Acoustic attenuation in a three-gas mixture: Results

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Acoustic attenuation in a mixture of gases results from the combined effects of molecular relaxation and the classical mechanisms of viscosity and heat conduction. Consequently, the attenuation depends on the composition of the gas mixture, acoustic frequency, temperature, and pressure. A model of the relaxational attenuation that permits the calculation of acoustic attenuation is used to predict the effect of composition, frequency, temperature, and pressure on the acoustic attenuation in a three-component gas mixture of nitrogen, methane, and water vapor. The attenuation spectrum is dependent upon the composition through the appearance of peaks in the spectrum related to the relaxation frequencies of the particular components and their relaxing complexes. The relaxation peak related to methane dominates except at low methane concentrations, where the nitrogen peak, which is dependent upon the water vapor and methane concentration, is evident. Temperature and pressure significantly alter the relaxation frequency and the degree of attenuation, but water vapor plays little role in the attenuation. © *2001 Acoustical Society of America.*
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I. INTRODUCTION

Molecular relaxation and the classical mechanisms of viscosity and heat conduction determine the acoustic attenuation in a mixture of gases, depending on the composition of the gas mixture, the acoustic frequency, the temperature, and the pressure. The absorption and dispersion of sound waves in polyatomic gases due to molecular relaxation has been studied for nearly seven decades.[1–6] The molecular relaxation processes can lead to a complicated mechanism of vibrational–translational and vibrational–vibrational energy transfer between different molecular energy levels resulting in several effective relaxation frequencies, depending on the vibrational modes of the species involved in the relaxation processes. The relaxational attenuation has been modeled for pure gases, binary mixtures of gases, and air with carbon dioxide in several ways.[5–9] We have recently extended the Schwartz, Slawsky, and Herzfeld model[5] for the relaxational component of attenuation to a mixture of three or more polyatomic gases at room temperatures based on molecular constants.[10] Although experimental data against which to compare the model are sparse, our theoretical prediction of attenuation for a binary mixture of nitrogen and water vapor and for pure methane match experimental results quite well.[10]

In this paper, we continue our earlier work by using our model to predict the effect of composition, frequency, temperature, and pressure on the acoustic attenuation in a three-component gas mixture of nitrogen, methane, and water vapor. We investigate this particular combination of gases for two reasons. First, the values of the molecular constants necessary to calculate the transition probabilities are available in the literature. Second, the nitrogen–methane–water mixture is representative of gas mixtures that are industrially important. For low concentrations of methane, the mixture is rep-resentative of a combustible air–fuel mixture, with the nitrogen and water vapor representing moist air. (Obviously, the neglect of oxygen in this simplified model is significant.) For high concentrations of methane, the mixture is representative of natural gas, which consists of 75%–99% methane with smaller quantities of higher hydrocarbons and inert components including nitrogen and water vapor.[11]

The focus in this paper is to investigate the effect of composition, frequency, temperature, and pressure on acoustic attenuation using the model from our earlier work.[10] While all of these factors are expected to play a role in the degree of attenuation, the dependence of attenuation on each of them is not readily apparent. The model from our earlier paper permits the independent variation of each of the factors to determine their impact on the attenuation. This allows the prediction of the acoustic attenuation under a variety of conditions in multicomponent gas environments.

II. THE MODEL FOR ACOUSTIC ATTENUATION

A complete description of the theoretical model that we used to calculated the results presented here is given in Dain and Lueptow.[10] Here we only describe the highlights of the model. The theory is based on the Euler gas equations to model a continuous medium consisting of a polyatomic gas mixture accompanied by nonlinear semimacroscopic population equations for the number of molecules in a given energy state.[12] We assume no diffusion of gas components and ignore the effect of rotational relaxation on the acoustic attenuation, since the rotational relaxation contribution is quite similar to the classical contribution at the frequencies that we are considering[9,13] and is negligible in the range of frequencies where the vibrational relaxation is significant.

The Euler equations are in the standard form except that the total energy of the gas mixture depends not only on the gas temperature, but also on the internal temperatures of the excited molecular mode. Molecules gain and lose vibrational

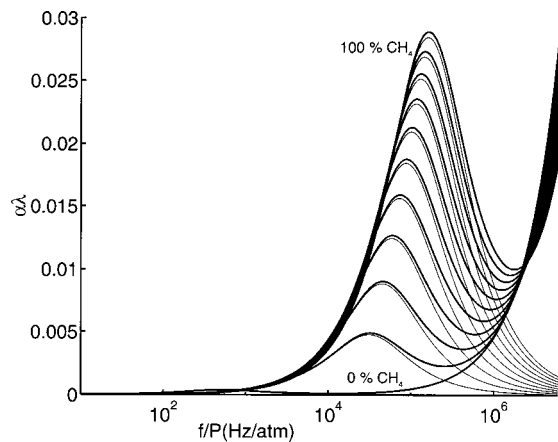[a]Electronic mail: r-lueptow@northwestern.edu

FIG. 1. Nondimensional acoustic attenuation spectrum for 0%,10%,20%, . . . ,100% methane concentrations (from lowest to highest at the relaxational peak) with 3% water vapor (except for 100% methane) and the remainder nitrogen at 297 K. Bold curves are the total attenuation (relaxational plus classical) and fine curves are the relaxational component only.

FIG. 2. Dimensional total acoustic attenuation spectrum for 0%,10%,20%, . . . ,100% methane concentrations (from lowest to highest at 10^5 Hz) with 3% water vapor (except for 100% methane) and the remainder nitrogen at 1 atm and 297 K.

and translational energy in collisions by vibrational–translational and vibrational–vibrational energy exchange. We assume that at room temperature only the lowest vibrational modes are significant and only one-quantum collisional reactions are possible. The relaxation equations are dependent on the collision rates of molecules based on kinetic theory for a gas of rigid spheres and the transitional probabilities of energy exchange per collision between different vibrational modes based on a solution of the Schrödinger equation.[6] The resulting system of first-order differential equations can be solved numerically for the internal temperatures related to the excited modes and substituted into the Euler energy equation, which is solved assuming a plane acoustic wave. The attenuation due to viscous dissipation and irreversible heat conduction are based on the classical formulation by Stokes and Kirchhoff[14] using the coefficient of shear viscosity, the thermal conductivity, and the specific heats of the gas mixtures calculated according to commercial software.[15]

In this paper we use the relaxation model along with the classical mechanisms to analyze the acoustic attenuation under a variety of conditions. We present the results of computational experiments to determine the effects of composition, frequency, temperature, and pressure. The goal of these computational experiments is to determine the nature of the effect of these variables on the acoustic attenuation.

III. RESULTS

A. Effects of composition

We first consider the effect of composition on the acoustic attenuation spectrum for a temperature of 297 K and a water vapor concentration of 3%, near its maximum value at this temperature and a pressure of 1 atm. Figure 1 shows the acoustic attenuation spectrum for 100% methane and for 0%, 10%,20%, . . . ,90% methane concentrations with 3% water vapor and the remainder nitrogen. Bold curves represent the total attenuation (relaxational plus classical) while the fine curves represent the relaxational component of attenuation
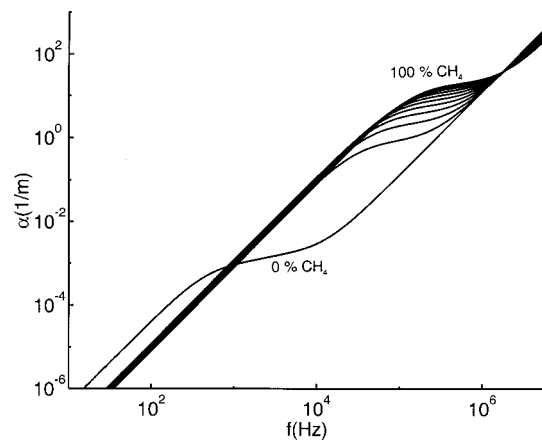
plotted against f/P, where f is the frequency and P is the pressure. This horizontal scale reflects the dependence of the relaxation time on energy exchange between molecules. The time between molecular collisions is inversely proportional to the pressure. Consequently, the relaxation frequency, which is the inverse of the relaxation time, is proportional to pressure. This proportionality is expressed by the dependence of attenuation on the quotient f/P. The acoustic attenuation α is nondimensionalized by the wavelength of the sound λ, which in turn is dependent on the frequency and speed of sound for that gas composition.

It is immediately evident from Fig. 1 that the relaxational component of attenuation dominates at low frequencies. The classical component of relaxation dominates at high frequencies. The peak in the curves at $f/P \sim 10^5$ Hz/atm is the relaxation frequency related to the relaxation of methane modified slightly by the presence of nitrogen and water. The attenuation at the relaxational frequency of methane is so large that it dominates classical attenuation and the relaxational frequency of nitrogen, which occurs at much lower frequencies and is not evident on the scale of Fig. 1. The relaxational frequency occurs at higher frequencies as the fraction of methane in the mixture increases. For pure methane, this relaxational frequency is at $f/P \sim 1.5 \times 10^5$ Hz/atm based on our model. The dominance of classical attenuation at high frequencies comes about because of the dependence of both shear viscosity and heat conductivity contributions to the attenuation on the square of the frequency.[14,16]

The results in Fig. 1 also show a strong dependence of the attenuation on composition in the frequency range 10^5 Hz/atm$<f/P<10^6$ Hz/atm. At low frequencies ($f/P<10^4$ Hz/atm) and in the range of frequencies where classical attenuation begins to dominate ($f/P>10^6$ Hz/atm), the dependence of the attenuation on composition is minimal.

It is helpful to plot the attenuation spectra at 1 atm using a dimensional scale for the attenuation, as shown in Fig. 2, to clearly show the wide range of attenuation. Again we show the attenuation for gas compositions ranging from 0% to 90% methane with 3% water and the remainder nitrogen as
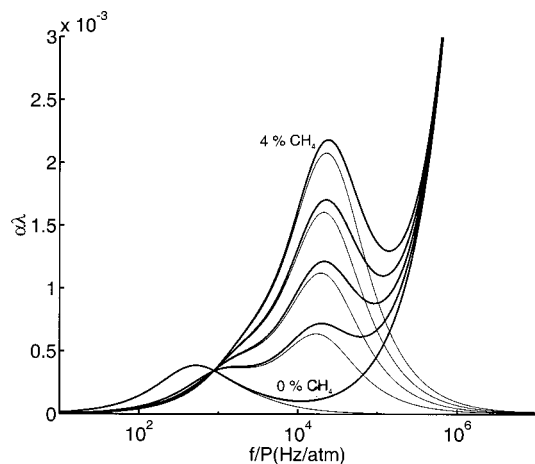
FIG. 3. Nondimensional acoustic attenuation spectrum for 0%, 1%, 2%, 3%, and 4% methane concentrations (from lowest to highest at 10^4 Hz/atm) with 3% water vapor and the remainder nitrogen at 297 K. Bold curves are the total attenuation and fine curves are the relaxational component only.
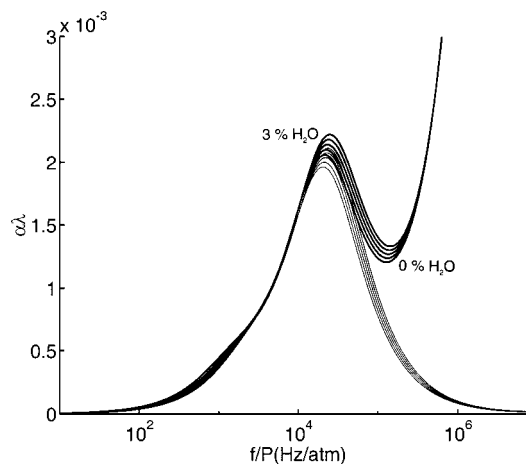

FIG. 4. Nondimensional acoustic attenuation spectrum for 0%, 1%, 2%, and 3% water vapor concentrations (from lowest to highest at 10^4 Hz/atm) with 4% methane and the remainder nitrogen at 297 K. Bold curves are the total attenuation and fine curves are the relaxational component only.

well as 100% methane. The knee at the lower frequency for 0% methane is related to the relaxation frequency of nitrogen. The knee at nonzero methane concentrations is associated with the relaxation frequency of methane. The attenuation is greatest at the highest frequencies. The dependence of the attenuation on the methane concentration is greatest for 10^5 Hz $< f < 10^6$ Hz. In this frequency range, the attenuation can vary be more than an order of magnitude with methane concentration.

We now return briefly to the issue of including the rotational relaxation contribution. Although we cannot calculate this contribution because the appropriate values for methane are not available, we can assume that the rotational relaxation contribution is less than the classical contribution. If a contribution this large were added to the classical contribution, the only effect in Fig. 1 would be a negligible leftward shift of the attenuation spectrum at the highest frequencies ($f/P > 10^6$ Hz/atm), where classical contributions dominate. Likewise, there would be a very slight upward shift in the dimensional curves in Fig. 2 for $f > 10^6$ Hz. Thus, qualitative results including rotational relaxation are identical to those shown and the quantitative results only change by an inconsequential amount.

As mentioned earlier, the relaxation frequency of nitrogen is not evident in Fig. 1 and is only visible for zero methane concentrations in Fig. 2. This is a consequence of the large relaxational effect of methane. The relaxational frequency of nitrogen becomes evident only at low concentrations of methane as shown in Fig. 3. Note that the vertical scale in Fig. 3 is greatly expanded compared to Fig. 1 to make visible the relaxation frequency of nitrogen at $f/P \sim 10^3$ Hz/atm. When no methane is present, only the relaxation frequency of nitrogen as modified by water is evident. The presence of water vapor increases the relaxational frequency above the relaxational frequency for pure nitrogen of about 9 Hz/atm.[17] The relaxation peak related to water vapor is too small to appear as a separate relaxational peak in the spectrum. The presence of even small quantities of methane (as small as 1%) results in the appearance of a strong relax-

ational peak for methane. As the fraction of methane increases, the relaxation frequency for the nitrogen shifts to higher frequencies and the attenuation due to the methane increases so that the methane peak dominates. The effect of nitrogen is evident only as a slight kink in the curve at 10^3 Hz/atm for 2% methane and higher concentrations.

Varying the water vapor concentration over nearly the full range of compositions thermodynamically possible at this temperature and pressure has little effect on the relaxational attenuation, as indicated in Fig. 4. The small effect of water vapor on the relaxational attenuation near 10^3 Hz/atm occurs because the relaxational peak for nitrogen is shifted to the right in the presence of water. The more obvious effect of water vapor is to increase the amplitude of the relaxational peak for methane near 10^4 Hz/atm and shift the peak to a slightly higher frequency due to the methane–water relaxational complex. Nevertheless, the influence of water vapor on the attenuation spectrum is much smaller than the influence of similar concentrations of methane.

Given the strong dependence of acoustic attenuation on the fraction of methane in the mixture, one might consider the relationship between the attenuation and the methane concentration by plotting the total dimensionless attenuation (relaxational plus classical) as a function of composition for several frequencies, as shown in Fig. 5. Three curves are plotted for each frequency corresponding to water vapor concentrations of 0%, 1.5%, and 3% with nitrogen making up the remainder of the mixture. (The concentration of water vapor is evident at the right end of the curves. The curve ending furthest to the left is 3% water vapor, and the curve ending furthest to the right is 0% water vapor.) The near overlap of the curves for different water vapor concentration confirms that the presence of water vapor is nearly inconsequential compared to the effect of methane concentration. At the lowest frequencies, the nondimensional attenuation is not a monotonic function of the methane fraction. The attenuation at the higher frequencies increases monotonically with methane fraction.

The dimensional attenuation at ten frequencies ranging

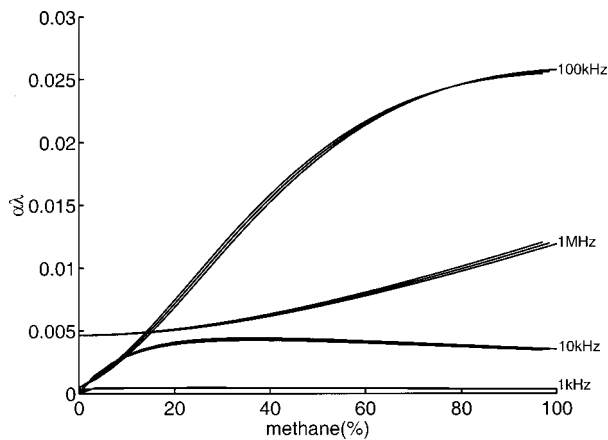Y. Dain and R. M. Lueptow: Attenuation in a three-gas mixture

FIG. 5. Dependence of nondimensional total attenuation on methane concentration for 0%, 1.5%, and 3% water vapor with the remainder of the mixture nitrogen at 297 K. (The curve ending furthest to the left at the right end is 3% water vapor, and the curve ending furthest to the right is 0% water vapor.)

from 100 kHz to 1 MHz is shown in Fig. 6. The dimensional attenuation is much larger at higher frequencies than at lower frequencies. However, the dimensional attenuation is not a monotonic function of methane concentration for high frequencies (800 kHz–1 MHz) at low methane concentrations or the lowest frequency (100 kHz) at high methane concentrations. At frequencies from 200 to 700 kHz the dimensional acoustic attenuation is monotonic, varies substantially over the range of methane concentrations, and is significant in magnitude. For instance, the attenuation at 500 kHz monotonically varies by nearly a factor of 6 from $\alpha = 3.3$ m^{-1} at 0% methane to $\alpha = 19.0$ m^{-1} at 100% methane.

The molecular relaxation not only affects attenuation, but also alters the sound speed. The sound speed c normalized by the equilibrium sound speed c_0 is plotted in Fig. 7 as a function of frequency. The equilibrium sound speed is that at low frequencies (much less than the relaxation frequency) calculated based on the classical equation using the translational temperature.[18,19] As shown in Fig. 7, the normalized sound speed increases slightly at the relaxation frequency of methane, but the increase is quite small, even for very large methane concentrations. This increase comes about when the
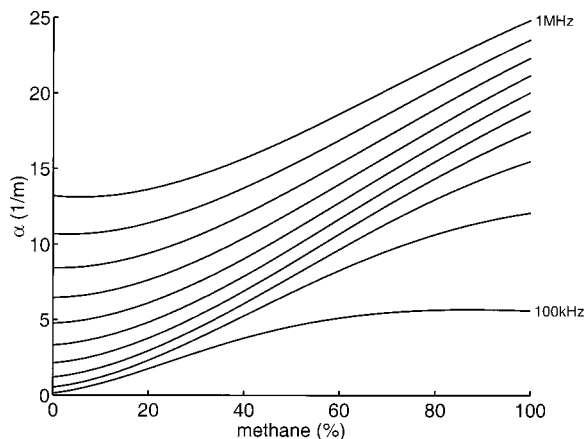

FIG. 6. Dependence of dimensional total attenuation on methane concentration for 0% water vapor with the remainder of the mixture nitrogen at 1 atm and 297 K. The curves correspond to 100 kHz increments in frequency.
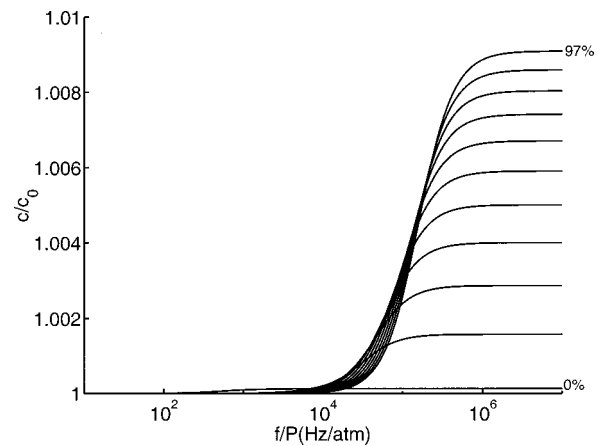

FIG. 7. Dependence of the sound speed normalized by the equilibrium sound speed on frequency for 0%,10%,20%,...,90%,97% methane concentrations (from lowest to highest at the highest frequency) with 3% water vapor and the remainder nitrogen at 297 K.

frequency of the sound wave is sufficiently high so that its period is less than the relaxation time of methane. Under these conditions, the specific heat at constant volume, which is based on the internal energy of the gas, is decreased because of the reduced contribution of the vibrational energy transfer resulting in a higher sound speed.[20] Of course, the increase in the equilibrium sound speed c_0 with methane concentration because of the decreased molecular weight of the mixture, which is not evident in Fig. 7 because of the normalization scheme, is much greater than the increase due to molecular relaxation at high frequencies.

B. Effect of temperature

The effect of temperature on the attenuation is shown in Fig. 8. In these figures, two curves are plotted at 297 and 323 K, one for 0% water vapor and the other for 3% water vapor. At the lowest temperature, 243 K, only 0% water vapor is considered because of the low partial pressure of water. At the low methane concentration, the effect of variation in temperature on the nondimensional attenuation is small, as shown in Fig. 8(a). However, at higher methane concentrations the effect of temperature is quite significant [Figs. 8(b) and (c)], particularly near the relaxational frequency of methane. In these cases, an increase in temperature results in a slight increase in the relaxational frequency and a substantial increase in the relaxational attenuation. The curves merge at low frequencies. At high frequencies, the classical attenuation increases substantially but the curves do not merge. In all cases, the water vapor plays little role in the effect of temperature on attenuation, as is evident from the curves for 0% and 3% water vapor concentrations overlaying each other. [In Fig. 8(a), the separate curves are only evident at the relaxational frequency of methane. In Figs. 8(b) and (c), the curves are so close that they appear only as thickened curves.]

C. Effect of pressure

All of the spectra to this point (except Fig. 2) have used the frequency divided by pressure as the independent vari-
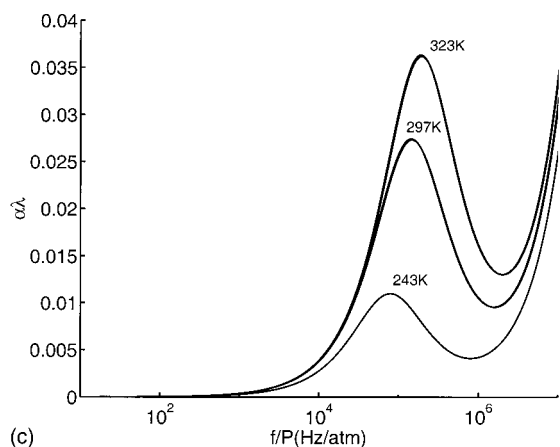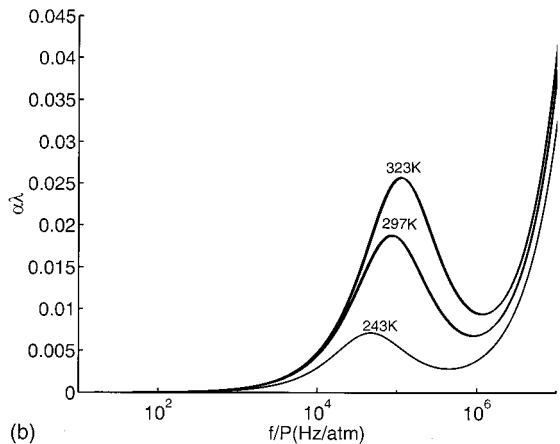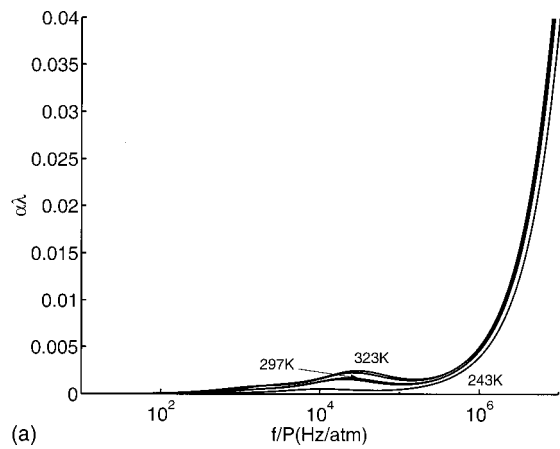
FIG. 8. Effect of temperature on the nondimensional total attenuation spectrum. For 297 and 323 K, the curves for 0% and 3% water vapor concentrations are shown, although they overlap in most cases. For 243 K, the water vapor concentration is zero: (a) 3% methane, 0% and 3% water vapor, and remainder nitrogen; (b) 50% methane, 0% and 3% water vapor, and remainder nitrogen; (c) 90% methane, 0% and 3% water vapor, and remainder nitrogen.

able reflecting the natural dependence of the nondimensional relaxational attenuation on pressure. It is, however, instructive to directly consider the effect of pressure on the spectrum of the attenuation, α, as shown in Fig. 9. The variation in pressure noticeably shifts the attenuation spectrum. However, the shape of the spectrum is essentially unchanged. Nevertheless, at any one frequency, the shift in the spectrum due to pressure has a significant effect on the attenuation at that frequency.
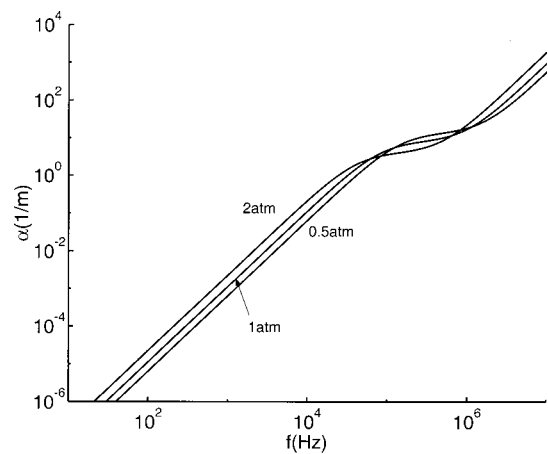

FIG. 9. Effect of pressure on the dimensional total attenuation spectrum for 50% methane, 3% water vapor, 47% nitrogen.

IV. SUMMARY

Our interest in a predictive model for acoustic attenuation came about because of the relation of the acoustic attenuation spectrum to gas composition. The key issue that arises is the dependence of acoustic attenuation on composition given the variability in temperature, pressure, and contaminants such as water vapor. Consider the acoustic attenuation at a frequency of 500 kHz for which the dependence of the attenuation on the fraction of methane was shown in Fig. 6. The attenuation is monotonic, relatively large, and varies by nearly an order of magnitude over the range of methane concentrations. But consider the extremes of the conditions for outdoor ambient temperatures from 243 to 323 K and water vapor concentrations from 0 to 3%. Except at the lowest methane concentration shown in Fig. 8, the attenuation varies substantially over this temperature range at 500 kHz. However, the variation of the attenuation with humidity at any particular temperature is negligible. We might also consider situations where the pressure changes. From Fig. 9, it is evident that the attenuation varies by a factor of 2 at 500 kHz for pressures from 0.5 to 2.0 atm.

To summarize, we have used a model of relaxational attenuation along with the model for classical attenuation to predict the total acoustic attenuation in a three-component mixture of nitrogen, methane, and water vapor. The attenuation spectrum is dependent upon the composition through the appearance of peaks in the spectrum related to the relaxation frequency of the particular components and their relaxing complexes. The relaxation peak related to methane dominates the spectrum except at very low methane concentrations, where the nitrogen peak is evident. Classical attenuation plays a significant role at high frequencies. Temperature and pressure significantly alter the relaxation frequency and the degree of attenuation. But the presence of water vapor plays little role.

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