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Calculation of Vibrational Relaxation Times in Multi-component Excitable Gases

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In the research field of acoustic propagation in excitable gases, one of the most critical parameters is the vibrational relaxation time, which determines the frequency of the acoustic dispersion step or the absorption maximum. In this paper, the vibrational relaxation equations given by Tanczos [J. Chem. Phys. 25, 439 (1956)] have been applied to calculate the vibrational multi-relaxation times in multi-component gases. The eigenvalues of the energy-transition-rate matrix are proven to be the reciprocals of the multi-relaxation times. Comparisons demonstrate that our relaxation frequencies calculated for various gas compositions, including carbon dioxide, methane, chlorine, nitrogen, and oxygen, agree with the experimental data.

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I. INTRODUCTION

A sound wave passing through an excitable (polyatomic or diatomic) gas will continuously exchange its mechanical energy with the kinetic energy of the constituent molecules of the gas by alternating compressions and expansions. The tendency toward equipartition of excess acoustic energy among all the molecular modes is a phenomenon called thermal relaxation [1]. During the compression phase, a certain amount of acoustic energy is fed from the translational to the internal (vibrational and rotational) energy of the molecules through molecular inelastic collisions. During the rarefaction phase, the translational and rotational modes ran through states of equilibrium almost instantly (generally within a few collisions). However, the vibrational mode is relatively quite longer (several thousand collisions) due to its large quantum level spacing, and thus suffers a time delay or phase lag relative to the phase of the sound. This time delay leads to a certain fraction of the excited vibrational energy being relaxed in the form of heat to raise the absorption and the dispersion of sound rather than being returned into mechanical energy after the expansion is finished [2]. This time delay of vibrational energy returning to equilibrium, namely, the relaxation time, determines the frequency of the acoustic dispersion step or the absorption maximum, which gives information on the rate of molecular energy transition [1, 3, 4]. Therefore, the calculation of the relaxation time is a key to theoretically investigating acoustic relaxation processes in excitable gases.

Herzfeld and Rice [5] initially assumed a relaxation equation to describe the vibrational relaxation process as an explanation of non-classical sound absorption. Kneser [6] treated the vibrational energy as if it were a two-state system to calculate the vibrational-translational (V-T) relaxation time. Landau and Teller [7] acquired the V-T relaxation time by considering the vibrational energy to be a multileveled system of a harmonic oscillator. Schwartz, Slawsky, and Herzfeld (SSH) [8] refined Landau and Teller's theory by including a one-for-one quantum exchange of vibrational-vibrational (V-V) energy transfer in two diatomic mixtures. Tanczos [9] extended the SSH theory to permit the two quanta for one quantum V-V exchange in pure polyatomic gases. However, these above theories for the relaxation time cannot be used for multi-component mixtures. More recent study

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of Dain and Lueptow [10] and Petculescu and Lueptow [11] employed the extended SSH relaxation equations to predict the relaxational absorption of sound in ternary mixtures. Unfortunately, their model did not provide a theoretical derivation for calculating the relaxation times in multi-component gases and only allowed for a one-for-one quantum V-V exchange. Consequently, it is still desirable to provide a physical model to calculate the relaxation times in multi-component gases whilst allowing for the two quanta for one quantum V-V exchange.

In this paper, first, we give the effective isochoric molar heat (IMH) by using the temperature fluctuation ratio between vibrational modes and the sound wave in a gas mixture. Second, we extend Tanczos relaxation equations [9] to apply to multi-component mixtures. Third, we obtain the relaxation times from the energy-transition-rate matrix based on the extended relaxation equations. To our knowledge, this work is unique in that it is the first application of Tanczos relaxation equations to multi-component gas mixtures for calculating vibrational relaxation times. We prove that the eigenvalues of the energy-transition-rate matrix are the reciprocals of the multi-relaxation times; there will be as many relaxation times as there are vibrational modes available to a gas, but the relaxation time of the primary relaxation process determines the frequency of the sound absorption maximum (*i.e.*, the relaxation frequency) in most cases.

II. OVERVIEW FOR A SINGLE-RELAXATION PROCESS

When an excitable gas is at thermal equilibrium, the translational and the vibrational instant temperatures are equal: $T = T^{vib}$ [12]. During every acoustic compression-rarefaction cycle, the vibrational temperature lags behind the translational (or acoustic) temperature. If T is assumed to be kept constant, T^{vib} will finally be in equilibrium with an external mode; *i.e.*, the vibrational energy $E(T^{vib})$ will tend towards $E(T)$. Equilibrium is considered to be achieved exponentially with the relaxation equation [13]

$$\{E(T^{vib})\}_t - E(T) = [\{E(T^{vib})\}_{t=0} - E(T)]\exp(-t/\tau), \tag{1}$$

Where $\{E(T^{vib})\}_t$ is the value of the vibrational energy at time t and τ is the relaxation time. When $t = \tau$, the equilibrium has been achieved. Because the difference between $\{E(T^{vib})\}_{t=0}$ and $E(T)$ is small, Eq. (1) can be rewritten as

$$dE(T^{vib})/dt = -[E(T^{vib}) - E(T)]/\tau. \tag{2}$$

In general, the degree of matching between the relaxation time τ and the acoustic angular frequency ω will determine the strength of the sound relaxational absorption, *i.e.*, how much acoustic energy will be converted to thermal energy during the transitions [2,12]. If the relaxation time is long ($\omega\tau \gg 1$) compared to the time for changes in the acoustic variables to take place, the internal energy state will not be populated, and there will be no absorption; if the relaxation time is short ($\omega\tau \ll 1$), the internal state will always be in equilibrium with the external states, and the absorption will again be absent; when the relaxation time is approaching the acoustic period ($\omega\tau \sim 1$), the absorption will come up. In short, there is no acoustic relaxational absorption at very low and very high sound frequencies, and maximum absorption emerges when a sound wave has a frequency that approximately equate the rate of adjustment of thermal equilibrium for vibrational relaxation processes. It is this characteristic that makes possible the investigation of molecular relaxations in gases by using acoustic measurements.

III. VIBRATIONAL RELAXATION TIMES IN A MULTI-COMPONENT GAS MIXTURE

1. Thermodynamic Energy Change of the Gas Mixture

In a gas mixture with W kinds of molecules, which consists of N kinds of vibrational modes ($W \leq N$), the sound propagation with small amplitude will induce a change in thermodynamic energy of the gases. First, the total energy change dQ can be divided into two parts: one belongs to the translational and rotational modes (dE'); the other, to the vibrational mode (dE) [1].Second, during the relaxation processes, because the deviations of the temperatures of all molecular modes from the equilibrium temperature T_0 are small, we can consider the value of the IMH of all modes to be the same as the values at T_0 [1,14]. Thus,

$$dQ = dE' + dE = C_V^{\infty} dT + \sum\nolimits_{j=1}^{N} a_j C_j^{vib} dT_j^{vib} = C_V^{eff} dT, \tag{3}$$

where C_V^{eff} is known as the IMH, denoting the macroscopic "footprint" of the inability of vibrational modes to follow the acoustic temperature fluctuations [15]. $C_V^{\infty} = \sum_{l=1}^{W} a_l C_l^{\infty}$ represents the non-relaxation part of the IMH, C_l^{∞} is the sum of the values of the IMH for translation and rotation for molecule l, a_l is the mole fraction of molecule l, and $\sum_{l=1}^{N} a_l = 1$. T_j^{vib} is the instantaneous temperature of vibrational mode j; C_j^{vib} and a_j are the IMH and the mole fraction of vibrational mode j, respectively. C_l^{∞} depends on molecular symmetry [15]: for a linear molecule, there are three translations and two rotations, so $C_l^{\infty} = 5R/2$ (R is the universal gas constant);

for a nonlinear molecule, $C_l^\infty = 3R$. C_j^{vib} is calculated by using the Planck-Einstein function for a harmonic oscillator [10];

$$C_j^{vib} = g_j R \left(\frac{\theta_j^{vib}}{T_0} \right) \frac{\exp(\theta_j^{vib}/T_0)}{(\exp(\theta_j^{vib}/T_0) - 1)^2}, \theta_j^{vib} = \frac{h\upsilon_j}{k_B}, \tag{4}$$

where h is Planck's constant, k_B is Boltzmann's constant and θ_j^{vib}, υ_j and g_j are the characteristic temperature, the vibrational frequency and the degeneracy of the vibrational mode j, respectively.

In Eq. (3), the temperatures of all translations and rotations are considered to be the same as the temperature of sound wave, because the energy transfer of those modes is rapid enough to catch up with the acoustic temperature fluctuations; however, the temperatures of the vibrational modes are different because the vibrational frequencies are commonly unequal. Thus, based on Eq. (3), the effective IMH of a relaxing gas mixture is [16]

$$C_V^{eff} = C_V^\infty + \sum_{j=1}^{N} a_j C_j^{vib} dT_j^{vib}/dT. \tag{5}$$

Here, dT_j^{vib}/dT is the temperature-fluctuation ratio between the vibrational mode j and the sound wave.

2. Extended Tanczos's Vibrational Relaxation Equations

To calculate dT_j^{vib}/dT, according to SSH theory [8], we need to consider two kinds of energy transitions: one is the V-T energy transfer from vibrational mode j to translational modes of molecule l; the other is the V–V energy exchange between vibrational mode j and k. Therefore, based on Tanczos relaxation equations [9], for W kinds of gas components consisting of N kinds of vibrational modes, we can obtain the general relaxation equations allowing for the two quanta for one quantum V-V exchange as

$$\frac{d\Delta T_j^{vib}}{dt} = (\Delta T - \Delta T_j^{vib}) k_{jj} - \sum_{k=1,k\neq j}^{N} (\Delta T - \Delta T_k^{vib}) k_{jk}, \quad j = 1, \ldots, N,$$

$$k_{jj} = k_{10}(j) + \sum_{k=1,k\neq j}^{V} [k_{01}^{10}(j,k) + 2\exp(-h\upsilon_j/k_B T_0) k_{01}^{20}(j,k) + \theta_k^{-1} k_{02}^{10}(j,k)] \theta_k^{-1} \theta_j g_k,$$

$$k_{jk} = k_{01}^{10}(j,k) + 2\exp(-h\upsilon_j/k_B T_0) \theta_j^{-1} k_{01}^{20}(j,k) + k_{02}^{10}(j,k)] \upsilon_j^{-1} \upsilon_k \theta_k^{-1} \theta_j g_k,$$

where $\theta_j = 1 - \exp(-h\upsilon_j/k_B T_o)$. ΔT and ΔT_j^{vib} denote the fluctuation of the translational and the vibrational temperature, respectively, and the phase delay between them essentially results in the molecular relaxation phenomena in excitable gases [1,8]. The V-T transition rate $k_{10}(j)$ is the number of transitions per second per molecule in which the energy goes from the first-excited-vibrational level into translational motion; *i.e.*, the state of mode j goes from $1 \to 0$ and the vibrational level of molecule l is unchanged:

$$k_{10}(j) = \sum_{l=1}^{W} a_l Z(j,l) \times P_{0-0(l)}^{1-0(j)} \times [1 - \exp(-h\upsilon_j/k_B T_0)]. \tag{6}$$

The V-V transition rate $k_{01}^{10}(j,k)$ is the rate when mode j goes from $1 \to 0$ and mode k from $0 \to 1$:

$$k_{01}^{10}(j,k) = a_k Z(j,k) \times P_{0-1(k)}^{1-0(j)}. \tag{7}$$

The V-V transition rates $k_{01}^{20}(j,k)$ and $k_{02}^{10}(j,k)$ are the energy transition rates involving a two-for-one interchange of quantum:

$$k_{01}^{20}(j,k) = a_k Z(j,k) \times P_{0-1(k)}^{2-0(j)},$$
$$k_{02}^{10}(j,k) = a_k Z(j,k) \times P_{0-2(k)}^{1-0(j)}. \tag{8}$$

Here, $P_{0-0(l)}^{1-0(j)}$ is the V-T transition probability; $P_{0-1(k)}^{1-0(j)}$, $P_{0-1(k)}^{2-0(j)}$ and $P_{0-2(k)}^{1-0(j)}$ are the V-V transition probabilities (the details of the calculation for those transition probabilities are in the Refs. 9, 11, and 12). $Z(j,l)$ is the hard-sphere collision rate between a molecule having mode j and molecule l, and $Z(j,k)$ is the collision rate between molecules having mode j and k[12]:

$$Z(j,k) = 2N_k \sigma_{jk}^2 (2\pi k_B T_0/\mu_{jk})^{1/2}, \tag{9}$$

where $N_k = a_k N_A P_0/RT_0$ is number of molecules having mode k in a unit volume (N_A is the Avogadro's constant and P_0 is the equilibrium pressure), $\sigma_{jk} = (\sigma_j + \sigma_k)/2$ is the molecular pair-wise collision diameter, $\mu_{jk} = m_j m_k/(m_j + m_k)$ is the reduced molecular mass of the collision pair, with m_j and m_k denoting the molecular masses of the components.

Under the perturbation of a sound field with small amplitude, we can write [8]

$$\Delta T_j^{vib} \cong T_j^{vib} - T_0, \Delta T \cong T - T_0. \tag{10}$$

As $T - T_0$ is proportional to $e^{i\omega t}$ ($i = \sqrt{-1}$and ω is the angular frequency of sound wave), $T_j^{vib} - T_0$ will also be proportional to $e^{i\omega t}$. Thus, substituting Eq. (10) into Eq. (6), we obtain the algebraic relaxation equations

$$\begin{aligned} y_j(k_{jj}+i\omega) - \sum_{k=1,k\neq j}^{N} y_k k_{jk} &= k_{jj} - \sum_{k=1,k\neq j}^{N} k_{jk}, y_j \\ &= \Delta T_j^{vib}/\Delta T, j = 1, ..., N. \end{aligned} \tag{11}$$

3. Calculation of Multiple Relaxation Times

We can rewrite the algebraic relaxation equations, Eq. (11), in a matrix form as

$$(\mathbf{R} + i\omega\mathbf{I})\mathbf{y} = \mathbf{H}, \tag{12}$$

where $\mathbf{R}$ is called the energy-transition-rate matrix, $\mathbf{y}_j = y_j$, $\mathbf{R}_{jj} = k_{jj}$, $\mathbf{R}_{jk} = -k_{jk}$, $\mathbf{H}_j = k_{jj} - \sum\limits_{k=1,k\neq j}^{N} k_{jk}$, and $j, k = 1, ..., N, j \neq k$; $\mathbf{I}$ is the identity matrix. $\mathbf{R}$ can be diagonalized:

$$\mathbf{R} = \mathbf{V}\mathbf{\Lambda}\mathbf{V}^{-1}, \tag{13}$$

where $\mathbf{\Lambda}$ and $\mathbf{V}$ are the eigenvalue matrix, and the eigenvector matrix of $\mathbf{R}$, respectively. Substituting Eq. (13) and $I = \mathbf{V}\mathbf{V}^{-1}$ into Eq. (12), we have

$$(\mathbf{I} + i\omega\mathbf{\Lambda}^{-1})\mathbf{y}' = \mathbf{H}', \tag{14}$$

where $\mathbf{y}' = \mathbf{V}^{-1}\mathbf{y}$ and $\mathbf{H}' = \mathbf{\Lambda}^{-1}\mathbf{V}^{-1}\mathbf{H}$.

From Eq. (14), we get

$$y_j^{'} = \frac{h_j^{'}}{(1 + \mathrm{i}\omega\lambda_j^{-1})}, \quad j = 1, 2, \ldots, N, \tag{15}$$

where λ_j is the eigenvalue of $\mathbf{R}$; $y_j^{'} = \sum_{k=1}^{N} V_{jk}^{'} y_k$ and $h_j^{'} = \lambda_j^{-1} \sum_{k=1}^{N} V_{jk}^{'} h_k$ are the entries of $\mathbf{y}'$ and $\mathbf{H}'$, respectively, and $V_{jk}^{'}$ is the entry of $\mathbf{V}^{-1}$. Because $\mathbf{y} = \mathbf{V}\mathbf{y}'$, we obtain

$$y_j = \sum_{n=1}^{N} V_{jn} y_n^{'}, j = 1, 2, \ldots, N, \tag{16}$$

where V_{jn} is the entry of $\mathbf{V}$. Putting Eq. (15) into Eq. (16), we get

$$y_j = \sum_{n=1}^{N} \frac{V_{jn} h_n^{'}}{(1 + \mathrm{i}\omega\lambda_n^{-1})}, \quad j = 1, 2, \ldots, N. \tag{17}$$

Because $y_j = \Delta T_j^{vib}/\Delta T = dT_j^{vib}/dT$, substituting Eq. (17) into Eq. (5), we rewrite the effective IMH, C_V^{eff}, of the mixture as

$$\begin{aligned} C_V^{eff} &= C_V^{\infty} + \sum_{n=1}^{N} \frac{C_n^*}{(1 + i\omega\lambda_n^{-1})}, \\ C_n^* &= h_n^{'} \sum_{j=1}^{N} a_j C_j^{vib} V_{jn}, n = 1, 2, \cdots, N. \end{aligned} \tag{18}$$

Bass *et al.* [17] and Bauer *et al.* [18] have pointed out that C_V^{eff} under a multimode vibrational relaxation would be expressed in a standard form of $C_V^{eff} = C_V^{\infty} + \sum_n C_n^*/(1 + i\omega\tau_n)$ as a result of V-V energy coupling, where C_n^* and τ_n are the coupled vibrational IMH and the relaxation time for one of the single-relaxation processes. Thus, from Eq. (18), we have proven that the reciprocals of the eigenvalues of the energy-transition-rate matrix $\mathbf{R}$ are exactly the relaxation times; that is,

$$\tau_n = \lambda_n^{-1}, \quad n = 1, 2 \cdots N. \tag{19}$$

Based on Eqs. (18) and (19), on one hand, multimode vibrational relaxation is the sum of its single-relaxation processes, one of which corresponds to a relaxation time; on the other hand, the number of relaxation times is the same as that of the vibrational modes available in the gas. From Eq. (6), every V-V energy exchange couples the differential relaxation equations because the rate at which a given mode relaxes depends upon the states of vibrational excitation of all other modes [8,9]. This means that molecular multimode relaxation is controlled by a very strong V-V coupling, which influences both the relaxation frequencies and the relaxation strengths [19,20]. Therefore, the relaxation times depend on the probabilities of transition between different quantum states after a collision. That is, the relaxation time τ_n contains the lifetimes of all quanta, which depend upon the transition probabilities of all V-T and V-V energy transitions. Thus, allocating τ_n to a particular vibrational mode is not possible [17].

The specific heat of a relaxing gas, C_V^{eff} in Eq. (18), is a complex value, resulting in the speed of sound c_e also being complex [2]:

$$c_e = \sqrt{\frac{P_0}{\rho_0}\gamma^{eff}} = \sqrt{\frac{P_0}{\rho_0}\frac{C_V^{eff} + R}{C_V^{eff}}}, \tag{20}$$

where P_0 and ρ_0 are the equilibrium density and pressure, respectively. Furthermore, from the expression for the complex wave number $k_e = \frac{\omega}{c} - i\alpha_r = \frac{\omega}{c_e}$, the frequency-dependent phase speed c and the relaxational absorption coefficient α_r can be obtained respectively [15]. As the presence of relaxing gases is manifested by relaxational peaks in the dimensionless absorption coefficient $\alpha\lambda$ (λ is the sound wavelength) as a function of the sound frequency f, the absorption spectrum $\alpha\lambda$ is conventionally used to emphasize the effects of relaxation on sound absorption [12].

Moreover, acoustic absorption due to a given vibrational state will be appreciable only when the period of the sound is close to the relaxation time for the state; thus, measuring the frequency-dependent sound absorption in gases is a powerful method to characterize vibrational relaxation [12,15]. Particularly, the relaxation time τ_n is obtained from the measured frequency of maximum absorption (*i.e.*, the relaxation frequency f_n^{relax}) according to the equation [1,3,16]

$$\tau_n = \frac{1}{2\pi f_n^{relax}} \sqrt{\frac{(C_V^{\infty} + C_n^*)(C_V^{\infty} + C_n^* + R)}{C_V^{\infty}(C_V^{\infty} + R)}}. \quad (21)$$

Additionally, we can give physical interpretations for the temperature T^{vib} in Eq. (2) in two cases. First, for a pure diatomic gas has only one kind of vibrational mode that can arouse one single-relaxation process. In this case, excited vibrational energy is converted totally into translational energy (*i.e.*, only V-T energy transfer occurs) thus, T^{vib} is just related to a particular mode. Second, however, for a multimode vibrational relaxation, the energies of all modes are coupled through rapid V-V energy exchanges [17]. (This is also shown in Eq. (18), as each C_n^* contains part of the IMH of every vibrational mode.) Thus, T^{vib} is connected with all modes. Consequently, the interpretation of T^{vib} for a multimode vibrational relaxation becomes the temperature and the relaxation time for a relaxation process.

IV. SIMULATION RESULTS AND DISCUSSION

The horizontal scale of the sound absorption spectrum reflects the dependence of the relaxation time on the energy exchange between molecules. For the point with the maximum height in a sound absorption curve, its position along the abscissa, *i.e.*, the relaxation frequency, can be determined by using the relaxation time (see Eq. (21)). Hence, we will confirm the validity of our proposed model by comparing theoretical calculations of the relaxation frequencies with experiment data. Table 1 provides the collisional diameter (σ) and the depth of the potential well (ε) of a molecule, as well as the characteristic frequency, amplitude coefficient ($\bar{A}^2$), degeneracy (g) and steric factor of the vibrational modes for nitrogen, oxygen, chlorine, methane, and carbon dioxide, respectively, which are necessary for our proposed model.

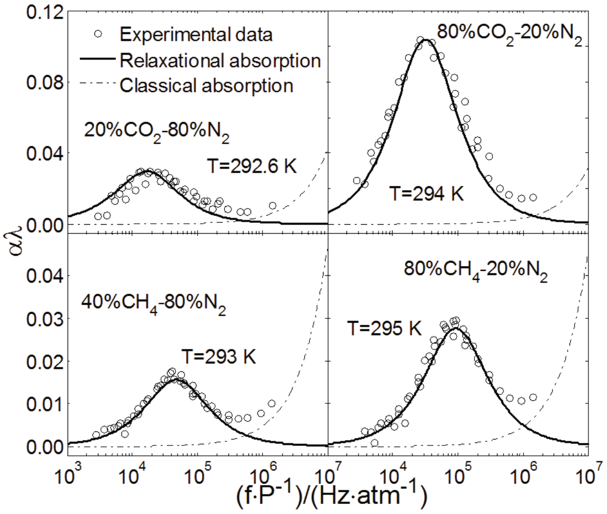

Fig. 1. Comparison of theoretical sound absorption spectra with experimental data from Ejakov *et al.* [21] for CO_2-N_2 and CH_4-N_2 mixtures around room temperature.

Table 1. Necessary parameters for the calculation of the vibrational energy transition probabilities for selected gases [12,21]

Gas	σ $(10^{-10}\mathrm{m})$	ε/k_B (K)	Normal modes of vibration (cm^{-1})	$\bar{A}^2$ (amu^{-1})	g	Steric factor
N_2	3.704	80.01	$v = 2331$	0.0714	1	1/3
O_2	3.541	88.17	$v = 1554$	0.0625	1	1/3
Cl_2	4.400	257.47	$v = 577$	0.0282	1	1/3
CH_4	3.759	154	$v_1 = 2915$	0.9921	1	2/3
			$v_2 = 1534$	0.9921	2	
			$v_3 = 3019$	0.9923	3	
			$v_4 = 1306$	0.8368	3	
CO_2	3.99	190.32	$v_1 = 1388$	0.05	1	2/3
			$v_2 = 677$	0.05	2	
			$v_3 = 2349$	0.05	1	

We first consider sound absorption spectra in the mixtures CO_2-N_2 and CH_4-N_2. In Fig. 1, comparisons of 20%CO_2-80%N_2, 80%CO_2-20%N_2, 20%CH_4-80%N_2, and 80%CH_4-20%N_2 show that the theoretical absorption spectra agree quite well with the experimental data from Ejakov *et al.* [21]. The total sound absorption $\alpha\lambda$ is the sum of the relaxational parts $\alpha_r\lambda$ and the classical parts $\alpha_c\lambda$ related with transport phenomena ($\alpha_c\lambda$ is calculated using the formulation of Stokes and Kirchhoff [2]). The classical absorption is generally so small compared with the relaxational absorption at values of $f/P < 10^6 Hz \cdot atm^{-1}$ (1 atm = 0.101325 MPa) that it can be considered to be negligible [12]. On the other hand, the time between molecular collisions is in-

Table 2. Calculations of the relaxation strengths and the relaxation times of single-relaxation processes at atmospheric pressure ($P = 1$ atm or 0.101325 MPa) in the gas media shown in Fig. 1.

Gas	*1*st process		*2*nd process		*3*rd process		*4*th process		*5*th process	
	ε_1	τ_1/s	ε_2	τ_2/s	ε_3	τ_3/s	ε_4	τ_4/s	ε_5	τ_5/s
20%CO_2-80%N_2	1.85^{-2}	9.93^{-6}	7.76^{-4}	5.74^{-5}	5.36^{-5}	1.01	3.91^{-11}	1.86^{-6}	\	\
80%CO_2-20%N_2	6.37^{-2}	6.26^{-6}	6.11^{-4}	2.20^{-6}	4.92^{-9}	2.47^{-6}	4.25^{-5}	8.80^{-2}	\	\
40%CH_4-80%N_2	9.87^{-3}	3.43^{-6}	4.05^{-8}	6.06^{-10}	1.40^{-12}	2.31^{-9}	8.96^{-10}	8.96^{-9}	5.74^{-5}	1.41^{-6}
80%CH_4-20%N_2	1.74^{-2}	1.82^{-6}	8.07^{-13}	6.05^{-10}	9.68^{-10}	2.70^{-9}	3.94^{-8}	1.69^{-10}	2.96^{-6}	4.27^{-7}

The notation x^y implies $x \times 10^y$.

Table 3. Comparisons of theoretical calculations and experiment data for the relaxations of gases with different compositions at atmospheric pressure ($P = 0.101325$ MPa).

Gas Composition	Coupled vibrational heat for the primary process ($J\,mol^{-1}K^{-1}$)	Calculated relaxation time for the primary process (s)	Theoretical relaxation frequency (Hz)	Experimental relaxation frequency (K) (Hz)	Temperature	Reference
N_2	1.32^{-2}	5.80	0.028	~0.063	297	[25]
O_2	2.83^{-1}	1.49^{-2}	10.8	~10	303.2	[26]
Cl_2	4.48	4.69^{-6}	4.02^4	~4.0^4	296.2	[27]
CH_4	2.34	1.36^{-6}	1.27^5	~1.6^5	299.15	[24]
CH_4	2.16	1.42^{-6}	1.20^5	~0.95^5	293.9	[21]
CO_2	7.57	5.01^{-6}	4.16^4	~3.9^4	296.15	[22]
CO_2	7.57	5.01^{-6}	4.16^4	~3.8^4	296.15	[28]
CO_2	7.65	4.90^{-6}	4.27^4	~4.5^4	298.15	[29]
20%CO_2-80%O_2	1.48	1.23^{-5}	1.37^4	~1.2^4	300	[30]
30%CO_2-70%O_2	2.17	1.08^{-5}	1.61^4	~1.8^4	300	[30]
60%CO_2-40%N_2	4.32	7.38^{-6}	2.55^4	~2.6^4	293.5	[21]
60%CH_4-40%N_2	1.29	2.52^{-6}	6.63^4	~7.3^4	293.4	[21]
98%CO_2-2%air	7.49	5.05^{-6}	4.08^4	~4.0^4	298	[31]
98%CH_4-2%air	2.25	1.39^{-6}	1.23^5	~1.3^5	298	[31]

The notation x^y implies $x \times 10^y$.

versely proportional to the pressure, making a lowering of ambient pressure equivalent to a raising of the sound frequency and vice versa. Thus, the sound absorption spectrum $\alpha\lambda$ is traditionally plotted as a function of the frequency divided by the pressure $f\ /P$ [11].

Interestingly, all four spectra in Fig. 1 have only one absorption peak. Because an absorption peak corresponds to a relaxation process, this means that only one significant relaxation process is formed and only a single relaxation time is observed in those four mixtures. This phenomenon actually exists in most excitable gases [1, 12]. However, according to Table 1, for example, there are four kinds of vibrational modes in the CO_2-N_2 mixture. Based on Eq. (19), there would have four single-relaxation processes in the mixture. Schafer first recognized that a single relaxation time would be observed even when more than one mode is relaxing as long as the energy relaxes by a fast V-V exchange through a gating mode, but his derivation failed to consider the quantum nature of the V-V energy exchange [3]. Thus, we need to give an other interpretation to avoid this contradiction.

As defined by Kneser [22], the relaxation strength of a single-relaxation process is

$$\varepsilon_n = \frac{C_n^* R}{(C_V^\infty + C_n^*)(C_V^\infty + R)}. \tag{22}$$

Moreover, because generally $C_n^* \ll C_V^\infty$ at room temperature, Eq. (22) can be simplified as $\varepsilon_n \approx C_n^* R/(C_V^{\infty 2} + C_V^\infty R)$. Table 2 gives the calculated relaxation strengths and relaxation times (at $P = 1$ atm) for all single-relaxation processes in the four mixtures of Fig. 1. We find that only the relaxation strength of the *1*st single-relaxation process is significant (*i.e.*, the *1*st single-relaxation process is the primary relaxation process) while the strengths of the other single-relaxation processes are too small to be considered. Thus, although there will be as many single-relaxation processes with different relaxation times as there are vibrational modes available in the gas, most of these processes will have small relaxation strengths; thus, their contributions to sound absorption can be ignored in practice. A similar interpretation can also be given qualitatively by using the phenomenological theory from BASS *et al.* [23]. As a consequence, in most cases, we just need to focus on the primary relaxation process, which corresponds to the single-relaxation process with the maximum strength ε_n or the maximum coupled vibrational IMH C_n^*.

Table 3 shows comparisons between theoretical calculations and experiment data for the relaxation frequencies of various gas compositions ($P = 1$ atm). For each composition in Table 3, according to the experimental data, only one peak appears in the absorption spectrum [18, 25–30]. Hence, we only need to investigate the relaxation time of the primary relaxation process. For N_2, because the relaxation frequency is far below the measurement capability, the experimental data actually did not catch up with the true relaxation frequency, resulting in a slight discrepancy between the theoretical and the experimental results. For CH_4, the theoretical value is midway between the experimental data from Gravitt *et al.* [24] and Ejakov *et al.* [21] For $20\%CO_2$-$80\%O_2$ and $30\%CO_2$-$70\%O_2$, the small difference may come from the sensitivity of the relaxation frequency in gases to impurities. For example, small concentrations of water can cause a large shift of the relaxation frequency [21]. For $100\%O_2$, $100\%Cl_2$, $60\%CO_2$-$40\%N_2$, and $60\%CH_4$-$40\%N_2$, our theoretical calculations agree well with the experiments. For the ternary mixtures $98\%CO_2$-2%air and $98\%CH_4$-2%air (where air is supposed to be comprised of 78% N_2 and 22% O_2), our results are also consistent with the experimental data. Overall, comparisons in Table 3 further validate our proposed model for calculating the vibrational relaxation times.

V. CONCLUSION

In this paper, we have provided a theoretical physical model that allows for the two quanta for one quantum V-V exchange to calculate the vibrational relaxation times in multi-component excitable gases. The eigenvalues of the energy-transition-rate matrix of the algebraic relaxation equations are proven to be the reciprocals of multi-relaxation times. We have quantitatively demonstrated that a vibrational multimode relaxation will have multiple relaxation times and that their number is equal to that of the vibrational modes available in gas. One of the multiple relaxation times includes lifetimes of all quanta, which depend upon the transition probabilities of all V-T and V-V energy transitions, and every relaxation time is related with all vibrational modes. Moreover, for most excitable gases, the relaxation frequencies calculated from the relaxation times of the primary processes are the relaxation frequencies.

Just as the SSH theory is limited for applications in the calculation of energy transition probabilities in strongly polar gases [8,12], the same deficiency also exists in our proposed model. Thus, in the future, some modified theories [11,32,33] should be used to enhance our model to accommodate polar gases with high concentrations.

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