

Acoustic attenuation in three-component gas mixtures—Theory

Y. Dain and Richard M. Lueptow^{a)}

Department of Mechanical Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3111

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Vibrational relaxation accounts for absorption and dispersion of acoustic waves in gases that can be significantly greater than the classical absorption mechanisms related to shear viscosity and heat conduction. This vibrational relaxation results from retarded energy exchange between translational and intramolecular vibrational degrees of freedom. Theoretical calculation of the vibrational relaxation time of gases based on the theory of Landau and Teller [Phys. Z. Sovjetunion **10**, 34 (1936); **1**, 88 (1932); **2**, 46 (1932)] and Schwartz *et al.* [J. Chem. Phys. **20**, 1591 (1952)] has been applied at room temperature to ternary mixtures of polyatomic gases containing nitrogen, water vapor, and methane. Due to vibrational-translational and vibrational–vibrational coupling between all three components in ternary mixtures, multiple relaxation processes produce effective relaxation frequencies affecting the attenuation of sound. The dependence of effective relaxation frequencies and the attenuation on mole fractions of the constituents was investigated. The acoustic attenuation in a mixture that is primarily nitrogen is strongly dependent on the concentrations of methane and water vapor that are present. However, the attenuation in a mixture that is primarily methane is only weakly dependent on the concentrations of nitrogen and water vapor. The theory developed in this paper is applicable to other multicomponent mixtures. © 2001 Acoustical Society of America. [DOI: 10.1121/1.1352087]

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I. INTRODUCTION

The anomalous absorption and dispersion of sound waves in polyatomic gases has been studied for nearly seven decades. The pioneering studies of Zener,¹ and Landau and Teller^{2–4} laid the foundation of the theory of vibrational energy transfer in diatomic gases. Later, the theory of vibrational relaxation was successfully applied by Kneser,⁵ Schwartz *et al.* (SSH),⁶ and Tanczos⁷ to explain the absorption and dispersion of sound waves in polyatomic gases. The further application of the SSH theory to the investigation of sound in pure gases and binary gas mixtures was reviewed by Herzfeld and Litovitz,⁸ Burnett and North,⁹ and Lambert.¹⁰ The complexity of molecular relaxation processes can lead to a complicated mechanism of vibrational-translational and vibrational–vibrational energy transfer between different molecular energy levels producing several effective relaxation frequencies depending on the vibrational modes involved in the relaxation process. Consequently, the effective relaxation frequencies of multi-component gas mixtures depend on the concentrations of the gases in the mixture.

Several phenomenological alternatives to the SSH theory have been used for binary and multi-component gas mixtures. Bauer developed a method to obtain relaxation equations for the phenomenological theory of simultaneous multiple relaxation processes.¹¹ His general theory calculates the eigenvalues of coupled relaxations in terms of the individual relaxation times including the cross terms. Each energy process between two vibrational levels is considered as a reaction. Zuckerwar and Miller applied Bauer's phenom-

enological treatment to the case of a mixture of nitrogen, oxygen, water vapor, and carbon dioxide.¹² They provided analytical expressions for coupled effective relaxation frequencies of oxygen and nitrogen in air depending on small concentrations of water vapor and carbon dioxide. Henderson and Herzfeld applied a similar analysis to air/water vapor mixtures using the semi-empirical dependence of the effective relaxation frequency of oxygen on water vapor.¹³ The general formalism of the theory of sound absorption of Bauer has been used to deduce relaxation equations with the functional form of relaxation frequencies of moist oxygen and nitrogen determined empirically from experimental measurements of sound absorption in air. A thorough review of the relaxation frequencies of nitrogen and oxygen as functions of humidity is provided by Bass *et al.*, with a focus on acoustic attenuation in the atmosphere.¹⁴

Townsend and Meador used the usual gas species continuity and momentum equations together with reaction kinetics to derive a wave equation for a single parameter (pressure or density) in a binary mixture.¹⁵ The absorption coefficient was decomposed into the sum of two contributions, which cannot be uniquely identified with either of the two species. This formula was used to calculate the absorption coefficient for a nitrogen/water vapor mixture, comparing favorably with experimental data of Zuckerwar and Griffin.¹⁶

Experimental results for multi-component mixtures of the gases that we consider in this paper are sparse. The dependence of the relaxation frequency of nitrogen on mole fractions of carbon dioxide and water vapor was experimentally investigated at 448 K by Henderson *et al.*¹⁷ They observed a synergistic effect of both additives resulting in a

^{a)}Electronic mail: r-lueptow@northwestern.edu

nonlinear shift of the relaxation frequency of nitrogen with the mole fraction of the additives. Zuckerwar and Griffin experimentally studied the vibrational relaxation peak in nitrogen/water vapor binary mixtures as a function of humidity and derived the reaction rate constants assuming that vibrational–vibrational energy transfer provides the dominant relaxation path.¹⁶

The present study is an investigation of the relaxational component of the attenuation coefficient in a ternary mixture of polyatomic gases at room temperatures based on the SSH theory. Specifically, we consider two cases: nitrogen with small amounts of water vapor and methane, and methane with small amounts of water vapor and nitrogen. This work is unique in that it is the first application of SSH theory to multi-component mixtures to our knowledge. Previously, SSH theory has only been applied to pure gases and binary mixtures of gases.

In this paper the plane acoustic wave propagation in a gas mixture is described by the Euler equations linearized around the equilibrium density, pressure, and temperature. The total gas energy is the sum of translational energy and internal molecular vibrational energies,⁶ depending on kinetic processes between vibrational modes of the constituents. The relaxation equations, which are written following Landau and Teller,² Schwartz *et al.*,⁶ and Tanczos⁷ establish a link between the internal molecular vibrational “temperatures” and the translational temperature of the gas. In the case of acoustic attenuation, the deviations from equilibrium temperature are small, and the relaxation system is a linear system of ordinary differential equations. Coefficients of the matrix of the relaxation system can be expressed in terms of transition probabilities. For the calculation of the transition probabilities, the SSH theory, which agrees relatively well with experimental data for nitrogen and methane at room temperature,¹⁰ is used.

II. THEORY FOR RELAXATION IN MULTI-COMPONENT MIXTURES

The theory is based on the Euler gas equations as the model of a continuous medium for a polyatomic gas mixture accompanied by nonlinear semi-macroscopic population equations for the number of molecules in a given energy state.¹⁸ In the acoustic approximation, these equations yield acoustical equations and a linear system of ordinary differential equations describing multiple relaxation processes. Consequently, we do not include the classical effects of viscosity and heat transfer on the acoustic attenuation. These effects can be calculated separately. Assuming that there is no diffusion of gas components, the acoustic equations for a gas mixture including the internal temperatures of molecular vibrational modes can be written in the form

$$\begin{aligned} \frac{p}{p_0} &= \frac{T}{T_0} + \frac{\rho}{\rho_0}, \quad \frac{\partial \rho}{\partial t} + \rho_0 \frac{\partial u}{\partial x} = 0, \quad \frac{\partial u}{\partial t} + \rho_0^{-1} \frac{\partial p}{\partial x} = 0, \\ \frac{\partial \epsilon}{\partial t} - p_0 \rho_0^{-2} \frac{\partial \rho}{\partial t} &= 0, \\ \epsilon &= c_v T + \alpha_1 c_1^{\text{vib}} T_1^{\text{vib}} + \alpha_2 c_2^{\text{vib}} T_2^{\text{vib}} + \alpha_3 (c_3^{\text{vib}} T_3^{\text{vib}} + c_4^{\text{vib}} T_4^{\text{vib}}), \end{aligned} \quad (1)$$

$$\sum_{i=1}^3 \alpha_i = 1, \quad c_v = \sum_{i=1}^3 \alpha_i c_v^i,$$

where p , ρ , u , ϵ , T , and T_j^{vib} are small fluctuations of pressure, density, velocity, energy, and temperatures around the equilibrium value. Here α_i are mole fractions of the three gas constituents, and c_v^i are the translational specific heat capacities of mixture constituents, i . For molecular vibrational mode j , c_j^{vib} are the vibrational specific heat capacities, and T_j^{vib} are the internal temperatures.

The fifth equation of Eq. (1) represents the fluctuation of the total energy ϵ of the gas mixture. The total energy depends not only on the gas temperature T , but also on the internal temperatures of excited molecule mode T_j^{vib} . We have assumed that there are only three gas components. The first two gases having mole fractions α_1 and α_2 are assumed to each have one vibrational mode with energies $c_1^{\text{vib}} T_1^{\text{vib}}$ and $c_2^{\text{vib}} T_2^{\text{vib}}$, respectively. We consider two vibrational modes with energies $c_3^{\text{vib}} T_3^{\text{vib}}$ and $c_4^{\text{vib}} T_4^{\text{vib}}$ for the third gas having mole fraction α_3 . As will be discussed later, nitrogen and water vapor are modeled with a single vibrational mode, while methane is modeled with two vibrational modes. Clearly the fifth equation of Eq. (1) could be extended to accommodate any number of constituent gases, each with any number of vibrational modes.

We assume that the translational degrees of freedom of each of the gases in the mixture are in equilibrium at equilibrium temperature T_0 . The mean equilibrium pressure and density are p_0 and ρ_0 , where

$$p_0 = \rho_0 R T_0, \quad R = \frac{R}{M}. \quad (2)$$

Here R is the gas constant per unit mass, R is the universal gas constant, and M is the mean molecular weight of the mixture. By definition, the total fluctuation of gas density of the mixture is

$$\rho = \sum_{i=1}^3 \alpha_i \rho_i. \quad (3)$$

Molecules gain and lose vibrational and translational energy in collisions. The kinetic nature of the collision process is thus of fundamental importance for investigation of relaxation processes and acoustic absorption. The relaxation equations for internal molecular temperatures depend to a large measure on the model of energy transitions and kinetic processes including: (1) vibrational-translational (V-T) energy exchange between vibrational and translational degrees of freedom for one type of molecule; (2) vibrational-translational (V-T) energy exchange for vibrational and translational degrees of freedom between different types of molecules; (3) vibrational–vibrational (V–V) energy exchange within a given type of molecule; (4) vibrational–vibrational (V–V) energy exchange between vibrational modes of different types of molecules. Thus the collisional reactions of excitation and deexcitation are of the form

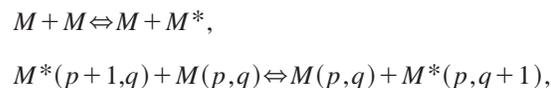
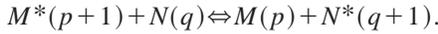
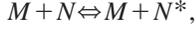


TABLE I. Vibrational frequencies and collisional parameters for Lennard-Jones potential (Refs. 10, 19).

	r_0 (Å)	ϵ_{LJ} (cal mol ⁻¹)	Normal modes of vibration (cm ⁻¹)	g	Vibrational amplitude coefficients (a.m.u. ⁻¹)
N ₂	3.749	159	$\nu=2331$	1	0.0354
H ₂ O	2.65	760	$\nu_1=3657$	1	0.9539
			$\nu_2=1596$	1	0.9527
			$\nu_3=3756$	1	0.9241
CH ₄	3.796	286	$\nu_1=2915$	1	0.9921
			$\nu_2=1534$	2	0.9921
			$\nu_3=3019$	1	0.9923
			$\nu_4=1306$	3	0.8368



Here M and N denote species of the mixture, and p and q are molecular vibrational modes. An asterisk indicates a molecule excited to the lowest vibrational level above the ground level.

Table I provides the vibrational modes ν_i of nitrogen, water, and methane. The subscripts are numbered according to the spectroscopic convention.¹⁹ The frequencies are expressed using the spectroscopic convention in terms of inverse wavelength. Multiplying the numerical value by the speed of light (3.00×10^{10} cm/s) provides the value for the mode in units of frequency (Hz).

In this analysis we consider only relatively low temperatures. We assume that only the lowest modes are significant, since the contribution of higher modes to molecular energy transfer at room temperature is small. Consequently, energy exchange occurs only between the following vibrational modes: $\nu=2331$ cm⁻¹ of N₂, $\nu_2=1596$ cm⁻¹ of H₂O, and $\nu_2=1534$ cm⁻¹ and $\nu_4=1306$ cm⁻¹ of CH₄. The second vibrational mode ν_2 of CH₄ is included along with the lowest modes of other constituents due to its near resonance with the mode $\nu_2=1596$ cm⁻¹ of H₂O. For notational simplicity, n_i denotes the vibrational modes when multiplied by the speed of light. Thus n_1 corresponds to the vibrational mode of N₂, n_2 corresponds to the lowest vibrational mode of H₂O, and n_3 and n_4 are the two lowest vibrational modes of CH₄.

The vibrational specific heats for the vibrational modes in Eq. (1) are given by the Planck–Einstein function²⁰ for a harmonic oscillator

$$c_i^{\text{vib}} = g_i R \left(\frac{\theta_i^{\text{vib}}}{T_0} \right)^2 \frac{\exp(\theta_i^{\text{vib}}/T_0)}{(\exp(\theta_i^{\text{vib}}/T_0) - 1)^2}, \quad \theta_i^{\text{vib}} = \frac{hn_i}{k}, \quad (4)$$

where $h=6.626 \times 10^{-34}$ J s is Planck's constant, $k=1.380 \times 10^{-23}$ J/K is Boltzmann's constant, θ_i^{vib} is the characteristic temperature for vibration, and g_i is the degeneracy of the mode (listed in Table I), which is related to the geometric structure of the molecule.

We assume that at room temperature only one-quantum collisional reactions are possible. By analogy to Landau and Teller² and Schwartz *et al.*⁶ we can deduce relaxation equations for the internal energies of the four vibrational modes n_j participating in the relaxation process of the form

$$\frac{dT_j^{\text{vib}}}{dt} = \frac{T - T_j^{\text{vib}}}{\tau_j^{\text{tran}}} + \sum_{\substack{k=1 \\ k \neq j}}^4 \frac{1}{\tau_{j,k}^{\text{vib}}} \frac{1 - \exp(-hn_j/kT_0)}{1 - \exp(-hn_k/kT_0)} \times \left[(T - T_j^{\text{vib}}) - \frac{n_k}{n_j} (T - T_k^{\text{vib}}) \right], \quad j=1, \dots, 4. \quad (5)$$

The translational (V-T) relaxation times that appear in Eq. (5) are

$$\frac{1}{\tau_j^{\text{tran}}} = \sum_{i=1}^3 \frac{\alpha_i}{\tau_{j,i}^{\text{tran}}}, \quad \frac{1}{\tau_4^{\text{tran}}} = \sum_{i=1}^2 \frac{\alpha_i}{\tau_{4,i}^{\text{tran}}} + \frac{\alpha_3}{\tau_{4,4}^{\text{tran}}}, \quad j=1, \dots, 3; \quad (6)$$

$$\tau_{j,i}^{\text{tran}^{-1}} = Z(j,i) P_{0 \rightarrow 0}^{1 \rightarrow 0}(j,i) (1 - \exp(-hn_j/kT)). \quad (7)$$

The paired vibrational (V-V) relaxation times for excitation processes with two vibrational modes involved are

$$\tau_{j,k}^{\text{vib}^{-1}} = \alpha_k g_k Z(j,k) P_{0 \rightarrow 1}^{1 \rightarrow 0}(j,k), \quad j, k=1, \dots, 4, \quad j \neq k, \quad \alpha_3 = \alpha_4. \quad (8)$$

Here $Z(j,k)$ are collision rates of molecules of specie j with molecules of specie k . $P_{0 \rightarrow 0}^{1 \rightarrow 0}(j,k)$ and $P_{0 \rightarrow 1}^{1 \rightarrow 0}(j,k)$ are transitional probabilities of V-T and V-V exchange of vibrational energy per collision between different vibrational modes.

The calculation of the number of collisions per molecule is conveniently based on the kinetic theory expression for a gas of rigid spheres¹⁰

$$Z(j,k) = 2N_k \left(\frac{\sigma_j + \sigma_k}{2} \right)^2 (2\pi kT(m_j + m_k)/m_j m_k)^{1/2}, \quad (9)$$

where N_k is the number of molecules of species k per unit volume, σ_j, σ_k are collision diameters, and m_j, m_k are the molecular masses of species.

The calculation of transition probabilities $P_{0 \rightarrow 0}^{1 \rightarrow 0}(j,k)$ and $P_{0 \rightarrow 1}^{1 \rightarrow 0}(j,k)$ is a more complicated problem. It is based on a solution of the Schrödinger equation for binary collisions of two molecules in a mixture. The solution depends on assuming special collisional conditions and is based on the molecular properties of the species. There are various approximations and approaches to estimate such a solution. Here we will use the approximate formulas of transition probabilities for polyatomic gases derived by Tanczos⁷ [Eq. (1)] for the evaluation of V-T and V-V transition probabilities $P_{0 \rightarrow 0}^{1 \rightarrow 0}(j,k)$ and $P_{0 \rightarrow 1}^{1 \rightarrow 0}(j,k)$. The general Tanczos equation for the transition probabilities is quite complicated and not included here. Suffice it to say that the equation depends on geometrical factors, collision cross-section factors, vibrational factors, the total change in translational energy, the Lennard-Jones potential, and an intermolecular force constant. Methods for determining these items are outlined by Tanczos.⁷ Values for constants for the three gases of interest are listed in Table I, based on Tables 1.1, 3.1 and 3.2 in the book by Lambert.¹⁰ The values for $P_{0 \rightarrow 1}^{1 \rightarrow 0}(j,k)$ are given in Table II.

The relaxation system Eq. (6) can be written in the vector form as

$$\frac{dT^{\text{vib}}}{dt} = -AT^{\text{vib}} + qT, \quad (10)$$

TABLE II. $P_{0 \rightarrow 1}^{1 \rightarrow 0}(j, k)$, where j is the row number, k is the column number.

not used	$1.43e-005$	$1.54e-006$	$1.12e-005$
$3.67e-007$	not used	0.12	0.41
$6.27e-009$	0.02	not used	0.05
$1.48e-007$	0.21	0.16	not used

where matrix $A = A(\alpha_1, \alpha_2, \alpha_3)$ of the system and the vector $q = q(\alpha_1, \alpha_2, \alpha_3)$ depend on the mole fractions α_i of gas constituents according to:

$$A_{jj} = \frac{1}{\tau_j^{\text{tran}}} + \sum_{\substack{k=1 \\ k \neq j}}^4 \frac{1}{\tau_{j,k}^{\text{vib}}} \frac{1 - \exp(-hn_j/kT_0)}{1 - \exp(-hn_k/kT_0)},$$

$$A_{jk} = -\frac{1}{\tau_{j,k}^{\text{vib}}} \frac{1 - \exp(-hn_j/kT_0)}{1 - \exp(-hn_k/kT_0)} \frac{n_k}{n_j}, \quad (11)$$

$$q_j = \frac{1}{\tau_j^{\text{tran}}} + \sum_{\substack{k=1 \\ k \neq j}}^4 \frac{1}{\tau_{j,k}^{\text{vib}}} \frac{1 - \exp(-hn_j/kT_0)}{1 - \exp(-hn_k/kT_0)} \left[1 - \frac{n_k}{n_j} \right],$$

$$j, k = 1, \dots, 4, j \neq k.$$

To summarize the calculation procedure for molecular relaxation: The collision rates $Z(j, k)$ and transition probabilities $P_{0 \rightarrow 0}^{1 \rightarrow 0}(j, k)$ and $P_{0 \rightarrow 1}^{1 \rightarrow 0}(j, k)$ at a given temperature and pressure are calculated based on Eq. (9) and the SSH-Tanzcos theory. Then the relaxation times $\tau_{j,k}^{\text{vib}}$, and τ_j^{tran} are calculated based on the constituent gas concentrations as well as the collision rates and transition probabilities using Eqs. (7) and (8). Substitution of these values into Eqs. (10) and (11) provides a system of first order differential equations that can be solved numerically for T_j^{vib} . Then these values can be substituted into the fifth equation of Eq. (1) for the total energy of the gas mixture. Finally Eqs. (1) are solved as described below.

III. SOLUTION PROCEDURE

The calculation of the attenuation of the acoustic wave in a gas mixture requires the solution of the united system of differential equations (1) and (10), is sought in the form of a harmonic plane wave with all quantities p, ρ, u, ϵ, T , and T_j^{vib} expressed in the plane wave form

$$f = \bar{f} e^{-i(\omega t - kx)}, \quad (12)$$

where \bar{f} is the amplitude of the quantity. The substitution of Eq. (12) into the system of differential equations leads to a homogeneous system of algebraic equations in terms of the amplitudes

$$\frac{\bar{p}}{\rho_0} = \frac{\bar{T}}{T_0} + \frac{\bar{\rho}}{\rho_0}, \quad -\omega \bar{p} + \rho_0 k \bar{u} = 0, \quad \omega \bar{u} - \rho_0^{-1} k \bar{p} = 0, \quad (13)$$

$$\bar{\epsilon} - p_0 \rho_0^{-2} \bar{\rho} = 0,$$

where

$$\bar{\epsilon} = c_v \bar{T} + \sum \alpha_i c_i^{\text{vib}} \bar{T}_i^{\text{vib}}. \quad (14)$$

Likewise, the substitution of Eq. (12) into the system of differential equations (10) leads to the algebraic equation

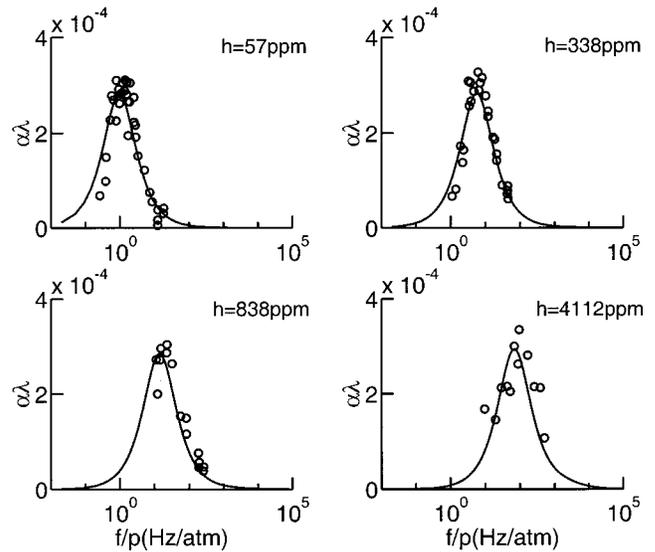


FIG. 1. Comparison of theoretical sound absorption curves with experimental data in N_2 - H_2O mixtures for different H_2O concentrations (h). Symbols: Experimental data from Zuckerwar and Griffin (Ref. 16). Curves: Theoretically predicted attenuation curves ($T = 297$ K, $P = 1$ atm).

$$(i\omega I + A) \bar{T}^{\text{vib}} = q \bar{T}. \quad (15)$$

This equation relates the amplitudes of the internal molecular temperatures \bar{T}^{vib} to the amplitude of the gas temperature \bar{T} , where the rows of the matrix A correspond to the vibrational modes under consideration, the columns correspond to the vibrational reactions, and I is the identity matrix.

Equations (13), (14), and (15) can be combined in matrix form as

$$\mathbf{B}y = 0, \quad y = (\bar{\rho}, \bar{u}, \bar{p}, \bar{T}, \bar{T}_1^{\text{vib}}, \bar{T}_2^{\text{vib}}, \bar{T}_3^{\text{vib}}, \bar{T}_4^{\text{vib}}), \quad (16)$$

where \mathbf{B} is an 8×8 matrix of coefficients. These coefficients depend on the gas concentration α_i , the frequency ω , and the coefficients of the matrix A calculated for the vibrational modes n_i under consideration. Setting the determinant of ma-

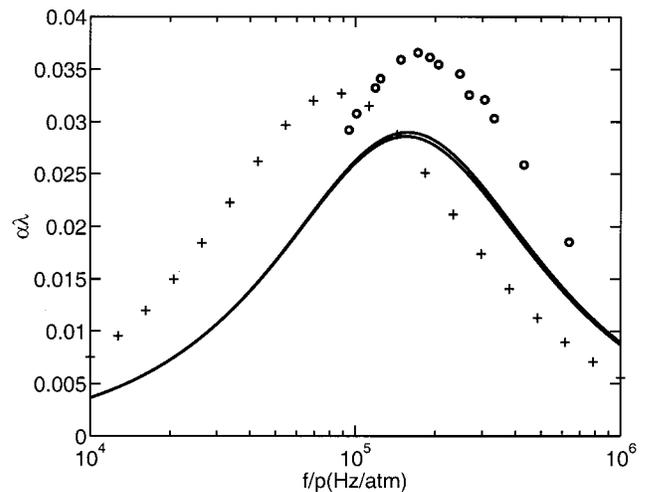


FIG. 2. Comparison of theoretical relaxation attenuation with experimental data for CH_4 . Symbols: Experimental data from Edmonds and Lamb (Ref. 22) ($T = 298.15$ K, $P = 1$ atm, curve fit through data, +), and Gravitt *et al.* (Ref. 24) ($T = 299.15$ K, $P = 1$ atm, circles). Curves: Theoretically predicted attenuation (lower curve 298.15 K, upper curve 299.15 K).

trix **B** equal to zero provides a dispersion relation, which can be solved numerically to provide k as a function of ω . The wave number k is in general a complex value: $k = k_R + i\alpha$. The real part is proportional to the reciprocal of the wavelength, $k_R = 2\pi/\lambda$, and determines the actual speed of wave propagation, $a = \omega/k_R$. The dimensionless attenuation coefficient per wavelength is $\alpha\lambda$.

To test our procedure, we compared our calculation of sound absorption in a binary N_2 - H_2O mixture with experimental results. In this case, the coefficient matrix is much simpler, since $\alpha_3 = 0$. Using the procedure described above, the attenuation can be calculated as a function of frequency. The results of the calculation are compared to the experimental data of Zuckerwar and Griffin¹⁶ in Fig. 1 for four different concentrations of water vapor. Although the theory slightly under-predicts the relaxation frequency at which the maximum attenuation occurs, the overall fit of the model to the experimental results is quite good.

The vibrational relaxation of methane has been measured based upon reverberation experiments, acoustic resonance tube measurements, and the ultrasonic velocity method.²¹⁻²⁵ The experimental results at room temperatures (shown in Table III) indicate a relaxation frequency either near 1.5×10^5 Hz, which agrees quite well with our calculations, or slightly less than 1.0×10^5 Hz. In two cases,^{22,24} it is possible to compare results over a range of frequencies, as

TABLE III. Comparison of theoretical calculations with experimental data for CH_4 relaxation.

Temperature (K)	Calculated relaxation frequency (10^5 Hz)	Experimental relaxation frequency (10^5 Hz)	Reference
382	3.10	1.89	Eucken and Aybar (Ref. 21)
298.15	1.46	0.85	Edmonds and Lamb (Ref. 22)
296	1.43	1.48	Parker and Swope (Ref. 23)
299.15	1.48	1.7	Gravitt <i>et al.</i> (Ref. 24)
303	1.53	0.94	Cottrel and Day (Ref. 25), 0.3% N_2

shown in Fig. 2. The amplitude of the calculated attenuation is somewhat less than the experimental value, but clearly in the proper range. The relaxation frequency matches one experiment quite well and is only slightly different from the other. Given the variability in the experimental results evident in Fig. 2 and Table III, it is clear that the calculations agree quite well with the experiments.

IV. RESULTS

We first consider a N_2 - H_2O - CH_4 mixture, when water vapor and methane are small additives with volume concentrations of 0.03. Evaluation of matrix A at a temperature of 297 K and a pressure of 1 atm produces the relaxation matrix

$$A = \begin{pmatrix} 1.17e+004 & -2.95e+003 & -715 & -4.05e+003 \\ -4.90e+003 & 4.28e+008 & -1.05e+008 & -2.88e+008 \\ -96.05 & -9.32e+006 & 4.31e+007 & -4.15e+007 \\ -1.94e+003 & -8.36e+007 & -1.36e+008 & 2.40e+008 \end{pmatrix}. \quad (17)$$

Eigenvalues λ_i of matrix (17) define effective relaxation frequencies $f_i = \lambda_i/2\pi$ of the ternary mixture which are equal to

$$\begin{aligned} f_1 &= 1860 \text{ Hz}, & f_2 &= 2.19 \times 10^4 \text{ Hz}, \\ f_3 &= 3.12 \times 10^7 \text{ Hz}, & f_4 &= 8.21 \times 10^7 \text{ Hz}. \end{aligned} \quad (18)$$

The corresponding normalized eigenvectors V_i of matrix A for eigenvalues λ_i are presented in Table IV. Elements of the eigenvectors describe the degree of participation of a vibrational mode in the relaxation of the complex. The first eigenvector V_1 in Table IV indicates that the nitrogen contribution to the relaxing complex is unity. Therefore, the effective relaxation frequency f_1 can be considered as the effective relaxation frequency of nitrogen as modified by the two small additives of water and methane. Eigenvector V_2 corresponding to the effective relaxation frequency f_2 has detectable but small nitrogen contribution. The effective relaxing complex comprises water and both modes of methane. The nitrogen contribution in relaxing complexes for eigenvectors V_3 and V_4 corresponding to effective relaxation frequencies f_3 and f_4 is negligible. The effective complex for f_3 is water and both modes of methane, whereas the relaxing complex for f_4 is water and mode n_4 of methane.

The results in Eqs. (17), (18), and Table IV are for a mixture of 3% water vapor, 3% methane, and 94% nitrogen. Of course similar results can be obtained for other concentrations of constituents. The constituent concentration alters the translational and vibrational relaxation times [Eqs. (6), (7), and (8)] thereby altering the relaxation matrix A . Thus the relaxation frequencies and eigenvectors can be found as functions of concentrations of water vapor and methane. Figure 3(a) shows the dependence of the lowest relaxation frequency f_1 on the concentration of methane and water vapor. The relaxation frequency is linearly dependent on the concentration of both methane and water vapor, except at very low methane concentrations. Likewise, the second lowest re-

TABLE IV. Normalized eigenvectors V_i of matrix A for 94% N_2 -3% H_2O -3% CH_4 .

	V_1	V_2	V_3	V_4
$N_2(\nu_1)$	1.000	-0.034	-0.000	0.000
$H_2O(\nu_2)$	0.005	0.529	0.717	-0.956
$CH_4(\nu_3)$	0.006	0.645	-0.223	-0.007
$CH_4(\nu_4)$	0.005	0.550	0.661	0.293

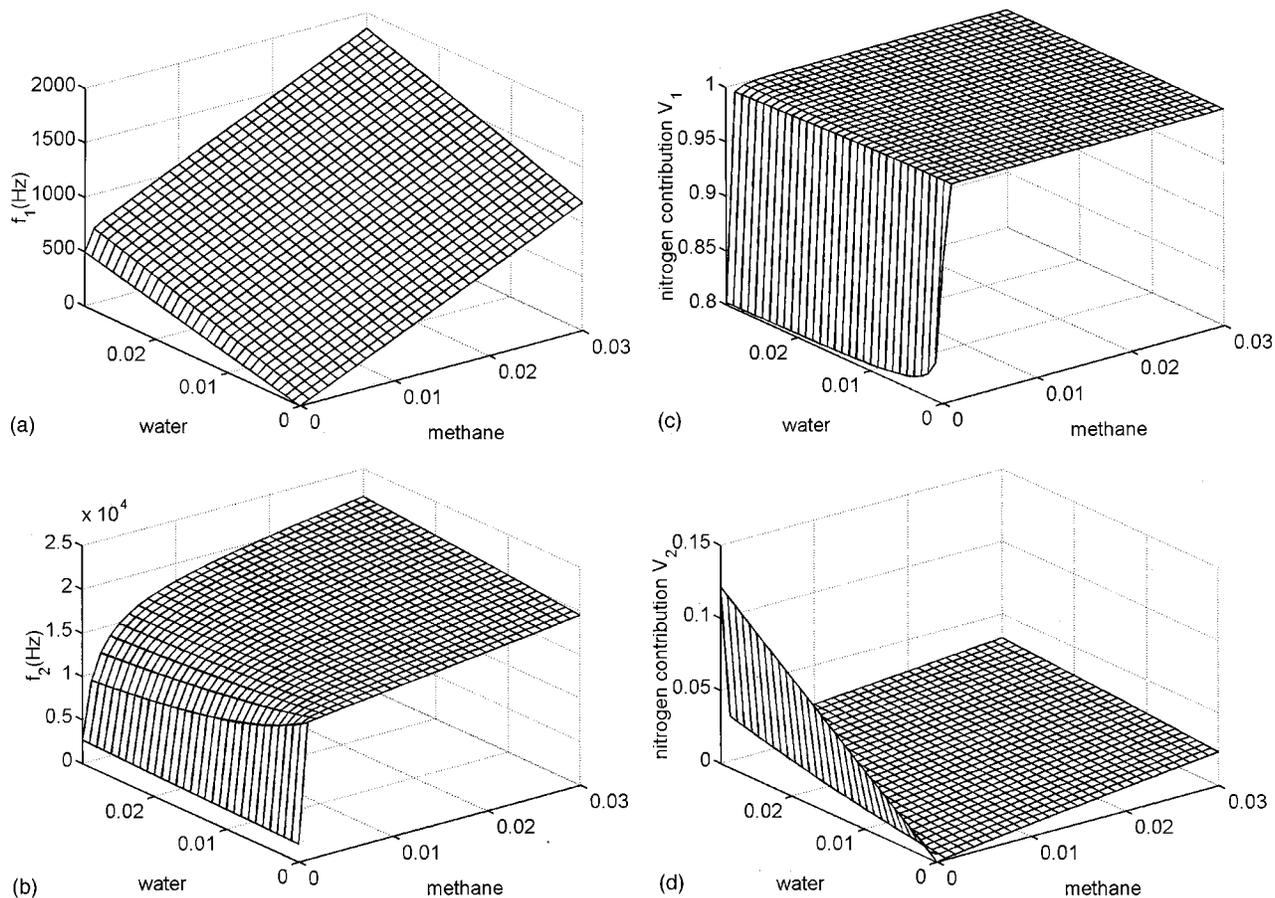


FIG. 3. Dependence of effective relaxation on the concentration in a ternary N_2 - H_2O - CH_4 mixture ($T=297$ K, $P=1$ atm). (a) Relaxation frequency f_1 ; (b) Relaxation frequency f_2 ; (c) Nitrogen contribution term of the eigenvector for f_1 ; (d) Nitrogen contribution term of the eigenvector for f_2 .

relaxation frequency f_2 is also linearly dependent on concentration except at low methane concentrations, as shown in Fig. 3(b). The reason for the nonlinearity at low concentrations of methane is evident from the nitrogen contribution to the relaxation as indicated in the first term of the eigenvector. The value of this term is plotted as a function of concentration in Fig. 3(c). This term has a value near unity except at very low methane concentrations where its value drops precipitously. The first term of the eigenvector related to the contribution of nitrogen is much smaller for the second lowest frequency f_2 . The plot of its value as a function of concentration in Fig. 3(d) shows a sharp change in its value at low methane concentration. The concentration for which the value changes sharply corresponds to the concentration for which the second relaxation frequency varies nonlinearly with methane concentration.

The third and fourth relaxation frequencies are linearly dependent on the water vapor and methane concentration as shown in Fig. 4. In both cases, the contribution of the nitrogen to the relaxation is so small that it does not result in any nonlinearity.

While the variation of the relaxation frequencies with concentration is of interest with respect to the physical phenomenon of vibrational relaxation, the key physical result is the attenuation of sound. The attenuation of sound is found by solving for the dispersion relation of Eq. (16). For a specified concentration of constituent gases in the mixture, the

dispersion relation provides the imaginary part of the wave number α , which is the sound absorption, as a function of frequency ω . Figure 5 shows the relaxational and classical attenuation curves of a 94% N_2 -3% H_2O -3% CH_4 mixture of gases as a function of frequency. For comparison, the relaxation attenuation of a 97% N_2 -3% H_2O and a 97% N_2 -3% CH_4 binary gas mixtures are also shown in the figure. Only the peak corresponding to effective relaxation frequency f_2 of the ternary mixture (bold curve) is evident. Effective relaxation frequencies f_3 and f_4 are at much higher frequencies and the absorption related to these frequencies is quite small. There is a slight inflection in the N_2 - H_2O - CH_4 curve near $f/p \approx 10^3$ Hz/atm that corresponds approximately to the peak in the N_2 - H_2O curve. The major peak at relaxation frequency f_2 in the N_2 - H_2O - CH_4 curve corresponds to the major peak in the N_2 - CH_4 curve, although a slight inflection is evident in the N_2 - CH_4 curve at a lower frequency, probably corresponding to the interaction with nitrogen.

For comparison, the classical attenuation due to viscosity and heat conduction was calculated for the gas mixture using the classical formula.⁸ The viscosity and thermal conductivity used in calculations were based on physical properties software.²⁶ The classical attenuation ranges from 4.5×10^{-7} to 4.5×10^{-3} for $100 \text{ Hz/atm} < f/p < 10^6 \text{ Hz/atm}$. Thus it is clear that the relaxational attenuation is dominant in the range of effective relaxation frequencies f_1 and f_2 .

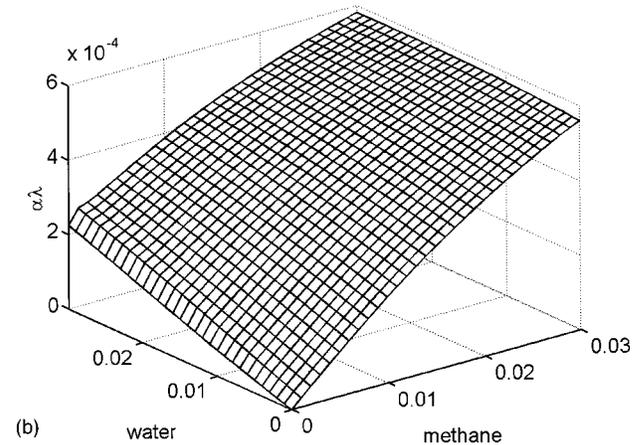
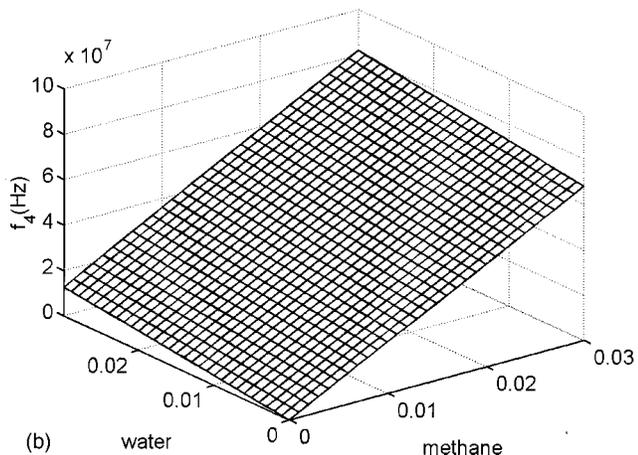
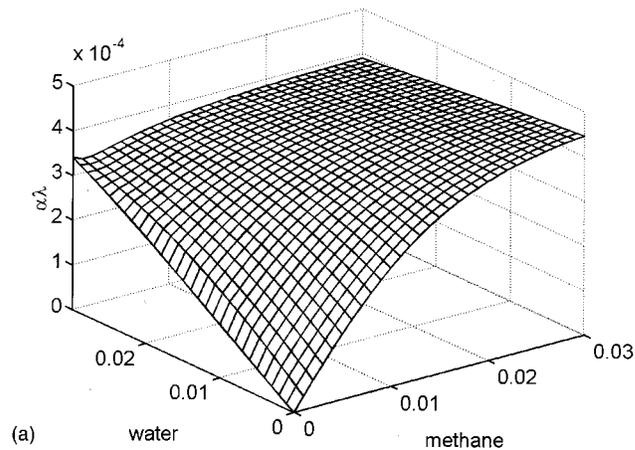
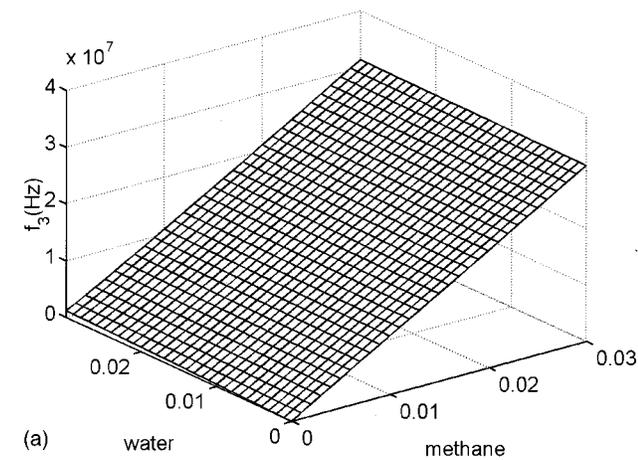


FIG. 4. Dependence of effective relaxation on the concentration in a ternary N_2 - H_2O - CH_4 mixture ($T=297$ K, $P=1$ atm). (a) Relaxation frequency f_3 ; (b) Relaxation frequency f_4 .

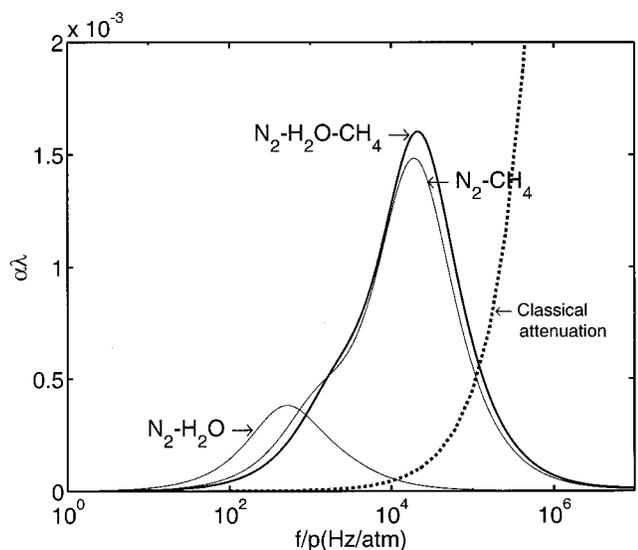


FIG. 5. Comparison of relaxation attenuation curves of a ternary N_2 - H_2O - CH_4 mixture with that for binary N_2 - H_2O and N_2 - CH_4 mixtures ($T=297$ K, $P=1$ atm), and classical attenuation. Bold Solid: Ternary N_2 - H_2O - CH_4 mixture with small H_2O and CH_4 additives. Fine Solid: Binary N_2 - CH_4 mixture with small CH_4 additive. Dotted: Classical attenuation for the ternary mixture. In all cases the concentration of the small additives is 0.03.

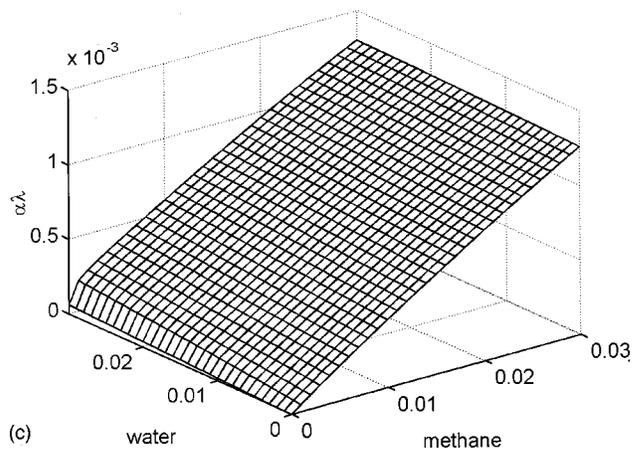


FIG. 6. Dependence of attenuation due to relaxation processes on small concentrations of water and methane for ternary N_2 - H_2O - CH_4 mixture ($T=297$ K, $P=1$ atm). (a) 1 kHz; (b) 2 kHz; (c) 10 kHz.

Classical attenuation dominates at higher frequencies.

Figure 6 shows the attenuation coefficient per wavelength versus concentration of the small additives water vapor and methane at different frequencies of the sound wave. At a frequency comparable with the effective relaxation frequency of nitrogen f_1 (1 kHz) the surface of the attenuation coefficient demonstrate nonlinear dependence on the concentrations of both small additives. When the concentration of one of the additives is equal to zero the attenuation coefficient is a monotonically increasing function of remaining

TABLE V. Normalized eigenvectors V_i of matrix A for 94% CH_4 -3% H_2O -3% N_2 .

	V_1	V_2	V_3	V_4
$\text{N}_2(\nu_1)$	1.000	-0.132	-0.000	0.000
$\text{H}_2\text{O}(\nu_2)$	0.000	-0.524	0.734	-0.999
$\text{CH}_4(\nu_3)$	0.000	-0.650	-0.172	-0.000
$\text{CH}_4(\nu_4)$	0.000	-0.546	0.657	0.010

additive's concentration. The attenuation coefficient is not a strong function of the concentrations of either constituent when the concentrations are sufficiently large. At 2 kHz, slightly above the lowest relaxation frequency f_1 , the attenuation almost linearly depends on concentrations of water and

methane. At 10 kHz, a frequency between relaxation frequencies f_1 and f_2 , the attenuation is more strongly dependent on methane concentration than on water concentration. Again it is helpful to consider the classical attenuation for comparison. The maximum classical attenuation for any of the three frequencies in Fig. 6 is 4.6×10^{-5} for 100% N_2 at 10 kHz/atm. Clearly, the relaxational attenuation is dominant at the frequencies shown in Fig. 6 except at very low methane and water concentrations.

Let us now examine attenuation of sound in a CH_4 - H_2O - N_2 mixture, when water vapor and nitrogen are small additives. Evaluation of matrix A at 297 K and 1 atm for a 94% CH_4 -3% H_2O -3% N_2 mixture produces the relaxation matrix

$$A = \begin{pmatrix} 2.37e+005 & -2.95e+003 & -2.24e+004 & -1.27e+005 \\ -157 & 1.34e+010 & -3.31e+009 & -9.01e+009 \\ -3.07 & -9.32e+006 & 1.12e+009 & -1.30e+009 \\ -61.8 & -8.36e+007 & -4.28e+009 & 5.10e+009 \end{pmatrix}. \quad (19)$$

The effective relaxation frequencies are

$$\begin{aligned} f_1 &= 3.77 \times 10^4 \text{ Hz}, & f_2 &= 1.40 \times 10^5 \text{ Hz}, \\ f_3 &= 9.75 \times 10^8 \text{ Hz}, & f_4 &= 2.15 \times 10^9 \text{ Hz}. \end{aligned} \quad (20)$$

The corresponding normalized eigenvectors V_i of matrix A for the eigenvalues are shown in Table V. Nitrogen plays a primary role only in the lowest relaxation frequency. The higher relaxation frequencies result from the relaxing complex of methane and water. In Fig. 7 only one peak corresponding to the effective relaxation frequency $f_2 = 1.4 \times 10^5$ is evident in the attenuation curve for the ternary mixture. The peak can be attributed to the relaxation of a water-methane complex modified slightly by the presence of nitrogen. The effective relaxation frequencies f_1 , f_3 , and f_4 do not play a significant role. The relaxation attenuation curves of a 97% CH_4 -3% H_2O and a 97% CH_4 -3% N_2 binary gas mixtures merge and are similar to the attenuation of a ternary mixture, indicating the dominant role of methane. The dependence of the effective relaxation frequency f_2 on the nitrogen and water vapor concentrations is quite small, varying by only about 2% over 0% to 3% CH_4 and 0% to 3% N_2 . The classical attenuation is negligible in the range of effective relaxation frequency f_2 , but dominates at higher frequencies.

Figure 8 shows the attenuation versus concentrations of the small additives water vapor and nitrogen at different frequencies of the sound wave. The attenuation linearly depends on concentrations of water and nitrogen for all frequencies, although the variation in attenuation is quite small. At 10 kHz, which is much smaller than the effective relaxation frequency f_2 , and at 1 MHz, which is much larger than the effective relaxation frequency f_2 , the attenuation due to

relaxation is quite small compared to the attenuation at 150 kHz, which is quite close to the effective relaxation frequency f_2 . The maximum classical attenuation over the range of concentrations is 2.9×10^{-5} at 10 kHz, 4.4×10^{-4} at 150 kHz, and 2.9×10^{-3} at 1 MHz. Thus the classical attenuation is quite small compared to the attenuation due to relaxation at the two lower frequencies. However, at the higher frequency, the classical attenuation is the same order as the relaxational attenuation.

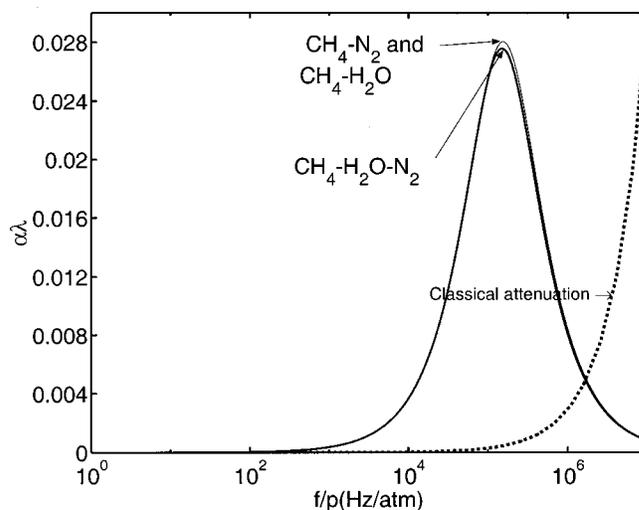


FIG. 7. Comparison of relaxation attenuation curves of a ternary CH_4 - H_2O - N_2 mixture with that for binary CH_4 - H_2O and CH_4 - N_2 mixtures ($T=297 \text{ K}, P=1 \text{ atm}$), and classical attenuation. Bold Solid: Ternary CH_4 - H_2O - N_2 mixture with small H_2O and N_2 additives. Fine Solid: Binary CH_4 - N_2 mixture with small N_2 additive and CH_4 - H_2O mixture with small H_2O additive. Dotted: Classical attenuation for the ternary mixture. In all cases the concentration of the small additives is 0.03.

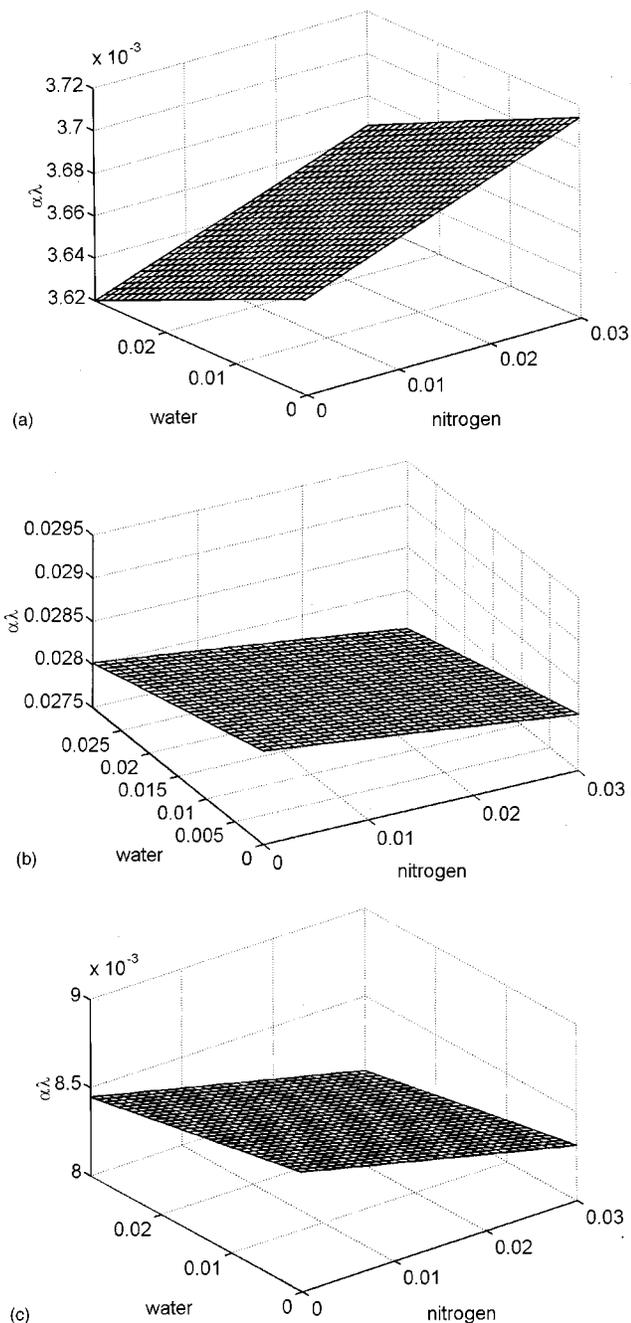


FIG. 8. Dependence of attenuation due to relaxation processes on the concentration of water and nitrogen for ternary $\text{CH}_4\text{-H}_2\text{O-N}_2$ mixtures ($T = 297 \text{ K}, P = 1 \text{ atm}$). (a) 10 kHz; (b) 150 kHz; (c) 1 MHz.

V. CONCLUSIONS

The attenuation due to relaxation processes is the major contributor to acoustic attenuation at low frequencies. Unfortunately, until now the attenuation due to relaxation has been quite difficult to calculate. In this paper we have applied the theory for vibrational energy transfer to multicomponent mixtures. Previously this theory had been applied to single-component and binary mixtures. We have extended the theory to three-component mixtures and indicated how the theory could be extended to mixtures with more components. The theory matches experimental data quite well for a $\text{N}_2\text{-H}_2\text{O}$ binary mixture and for pure methane.

We have applied the theory to mixtures of nitrogen, wa-

ter vapor, and methane where either nitrogen or methane has been the dominant component of the mixture. The relaxation frequencies that were calculated are strongly dependent on the concentration of small additives, even though the concentration of small additives never exceeded 3%. Two relaxation frequencies appear for a mixture that is primarily nitrogen, although one is so strong that it overwhelms the other. Only one relaxation frequency resulted for the attenuation of the gas mixture that was primarily methane.

The important role of small additives is also evident in the acoustic attenuation resulting from the relaxation processes. In the case where nitrogen is the primary component, the attenuation is strongly dependent upon the small concentration of the additives. The influence of additives on the attenuation in a gas mixture that is primarily methane is much smaller. Nevertheless, the attenuation due to relaxation processes is much larger than that due to classical attenuation at low frequencies.

The analysis in this paper makes it clear that the theory of vibrational relaxation can be extended to multi-component mixtures to calculate the attenuation of sound. The weakest portion of the model is the estimation of the transition probabilities in SSH-Tanczos model where the quasi-classical approximation was used for the Lennard-Jones potential at relatively low temperatures. More realistic collision potential functions and the use of molecular dynamics to determine transition probabilities could significantly improve the model. Nevertheless, the model provides a theoretical means to investigate the influence of various conditions including temperature, pressure, and constituent gas concentrations on relaxational attenuation.

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- ¹C. Zener, *Phys. Rev.* **37**, 556–569 (1931).
- ²L. Landau and E. Teller, *Phys. Z. Sowjetunion* **10**, 34–43 (1936).
- ³L. Landau, *Phys. Z. Sowjetunion* **1**, 88–98 (1932).
- ⁴L. Landau, *Phys. Z. Sowjetunion* **2**, 46–51 (1932).
- ⁵H. O. Kneser, *J. Acoust. Soc. Am.* **5**, 122–126 (1933).
- ⁶R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, *J. Chem. Phys.* **20**, 1591–1599 (1952).
- ⁷F. I. Tanczos, *J. Chem. Phys.* **25**, 439–447 (1956).
- ⁸K. F. Herzfeld and T. H. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic, New York, 1959).
- ⁹G. M. Burnett and A. M. North, *Transfer and Storage of Energy by Molecules* (J. W. Arrowsmith Ltd., Bristol, 1969), Vol. 2.
- ¹⁰J. D. Lambert, *Vibrational and Rotational Relaxation in Gases* (Clarendon, Oxford, 1977).
- ¹¹H. J. Bauer, "Phenomenological theory of the relaxation phenomena in gases," in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1965), Vol. 2, Pt. A, Chap. 2, Sec. E, pp. 47–131.
- ¹²A. J. Zuckerwar and K. W. Miller, *J. Acoust. Soc. Am.* **84**, 970–977 (1988).
- ¹³M. C. Henderson and K. F. Herzfeld, *J. Acoust. Soc. Am.* **37**, 986–988 (1965).
- ¹⁴H. E. Bass, L. C. Sutherland, J. Piercy, and L. Evans, "Absorption of Sound by the Atmosphere," in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, Orlando, 1984), Vol. XVII, pp. 145–232.
- ¹⁵L. W. Townsend and W. E. Meador, *J. Acoust. Soc. Am.* **99**, 920–925 (1996).

- ¹⁶A. J. Zuckerwar and W. A. Griffin, *J. Acoust. Soc. Am.* **69**, 150–154 (1981).
- ¹⁷M. C. Henderson, K. F. Herzfeld, J. Bry, R. Coakley, and G. Carriere, *J. Acoust. Soc. Am.* **45**, 109–114 (1969).
- ¹⁸M. N. Kogan, *Rarefield Gas Dynamics* (Plenum, New York, 1969).
- ¹⁹G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1945).
- ²⁰J. P. Holman, *Thermodynamics* (McGraw-Hill, New York, 1988), p. 684.
- ²¹A. Eucken and S. Aybar, *Z. Phys. Chem. Abt. B* **46**, 195–211 (1940).
- ²²P. D. Edmonds and J. Lamb, *Proc. Phys. Soc. London* **72**, 940–948 (1958).
- ²³J. G. Parker and R. H. Swope, *J. Chem. Phys.* **43**, 4427–4434 (1965).
- ²⁴J. C. Gravitt, C. N. Whetstone, and R. T. Langemann, *J. Chem. Phys.* **44**, 70–72 (1965).
- ²⁵T. L. Cottrell and M. A. Day, *J. Chem. Phys.* **43**, 1433–1434 (1965).
- ²⁶PPDS2 for Windows (National Engineering Laboratory, England, 1998).