



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



Kesheng Zhang<sup>a,b</sup>, Yi Ding<sup>c</sup>, Ming Zhu<sup>c,\*</sup>, Mingzhe Hu<sup>d</sup>, Shu Wang<sup>c</sup>, Yingqun Xiao<sup>a</sup>

<sup>a</sup> Guizhou Key Laboratory of Electric Power Big Data, Guizhou Institute of Technology, Guiyang 550003, Guizhou, China

<sup>b</sup> School of Information Engineering, Guizhou Institute of Technology, Guiyang 550003, Guizhou, China

<sup>c</sup> School of Electronic Information and Communications, Huazhong University of Science and Technology, Wuhan 430074, Hubei, China

<sup>d</sup> Department of Physics and Electronics, Liupanshui Normal University, Liupanshui, Guizhou 553004, China

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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.

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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].

\* Corresponding author.

E-mail address: [zhuming@mail.hust.edu.cn](mailto:zhuming@mail.hust.edu.cn) (M. Zhu).

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 **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

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

$$j, k = 1, \dots, N, j \neq k. \quad (1)$$

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

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

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,  $\nu_j$  and  $\nu_k$  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,  $T_j^{\text{vib}}$  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

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