Calculating vibrational mode contributions to sound absorption in excitable gas mixtures by decomposing multi-relaxation absorption spectroscopy

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ABSTRACT

Sound relaxational absorption spectroscopy of excitable gas mixtures is potentially applied for gas composition detection. The relaxation of vibrational modes of gas molecules determines the sound relaxational absorption. However, to our knowledge, the contribution of each vibrational mode available in gas mixtures to sound multi-relaxation absorption has not been calculated in existing literature. In this paper, based on the decoupled expression of the effective isochoric molar heat for a gas mixture, a sound multi-relaxation absorption spectrum is decomposed into the sum of single-relaxation spectra. From this decomposable characteristic, the contribution of each vibrational mode available in the gaseous medium to the multi-relaxation absorption is obtained at room temperature. For various gas compositions including carbon dioxide, methane, nitrogen etc., the calculated contributions of vibrational modes are verified by the comparison with experiment data. We prove the following views with quantifiable outcomes that the primary molecular relaxation process associated with the lowest mode plays the major role in acoustic relaxational absorption of gas mixtures; the mode with lower vibrational frequency provides higher contribution to the primary relaxation process. This work could provide a deeper insight into the relationship between the sound relaxational absorption spectroscopy and gas molecules.

Keywords: sound absorption; Molecular vibrational relaxation; Mode contributions; Decomposing multi-relaxation absorption spectra

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1. Introduction

Acoustic relaxational absorption spectroscopy of gas mixtures is potentially applied for gas composition detection, such as practical applications for real-time monitoring of natural gas [1-8]. The propagation of acoustic waves in gases is fundamentally a molecular phenomenon [9]. The sound absorption in excitable gases (polyatomic or diatomic gases or their mixtures) is caused by two mechanisms: the classical absorption associated with transport phenomena (e.g., heat conduction and viscosity) and the non-classical, or relaxational absorption associated with the lag in adjustment between the internal states of the molecules and their external energy [10]. In a thermal equilibrium, the energy distribution of a gas between the external (translational) molecular kinetic energy and the internal (e.g., vibrational, rotational) states of energy of the molecules only depends on the temperature of the gas. When the equilibrium is disturbed by the propagation of an acoustic wave through the gas, there is an instantaneous increase (due to compression) in the external energy. By molecular collisions, some of this energy increase enters into the internal states. A certain relaxation time (or time lag) is required for this energy to be transferred back to the external form to reestablish equilibrium. As a result of that, much of this energy released on de-excitation will be released as heat to give rise to a net absorption of acoustic energy—the relaxational absorption. For most simple molecules at room temperature, the rapid equilibration between rotation and translation makes Vibrational-Rotational plus Rotational-Translational energy transfer process indistinguishable from the Vibrational-Translational (V-T) process. Thus, rotation is usually classified as translation as “external” degrees of freedom (DOF) to distinguish from vibration as the “internal” DOF which takes a longer time to adjust [10]. Thus, the internal DOF thermal relaxation is almost entirely attributed to the vibrational modes, whose relaxation processes are the cause for the sound relaxational absorption around room temperature [3].

Herzfeld and Rice made the first application of a vibrational relaxation process to the theoretical calculation of acoustic absorption [11]. Landau and Teller treated the vibrational energy as the multileveled system of a harmonic oscillator to calculate V-T relaxation time [12]. Schwartz, Slawsky, and Herzfeld (SSH) refined the Landau and Teller’s theory by including a one-for-one quantum exchange of vibrational–vibrational (V–V) energy transfer in two diatomic mixtures [13]. Tanczos developed the SSH theory to calculate the absorption and dispersion of acoustic wave in pure polyatomic gases allowing for the two quanta for one quantum V-V exchange [14]. Dain, Lueptow (DL) and Petculescu predicted the sound relaxational absorption in

ternary mixtures with the extended SSH relaxation equations, and attempted to describe the degree of participation of a vibrational mode in the acoustic relaxation by using normalized eigenvectors of matrix $\mathbf{A}$ [15,16]. Recently, we presented the models to predict sound relaxational absorption spectra in multi-component gas mixtures [17] and decoupled the extended SSH energy relaxation equations to explain how a multimode relaxation leads to the peaks in the corresponding sound absorption spectrum [18]. We also developed an algorithm [4] to capture the primary vibrational relaxation processes from the acoustic measurements at two operating frequencies and applied the algorithm into gas composition detection by employing the absorption spectral peak locations and effective relaxation area (ERA) of spectral peaks in gas mixtures [6-8]. Generally, an excitable gas contains two or more molecular vibrational modes to arouse a multi-relaxation process which is synthesized by the complicated strong vibrational–vibrational (V–V) energy coupling [19,20]. As far as we know, in excitable gas mixtures, the contribution of each vibrational mode to acoustic multi-relaxation absorption has not been calculated or measured in existing literature. Therefore, it is still desirable to obtain this straightforward relation between vibrational modes and acoustic absorption.

In this paper, based on the decoupled effective isochoric molar heat (IMH) derived from the extended Tanczos relaxation equations, we demonstrate that the sound relaxational absorption spectrum due to a multi-relaxation process can be decomposed into the sum of spectra ascribed to a set of single-relaxation processes which belong to the multi-relaxation process (In our previous works [17,18], we directly calculated the multi-relaxation absorption spectrum, while we will obtain the multi-relaxation absorption spectrum by the sum of its single-relaxation absorption spectra in this paper). This decomposition means that the acoustic absorption in excitable gases not only can be traditionally divided into the classical absorption part and the relaxational absorption part, the relaxational absorption part under a multi-relaxation process can be further decomposed into the sum of single-relaxation processes spectra. From this decomposable characteristic of multi-relaxation absorption, we can calculate the contribution of each vibrational mode available in the gaseous medium to the sound relaxational absorption. The quantitative relation between the molecular makeup of gas mixtures and acoustic absorption revealed in this paper will improve our understanding in the practical applications of gas detection with acoustic absorption spectroscopy.

This paper is organized as follows. In Section 2, the vibrational relaxation

equations given by Tanczos [14] have been extended to multi-component gas mixtures. Apart of that, based on the decoupled expression of the effective IMH, we demonstrate that an acoustic relaxation process aroused by multiple vibrational modes is the sum of single-relaxation processes with different relaxation times and strengths, showing a multi-modes process is a multi-relaxation process that can be expressed in terms of the process IMHs and the relaxation times of the single-relaxation processes. Section 3 demonstrates a sound multi-relaxation absorption spectrum can be decomposed into the sum of single-relaxation absorption spectra, and thus we can calculate the vibrational mode contributions to the acoustic relaxational absorption. In Section 4, we compare the calculations of decomposed sound absorption spectra and vibrational mode contributions with the experimental data to validate the proposed model. Section 5 concludes this paper.

2. Decoupled effective isochoric molar heat of gas mixture

2.1. Extended Tanczos relaxation equations

In our previous work [17,18], we have applied the SSH coupled relaxation equations, which only allows for a one-for-one quantum exchange of V-V energy transfer, into a multi-component gas mixture. Similarly, for a gas mixture with W kinds of molecules including N vibrational modes, we can extend the Tanczos relaxation equations [14], which permit two quanta for one quantum V-V exchange, to a general form as

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

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

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

where h is Planck's constant, k_B is Boltzmann's constant, g_k is the degeneracy of mode k . $\theta_j = 1 - \exp(-h\nu_j / k_B T_0)$ is the characteristic temperature of vibrational mode j , T_0 is the equilibrium temperature, ν_j and ν_k are the characteristic frequencies of mode j and mode k respectively. $\Delta T = T - T_0$ and $\Delta T_j^{\text{vib}} = T_j^{\text{vib}} - T_0$ are the fluctuations of the translational and vibrational temperature respectively, T is the instantaneous temperature of external DOF, T_j^{vib} is the instantaneous temperature of vibrational mode j . 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 $1 \rightarrow 0$ and the vibrational level of molecule l is unaltered; the V-V transition rate $k_{01}^{10}(j,k)$ is the rate when mode j goes from $1 \rightarrow 0$ and mode k goes from $0 \rightarrow 1$ [18,21]. 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

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

Here, a_k is the mole fraction of mode k , $Z(j,k)$ is the hard sphere collision rate between the molecules having the mode j and k [21]. $P_{0-0(l)}^{1-0(j)}$ is the V-T transition probability (i.e. the probability that the state of mode j goes from $1 \rightarrow 0$ and the vibrational level of molecule l is unchanged). $P_{0-1(k)}^{1-0(j)}$ is the V-V transition probability that during a binary collision the mode j of one molecule will change its quantum state from 1 to 0, while simultaneously a second mode k in the other molecule will change its state from 0 to 1. $P_{0-1(k)}^{2-0(j)}$ and $P_{0-2(k)}^{1-0(j)}$ are the V-V transition probabilities involving a two-for-one interchange of quantum. The calculation expressions for those transition probabilities are given by Tanczos [14,16,21]. Table 1 in ref. [18] provides all the necessary parameters to calculate the vibrational transition probabilities for nitrogen, oxygen, chlorine, methane, and carbon dioxide.

2.2. Decoupled effective isochoric molar heat

The effective IMH represents the macroscopic “footprint” of vibrational relaxation effects [3]. For the relaxing mixture, its effective IMH C_V^{eff} is [18]

$$C_V^{\text{eff}} = C_V^{\infty} + \sum_{j=1}^N a_j C_j^{\text{vib}} dT_j^{\text{vib}} / dT. \quad (3)$$

where $C_V^{\infty} = \sum_{l=1}^W a_l C_l^{\infty}$ is the external IMH of the mixture or the non-relaxation part of heat capacity, a_l is the mole fraction of molecule l ($\sum_{l=1}^W a_l = 1$), C_l^{∞} is the external IMH of molecule l . For a linear molecule, there are 3 translations and 2 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 the vibrational IMH of mode j calculated by the Planck-Einstein function [15], a_j is the mole fraction of mode j , dT_j^{vib} / dT is the ratio of vibrational-to-acoustic temperature fluctuations of mode j .

To calculate dT_j^{vib} / dT in Eq. (3), we need convert the relaxation equations into its algebraic form. In an acoustic field with small amplitude of harmonic plane wave of angular frequency ω , Eq. (1) becomes the following algebraic relaxation equations [18]

$$y_j(k_{jj} + i\omega) - \sum_{\substack{k=1 \\ k \neq j}}^N y_k k_{jk} = k_{jj} - \sum_{\substack{k=1 \\ k \neq j}}^N k_{jk}, \quad (4)$$

$$y_j = \Delta T_j^{\text{vib}} / \Delta T \cong dT_j^{\text{vib}} / dT, \quad j, k = 1, \dots, N, j \neq k.$$

Then, Eq. (4) can be expressed in a matrix form

$$(i\omega \mathbf{I} + \mathbf{R})\mathbf{y} = \mathbf{H}, \quad (5)$$

where $\mathbf{y}_j = y_j$, $\mathbf{R}_{jj} = k_{jj}$, $\mathbf{R}_{jk} = -k_{jk}$, $\mathbf{H}_j = k_{jj} - \sum_{k=1, k \neq j}^N k_{jk}$, $j, k = 1, \dots, N, j \neq k$; $\mathbf{I}$

is the identity matrix. Eq. (5) links the temperature fluctuations of the vibrational mode and external DOF. If the energy-transition-rate matrix $\mathbf{R}$ can be diagonalized in the form as $\mathbf{R} = \mathbf{V}\mathbf{\Lambda}\mathbf{V}^{-1}$, from Eq.(5), we have [18]

$$y_j = \sum_{n=1}^N \frac{V_{jn} h'_n}{(1 + i\omega \lambda_n^{-1})}, \quad j = 1, 2, \dots, N. \quad (6)$$

Where V_{jn} is the entry of matrix $\mathbf{V}$, λ_j is the eigenvalue of $\mathbf{R}$, $h'_n = \lambda_n^{-1} \sum_{k=1}^N V_{nk} h_k$ (λ_n^{-1} is the reciprocal of eigenvalue of $\mathbf{R}$, V_{nk} and h_k are the entries of matrix $\mathbf{V}^{-1}$ and $\mathbf{H}_j$ respectively).

Noting that $y_j \cong dT_j^{\text{vib}} / dT$ and substituting Eq. (6) into Eq. (3), we obtain the decoupled expression of the effective IMH for the mixture as

$$C_V^{\text{eff}} = C_V^{\infty} + \sum_{n=1}^N \frac{h'_n \sum_{j=1}^N a_j C_j^{\text{vib}} V_{jn}}{(1 + i\omega \lambda_n^{-1})} = C_V^{\infty} + \sum_{n=1}^N \frac{C_n^*}{(1 + i\omega \tau_n)}, \quad n = 1, 2, \dots, N. \quad (7)$$

Where $C_n^* = h'_n \sum_{j=1}^N a_j C_j^{\text{vib}} V_{jn}$ and $\tau_n = \lambda_n^{-1}$, they are the process IMH and the isothermal relaxation time for one of decoupled single-relaxation processes respectively [18]. The effect of the delay in the transfer of energy between the internal and external DOF, i.e. the vibrational relaxation, is clearly displayed in the frequency dependence of C_V^{eff} . In Eq. (7), the equilibrium external and vibrational IMH are

C_V^{∞} and $\sum_{n=1}^N C_n^*$ respectively. As the frequency of state alteration increases, an obvious decrease in the modulus of C_V^{eff} will happen, making C_V^{eff} ultimately reach the minimum limiting value C_V^{∞} when $\omega \rightarrow \infty$ (when the internal energy state is not populated). Inversely, the equilibrium thermodynamic heat capacity reaches the maximum limiting value $C_V^{\infty} + \sum_{n=1}^N C_n^*$ when $\omega \rightarrow 0$ (when the internal state is in equilibrium with the external states). At frequencies where the period of the compression-rarefaction cycle is comparable with the relaxation time, the

frequency-dependent C_v^{eff} leads to the sound relaxational absorption [22].

In Eq. (7), N identifies the number of the decoupled single-relaxation processes, which is equivalent to the number of the vibrational modes as shown in Eq. (3). Actually, an excitable gas can be treated as a mixture of its DOF. Since every V–T transfer can provide a deexcitation path for the resident acoustic energy to the translational energy [10,18], the number of the vibrational modes would be the same as the number of the single-relaxation processes. Therefore, a multimode relaxation process is a multi-relaxation process and it can be expressed in terms of the vibrational IMHs and the relaxation times of the single-relaxation processes.

Furthermore, the relation between C_v^{eff} and the sound propagation characteristics is connected by the effective thermodynamic sound speed $c_e = \sqrt{P_0(C_v^{\text{eff}} + R)/(\rho_0 C_v^{\text{eff}})}$ (P_0 and ρ_0 are the equilibrium pressure and density respectively) [10]. From this relation, we obtained the sound multi-relaxation absorption spectrum $\alpha_r \lambda = -2\pi \cdot \text{Im}(c_e^{-1}) / \text{Re}(c_e^{-1})$ (λ is the sound wavelength) for the mixture in the previous works [17,18].

3. Vibrational mode contribution for sound absorption

3.1. Decomposition of sound multi-relaxation absorption spectrum

The features of a sound absorption spectrum in excitable gases are determined by the characteristics of the resultant effective IMH [23]. Eq. (7) implies that there are exactly N decoupled single-relaxation processes characterized by relaxation times τ_n ($n=1,2,L,N$) and process IMHs C_n^* ($n=1,2,L,N$) in the relaxing gas with N vibrational modes. For those single-relaxation processes, the external IMH C_v^∞ is the same; so the differences of absorption spectra due to those single-relaxation processes only result from their process IMHs and relaxation times.

From the measurements of acoustic absorption and speed at two frequencies, Petculescu and Lueptow (PL) propose a reconstructive algorithm [3] to synthesize the effective IMH of a single-relaxation process. Based on the PL algorithm, when considering a single-relaxation process with the relaxation time τ_n and the process IMH C_n^* , we can define the effective IMH of the single-relaxation process in the mixture as

$$C_n^{\text{eff}} = C_v^\infty + C_n^* / (1 + i\omega\tau_n), \quad (9)$$

Acoustic propagation under the single-relaxation process of relaxing gas can be described in terms of its effective thermodynamic acoustic speed

$$c_n^e = \sqrt{(P_0 / \rho_0) / [(C_n^{\text{eff}} + R) / C_n^{\text{eff}}]}, \quad (10)$$

By using the relation between the effective speed c_n^e and its effective wave number

k_e , i.e. $k_e = \omega/c - i\alpha_n = \omega/c_n^e$ (c is the phase speed of sound), the frequency dependent sound relaxational absorption spectrum $\alpha_n \lambda$ (i.e. the absorption coefficient per wavelength due to the n th single-relaxation process) is [17]

$$\alpha_n \lambda = 2\pi \cdot \{[(B_n / C_n)^2 + 1]^{1/2} - B_n / C_n\}, \quad (11)$$

$$B_n = x_n^2(\omega) + y_n^2(\omega) + R x_n(\omega), C_n = R y_n(\omega).$$

Here $x_n(\omega) = \text{Re}(C_n^{\text{eff}}) = C_V^\infty + \frac{C_n^*}{1 + (\omega\tau_n)^2}$, and $y_n(\omega) = -\text{Im}(C_n^{\text{eff}}) = \frac{\omega\tau_n C_n^*}{1 + (\omega\tau_n)^2}$.

In the works of Bauer [19,20], Bass[24] and Shields[25], they suppose that a multimode relaxation absorption spectrum can be decomposed into a sum of single-relaxation absorption spectra, each of them has a different relaxation time and relaxation strength. Thus, we assume that the relaxational absorption spectrum $\alpha_r \lambda$ due to a multi-relaxation process can be decomposed into the sum of the spectra due to the decoupled single-relaxation processes characterized by τ_n ($n=1,2,L,N$) and C_n^* ($n=1,2,L,N$), that is

$$\alpha_r \lambda = \sum_{n=1}^N \alpha_n \lambda. \quad (12)$$

3.2. Vibrational mode-contribution for sound absorption

The presence of relaxing gases is obviously manifested by relaxational peaks in the bell-shaped absorption spectrum [10,21]. The most important point in a single-relaxation absorption spectrum is its absorption maximum, the frequency and height of which are used to obtain the relaxation time and the relaxation strength respectively [4,6]. From Eq. (11), the minimum value of B_n / C_n corresponds to the maximum height of $\alpha_n \lambda$. Thus, setting $d(B_n / C_n)/d\omega = 0$, the frequency of absorption maximum (i.e. the relaxation frequency) for $\alpha_n \lambda$ is

$$f_n^m = \frac{1}{2\pi\tau_n} \sqrt{\frac{(C_V^\infty + C_n^*)(C_V^\infty + C_n^* + R)}{C_V^\infty (C_V^\infty + R)}}. \quad (13)$$

When $\omega = 2\pi f_n^m$, the height of absorption maximum $(\alpha_n \lambda)_m$ can be inferred from Eq. (13) as

$$(\alpha_n \lambda)_m = \frac{\pi}{2} \frac{\varepsilon_n}{\sqrt{1 - \varepsilon_n}}, \quad \varepsilon_n = \frac{C_n^* R}{(C_V^\infty + C_n^*)(C_V^\infty + R)}. \quad (14)$$

where ε_n is the relaxation strength defined by Kneser [24]. It is generally true that $C_n^* \ll C_V^\infty$ to make $\varepsilon_n \ll 1$ around room temperature [24]. Thus, we can rewrite $(\alpha_n \lambda)_m$ in Eq. (14) as

$$(\alpha_n \lambda)_m \approx \frac{\pi}{2} \frac{C_n^* R}{C_V^\infty (C_V^\infty + R)}. \quad (15)$$

Eq. (15) shows that the height of absorption maximum is proportional to the corresponding process IMH C_n^* , which means the bigger C_n^* a single-relaxation process has, the stronger relaxation strength it possesses.

In our previous works [4], we have proven that a single-relaxation absorption spectrum $\alpha_n \lambda$ in the whole frequency range can be reconstructed from the point of absorption maximum, that is

$$\alpha_n \lambda = (\alpha_n \lambda)_m \frac{2 f_n^m f}{f^2 + (f_n^m)^2}. \quad (16)$$

Here f is the frequency of sound. Eq. (16) shows that the absorption spectrum reaches a maximum when f matches f_n^m . Thus, for a single-relaxation absorption spectrum, the differences in the heights of absorption at different frequencies just come from the matching degrees between f and f_n^m (or τ_n based on Eq. (13)). The matching degrees determine how much the acoustic energy retained by the vibrational modes will be converted to thermal energy during the relaxation transitions. Therefore, although the absolute contribution of a vibrational mode available in the mixture to the relaxational absorption is different at various frequencies in a single-relaxation absorption spectrum, the percent contribution will be the same at any frequency.

From Eqs. (15) and (16), we can see $(\alpha_n \lambda)_m$ is linearly proportional to C_n^* and the single-relaxation absorption spectrum $\alpha_n \lambda$ can be reconstructed from the point of absorption maximum; on the other hand, the vibrational modes only changes the value of C_n^* . Hence the percent contribution of vibrational modes to the absorption spectrum $\alpha_n \lambda$ is equivalent to C_n^* . Consequently, based on Eq. (7), we define $Z_{j,n}$ as the contribution of mode j for C_n^* or the n th single-relaxation process; that is

$$Z_{j,n} = a_j C_j^{\text{vib}} V_{jn} h_n', \quad j, n = 1, 2, L, N. \quad (17)$$

Eq. (17) shows that $Z_{j,n}$ is decided by four factors: i) The mole fraction a_j . ii) The vibrational IMH C_j^{vib} , which is proportional to the ambient temperature and varies inversely with the characteristic frequency of mode j [18]. iii) The entry of the eigenvector matrix of the energy-transition-rate matrix V_{jn} , which is related to the V-V and V-T energy transition rates between mode j and the other modes. iv) h_n' is the outcome from the interactions among all modes, which is the same for all vibrational modes. In short, Eq. (17) demonstrates that the contribution of mode j to the n th single-relaxation process is not just decided by itself but also dependent upon its interactions with the other modes.

By combining Eqs. (7) and (17), the process IMH C_n^* can be rewritten as $C_n^* = \sum_{j=1}^N Z_{j,n}$, demonstrating the IMH of a single-relaxation process is the sum of contributions from all vibrational modes, in other words, a relaxational absorption peak is related to all vibrational modes available to the gas. Further, the mode contribution $Z_{j,n}$ can be expressed in percentage as

$$P_{j,n} = (Z_{j,n} / \sum_{j=1}^N Z_{j,n}) \times 100\% . \quad (18)$$

4. Simulations and discussion

4.1. Decomposing multi-relaxation absorption spectrum

To verify our model for decomposing the multi-relaxation absorption spectra in excitable gases, we consider the mixtures of 20%CH₄-80%N₂, 40%CH₄-60%N₂, 60%CH₄-40%N₂, 80%CH₄-20%N₂, 20%CO₂-80%N₂, 40%CO₂-60%N₂, 60%CO₂-40%N₂ and 80%CO₂-20%N₂ at room temperature. In our previous works [17,18], we directly calculated the multi-relaxation absorption by $\alpha_r \lambda = -2\pi \cdot \mathbf{Im}(c_e^{-1}) / \mathbf{Re}(c_e^{-1}) (c_e = \sqrt{P_0(C_v^{\text{eff}} + R) / (\rho_0 C_v^{\text{eff}})})$. In contrast, in this paper, we will obtain the multi-relaxation absorption by the sum of all single-relaxation absorption spectra, i.e. $\alpha_r \lambda = \sum_{n=1}^N \alpha_n \lambda$ (Eq. (12)). CH₄ has four vibrational modes, CO₂ has three modes, and N₂ has one mode [18]. So, for the mixture CH₄-N₂, its acoustic multi-relaxation process would contain five single-relaxation processes; for the mixture CO₂-N₂, four single-relaxation processes.. In Figures 1 and 2, the total acoustic absorption $\alpha \lambda$ (solid line) is the sum of the multi-relaxation absorption $\alpha_r \lambda$ (dash line) calculated by Eq. (12) and the classical absorption $\alpha_c \lambda$ (dotted line) associated with transport phenomena got from the Stokes and Kirchhoff formulation [10,26]. Comparisons show that the theoretical absorption spectra $\alpha \lambda$ agree fairly well with the experimental data (circles) from Ejakov et al [27].

Fig. 1. Comparison of theoretical acoustic absorption spectra with experimental data from Ejakov et al. [27] for CH₄-N₂ mixtures around room temperature.

Fig. 2. Comparison of theoretical acoustic absorption spectra with experimental data from Ejakov et al. [27] for CO₂-N₂ mixtures around room temperature.

The calculations of relaxation strengths by Eq. (14) and relaxation times by Eq. (7) (at $P = 1$ atm) for all single-relaxation processes in the mixtures of Figs. 1 and 2 are given in Table 1. For 40%CH₄-60%N₂, 60%CH₄-40%N₂, 80%CH₄-20%N₂, 20%CO₂-80%N₂, 60%CO₂-40%N₂ and 80%CO₂-20%N₂, it is found that only the relaxation strengths of 1st processes are significant while the relaxation strengths of other processes are too small. So, the 1st process is the primary relaxation process. As illustrated in Figures 3 and 4, if we just consider the influence of 1st process to the acoustic propagation for each of those six mixtures, the 1st single-relaxation absorption $\alpha_1 \lambda$ calculated by Eq. (11) is overlapped with multi-relaxation absorption $\alpha_r \lambda$ (40%CH₄-60%N₂: $C_I^* = 0.850 \text{ J mol}^{-1} \text{ K}^{-1}$; 60%CH₄-40%N₂: $C_I^* = 1.29 \text{ J mol}^{-1} \text{ K}^{-1}$; 80%CH₄-20%N₂: $C_I^* = 1.76 \text{ J mol}^{-1} \text{ K}^{-1}$; 20%CO₂-80%N₂: $C_I^* = 1.43 \text{ J mol}^{-1} \text{ K}^{-1}$; 60%CO₂-40%N₂: $C_I^* = 4.33 \text{ J mol}^{-1} \text{ K}^{-1}$; 80%CO₂-20%N₂: $C_I^* = 5.96 \text{ J mol}^{-1} \text{ K}^{-1}$.). Therefore, although Eq. (12) shows that a multi-relaxation absorption spectrum can be decomposed into the sum of spectra due to the single-relaxation processes, whose number is the same as that of the vibrational modes available in the gas, the relaxation strengths of the most of these processes are so small that their influences to acoustic absorption can be ignored in practice.

Table 1. 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 mixtures of Figs. 1 and 2.

Gas	1st process		2nd process		3rd process		4th process		5th process	
	$\mathcal{E}_1$	τ_1/s	$\mathcal{E}_2$	τ_2/s	$\mathcal{E}_3$	τ_3/s	$\mathcal{E}_4$	τ_4/s	$\mathcal{E}_5$	τ_5/s
20%CH ₄ -80%N ₂	2.83 ⁻³	6.21 ⁻⁶	2.67 ⁻³	3.94 ⁻⁶	5.83 ⁻⁸	2.28 ⁻⁹	1.29 ⁻⁹	3.18 ⁻⁸	2.17 ⁻¹²	8.94 ⁻⁹
40%CH ₄ -60%N ₂	9.87 ⁻³	3.43 ⁻⁶	5.74 ⁻⁵	1.41 ⁻⁶	4.05 ⁻⁸	6.06 ⁻¹⁰	8.96 ⁻¹⁰	8.96 ⁻⁹	1.40 ⁻¹²	2.31 ⁻⁹
60%CH ₄ -40%N ₂	1.38 ⁻²	2.52 ⁻⁶	3.72 ⁻⁸	2.88 ⁻¹⁰	1.72 ⁻⁸	7.12 ⁻⁷	8.64 ⁻¹⁰	4.48 ⁻⁹	9.48 ⁻¹³	1.06 ⁻⁹
80%CH ₄ -20%N ₂	1.74 ⁻²	1.82 ⁻⁶	2.96 ⁻⁶	4.27 ⁻⁷	3.94 ⁻⁸	1.69 ⁻¹⁰	9.68 ⁻¹⁰	2.70 ⁻⁹	8.07 ⁻¹³	6.06 ⁻¹⁰
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 ⁻¹²	1.86 ⁻⁶	\	\
40%CO ₂ -60%N ₂	2.84 ⁻²	7.66 ⁻⁶	9.45 ⁻³	1.18 ⁻⁵	4.42 ⁻⁵	1.61 ⁻¹	1.53 ⁻¹¹	2.80 ⁻⁶	\	\
60%CO ₂ -40%N ₂	4.92 ⁻²	7.38 ⁻⁶	2.32 ⁻³	3.97 ⁻⁶	8.48 ⁻¹⁰	3.11 ⁻⁶	4.26 ⁻⁵	7.79 ⁻²	\	\
80%CO ₂ -20%N ₂	6.37 ⁻²	6.26 ⁻⁶	6.11 ⁻⁴	2.20 ⁻⁶	4.25 ⁻⁵	8.80 ⁻²	4.92 ⁻⁹	2.47 ⁻⁷	\	\

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

Fig. 3. Comparison of multi-relaxation absorption spectra with decomposed single-relaxation absorption spectra for CH₄-N₂ mixtures around room temperature. $\alpha_r\lambda$: multi-relaxation absorption; $\alpha_1\lambda$: 1st single-relaxation absorption; $\alpha_2\lambda$: 2nd single-relaxation absorption.

Fig. 4. Comparison of multi-relaxation absorption spectra with decomposed single-relaxation absorption spectra for CO₂-N₂ mixtures around room temperature. $\alpha_r\lambda$: the multi-relaxation absorption; $\alpha_1\lambda$: 1st single-relaxation absorption; $\alpha_2\lambda$: 2nd single-relaxation absorption.

In conventional notion, one measurement absorption peak just corresponds to one single-relaxation process, i.e., if one absorption peak is measured, its corresponding single-relaxation process is found [10,19,21]. However, interestingly, although only one absorption peak is measured in the mixtures of 20%CH₄-80%N₂ and 40%CO₂-60%N₂, in fact there are two single-relaxation processes with significant relaxation strengths (i.e., the 1st and 2nd processes) shown in Table 1. For those two mixtures, the ultrasonic measurement cannot establish the maximum value of the absorption per wavelength for those two individual relaxation processes respectively. While based on our model, the two absorptions $\alpha_1\lambda$ and $\alpha_2\lambda$ of two single-relaxation processes can be found. The similar case that two relaxation processes contribute to one acoustic absorption peak is also reported by Beyer [28], who named this phenomenon as the “Double relaxation effects”. From Figures 3 and 4, the sum of 1st single-relaxation absorption $\alpha_1\lambda$ and 2nd single-relaxation absorption $\alpha_2\lambda$ is overlapped with $\alpha_r\lambda$ (20%CH₄-80%N₂: $C_1^* = 1.43 \text{ J mol}^{-1} \text{ K}^{-1}$, $C_2^* = 0.0566 \text{ J mol}^{-1} \text{ K}^{-1}$; 40%CO₂-60%N₂: $C_1^* = 2.29 \text{ J mol}^{-1} \text{ K}^{-1}$, $C_2^* = 0.710 \text{ J mol}^{-1} \text{ K}^{-1}$).

Consequently, not only the total acoustic absorption in excitable gases can be traditionally divided into two parts as classical and relaxational absorption, but also the relaxational absorption part under a multi-relaxation process can be further decomposed into the ones ascribed to the single-relaxation processes. Hence, for the expression of total acoustic absorption $\alpha\lambda = \alpha_c\lambda + \alpha_r\lambda$ [10] in excitable gases, it can be updated as

$$\alpha\lambda = \alpha_c\lambda + \sum_{n=1}^N \alpha_n\lambda . \quad (19)$$

4.2. Vibrational mode contributions to acoustic absorption

From Eq. (7), each C_n^* contains parts of the mole-fraction heat capacities of all the vibrational modes available to the mixture, which is generated from the V-V energy coupling formulated by the differential relaxation equations (Eq. (1)). On the other hand, each τ_n includes the lifetimes of all excited states which depend upon the transition probabilities of all V-T and V-V energy transitions. They mean that a multi-relaxation process is controlled by a strong V-V coupling, which influences both the relaxation frequencies and the relaxation strengths. Thus, every single-relaxation process relates with all vibrational modes. That is, for an acoustic multi-relaxation process, it would not be possible to allocate any single-relaxation process or decomposed single-relaxation absorption spectrum to a particular vibrational mode [18,29]. Moreover, an excitable gas can be treated as a mixture of its three kinds of DOF—translation, rotation, and vibration. In Eq. (9), the process effective IMH C_n^{eff}

has three elements C_V^∞ , C_n^* and τ_n . Translation and rotation affect the value of C_V^∞ , while vibration affects C_n^* and τ_n . Thus, based on Eqs. (13) and (14), we can find that the different parts (i.e. translation, rotation, and vibration) of a component molecule would have different (increasing or decreasing) effects on f_n^m and $(\alpha_n \lambda)_m$. This indicates that a single-relaxation absorption spectrum is the result of complicated interactions among all DOF of the gas molecules. So, strictly speaking, it is just possible for us to assign a relaxational absorption spectrum to a relaxation process or the whole mixture rather than a gas component or a DOF. Fortunately, using the simplified expression of $(\alpha_n \lambda)_m$ given by Eq. (15), we can calculate the contributions of vibrational modes to a single-relaxation process or the maximum height of absorption spectrum.

To analyze the contributions of vibrational modes to acoustical relaxational absorption, we have the following steps. Firstly, we calculate the vibrational mode contributions in pure gases CH₄ ($T=299.15\text{K}$) and CO₂ ($T=296.15\text{K}$). The four vibrational modes of CH₄ lead to four single-relaxation processes (Table 2), but only the 1st process has significant relaxation strength to cause an obvious acoustic absorption peak as measured by the experiments. Therefore, in this case, we can ignore the other non-primary relaxation processes, just analyze mode contributions to the 1st process or the primary relaxation process ($\varepsilon_1 = 0.0215$, $C_l^* = 2.34\text{J mol}^{-1}\text{K}^{-1}$).

Table 2. Calculations of the relaxation strengths and relaxation times of the four single-relaxation processes in pure CH₄ ($T=299.15\text{K}$, $P=1\text{ atm}$).

Process	ε_n	τ_n (s)
1st	2.15×10^{-2}	1.36×10^{-6}
2nd	4.44×10^{-8}	1.11×10^{-10}
3rd	1.22×10^{-9}	1.82×10^{-9}
4th	8.18×10^{-13}	3.93×10^{-10}

Based on Eqs. (17) and (18), the vibrational mode contributions $Z_{j,1}$ and $P_{j,1}$ ($j=1,2,\dots,4$) to the 1st single-relaxation process in pure CH₄ are given in Table 3. The mode $\nu_4=1306$ provides about 79.2% contribution for the relaxational absorption, $\nu_2=1534$ contributes the remaining 20.8%, while the contributions of $\nu_1=2915$ and $\nu_3=3019$ can be ignored. It is demonstrated that the contributions of modes decrease as the vibrational frequencies of the modes increase for pure CH₄. This phenomenon can be explained by the fact that a vibrational mode with the lower frequency has the larger vibrational heat capacity to detained more acoustic energy. So, the more acoustic energy relaxed from this mode in the form of heat, the more weight on the contribution to sound absorption.

Table 3. Vibrational mode contributions to the 1st single-relaxation process (the primary relaxation process) in pure CH₄ ($T=299.15\text{K}$).

Modes (cm ⁻¹)	$Z_{j,1}$ (J mol ⁻¹ K ⁻¹)	$P_{j,1}$
CH ₄ ($\nu_4=1306$)	1.85	79.2%
CH ₄ ($\nu_2=1534$)	0.486	20.8%
CH ₄ ($\nu_1=2915$)	5.96×10^{-4}	~0%
CH ₄ ($\nu_3=3019$)	3.74×10^{-4}	~0%

To further confirm our calculations on mode contributions for CH₄ ($T=299.15\text{K}$), we compare the absorption spectra due to the primary relaxation processes when considering different vibrational modes. Selecting different vibrational modes will lead to different C_n^* and τ_n , these parameters will affect the frequency and the height of absorption maximum due to the primary relaxation process (as shown in Eqs. (13) and (15)). In Fig. 5, the height of relaxational absorption maximum is about 0.0360 given by the experimental data from Gravitt (crosses) and 0.0340 from Edmonds (circles) [15]. From our theoretical spectra (Solid), when considering the modes $\nu_2=1534$ and $\nu_4=1306$ together, the height is 0.0352 with less than 1% relative error compared with the average value (0.0350) of experimental data; only considering the mode $\nu_2=1534$, the height is 0.0076; for the case of mode $\nu_4=1306$, the height becomes 0.0276. Therefore, the mode $\nu_2=1534$ provides about 21% contribution to the total height, and $\nu_4=1306$ supplies the remaining 79%. The shifts of the relaxation frequencies (i.e., the frequency of absorption maximum) with different modes are resulted from the corresponding different relaxation times. The same results of mode contributions for the primary relaxation process have been obtained in Table 3. This result confirms that the mode contributions for the process IMH of a single-relaxation process are equivalent to those for the maximum height of absorption spectrum.

Fig. 5. Sound relaxational absorption for pure CH₄. Symbols: Experiment data from Edmonds ($T=298.15\text{K}$, crosses), and Gravitt ($T=299.15\text{K}$, circles) [15]. Curves: theoretical absorption ($T=299.15\text{K}$, solid) due to the primary relaxation process, when considering the vibrational mode $\nu_2=1534\text{ cm}^{-1}$, $\nu_4=1306\text{ cm}^{-1}$, and $\nu_2 \& \nu_4$, respectively (from lowest to highest).

Pure CO₂ ($T=296.15\text{K}$) has three vibrational modes [18]. Table 4 provides the calculations of the corresponding relaxation strengths and relaxation times for three single-relaxation processes in the gas. Compared with the relaxation strength of 1st process ($\varepsilon_1=0.0763$, $C_l^*=7.57\text{ J mol}^{-1}\text{K}^{-1}$), the relaxation strengths of the other two processes are so small that their effects on the absorption can be ignored. So we just need to analyze the mode contributions of the 1st process (i.e., the primary process). In Table 5, the bending mode $\nu_2=677$ contributes 96.2% to the primary process, providing an overwhelming contribution compared with other modes. Mode $\nu_1=1388$ gives 3.8% contribution, while the contribution of $\nu_3=2349$ is negligible. Therefore, the most decisive factor for the relaxational absorption in pure CO₂ is the low-lying bending vibration of the molecule. This phenomenon can be explained by the fact that the energy gaps between the upper modes are usually much smaller than the energy level of the lowest mode which has the lowest characteristic frequency, so the rapid V–V energy transitions maintain the continuous equilibrium of vibrational energy among all vibrational modes. Thus almost all resident acoustic energy relaxes through the V–T deexcitation path provided by the lowest mode to arouse the primary relaxation process. This result also confirms that the mode with lower vibrational frequency holds more weight about the contribution to the primary relaxation process.

Table 4. Calculations of the relaxation strengths and relaxation times of the three single-relaxation processes in pure CO₂ ($T=296.15\text{K}$, $P=1\text{ atm}$).

Process	ε_n	τ_n (s)
1st	7.63×10^{-2}	5.01×10^{-6}
2nd	4.30×10^{-4}	1.45×10^{-6}
3th	4.47×10^{-5}	9.08×10^{-2}

Table 5. Vibrational mode contributions to the 1st single-relaxation process (the primary process) in pure CO₂ ($T=296.15\text{K}$).

Modes (cm ⁻¹)	$Z_{j,1}$ (J mol ⁻¹ K ⁻¹)	$P_{j,1}$
CO ₂ ($\nu_2=677$)	7.28	96.2%
CO ₂ ($\nu_1=1388$)	0.29	3.8%
CO ₂ ($\nu_3=2349$)	~ 0	$\sim 0\%$

In Fig. 6, the relaxational absorption spectrum due to the primary relaxation process with $\nu_2=677$ (Dashed curve) is nearly overlapped with the one (Dotted line with cross markers) from the modes ν_1 and ν_2 or the one (Solid curve) from ν_1 , ν_2 and ν_3 . These three theoretical spectra match with the experiment data from Kneser [24] (Circles) and Angona [30] (Squares) very well. These comparisons in CO₂ confirm the correctness of our calculations on the vibrational mode contributions to acoustic relaxational absorption again.

Fig. 6. Sound relaxational absorption for pure CO₂. Symbols: Experiment data from Kneser [24] (Circles), and Angona [30] (Squares). Curves: Theoretical calculations from the primary relaxation process when considering the mode $\nu_2=667\text{ cm}^{-1}$ (Dashed), ν_2 & $\nu_1=1388\text{ cm}^{-1}$ (Dotted line with cross markers) and ν_1 , ν_2 & $\nu_3=2349\text{ cm}^{-1}$ (Solid), respectively.

Secondly, we calculate the vibrational mode contributions in the two-component mixture of 5%CH₄-95%N₂ ($T=300\text{K}$). In Table 6, we find that the relaxation strengths of 1st and 2nd single-relaxation processes are significant for the mixture. Hence, we just need consider the absorption spectra due to the 1st and 2nd single-relaxation processes. In Fig. 7, the sum (dotted line with cross markers) of 1st single-relaxation absorption $\alpha_1\lambda$ (Dashed, $C_1^* = 0.107\text{J mol}^{-1}\text{K}^{-1}$) and 2nd single-relaxation absorption $\alpha_2\lambda$ (Dash-dotted, $C_2^* = 0.0188\text{J mol}^{-1}\text{K}^{-1}$) is overlapped with multi-relaxation absorption $\alpha_r\lambda$ (Solid). Thus, the multi-relaxation absorption $\alpha_r\lambda$ can be decomposed by the sum of $\alpha_1\lambda$ and $\alpha_2\lambda$ with two obvious absorption peaks. Similarly, the two relaxational absorption peaks of 5%CH₄-95%N₂ are also predicted by DL model [3] (Dotted).

Table 6. Calculations of the relaxation strength and relaxation times of the five single-relaxation processes in the mixture of 5%CH₄-95%N₂ ($T=300\text{K}$, $P=1\text{ atm}$).

Process	ε_n	τ_n (s)
1st	1.45×10^{-3}	4.75×10^{-6}
2nd	2.54×10^{-4}	8.61×10^{-5}
3rd	2.52×10^{-7}	3.62×10^{-8}
4th	1.09×10^{-8}	3.79×10^{-7}
5th	4.39×10^{-11}	1.31×10^{-7}

Fig. 7. Decomposing the sound multi-relaxation absorption spectrum in the mixture of 5%CH₄-95%N₂. $\alpha_r\lambda$: multi-relaxation absorption curve; $\alpha_1\lambda$: 1st single-relaxation absorption; $\alpha_2\lambda$: 2nd single-relaxation absorption.

We also give the calculated mode contributions for the 1st and 2nd single-relaxation processes for the mixture of 5%CH₄-95%N₂. From Eq. (17), for a gas mixture, besides the vibrational frequency, the mole fraction of molecule and the other molecular natures (such as molecular weight, the depth of molecular potential well, collision diameter, etc.) both affect the mode-contribution in a mixture. In Table 7, for the 1st process, the mode CH₄($\nu_4=1306$) provides 79.5% contribution, CH₄($\nu_2=1534$) makes 20.9%, while the contributions of CH₄($\nu_1=2915$) and CH₄($\nu_3=3019$) are ignorable (0.02% and 0.01% respectively). N₂($\nu=2331$) provides the negative value -0.4%, denoting that it is possible for a vibrational mode, which provides the V–T deexcitation path for a single-relaxation process, to acquire slightly more energy in its V–V energy exchanges than the relaxing energy by its V–T transfer. For the mode contributions to the 2nd process, CH₄($\nu_4=1306$) is 44.8%, CH₄($\nu_2=1534$) is 11.8%, N₂($\nu=2331$) is 43.4%, the other two modes together provide negligible contributions (about 0.09%). The contributions of CH₄($\nu_1=2915$) and CH₄($\nu_3=3019$) for the absorption are so small that can be ignored in the prediction of sound relaxational absorption in practice. In this case, the mode contributions no longer decrease as the vibrational frequency increases.

Table 7. Vibrational mode contributions to 1st and 2nd single-relaxation processes in the mixture of 5%CH₄-95%N₂ ($T=300\text{K}$).

Modes (cm ⁻¹)	$Z_{j,1}$ (J mol ⁻¹ K ⁻¹)	$P_{j,1}$	$Z_{j,2}$ (J mol ⁻¹ K ⁻¹)	$P_{j,2}$
CH ₄ ($\nu_4=1306$)	8.51×10^{-2}	79.5%	8.41×10^{-3}	44.8%
CH ₄ ($\nu_2=1534$)	2.24×10^{-2}	20.9%	2.21×10^{-3}	11.8%
CH ₄ ($\nu_1=2915$)	2.10×10^{-5}	~0%	1.15×10^{-5}	~0%
CH ₄ ($\nu_3=3019$)	1.41×10^{-5}	~0%	6.53×10^{-6}	~0%
N ₂ ($\nu=2331$)	-4.49×10^{-4}	-0.4%	8.15×10^{-3}	43.4%

Thirdly, we give the calculations of the vibrational mode contributions in the three-component mixture of 30%CL₂-55.30%N₂-14.70%O₂ (i.e., 30%CL₂-70% dry Air, $T=300\text{K}$). For this mixture, only the relaxation strengths of 1st single-relaxation processes are significant in Table 8; the 1st single-relaxation absorption $\alpha_1 \lambda$ (dotted line with cross markers, $C_I^* = 1.37 \text{ J mol}^{-1} \text{ K}^{-1}$) is overlapped with multi-relaxation absorption $\alpha_r \lambda$ (Solid) in Fig. 8. In Table 9, CL₂($\nu=577$) provides about 100% contribution for the 1st process because of its quite low vibrational frequency, while the contributions of N₂($\nu=2331$) and O₂($\nu=1554$) are negligible (resulting in $Z_{1,1} = C_I^*$).

Table 8. Calculations of the relaxation strength and relaxation times of the three single-relaxation processes in the mixture of 30%CL₂-55.30%N₂-14.70%O₂ ($T=300\text{K}$, $P=1\text{ atm}$).

Process	ϵ_n	τ_n (s)
1st	1.76×10^{-2}	2.51×10^{-6}
2nd	2.01×10^{-4}	3.03×10^{-3}
3rd	5.31×10^{-5}	2.01×10^{-2}

Fig. 8. Acoustic relaxational absorption in the mixture of 30%CL₂-55.30%N₂-14.70%O₂. $\alpha_r \lambda$: multi-relaxation absorption curve; $\alpha_1 \lambda$: 1st single-relaxation absorption.

Table 9. Vibrational mode contributions to the 1st single-relaxation process in the mixture of 30%CL₂-55.30%N₂-14.70%O₂ ($T=300\text{K}$).

Modes (cm ⁻¹)	$Z_{j,1}$ (J mol ⁻¹ K ⁻¹)	$P_{j,1}$
CL ₂ ($\nu=577$)	1.37	~100%
N ₂ ($\nu=2331$)	1.01×10^{-11}	~0
O ₂ ($\nu=1554$)	-9.56×10^{-6}	~0

5. Conclusions

In this paper, we demonstrate how a sound multi-relaxation absorption spectrum is decomposed into the sum of single-relaxation processes spectra. Based on this decomposable characteristic, we calculate the vibrational mode contributions to the

sound relaxational absorption in excitable gas mixtures at room temperature.

We show that not only the total sound absorption in excitable gases can be traditionally divided into two parts as classical and relaxational absorption, but also a multi-relaxation absorption can be further decomposed into the ones ascribed to the single-relaxation processes. We prove that the mode contributions for the process IMH of a single-relaxation process are equivalent to those for the maximum height of absorption spectrum. In most excitable gases, the primary relaxation process plays a decisive role in arousing the sound relaxational absorption and the mode with lower vibrational frequency provides higher contribution to the primary relaxation process in pure polyatomic gases. For pure CH₄, the vibrational mode $\nu_4=1306$ has 79.2% contribution to the primary process, $\nu_2=1534$ provides 20.8% contribution, and the contributions of $\nu_1=2915$ and $\nu_3=3019$ are ignorable. For CO₂, the bending mode $\nu_2=677$ has an overwhelming weight, 96.2% contribution, for the primary process; the mode $\nu_1=1388$ gives 3.8% and the contribution of $\nu_3=2349$ is negligible. For a gas mixture, besides the vibrational frequency, the mole fraction of molecule and the other molecular natures (such as molecular weight, the depth of molecular potential well, collision diameter, etc.) would jointly affect the mode-contribution. In short, our work provides an effective model to decompose a sound multi-relaxation absorption spectrum and calculate the vibrational mode contributions to sound relaxational absorption. Additionally, we find that in some situations such as in the mixtures of 20%CH₄-80%N₂ and 40%CO₂-60%N₂, there are two significant single-relaxation processes affecting the sound absorption, although only one absorption peak or a single-relaxation process can be measured by using acoustic approach.

Since the approach based on acoustic absorption spectra has been employed in moderate-sensitivity gas composition sensing [1-8], the quantitative relation between the molecular makeup of gas mixtures and acoustic absorption revealed in this paper can be used to guide the implementation of gas detection with acoustic absorption spectra.

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