\frac{1}{2}}$$

$$= (M)_{ji} \qquad \text{q.e.d.}$$

So that a matrix $\underline{B}$ can be found such that: $\underline{\tilde{B}}\ \underline{M}\ \underline{B} = (1/\underline{\tau})$, and: $\underline{\tilde{B}}\ \underline{B} = \underline{1}$, where $(1/\underline{\tau})$ is a diagonal matrix. Rewriting (48) and (49):

$$\underline{\tilde{B}}\ x^{\frac{1}{2}}\ \bar{\mu} = \frac{RT}{n}\ \underline{\tilde{B}}\ \underline{x}^{-\frac{1}{2}}\ \bar{n} - \frac{1}{T}\ \underline{\tilde{B}}\ \underline{x}^{\frac{1}{2}}\ \bar{E}\ \Delta T \tag{50}$$

$$\underline{\tilde{B}}\ \underline{x}^{-\frac{1}{2}}\ \dot{\bar{n}} = -\ (1/\underline{\tau})\ \underline{\tilde{B}}\ \underline{x}^{\frac{1}{2}}\ \bar{\mu} \tag{51}$$

Combine To eliminate $\bar{\mu}$ and assume, as above, $\dot{\bar{n}} = j\omega\bar{n}$

$$j\omega\underline{\tilde{B}}\ \underline{x}^{-\frac{1}{2}}\ \bar{n} = -\ (1/\underline{\tau})\ \{\frac{RT}{n}\ \underline{\tilde{B}}\ \underline{x}^{-\frac{1}{2}}\ \bar{n} - \frac{1}{T}\ \underline{\tilde{B}}\ \underline{x}^{\frac{1}{2}}\ \bar{E}\ \Delta T\} \tag{52}$$

$$\underline{\tilde{B}}\ \underline{x}^{-\frac{1}{2}}\ \bar{n} = (j\omega + \frac{RT}{n}\ (1/\underline{\tau}))^{-1}\ (1/\underline{\tau})\ \frac{1}{T}\ \underline{\tilde{B}}\ \underline{x}^{\frac{1}{2}}\ \bar{E}\ \Delta T \tag{53}$$

$$\begin{aligned} \bar{E}\cdot\bar{n} &= \bar{E}\ \cdot\ (\underline{\tilde{B}}\ \underline{x}^{-\frac{1}{2}})^{-1}\ (j\omega + \frac{RT}{n}\ (1/\underline{\tau}))^{-1}\ (\frac{1}{\underline{\tau}})\ \frac{1}{T}\ \underline{\tilde{B}}\ \underline{x}^{\frac{1}{2}}\ \bar{E}\ \Delta T \\ &= (\bar{E}\ \underline{x}^{\frac{1}{2}}\ \underline{B})\ (j\omega + (1/\tau'))^{-1}\ (\frac{n}{RT})\ (\frac{1}{\underline{\tau}'})\ \frac{1}{T}\ (\underline{\tilde{B}}\ \underline{x}^{\frac{1}{2}}\ \bar{E})\Delta T \end{aligned} \tag{54}$$

Where $(1/\underline{\tau}') \equiv \frac{RT}{n}\ (1/\underline{\tau})$

$$\therefore\ \bar{E}\cdot\bar{n} = \sum_{i} \delta_i C_p/(1 + j\omega\tau_i) \tag{55}$$

where

$$\delta_i C_p \equiv |\tilde{\underline{B}}\, \underline{x}^{\frac{1}{2}} \frac{\bar{E}}{RT}|^2 Rn$$

giving finally

$$C_p(\omega) = C_p^{\infty} + \sum_i \frac{\delta_i C_p}{(1 + j\omega\tau_i)} \tag{56}$$

This is the form used in all calculations and the program for the rate calculations, AMD004 and the calculation of C_p, AMD005, are outlined in the Appendix. The problem of going from a set of rates to acoustical results is formally solved. By using this procedure the method of going from a set of rates to acoustical data is reduced from numerically solving a set of coupled differential equations to diagonalizing a matrix, a substantial reduction of computer time and programming effort. Admittedly the above derivation is rather complicated, and it is only an outline of the more complete and formal presentation by Bauer(13,14). It is not a difficult procedure to use in practice and an outline of the steps necessary to use the program is presented below.

1. Set up a reaction scheme matrix, $\nu_{i\alpha}$.
2. Calculate the diagonal $\underline{L}$ matrix containing the reaction rates.
3. Calculate the concentration of each specie, X_i.
4. Form matrix $\underline{M}$ by:

$$(\underline{M})_{ij} = \sum_{m=1}^{R} x_j^{-\frac{1}{2}} \nu_{jm} L_{mm} (\tilde{\underline{\nu}})_{mi} x_i^{-\frac{1}{2}}$$

5. Diagonalize $\underline{M}$ with a matrix $\underline{B}$ giving eigenvalues, $(1/\tau_i)$ and the corresponding eigenvectors, $\bar{b}_i$ from the columns of $\underline{B}$.
6. Calculate the internal energy of each specie, E_i.

7. For each non zero eigenvalue calculate $\delta_i C_p$ from the corresponding eigenvector by:

$$\delta_i C_p = \frac{n}{RT^2} \{ \sum_{j=1}^{N} [(\bar{b}_i)_j \, x_j^{\frac{1}{2}} \, E_j]^2 \}.$$

8. Calculate $(C_p)_{eff} = C_p + \sum_i \delta_i C_p/(1 + j\omega\tau_i)$.

9. Use $(C_p)_{eff}$ to calculate $(\alpha\lambda(\omega))_{int}$ and v^2/v_o^2.

In practice several of the above steps can be combined and the process becomes even simpler.

Vibration - Rotation Rates

This section deals with the formalism involved in calculating the vibration - rotation energy transfer rates for two reactions.

$$CO_2\ (010) + H_2\ (J=1,\ \nu=0) \rightarrow CO_2\ (000) + H_2\ (J=3,\ \nu=0)$$

$$CO_2\ (010) + H_2\ (J=2,\ \nu=0) \rightarrow CO_2\ (000) + H_2\ (J=4,\ \nu=0)$$

As this procedure is described in more detail in other works(17-22) only a brief outline will be given mainly for completeness and which deals primarily with the assumptions and approximations of the model. Mathematical details are presented in a series of three papers by Rabitz and Gordon(17-19) and a presentation here would only be a rederivation of their results. The problem of calculating the probability of an inelastic transfer of energy between the carbon dioxide and hydrogen molecules is solved by a semiclassical approximation. The translational motion of the two molecules is treated classically and the potential between the colliding molecules is a sum of multipole potentials which is truncated after the first nonvanishing term. Further the assumption is made that the classical trajectory can be approximated by a straight line for large impact parameters.

The important point to note about this type of calculation is its region of validity. As mentioned it is useful only for small changes in the total internal energy of the two molecules and this implies that it should be used for near resonant energy exchanges. It could not be expected to work in systems where the change in rotational quantum numbers would be very large. The approach does not conserve angular momentum and errors because of this should be kept to a minimum. Rabitz and Gordon(17) give a general criterion:

$$\Delta E/kT < 1$$

and

$$\Delta J/L < 1$$

where: ΔE is the change of internal energy, and $L = m\ v\ b/h$ = a measure of the angular momentum of the system, b is the impact parameter, ΔJ = change in rotational quantum number.

The potential used is the first nonvanishing term of Equation (8) for impact parameters greater than a certain cut off parameter, d, and the transition probability for the system going from one set of quantum numbers, i, to another, f is calculated. In the case of carbon dioxide - hydrogen the transition dipole moment for carbon dioxide is used, while the quadrapole moment of hydrogen is used. There is no assurance that the actual potential can be represented by such a truncation, but that assumption is made. The calculation is straight forward, and the result is a transition probability parameterized by ΔE, v (relative velocity of colliding molecules), and b: $P(\Delta E,v,b)$.

The general, and complicated, final result is:(42)

$$P_{\ell_1\ell_2} = \frac{4(2\ell_1 + 2\ell_2)!}{(2\ell_1 + 1)!\ (2\ell_2 + 1)!}\ G_{\ell_1+\ell_2}(\omega\tau)\,|<n_1{}^1|Q^{(1)}_{\ell_1}|n_1>|^2$$

$$x\ |<n_2{}^1|Q^{(2)}_{\ell_2}|n_2>|^2 \quad C^2(j,\ell,j_1{}^1;00)$$

$$x\ C^2(j_2\ \ell_2\ j_2{}^1;\ 00)/(\hbar^2\ v^2\ b^{2(\ell_1+\ell_2)}) \qquad (57)$$

Where

$\omega = \Delta E/\hbar$

$\tau = b/v$

$G_\ell(x) = \sum_{\mu=\ell}^{\ell} [(\ell+\mu)!\ (\ell-\mu)!]^{-1}\ x^2\ K_\mu^2(x)$

$K_\mu(x)$ = modified Bessel function

$<n_i{}^1|Q^{(i)}_{\ell_i}|n_i>$ = matrix element for Q_{ℓ_i} multipole moment of molecule i.

In the case considered here the transition is summed over all possible values of the rotation quantum numbers for the carbon dioxide molecule, while the hydrogen molecule is assumed to be in the ground vibrational state. This transition probability is averaged over the velocity by using a Maxwell-Boltzman distribution of velocities:(41)

$$dN_v = (4N/\sqrt{\pi})(m/2kT)^{3/2}\ v^2\ \exp\ (-mv^2/2kT)dv$$

giving

$$P(T,w,b) = \int_{v=o}^{\infty} P(v,w,b)\ vdN_v / \int_{v=o}^{\infty} vdN_v$$

Some manner of averaging over the impact parameter, b, is then formulated. Sharma and Brau(42) calculate an approximate for P(b=0) and then assume:

$$P(b < d) = P(b = 0) + (b/d)^2 \, (P(b = d) - P(b = 0)).$$

There are other ways of handling this averaging,(17) one being:

$$P(b < d) = 1$$

$$P(b \geq d) = P_{calc.}$$

In each case d is the cut off parameter that reflects the fact that a zero impact parameter in the straight line trajectory model would imply that the molecules passed straight through each other. The value of P can be sensitive to the choice of d. The usual choice is the hard sphere diameter of the molecule obtained from the Lennard - Jones 6 - 12 potential, but it can be treated as an adjustable parameter. It was not in the carbon dioxide - hydrogen calculation.

The P(w,T) obtained after averaging is often referred to as a transition probability or cross section. Clearly it is not a transition probability in the usual quantum mechanical sense. It is connected to a reaction rate by multiplication by the number of collisions per second between the two initial states of the colliding molecules normalized to a standard density. The density chosen for all of the rates was one atmosphere at the temperature of the calculation.

Although the final result is relatively simple, especially if one has access to a computer, discretion must be exercised in its use. As noted there are several assumptions made in deriving the final form, and the system on which the model is used should not contradict these assumptions. It does have advantages in that it can be used to predict transition probabilities that are difficult to define if the internal motion of the molecule is treated classically. A further discussion of this semiclassical model is presented in Chapter V.

CHAPTER IV

COMPARISON OF THEORY AND EXPERIMENT

Computational Techniques

Using Bauer's ideas a model of the system was made which allowed various types of reaction schemes to be tested against the data. Although the model can predict absorption and dispersion the theory and experiment are compared through relaxation times. The theoretical absorption data was fitted to a single relaxation curve and a theoretical relaxation time was extracted much in the same manner in which a relaxation time is inferred from experimental data. A flow chart for this scheme is shown in Figure 25. This was done to keep with what appears to be the standard practice of reporting not the acoustic data, but the relaxation times inferred from it. The relaxation times so inferred would correspond to vibrational relaxation times, but as is noted below the processes involved can include the rotational degrees of freedom. Figure 26 shows the acoustic and shock tube vibrational relaxation times. The shock tube work is due to Simpson and Chandler of Great Britain.

The rates used are calculated according to three different theories. The vibration - translation (V-T) rates are calculated according to the Schwartz, Schlawsky and Herzfeld (SSH) model(10), the rotation - translation (R-T) rates were calculated according to a model proposed by Raff and Winter(23), and the vibration - rotation (V-R) rates were cal-

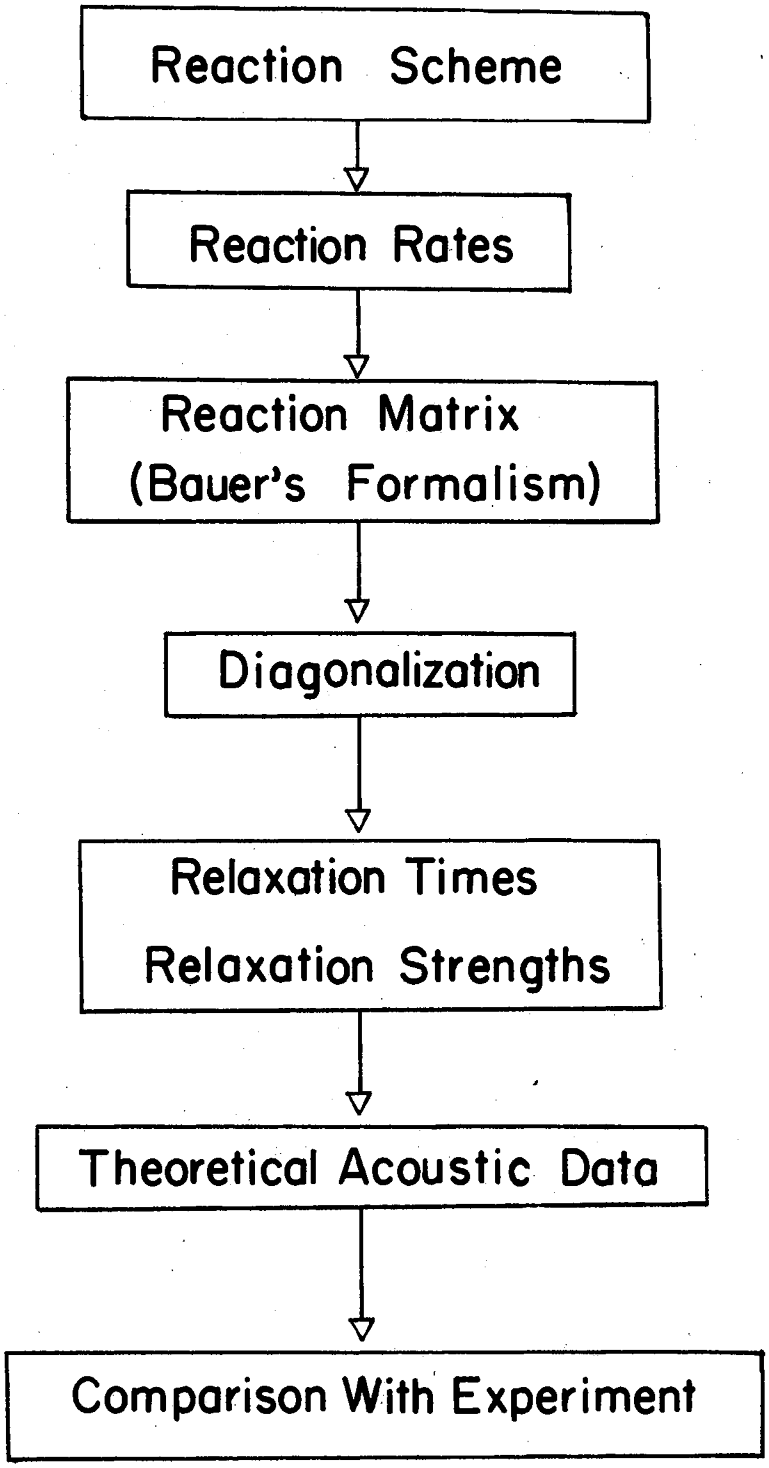

Figure 25. Flow Diagram for Using Bauer's Approach

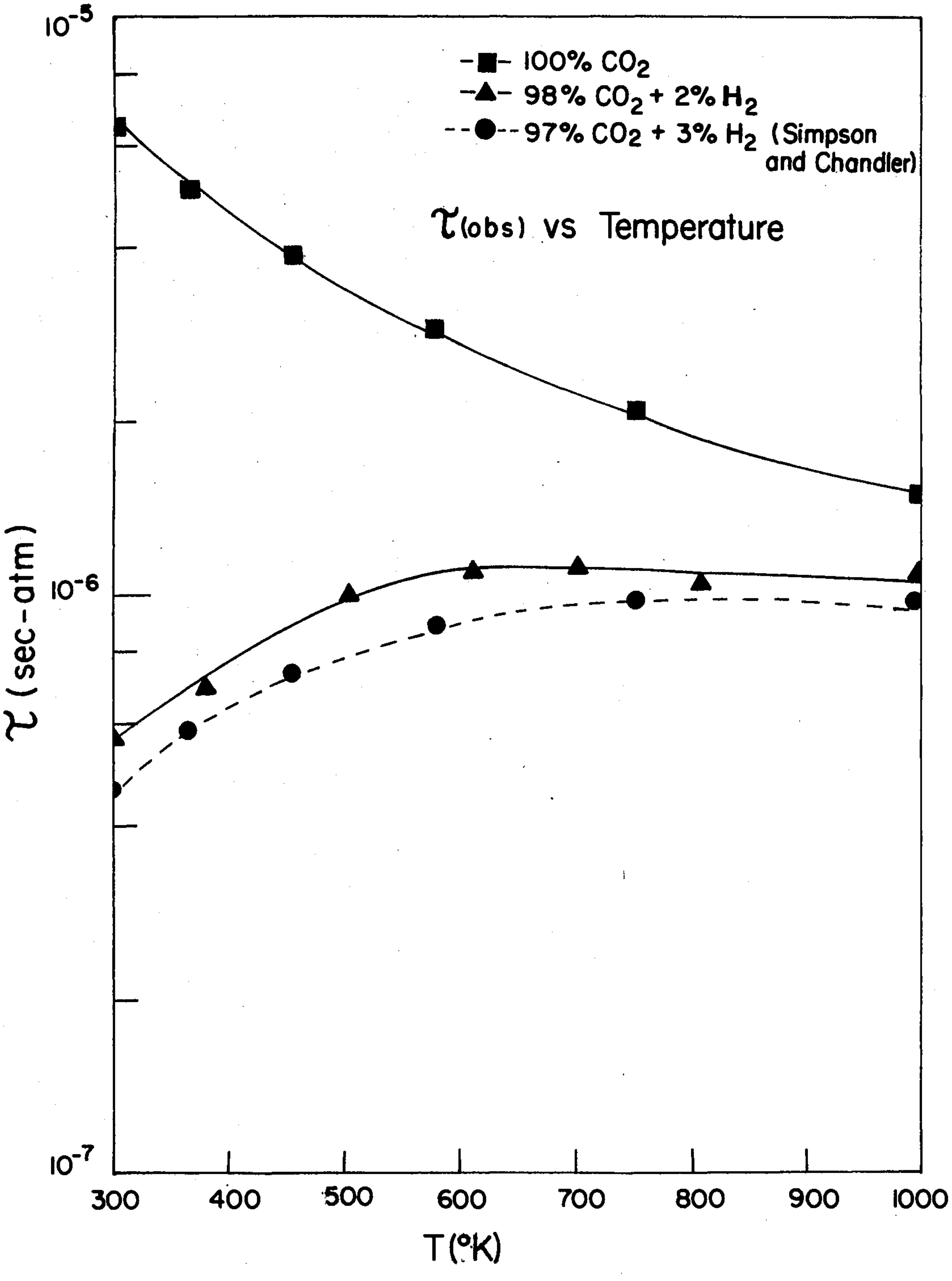

Figure 26. Observed CO_2 Relaxation Times Versus Temperature

culated to Sharma's model(22). The Raff and Winter calculation was modified to allow for ΔJ, the change in rotation quantum number, to be equal to two. The $\Delta J = 1$ assumption of the published Raff and Winter calculation was not critical to the conclusions from their calculations(23), but because of the nature of the model of the gas used in this work it is necessary to keep the system as physically realistic as possible. Because inelastic collisions causing a change in the nuclear orientations of the hydrogen molecule would confuse the results of the model this change was deemed necessary. It should be pointed out however that this would in no way invalidate the conclusions of the Raff and Winter paper with respect to the origin of the temperature dependence of the rotational relaxation times being contained in the rotational level populations. Another point to note is that in these calculations the value of Z, the number of collisions per second experienced by one molecule in a gas at one atmosphere pressure is slightly different than that used by most authors. The Z used differs by the inclusion of a term called $\Omega^{(2,2)}$ by Hirschfelder, Curtiss and Bird(33) which allows to some extent the dynamics of the collision process to enter into the calculation of Z. The use of $\Omega^{(2,2)}$ gives the same effect as deducing the value of Z from viscosity measurements(7). The difference in rates using this form of Z can be as much as 30% from that gotten using a hard sphere model of the collision. In all cases the rate for a reaction is inferred from:

$$\text{Rate} = \text{Probability of transition/collision} * (Z^*)$$

Where: Z^* = number of collisions per second of reaction species normalized to a standard density (1 atmosphere)

Pure Carbon Dioxide

Using the formalism a reaction scheme was developed which allowed for only carbon dioxide - carbon dioxide collisions and the results were compared with the relaxation times for pure carbon dioxide, Figure 27. It was found that although the general temperature dependence of the relaxation times could be predicted by the SSH theory without any adjustment the slope of the Log(τ) vs. temperature curve was not correct. Since it is essential that the theory be able to predict the results in pure substances before the effect of impurities could be inferred the carbon dioxide - carbon dioxide SSH rates were adjusted by an empirical adjustment of 300/temperature. As can be seen in Figure 27 this adjustment reproduces the experimental relaxation times fairly well in the temperature range 300 to 1000 degrees Kelvin. The fact that an adjustment less than one was necessary reflects a fact noted repeatedly in this work, namely that the SSH theory gives rates that are in general too large. For carbon dioxide - carbon dioxide collisions there are any number of reasons why the SSH theory is not exact. The theory was not, nor was it intended to be, a rigorous calculation. It is employed mainly because it seems to predict the general temperature dependence and correct order of magnitude of a large number of relaxation times, and it is easy to use. The calculation as outlined can be susceptible to rounding errors on the computer, especially the diagonalization procedure. Therefore, all calculations were done using the double precision mode of the computer, and IBM 360/65 system. In all calculations it was necessary to include a rather large number of levels and a cut off population of 10^{-3} % was used when the population of the various vibrational levels were calculated. An inclusion of more levels resulted in a change of

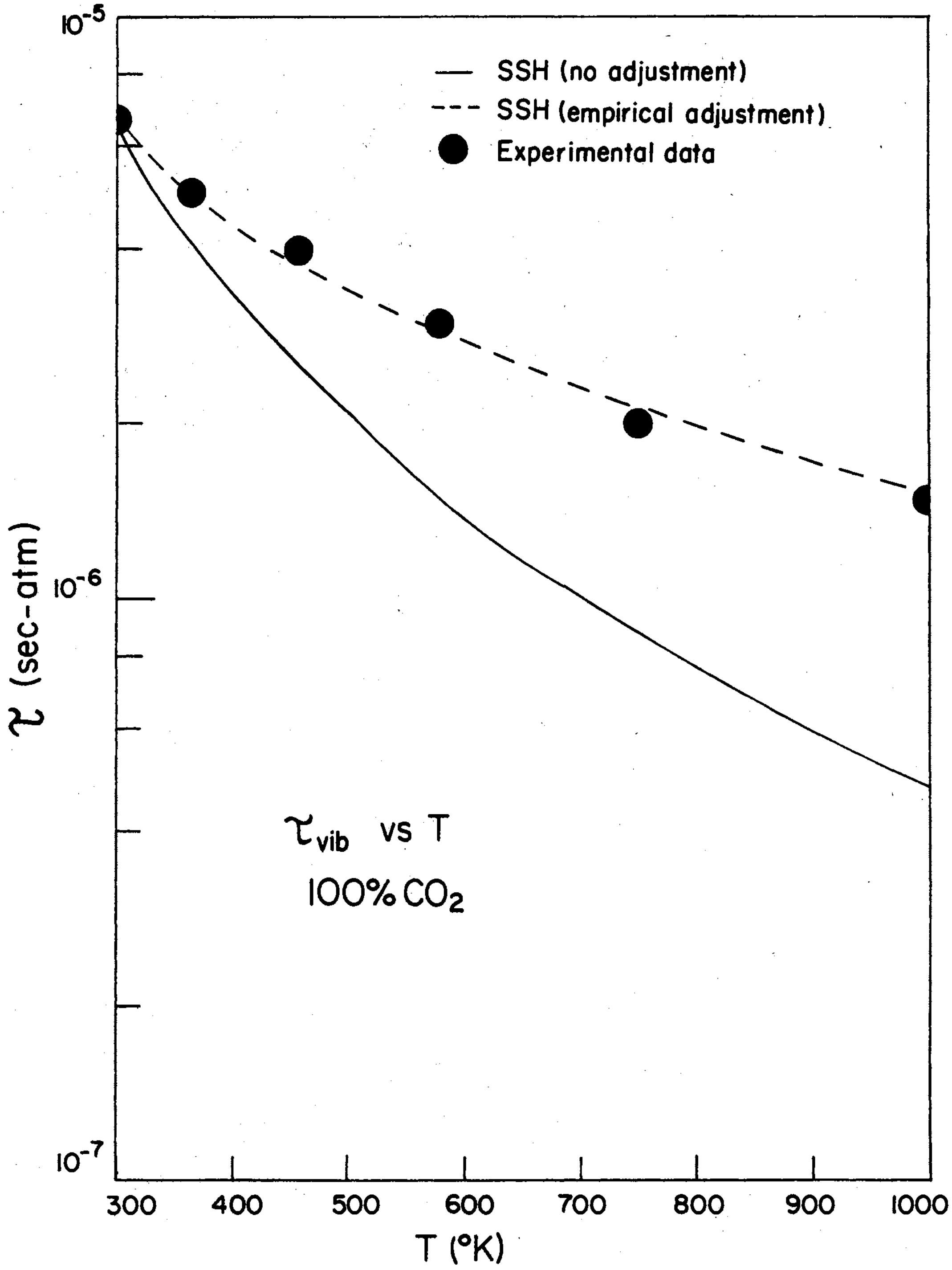

Figure 27. Comparison of Theory and Experiment for 100% CO_2

peak height of less than 1% and it was decided to trade off a greater accuracy in the peak height, which is related to the relaxation strength, for computational speed, and a reduction of the core size necessary to run the program.

Pure Hydrogen

A reaction scheme was then formulated for pure hydrogen, and the results are shown in Figure 28. As explained by Raff and Winter$^{(23)}$ the rates are given by:

$$K_{ij} = N(\pi\sigma^2 p)(8kT/\pi\mu)^{\frac{1}{2}} \exp(-\alpha^2 \Delta E_{ij}/kT) \qquad (58)$$

Where: N = Number of molecules in the system at one atmosphere

p = an adjustable parameter

T = temperature

μ = reduced mass of colliding pair

$\Delta E_{ij} = E_i - E_j$

α^2 = an adjustable parameter

The parameters α and p were adjusted to give a good fit to the data of Hill$^{(50)}$ at 300 degrees Kelvin. The values used were:

$$\alpha^2/k = 2440 \text{ (degrees/ev)}$$

$$\pi\sigma^2 p = 0.63 \text{ (a.u.)}^2 = 1.8 \times 10^7 \text{ barn}$$

Probably because of the different method for connecting the acoustic data to the microscopic rates the relaxation times are different than

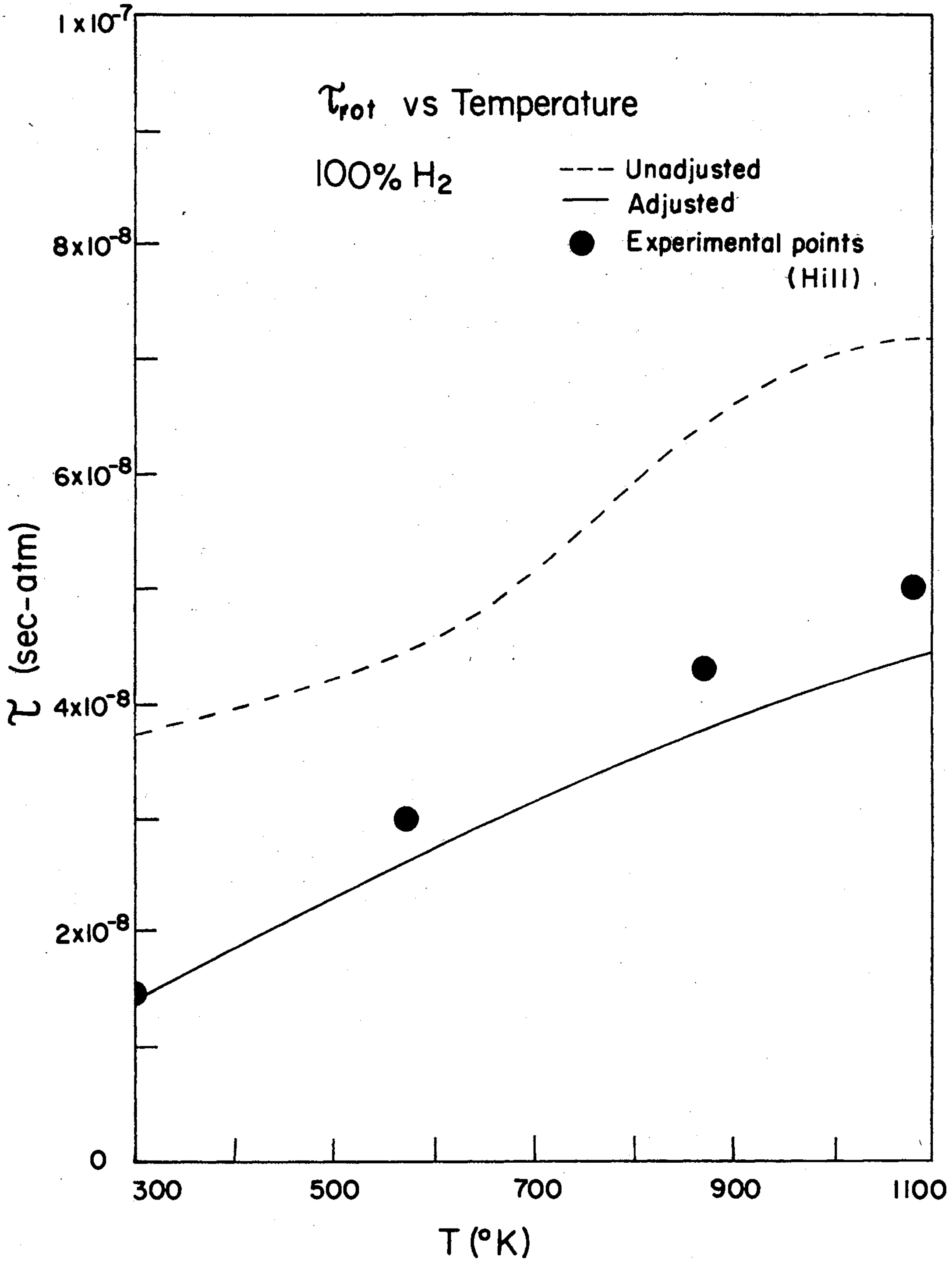

Figure 28. Comparison of Theory and Experiment for 100% H_2

those used by Raff and Winter for their $\Delta J = 2$ calculations$^{(23)}$. The results of using their parameters are also shown in Figure 28 as the dashed line.

As mentioned above the main effect of including a large number of levels is to change the peak height slightly. This effect can be noted for the case of pure hydrogen in Table I, where the total relaxation strength, δCP_i, is given for different values of the maximum rotational quantum number considered. In no case was the inferred value of the relaxation seen to change, so the effect of adding more levels would be to change slightly the peak shape, but it should not effect the value of the relaxation time inferred. In other words the frequency of maximum absorption does not change, but the absolute magnitude of the maximum does.

Carbon Dioxide - Hydrogen Mixtures

Three different mixtures of carbon dioxide were analyzed, 2% H_2, 3% H_2, and 15% H_2 concentrations. Using the SSH theory to predict the V-T transition for the reaction:

$$CO_2^* + H_2 \text{ --- } CO_2 + H_2 + \text{kinetic energy}$$

yields the results shown by the lower line in Figure 29. It is obvious that this does not agree with the data even within an order of magnitude, and an adjustment on the SSH CO_2 - H_2 rates of 1/50 yields the results shown by the dashed line in Figure 29. The solid line through the data is simply a reference line. In all subsequent calculations where the carbon dioxide - hydrogen rates are used this adjustment has been made. The carbon dioxide - carbon dioxide SSH rates have been modified by the

TABLE I

EFFECT OF INCLUDING ADDITIONAL ROTATIONAL LEVELS IN THE REACTION SCHEME FOR HYDROGEN AT 300 °K

J_{max}	% of Molecules in Rotational Level J_{max}	$\sum_i \delta_i C_p$	τ(best fit)
5	1	0.9584	1.501×10^{-8}
6	.1	0.9597	1.501×10^{-8}
7	.01	0.9598	1.501×10^{-8}
8	10^{-4}	0.9599	1.501×10^{-8}
9	10^{-6}	0.9599	1.501×10^{-8}
10	10^{-10}	0.9599	1.501×10^{-8}
11	10^{-12}	0.9599	1.501×10^{-8}
12	10^{-14}	0.9599	1.501×10^{-8}

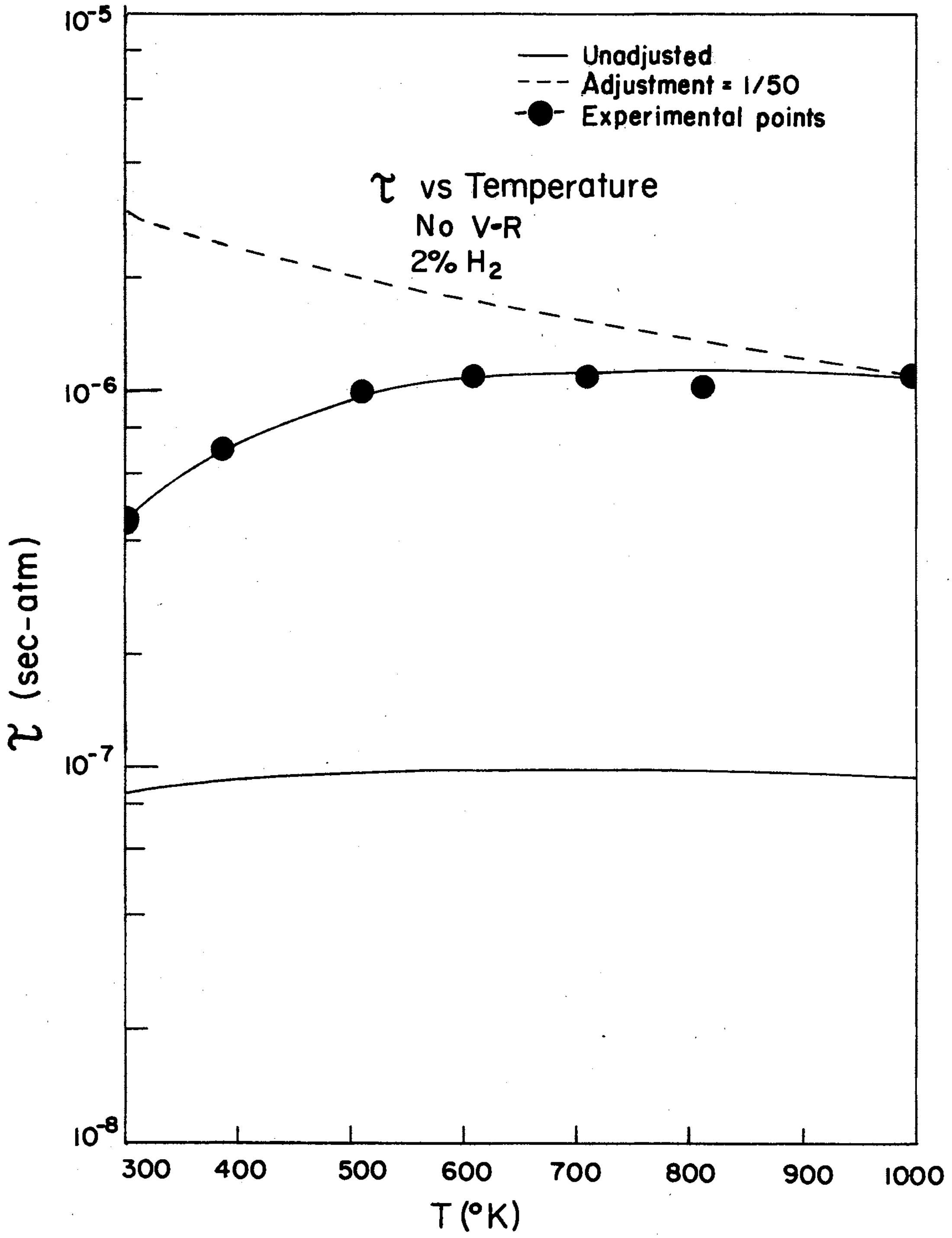

Figure 29. Comparison of Theory and Experiment Allowing No V-R Reactions for 98% CO_2 + 2% H_2

empirical factor noted above. Figure 30 shows the same reaction for a 3% hydrogen concentration. As can be seen the temperature dependence of the relaxation times is certainly different than the pure carbon dioxide relaxation times, but the curve is not representative of the data as the slope is wrong. It appears that the SSH theory does not predict relaxation times that increase with temperature, as the data implies. For this reason a reaction scheme which included vibration - rotation energy transfer was formulated. There are two different V-R reactions treated:

$$CO_2(010) + H_2(J=2) \quad ---- \quad CO_2(000) + H_2(J=4)$$

$$CO_2(010) + H_2(J=1) \quad ---- \quad CO_2(000) + H_2(J=3)$$

In reference 22 Sharma calculated the rates for these reactions, but in his discussion he does not compare the theory and experiment in a way that is analogous to that presented here.

Figure 31 shows the results of a reaction scheme which allows only V-R type interactions between the carbon dioxide and hydrogen while using carbon dioxide - carbon dioxide rates that have not been adjusted by the empirical temperature dependent factor. The effect of the inclusion of the V-R rates is to lower the relaxation time at 300 degrees Kelvin and the relaxation time increases until it approaches that of the pure carbon dioxide results. This behavior is understandable through a rather crude model of the internal processes. If the assumption is made that at the lower temperatures the internal energy goes from the vibration of the carbon dioxide into the rotation of the hydrogen faster than it goes from the vibration of carbon dioxide through carbon dioxide - carbon dioxide energy exchange processes the relaxation times will follow the temperature of the V-R rate inversely, i.e., if the V-R rate decreases

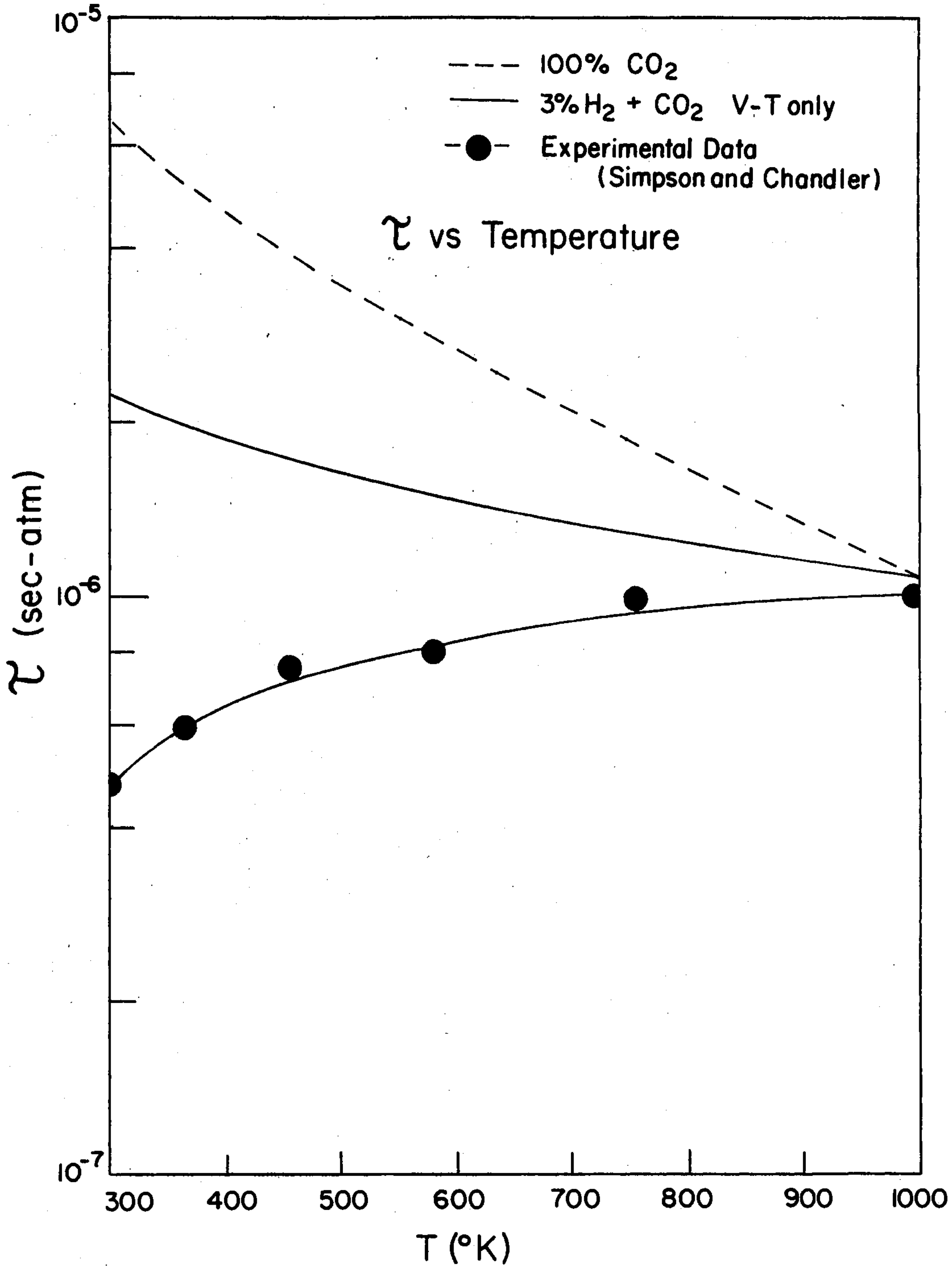

Figure 30. Comparison of Theory and Experiment Allowing No V-R Reactions for 97% CO_2 + 3% H_2

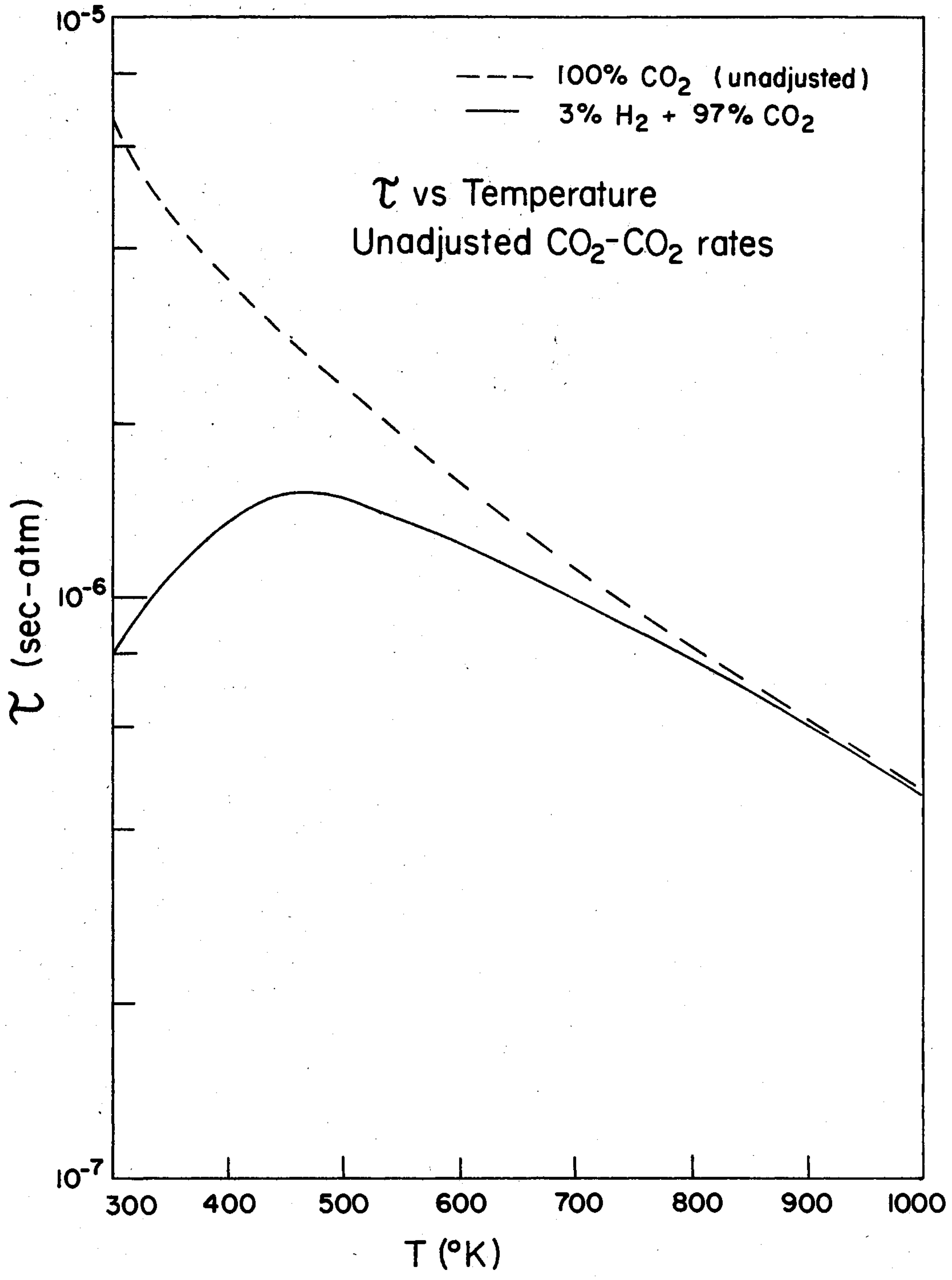

Figure 31. Theoretical Results Allowing V-R But Using Unadjusted CO_2 - CO_2 Rates

with temperature the relaxation time will generally increase with temperature. While the V-R rate decreases with temperature the carbon dioxide - carbon dioxide rates are increasing with temperature and the system will at some point begin to follow a temperature dependence that is inversely related to this faster rate. Although this is a gross simplification of the actual process it seems that the relaxation will follow the temperature dependence of the faster process.

Adjusting the carbon dioxide - carbon dioxide rates by the empirical factor so that they do not increase with temperature quite as fast as the SSH theory indicates gives relaxation times that agree more closely with the experiment as shown in Figure 32. Allowing both V-R and V-T (adjusted) type interactions between carbon dioxide and hydrogen yields the results shown in Figure 33. The relaxation times are in general too large for the mixtures, but the theory seems to reproduce the general temperature dependence of the experimental data which the V-T theory could not do.

Figure 34 shows a summary of the results for a 3% hydrogen concentration where some feeling for the effect of different types of reactions on the relaxation time can be gotten. The curves indicate that in this model the effect of V-R transitions is important at low temperatures while at higher temperatures the relaxation times seem to indicate a V-T type transition predominates.

Carbon Dioxide - Nitrogen Mixtures

Measurements on carbon dioxide - nitrogen mixtures were also made by Simpson and Chlander(36) using a 60% concentration of nitrogen. The temperature dependence of these relaxation times is plotted in Figure

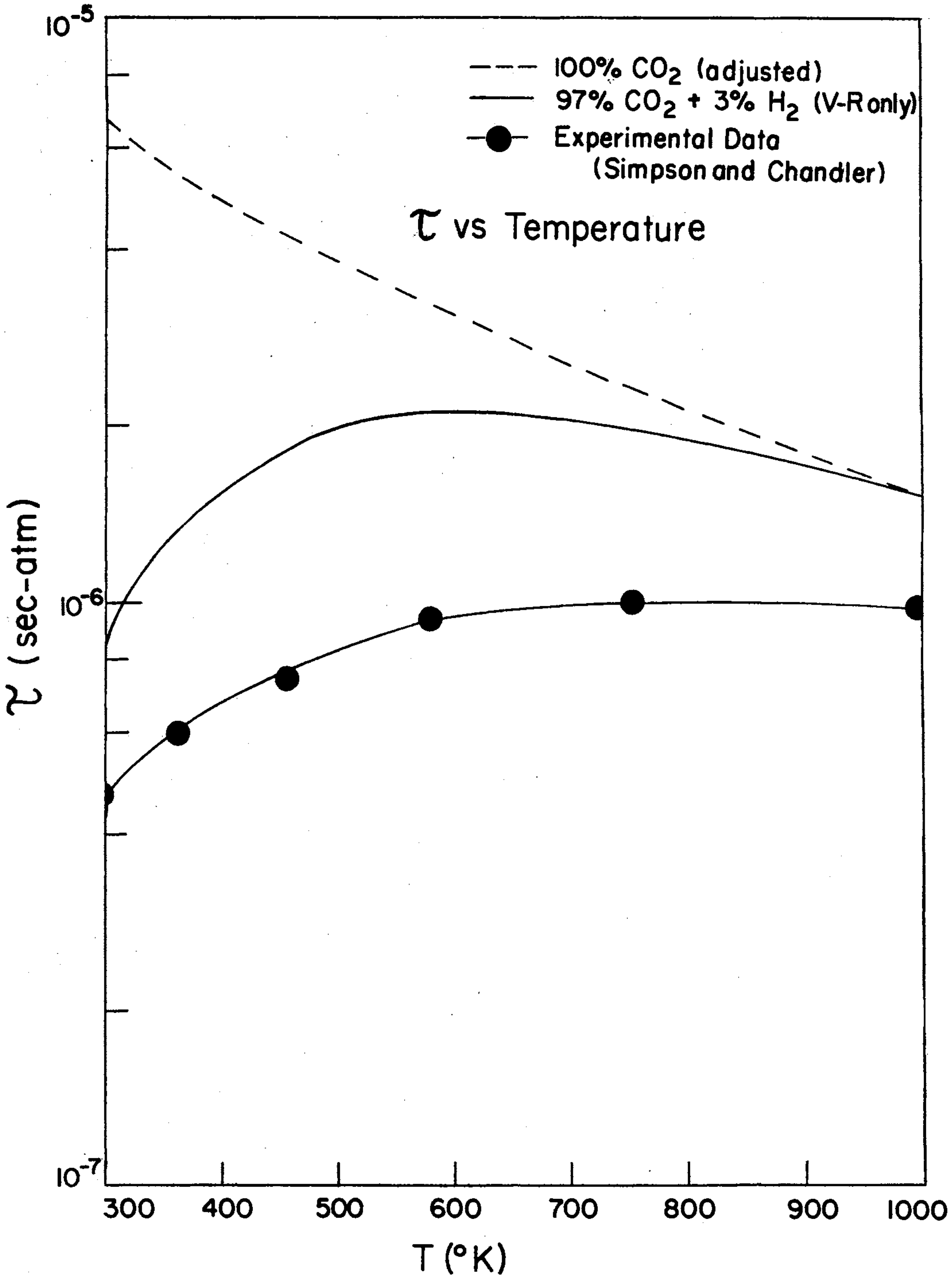

Figure 32. Comparison of Theory and Experiment Allowing V-R With Adjusted CO_2 - CO_2 Rates for 97% CO_2 + 3% H_2

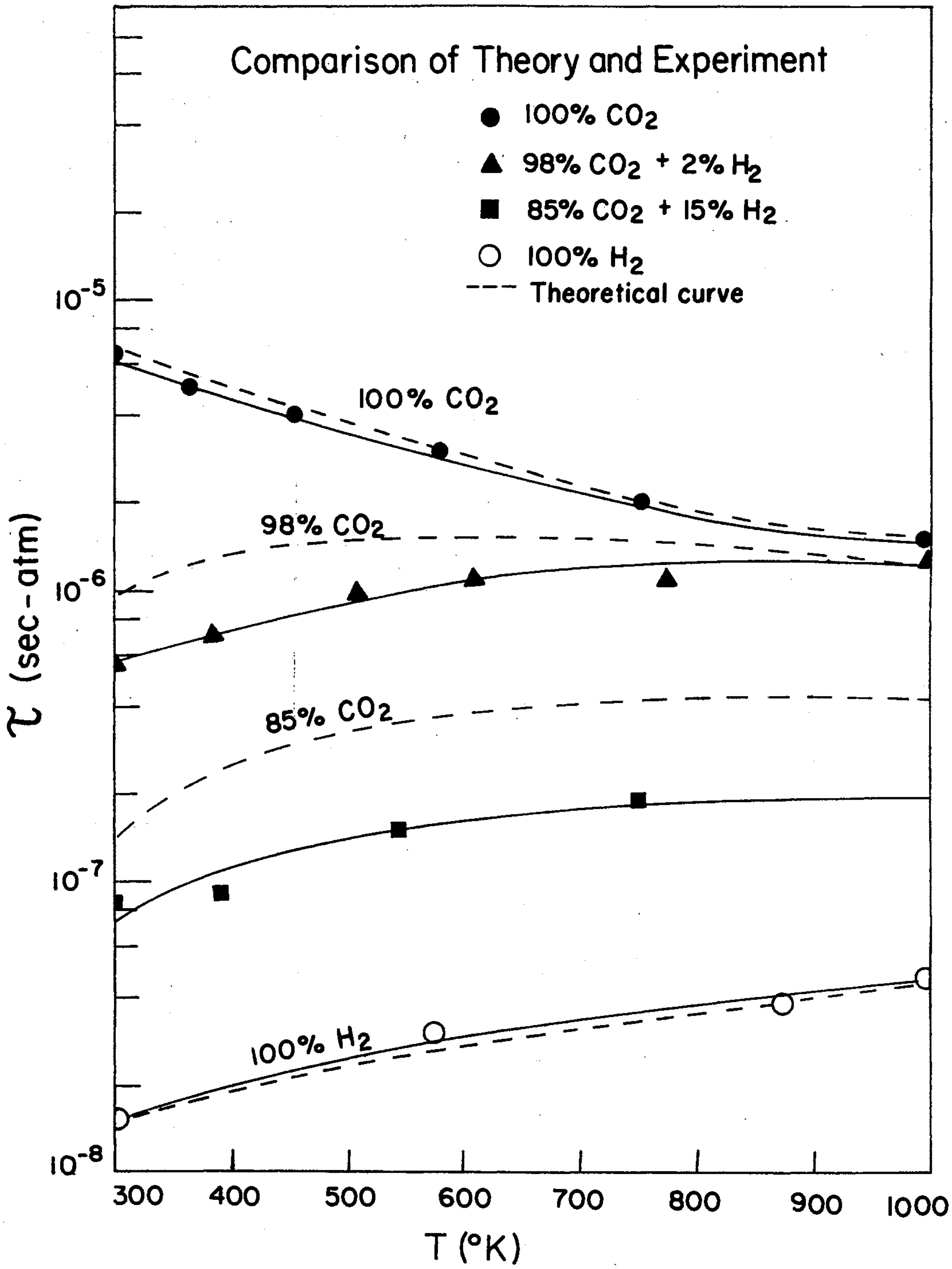

Figure 33. Comparison of Theory and Experiment Allowing V-R and V-T CO_2 - H_2 Reactions

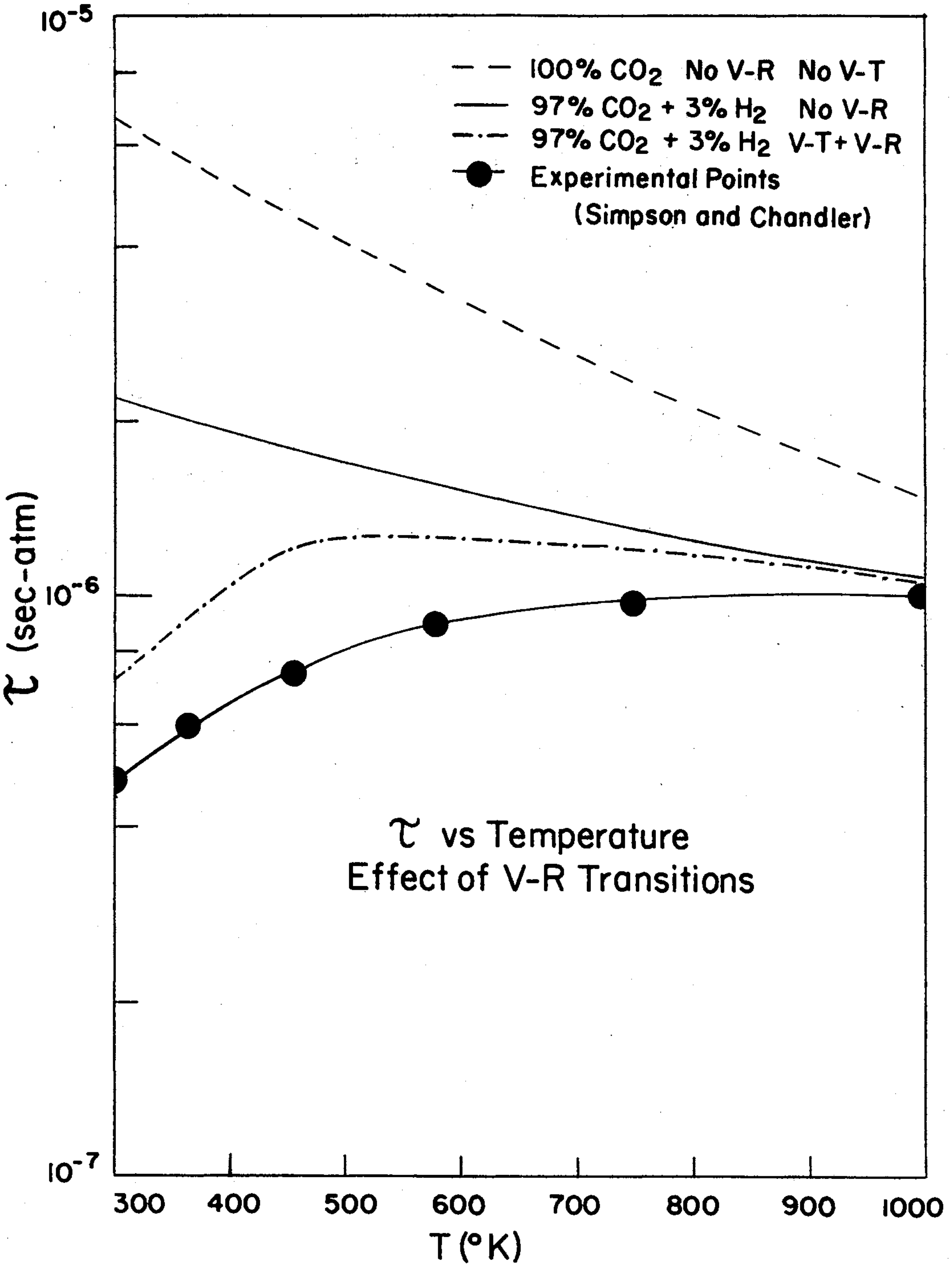

Figure 34. Effect of Including V-T and V-T + V-R on 97% CO_2 + 3% H_2 Mixture

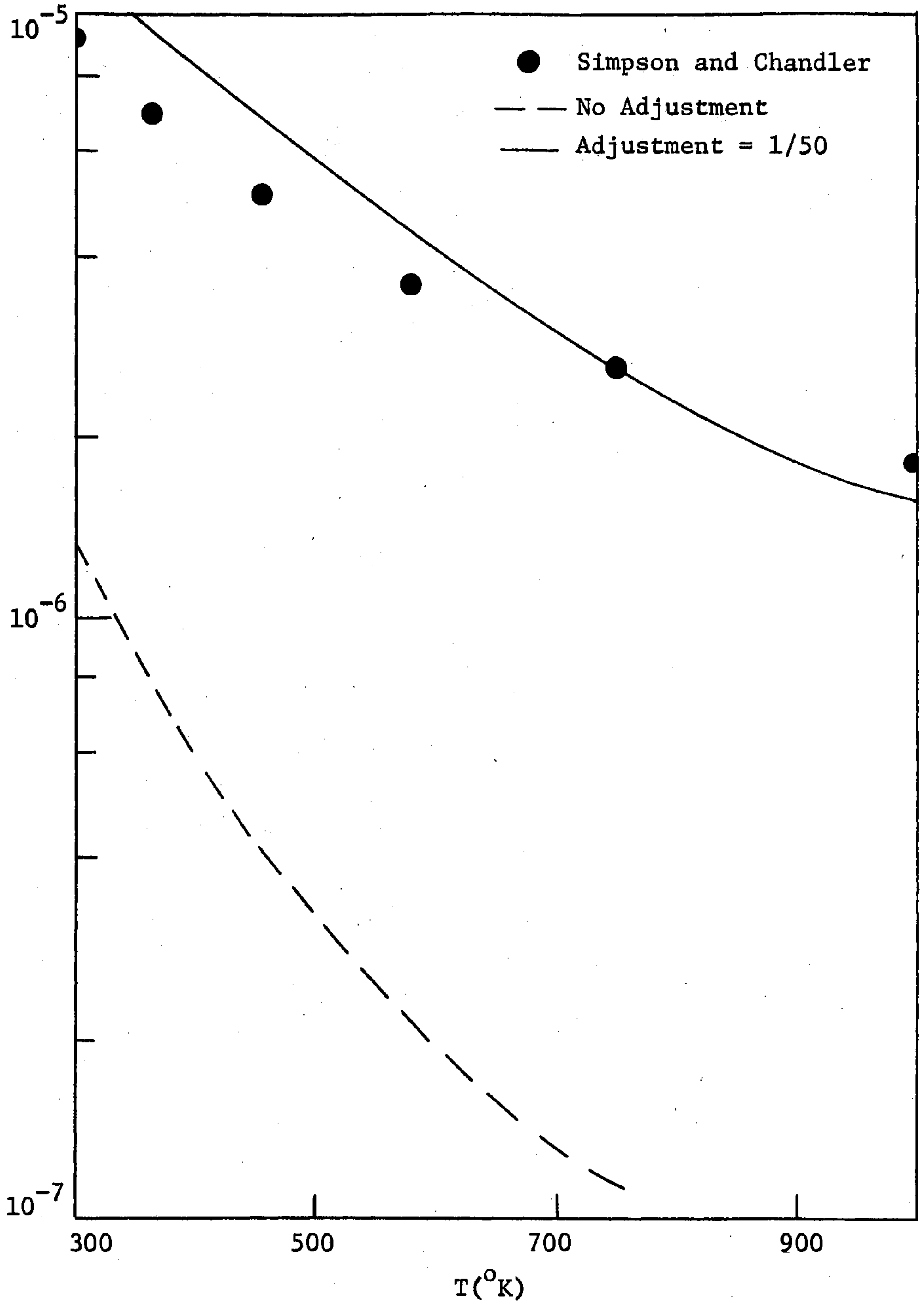

Figure 35. Comparison of Theory and Experiment for 40% CO_2 + 60% N_2 With V-T Type CO_2 - N_2 Reactions Only

35, and it appears that the addition of nitrogen raises the relaxation time above that of the pure carbon dioxide values. A similar effect was noted by Treadaway(43) using the high pressure acoustic interferometer described earlier. This effect is not predicted by the SSH theory as shown by the lower line in Figure 35. The SSH theory predicts that the relaxation time of the mixture should be lower. In this reaction the carbon dioxide and nitrogen were allowed to interact by a V-T type process only. If the carbon dioxide - nitrogen SSH V-T rates are adjusted by a factor 1/50, the same adjustment as used for the carbon dioxide - hydrogen V-T rates, the results agree more closely with experiment. This effect is also plotted in Figure 35.

A great deal of importance should probably not be attached to the fact that the adjustment has the exact same numerical value, although several other values were tried and 1/50 seems to give the closest fit to the data. The agreement implies only that the SSH theory predicts rates that are consistently too high by about a factor of 0.01 -- 0.03 for carbon dioxide - hydrogen and carbon dioxide - nitrogen V-T rates. Although the value of the adjustment happens to be the same in both cases a different reaction scheme may well imply that a different adjustment, or no adjustment, would be necessary.

CHAPTER V

CONCLUSIONS

Experimental Conclusions

From the comparison of the theory and experiment it appears as though the model used can predict the general temperature dependence of the relaxation times of pure carbon dioxide, pure hydrogen, carbon dioxide - hydrogen and carbon dioxide - nitrogen mixtures. In carbon dioxide - hydrogen mixtures it appears necessary to allow for vibration to rotation energy transfer between the carbon dioxide and the hydrogen molecules, and Sharma's theory gives rates for this process that appear to predict the general temperature dependence of the relaxation times. In carbon dioxide - nitrogen mixtures the general temperature dependence of the relaxation times seem to be predicted by considering V-T type collisions only. This implies that a V-R process is important in carbon dioxide - hydrogen systems, but not carbon dioxide - nitrogen systems.

Multiple Relaxation

In order to predict the relaxation times it is necessary to include a complete model of the system. It is sometimes assumed(36,44) that when V-R transitions are considered it is not necessary to allow for R-T reactions also, but in order that the model be complete this effect must also be considered. Figure 36 shows the effect of using R-T rates that are a factor of 100 larger than those used in the previous calculations

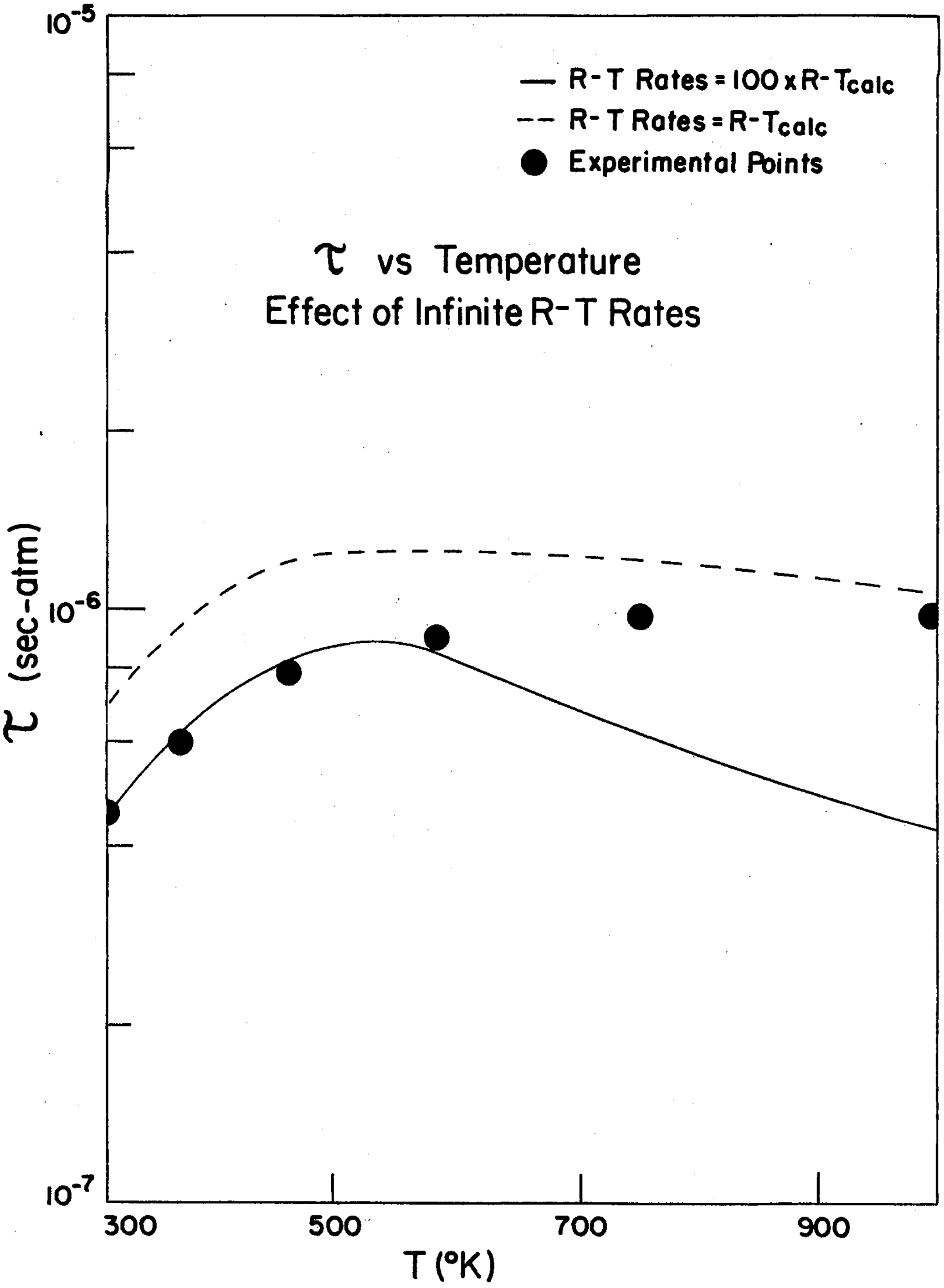

Figure 36. Effect of Infinite R-T Rates for 97% CO_2 + 3% H_2

(effectively infinite rates) for a 3% hydrogen mixture. The low temperature data agrees rather well with the experimental results, but at 1000 degrees Kelvin the results are too low by a factor of two. More importantly the temperature dependence of the relaxation times appears to be wrong. Although no claim for the exactness of the rates used is made this result implies that the resultant relaxation times are closely connected to the rates and the reaction scheme used in the model. Only by considering the total model of the gas can conclusions about the correctness of various theories be made.

The formalism of Bauer for going from a set of microscopic rates to macroscopic data is very useful. Figures 37 through 39 show the experimental absorption and the predicted absorption gotten from Bauer's formalism at 300 degrees Kelvin. Although the theory is complicated and its original English publication(14) is difficult to understand it is easily used in practice. It is also very fast. The importance of using a complete reaction scheme has been recognized by several authors(23,45), but detailed calculations on systems with a large number of internal levels has been hampered by the restrictions of computer size and speed (23). Using Bauer's approach the system of differential equations, the rate equations, can be solved quite easily, and although the approach will not work when there are large perturbations from equilibrium yielding non linear effects nevertheless it appears to be useful in a large number of situations where a relaxation process is important. Besides acoustic phenomena the same approach can be easily extended to the study of laser flourescence, where the measurement also the results of the effect of more than one reaction rate(46).

The formalism has been used to go from a postulated reaction scheme

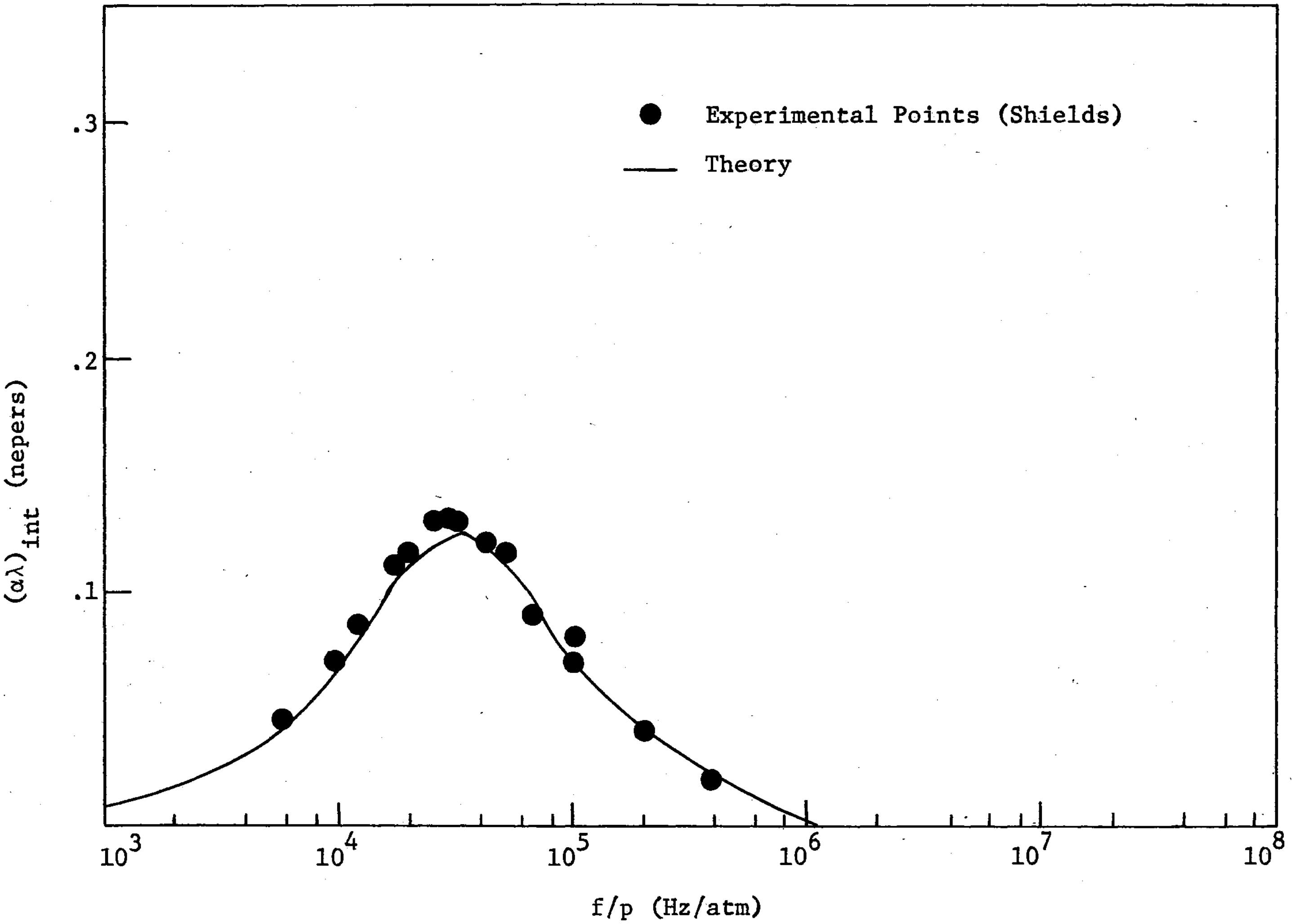

Figure 37. Comparison of Theoretical and Experimental Ultrasonic Absorption in CO_2 at 298°K

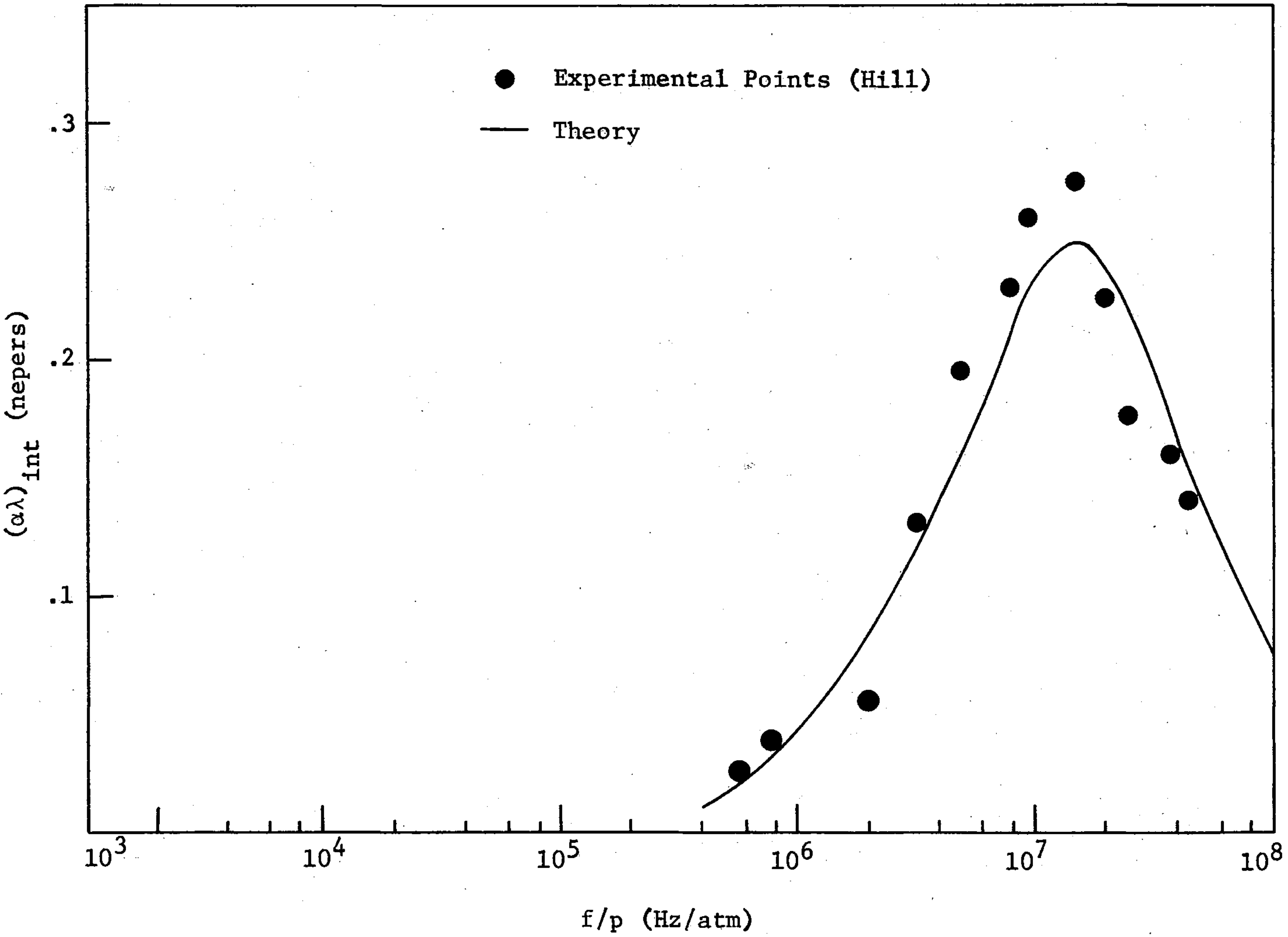

Figure 38. Comparison of Theoretical and Experimental Ultrasonic Absorption in H_2 at 298°K

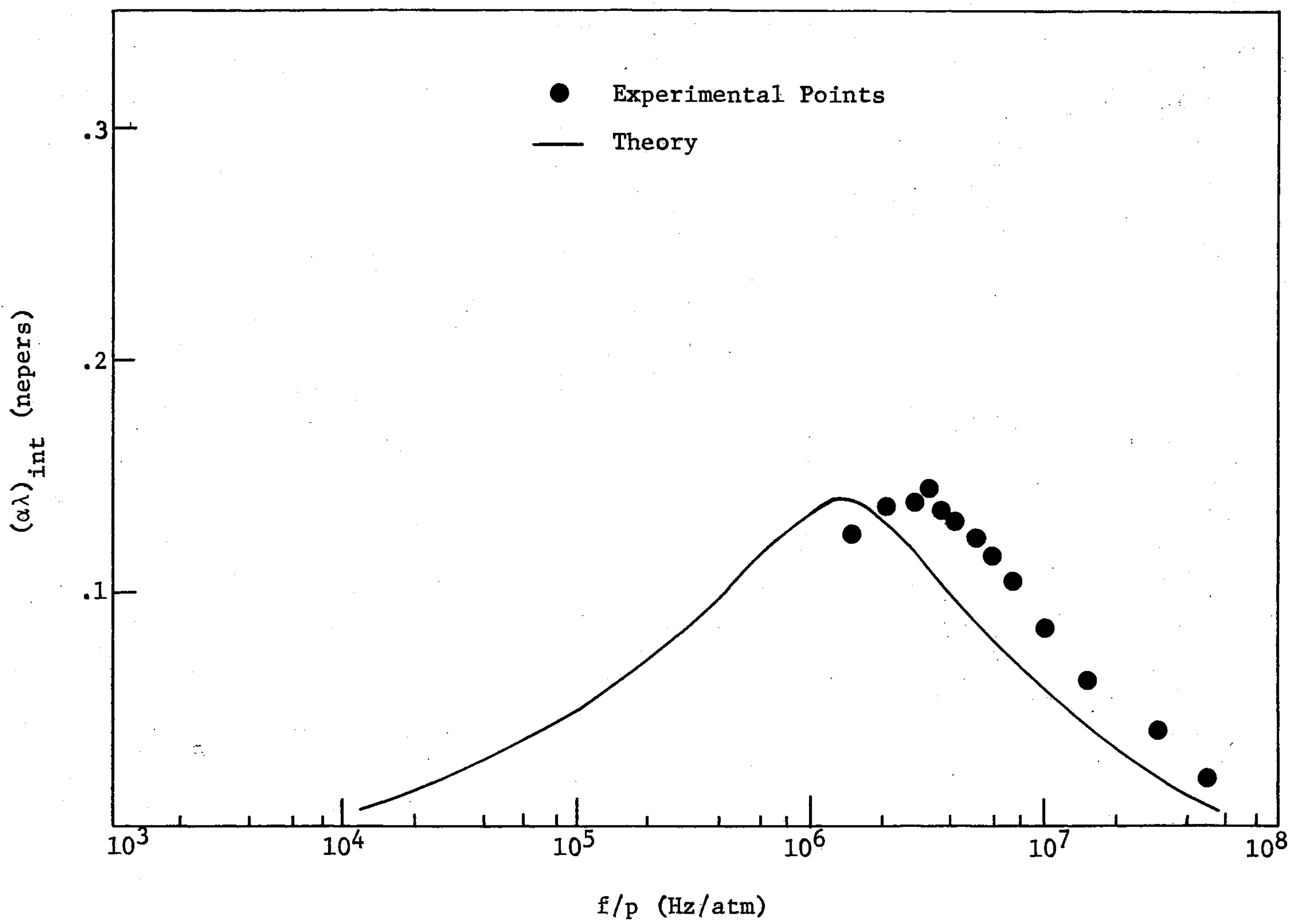

Figure 39. Comparison of Theoretical and Experimental Ultrasonic Absorption in 85% CO_2 + 15% H_2 at 298°K

to theoretical results which can be compared with experiment. It is not believed that the formalism can be used in reverse. Although it would be desirable to go from experimental data to reaction rates, and it has been suggested that such an approach may be possible(17) there are serious problems in attempting such a procedure from Bauer's formalism.

This work has implied that one must consider a complicated set of reactions that is, at the least, complete within itself. In other words if a V-R reaction is in the reaction scheme the corresponding R-T reaction must also be considered. In going from experimental data to rates there appears to be no assurance that the rates so produced are unique, and other rates coupled with a different reaction scheme might also yield the same agreement with experiment with different rates. Although a procedure to go from the data to the rates can be written there is some question as to the validity of the rates so obtained. It appears that one would be attempting to reverse the flow of information from the macroscopic to microscopic. It may be that such an attempt could be predicted to fail a priori, since it appears to be an attempted "retrodiction"(47)--prediction of the probability that an event will occur based on the experimental fact that it did occur. Further comment should be deferred until the results of such an effort can be analyzed completely.

The formalism can be used, however, to decide whether or not a theoretical prediction can be checked by a given experimental situation. An example ~~concerns~~ Kolker's(46) calculation of the rates for two reactions:

$$CO_2(001) + H_2(J=3) \text{ ---- } CO_2(020) + H_2(J=5)$$

$$CO_2(001) + H_2(J=2) \text{ ---- } CO_2(100) + H_2(J=4)$$

The results of including these reactions into the reaction scheme for a 3% hydrogen are compared to those gotten by omitting these rates from the reaction scheme in Table II. Although there is a slight difference in the results at 364 and 579 degrees Kelvin the experimental relaxation times would have to be known to an accuracy of better than 1% to observe the effect. Relaxation times to this accuracy could not be resolved with the available instrument. In a laser flourescence experiment which observes specifically the deactivation of the (001) mode of carbon dioxide the accuracy of the results could be checked, but again one would have to consider all reactions involved and not just the ones calculated above.

Rate Calculations

There are three distinct types of rate calculations used: Raff and Winter(23), SSH(10), and Sharma's multipole moment method(22). They will be considered separately. The Raff and Winter calculation for the R-T rates is admittedly unrealistic(23) as it assigns a constant transition probability irregardless of the quantum numbers identifying the reacting species. That it can predict the temperature dependence of the acoustic data is probably due not to the correctness of the rates, but the discrete level nature of the rotational energy. This was the conclusion of the work of Raff and Winter(23), and it is not contradicted by this work. It seems to be strengthened by the fact that the same model can predict the temperature dependence of the relaxation times when a reaction scheme of $\Delta J = 1$ or $\Delta J = 2$ is used. Of course it could be that the fact that there are two adjustable parameters in the theory might be forcing the model to fit, but the parameters are adjusted only once at

TABLE II

EFFECT OF INCLUDING KILKER'S V-R DEACTIVATION OF CO_2 (001) BY H_2 IN THE REACTION SCHEME

Temperature (degrees Kelvin)	τ (sec-atm) With Kolker Rates	τ (sec-atm) Without Kolker Rates
300	6.93×10^{-7}	6.93×10^{-7}
364	9.11×10^{-7}	9.12×10^{-7}
455	1.24×10^{-6}	1.24×10^{-7}
579	1.24×10^{-6}	1.25×10^{-7}
751	1.20×10^{-6}	1.20×10^{-7}
1000	1.08×10^{-6}	1.08×10^{-6}

300 degrees Kelvin so that the magnitude of the relaxation time and the shape of the absorption curbe agree with the data. There is then no apparent reason for the fact that the temperature dependence of the relaxation times should follow from this one adjustment. The fact that it does implies that indeed it is the changing population of the levels with temperature that is causing the effect and not to any large extent the temperature dependence of the rates due to a change in the average velocity of the molecules. Although the assignment of a constant transition probability to each reaction was for computational convenience, detailed calculations by Shimamura and Takayanagi(45) on para-hydrogen using a potential that averages long range forces over molecular orientations indicate that the cross sections for the two reactions:

$$H_2(J=0) + H_2(J=0) \text{ ---- } H_2(J=0) + H_2(J=2), \text{ and}$$

$$H_2(J=0) + H_2(J=2) \text{ ---- } H_2(J=2) + H_2(J=2)$$

are the same to within 2% over a wide range of relative velocities. Although this does not mean that the parameters chosen are in any sense correct, it does imply that the model is not completely wrong, and the fact that the theory agrees with the acoustic data implies that the rates themselves are probably within an order of magnitude of being correct.

The SSH rate calculations have been applied to a large number of various gases(48), and the basic calculations have been modified by several authors(11,12) to make calculations on a large number of systems. The calculation does not appear to be accurate in all cases, but it has been found to predict the temperature dependence of relaxation times in relatively simple systems with surprising accuracy considering the crudeness of the model.

Previous comparison of the SSH calculation with experiment has indicated that the rates were in general too large(48), and this has been verified in this work. Although the calculations are admittedly crude and some of the assumptions made in making them are possibly not valid, the SSH model is the best available for V-T and V-V rates, and for this reason it has been used extensively.

The V-R calculation due to Sharma is most noted for its lack of adjustable parameters, although the impact parameter used can be in some sense considered a parameter indicating an arbitrary cut-off for the potential. If the parameter used is the hard sphere radius of the molecule then this parameter is really not adjustable. The calculation, when used with a complete reaction scheme, seems to work. It can predict the temperature dependence of the relaxation times for carbon dioxide - hydrogen systems while a V-T theory only does not. The magnitude of the relaxation times is not correct, but the error is not severe. It is most noteworthy that what fit there is occurs with no empirical modification of the V-R calculation.

The method of calculation using the multipole moment approach seems to be a powerful and easily used tool for making rate calculations. It has been applied to other types of collisions(17-19) and will probably come into greater use. It should be noted that the accuracy and usefulness of the calculation depend on several factors: (1) The validity of the trajectory and impact parameter approximations, (2) the validity of the perturbation truncation, and (3) the availability of multipole moment matrix elements. Rabitz and Gordon(17) have discussed the validity of these approximations in first and higher order perturbation theory.

It appears that other transition probabilities could be calculated by this method. Since all but the translation degrees of freedom are quantized the model can predict transition probabilities that are difficult to define classically, and it can be understood by elementary quantum mechanical theories. The calculation seems to require a minimum amount of approximations that maintain the quantum nature of the system while keeping the calculation tractable.

An estimate of the accuracy of the rates as calculated is difficult because the system is so complicated. A question arises as to whether the disagreement between theory and experiment is due to the V-T, V-V, R-T, or V-R rates being in error. No claim for the accuracy of the rates used is made except for that which can be inferred by the agreement, or disagreement between the theory and experiment. Certainly if the SSH theory is to be believed for the V-T rates then some sort of V-R transition must be included in the reaction scheme to account for the observed temperature dependence of the experimental relaxation times. Someday someone with a large computer will make a full quantum calculation for a system for which a calculation based on the multipole moment appraoch has been made, and the results will be compared. A start in this direction has been made and there is a book in print(49) directed to the necessary computational techniques. All that can be claimed at this time is that the rates as calculated appear to predict the correct temperature dependence of the relaxation times as long as they are understood as a part of a total reaction scheme.

Rates Used

It would not be feasible to list all of the rates used for calculations in this work. In some cases the number of reactions is in the thousands, and since analytic formulas exist for all of the rates used any listing of the rates for specific temperatures would be redundant. The SSH theory used was that derived in the original paper by Schwartz, Schlawsky, and Herzfeld$^{(10)}$, and modified slightly in a later paper by Tancoz$^{(11)}$. The R-T rates were calculated by the formula given by Raff and Winter$^{(23)}$ and reproduced in Equation 58. The value of the adjustable used are:

$$\alpha^2/K = 2440 \text{ (deg/ev)}$$

$$\pi\sigma^2 p = 0.63 \text{ (a.u.)}^2$$

The V-R rates were calculated by Sharma$^{(22)}$ by averaging Equation 57 over all possible values of the carbon dioxide rotational quantum numbers$^{(22)}$. Since Sharma calculated the numerical value of the rates it is easiest to use his numbers. They were reproduced as a polynomial in the temperature:

$$P_{13} = \sum_{i=o}^{3} a_i T^i$$

$$P_{24} = \sum_{i=o}^{3} b_i T^i - P_{13}$$

Where T is the temperature in degrees Kelvin. The values of the coefficients used were:

$$a_0 = 7.368 \times 10^{-3} \qquad b_0 = 6.958 \times 10^{-3}$$

$$a_1 = -1.58 \times 10^{-5} \qquad b_1 = -1.289 \times 10^{-5}$$

$$a_2 = 1.470 \times 10^{-8} \qquad b_2 = 1.004 \times 10^{-8}$$

$a_3 = -5.556 \times 10^{-12} \quad b_3 = -3.194 \times 10^{-12}$

It must be emphasized again that the rates should be considered in the reaction scheme used. Although no universality is claimed for the rates, with the reaction used they can predict the general temperature dependence of the relaxation times.

Further Study

The areas of further study can be divided into two classes; use of Bauer's formalism and rate calculations. There are several areas where the rate calculations of the type done by Sharma could be used. It seems that rotationally inelastic cross sections for H_2 systems could be calculated using a calculated quadropole moment of the H_2 molecule, but calculations by Shimamura and Takayanagi(45) seem to indicate that a shorter range potential might be necessary. The multipole moment method seems useful for long range forces with near resonant energy exchange because of the trajectory and impact parameter approximations. One can check the trajectory approximation by using an equation for the relative motion of the two molecules, $\bar{R}(t)$, derived from classical considerations using a potential surface calculated quantum mechanically or one of the semi-empirical potentials, such as the Lennard - Jones 6 - 12 potential.

The outline of Bauer's formalism given here was directed specifically to the acoustic case. The theory is much more general than that and can be used in almost any system where the perturbation from equilibrium is small and the return to equilibrium is governed by a set of microscopic rate equations. With the advent of tunable lasers the number flourescence studies should increase and Bauer's theory can be easily used to treat this case. Instead of acoustic absorption one predicts the intensity of emitted light as a function of time(15).

The fact of nature is that one usually can not measure one rate in a given experiment but rather some sort of an effective rate which can be a complicated function of all the rates. This is unfortunate because one would like to be able to compare one rate at a time with the experiment. At least in Bauer's formalism there exists a straightforward, fast and fairly rigorous method to compare all the rates and the experiment.

Conclusions

The conclusions of this work are summarized as follows:

(1) There is a V-R process present in the deactivation of carbon dioxide by hydrogen, and Sharma's calculation of this rate, when coupled with a reaction scheme that allows for several different types of reactions, yields relaxation times whose temperature dependence generally agree with experiment.

(2) Rates calculated according to the SSH theory for vibrational energy transfer seem to be generally too large.

(3) That the rotational relaxation times agree with experiment strengthens the conclusion of Raff and Winter with respect to the origin of the temperature dependence of the relaxation times being connected to the level structure of the system more closely than they are connected to some velocity dependence of the reaction rates.

(4) Bauer's formalism is an easily used method for connecting reaction rates to the macroscopic data. Because of its ease of use and the relatively rigorous connection of the rates to thermodynamic quantities

it appears to be preferable to a brute force method of numerically integrating the rate equations.

(5) The method of calculation energy transfer rates by the semiclassical approach of quantizing all but the translational degrees of freedom seems to be effective when the rotational energy is postulated as taking a part in the process. The results of these calculations must be compared with experiment within the framework of a total reaction scheme in order that the comparison be meaningful.

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APPENDIX I

OUTLINE OF COMPUTER PROGRAMS

A brief outline of the computer programs used in data reduction and comparison of theory and experiment is presented below. All programs are useful only for the systems under consideration here, but they could be modified for use with other systems. A listing of all programs is available upon request, but experience has shown that unless the program was written with a general application as an end, the program itself can only serve as a general guide to specific problems. The programs were written to handle carbon dioxide, carbon dioxide - hydrogen, and carbon dioxide - nitrogen mixtures and modifications for use with other types of gases would be necessary.

AMD001

This program is very straightforward. Designed to handle one gas with two relaxation times in a parallel relaxing situation it attempts to find the smallest value of the sum over all data points of the absolute value of the calculated absorption minus the observed absorption. The input to the program includes the transport coefficients and the temperature as well as the absorption and corresponding pressure for each data point. The program was written in IBM's Fortran (G) compiler using the available options and built in mathematical functions. At the time the program was written there existed no on line method of taking the real or imaginary part of a double precision variable (although the functions have since been implemented) and function subroutines were included for this purpose. The program assumes the absorption to be in db/in and the pressure to be in lbs/sq. in. Output includes the calculated internal absorption, experimental absorption, and velocity dispersion as a function of frequency/pressure. Also included in the output is the values of the difference between theory and experiment for each of the 100 possible pairs of relaxation times searched. The program will search a maximum of ten possible values for each of the two relaxation times, and can internally reduce the range of relaxation times searched if convergence does not occur at either the upper or lower limit of the relaxation times (input). The thermal conductivity is frequency dependent.

AMD002

This program is similar to AMD001 except that the transport coefficients are computed as the values they would have in a gas mixture. There is no provision for calculating the effect of mass diffusion and the program is therefore useful only for small impurity concentrations.

AMD003

The essential points of this program are outlined in the body of the thesis. It was written to analyze the data from carbon dioxide - hydrogen mixtures, and it will calculate the theoretical absorption by assuming three parallel relaxation times correspond to the vibration and rotation of carbon dioxide and the rotation of hydrogen. The specific heat is calculated as a function of pressure (probably not necessary) as well as the concentration of various species, and the effect of mass diffusion is calculated. A vector of integers (input) determines the order in which the relaxation times are searched. This program was written to be compiled by IBM's Fortran (H) compiler, and although a great deal of the physical body of the program deals with bookkeeping for the searching procedure the greatest amount of execution time is spent calculating the theoretical absorptions. The output includes the difference between the calculated and measured absorption at each pair of relaxation times searched as well as the calculated and measured absorption as a function of frequency/pressure for the best relaxation times.

AMD004

This procedure calculates the rates and reaction scheme as input to Bauer's formalism. The program will calculate SSH, Raff and Winter, and Sharma rates (if the gas impurity is hydrogen) and was intended for either nitrogen or hydrogen as the impurity gas. The procedure was written to be compiled of IBM's PL/I (F) compiler version 5.1, and makes use of a large number of the available options. The input for each new set of rates is gotten by a GET DATA statement and as a consequence all parameters need not be read in each time. The input parameters keep their initial values unless specified explicitly on the data card. The input for each new calculation is separated by a semicolon from the proceeding stream. The program will internally generate the reaction species, population of various species, energy of each specie and a reaction scheme. All data is written on an external file (intended to be a tape) for use as input to AMD005. A DD card must be included for this file and one scratch file (tape or direct access device), and the block-size for these external files should be greater than 7230 if the program is to generate more than 900 rates. The rates are put on the external file in blocks of 900 which, since the rates are double precision, is approximately the largest single write statement available. Two notes of caution, several variables (vectors) have different meanings in the flow of the program in order to conserve core space. This is similar to having the variables equivalenced in Fortran, except that the variables keep the same name. Also several of the variables are declared with the CONTROLLED VARIABLE attribute which means that their dimensions are set at execution time, and not all variables are active throughout the program. The program also generates an indexing vector from which AMD005 deduces the nature of the rates and reaction scheme.

AMD005

This procedure (IBM PL/I (F) version 5.1) uses the data created by AMD004 in Bauer's formalism. The first part of the program is mainly bookkeeping as the procedure was written to be run from a private library so that many possible variations (printing of output, skipping of various segments, etc.) can be controlled by data input rather than having to recompile the procedure. The options are read in as string variables and each set of options is indicated with a card completely blank except for %% in any two consecutive columns. This card can then be followed by a new set of options. Diagonalization is done by a modified version of an IBM PL/I SSP routine MSDU contained in AMD005 as an external procedure. The fit of the theoretical data is done by an external procedure, ACOUTIC, also contained in AMD005. A note of caution in that there are approximately 25 separate options available to the procedure and all possible combinations have not been checked. The procedure assumes that the data will be inputed from an external file and that the rates and reaction scheme will be inputed in groups containing less than 901 separate reactions. Various rates themselves can be modified by this program so that it has been the usual practice to calculate the rates in AMD004 with no empirical adjustments and make any adjustments in AMD005. The procedure does not destroy the rates created by AMD004.

APPENDIX II

COMPLEX QUANTITIES IN ACOUSTIC EQUATIONS

It is often convenient to introduce complex notation into the equations which describe the acoustic properties of a system. A variable q(x,t) which depends harmonically on x or t is written:

$$q(x,t) = q_0 \exp(-i(wt - kx)).$$

The quantities k, the wave vector, and w, the angular frequency, may also be treated as complex quantities. A question of interpretation arises when attempts to measure these complex quantities are made. There are two distinct types of complex quantities under consideration, those that are harmonic functions of x and/or t, such as q(x,t) above, and those which are not, like k or w, but which are made complex for notational convenience.

In the case of complex quantities of the first type A convention is established depending on whether the quantity itself or its square is to be of interest. Considering, for simplicity, a function of time, t, only, $q(t) = A \exp(iwt)$, where A is complex and $A = A_r + iA_i$. A first, and obvious, choice would be to take the real part of q(t) as corresponding to that which is measured.

$$q(t)_m = B \cos(wt - \emptyset)$$

$$\text{Where: } B^2 = A_r^2 + A_i^2, \text{ and}$$

$$\emptyset = \tan^{-1} (A_i/A_r) .$$

B refers to the amplitude of the oscillation and $\emptyset$ is a phase angle. This is convenient as long as q(t) and not $q(t)^2$ is the quantity considered. When it is the square of an harmonic quantity that is being considered a slightly different convention is used.

When the square of an harmonic quantity is considered it is the time average that is of importance. For a simple periodic function of time the time average:

$$\bar{q}(t) = \frac{1}{T} \int_0^T q(t) \, dt = 0,$$

where T is the periodicity of the function. In these the time average of the square of the quantity is taken and the magnitude of the quantity, q, is taken to be, $q = (((\bar{q})^2))^{\frac{1}{2}}$, and is the root mean square amplitude of the actual variable, q(t). The peak value will then be given by:

$$q_{peak} = \sqrt{2} \; xq,$$

since the time averaging introduces a factor of ½. It is simply a matter of convention whether the amplitude of a complex quantity, q(t), refers to the quantity B, defined above, or the root mean square value, or the peak value. As long as the convention has been established the interpretation is straightforward.

As noted above it is sometimes convenient to make k or w complex quantities. It is usually one or the other that is complex, not both. Assuming:

$$k = k_r - ik_i$$

a convention for interpretation will be established which agrees with that established by several authors referenced in this work. The convention used is that the phase velocity, V_p, is given by:

$$V_p = w/k_r,$$

and the absorption coefficient for the amplitude is given by:

$$\alpha = k_i \,..$$

In order to illustrate this convention its introduction into the acoustic equation will be illustrated. Consider the case of a shear wave in a fluid

$$\frac{d^2q}{dt^2} = \eta/\rho \frac{d}{dt} \frac{d^2}{dx^2} (q)$$

Assuming $q = q_0$ exp (i(wt = kx)) the equation reduces to:

$$-w^2 = -iwk^2\eta/\rho$$

$$-w^2 = -iw\eta/\rho(k_r^2 - k_i^2 - 2ik_rk_i)$$

equating imaginary parts: $k_r = k_i = k$

Equating real parts: $w^2 = 2wk^2\eta/\rho$, or $k^2 = \rho w/(2\eta)$.

According to Bhatia(52) the phase velocity, V_p, is interpreted as:

$$V_p = w/k_r = (2\eta w)^{\frac{1}{2}}/\rho$$

Obviously the wave will be quite dispersive.

Cottrell and McCoubrey(37) treat the problem in a different manner. They write the solution to the wave equation as:

$$q(x,t) = q_0 \exp (iw(t - x/v))$$

where the "velocity", v, is complex; $v = v_i + v_r$, but the phase velocity is interpreted as $V_p = \frac{V_r^2 + V_i^2}{V_r}$, but this is really no different than the situation of allowing k to be complex and having the phase velocity given by w/k_r. For Cottrell and McCoubrey's equation can be rewritten as:

$$q(x,t) = q_0 \exp (iw(t - \frac{x V_r}{V_r^2 + V_i^2}) - \frac{V_i x}{V_r^2 - V_i^2})$$

which is the same as having the real part of k given by

$$k_r = \omega/V_p = \frac{V_r \omega}{V_r^2 + V_i^2}$$

and as before the phase velocity is given by w/k_r.

The idea of the phase velocity given by w/k_r is also explicitly stated by Markham, Beyer and Lindsay(53) who set $k = k_r + k_i$ and state "The phase velocity in general is given by $C^2 = w^2/k_r^2$." This seems to be the convention adopted by Herzfeld and Litovitz also(7). The question arises whether this convention, and it is really a convention, is different from assuming that a complex quantity, when measured, yields a value $X_m = (X_r^2 + X_i^2)^{\frac{1}{2}}$. Consider the case of molecular absorption and no classical absorption(7). In this case the specific heat becomes a complex and the equation reduces to(7):

$$(k/w)^2 = \frac{M}{RT}\left(\frac{C_v}{C_p}\right)$$

$$\left(\frac{k_r}{w} - \frac{ik_i}{w}\right)^2 = \frac{M}{RT}\left(\frac{C_v}{C_p}\right)$$

If the measured velocity (insofaras the phase velocity is the measured velocity) is assumed to be w/k_r the equation for the velocity becomes, from the real part of the above equation:

$$\left(\frac{1}{v}\right)^2 = \mathrm{Re}\left(\frac{M}{RT}(C_v/C_p)\right) + \frac{k_i^2}{w^2}$$

But stating that the real part is what is measured would be equivalent to adopting the convention that

$$V_r^2 = \mathrm{Re}\left(\frac{RT}{M}C_p/C_v\right) + V_i^2 = V_m^2 .$$

Adopting the convention that $\mathrm{Re}\left(\frac{RT}{M}C_p/C_v\right)$ is interpreted as V_r^2 and the measurement is of $V_m^2 = V_r^2 + V_i^2$ then the two conventions are equivalent. The problem seems to be one of deciding which convention has been adopted. The references used in compiling this thesis adopt the convention that the measured velocity corresponds to w/k_r, but they do not interpret $\mathrm{Re}\left(\frac{RT}{M}C_p/C_v\right)$ as V_r^2. It really makes no difference which convention is used as long as one is consistent. As a matter of fact for the case of acoustic compressional waves propagating in a "dense" gas one need not worry about the problem at all. Using the convention adopted it is always the case that k_i^2/w^2 is much smaller than Re $(\frac{M}{RT} C_v/C_p)$ or in the other convention, the imaginary part of the velocity is much smaller than the real part so that the measurement is of the real part, and in fact Cottrell and McCoubrey state, "V_p is set equal to V_r and is simply written V."(37)

VITA 2

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