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ABSORPTION OF SOUND IN AIR

By

L.B. Evans
L.C. Sutherland

Work Performed Under Contract DAH C04-69C 0088

July 1970

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ABSTRACT

Experimental measurements of the absorption of sound in still air exhibit a distinct deviation from the theoretical predictions based on known classical and molecular relaxation absorption losses. Investigation of published laboratory data has verified that Kneser's theory for molecular relaxation accurately describes the absorption loss near and above the relaxation frequency. At frequencies less than about 0.1 of the relaxation frequency, a different mechanism becomes predominant and results in an absorption loss component which varies directly with the frequency and is essentially independent of humidity. The objective of the effort in this contract was to carry out a detailed experimental and analytical investigation of this anomaly to allow numerical calculations to be made of air absorption for a variety of atmospheric conditions in still air.

An extensive literature survey has revealed that the anomaly is probably due to an as yet undefined vibrational relaxation process in moist air. With this in mind experimental measurements of audible sound in air were made over the humidity range of 0 percent to 100 percent relative humidity. Analysis of the data from these measurements show the same type anomaly and the same agreement with Kneser's relaxation theory (single relaxation). The anomaly in these measurements is not as large as that of previous investigators. It is thought that the anomaly is due to the vibrational relaxation of nitrogen catalized by either water vapor, carbon dioxide, or a combination of both. To verify this a set of experiments needs to be performed in which both water vapor content and carbon dioxide content can be accurately controlled. Experimental sound absorption measurement were also made in humid nitrogen at room temperature. The relaxation frequencies from these nitrogen measurements agree fairly well with values deduced from Harris' air data.

A scheme based on previous data has been devised for predicting sound absorption in still air. Vertical profiles of air absorption utilizing real weather conditions have been made and reveal that the absorption coefficient at a given frequency on the ground quite often does not at all describe the sound absorption at higher altitudes. Also existing field data has been compared to the prediction scheme for sound absorption with fair agreement between the two.

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LIST OF SYMBOLS

a	-	surface absorption coefficient
a_d	-	molecular diffusion constant for O_2 and N_2 mixture
c	-	speed of sound in air
C'	-	internal or relaxing specific heat
C_p	-	specific heat at constant pressure
C_v	-	specific heat at constant volume
D_{12}	-	diffusion coefficient for O_2 and N_2 mixture
E	-	energy
E_j	-	energy level of rotational energy modes
$\mathcal{E}$	-	energy per unit volume
f	-	frequency
f_m	-	frequency of maximum absorption or relaxation frequency
h	-	percent mole ratio
h_s	-	saturated vapor density
$\hbar$	-	$h/2\pi$ - Planck's constant
H	-	percent relative humidity
I	-	intensity of sound wave - moment of inertia in Section 6.0
I_0	-	intensity of sound source
j	-	rotational quantum number
J_n	-	rotational level of greatest excitation

k_{ij}	-	chemical rate constant
K	-	Boltzman's constant
m	-	intensity absorption coefficient - mass in Section 6.0
m_{cl}	-	classical intensity absorption coefficient
m_{max}	-	maximum intensity absorption coefficient
m_{mol}	-	molecular intensity absorption coefficient
M	-	mass of air
M_w	-	mass of water
N	-	decay rate of sound in dB/sec
N_{air}	-	decay rate of sound in air
N_{N_2}	-	decay rate of sound in nitrogen
P, P_0	-	pressure
R	-	universal gas constant in Section 2.0 - Total absorption of room in Section 3.0
R_{air}	-	total intensity absorption in air
R_{cal}	-	total intensity absorption in room filled with calibration gas
R_{mol}	-	m_{mol}
R_{N_2}	-	total intensity absorption in nitrogen
t	-	time
T	-	temperature

1.0 INTRODUCTION

1.1 General Remarks

A basic characteristic of sound propagation is the attenuation with distance due to various irreversible processes which remove energy from an acoustic wave and convert it to heat. Prediction of sound propagation in air over long distances has become a matter of increasing practical significance in several areas including:

- Prediction of community noise levels around airports.
- Analysis or acoustic detection of tactical equipment or aircraft.
- Evaluation of very low frequency sound propagation in the atmosphere from rocket powered space vehicles or from natural sources such as tidal motion, earthquakes, wind storms, etc.
- Investigation of the vertical propagation of sonic disturbances from signaling grenades or sonic booms.

A number of studies on sound absorption in moist air have been carried out culminating recently in the extensive investigation by Professor C.M. Harris, Columbia University, (Reference 1) and the results of the past year's effort presented in this report.

In the past year the literature has been surveyed extensively for previous work which is related to sound absorption in the atmosphere. This literature review has supplied many answers and has helped to direct the experimental efforts. A set of experiments, covering the humidity range of approximately 1.8 to 100 percent relative humidity, has been performed on sound absorption in air. The results have been tabulated and comparisons have been made to previous investigations.

A set of engineering equations have been developed which is offered as a tentative solution for the description of sound absorption in humid air; however, there are several areas which need further investigation. Even though significant progress has been made, there are still many unsolved problems, and further refinement, along with further experimental data, is needed for the solution of these problems.

In any program where it is necessary to make field measurements of sound, the absorption of sound by the atmosphere enters into these measurements. It is often necessary for design purposes to correct these measurements so as to know the sound pressure levels at the source. One example of this is for aircraft or helicopter flyovers. At times it is also necessary for detectability criterion to be able to predict the distance required for doubling of sound pressure levels, e.g., how much lower can a helicopter fly before the sound pressure level is doubled? In all of these problems a very large part of the total sound absorption is due to the internal structure of the molecules in air, i.e., molecular relaxation processes. In fact for free field propagation the molecular absorption is often the largest mechanism absorbing the sound energy, and the magnitude of the absorption is very

dependent upon the ambient weather conditions. The temperature and humidity profiles of the atmosphere are very important in outdoor sound measurements. For example, at high altitudes the molecular absorption is higher for low frequencies than for high frequencies. This is because of the low humidity found at high altitudes. The completion of this investigation will give the field or design engineer a set of equations with which outdoor sound absorption data can be corrected for these meteorological anomalies.

1.2 Review of General Characteristics of Sound Propagation in the Atmosphere

Whenever an outdoor sound absorption measurement is made, the question always arises "how much should the measurement be adjusted for sound absorption due to atmospheric effects?" In open air, effects such as thermal inhomogeneities, turbulence, dust, fog, ground reflections, scattering, diffraction, inverse-square law spreading, classical absorption and molecular absorption are all factors which can distort sound measurements.

If the noise generation characteristics of a particular noise source such as a helicopter can be defined as a function of its flight configuration and ambient atmospheric conditions, the sound observed at any point in its vicinity is then dependent upon the sound propagation path. Propagation characteristics are dependent upon (a) atmospheric conditions, (b) the position of the source relative to the ground, and (c) the terrain/vegetation features adjacent to the sound path. The above listed factors which effect the intensity of the sound arriving at the observer can be classified as follows: (See for example Reference 2).

Spreading Losses

- Uniform spherical spreading (Inverse Square Law) losses
- Non-uniform spreading
 - reflection by finite boundaries
 - refraction by non-uniform atmosphere
 - diffraction (scattering) by non-stationary atmosphere

Absorption Losses

- Absorption by ground and ground cover
- Absorption by atmosphere
 - classical absorption
 - molecular relaxation absorption

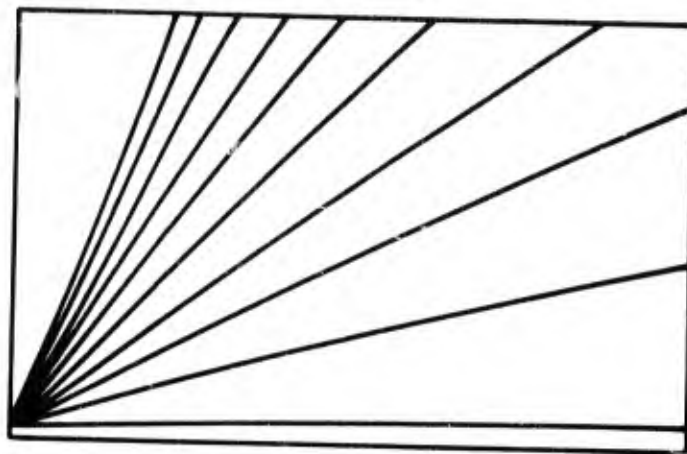
Of these sound propagation effects, different ones may be the controlling factor for different atmospheric meteorological conditions; however for any type of condition or any type of sound propagation path the absorption due to classical and molecular effects are fixed and are functions only of the propagation path distance, the humidity

content, and the temperature. Before the more variable propagation effects can be accurately accessed it is necessary to establish the proper values for the fixed absorption losses. Following are short discussions of the various different propagation effects.

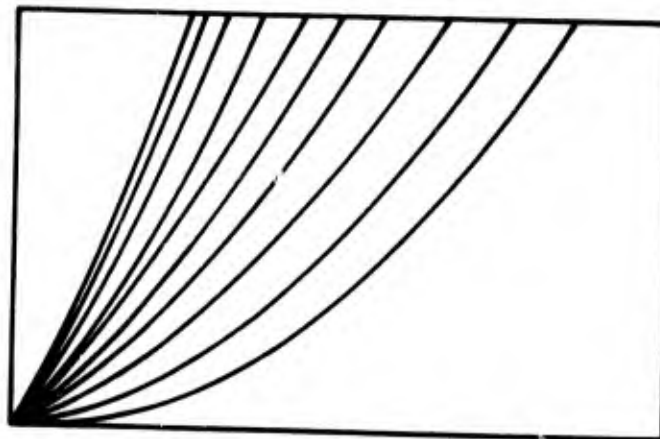
1.2.1 Spreading Losses

- Uniform Spherical Spreading — In an ideal medium, the total sound power radiated through an expanding spherical wave front remains constant so that sound pressure levels are reduced by 6 dB each time the distance from the source doubles. Two effects cause deviations from this rule at small source to receiver distances which are within the "near field". Firstly, the near field is a region in which the physical dimensions of the source region are important so that sound reaches the observer from various directions. Secondly, at distances which are small compared with typical sound wavelengths, non-propagating "hydrodynamic" pressure fluctuations amplify the apparent sound levels.
- Reflection by Boundaries — If the source is within a few wavelengths of the ground, sound reflection effects will affect propagation characteristics. These include amplifications due to an effective increase in source power when the height is small compared with a wavelength and due to interference between the direct and reflected signals. Variations in the far field sound levels of up to 6 dB are possible. Theoretical predictions of this ground reflection effect have been verified experimentally (Reference 3).
- Refraction by Non-Uniform Atmosphere — Atmospheric wind velocity and temperature gradients change the directionality characteristics of a source by bending the sound rays such as illustrated in Figure 1. As noted in Figure 1b, a "shadow zone" is formed in the presence of a negative vertical velocity of sound gradient caused by vertical changes in either wind speed or velocity. Conversely, a positive vertical velocity of sound gradient (Figure 1c) will cause the sound rays to be bent back towards the ground, resulting in a phenomenon known as "focusing". In the case of a negative temperature gradient the shadow zone is in the shape of a circle with the source as center; however, in the presence of wind the shadow zone is as illustrated in Figure 2. Here the shadow zone begins upwind and has the boundary as sketched. Downwind, however, there is a "focusing" of the sound rays similar to that shown in Figure 1c. Within the shadow zone itself, the sound radiated by the source suffers an excess attenuation which approaches the constant value indicated in Figure 2 at distances greater than about 1500 feet from the source. This excess attenuation is based upon a theoretical model outlined in References 4 and observed experimental data (References 5 and 6).

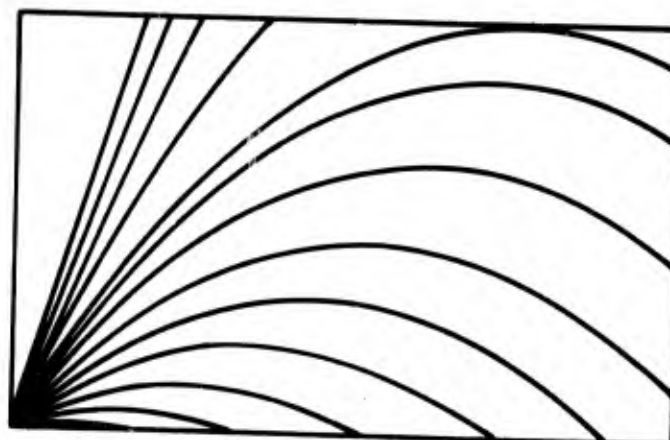
Evidence of the reduced effect of refraction for air-to-ground propagation is reported in an extensive study of air-to-ground propagation losses by Sabine et al (Reference 6). They show that the fixed shadow-zone attenuation is



a) Ray Paths in Air When Vertical Velocity Gradient is Zero



b) Ray Paths in Air When Vertical Velocity Gradient is Negative



c) Ray Paths in Air When Vertical Velocity Gradient is Positive

Figure 1. Acoustic Ray Path Variation as a Function of Vertical Speed of Sound Gradient and Vertical Temperature Gradient

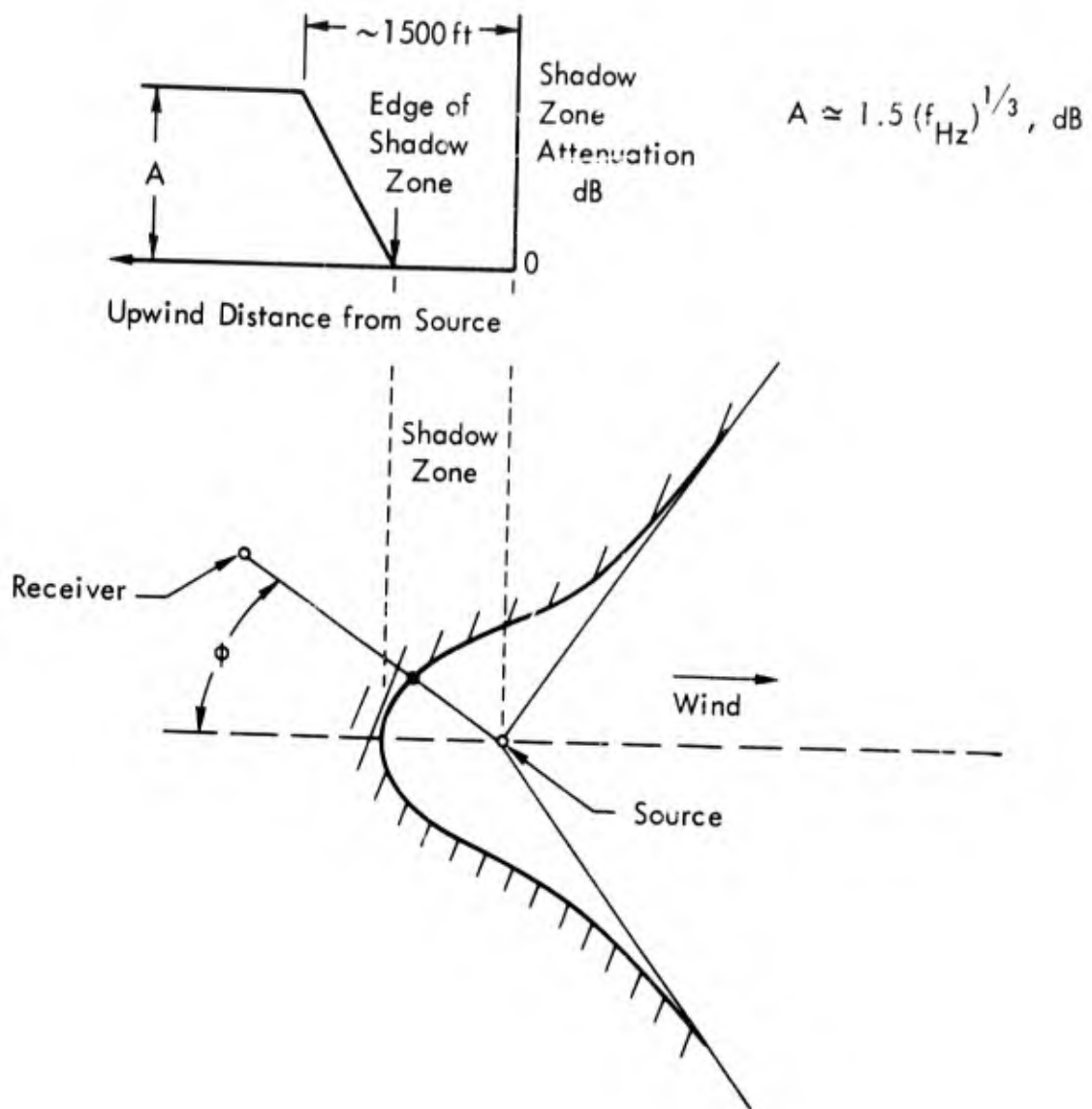


Figure 2. Excess Attenuation of Sound in an Upwind Shadow Zone

reduced by a factor of 2 to 10 for sound source elevation angles greater than 5 degrees. This trend is also verified by theory as shown in Figure 1 where it is clear that rays with an initial direction approaching the vertical are refracted much less than those with a more horizontal initial angle.

- Scattering by Non-Stationary or Turbulent Atmosphere — Turbulence scattering is a further important source of atmospheric attenuation for low frequency sound. It does not involve a dissipation of sound energy, but a redirection of it. Its principal effect, on a directional sound field, is to equalize acoustic energy propagating in all directions at large distances from the source. This is a direct result of the scattering of the sound field by the non-uniform sound velocity distributions in atmospheric turbulence. Thus, a highly directional sound profile can be gradually rounded out, tending to a non-directional pattern at great distances from the source. This scattering or redistribution of sound energy is, in fact, the basis for a finite limitation in the excess attenuation in a shadow-zone discussed in the previous paragraph. This scattering loss phenomena has been analyzed in some detail and has led to tentative empirically-derived expressions for the apparent propagation loss, (Reference 1). In the frequency range of 60 - 100 Hz, the observed scattering loss coefficient for ground to ground propagation of sound is of the order of 0.4 dB/1000 ft. This appears to be a characteristic frequency range for maximum scattering attenuation for ground to ground propagation. A similar indication of a maximum value for attenuation anomalies in this frequency range for ground to ground propagation has been reported in Reference 7. However, it is quite impossible to make accurate quantitative estimates of this scattering attenuation until a valid baseline for absorption losses in a stationary, homogeneous atmosphere are clearly defined.

1.2.2 Atmospheric Absorption Losses

Atmospheric absorption losses have two basic forms: 1) classical losses associated with the change of acoustical energy (or kinetic energy of molecules) into heat by fundamental gas transport properties of a gas, and 2) for polyatomic gases, relaxation losses associated with the change of kinetic or translational energy of the molecules into internal energy within the molecules themselves.

The classical losses can be further sub-divided into (Reference 8)

- Viscous Losses
 - Heat Conduction Losses
 - Diffusion Losses
 - Radiation Losses
- } Stokes-Kirchhoff Loss

Only the first two components are considered significant for air under normal atmospheric conditions and at values of the acoustic frequency divided by the atmospheric pressure of less than about 100 MHz/atm.

Relaxation absorption losses in polyatomic gases are known to have the following forms. (A thorough review of the theory of relaxation losses is given by Kneser (Reference 9)).

- Thermal relaxation between translational energy and vibrational energy states of the molecules
- Thermal relaxation between a close vibrational resonance of two different molecules
- Thermal relaxation between the vibration of one molecule and the rotation of a different molecule
- Thermal relaxation between translational energy and rotational energy states of the molecules
- Electromagnetic relaxation between translational energy and allowable energy states of external electrons of the molecule

For acoustic frequencies below 100 MHz/atm in air, rotational relaxation varies with frequency in the same manner as, and adds a small component to, classical absorption so that these two components of atmospheric absorption can be considered together (Reference 10). As far as is known, electromagnetic relaxation is known to be significant for only one common gas, nitric oxide, NO, and then, only at very high ultrasonic frequencies (References 9 and 11).

1.2.3 Ground Absorption Losses

Terrain effects range from the dissipation of acoustic energy at the boundary of a sound wave traveling parallel to the ground to the direct impedance offered to a sound wave penetrating a leafy jungle. Limited data on these effects are available and those experiments which have been performed (e.g., References 4, 12-16) have provided results which often conflict with each other largely because of the large number of propagation effects which must be taken into consideration. Again, lack of an adequate or consistent baseline for the inherent atmospheric absorption loss adds to the lack of consistency in the available experimental data. A particularly striking example of this is given in Reference 16. Here, the use of an empirical procedure for estimating atmospheric losses (Reference 17) has produced misleading results on ground absorption since the empirical air absorption method is not defined at low frequencies. Attempts are being made to produce an accurate ground absorption model through both theoretical analysis and laboratory scaled experiments; however, an accurate base line for air absorption will be needed for field calibration and evaluation of such a ground absorption model.

1.3 Summary of Balance of Report

The following section contains a description of sound absorption due to classical effects and molecular effects. A comparison of previous molecular absorption data to theory is also given. Section 3.0 contains a description of the experimental results in air. The experiment theory and design are described and the experimental results are presented. Section 4.0 gives a tentative prediction method for atmospheric absorption in still air and the following section presents a comparison of this prediction method to field data. The last section gives a summary of the results and conclusions which have been drawn.

2.0 THEORY

All sonic disturbances lose energy in propagating through air due to the irreversible conversion of acoustical energy into heat energy. This energy transfer process may be broken down into two types: classical absorption losses which are inherent in all gases due to basic gas transport phenomena and molecular absorption losses which are associated with resonance phenomena within polyatomic gases.

At thermal equilibrium, the various molecular energy states of the constituent gases in air are populated according to Maxwell-Boltzman statistics. Although energy is continually exchanged between internal and translational degrees of freedom by collisional processes, the various internal states are time invariant, and since individual collisional processes cannot be distinguished experimentally, the rate of energy exchange cannot be measured for a system at thermal equilibrium. However, perturbation of the thermal equilibrium by a sound wave produces heat adiabatically in the compressional phase which is dissipated in the expansion phase. This heat energy is initially in the translational degrees of freedom and is then distributed among the internal degrees of freedom by collisions and this distribution requires time. If the frequency of the sound wave becomes sufficiently high, there may not be enough time in the compressional phase for the heat energy to be transferred to some of the internal degrees. When this happens the effective number of degrees of freedom of the gas has been lowered.

For molecular gases, as the sound frequency is increased from zero, the vibrational modes are the first to fail to keep in equilibrium. As the frequency is further increased the rotational modes are the next which undergo this transition, and when the wavelength of the sound wave becomes approximately the same as the mean-free-path of the gas molecules, the translational degrees are affected.

Experimental studies of the effects produced by equilibrium perturbation are in general called relaxation studies. The relaxation of the vibrational modes has received the most study both experimentally and theoretically since usually this relaxation occurs at frequencies which are easily obtainable. For the case of audible sound in still air most of the absorption effects are due to the vibrational relaxation of oxygen; however, other processes appear to be extremely important under certain conditions of humidity, temperature and sound frequency.

The intensity of a plane wave, I , received a distance, x , from the source, I_0 , in still air is given by

$$I = I_0 e^{-2\alpha x} = I_0 e^{-mx}$$

where α is the total amplitude absorption coefficient and m is the total intensity absorption coefficient and is equal to 2α . This total absorption coefficient can be broken into several additive terms as long as the transport properties of the gas are not frequency dependent, and the frequency regions important to vibration and rotation are not coupled. These conditions are met in the case of air at all frequencies below several hundred megahertz.

The absorption coefficient is then given by

$$\alpha = \alpha_{cl} + \alpha_{mol}$$

where α_{cl} is the absorption due to classical effects and α_{mol} is the absorption due to the internal structure of the molecule.

The classical absorption can be further broken down into several parts

$$\alpha_{cl} = \alpha_{\eta} + \alpha_K + \alpha_D + \alpha_{rad}$$

where α_{η} is the viscosity effect; α_K is the thermal conductivity effect; α_D is due to diffusion; and α_{rad} is due to heat radiation.

2.1 Classical Absorption

Classical absorption of sound in air is due to the energy losses as a result of the transport properties of gases. These losses can generally be placed in four groups (see for example References 16-18).

- Viscous Losses
- Heat Conductivity Losses
- Diffusion Losses
- Heat Radiation Losses

2.1.1 Viscous Losses

The cause of the viscous loss is attributed to the viscous drag forces opposing "particle" motion of sound waves. The absorption due to these drag forces is given by

$$\alpha_{\eta} = \frac{2\pi^2 f^2}{\gamma P_0 c} \left\{ \frac{4\eta}{3} \right\} \frac{np}{\text{unit distance}}$$

2.1.2 Heat Conduction Losses

The cause of the heat conductivity loss of energy is due to heat transfer between adjacent condensation and rarefaction regions within the gas. The absorption due to these compressions and rarefactions is given by

$$\alpha_K = \frac{2\pi^2 f^2}{\gamma P_0 c} \left\{ \frac{\gamma - 1}{C_p} k \right\} \frac{np}{\text{unit distance}}$$

The sum of the viscous and heat conductivity terms is generally called the Stokes-Kirchhoff absorption.

2.1.3 Diffusion Losses

The cause of the diffusion losses is the mutual diffusion (mixing) between the oxygen and nitrogen molecules in air. The expression for this loss is

$$\alpha_D = \frac{2\pi^2 f^2}{\gamma P_0 c} (\gamma a_d D_{12} \rho) \frac{np}{\text{unit distance}}$$

2.1.4 Heat Radiation Losses

The cause of the heat radiation loss is due to the radiation of heat from the compressional part of the sound wave. The exact formulation of this term has not been determined but estimates of its magnitude have been made. Calvert, et al., Reference 19 estimates that the radiation absorption due to the 25μ infrared band of H_2O is the largest cause of sound absorption due to radiation. His estimates show that the radiative absorption term is approximately equal to the Stokes-Kirchhoff term at 55 Hz and becomes much larger than the Stokes-Kirchhoff absorption at infrasonic frequencies. So, for absorption of audible sound the heat radiation term can be neglected.

2.1.5 Total Loss Due to Classical Effects

The total absorption due to classical effects can be written as

$$\alpha_{cl} = \alpha_\eta + \alpha_\kappa + \alpha_D$$

$$\alpha_{cl} = \frac{2\pi^2 f^2}{\gamma P_0 c} \left[\frac{4}{3} \eta + \frac{\gamma - 1}{C_p} \kappa + \gamma a_d D_{12} \rho \right]$$

and this expression can be evaluated in terms of the viscosity as

$$\alpha_{cl} = \frac{2\pi^2 f^2}{\gamma P_0 c} [1.900] \eta.$$

2.2 Molecular Absorption

The molecular or internal absorption is attributed to the vibrational and rotational degrees of freedom of the molecules. The molecular absorption is given by (see for example References 16-18)

$$\alpha_{mol} = \frac{\pi C' (\gamma - 1)}{c C_p} \frac{f^2 f_m}{f^2 + f_m^2}$$

In general the above equation is applicable to any region of molecular absorption by proper definition of the internal specific heat C' . For the case of air at audio-frequencies, C' is the vibrational specific heat of the diatomic components; however, there is also some absorption due to the rotational degrees of freedom even at low frequencies (Reference 20). The rotational degrees of freedom relax at very high frequencies and for the case of air the regions of vibrational and rotational relaxation are well separated and the excess absorption due to the rotational degrees of freedom can be simply subtracted from the total molecular absorption, i.e.,

$$\alpha_{\text{mol}} = \alpha_{\text{vib}} + \alpha_{\text{rot}}$$

2.2.1 Rotational Absorption

Inspection of the equation for molecular absorption reveals that at frequencies well below the frequency of maximum absorption, i.e., $f \ll f_m$

$$\alpha_{\text{mol}} = \frac{\pi C' (\gamma - 1)}{c C_p} \frac{f^2}{f_m}$$

where in this case f_m is the frequency of maximum absorption for the rotational degree of freedom. Also for air the internal specific heat, C' , due to rotation is equal to R , and C_p and γ are given by $7/2R$ and $7/5$, respectively. So

$$\alpha_{\text{rot}} \approx \frac{4}{35} \frac{\pi}{c f_m} f^2$$

which is valid only at low frequencies, i.e., $f \ll f_m$. Values of f_m can be taken from Sessler (Reference 21) or Winter and Hill (Reference 22).

Experimental values for the sum of α_{cl} and α_{rot} for air at low frequencies can be predicted from Greenspan's (Reference 10) data as

$$\alpha_{\text{cl}} + \alpha_{\text{rot}} = \frac{2 \pi^2 f^2}{\gamma P_0 c} [2.50] \eta$$

or in terms of temperature it can be expressed to a close approximation over the normal temperature range by:

$$\alpha_{\text{cl}} + \alpha_{\text{rot}} \approx 18.0 \times 10^{-12} (1 + 0.001 T^{\circ}\text{C}) \frac{f^2}{P}, \text{ m}^{-1}$$

where f is in Hertz and P is in atmospheres

2.2.2 Vibrational Absorption

All that remains to be evaluated is the molecular absorption due to the vibrational energy states. Remembering that for temperatures in the range expected outdoors, the internal specific heat for O_2 and N_2 are quite small so that C_p can be closely approximated by $7/2R$ and γ by $7/5$. The absorption equation due to vibration is then given by

$$\alpha_{vib} = \frac{4 \pi C'}{35 R c} \left[\frac{f}{f_m/f + f/f_m} \right]$$

and the absorption per wavelength $\alpha_{vib} \lambda$ is given by

$$\alpha_{vib} \lambda = \frac{4 \pi C'}{35 R} \frac{1}{f_m/f + f/f_m} .$$

The maximum absorption occurs when $f_m = f$ and this gives

$$2 (\alpha_{vib} \lambda)_{max} \equiv \mu_{max} = \frac{4 \pi C'}{35 R}$$

It is obvious from this that the maximum absorption due to vibrational effects is only a function of the vibrational specific heat which is directly related to temperature. So, it is seen that the peak of the molecular absorption curve is controlled only by temperature. The internal specific heat of nitrogen at room temperature is approximately $0.002R$ while that for oxygen is about $0.03R$. From this it is determined that the molecular absorption in air is due almost entirely to the oxygen content; however, at frequencies such that $f/f_m < 0.1$, Sutherland (Reference 23) has shown an anomalous excess absorption which can perhaps be attributed to the nitrogen content (Reference 24).

2.2.3 Temperature and Pressure Variation in Relaxation Frequency

For prediction of sound through the stratosphere or for sound propagating under unusual weather conditions, some rational method is required for predicting the variation in f_m with temperature and pressure. Harris has provided significant data on these effects (References 25 and 26). His data on f_m at reduced pressure confirm theoretical predictions that f_m is directly proportional to ambient pressure. This variation with pressure will be significant when attempting to compute relaxation losses for propagation of sound through the atmosphere.

The absorption equation is given by

$$\alpha_{vib} \lambda = \frac{4 \pi C'}{35 R} \frac{1}{\frac{f_m/P}{f/P} + \frac{f/P}{f_m/P}}$$

or if we normalize $\alpha_{\text{vib}} \lambda$ we have

$$\frac{\mu}{\mu_{\text{max}}} = \frac{2 (f/P) (f_m/P)}{(f/P)^2 + (f_m/P)^2}$$

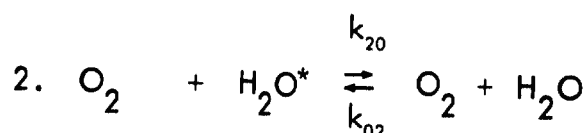
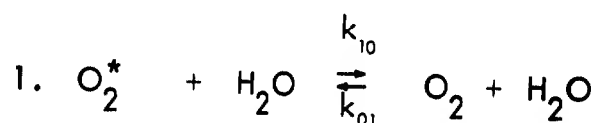
Data on the variation in relaxation frequency in air with temperature are not as definitive as those for pressure effects. In fact, an accepted theoretical model is not available for temperature effects on relaxation frequency in a composite mixture of gases, such as air. The temperature dependence of f_m is still somewhat of an unanswered question. Harris (Reference 1) has found a negative temperature dependence, i.e., f_m decreases with increasing temperature.

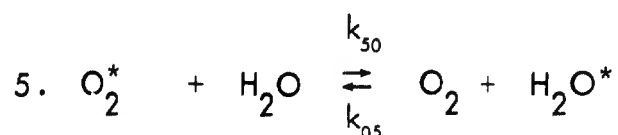
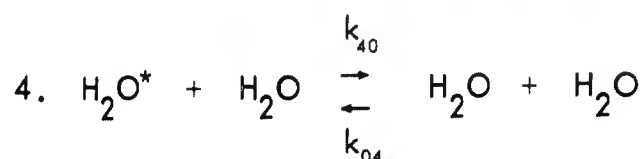
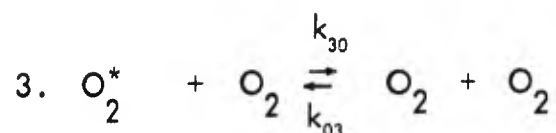
2.2.4 Humidity Dependence of Vibrational Relaxation

In the introduction five types of relaxation processes are listed. Of these five, two have been utilized to predict the humidity dependence of sound absorption in humid air:

- Thermal relaxation between translational energy and vibrational energy states of the molecules
- Thermal relaxation due to a close vibrational resonance between two different molecules

Historically the first of these processes was thought to be the cause of acoustic absorption in the audio frequency range in gases. However, according to the chemical kinetics of bimolecular collision processes there should be a linear shift in relaxation frequency with mole percent of an added impurity, (see for example Reference 16). This effect has been shown to be true for many molecular collision processes; however, one of the first systems which did not obey this simple theory was the case of oxygen and water vapor mixtures (Reference 27). The $\text{O}_2 - \text{H}_2\text{O}$ acoustical absorption data clearly revealed a quadratic shift in relaxation frequency with percent mole ratio of water vapor. This anomaly was explained by Tuesday and Boudart (Reference 28) in 1954, using a combination of the two above listed types of relaxation processes. They considered the following set of chemical reaction equations to explain the anomaly:



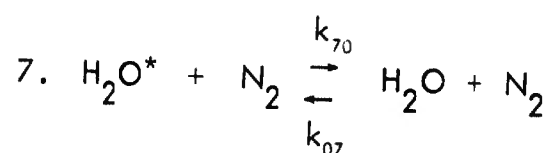
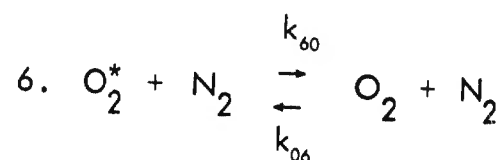


The asterisk (*) indicates an excited vibrational mode in that particular molecule.

Of these five equations, the first four represent thermal relaxations between the vibrational energy state of one molecule to the translational energy state of the other. The fifth equation represents a direct interchange of energy between the vibrational mode of one molecule to the vibrational energy state of the other. This is considered possible since a near resonance exists between the first vibrational energy state of oxygen and one of the bending vibrational energy states of the water vapor molecule.

This analysis by Tuesday and Boudart (Reference 28) did predict the quadratic dependence of the relaxation frequency of oxygen on the mole percent water vapor present. It was recognized by others that this type of analysis could perhaps be used to predict other systems which might show a quadratic dependence on mole percent added impurity. A system which was recognized to exhibit the same general characteristics as the $\text{O}_2 - \text{H}_2\text{O}$ system was $\text{O}_2 - \text{CH}_4$, and in this case the near vibrational resonance was much closer than in the case of $\text{O}_2 - \text{H}_2\text{O}$. Therefore, it was thought that this system should also exhibit a quadratic dependence on percent of added impurity. Investigation of the $\text{O}_2 - \text{CH}_4$ system by Schnaus (Reference 29) and also by Parker (Reference 30) showed conflicting results and a further study was made by Evans and Winter (Reference 31). The results of Schnaus, and Evans and Winter were very close and neither of these experiments showed the expected quadratic dependence. Further investigation revealed that in order to obtain a quadratic dependence the impurity molecule must be able to de-excite its own vibrations very rapidly which is the case with water vapor but is not true with methane, i.e., in the fourth chemical rate equation the rate constant k_{40} is very large.

The analysis by Tuesday and Boudart has been extended by Henderson and Herzfeld (Reference 32) to explain the relaxation frequency of air as a function of mole percent water vapor. Their work still did not fit the experimental data exactly, and Monk (Reference 33) further extended their work. Henderson and Herzfeld considered these following chemical reactions in addition to the ones considered by Tuesday and Boudart to explain the relaxation in air. Monk re-evaluated the rate constants to obtain a better fit to the experimental data.



The final expression by Monk appears to fit the experimental data over a large range of humidities and is given by:

$$f_m = 1750h + 61400h \left[\frac{1.12 + 10h}{10.4 + 10h} \right]$$

Monk has suggested that the preceding equation can be closely approximated for $0.1 < h < 1.0$ by

$$\frac{f_m}{p} = 38,600h^{1.45}$$

However, close inspection of the accumulated data of Knotzel, Pennsylvania State University, Evans and Beazley, Pohlman, Harris, and Monk (References 25-26, 34-38) as shown in Figure 3 reveals that

$$\frac{f_m}{p} = 40,000h^{1.45}$$

is a better approximation over a wider humidity range.

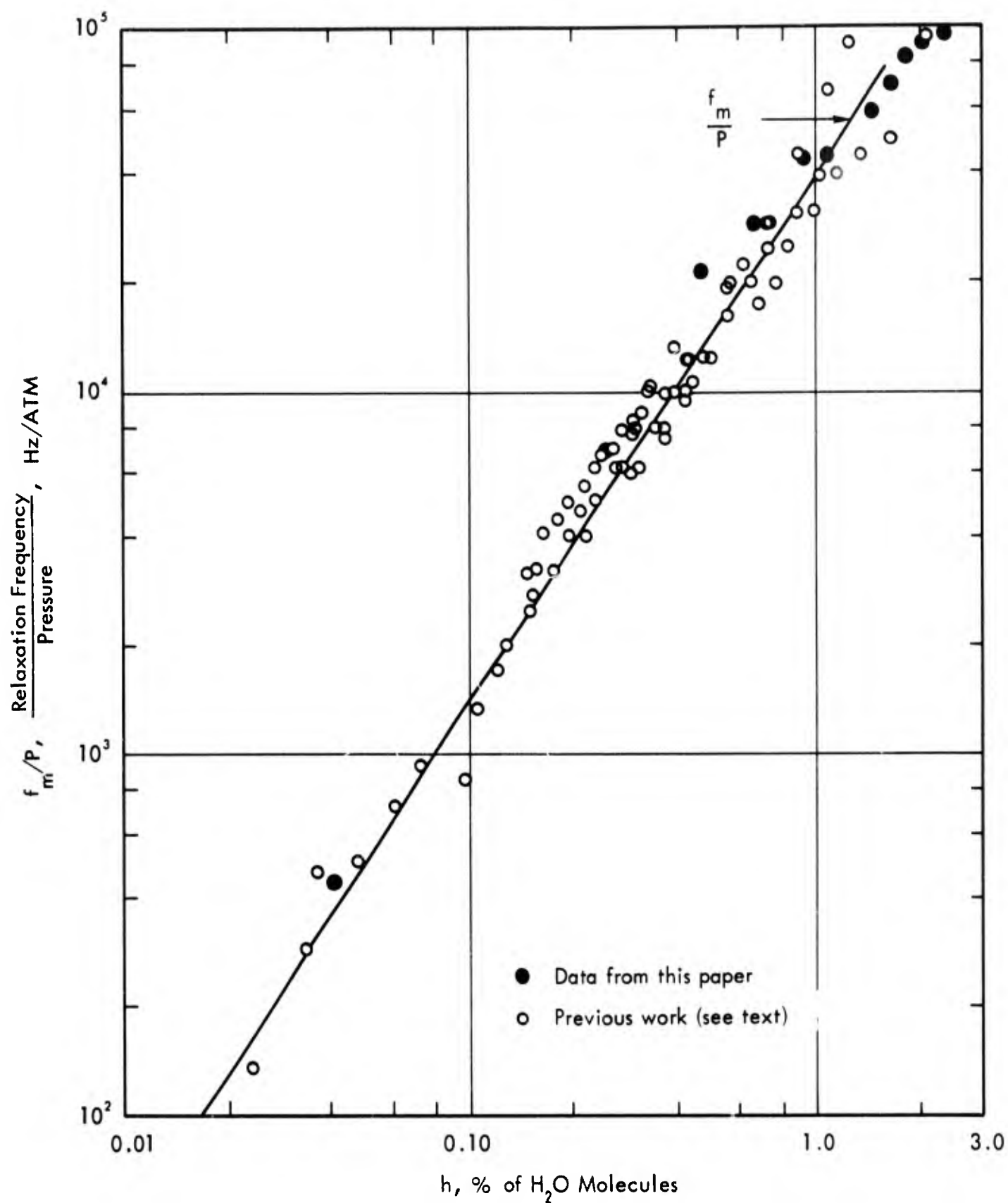


Figure 3. Observed Relaxation Frequency in Air

2.2.5 Comparison of Previous Molecular Absorption Data with Theory

Based on the preceding techniques for defining $\mu_{\max}$ and f_m , the detailed results of Harris (Reference 1) and Harris and Tempest (Reference 26) have been analyzed. The Normalized data are compared in Figure 2 with Kneser's (Reference 9) theoretical prediction (single relaxation theory). It appears that theory does indeed predict the observed results very well for $f/f_m \geq 0.3$ but that below this normalized frequency, the data exhibit a definite and systematic deviation. The latter can be described by an added loss term which varies directly with the first power of frequency instead of the second power. A purely empirical expression, shown in Figure 4, has been developed to describe the data over the entire range of f/f_m for which results are available. Several points should be emphasized about the results in Figure 4.

- 1) A careful analysis of the data (based on smoothed values presented by Harris and Tempest) rejects the possibility of simply adding a new linear term. This would have caused a significant deviation, on the order of 20 percent, between data and theory for $f/f_m \approx 0.3$.
- 2) The normalized data for $f/f_m < 0.05$ are insensitive to f_m . The latter is a normalizing factor in the denominator of both abscissa and ordinate scales. Thus, any change in f_m causes the normalized data point to shift along a line with the same unity slope as the empirical line. This indicates that the anomalous loss is insensitive to humidity content.
- 3) There is insufficient data to validate the accuracy of the empirical expressions for $f/f_m \geq 3$.
- 4) A brief review of other published data on laboratory measurements of air absorption indicates a similar trend to that shown in Figure 4.
- 5) The empirical expression shown in this figure is only one possible form that might be used. An alternate form might consist of an added linear (with frequency) term which approaches a maximum value near a value of $f/f_m \geq 0.1$.
- 6) There is no available theoretical guidance for selection of any one empirical form.

The purpose of this study was to investigate this anomalous low frequency sound absorption. The study was to consist of an extensive literature survey, an experimental investigation, and the development of a set of equations to predict the absorption of audible sound in still air.

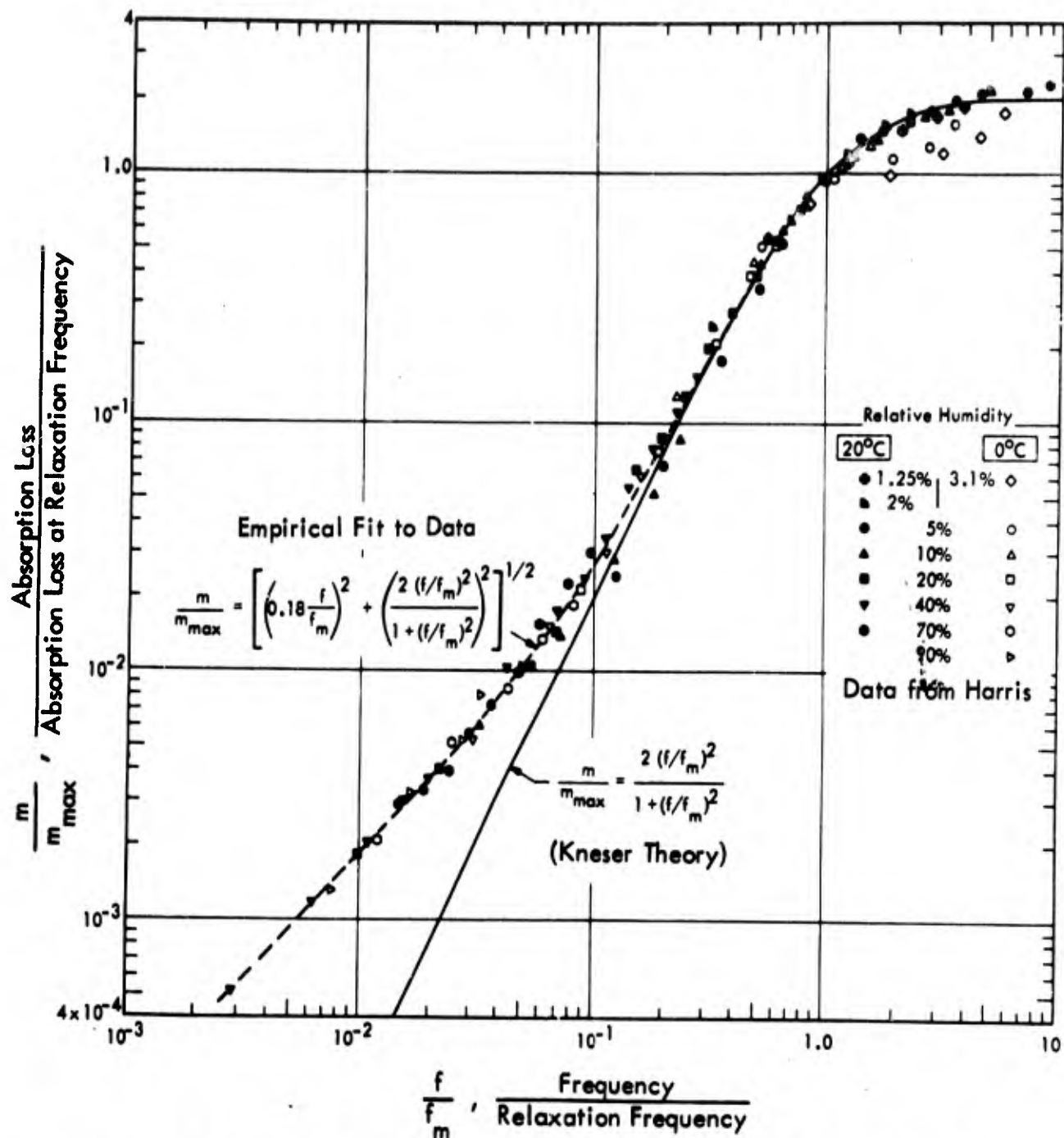


Figure 4. Comparison of Laboratory Measurements of Molecular Absorption Loss With Kneser Theory

3.0 EXPERIMENTAL RESULTS IN AIR

Of the different types of absorption mechanisms applicable to air the only two which were thought to possibly have bearing on the low frequency anomalous absorption were heat radiation or an, as yet, undefined molecular absorption. Effects of heat radiation on sound absorption in gases has not been extensively studied experimentally. However, it seems plausible that if heat radiation is the cause of the anomalous absorption then it must be due to an infrared active band in one of the polar molecules in air, i.e., carbon dioxide, water vapor, or ozone. Neglecting ozone, the principle regions responsible are expected to be the rotation and 6- μ bands of water vapor, and the 15- μ band of carbon dioxide (Reference 19). These regions do not overlap to any great degree, so their contributions to the acoustic absorption will be additive. According to Kyle (Reference 39) of these two molecules, the most important is water vapor since it is usually present in larger quantities than CO_2 . This indicates that if the anomalous absorption in air is due to thermal radiation then the effect should also appear in oxygen-water vapor sound absorption data. Figure 5 shows the $\text{O}_2\text{-H}_2\text{O}$ data of Harris and Tempest (Reference 26) and it is apparent that at low normalized frequency ratios the data is well behaved and is well described by single relaxation theory. This then eliminates thermal radiation as a cause of the anomalous low frequency absorption.

Having eliminated all the parts of classical absorption this leaves only relaxation effects due to molecular absorption. As has been pointed out, oxygen is responsible for most of the molecular absorption in air. However, since the low frequency anomalous absorption is well below the absorption peak it is felt that perhaps nitrogen may also contribute significantly at the lower frequencies. To closer investigate the low frequency absorption an experiment on sound absorption in humid air was performed.

3.1 Experimental Theory

To determine the vibrational relaxation in air at audio frequencies, several different approaches may be taken. The method which appeared to have the greatest chance of success for these experiments was the reverberation technique. In this technique the physics of sound absorption in a room is utilized to determine the absorption due to the internal molecular structure of the air inside the room. The measured physical quantity is the reverberation time which is a measure of the time needed for a sound of a given frequency to decay to 60 dB below its original value.

The length of the reverberation time is a function of the absorptive qualities of the surface areas of the boundaries of the room, the volume of air in the room, and the internal molecular structure of the air. The rate of decay of diffuse sound energy is then given by (Reference 40)

$$\left(\frac{dE}{dt}\right)_{\text{volume}} + \left(\frac{dE}{dt}\right)_{\text{air}} + \left(\frac{dE}{dt}\right)_{\text{surface}} = 0$$

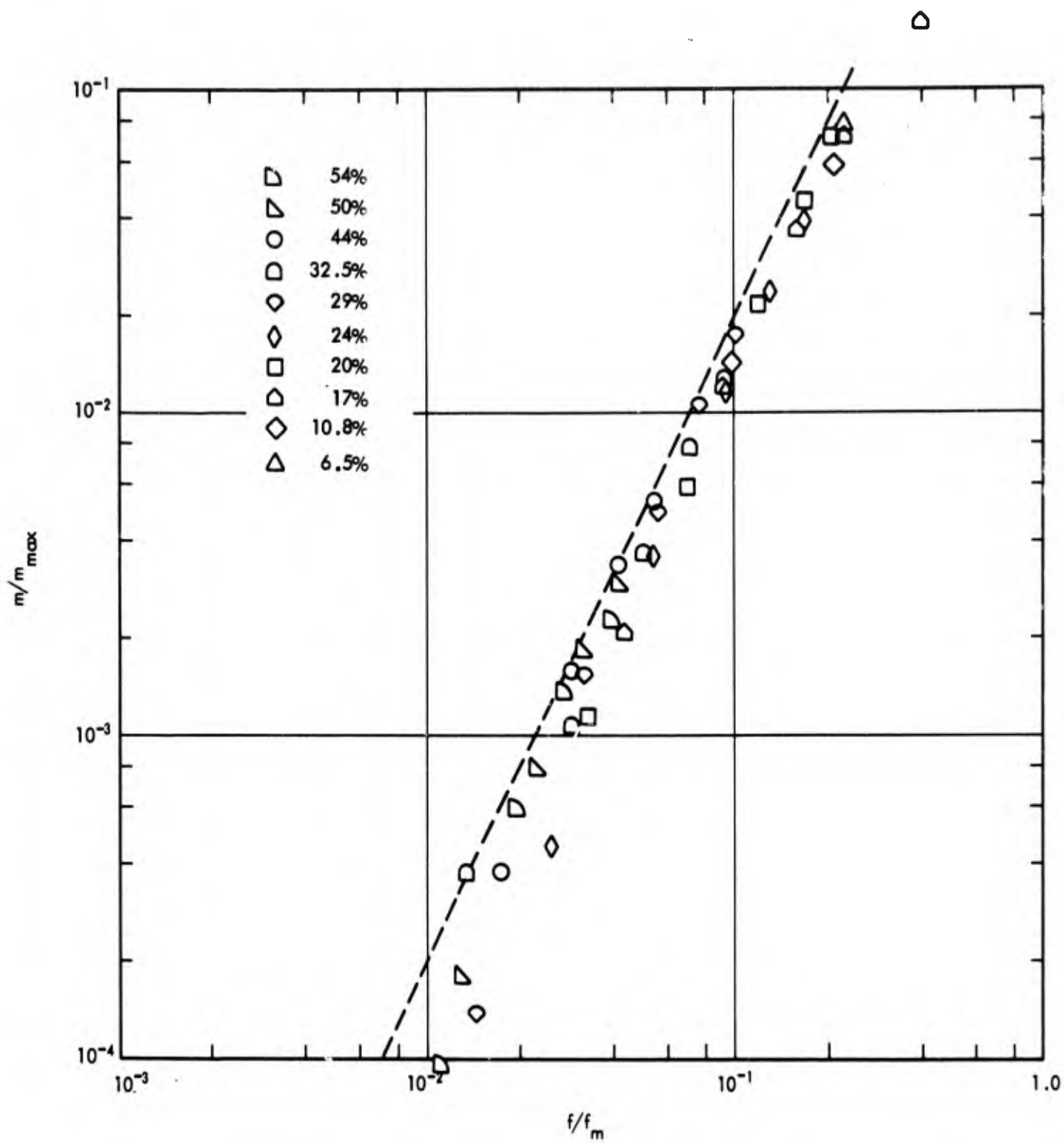


Figure 5. Comparison of Laboratory Measurements of Molecular Absorption Loss with Single Relaxation Theory for Humid O_2 . From Harris and Tempest (Reference 26)

or this can be written as

$$\frac{V d\mathcal{E}}{dt} + mcV\mathcal{E} + \frac{\mathcal{E}ca}{4} = 0$$

The solution to this equation in terms of the intensity is

$$I = I_0 e^{-(m + a/4V) ct}$$

Now since the physically measured quantity is the reverberation time or rate of decay this equation can be written as

$$\log_{10} (I_0/I) = 0.434 (m + a/4V) ct$$

and since

$$dB \equiv 10 \log (I_0/I)$$

$$\# dB = 4.34 (m + a/4V) ct$$

The rate of decay in the room is then

$$\# dB/sec = N = 4.34 (m + a/4V) c$$

where N (the rate of decay) is the experimentally measured quantity.

In the above equation the unknown quantities are the total intensity absorption, m , and the term due to the wall absorption, $a/4V$. In order to calculate $a/4V$, precise values of both the volume of the room and the surface absorption coefficients are needed. To experimentally find precise values for each of these quantities is a difficult task; however, the ratio itself may be found very precisely.

If one considers a monatomic gas, there is no internal structure to absorb the sound energy and the decay rate which is measured will then be due to only the wall losses and the classical absorption of the molecules. Now define the total absorption in the room to be

$$R \equiv N/4.34c = m + a/4V$$

where m can be subdivided into

$$m = m_{cl} + m_{mol}$$

The quantity m_{cl} is the absorption due to the classical effects of the molecules, and m_{mol} is the absorption due to the internal structure of the molecules. So, if the decay

rate is measured in the room when it is filled with a monatomic gas, or a molecular gas which does not exhibit absorption due to its internal structure, then the intensity absorption due to internal structure of the gas of interest will be the difference between the two experimentally determined intensity absorptions, i.e.,

$$R_{\text{mol}} \equiv R - R_{\text{cal}}$$

where R_{mol} is the intensity absorption due to the molecular structure of the gas of interest, R is the total absorption in that gas, and R_{cal} is the intensity absorption in the calibration gas.

In the case of air, pure dry nitrogen has the best characteristics for the calibration gas. There is very little mass difference between nitrogen and air so the impedance match between the gas and room walls should be the same for both N_2 and air. Also, pure dry nitrogen does not exhibit any relaxation effects due to its internal structure in the audio frequency range. Since air is composed of approximately 80 percent nitrogen the absorption due to classical and rotational effects can be taken as equal to that of air. There is some slight difference between the two but the difference should always be very much less than the experimental error and can therefore be neglected. So, for air

$$R_{\text{mol}} = R_{\text{air}} - R_{N_2}$$

or

$$R_{\text{mol}} = (m_{\text{cl}} + m_{\text{mol}} + a/4V)_{\text{air}} - (m_{\text{cl}} + a/4V)_{N_2}$$

$$R_{\text{mol}} = m_{\text{mol}} = N/4.34c = N/4.34f\lambda$$

The total intensity absorption per wavelength, μ is then given by

$$m_{\text{mol}}\lambda \equiv \mu = \frac{N_{\text{air}} - N_{N_2}}{4.34f}$$

where f is the frequency at which the decay rates are measured.

3.2 Experimental Design

In order to make accurate experimental decay time measurements, a room is needed in which the external parameters can be precisely controlled. For this set of experiments a large space simulation chamber was utilized (Figures 6 and 7). The volume of the chamber was approximately five hundred cubic feet and it was constructed of aluminum which has a small surface absorption coefficient. The chamber had vacuum capabilities which were desirable for removing the ambient air so that pure dry air could be used.

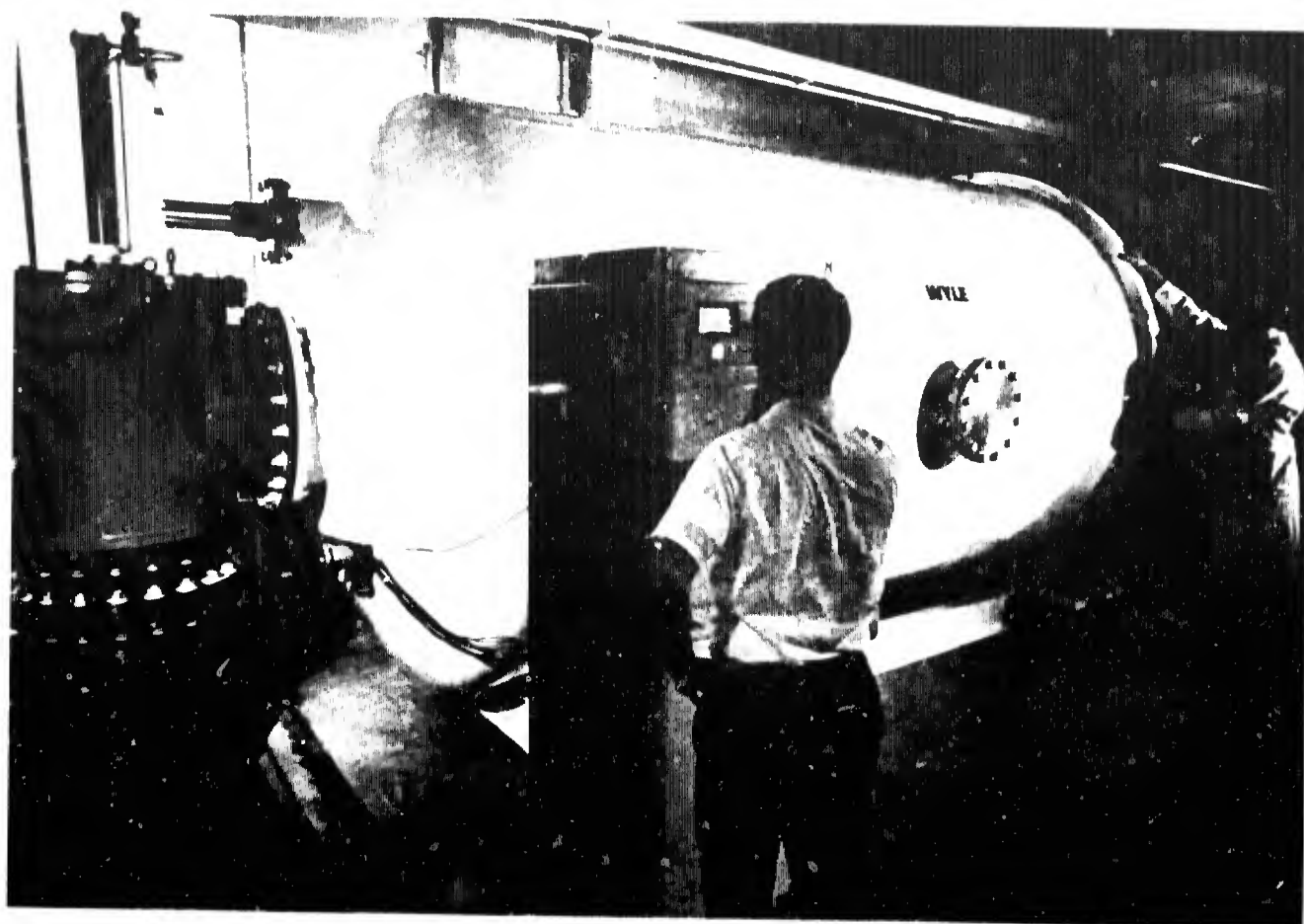


Figure 6. Reverberation Chamber

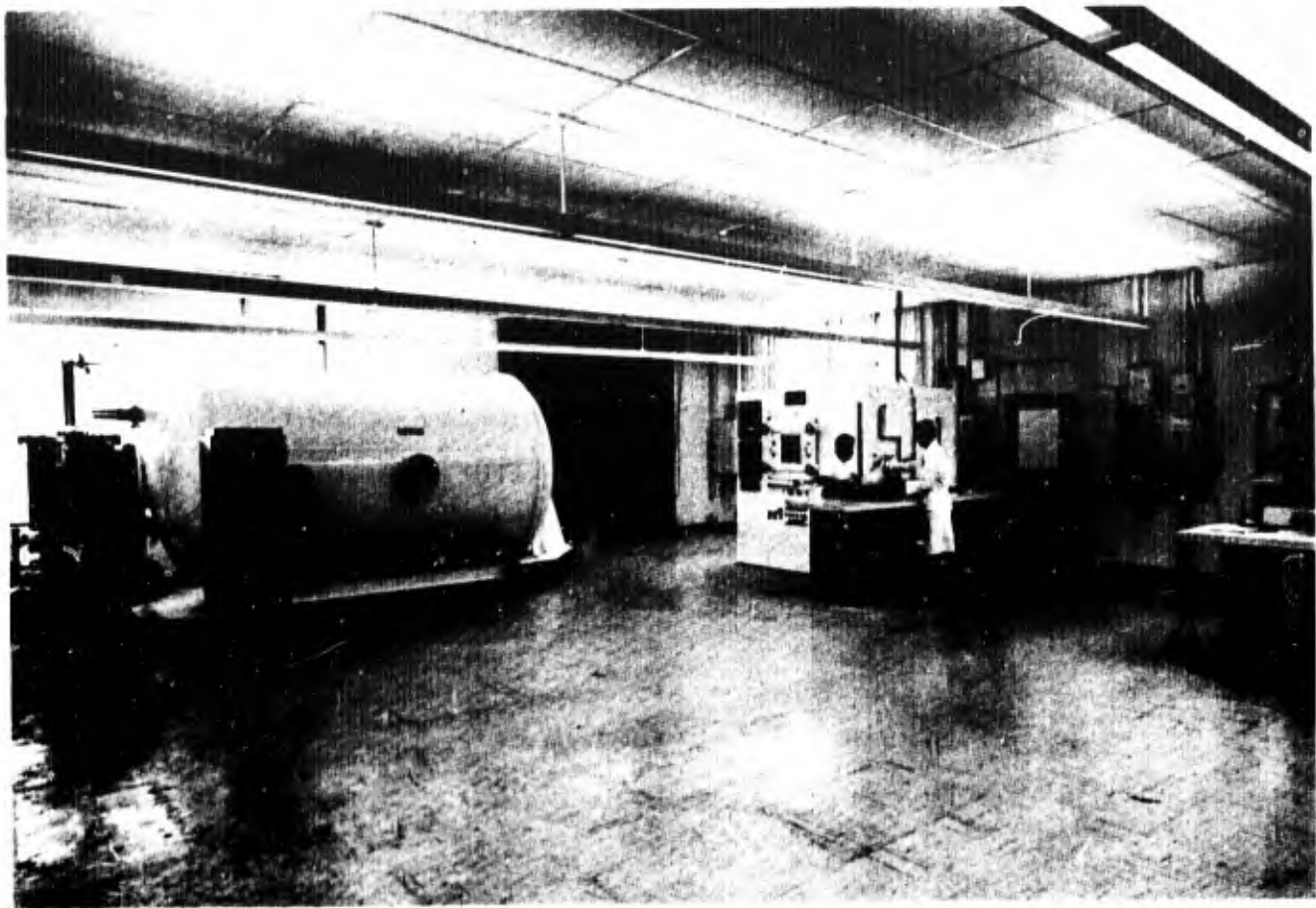


Figure 7. Reverberation Chamber

A system to control the humidity in the chamber was devised and three humidity sensors and three thermocouples were mounted in the chamber. The humidity sensors were Phys-Chemical Research Corporation, Inc. Type PC-55 and were calibrated to within three percent at the factory. This calibration was checked against a lab standard sling psychrometer which could be traced to the Bureau of Standards. Between 10 percent humidity and 95 percent relative humidity these units could always be read even closer than the 3 percent factory calibration. Outside of these values the accuracy fell off rapidly and estimations had to be made.

A wide range high fidelity acoustic driver and a crystal microphone were mounted in the chamber. The placement and orientation of these were determined experimentally and were fixed at the points where the received nodal density was the greatest. Wide range pink noise was played into the chamber and the decay rates were measured on a high speed level recorder after being passed through a one-third octave filter set. Figure 8 shows a block diagram of the instrumentation. The decay rates in dB/sec were read directly from the level recordings. Three recordings were made of each decay rate and an average was taken.

3.3 Experimental Results

Figures 9-18 show the normalized intensity absorption per wavelength versus frequency for air over the humidity range of approximately 1.8 percent relative humidity to 100 percent relative humidity. The solid curves in the figures are the prediction of single relaxation theory. The frequencies which correspond to the peak of these curves is the relaxation frequency and these values agree very well with previous experimental results and also with Monk's prediction scheme as shown in Figure 3. The low frequency measurements at the higher frequencies were of primary importance in this study. Inspection of the data points readily reveals that the low frequency values approach a constant value of approximately 0.1. This consistency indicates that the absorption coefficients are independent of humidity at low frequencies in relation to the absorption peak.

Figure 19 shows a plot of the normalized intensity absorption versus the normalized frequency. It is evident that at frequency ratios greater than approximately 0.1, single relaxation theory adequately describes the data. However, below that ratio there is a definite deviation from the single relaxation curve. It is interesting to note that the deviation in this data is somewhat less than that in Harris' data (Figure 4). An empirical curve which seems to fit this data best is

$$\frac{m}{m_{\max}} = \left\{ (0.1 f/f_m)^2 + \left[\frac{2 (f/f_m)^2}{1 + (f/f_m)^2} \right]^2 \right\}^{1/2}$$

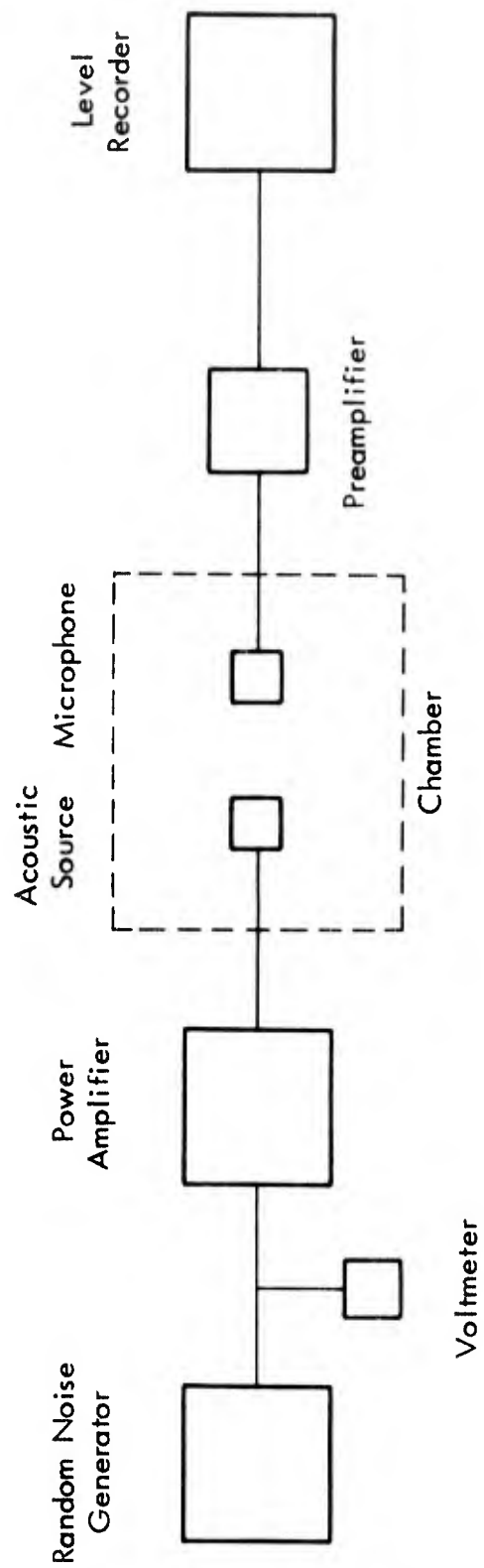


Figure 8. Instrumentation

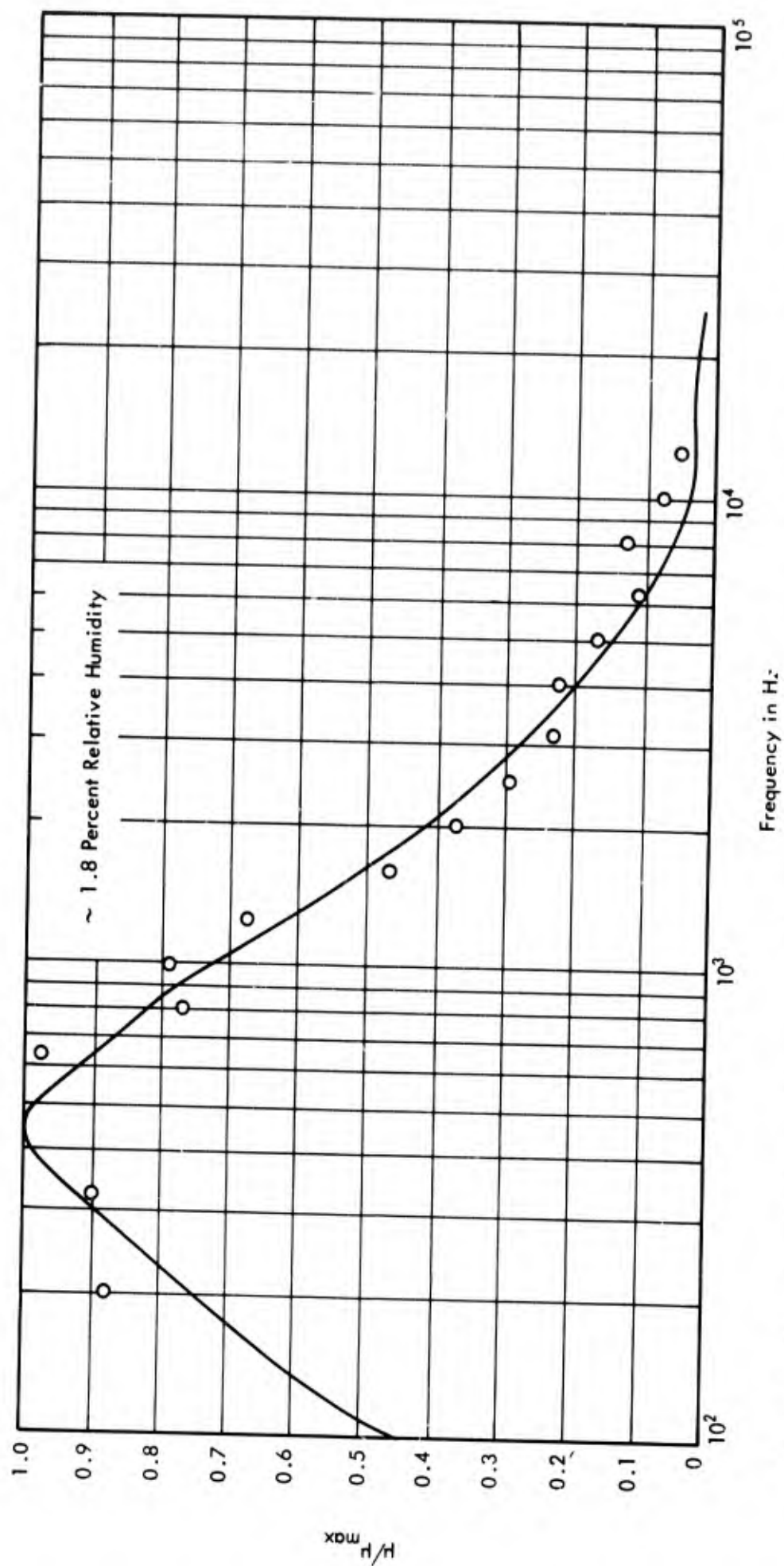


Figure 9. Comparison of Laboratory Measurements of Molecular Absorption Loss with Single Relaxation Theory for Air Containing Approximately 1.8 Percent Relative Humidity

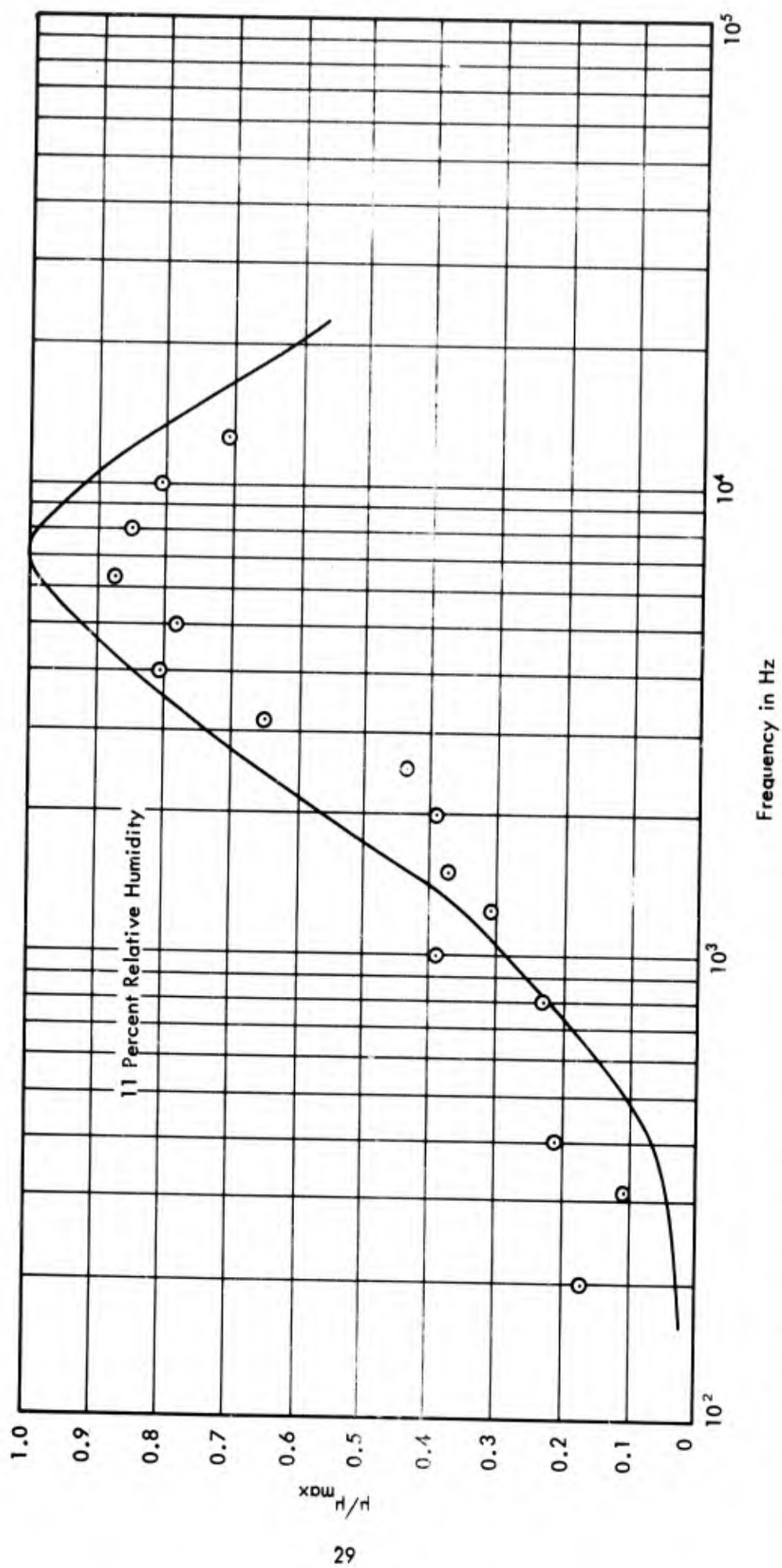


Figure 10. Comparison of Laboratory Measurements of Molecular Absorption Loss with Single Relaxation Theory for Air Containing Approximately 11 Percent Relative Humidity

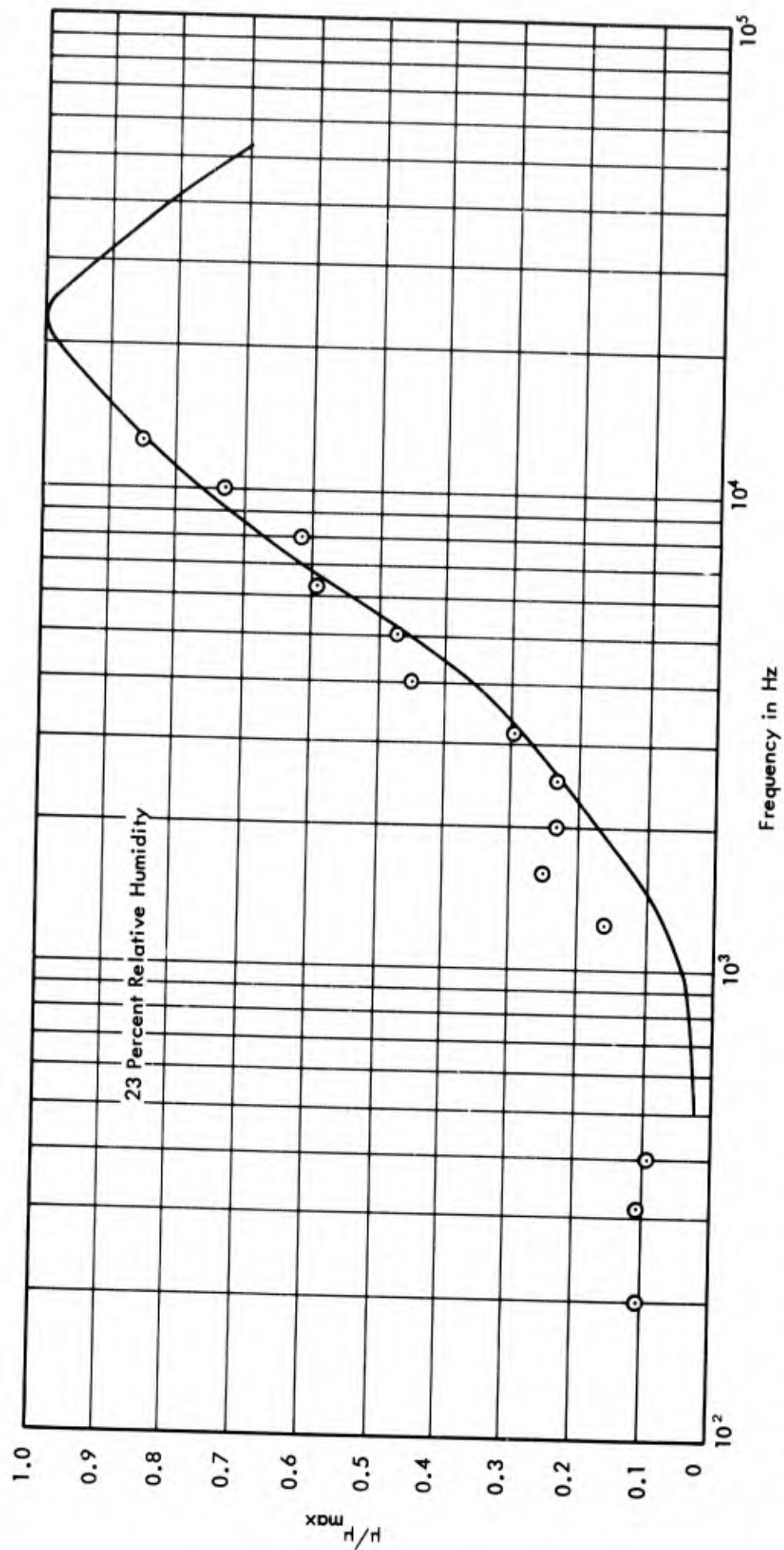


Figure 11. Comparison of Laboratory Measurements of Molecular Absorption Loss with Single Relaxation Theory for Air Containing Approximately 23 Percent Relative Humidity

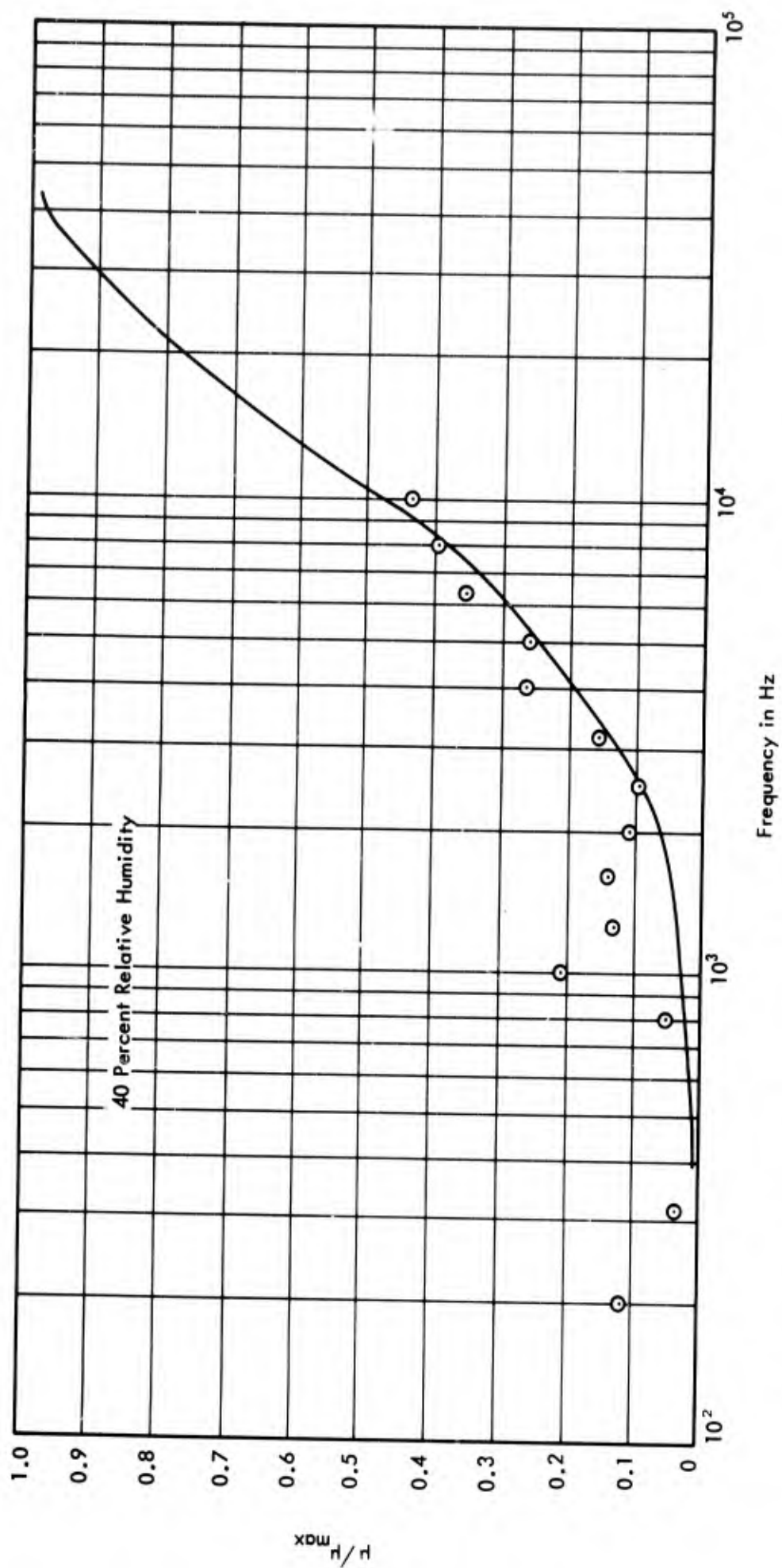


Figure 12. Comparison of Laboratory Measurements of Molecular Absorption Loss with Single Relaxation Theory for Air Containing Approximately 40 Percent Relative Humidity

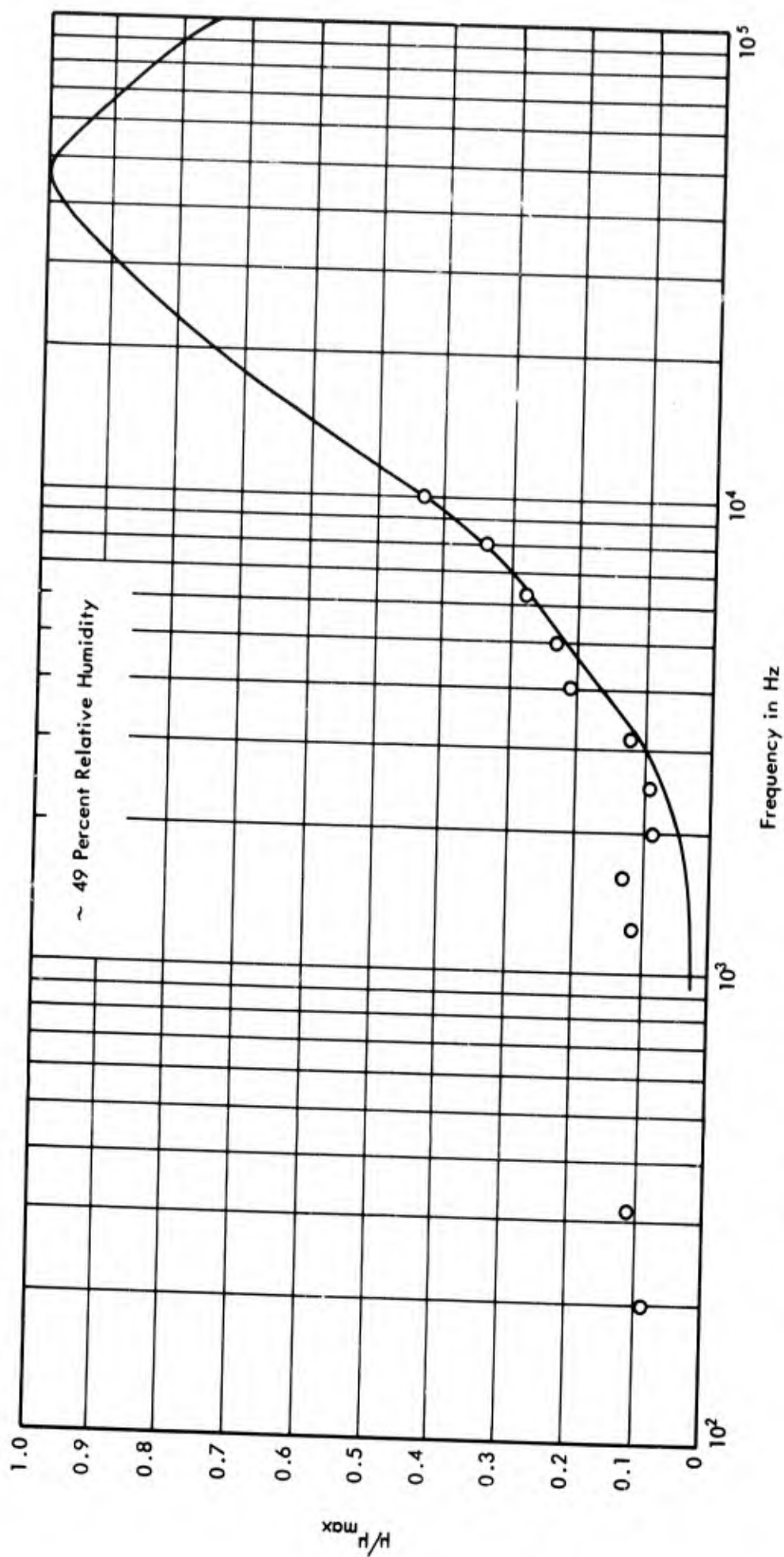


Figure 13. Comparison of Laboratory Measurements of Molecular Absorption Loss with Single Relaxation Theory for Air Containing 49 Percent Relative Humidity

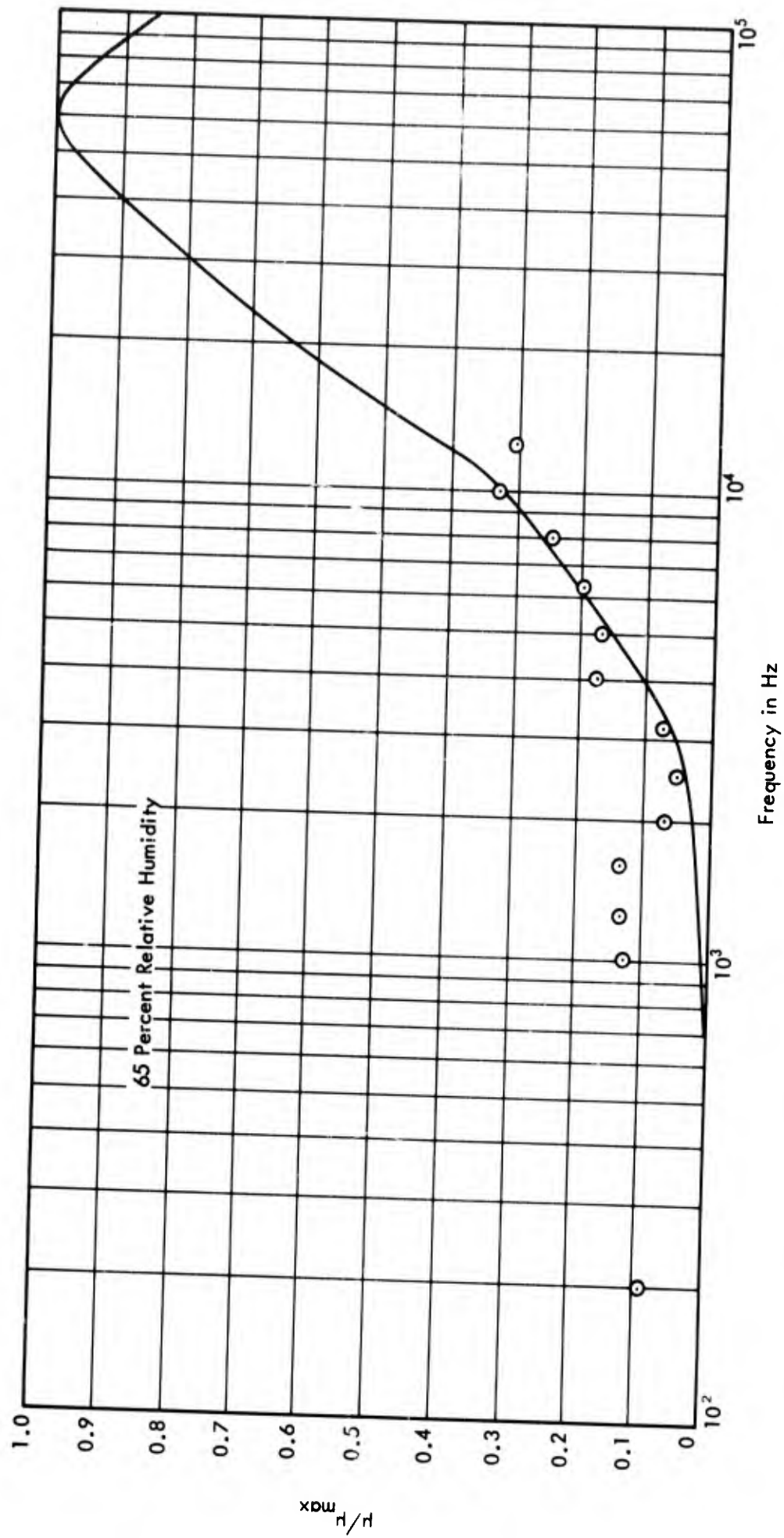


Figure 14. Comparison of Laboratory Measurements of Molecular Absorption Loss with Single Relaxation Theory for Air Containing Approximately 65 Percent Relative Humidity

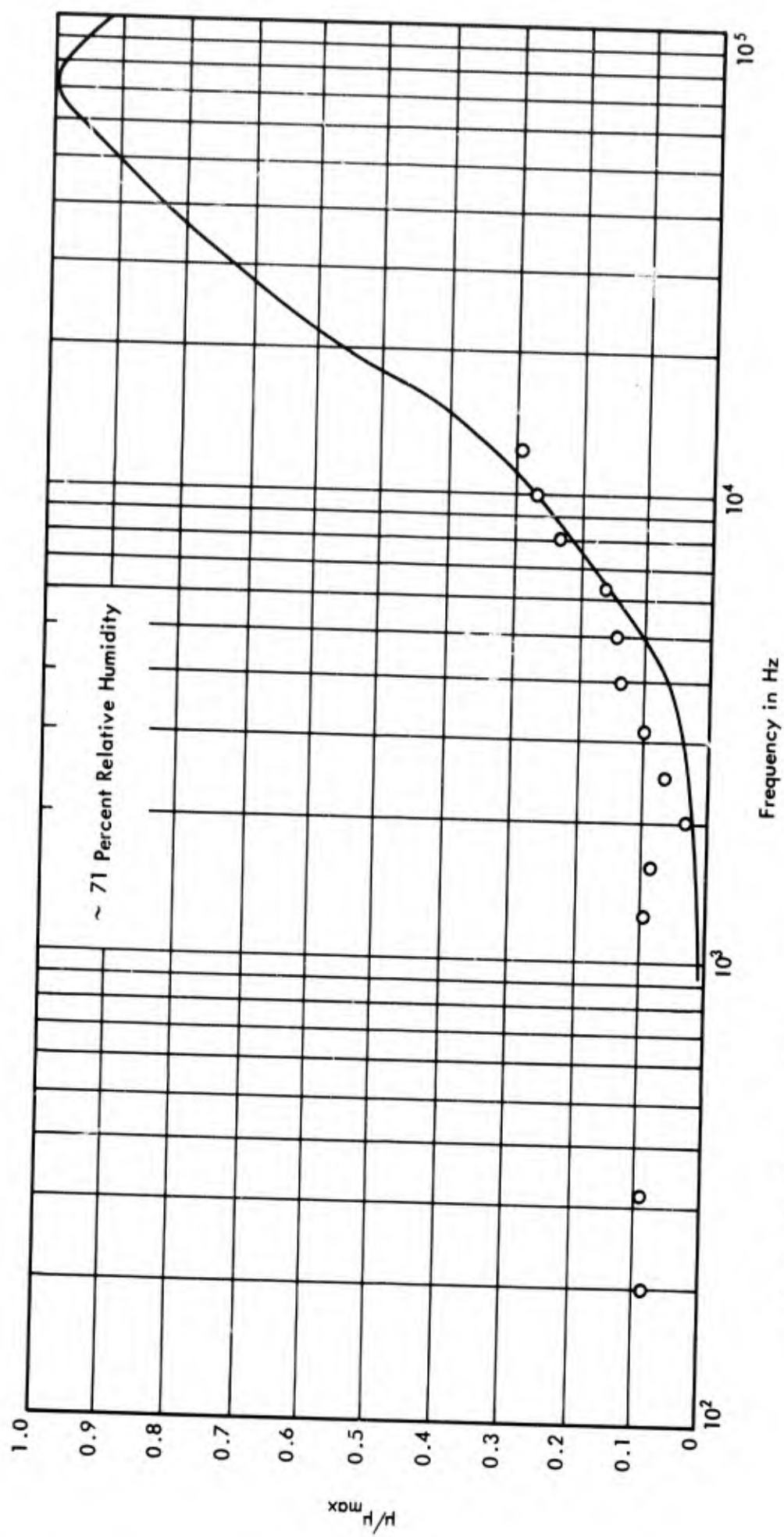


Figure 15. Comparison of Laboratory Measurements of Molecular Absorption Loss with Single Relaxation Theory for Air Containing 71 Percent Relative Humidity

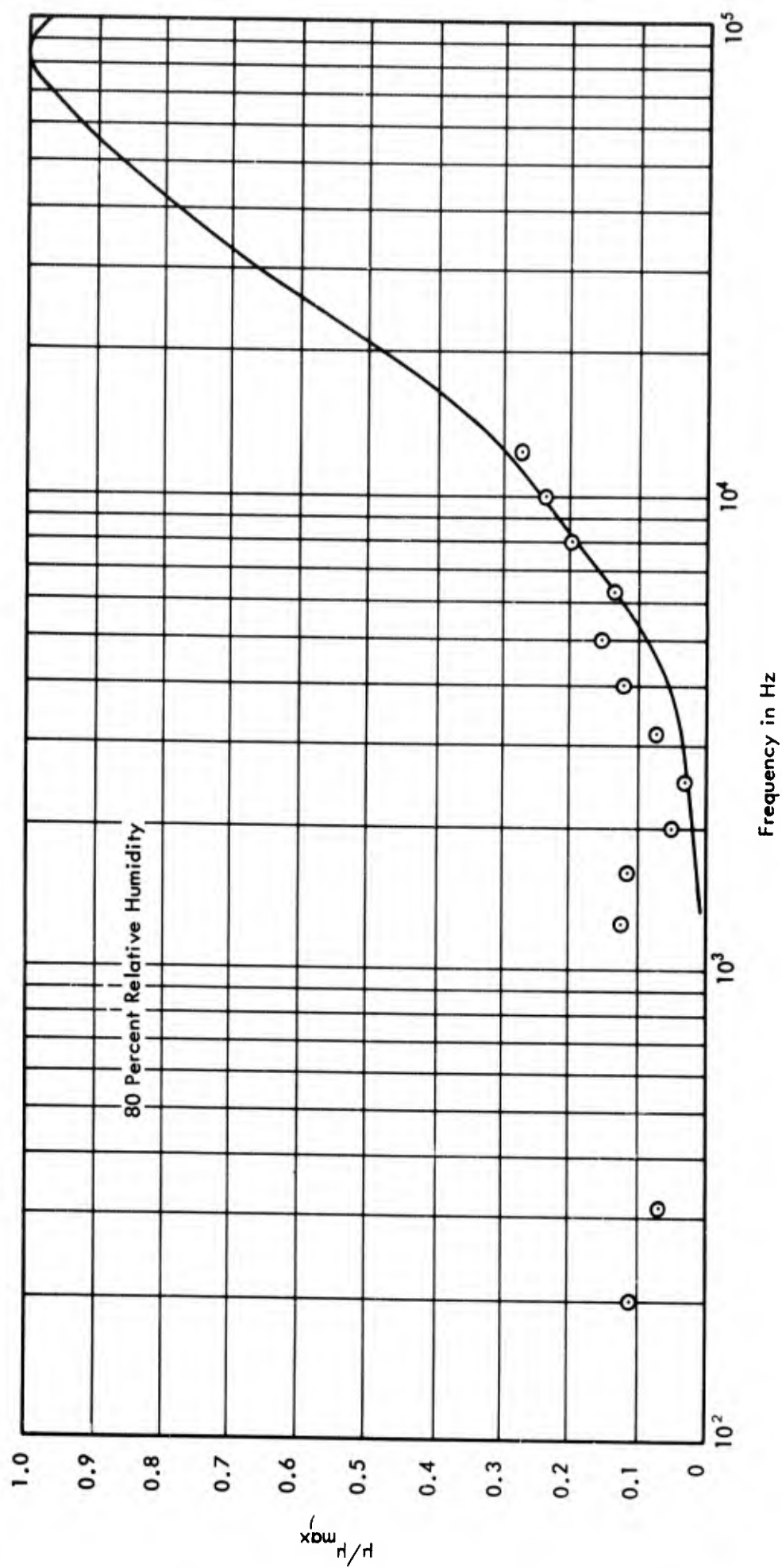


Figure 16. Comparison of Laboratory Measurements of Molecular Absorption Loss with Single Relaxation Theory for Air Containing Approximately 80 Percent Relative Humidity

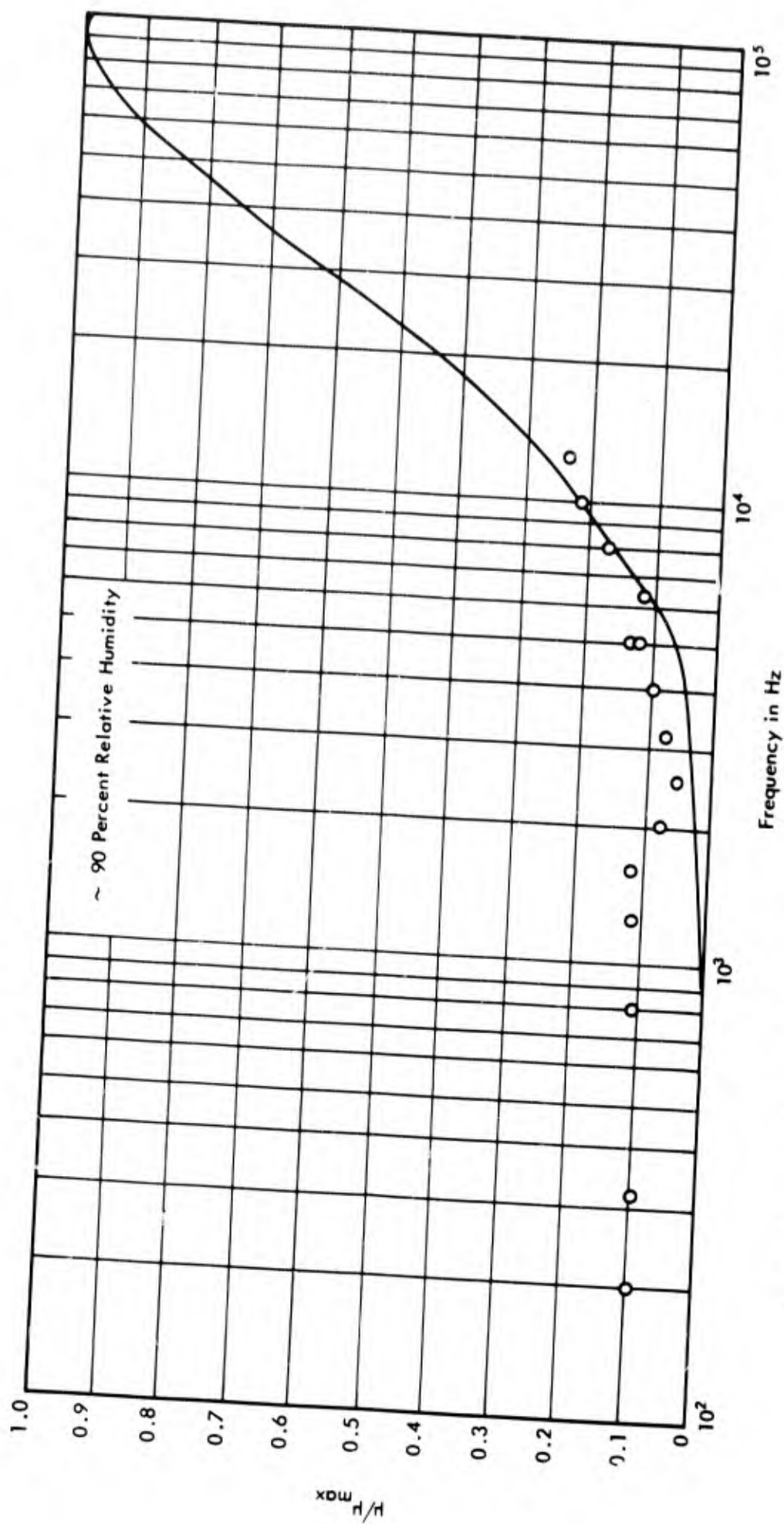


Figure 17. Comparison of Laboratory Measurements of Molecular Absorption Loss with Single Relaxation Theory for Air Containing 90 Percent Relative Humidity

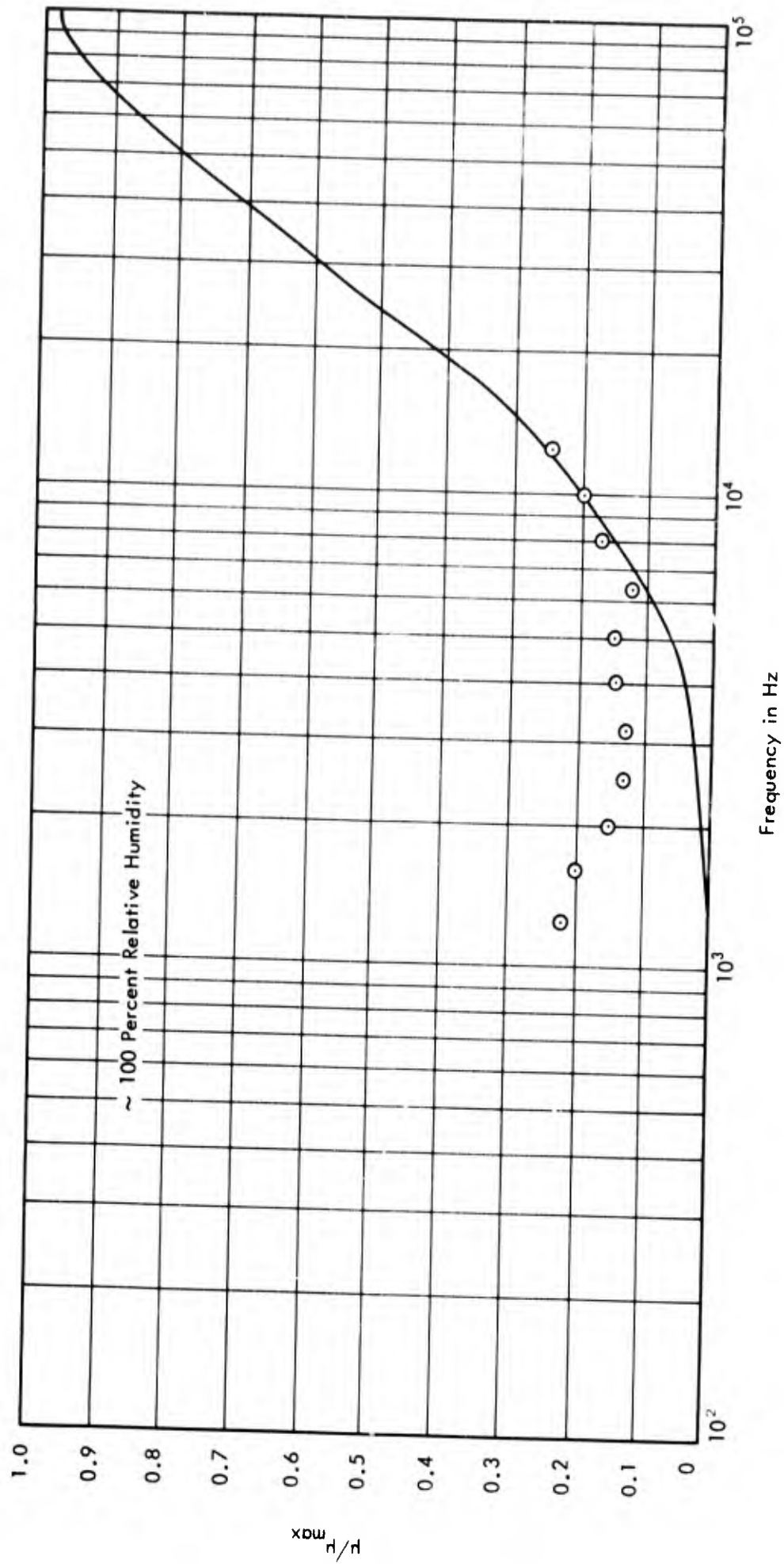


Figure 18. Comparison of Laboratory Measurements of Molecular Absorption Loss with Single Relaxation Theory for Air Containing Approximately 100 Percent Relative Humidity

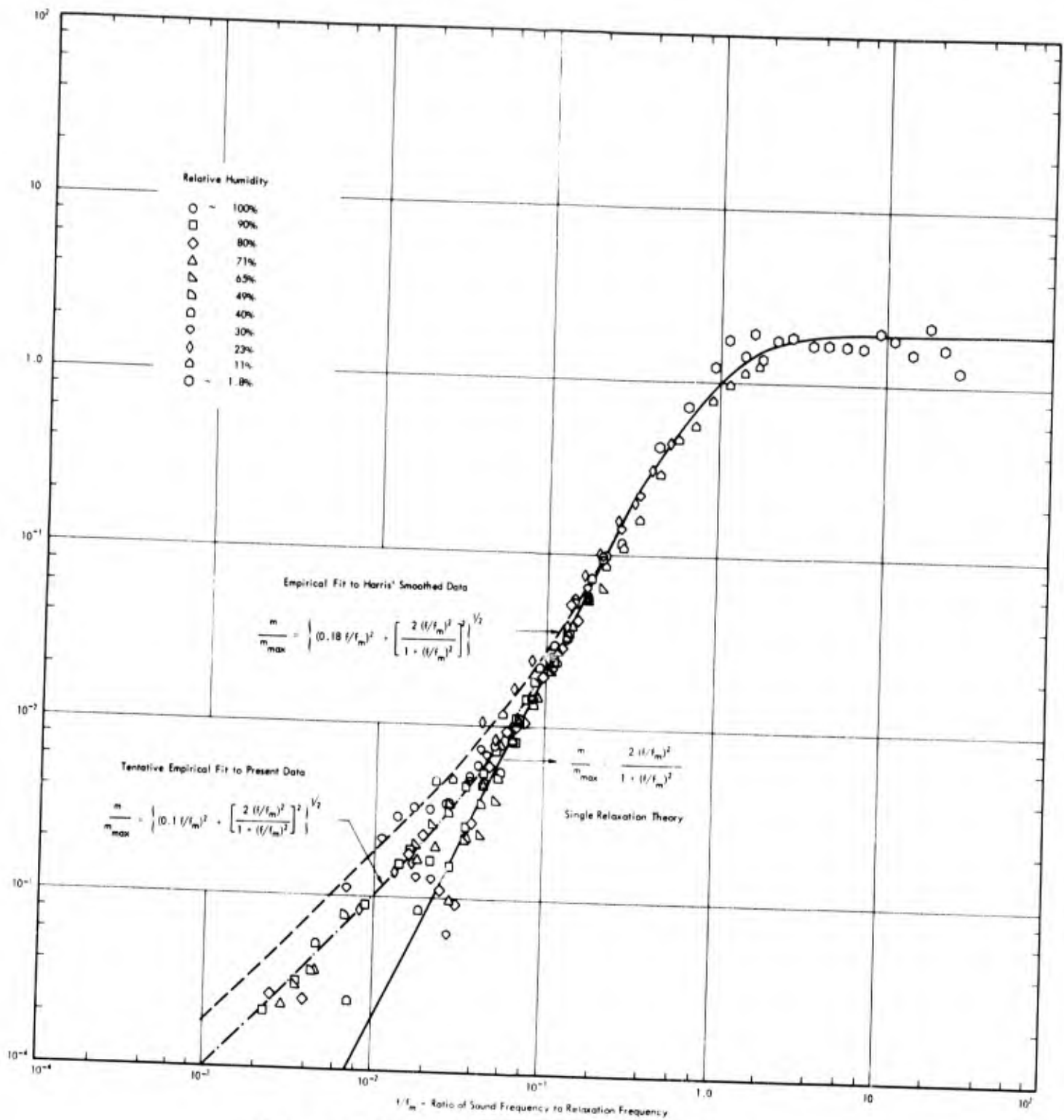


Figure 19. Comparison of Laboratory Measurements of Molecular Absorption Loss with Single Relaxation Theory

This differs from the fit Sutherland (Reference 23) made to Harris' smoothed data, only in the numerical coefficient of the first term. Again, one must remember that there is no theoretical basis for this type of empirical fit. This is just a modification of the single relaxation equation which seems to predict the general trend of the observed sound absorption data.

Since classical effects have been eliminated as a cause of this anomalous adsorption and since single relaxation theory does not describe all of the data, the next step is to assume that there is another relaxation process occurring. Inspection of Harris' data and the present data both reveal that this may well be the case.

Classical, rotational, and vibrational absorption for oxygen have all been subtracted from Harris' air data and the remainder fitted to single relaxation theory assuming that the peak is caused by the nitrogen content. The results of this effort are shown in Figure 20 as a plot of the relaxation frequency of nitrogen versus the percent mole ratio of water vapor. Even though the values are quite scattered the results do show a significant shift in the relaxation frequency with increasing humidity. The best straight line fit to the data is given by

$$\left(\frac{f_m}{P} \right)_{N_2} \approx 450h$$

where h is the percent mole ratio of water vapor. At this time this technique has not been applied to the air data from the present study; however, absorption measurements were made in humid nitrogen at room temperature which can be compared to the results from Harris' air data.

Figures 21 and 22 show this humid nitrogen data and the "best fit" to single relaxation theory. Two fits have been made in Figure 21 - one putting the curve through the greatest number of points and the other fitted to the peak of the curve. There is considerable difference between the relaxation frequencies predicted by the two different fits. In Figure 22, only one fit to theory is made.

While there is considerable scatter in this humid nitrogen data, the data does show a definite relaxation trend and that the peak is shifted by water vapor. As far as these authors know this is the only humid nitrogen data at room temperature. When compared to the nitrogen values reduced from Harris air data the relaxation frequencies are somewhat below those predicted by the $f_m/P = 450h$ curve.

3.3.1 Calculation of $\mu_{\max}$

All of the absorption data from this experiment was normalized by dividing the measured values, μ , by the maximum values, $\mu_{\max}$. The difficulty of this technique lies in determining the correct values of the relaxing specific heats. The magnitude of the absorption coefficient is given by

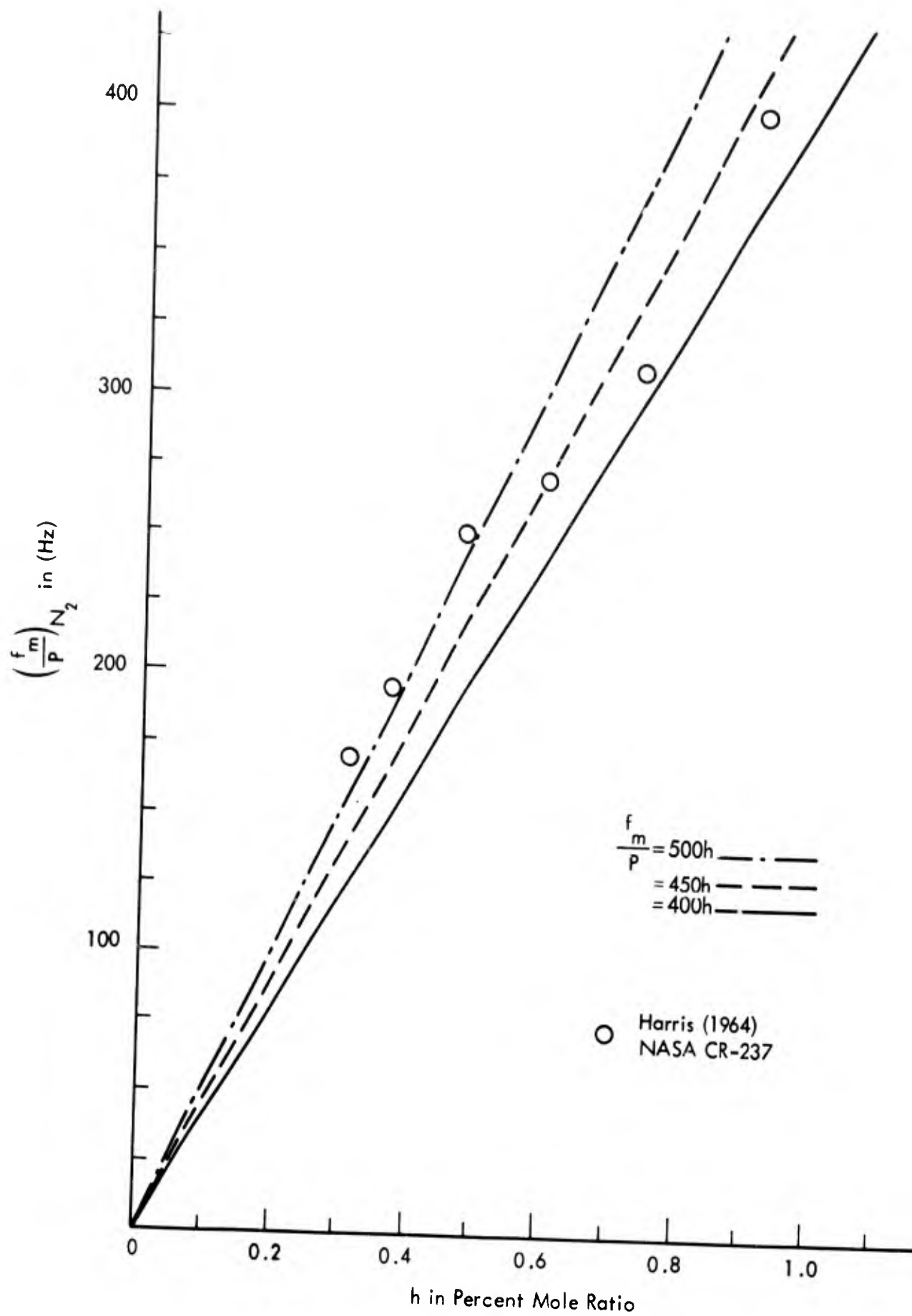


Figure 20. Relaxation Frequency of N_2 Versus Percent Mole Ratio of Water Vapor as Reduced from Humid Air Data

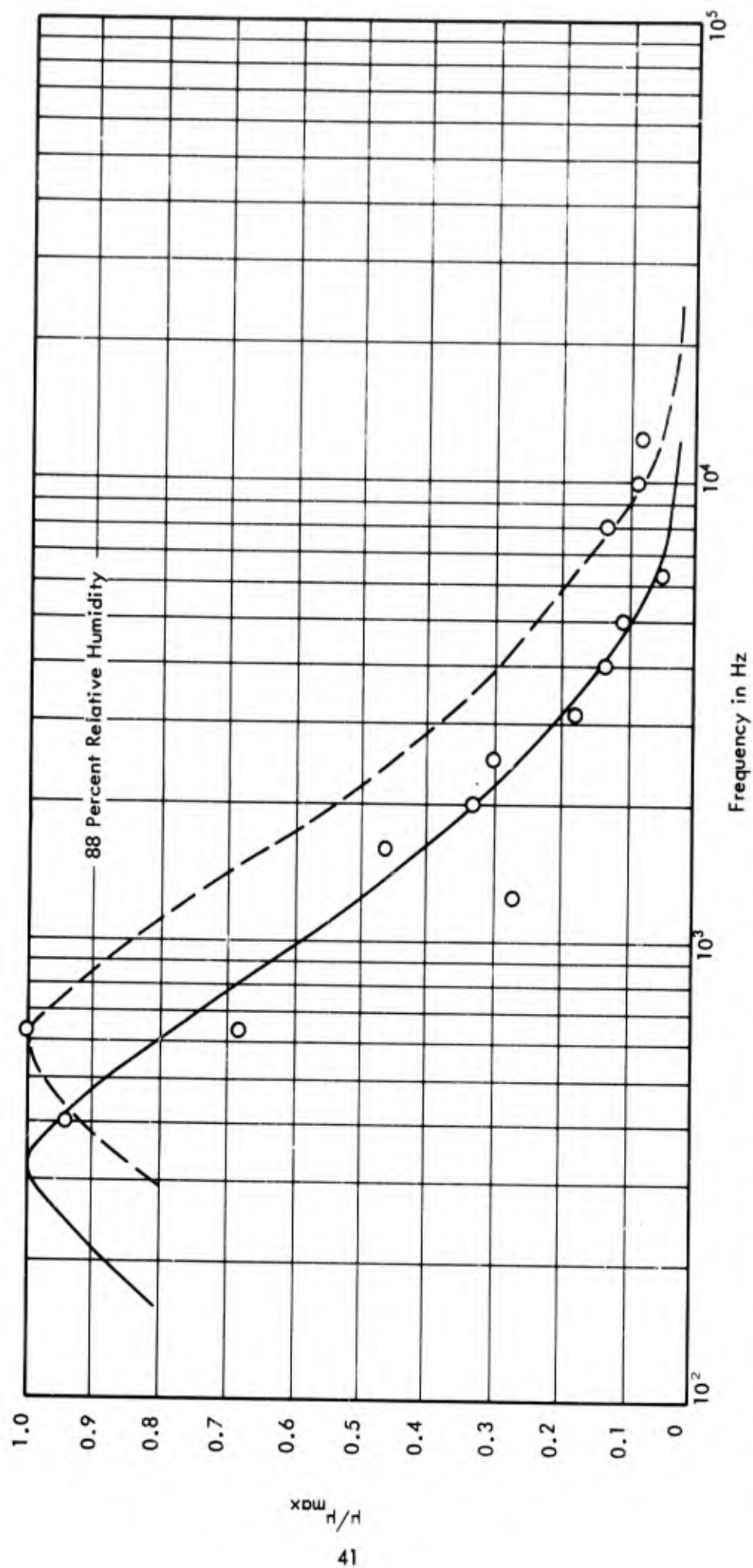


Figure 21. Comparison of Laboratory Measurements of Molecular Absorption Loss with Single Relaxation Theory for Nitrogen Containing 88 Percent Relative Humidity

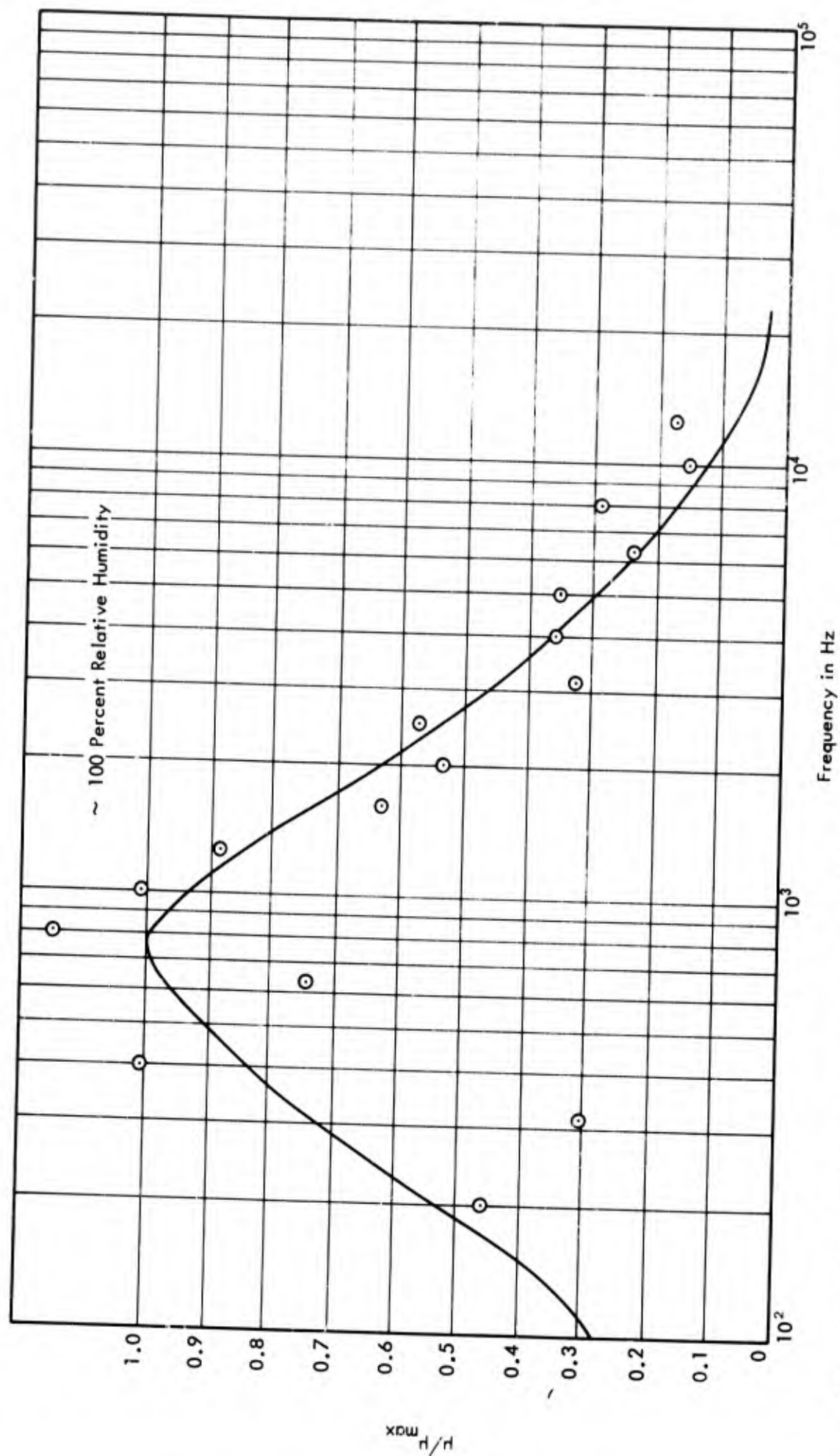


Figure 22. Comparison of Laboratory Measurements of Molecular Absorption Loss with Single Relaxation Theory for Nitrogen Containing Approximately 100 Percent Relative Humidity

$$\mu_{\max} = \frac{4\pi}{35} \frac{C'}{R}$$

where C' is the internal or relaxing specific heat of the molecule in question. In the case of air it is well known that this internal vibrational specific heat is that of oxygen.

It is common practice to use the Planck-Einstein relationship

$$\frac{C'}{R} = \left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{(e^{\theta/T} - 1)^2}$$

to predict the vibrational specific heat of diatomic molecules such as O_2 . However, there are errors inherent in this technique.

The Planck-Einstein relationship was derived for a simple harmonic oscillator and does not consider the unharmonicity which a real molecule may possess in its vibrational modes. Another error which is inherent in the use of the Planck-Einstein relationship is that θ , the characteristic temperature of vibration, differs slightly for the different isotopes of a given molecule.

If accurate experimental data is available for a given molecule, then the internal specific heat may be determined from these values. From kinetic theory the principle of equipartition of energy reveals that any degree of freedom of a molecule which has a squared term in its energy contribution - i.e., kinetic energy = $1/2 m v^2$ or $1/2 I \omega^2$ or potential energy = $1/2 K x^2$ - will contribute $1/2 R$ to the specific heat when fully excited. For a diatomic molecule such as oxygen the degrees of freedom which fit this criterion are

- Three translation degrees
- Two rotational degrees
- Vibrational degree due to kinetic energy
- Vibrational degree due to potential energy

This then means that

$$C_{V, \text{trans}} = 3/2 R$$

$$C_{V, \text{rot}} = R$$

$$C_{V, \text{vib}} = R ;$$

however, it must now be determined which of these degrees are fully excited at the temperature of interest.

It is well known that the translational degrees of freedom are completely occupied at very low temperatures and that the rotational degrees usually are fully occupied at normal ambient temperatures. This then indicates that

$$C_{V,trans} + C_{V,rot} = 5/2R$$

If accurate experimental specific heat data is available, then the vibrational specific heat will be

$$C_{V,vib} = C_{V,exp} - 5/2R \equiv C'$$

or as is usually the case

$$C_{P,vib} = C_{P,exp} - 7/2R \equiv C'$$

Figure 23 shows a plot of available maximum absorption data for air as a function of temperature. It is obvious that the experimental values of C' give the best fit; however, in the case of oxygen the Planck-Einstein relationship multiplied by 1.05 also fits the data over a fair temperature range. When using this method, one should be sure to correct the experimental values for non-ideal gas effects.

Figure 24 shows a similar plot for nitrogen data. In this case it appears that the Planck-Einstein relationship gives better results than the available experimental specific heat data. In fitting the data in this set of experiments the oxygen specific values were taken from Reference 41 while the nitrogen data were fitted using the Planck-Einstein relationship.

OXYGEN

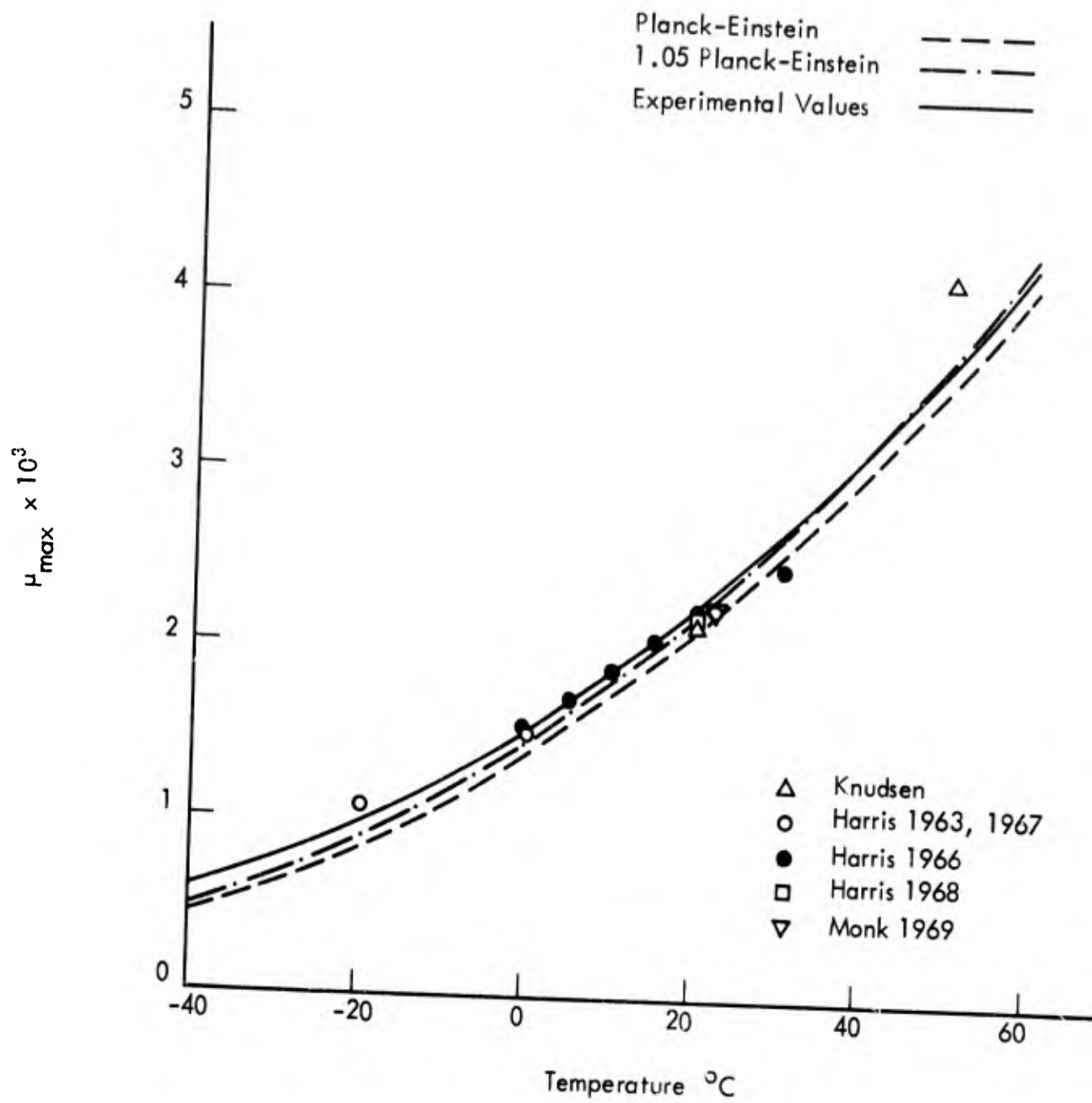


Figure 23. Maximum Absorption in Air as a Function of Temperature

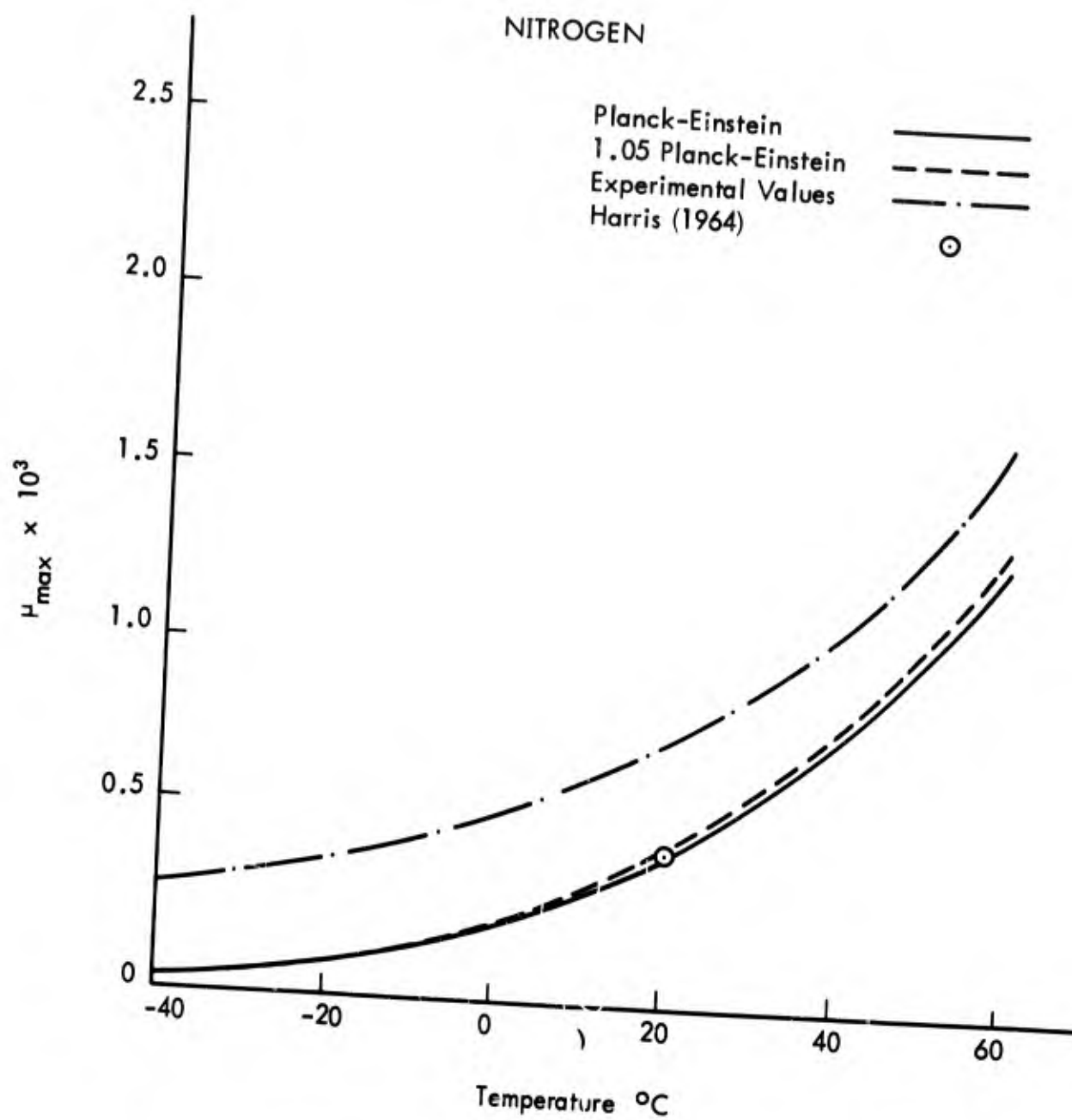


Figure 24. Maximum Absorption in Nitrogen as a Function of Temperature

4.0 TENTATIVE PREDICTION METHOD FOR ATMOSPHERIC ABSORPTION IN STILL AIR

Quite often in practical engineering problems it is important to be able to correct outdoor sound level measurements for the effects of atmospheric absorption. As has been previously pointed out effects such as thermal inhomogeneities, turbulence, dust, fog, ground reflections, scattering, diffraction, and inverse square law spreading are all mechanisms which can change the character of sound propagation from laboratory predictions. However, laboratory predictions of the classical and molecular absorptions can be applied with success to a still atmosphere. The ability to make such a correction depends upon the available meteorological data. If for noise measurement from aircraft flyovers the temperature and humidity are known as a function of altitude then the atmosphere can be broken into layers. If on the other hand only ground meteorological data is available some information is still obtainable but not with the same reliability as when the vertical profiles are known.

To make corrections for classical and molecular effects the temperature and water vapor content are both needed. Usually the water vapor content is either given in percent relative humidity or as the dew point. If the dew point temperature is given, the relative humidity can be obtained by referring to tables such as those in the Handbook of Chemistry and Physics (Reference 42). The water vapor content is actually needed in the percent mole ratio of water vapor in air. This can be calculated from the relative humidity by

$$h = \frac{H}{\left(\frac{p}{h_s} \frac{M_w}{M} - 1 \right)}$$

Over the temperature range of 32°F - 77°F (0°C - 25°C) this can be reduced to

$$h = \frac{H}{\left\{ (5.6) [30 - T/10] e^{-0.0665T} - 1 \right\}}$$

where T is in degrees centigrade.

Next calculate the frequency of maximum molecular absorption from the relationship given by Monk (Reference 35)

$$f_m = 1750h + 61400h \left[\frac{1.12 + 10h}{10.4 + 10h} \right],$$

and then calculate the value of maximum molecular absorption per wavelength by

$$\mu_{\max} = (0.079) \left(\frac{2239}{T} \right)^2 \frac{e^{2239/T}}{(e^{2239/T} - 1)^2}$$

where T = temperature in $^{\circ}\text{K}$.

Now calculate the maximum molecular absorption at any frequency f by

$$\alpha_{\text{mol}} = (1.32) \left[(0.18 f/f_m)^2 + \left(\frac{2 (f/f_m)^2}{1 + (f/f_m)^2} \right)^2 \right]^{1/2} \left(\frac{\mu_{\max} f_m}{(331.5 + 0.607T)} \right)$$

where T is in $^{\circ}\text{C}$ and the units of α_{mol} are in dB/ft.

The classical absorption plus the rotational absorption can be calculated at any frequency f by

$$\alpha_{\text{cl}} + \alpha_{\text{rot}} = 47.7 \times 10^{-12} (1 + 0.001 T) f^2$$

where the units are dB/ft and T is in $^{\circ}\text{C}$.

The total atmospheric absorption in dB/ft is then

$$\alpha_{\text{total}} = \alpha_{\text{mol}} + \alpha_{\text{cl}} + \alpha_{\text{rot}}.$$

There are several points in this prediction scheme at which errors are inherent. The largest error is probably due to not knowing the temperature dependence of the frequency of maximum absorption. This is an area in which further experimental work is needed. Also the α_{mol} expression given is that from Harris' data. This has been used since the CO_2 content was well documented. Another small error is introduced in using the Planck-Einstein relationship to predict $\mu_{\max}$. However, the outlined procedure should be fairly accurate over the temperature range $0^{\circ}\text{C} - 30^{\circ}\text{C}$.

5.0 FIELD DATA

The ultimate utilization of the prediction scheme given in the previous section is to correct field sound data for molecular and classical absorption. The prediction method given would work very well in a still atmosphere with no temperature or humidity gradients and it would also work well if these gradients were known.

In Figure 25 the verticle temperature and humidity profiles are shown for two different times of day. These were taken from actual data supplied by ESSA for Pendleton, Oregon (Reference 43). Also shown are the molecular absorption coefficients as a function of altitude for the two different times of day. As can be readily seen, ground measurement may have little or no correlation to values at higher altitudes. Figure 26 shows the molecular absorption coefficient as a function of height for two days approximately three months apart. These were also calculated from actual meteorological data for Pendleton, Oregon.

In Figures 27-32 the absorption coefficient in dB/1000 feet versus frequency are shown for several sets of field data for which only ground weather data was available. Figure 33 shows a plot of humidity versus temperature with different data sets grouped together. The number of these groups corresponds to the numbers on the absorption versus frequency curves. The meteorological data is averaged over these individual groups for analysis purposes. The α_{tot} line on the plots has been calculated from the method outlined in the previous section; while, the $\alpha_{mol} + \alpha_{cl}$ line assumes that oxygen alone has molecular absorption. Several of the plots show fair agreement with the prediction method and the agreement is really outstanding when one considers that only ground meteorological data was available. The plots do show that a molecular absorption prediction scheme which only considers oxygen as having internal absorption will not give large enough values, particularly at low frequencies.

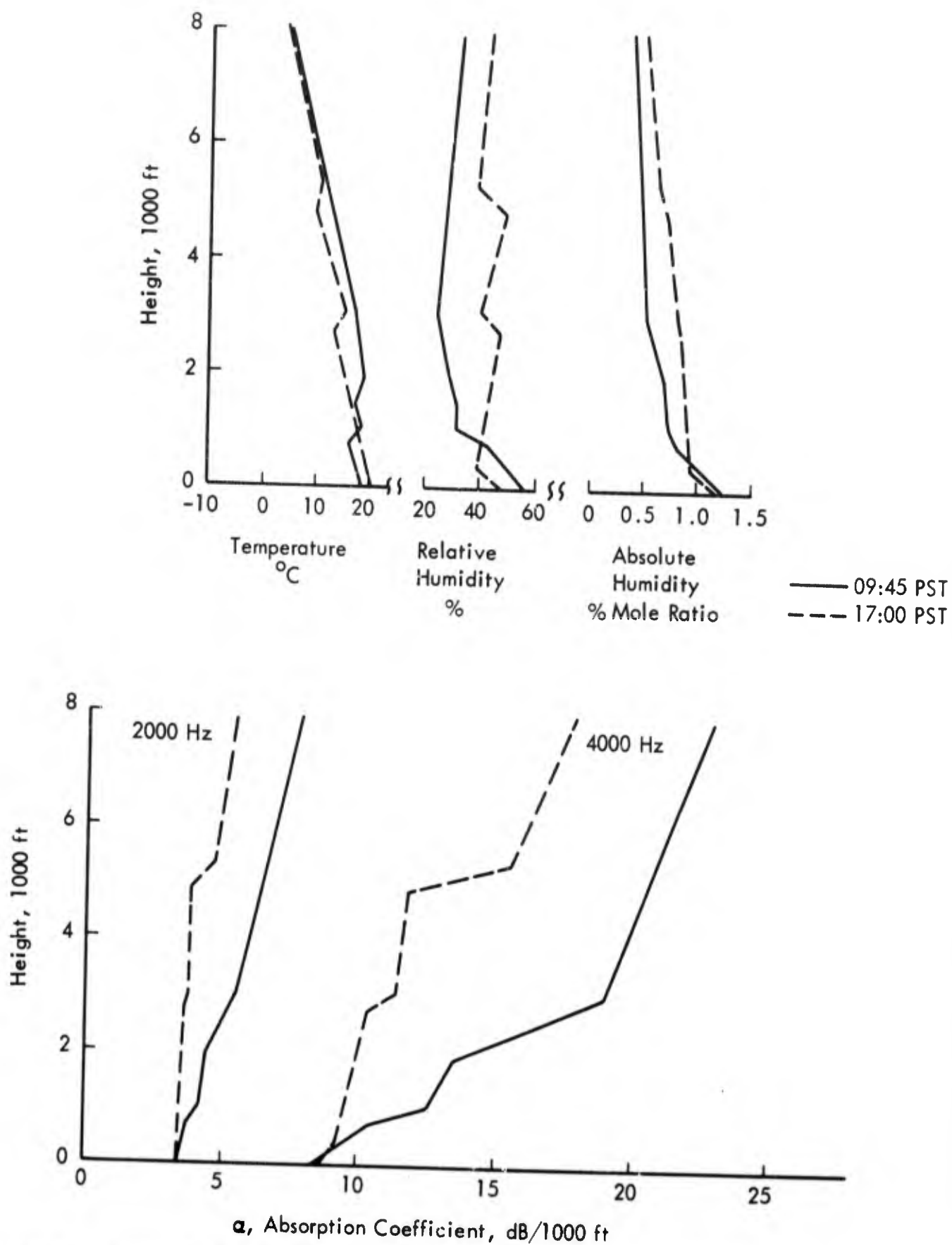


Figure 25. Vertical Profile of Weather and Computed Atmospheric Absorption Coefficient for ESSA Site, Pendleton, Oregon, Over 7 Hour Time Span on October 22, 1969

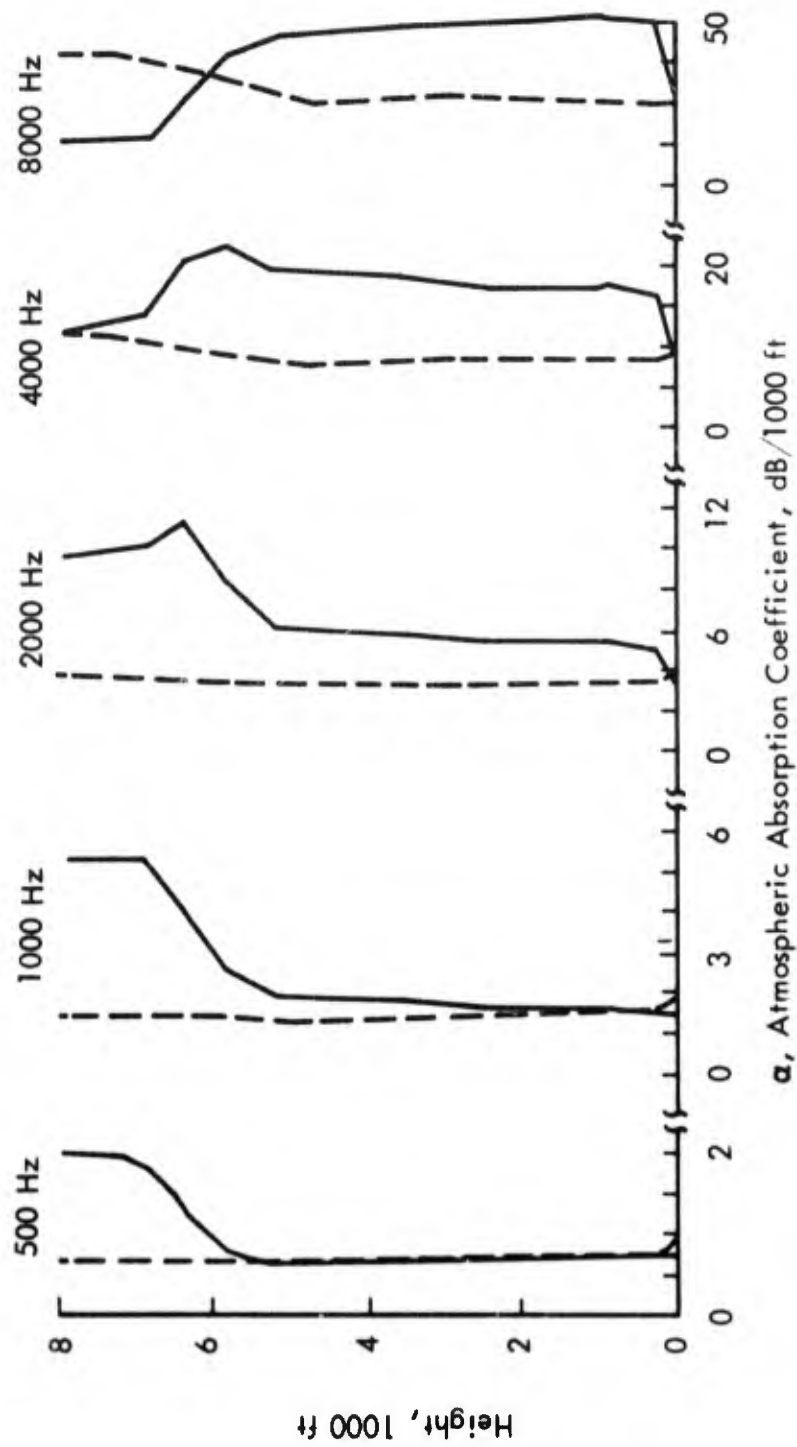


Figure 26. Vertical Profile of Variation in Computed Atmospheric Absorption Coefficient for ESSA Site, Pendleton, Oregon (Solid Lines for April 1, 1969, Dashed Lines for July 2, 1969)

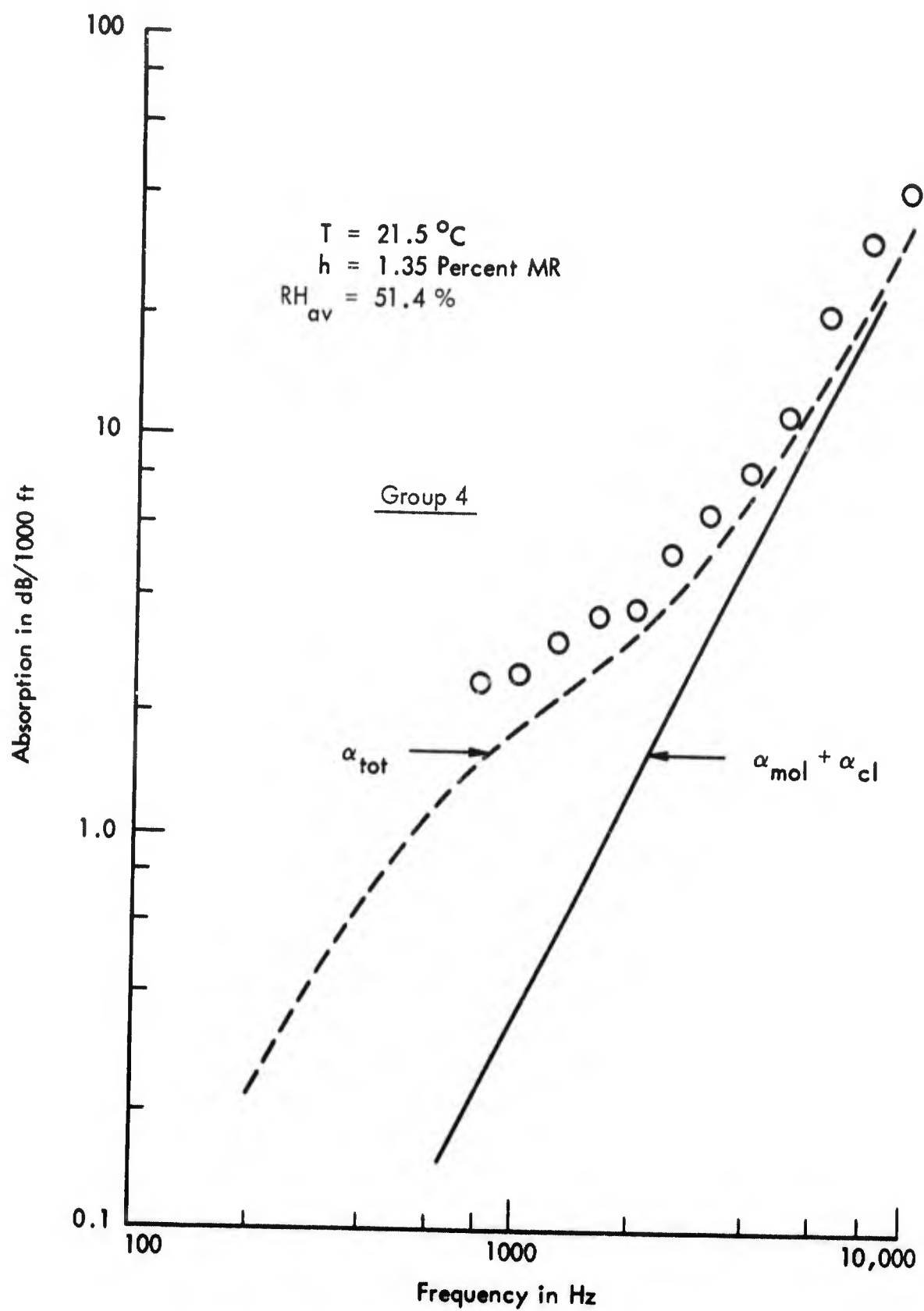


Figure 27. Comparison of Molecular Relaxation Reduced from Field Data to Single Relaxation Theory

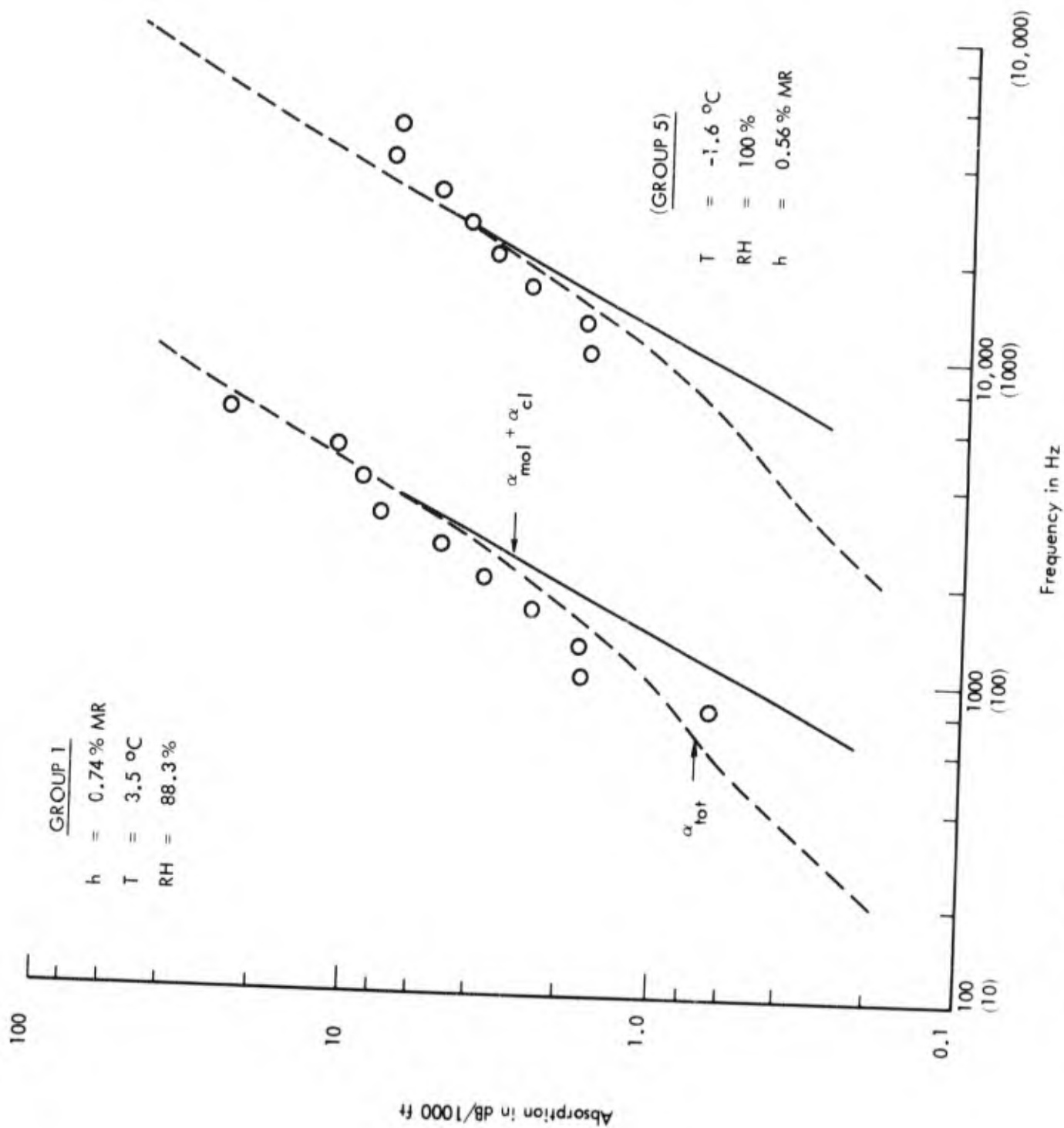


Figure 28. Comparison of Molecular Relaxation Reduced from Field Data to Single Relaxation Theory

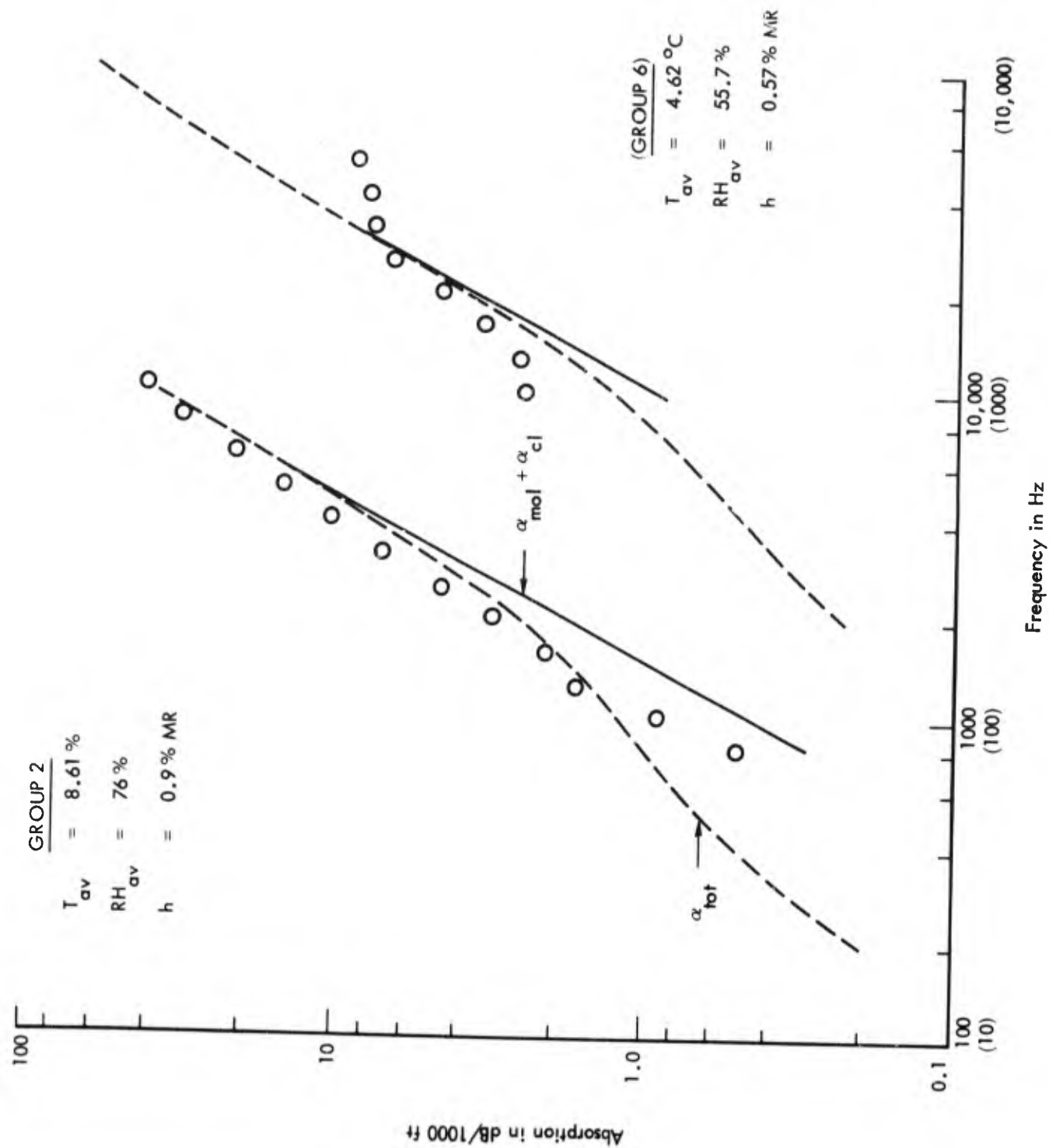


Figure 29. Comparison of Molecular Relaxation Reduced from Field Data to Single Relaxation Theory

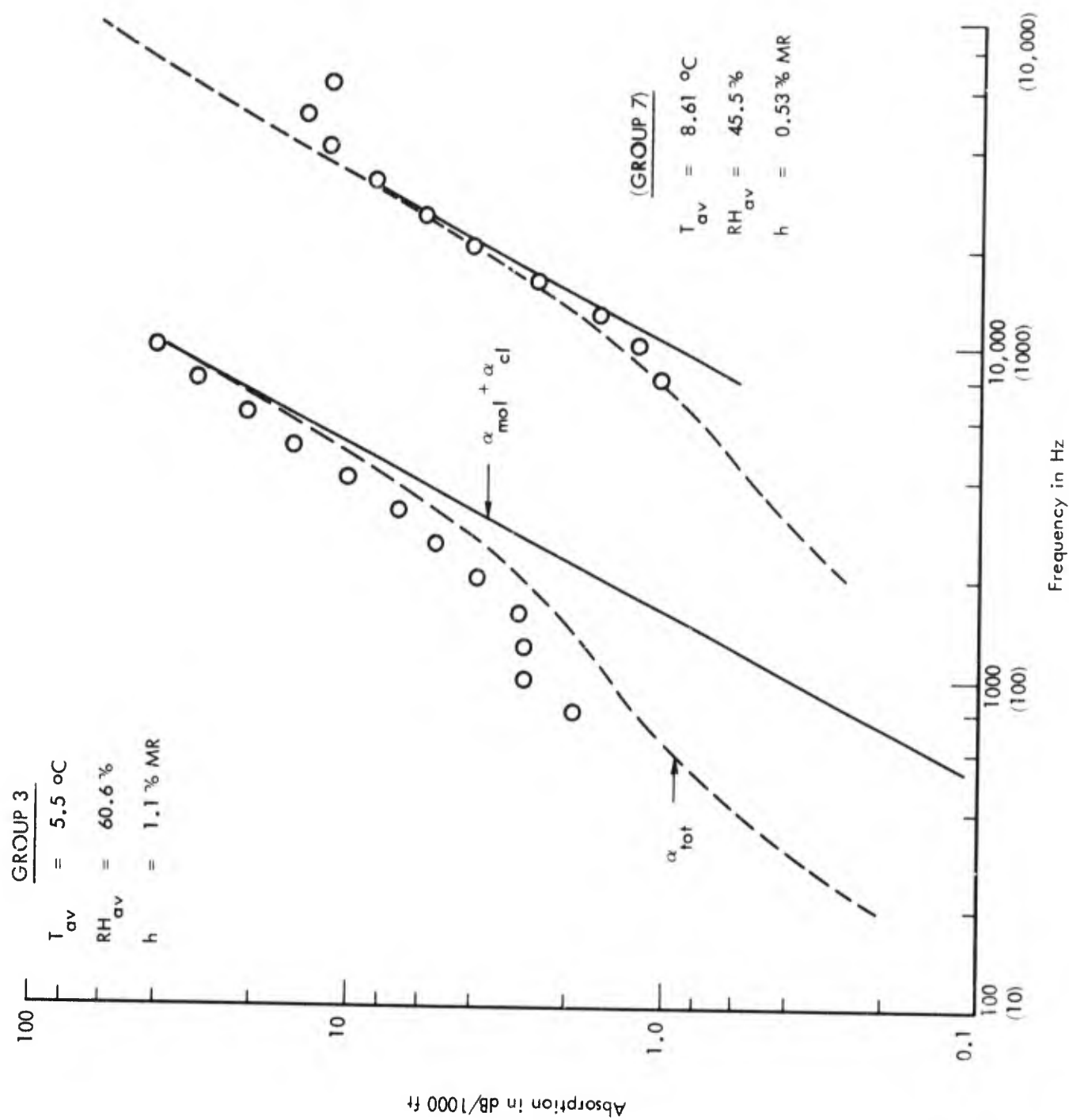


Figure 30. Comparison of Molecular Relaxation Reduced from Field Data to Single Relaxation Theory

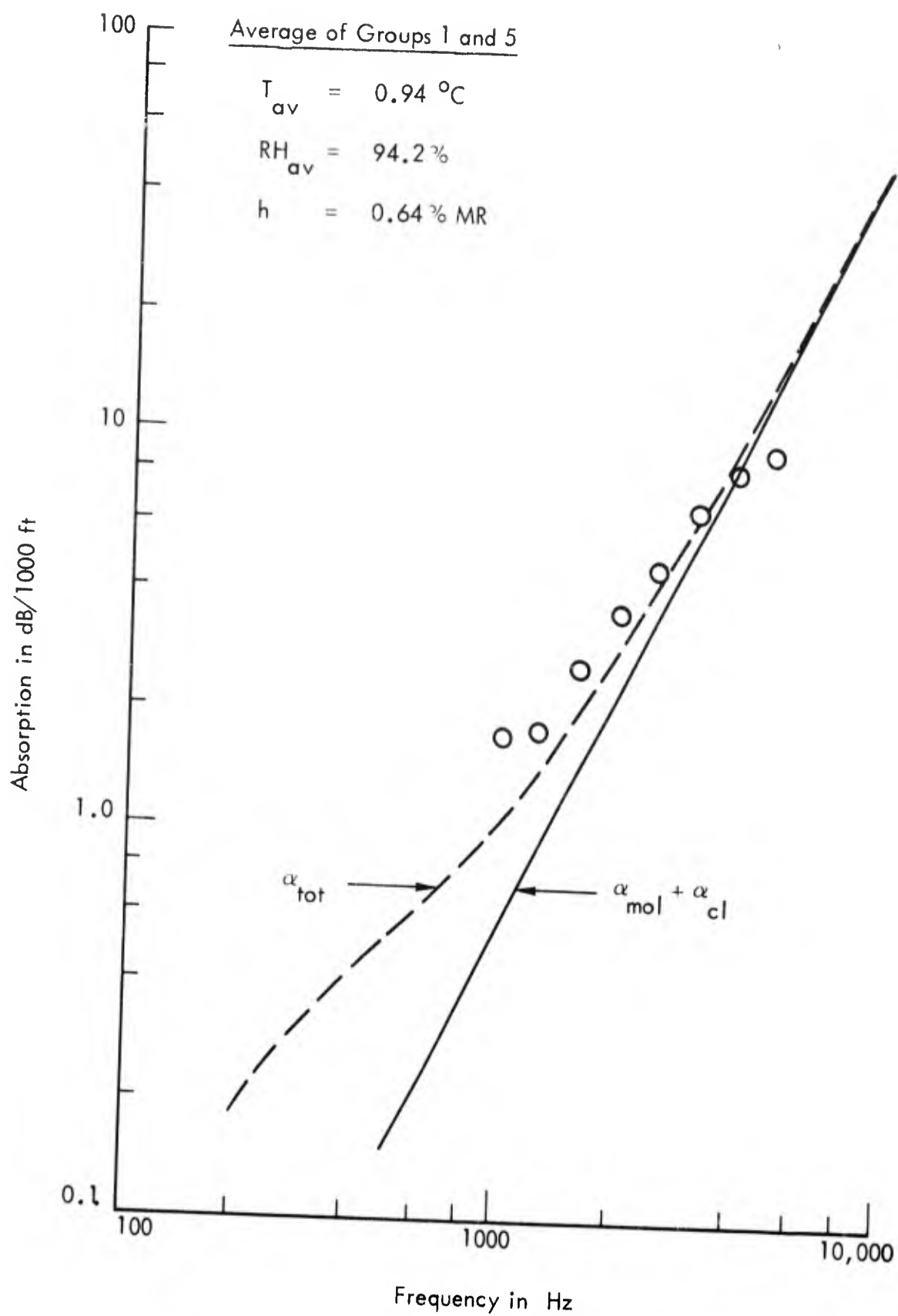


Figure 31. Comparison of Molecular Relaxation Reduced from Field Data to Single Relaxation Theory

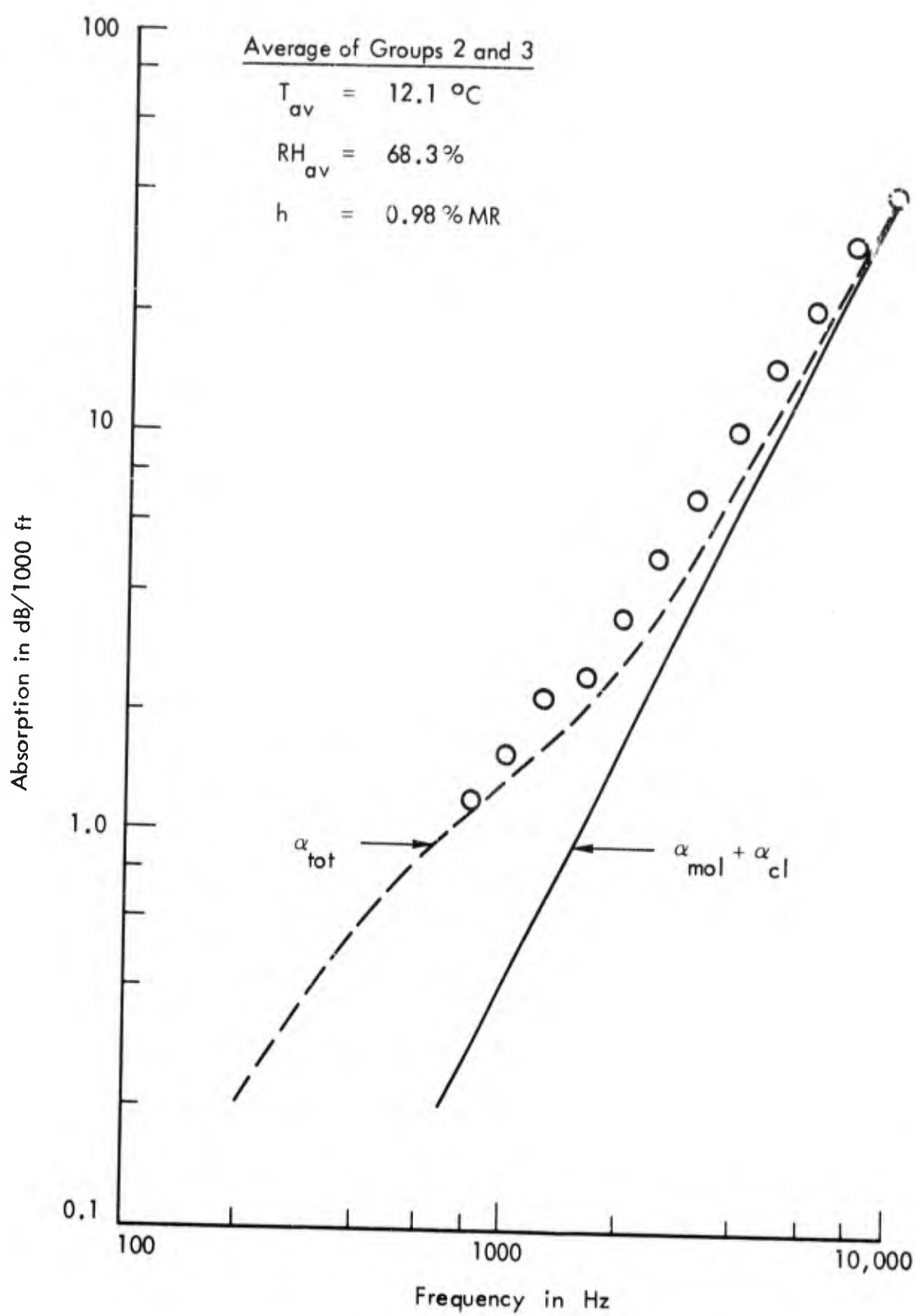


Figure 32. Comparison of Molecular Relaxation Reduced from Field Data to Single Relaxation Theory

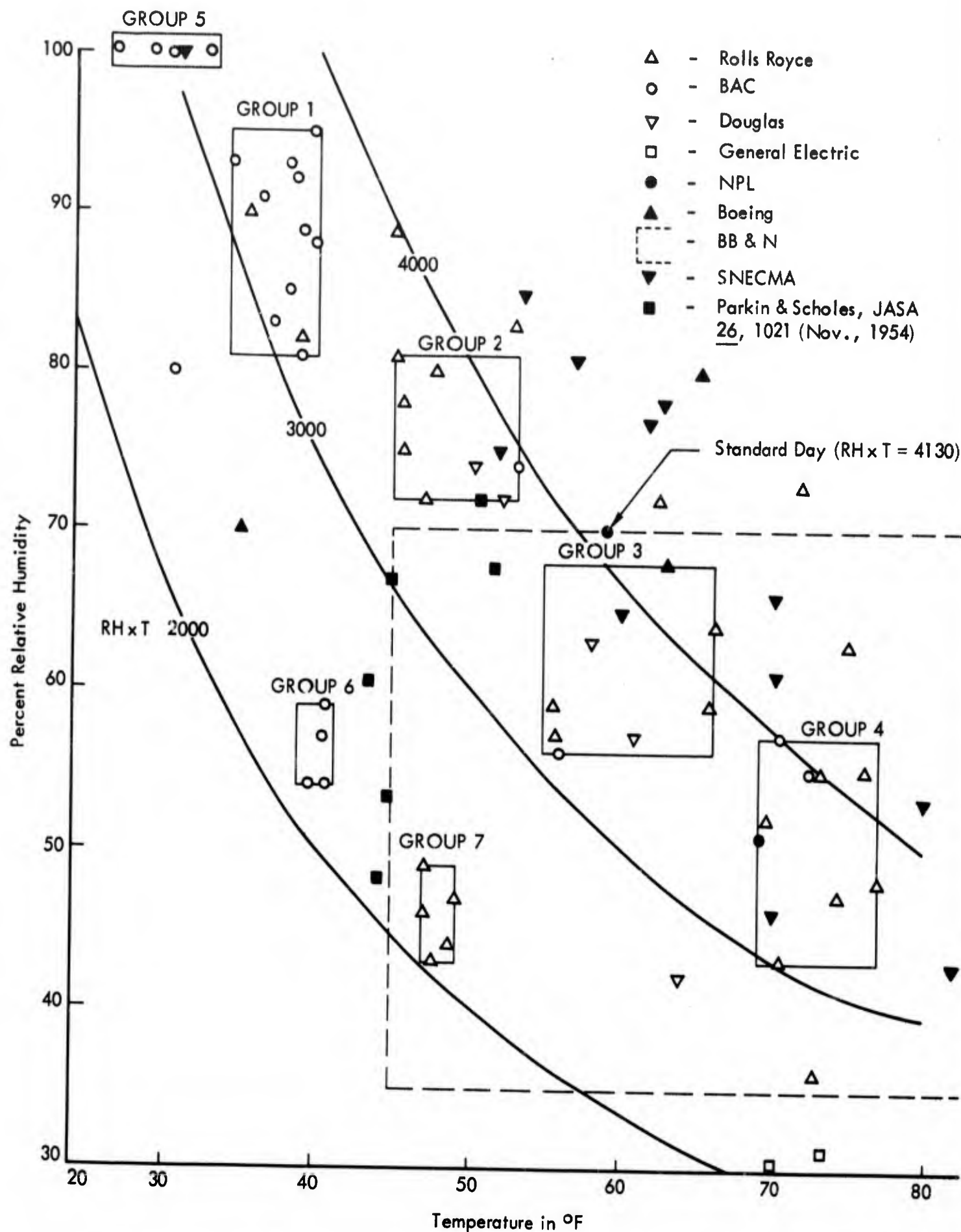


Figure 33. Range of Ground Conditions for Atmospheric Absorption Data

6.0 SUMMARY AND CONCLUSIONS

The purpose of this study was to investigate the low frequency sound absorption anomaly in air and to produce a set of engineering equations which would predict the total absorption due to both classical and molecular effects as a function of humidity and possibly temperature. To accomplish these goals an extensive literature survey was made, a set of experiments was performed, and a tentative set of equations was written.

The important results of this study can be summarized as follows:

- A value of 5 Hz has been found to be the relaxation frequency of dry air (Reference 44)
- The internal specific heats of diatomic gases may or may not obey the Planck-Einstein relationship
- There is definitely some other molecular relaxation mechanisms other than oxygen active in air at low frequencies
- Thermal radiation has been ruled out as a cause of the low frequency absorption anomaly
- The low frequency absorption anomaly is most likely due to nitrogen
- The low frequency absorption in air is humidity independent but the magnitude of the absorption coefficients at low frequencies are not consistent from one set of experiments to the next
- A tentative set of engineering equations has been developed which will predict the absorption coefficient of sound accurately as a function of humidity over a small temperature range
- This prediction scheme has been utilized to find the absorption coefficients as a function of altitude for real weather conditions
- This prediction scheme has also been utilized to analyze field data when only ground weather conditions were known with fair accuracy
- Low frequency sound absorption measurements have been made on humid nitrogen at room temperature and the relaxation frequency predicted

As yet the zero humidity value of relaxation frequency for air has not been utilized. Use of this value may change some of the coefficients in Monk's equation for f_m as a function of humidity.

The low frequency experimental results of Harris (Reference 1), Knudsen (Reference 27), and this work have all been different, and single relaxation theory does not adequately explain the observed absorption found in any of these experiments. All of the results appear to become independent of humidity in the low frequency range, but the magnitudes of the absorption coefficients are all different. Knudsen's data appears to approach a constant value of normalized absorption of 0.4; Harris's data approaches 0.2; and Evans and Sutherland's data approaches a value of 0.1.

It was originally thought by these authors that a relaxation in nitrogen catalized by water vapor was the cause of this low frequency absorption, but since the values are so different among the different investigators it is now felt that perhaps some other impurity molecule such as CO_2 may be helping to catalize the excess absorption. It is still felt that the excess low frequency absorption is essentially due to the nitrogen content of air and the problem now is to determine which impurity is causing the frequency to shift into the audible frequency range. Nitrogen and carbon dioxide have a well known near vibrational resonance (Reference 45) which is a very efficient collision process. If the trace amounts of carbon dioxide in air can be rapidly de-excited by some other molecule such as maybe water vapor, then CO_2 may be the cause of the low frequency anomaly. This vibrational resonance of N_2 and CO_2 is the basis of the high power continuous wave CO_2 laser. A way to check the importance of CO_2 would be to perform a set of experiments in which the CO_2 content can be closely controlled. It has been shown by Parker and Swope (Reference 46) that CO_2 is an efficient collision partner to de-excite vibrationally excited O_2 , but the order of magnitude of this relaxation effect is not large enough to explain the anomalous low frequency absorption in air.

Experimental evidence has appeared in the literature that leads these authors to believe that many of the vibration→translation relaxation processes used to determine the relaxation frequency dependence of air on water vapor content may indeed be vibration→rotation relaxation processes. This may particularly be true at low temperatures. This evidence includes:

- A negative temperature dependence found by Harris for the relaxation frequency of air for room temperature and below, i.e., as temperature increases the relaxation frequency decreases (Reference 1)
- A temperature independence found by Knotzel in air for $20^\circ\text{C} - 55^\circ\text{C}$ (Reference 36)
- Work by Cottrell which shows strong possibilities for vibration to rotation energy transfer (References 47-50)
- Work by Milliken and Osburg which reveals that para-hydrogen is a much better collision partner for carbon monoxide than is ortho-hydrogen (Reference 51)

The combined work of Harris (Reference 1) and Knotzel (Reference 36) indicates that perhaps the relaxation frequency in air as a function of temperature is showing a minimum value. This is contrary to the Landau-Teller (Reference 16) theory which predicts that the relaxation frequency should vary linearly with $T^{-1/3}$. Cottrell's (References 47-50) work with rather exotic molecules indicates that there are many cases in which vibration to rotation energy transfer is much more probable than vibration to translation energy transfer. Milliken and Osburg's (Reference 51) results indicate that rotation must be very important when H_2 is used as an impurity collision molecule with carbon monoxide, since the only difference between parahydrogen and orthohydrogen are the rotational energy levels available for occupation. All of these things appear to be indicating the importance of the vibration→rotation energy transfer process as one of the controlling mechanisms for the temperature dependence of the relaxation frequency of air at audio frequencies.

As outlined previously the frequency of maximum absorption as a function of humidity has been rather well defined by Monk as:

$$f_m = 1750h + 61400h \left[\frac{1.12 + 10h}{10.4 + 10h} \right]$$

However, this equation is valid only for 20°C temperature. The only credible experimental data available on f_m at other temperatures are those of Harris (Reference 1) and Knotzel (Reference 36).

Harris has found a negative temperature dependence for f_m over the temperature range of -40°C - +20°C; whereas Knotzel found f_m to be essentially independent of temperature from 20°C - 55°C. These two different sets of experiments can be taken to be conflicting, or assumed to be correct and indicating that perhaps a minimum or inflection point is occurring in the f_m versus temperature curve.

If it is assumed that the previous work is correct and that a minimum is occurring in the f_m versus T curve, then this may lend credence to the possibility of a vibrational to rotational energy transfer process as the controlling mechanism (or at least as a major factor) of the temperature dependence. For molecules such as H_2 , H_2O and other hydrogen containing molecules there is usually at least one principal axis of rotation about which the moment of inertia is rather small. This means that this rotational degree-of-freedom is highly quantized and is capable of high rotational (tangential) velocities in a discrete quantum state. In fact, it is possible for the rotational velocity to have magnitudes as great or greater than the translational velocity of the molecule. This indicates that in a collision with a vibrational excited molecule the probability of a vibrational to rotational energy transfer may be as great or greater than a vibrational to translational energy transfer.

The spacing of the energy levels of the rotational modes of a molecule are given by

$$E_j = j(j+1) K \theta_r$$

where j is the rotational quantum number, K is Boltzman's constant, θ_r is the characteristic temperature of rotation given by

$$\theta_r = \frac{h^2}{2KI}$$

where h is Planck's constant and I is the moment of inertia. The level of greatest population for a given temperature is given by

$$J_n \approx \left(\frac{T}{2\theta_r} \right)^{1/2}$$

where T is the absolute temperature.

The tangential velocity of an excited rotational mode at a given temperature is then given by

$$v_T^2 = \frac{2 J_n (J_n + 1) K \theta_r}{m}$$

where m is the mass of the molecule.

Now the most probable translational velocity from the Maxwell velocity distribution is given by

$$v^2 = \frac{2KT}{m}$$

The ratio of the tangential velocity to the translational velocity is then

$$\frac{v_T^2}{v^2} = \frac{J_n (J_n + 1) \theta_r}{T}$$

If we now consider water vapor whose three principal moments of inertia are:

$$I_a = 1.0224 \times 10^{-40} \text{ gm cm}^2$$

$$I_b = 1.9180 \times 10^{-40} \text{ gm cm}^2$$

$$I_c = 2.9404 \times 10^{-40} \text{ gm cm}^2$$

and using the smallest of these gives:

$$\frac{v_T^2}{v^2} = \frac{40 J_n (J_n + 1)}{T}$$

This ratio indicates that the rotational tangential velocity and the translational velocity are very nearly equal over a fairly wide temperature range.

This ratio also indicates that the probability of vibrational energy transfer to a rotational mode is as great as the probability of transfer to a translational mode; however, this in itself does not predict the lessening of collision efficiency as is indicated by the observed negative temperature dependence.

Considering the nature of the collision processes, one sees that when a vibrational quanta of energy is transferred to a rotational mode of a different molecule the rapidity with which this process occurs is dependent upon the rate of de-excitation of the rotationally excited molecule, i.e., the rotationally excitable molecule must be made available to absorb another vibrational quanta. The theory of Raff and Winter (Reference 52) for homo-nuclear molecules, the theory of Zeleznik (Reference 53) for polar molecules along with the experimental work of Winter and Hill (Reference 54) and Evans et al., (Reference 59) all indicate that as the temperature is increased the rotational relaxation frequency decreases, i.e., the rotational $\rightarrow$ translation energy transfer process becomes less efficient with increasing temperature, or another way to explain the phenomena is that more collisions are necessary before an energy quanta can be transferred. The work of Evans et al., (Reference 39) also indicates that the greater the dipole moment of a polar molecule the larger the negative shift of the rotational relaxation frequency with increasing temperature. Since water vapor has a very large dipole moment a similar shift would be expected with temperature. The meaning of all of this as related to humid air is that as the temperature is increased the water vapor molecules become less and less available to absorb vibrational energy quanta by its rotational degrees-of-freedom. This means that the relaxation frequency could very well decrease with increasing temperature as is indicated by Harris's experimental data.

Pursuing this line of thought even further, as the temperature becomes higher, the translational velocities become greater, and can more easily interact with the vibrational modes. This could mean that a minimum may occur in the frequency of maximum absorption versus temperature curve. Then a positive temperature dependence may be observed. It should be pointed out that such a minimum has been observed in $\text{CO}_2 - \text{N}_2$ relaxation data (Reference 45).

Essentially, this is postulating that the previous temperature dependence found by Harris and that found by Knotzel may be correct. The rate controlling mechanism at low temperatures would be a vibration→rotation→translation collision process; whereas, at higher temperatures the rate controlling mechanisms would be a vibrational→translation mechanism. Further experimental work is clearly needed to help clarify these mechanisms and their relationships to sound absorption in humid air.

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