N O T I C E

DEPARTMENT OF PHYSICS
SCHOOL OF SCIENCES AND HEALTH PROFESSIONS
OLD DOMINION UNIVERSITY
NORFOLK, VIRGINIA

THE CONTRIBUTION OF MOLECULAR RELAXATION IN NITROGEN TO THE ABSORPTION OF SOUND IN THE ATMOSPHERE

By

Allan J. Zuckerwar, Principal Investigator

and

Roger W. Meredith, Graduate Research Assistant

Final Report

April 1980

OLD DOMINION UNIVERSITY RESEARCH FOUNDATION

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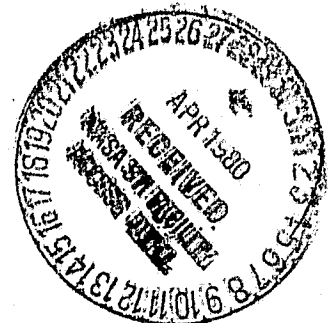
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SUMMARY

Work accomplished during the final two quarters of NSG 1324 falls into two broad categories: first, sound absorption in N_2-H_2O binary mixtures at room temperature—changes in final results and statistical analysis; secondly, sound absorption in N_2-H_2O binary mixtures at elevated temperatures—experimental procedure, temperature effects, and preliminary results. A summary of publications resulting from research performed under this grant is included.

SOUND ABSORPTION IN N_2-H_2O BINARY MIXTURES AT ROOM TEMPERATURE

A. Changes in Final Results

A few changes regarding the evaluation of the data presented at the 97th Meeting of the Acoustical Society of America have led to a slight modification of the experimentally determined relationship between humidity h and the location of the N_2 vibrational relaxation peak on the frequency/pressure (f/P) axis.[1,2] Theoretical considerations suggest that the relationship should be linear:

$$(f/P)_{max} = a_0 + a_1 h \qquad (Hz/atm) \; . \tag{1}$$

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A weighted least-squares regression analysis yields the following updated values for the constants:

$$a_0 = 0.013 \pm 0.012 \quad \text{Hz/atm}$$

$$a_1 = 0.0200 \pm 0.0018 \quad \text{Hz/atm} \cdot \text{ppm}. \tag{2}$$

The water vapor content h is expressed in parts per million (ppm). The limits of error represent the 95% confidence intervals for the random error only, which was obtained by the computational procedure described below. The systematic error, by far less significant, is still being formulated and is expected to amount to less than ±5% of the above values. The correlation coefficient of the fit is 0.9938—which indicates an excellent linear fit. The changes from the previous data include the addition of a new point (at $h = 18\ 800$ ppm), the correction of a numerical error (5237 ppm corrected to 5327 ppm), the deletion of a point in which the dew point was not taken immediately after the measurement, and improved rounding consistency.

B. Statistical Analysis

Figure 1 shows the sound absorption per unit wavelength μ in N_2 vs. (f/P) for four selected values of water vapor concentration. The solid lines are the best fit of the experimental data points (circles) to the theoretical Debye relaxation curve:

$$\mu = 2\mu_{max} \cdot \frac{(f/P)(f/P)_{max}}{(f/P)^2 + (f/P)^2_{max}} . \tag{3}$$

The peak height μ_{max} is known from thermodynamic considerations. The value of (f/P) at which the crest of the peak occurs is called the "relaxation f/P" and is designated by $(f/P)_{max}$, the only adjustable parameter in Eq. (3). Table I lists corresponding values of humidity and $(f/P)_{max}$, together with the 95% confidence intervals on $(f/P)_{max}$, for ten sets of data taken during the course of the experiment.

The ten sets of data listed in Table I are shown in the plot of Fig. 2. The solid line is a plot of Eq. (1) with the best-fitted values of slope a_1

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and intercept a_0 given in Eq. (2). The error bars are the 95% confidence intervals on $(f/P)_{max}$ as listed in Table I, and, it is emphasized, include only the random error.

The problem of computing the random error consists of two parts: first, to determine the bounds on each $(f/P)_{max}$ upon fitting the sound absorption data to the theoretical curves given by Eq. (3); secondly, to determine the bounds on a_0 and a_1 in the linear fit of Eq. (1). The statistical distributions used here are explained in many standard texts on the subject.[3,4,5]

In the procedure for determining the best value of $(f/P)_{max}$ to fit a set of absorption data to Eq. (3), it is convenient to simplify notation by using $A = 1/(f/P)_{max}$ as the adjustable parameter. Then, for the ith point of a given set of data let $\mu_i(A)$ be the estimated value of absorption according to Eq. (3) and M_i the measured value of absorption. The quantity $S(A)$, the sum of the squares of the deviations, is minimized to determine the value of A which gives the best fit:

$$S(A) = \sum_i [\mu_i(A) - M_i]^2. \tag{4}$$

This is done numerically on an HP Model 9830A desk calculator. Initially a rough estimate of A, designated as A_0, is obtained from the location of the peak on a graph and $S(A_0)$ is computed. Then A is changed by small increments about A_0 and $S(A)$ recomputed until it reaches a minimum value. The corresponding value of A, designated by $\hat{A}$, yields the best fit and is determined to three significant figures.

The statistical problem may be stated as follows: How far can A deviate from $\hat{A}$ before the difference between $S(A)$ and $S(\hat{A})$ becomes significant at a given confidence level? This problem is resolved with the aid of the "F distribution," which is designed to test the equality of two variances, such as $S(A)$ and $S(\hat{A})$, and is suitable for small samples.*

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*The variance is actually Eq. (4) divided by the number of samples, but the F distribution may be applied to $S(A)$ and $S(\hat{A})$ directly since the number of samples is the same for both.

If $S(A)$ is computed for an arbitrary value of A, the F distribution is defined* such that

$$S(A) \leq S(\hat{A}) \left[1 + \frac{P}{N-P} F(P, N-P, 1-\alpha)\right] . \tag{5}$$

Here P is the number of adjustable parameters, N the number of data points, and $1-\alpha$ the confidence interval. In the present analysis $P = 1$ since A is the only adjustable parameter, and $1-\alpha$ is taken to be 0.95, which corresponds to twice the standard deviation of a Gaussian distribution. Knowing P, N, and $1-\alpha$, one can find F from available F distribution tables. Then the entire right side of Eq. (5) is known. The parameter A is varied until $S(A)$ equals the right side of Eq. (5). There are two values of A, designated as $A\overset{+}{\alpha}$ and $A\overset{-}{\alpha}$, which fulfill this requirement:

$$A\overset{-}{\alpha} < A < A\overset{+}{\alpha} . \tag{6}$$

The difference $(A\overset{+}{\alpha} - A\overset{-}{\alpha})$ represents the "95% confidence interval" on A. The error bound on $(f/P)_{max}$, defined here as

$$B = (A\overset{-}{\alpha})^{-1} - (A\overset{+}{\alpha})^{-1} , \tag{7}$$

is an estimator of four times the standard deviation of $A^{-1} = (f/P)_{max}$. Because $S(A)$ is an asymmetric function of A, the bound is given as B in Table I and not in the form $\pm \delta(f/P)_{max}$.

Once the best values of A, thus $(f/P)_{max}$, and their confidence intervals are established, the ten sets of data of Table I are fitted to Eq. (1) by a weighted linear regression analysis. The need for weighting stems from the fact that the ten observations are not samples from the same parent distribution, and the dependent variable—the $(f/P)_{max}$'s—are characterized by widely diverging variances. In accordance with established practice, the data are weighted by the reciprocals of the variances, which in the present analysis are represented by the estimator B:

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*Eq. (5) is approximate because the theoretical relaxation curve, Eq. (3), is nonlinear in $(f/P)_{max}$, the quantity for which $\hat{A}^{-1}$ is an estimator.

$$w_j = B_j^{-2} \quad (j = 1, 2, \ldots, 10). \tag{8}$$

The best values of a_0 and a_1 are derived from the usual formulas:

$$a_0 = \frac{(\Sigma w_j y_j)(w_j x_j^2) - (\Sigma w_j x_j y_j)(\Sigma w_j x_j)}{(\Sigma w_j)(\Sigma w_j x_j^2) - (\Sigma w_j x_j)^2}, \tag{9}$$

$$a_1 = \frac{(\Sigma w_j)(\Sigma w_j x_j y_j) - (\Sigma x_j)(\Sigma y_j)}{(\Sigma w_j)(\Sigma w_j x_j^2) - (\Sigma w_j x_j)^2}, \tag{10}$$

in which x_j is the humidity h and y_j the value of $(f/P)_{max}$ for the jth set of data. The error limits on a_0 and a_1 are set equal to the 95% intervals of a "Student's t" distribution, which for small samples provides improved estimators for the mean and standard deviation. The distribution is defined in the following equation:

$$\langle a \rangle = \bar{a} \pm t_c \frac{s}{\sqrt{N - 2}}, \tag{11}$$

where $\langle a \rangle$ is the true mean, $\bar{a}$ the sample mean, c the confidence level, t_c the confidence coefficient, s the sample standard deviation, and N the number of samples or data sets. Values for t_c, which depends only upon c and N (more exactly, the number of degrees of freedom), are found in readily available t distribution tables. In the present analysis $\bar{a}$ is the best-fitted value of a_0 or a_1, and c is again chosen to be 0.95. The standard errors s_0 and s_1, for a_0 and a_1 respectively, are used to represent s in Eq. (11):

$$s_0 = \left\{ \frac{[\Sigma w_j (y_j - Y_j)^2](\Sigma w_j x_j)^2}{\Delta \Sigma w_j} \right\}^{1/2}, \tag{12}$$

$$s_1 = \left[\frac{\Sigma w_j (y_j - Y_j)^2}{\Delta} \right]^{1/2}, \tag{13}$$

$$\Delta = \Sigma w_j x_j^2 - \frac{(\Sigma w_j x_j)^2}{\Sigma w_j} \, ,$$

x_j = measured value of humidity h,

y_j = measured value of $(f/P)_{max}$,

Y_j = estimated value of $(f/P)_{max}$, Eq. (1).

The factor $(N - 2)$ appears in the denominator of Eq. (11) because the two unknowns, slope and intercept, remove two degrees of freedom. For 8 degrees of freedom $t_{.95} = 2.306$. Upon substituting the data of Table I into Eqs. (8) to (13) one obtains the best-fitted values and confidence intervals given in Eq. (2).

SOUND ABSORPTION MEASUREMENTS IN N_2-H_2O BINARY MIXTURES AT ELEVATED TEMPERATURES

A. Experimental Procedure for Measurement of Sound Absorption at Elevated Temperatures

The first part of the experimental procedure has remained the same as before. The entire system is evacuated to 5×10^{-5} Torr, and if an impurity—H_2O or CO_2—is to be used, it is admitted to the system first. Nitrogen is then admitted into the tube to a desired pressure. Mixtures of $N_2 + H_2O$ are allowed four days to homogenize to insure uniformity. A gas sample is taken for independent analysis by gas chromatography.

The tube temperature is initially set at 298°K, a set of acoustical data is taken, the pressure, dew point, and temperature are measured. The temperature is reset to 342°K, and the tube is left to stand overnight to come to thermal equilibrium. The acoustical and ancillary data are obtained at the new temperature, and this process is repeated again at 387°K. A second gas sample is taken upon completion of the acoustical measurements.

There has been a slight modification in the procedure for measuring the dew point with the Cambridge Systems Model 992 Dew Point Hygrometer. The piping between the tube and hygrometer is evacuated to 5×10^{-5} Torr prior to being flushed with pure N_2. Then the test gas is used as a final flushing

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agent. The hygrometer has a feature allowing long-term measurement of dew point by operating with the "auto balance" switch in the "on" position. It has been determined that in the present experiments the precision of the instrument is increased with the switch turned off. In addition, less gas is needed for accurate readings at high values of humidity. This is important because at low pressure the dew point was found to vary with presure.[6] Finally, multiple dew point measurements of test gases are made before and after the acoustical data are taken; the reproducibility of the dew point measurement is within 1%.

B. Temperature Effects

Each time the tube temperature is changed the dew point of the N_2-H_2O mixture also changes. At higher temperatures the water vapor previously adsorbed onto the walls of the tube during the initial charging returns to the vapor state when the wall is heated. Typical results for two different mixtures are shown in Fig. 3.

The elevated temperatures also cause the broadband background noise of the PCB quartz microphone to increase as much as fivefold. A water-cooling system affixed to the microphone proved to be ineffective in reducing the noise levels. The primary sources of the noise appear to be the increased electronic noise of the microphone and increased thermal noise of the gas inside the tube. Fortunately the length and quality of the acoustic decay curves are not seriously affected.

C. Preliminary Results

A summary of the range of parameters—temperature, pressure, humidity—and some corresponding values of $(f/P)_{max}$ appear in Table II. In addition, five sets of N_2-CO_2 data were taken to provide background values for (f/P) < 3 Hz/atm. A plot of three sets of data, one at each selected temperature, is shown in Fig. 4. Measurements at room temperature were taken for the purpose of control. As before, the peak heights are known from thermodynamics and the peak locations are determined from the best fit to Eq. (3). Without exception all the data evaluated thus far indicate that the slope a_1 in Eq. (1) _decreases_ with increasing temperature—a surprising and unexpected result with potentially far-reaching theoretical consequences.

For this reason more sets of data will be taken at elevated temperatures than originally planned.

PUBLICATIONS

The measurements of sound absorption in N_2-H_2O mixtures, conducted under NSG 1324, are the basis of a doctoral thesis and a master's thesis, both in preparation.

The following article has been accepted for publication:

A.J. Zuckerwar and W.A. Griffin, "Resonant Tube for Measurement of Sound Absorption in Gases at Low Frequency/Pressure Ratios," J. Acoust. Soc. Am., scheduled for July 1980.

The manuscript for a sister article, "Effect of Water Vapor on Sound Absorption in Nitrogen at Low Frequency/Pressure Ratios," is presently in preparation. Additional articles covering the scope of the research grant are being planned, as is a comprehensive Contractor's Report.

The following are published abstracts of presentations made at professional society meetings:

1. W.A. Griffin, "Argon Calibration Study of a Resonance Tube at Low f/P Ratios," Virginia Academy of Science, 56th Annual Meeting, May 1978.

2. A.J. Zuckerwar and W.A. Griffin, "Resonant Tube for Measurement of Sound Absorption in Gases at Low f/P Ratios," J. Acoust. Soc. Am. 64, Suppl. No. 1, S61, 1978.

3. W.A. Griffin and A.J. Zuckerwar, "Location of the Nitrogen Vibrational Relaxation Peak on the Frequency/Pressure Axis as a Function of Humidity in N_2-H_2O Mixtures," J. Acoust. Soc. Am. 65, Suppl. No. 1, S48, 1979.

4. A.J. Zuckerwar, "Radiation Losses in Resonant Tubes," J. Acoust. Soc. Am. 65, Suppl. No. 1, S75, 1979.

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1. W.A. Griffin and A.J. Zuckerwar, "Location of the Nitrogen Vibrational Relaxation Peak on the Frequency/Pressure Axis as a Function of Humidity in N_2-H_2O Mixtures," J. Acoust. Soc. Am. 65, Suppl. No. 1, S48 (1979).

2. A.J. Zuckerwar and W.A. Griffin, Technical Report PR-79-6, Old Dominion University, Department of Physics, August 1979.

3. N.R. Draper and H. Smith, Applied Regression Analysis, Wiley, 1966.

4. K. Rektorys, Editor, Survey of Applicable Mathematics, MIT Press, 1969.

5. P.G. Hoel, Introduction to Mathematical Statistics, Wiley, 1962.

6. See reference 2.

Table I. Relaxation $(f/P)_{max}$ vs. Humidity in Sound Absorption Measurements in N_2-H_2O Binary Mixtures at Room Temperature (297°K)

Data Set	Humidity h (ppm)	$(f/P)_{max}$ (Hz/atm)	Bounds on $(f/P)_{max}$ [a]
1	2.5	0.063	0.058 - 0.070
2	57	1.18	1.06 - 1.31
3	167	3.03	2.43 - 3.66
4	338	6.17	5.62 - 6.76
5	838	20.2	18.0 - 22.6
6	4112	96.2	69.4 - 129
7	5327	97.1	62.5 - 143
8	9026	196	133 - 278
9	14 400	304	231 - 402
10	18 800	435	321 - 588

[a] 95% confidence interval using the F distribution.

Table II. Range of Data and Preliminary Results for Sound Absorption Measurements in N_2-H_2O Binary Mixtures at Elevated Temperatures

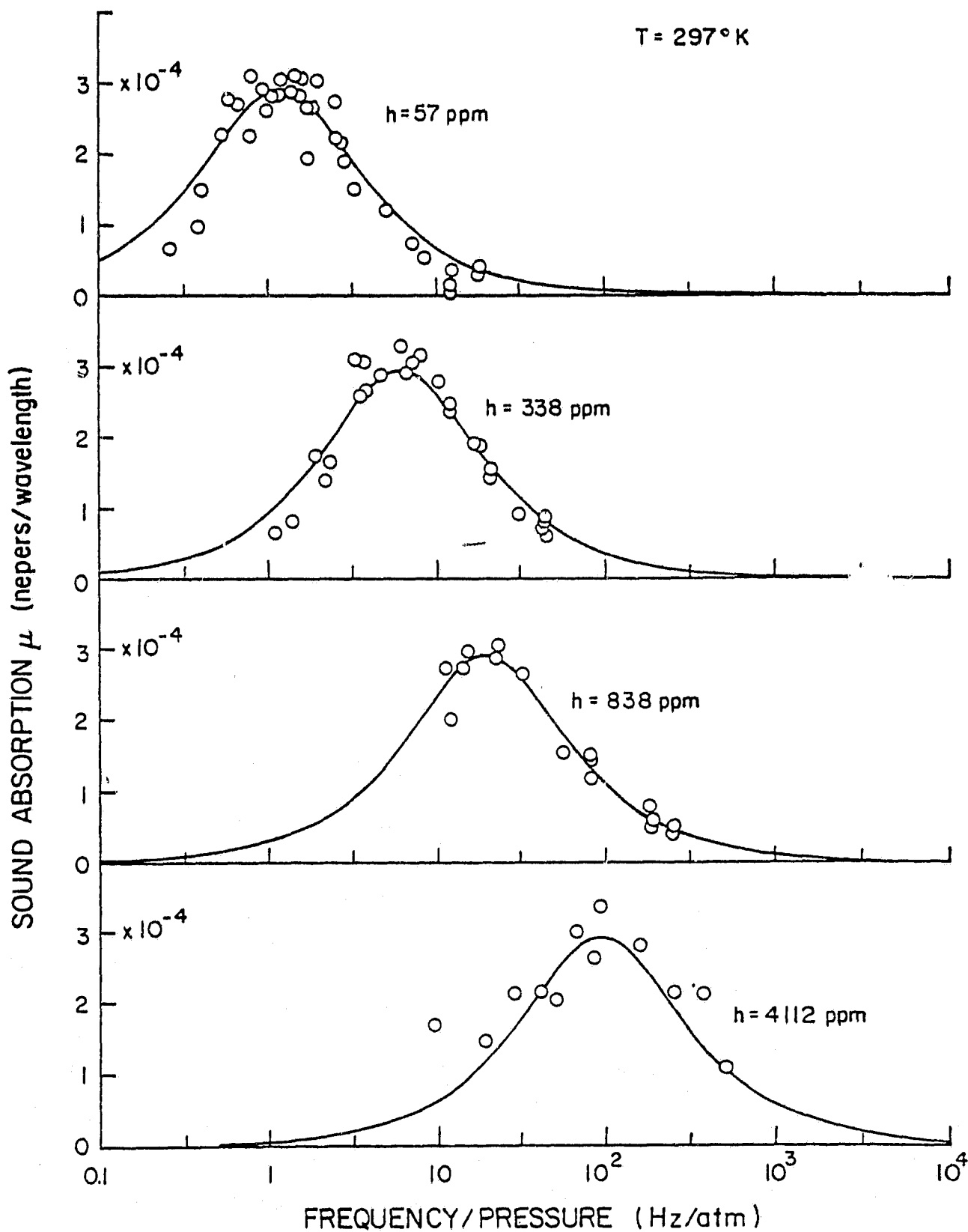| Temperature (°K)	Pressure (atm·abs)	Humidity (ppm)	$(f/P)_{max}$ (Hz/atm)
298	1.0	18 500	a
	1.0	7410	a
	35.4	110.1	2.11
	35.4	17.1	0.267
	80.5	<1.5	0.046
342	1.2	21 840	a
	1.2	8770	a
	43.7	84.8	1.23
	43.7, 89.4	<1.5	0.0327
387	1.3	24 710	a
	1.3	10 430	a
	53.4	217.1	2.10
	53.4, 105.5	10.9	0.175

[a] Sound absorption data not yet evaluated.

Figure 1. Sound absorption versus frequency/pressure ratio for four selected
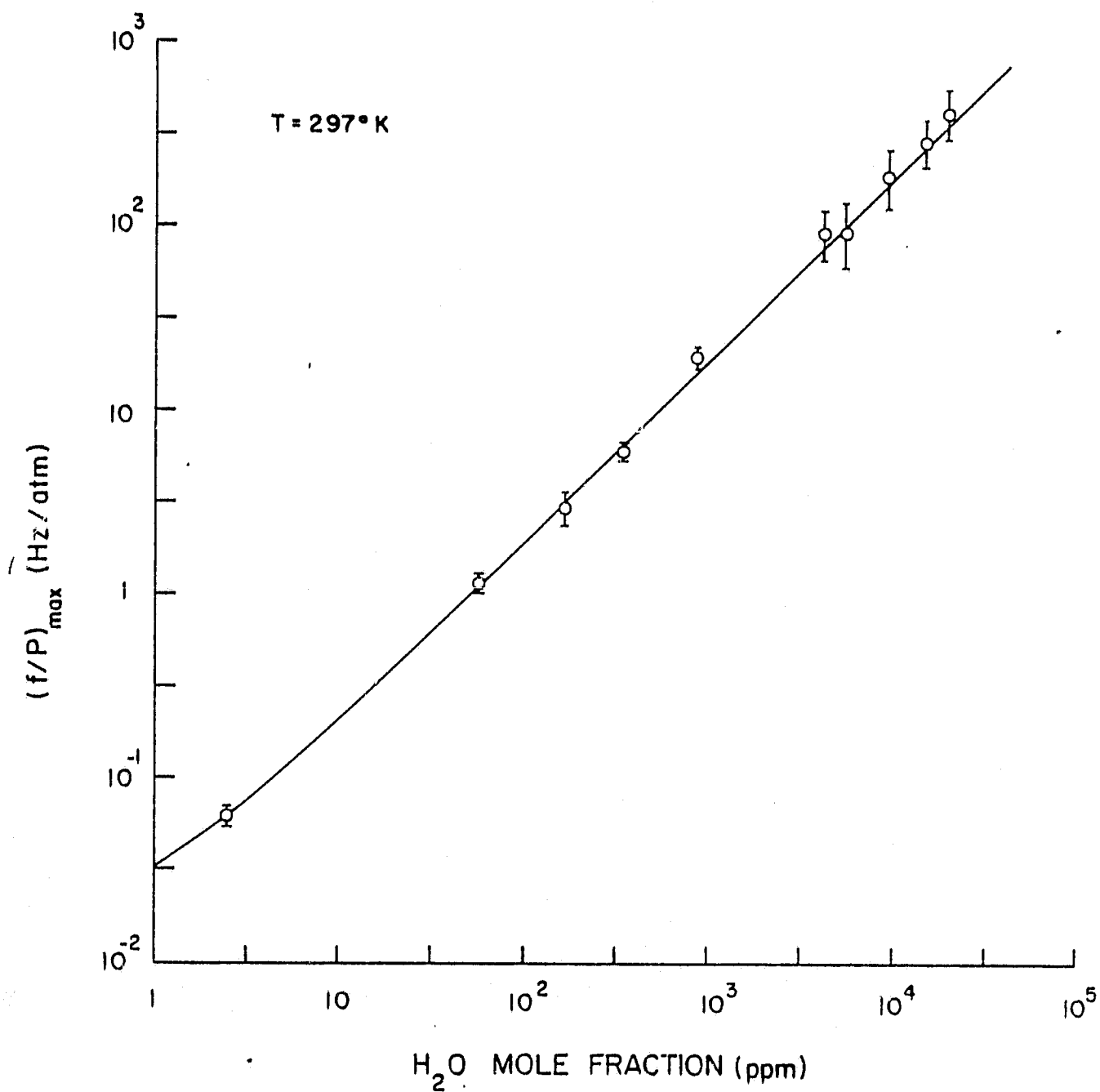N₂-H₂O binary mixtures at 297°K. The solid lines are best fits
to Eq. (3).

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Figure 2. Relaxation frequency/pressure ratio $(f/P)_{max}$ versus humidity h
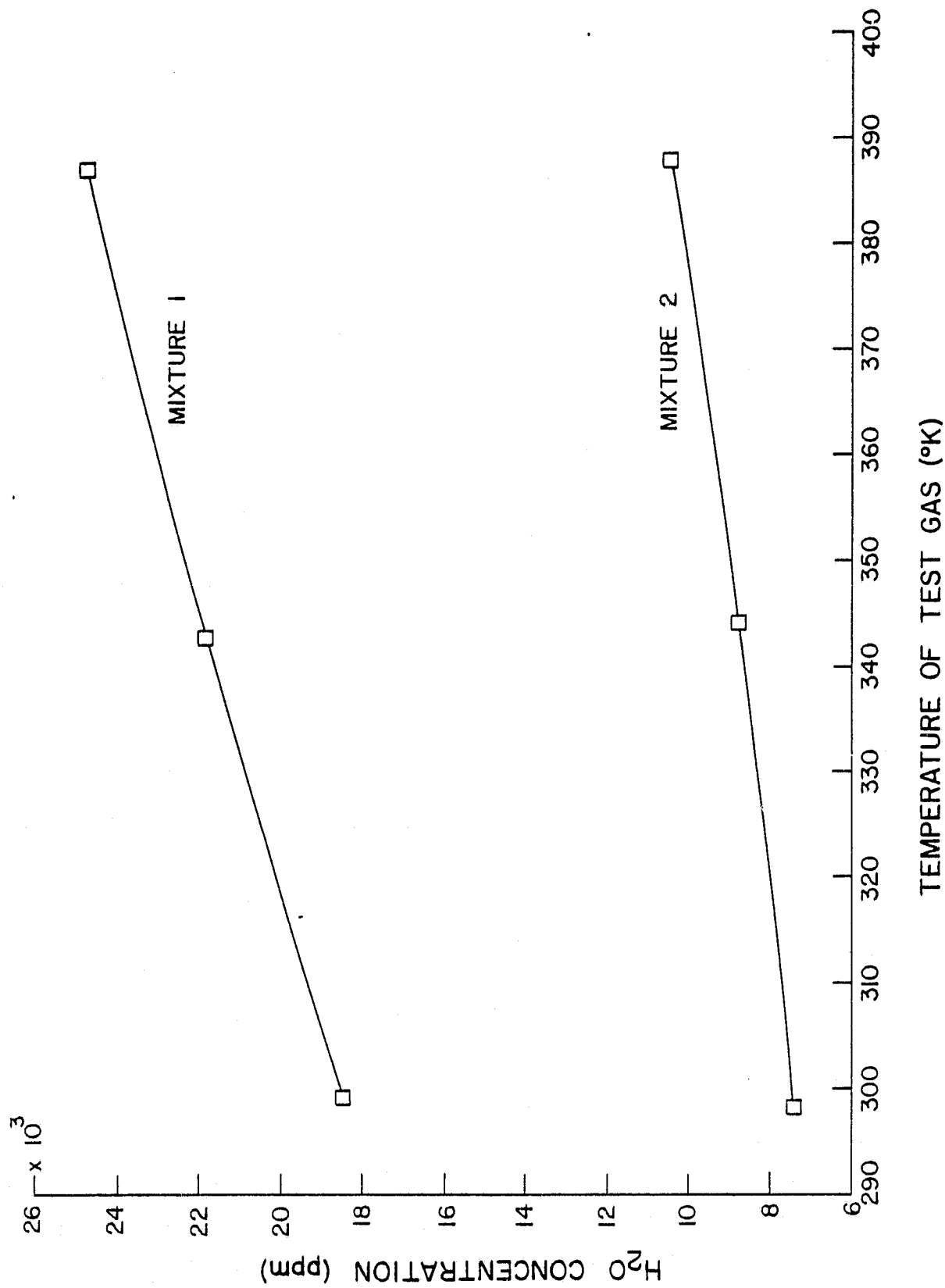in N_2-H_2O binary mixtures at 297°K. The error bars designate
95% confidence intervals.

Figure 3. Water vapor concentration versus temperature for two different N_2-H_2O mixtures. With increasing temperature adsorbed water leaving the walls of the tube enriches the mixture.
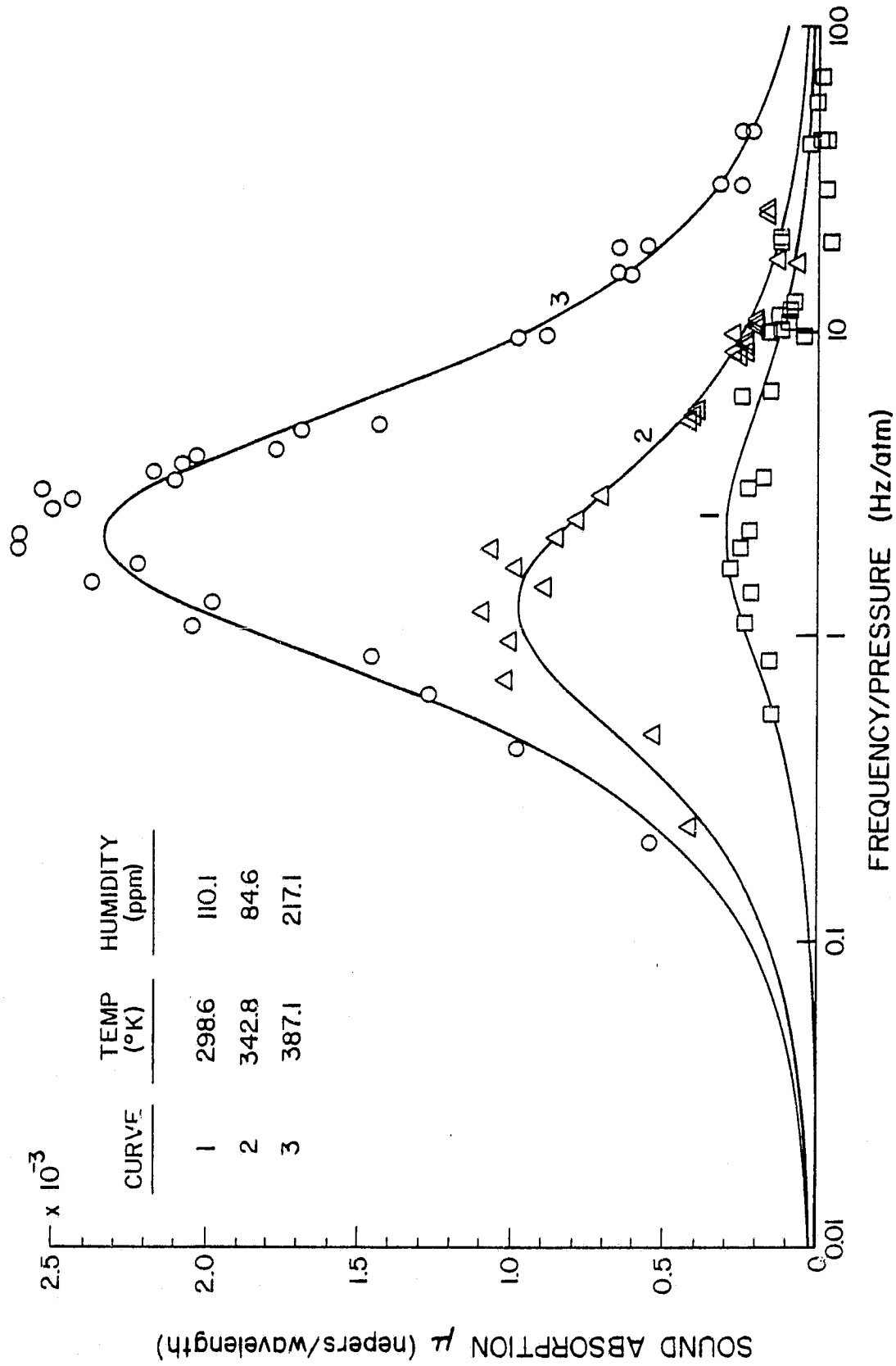
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Figure 4. Sound absorption versus frequency/pressure ratio for N_2-H_2O binary mixtures at three different temperatures. The solid lines are best fits to Eq. (3).

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