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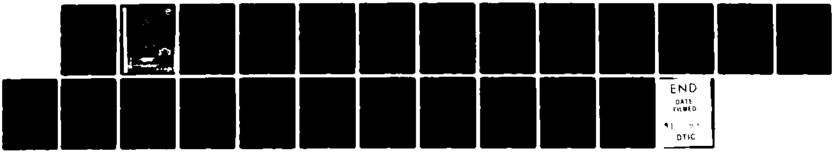

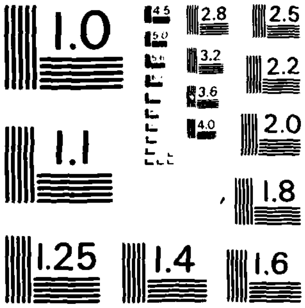

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PROPOGATION OF SOUND THROUGH A GAS WITH AN OVER-POPULATION OF EXCITED VIBRATIONAL STATES

by

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The Propagation of Sound Through a Gas with an Over-Population of Excited Vibrational States

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Abstract

Calculations have been made which predict sound amplification under certain conditions when propagated through a gas with an overpopulation of vibrationally excited states. Three metastable states have been analyzed where the vibrational temperature is varying slowly on the scale of the sound period. The first is that of a long-lived vibrational mode in a diatomic gas. Calculations were made for N_2, CO, O_2, and Cl_2. The second is that of a fast v-v exchange followed by a slow v-t. Calculations were made for CD_4 as an example of this situation. And the third is that of a slow v-v followed by a fast v-t. Calculations were made for a mixture of $N_2/CO_2/He$ as an example of this situation. Some of the difficulties in experimentally observing the gain are discussed.

Propagation of Sound through Gases with an Overpopulation of Excited Vibrational States

Introduction

The propagation of sound through gases under a variety of non-equilibrium conditions has been studied the past ten years. These studies have predicted sound amplification in the presence of a chemical reaction[1-4] or optical pumping of vibrational states[5-7]. Bauer and Bass have named the later process "SACER", which is an acronym for "sound amplification from controlled excitation reactions." The predicted amplification is attributed to the preferential heating of the compression part of the sound wave either by the pumping process or the relaxation process or both. The amplification due to pumping results from the selective absorption of pumping energy in the compression part of the sound cycle. The amplification due to relaxation results from the temperature and pressure dependence of the vibrational energy transition rate. The increase in the rate of v-t energy transfer with temperature and pressure causes the relaxing vibrational energy to be selectively "dumped" into the hot (or compressional) part of the sound cycle. When the sound wave is propagated in the presence of pumping, both effects are likely to be operative and the two will be difficult to separate. In addition, the non-equilibrium conditions produced by the pumping make accurate measurement of the sound amplification or absorption difficult.

A situation more amenable to experimental study results if the pumping process can be terminated and a metastable state allowed to develop in the gas before the sound wave is introduced. In this case it is obvious that the decay time must be long compared to the sound period. Three typical situations where such a condition could be produced by pumping energy into a particular vibrational mode are:

(1) A single long lived relaxing mode. Most stable diatomic gases fall into this category. Bauer and Bass have considered the case of a mixture of CO and H_2 and predict large amplification when the period of the wave is close to the relaxation time of the excited state[7]. As mentioned above, if the measurements are made after the pumping mechanism is removed, frequencies in this range are ruled out. This study considers the possibility of observing the amplification when the sound has a period that is short compared to the relaxation time.

(2) Fast v-v and slow v-t exchange. For most pure polyatomic gases, and in some gas mixtures, vibrational energy exchanges rapidly between modes by a fast v-v exchange and then more slowly with translation by a slow v-t exchange. It was early recognized that such a "fast series process" would lead to single-relaxation-time sound absorption and dispersion curves and the process was invoked to explain the single-relaxation times observed for most polyatomic gases[8,9].

If a vibrational level of such a gas is pumped, a metastable state with different vibrational modes at different temperatures results. The whole manifold of vibrational states then decays at a slow rate. The resonant v-v exchange within a given mode is still fast compared to v-v exchange between modes. An example of this situation treated below is CD_4. In this gas the v-v rates are about 400 times the v-t rate and the gas behaves much the same way as the diatomic gas with a single relaxing mode. However, this gas is more amenable to experimental study since the vibration can be excited optically and the relaxation times are shorter allowing measurements at higher frequencies and with smaller volumes.

(3) Slow v-v and fast v-t. In some cases the v-v rate may be slower than the v-t rate. SO_2 is an example of this situation[12]. The v-t rate

is about 10 times the v-v rate. In this case, which might be compared to the two step decay of a radioactive isotope, energy pumped into the long-lived mode feeds by v-v transfer a second mode that is communicating with translation by v-t transfer and maintains its vibrational temperature above the equilibrium value for periods comparable to the v-v relaxation time rather than the v-t time. The metastable condition requires that the energy flow out of the pumped mode, through the other modes and into translation at a constant rate. This rate is determined by the first v-v transfer time which is long compared to the sound period. In this case also experimental observation of sound amplification may be possible and measurements may give valuable knowledge about the energy transfer process.

The Reaction Equation

The sound absorption (or amplification) and velocity can be obtained from the imaginary and real parts of the propagation constant for plane waves (k_s). For this purpose we write

$$k_s = \omega \sqrt{\frac{M}{RT}} \sqrt{\frac{C_v}{C_p}} , \tag{1}$$

where ω is the angular frequency, M is molecular weight, R is the gas constant, T is absolute temperature, and C_v and C_p are the specific heat at constant volume and pressure. In the presence of relaxation, C_v and C_p are time dependent or, for a sinusoidal wave, complex and frequency dependent. The sound absorption (α_s) and velocity (v_s) are given by

$$\begin{aligned} \alpha_s &= \text{Imaginary part of } k_s \\ v_s &= \omega \times [\text{Real part of } k_s]^{-1} \end{aligned} \tag{2}$$

The problem of calculating the sound absorption and velocity is thus reduced to finding the real and imaginary parts of the complex, frequency-dependent specific heats, C_v and C_p.

For this purpose, we begin with the reaction equation which gives the time rate of change of energy in a vibrational mode. We will assume that the normal modes of vibration can be treated as harmonic oscillators and that resonant exchange of energy between the vibrational levels within a single mode rapidly establish a Boltzmann distribution within the mode characterized by a "vibrational temperature"[13,14]. In the metastable state here considered, the vibrational temperatures for the different modes may differ from each other and from the translational temperature and will be changing slowly on the time scale of the sound-wave period.

The time rate of change of energy in the ath vibrational mode can be written as[15]

$$\dot{E}_a = \sum_{i,j} ih\nu_a \mathcal{P} \sum_{\alpha=0}^{\infty} \sum_{\beta=0}^{\infty} \Big(k^{\alpha\rightarrow\alpha+i,\,\beta\rightarrow\beta+j}(a,b)\frac{n_\alpha(a)n_\beta(b)}{N_b}$$

$$- k^{\alpha+i\rightarrow\alpha,\,\beta+j\rightarrow\beta}(a,b)\,\frac{n_{\alpha+i}(a)n_{\beta+j}(b)}{N_b}\Big). \qquad (3)$$

This equation assumes that mode "a" is exchanging energy with a second mode "b", and with translation. Modes a and b can be in the same molecule, or, in the case of a gas mixture, in different molecules. The inclusion of additional modes of interaction is straight forward[15]. α and β refer to the vibrational quantum number of modes a and b, h is Planck's constant, ν_a is the fundamental vibrational frequency of mode a, $\mathcal{P}$ is pressure, N_b is the total number of molecules carrying mode b, n_α and n_β are the number of molecules with α and β quanta in modes a and b, respectively, $k^{\alpha\rightarrow\alpha+i,\,\beta\rightarrow\beta+j}(a,b)$ is the composition-averaged rate constant in the dimensions (time x pressure)$^{-1}$ for the particular process in which α changes to $\alpha+i$ and $\beta\rightarrow\beta+j$ in the mixture. The summations over α and β gives a net rate constant for transitions where mode a gains i quanta and mode b gains j quanta. In general, only transitions where i and j have different signs are likely to occur, i.e., mode a gains i quanta and mode b loses j quanta or vice versa.

For linear pertubations of harmonic oscillators,

$$k^{\alpha\to\alpha-i,\beta\to\beta+j}(a,b) = \{[\alpha(\alpha-1)\cdots(\alpha-i+1)] \times [(\beta+j)(\beta+j-1)\cdots(\beta+1)]/i!j!\} \times k^{i\to o,o\to j}(a,b) \qquad (4)$$

In terms of collision efficiencies, $k^{\alpha\to\alpha+i,\beta\to\beta+j}$ can be written

$$k^{\alpha\to\alpha+i,\beta\to\beta+j} = \Sigma_p x_p M_p P^{\alpha\to\alpha+i,\beta\to\beta+j}(a,b,p), \qquad (5)$$

where $P^{\alpha\to\alpha+i,\beta\to\beta+j}(a,b,p)$ is the collision efficiency for the designated transitions, p denotes the collision partner (if the collision does not allow the transition $P = 0$), and M_p is the collision rate of a molecule of type a in a gas of type p at unit pressure. $M_p P^{\alpha\to\alpha+i,\beta\to\beta+j}(a,b,p)$ is, therefore, the usual rate constant. x_p is the mole fraction of gas of type p.

We now assume that resonant exchanges of energy between levels of a single mode rapidly establish a Boltzmann distribution of energy within each mode so that we can write

$$n_\alpha = n_0(a)e^{-\alpha h\nu_a/kT_a} = N_a(1-e^{-h\nu_a/kT_a})e^{-\alpha h\nu_a/kT_a}. \qquad (6)$$

N_a is the number of molecules with mode a. Thus, each mode has its own temperature which in the general case is different from the translational temperature. Following conventional notation we set

$$\frac{h\nu_a}{k} = \theta_a, \text{ and } 1-e^{-\theta_a/T} = \chi_a(T). \qquad (7)$$

(Note that this is a change in notation from ref. 15.)

Using equations 4 and 6, the reaction equation (Eq. 3) can be summed over α and β. For this purpose note that

$$\Sigma_\alpha (\alpha+i)(\alpha+i-1)\cdots(\alpha+1)x^\alpha = \frac{d^i}{dx^i}\left(\frac{1}{1-x}\right) = \frac{i!}{(1-x)^{i+1}}$$

After summing over α and β Eq. 3 becomes

$$\dot{E}_a = \sum_{i,j} iN_a h\nu_a \mathcal{P}[k^{i\to o,o\to j}(a,b)e^{-i\theta_a/T_a} - k^{o\to i,j\to o}(a,b)e^{-j\theta_b/T_b}]/$$

$$([\chi_a(T_a)]^i[\chi_b(T_b)]^j). \qquad (8)$$

For a discussion of the case where the modes are degenerate, see ref. 15.

A Single Long-Lived Relaxing Mode

If the vibrational temperatures can be determined, Eq. 8 allows the determination of the sound absorption and velocity in the excited gas. The three cases discussed in the introduction would be delineated by the choice of transition rates. To illustrate, we specialized first to the simplest case, that of a gas with a single long-lived relaxing mode. In this case j = 0 and i = 1. The sum over i and j has only one term and Eq. 8 becomes, after some manipulation,

$$\dot{E}_a = -\mathcal{P}k^{10}\chi_a(T)[E_a(T_a) - E_a(T)], \qquad (9)$$

where $E_a(T_a) = N_a k\theta_a e^{-\theta_a/T_a}/\chi_a(T_a)$ and $E_a(T) = N_a k\theta_a e^{-\theta_a/T}/\chi_a(T)$. This of course, is the expected relaxation equation with the relaxation time, τ, equal to $[\mathcal{P}k^{10}\chi_a(T)]^{-1}$.

Now consider the case where a sound wave is propagated through a slowly relaxing gas. Either by differentiating Eq. 9 or be differentiating Eq. 3 and the summing over α and β, we obtain

$$\Delta\dot{E}_a = \dot{E}_a^o\{[\frac{1}{p}\frac{dp}{dT} + \frac{1}{k^{10}}\frac{dk^{10}}{dT} - \frac{\theta_a e^{\theta_a/T}}{T^2\chi_a(T)}]\Delta T - \frac{\Delta E_a(T_a)-\Delta E_a(T)}{\tau \dot{E}_a^o}\}. \qquad (10)$$

Here we make use of the fact that the transition rate is a function of translational temperature only and we neglect higher order terms in the sound variables. E_a^o, T_a and T now represent unperturbed values, i.e., values without the sound wave. Introducing the sinusoidal time dependence and setting $\Delta E_a(T_a) = C_a(T_a)\Delta T_a$, $\Delta E_a(T) = C_a(T)\Delta T$, and $\dot{E}_a^o = -\frac{E_a(T_a)-E_a(T)}{\tau}$, this equation becomes

$$(1+j\omega\tau)\frac{\Delta T_a}{\Delta T} = [\frac{\dot{E}_a^o\tau}{C_a(T_a)}] \times [\frac{1}{p}\,\frac{dp}{dT} + \frac{1}{k^{10}}\,\frac{dk^{10}(a)}{dT} - \frac{\theta_a e^{-\theta_a/T}}{T^2\chi_a(T)}] + \frac{C_a(T)}{C_a(T_a)} \quad (11)$$

In this form, it is easy to see the effect of the overpopulation of excited states on the usual absorption due to relaxation. In the "usual case", that is when the gas has not been "pumped", $\dot{E}_a^o = 0$, and $T_a = T$, and the right hand side of Eq. 5 is unity. Then $\Delta T_a/\Delta T = (1+j\omega\tau)^{-1}$. Writing the frequency independent part of the specific heat as C_∞, the frequency dependent specific heats become

$$C_v(\omega) = C_\infty + C_a\Delta T_a/\Delta T = C_\infty + C_a(1+j\omega\tau)^{-1} \quad (12)$$

and

$$C_p(\omega) = C_v(\omega) + R \quad (13)$$

The familiar absorption and velocity versus frequency curves are those corresponding to a single-relaxation-time process.

When $T_a \neq T$, $\dot{E}_a^o \neq 0$ and the frequency dependent specific heats are

$$C_v(\omega) = C_\infty + C_a'/(1+j\omega\tau) \quad (14)$$

with

$$C_a' = \dot{E}_a^o\tau[\frac{1}{T} + d[\ln k_{10}(a)]/dT - \frac{\theta_a e^{-\theta_a/T}}{T_a^2\chi_a(T)}] + C_a(T) \quad (15)$$

and

$$C_p(\omega) = C_v(\omega) + R - \frac{\dot{E}_a^o\tau}{T(1+j\omega\tau)}\ . \quad (16)$$

Here R is the universal gas constant and $\frac{1}{p}\frac{dp}{dT}$ has been given its ideal gas value of $\frac{1}{T}$. The extra term in C_p results from the fact that, at constant pressure, $\partial p/\partial T = 0$.

It is possible, therefore, to plot $C_p(\omega)$ and $C_v(\omega)$ as $\omega \to 0$, and the sound absorption and dispersion in a particular gas as a function of the decay rate, $\dot{E}_a^o$. Bauer and Bass have done this for a CO/H_2 mixture, treating the CO as having two vibrational states. If $\dot{E}_a^o$ is set equal to the negative of their pumping rate, the two treatments give similar results.

For the purposes considered here, it is more useful to set

$$\dot{E}_a^o = -\tau^{-1}[E_a(T_a) - E_a(T)] \qquad (17)$$

and express the results in terms of the vibrational temperature T_a. Sound amplification will occur when C_a' becomes negative. (Note that $\dot{E}_a^o$ is negative.) We now seek to determine values of T_a needed to produce this sound amplification, the magnitude of the amplification, and the experimental conditions under which it can be observed.

Bauer and Bass point out that when $C_a(\omega=0) < -C_\infty(\omega=0)$ the gas is unstable. This means that it is not possible to maintain a steady difference between T_a and T large enough to make $C_a(\omega=0) < -C_\infty(\omega=0)$ by controlling the pumping rate. This restriction upon the difference between T_a and T does not apply in the metastable case where T_a and T are changing but on a time scale slow compared to the sound period.

Calculation and Observation of the Sound Amplification: For most diatomic gases, (the halogens would be an exception), the relaxation time is so long in the pure gas that collisions with impurity molecules usually control the relaxation process. For such collisions, $\frac{d(\ln k_{10})}{dT}$ is of the order of a few one hundreds[16] and amplification will occur when T_a-T is a few tens of degrees.

However, observing this amplification in a metastable state in the absence of pumping is difficult. For frequencies where the sound period is short compared to the relaxation time (a requirement for the metastable state to persist over a number of sound vibrations), $\omega\tau$ will be large and the gain per unit length of sound path will be small. Furthermore, the length of the sound path is restricted since the transit time for the sound wave through the gas must be small compared to the relaxation time.

This means that high vibrational temperatures are needed to produce observable amplification of the sound in the diatomic case. Table 1 gives values of the gain in db/wavelength for some typical diatomic gases as calculated from Eqs. 1,2,11,12 and 13. In these calculations $\omega\tau$ is set equal 100 and, in this range, the gain is approximately inversely proportional to $\omega\tau$. However, values much smaller than 100 violate the metastable state requirement since at this value τ corresponds to approximately 16 sound periods. The value of $\frac{d}{dT} \ln k_{10}$ has been taken to be 0.01, which, as mentioned above, seems to be representative.

Table 1. Sound amplification in db per wavelength for typical diatomic gases at 300°K with elevated vibrational temperatures, T_a. The derivative of the natural logarithm of the transition rate, $d(\ln k_{10})/dT$, has been set equal to 0.01. The amplification is approximately inversely proportional to $\omega\tau$.

Gas	$\nu(cm^{-1})$	Amplification Factor (dB/λ)					
		T_a=500°K	1000°K	2000°K	3000°K	4000°K	6000°K
N_2	2331	0.0027	0.082	0.52	1.1	1.7	2.9
CO	2143	0.0042	0.10	0.56	1.2	1.8	3.0
O_2	1556	0.015	0.18	0.73	1.4	2.0	---
Cl_2	557	0.075	0.37	1.00	---	---	---

For the temperature and $\omega\tau$ values considered in Table 1, the sound velocity will differ at most by only a few tenths of a percent from the high frequency sound velocity calculated with $T_a = T$.

To get the expected gain in the sound wave in transversing the excited gas, the values in Table 1 are multiplied by the number of wavelengths in the sound path. However, this path length is limited since the transit time for the sound to pass through the gas must be short in comparison to the relaxation time for the excited states. Making use of the fact that the gain at high frequency is approximately inversely proportional to $\omega\tau$

$$\text{Gain} = \alpha\lambda_{100} \times \frac{100}{2\pi} \times (\text{transit time/relaxation time}) \qquad (18)$$

where $\alpha\lambda_{100}$ represents values in Table 1. If the ratio of the transit time to the relaxation time (t.t./r.t.) is not small the overpopulation of excited states decays away before the sound wave can transverse the gas. Further, the translational temperature is increasing as the vibrational temperature decreases. For t.t./r.t. =0.10, the vibrational temperature decreases about 10% while the sound wave transverses the gas and the total gain obtainable independent of frequency is about 1.6 times the values in Table 1.

Polyatomic Molecules with v-v and v-t Exchanges

The case of a small amplitude sound wave propagating in a metastable gas with more than one excited vibrational mode can be treated by either differentiating Eq. 3 and summing over the vibrational levels in each mode or by summing first to get Eq. 8 and then differentiating. By the chain rule of differentiating a product, the result can be written as

$$\begin{aligned}\Delta\dot{E}_a = &-\sum_{i,j} \frac{iN_a h\nu_a \mathcal{P}}{\chi_a(T_a)^i \chi_b(T_b)^j}\{k^{io,oj}(a,b)e^{\frac{-i\theta_a}{T_a}}[\frac{\Delta p}{p} + \frac{\Delta k^{io,oj}(a,b)}{k^{io,oj}(a,b)}\\ &+ \Delta\frac{[\chi_a(T_a)^{-i}\chi_b(T_b)^{-j}]}{\chi_a(T_a)^i\chi_b(T_b)^j} + \frac{\Delta e^{\frac{-i\theta_a}{T_a}}}{e^{\frac{-i\theta_a}{T_a}}}] + k^{oi,jo}(a,b)e^{\frac{-i\theta_a}{T}}[\frac{\Delta p}{p}\\ &+ \frac{\Delta k^{oi,jo}(a,b)}{k^{oi,jo}(a,b)} + \frac{\Delta[\chi_a(T_a)^{-i}\chi_b(T_b)^{-j}]}{\chi_a(T_a)^{-i}\chi_b(T_b)^{-i}} + \frac{\Delta e^{\frac{-j\theta_b}{T_a}}}{e^{\frac{-j\theta_b}{T}}}]\}\end{aligned} \tag{19}$$

The Δ's indicate changes produced by the sound wave and, according to the small amplitude assumption, only first order in the Δ's has been retained.

Substituting $\omega C_a(T_a)\Delta T_a$ for $\Delta\dot{E}_a$, this equation can be written as

$$C_{aa}\Delta T_a + C_{ab}\Delta T_b + C_{ac}\Delta T_c + \ldots = C_{aT}\Delta T. \tag{20}$$

There will be a similar equation for each relaxing mode, and the left side includes a term for each mode exchanging energy with mode *a*. The coefficients are given by

$$\begin{aligned}C_{aa} = &\, j\omega - \sum_{i,j,b} \frac{i^2\mathcal{P}}{\chi_a(T_a)^{i-1}\chi_b(T_b)^j}[e^{-(i-1)\theta_a/T_a}k^{io,oj}(a,b) - e^{-j\theta_b/T_b}k^{oi,jo}(a,b)],\\ C_{ab} = &-\sum_{i,j} ij\mathcal{P}\frac{\theta_b}{\theta_a}\frac{T_a^2}{T_b^2}[\frac{e^{-(i-1)\theta_a/T_a}e^{-\theta_b/T_b}k^{io,oj}(a,b) - e^{\frac{\theta_a}{T_a}}e^{\frac{-j\theta_b}{T_b}}k^{oi,jo}(a,b)}{\chi_a(T_a)^{i-2}\chi_b(T_b)^{j+1}}],\\ C_{aT} = &-\sum_{i,j,b} ie^{\theta_a/T_a}\frac{T_a^2}{\theta_a}\frac{\mathcal{P}}{\chi_a(T_a)^{i-2}\chi_b(T_b)^j}[k^{io,oj}(a,b)e^{-i\theta_a/T_a}(\frac{1}{T} + \frac{d\ln k^{io,oj}(a,b)}{dT})\\ &-k^{oi,jo}(a,b)e^{-j\theta_b/T_b}(\frac{1}{T} + \frac{d\ln k^{io,oj}(a,b)}{dT} - \frac{i\theta_a}{T^2} - \frac{j\theta_b}{T^2})];\end{aligned} \tag{21}$$

where the sum over b indicates a sum over modes coupled to mode a.

In most cases, two modes are coupled by a *specific type* of v-v exchange, i.e., a one quantum for one quantum exchange or a one quantum for two quantum exchange and the sum over i and j has only one term. Unfortunately, the matrix of coefficients in the coupled equations is not symmetric, and therefore, not amenable to an eigenvalue analysis. However, the equations can be solved for the complex, frequency dependent ratios

$\Delta T_a/\Delta T$, $\Delta T_b/\Delta T$, ... and the complex frequency dependent specific heat at constant volume obtained by an extension of Eq. 12. This solution will have to be repeated for $C_p(\omega)$ since the C_{aT} coefficients in this case will not contain the $\frac{1}{T}$ term which arises from $(\frac{dp}{dT})_v$.

Fast v-v Slow v-t

The two types of metastable states for polyatomic molecules that were discussed above correspond to the proper choice of transition rates and vibrational temperatures in Eq. 2. As an example of the fast v-v exchange with a slow v-t consider the gas CD_4 which has the properties that make it amenable to experimental investigation. The ν_4 mode can be pumped by readily available high-powered CO_2 lasers and its relaxation time is relatively long (for a polyatomic) allowing the acoustic measurements at experimentally accessible frequencies. In addition, the large vibrational specific heat at room temperature gives rise to a large relaxation absorption (or gain). A variety of measurements have indicated that energy deposited in the ν_4 mode by the absorption of laser light is quickly shared by a one-for-one quantum exchange with the ν_2 mode and a two-for-one quantum exchange with the ν_3 and ν_1 modes[17].

After the vibrational modes have equilibriated by such exchanges, the whole manifold of vibrational energy relaxes with a relaxation time of approximately 4.2 μsec atm which corresponds to a transition rate of 2.4 x $10^5 sec^{-1} atm^{-1}$. From the rate of rise of flourescent radiation from the ν_3 mode, previous studies indicate the v-v exchanges are on the order of 400 times this rate. $\frac{d\ln k^{10}}{dT}$ for the v-t transition to the lowest mode (ν_4) is approximately 0.009 $(°K)^{-1}$[18]. If we assume that the different modes have equilibriated in the metastable state by the fast v-v transfers, then the ratios of the vibrational temperatures are fixed by the condition that

$$k^{io}_{oj}\, e^{-i\theta_a/T_a} = k^{oi}_{jo}\, e^{-j\theta_b/T_b}, \qquad (22)$$

which expresses the principle of detail balancing. Since k^{io}_{oj} and k^{oi}_{jo} are functions of translational temperature only, $k^{io}_{oj}/k^{oi}_{jo} = e^{(i\theta_a - j\theta_b)/T}$ and Eq. 22 leads to the familiar expression[11] relating translational and vibrational temperatures in a metastable state

$$\frac{i\theta_a - j\theta_b}{T} = \frac{i\theta_a}{T_a} - \frac{j\theta_b}{T_b} \qquad (23)$$

An examination of Eq. 19 shows that the v-v terms produce no gain, since the modes coupled by v-v exchange are in metastable equilibrium.

Sound amplification and velocities calculated for CD_4 are given in Table 2. The v-t relaxation is assumed to take place through the lowest energy mode 4. A one for one quantum exchange is assumed between mode 4 and mode 2 and a two for one between modes 2 and 3. Modes 1 and 3 with corresponding degeneracies, are lumped together into a single mode with an assumed frequency equal to the average of the two. The temperature of ν_4 was assigned values shown in the table and the temperature of the other modes calculated using Eq. 23. As in Table 1, $\omega\tau$ is set equal to 100, where τ is the v-t relaxation time for ν_4 given above (= 4.2 μsec atm). The velocities are given as a ratio of v to the high-frequency velocity ($v_\infty = \sqrt{RT(C_\infty+1)/(MC_\infty)}$). It might be worth noting that as $\omega \to \infty$, v approaches v_∞ from below if $C_a < -C_\infty$, and from above (as in Bauer & Bass) if $C_a < -C_\infty$.

Table 2. Sound amplification in CD_4. The translational temperature is 300°K, $d\ln k_{10}/dT = 0.009°K^{-1}$, and $\omega\tau = 100$. T_a is the vibrational temperature of mode 4 (ν=995.6cm^{-1}). The vibrational temperature for the other modes are calculated using Eq. 23 assuming a one-for-one quantum exchange between modes 4 and 2 and a two for one quantum exchange between modes 2 and 1 and 3. Velocities are given as a ratio between the calculated velocity and the high frequency sound velocity ($\nu_\infty = \sqrt{RT(C_\infty+1)/(MC_\infty)}$).

T_a	500	1000	2000	3000	4000°K
$\alpha(db/\lambda)$	0.095	0.60	1.65	2.48	3.12
v/v_∞	1.000	0.997	0.986	0.974	0.962

Slow v-v followed by fast v-t

The third situation where a metastable state can exist is the case where an excited mode decays slowly by a v-v exchange into a mode decaying more rapidly by v-t. An example of this situation is a mixture of N_2, CO_2 and He. The N_2 vibration is strongly coupled with the ν_3 mode in CO_2. These two modes together relax slowly by v-v processes involving multiple quantum exchanges with the ν_1 and ν_2 modes in CO_2. The ν_1 and ν_2 modes are also strongly coupled by a Fermi resonance. Practically all of the vibrational energy gets into translation through a v-t transfer from the lowest level of the ν_2 mode in CO_2/He collisions.

Therefore, we can diagram the relaxation process as follows:

$$E(N_2,\nu_3) \rightarrow E(\nu_1,\nu_2) \rightarrow \text{Translation.}$$

For a 50,25,25%mixture of He, N_2, CO_2 as an example, the first step takes place at a composition-averaged rate of about $4.5 \times 10^4 sec^{-1}atm^{-1}$[16]. The second step takes place at a rate of about $2 \times 10^6 sec^{-1}atm^{-1}$ due primarily to CO_2/He collisions, and the value of $d\ln k_{10}/dT$ for this v-t rate is about 0.003[19].

Now, if the angular sound frequency is large compared to 4.5 x 10^4 $sec^{-1}atm^{-1}$ the vibrational temperature will be changing little in a sound period. The long-lived (N_2,ν_3) vibrational feeds the $\nu_1\nu_2$ modes maintaining them above the translational temperature while energy passes through them at a constant rate.

The temperature of ν_2 can be calculated using Eq. 8. Since the amount of energy in ν_2 is changing slowly

$$\dot{E}_2 = \frac{3Nh\nu_2\mathcal{P}}{\chi_2(T_2)^3\chi_3(T_3)}\,[k^{30}_{01}(2,3)e^{-3\theta_2/T_2}-k^{03}_{10}(2,3)e^{-\theta_3/T_3}]$$

$$-\frac{Nh\nu_2\mathcal{P}}{\chi_2(T_2)}\,[k^{10}(2)e^{-\theta_2/T_2}-k^{10}(2)] = 0.$$

Here we have assumed a 3 for 1 quantum exchange between ν_2 and ν_3. As an example when T is 300°K and T_2 is 400°K, this equation gives T_3 = 1163, when the rates have the values listed above. Figure 1 shows the sound absorption when the vibrational temperatures are equal to the translational temperature (curve A) and the sound amplification (notice the change in scale on the negative axis) when T = 300, T_2 = 400 and T_3 = 1163 °K (curve B). T_1, as determined from T_2 by Eq. 23, is 341°K.

Conclusion

Calculations have shown that sound will be amplified when propagated through a gas with an overpopulation of vibrationally excited states. However, the conditions under which the gain can be experimentally observed are difficult to obtain. In the case of a single long-lived vibrational mode observable gain results from vibrational temperatures of a few thousand °K. The case of fast v-v followed by slow v-t is very similar to the diatomic case but the vibrational modes are likely to be more easily excited optically. The case where the most gain is likely to be observed is that of slow v-v followed by fast v-t. Calculations indicate that for this case significant gain should be possible at experimentally obtainable conditions.

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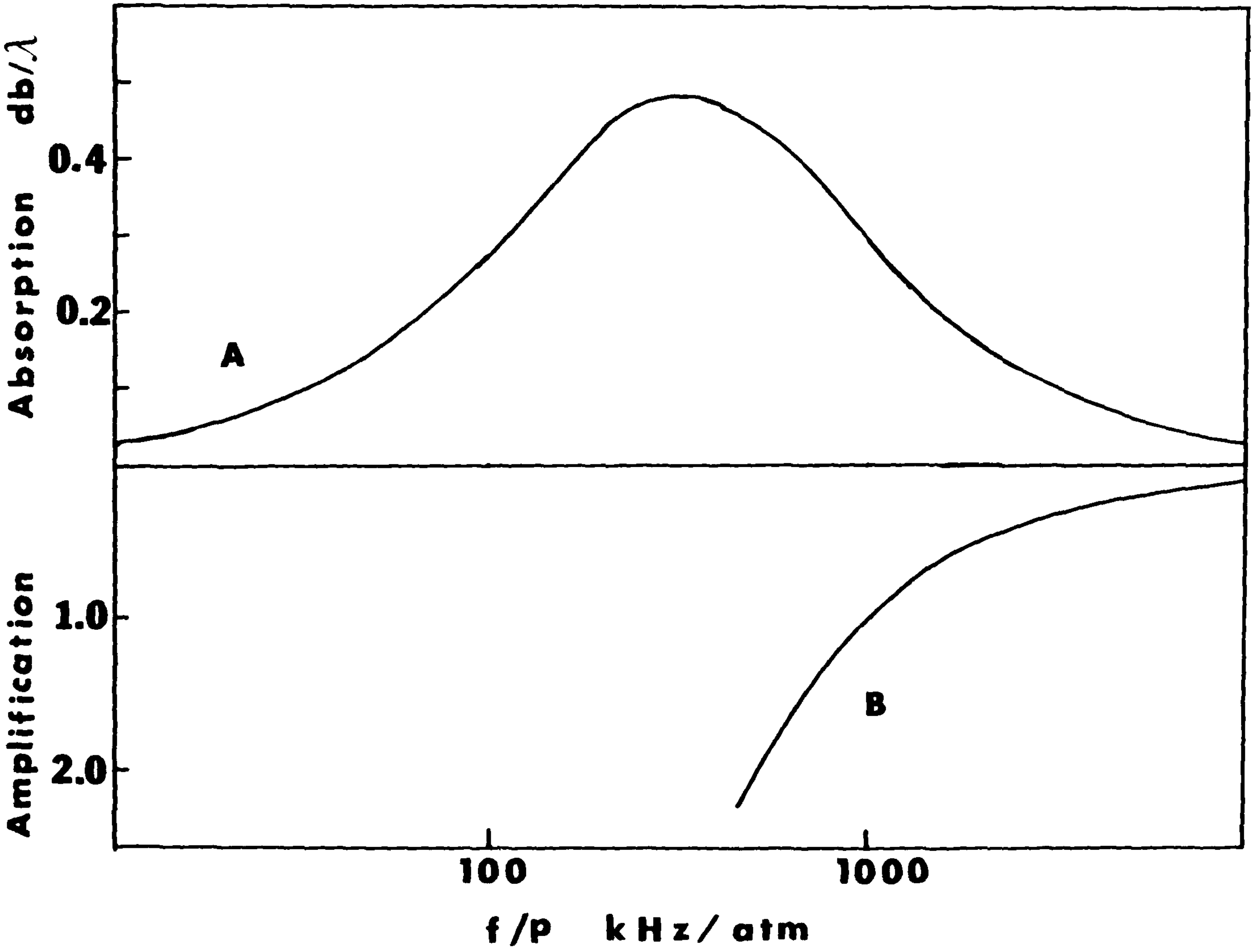

Fig.1. Sound absorption and amplification in a 50/25/25% mixture of He/CO_2/N_2. Curve A is the absorption assuming translational and vibrational temperatures all equal to 300° K. Curve B (note the difference in scale on the negative axis) is the amplification when T = 300°, T_1 = 341°K, T_2 = 400°, T_3 = 1163°

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