



# Analytical relationship between sound relaxational absorption and sound speed dispersion in excitable gases

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## Abstract

Whether sound relaxational absorption and sound speed dispersion can be used as two independent acoustic parameters for gas sensing or not is still uncertain. In this paper, the analytical relationship between the frequency-dependent sound relaxational absorption and sound speed dispersion in excitable gases is derived and analyzed. First, the coefficient of compressibility in the Newton–Laplace equation of sound speed is extended to an effective one for relaxing gas. Second, using the relationship between the effective coefficient of compressibility and the effective wave number, we obtain the analytical relationship between sound relaxational absorption and sound speed dispersion from the high-frequency and the low-frequency sound speeds, respectively. The derivation and the simulation results for gas mixtures, including carbon dioxide, methane, and nitrogen, demonstrate that the ratio of the high-frequency sound speed to the low-frequency sound speed determines the amplitude of acoustic relaxation absorption peak, that the inflection frequency of sound speed dispersion is consistent with the relaxation frequency of sound relaxational absorption, and that sound speed dispersion contains all molecular information carried by sound relaxational absorption and is more applicable to acquiring the molecular geometry, the vibration frequency, and other gas molecular characteristics. This paper provides a more theoretical basis on using acoustic speed dispersion for gas sensing.

**Keywords** Sound speed dispersion · Sound relaxational absorption · Coefficient of compressibility · Gas sensing

## 1 Introduction

Acoustic relaxational absorption and speed dispersion in excitable (non-monoatomic) gases carry the essential characteristic information of molecules, such as the molecular structure, force, energy level of internal degrees of freedom (DOF), and energy transfer of gas molecules [1–3]. Thus, they are potentially being applied to the field of intelligent gas sensing [4–10]. The sound speed has a long history of being used to detect the concentration of binary mixtures [11]. Using sound speed while ignoring the effect of dispersion, Joos et al. measured the concentration of carbon

dioxide or SF<sub>6</sub> in the air [12], and Lueptow and Phillips monitored the methane component in natural gas [13]; sound absorption has also been independently applied to the quantitative analysis of an ethane and oxygen binary gas [14]. To cope with the situation with multi-component gas composition, some scholars tried to use the sound speed and sound absorption together for gas composition analysis. For examples, when considering acoustic classical absorption and ignoring acoustic relaxation absorption, Terhune and Calif [15] designed a method and device for quantitatively detecting the ternary mixed gas of hydrogen, oxygen, and water vapor by the measurements of sound speed and sound absorption at a certain frequency; while ignoring the dispersion of the sound speed, Philliips et al. [16] proposed a concept for a real-time gas sensor for multi-component composition based on acoustic speed and relaxational absorption; then, Zhu et al. [17] provided an algorithm to detect the concentration of carbon monoxide in moist air using acoustic dispersion and sound relaxational absorption together.

In an excitable gas media, the disturbance from the passage of a sound wave arouses thermal relaxational processes

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between molecular internal energy levels and external energy levels via non-elastic molecular collisions [1]. Because the vibrational relaxation time at room temperature is generally several orders of magnitude larger than the rotational relaxation time, the vibrational modes dominate the acoustic relaxation at middle-to-low frequency (i.e., the ratio of sound frequency to pressure  $f/P$  is less than  $10^6$  Hz/atm, where  $f/P$  indicates that raising the sound frequency is equivalent to lowering the pressure, because the relaxation time varies inversely with the ambient pressure) to cause the frequency-dependent acoustic speed dispersion and relaxational absorption [1, 18]. On one hand, classical absorption relating with the viscosity and conductivity contributes to acoustic absorption, as well. However, classical absorption is so small compared with relaxational absorption that it can be omitted in at middle-to-low frequency for most gas molecules without loss of generality [2, 19]. On the other hand, vibrational relaxation triggers acoustic relaxational absorption and speed dispersion at the same time, so ignoring either of them when analyzing the acoustic propagation in excitable gases is unreasonable. Therefore, when using sound speed (which is equal to the sound speed dispersion at a certain frequency) and sound absorption together to sense an excitable gas, the acoustic speed dispersion and the relaxation absorption need to be classified as to whether these two basic acoustic parameters are independent of each other or not, and if not, what is the analytical relationship between them, and which carries more molecular information and is more applicable to gas detection.

Dain, Lueptow and Petculescu (DLP) proposed a physical model to predict the acoustic relaxation absorption and speed dispersion in multi-component gas mixtures with the extended SSH relaxation equations [2, 20]. We also present the prediction models with decoupled SSH relaxation equations and Tanczos relaxation equations, and use the models to calculate the vibrational relaxation times and vibrational-mode contributions to sound absorption based on the effective heat capacity of relaxing gases [18, 19, 21, 22]. Unfortunately, the model of DLP only provides a numerical calculation for acoustic relaxational absorption and speed dispersion, and our previous models are too complicated to get the analytical relationship between them. In this paper, based on Kneser's acoustic relaxation theory [23], we extend the coefficient of compressibility in the Newton–Laplace equation of sound speed to the effective one for relaxing gases and use the relationship between the effective coefficient of compressibility and the effective wave number to obtain the analytical relationship between acoustic relaxational absorption and speed dispersion. Comparisons demonstrate that our constructed relaxational absorption calculated from sound speed dispersion based on the analytical relationship between acoustic relaxational absorption and speed dispersion, for various gas compositions including

carbon dioxide, methane, and nitrogen, agree with the experimental data quit well. The derivation and the simulation results show that acoustic relaxational absorption and speed dispersion can be converted to each other analytically, that the peak amplitude of sound relaxational absorption is determined by the ratio of the high-frequency sound speed to the low-frequency sound speed, that the relaxation frequency of sound relaxational absorption and the inflection frequency of sound speed dispersion are the same, and that the sound speed dispersion contains all information provided by sound relaxational absorption and is more applicable to gas sensing than sound relaxational absorption.

## 2 Acoustic relaxation equations

1. Acoustic relaxation equations of vibration temperature under different thermodynamic conditions

The propagation of a sound wave in a gas media is a series of periodic changes of adiabatic compression and adiabatic expansion. Especially, in an excitable gas, not only the density and the pressure of the gas, but also the temperatures of the inner and the outer degrees of freedom (DOF) of the gas molecules will fluctuate periodically with the spatial position due to the disturbance caused by a sound wave [23]. Because the molecular vibration modes have large energy level intervals, the relaxation process of a vibration temperature  $T^{\text{vib}}$  returning to a thermal equilibrium state has a certain lag time for the return process of the translation temperature  $T$ . This lag time is called the vibrational relaxation time [18]. The rapid energy equilibration between rotation and translation makes the (Vibration–Rotation) + (Rotation–Translation) process equal to the Vibration–Translation process; thus, it is conventional to classify the rotation as the translation as the external DOF to differentiate from the vibration as the internal DOF in the study of vibrational relaxation (hereinafter, we abbreviate vibrational relaxation as relaxation) [24]. Under an adiabatic condition (the gas temperature or the translation temperature  $T$  is not constant, but the entropy  $S$  is constant), the relaxation equation for  $T^{\text{vib}}$  is [23, 25]:

$$\frac{d(T^{\text{vib}} - T_0^{\text{vib}})}{dt} = \frac{dT^{\text{vib}}}{dt} = -\frac{1}{\tau} \left[ \frac{C_p^0}{C_p^\infty} (T^{\text{vib}} - T_0^{\text{vib}}) - \frac{RT}{PC_p^\infty} (P - P_0) \right], \quad (1)$$

where  $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$  is the molar universal gas constant,  $P$  is the gas pressure,  $P_0$  is the gas equilibrium pressure,  $T_0^{\text{vib}}$  is the equilibrium value of vibration temperature and the gas equilibrium temperature as well,  $C_p^0 = C_p^\infty + C_{\text{vib}}^*$  is the static isobaric molar heat,  $C_p^\infty$  is the isobaric molar heat capacity of the external DOF

(the sum of isobaric molar heat of molecular translation and rotation),  $C_{\text{vib}}^*$  is the coupled vibrational molar heat, which is the coupling result from the vibrational–vibrational energy exchanges by all vibrational modes [21], and  $\tau$  is the isothermal relaxation time.

For Eq. (1), if the pressure  $P$  is also constant (i.e.,  $P = P_0$ ), the relaxation equation under an adiabatic and isobaric condition is:

$$\frac{dT^{\text{vib}}}{dt} = -\frac{1}{\tau_{PS}}(T^{\text{vib}} - T_0^{\text{vib}}) = -\frac{1}{\tau} \frac{C_P^0}{C_P^\infty}(T^{\text{vib}} - T_0^{\text{vib}}), \tag{2}$$

where  $\tau_{PS} = \tau C_P^\infty / C_P^0$  is adiabatic constant pressure relaxation time. Similarly to Eq. (1), after the fluctuation of  $T$  is written in the form expressed by volume  $V$  and  $T_0^{\text{vib}}$ , the relaxation equation under an adiabatic constant volume condition becomes [25]:

$$\frac{dT^{\text{vib}}}{dt} = -\frac{1}{\tau_{VS}}(T^{\text{vib}} - T_0^{\text{vib}}) = -\frac{1}{\tau} \frac{C_V^0}{C_V^\infty}(T^{\text{vib}} - T_0^{\text{vib}}), \tag{3}$$

where  $C_V^0 = C_V^\infty + C_{\text{vib}}^*$ ,  $C_V^0$  being the static isochoric molar heat and  $C_V^\infty$  the isochoric molar heat capacity of the external DOF.  $\tau_{VS} = \tau C_V^\infty / C_V^0$  is the adiabatic constant volume relaxation time.

2. Acoustic relaxation equation of gas density

For an acoustic field of a harmonic plane wave with small amplitude  $P = Ae^{i(\omega t - kx)}$  (where  $P$  is the sound pressure,  $A$  is the sound pressure amplitude,  $\omega$  is the sound angle frequency,  $k$  is the sound wave number),  $T^{\text{vib}} - T_0^{\text{vib}}$  and  $P - P_0$  vary periodically with time, i.e., are proportional to  $e^{i\omega t}$ ; thus, the operation  $d/dt$  in Eq. (1) is equivalent to multiplying by  $i\omega$  ( $i = \sqrt{-1}$ ), so the relaxation equation, Eq. (1), can be rewritten in the algebraic form:

$$(T^{\text{vib}} - T_0^{\text{vib}}) = \frac{RT}{PC_P^0}(P - P_0)(1 + i\omega\tau_{PS})^{-1}. \tag{4}$$

Affected by an acoustic relaxation process, the change in the gas density relative to the equilibrium state is not only related to a change in the gas pressure, but also to a change in the vibrational temperature; then, one has (only the first-order series expansion is considered) [23]:

$$\rho - \rho_0 = \left(\frac{\partial\rho}{\partial P}\right)_{ST^{\text{vib}}}(P - P_0) + \left(\frac{\partial\rho}{\partial T^{\text{vib}}}\right)_{PS}(T^{\text{vib}} - T_0^{\text{vib}}), \tag{5}$$

where  $\rho$  is the gas density, and  $\rho_0$  is the gas equilibrium density. Because the vibration temperature  $T^{\text{vib}}$  is changed under the condition of an adiabatic constant pressure, the energy increased by the vibration modes is equal to the energy decreased by the external DOF, i.e.,

$-C_{\text{vib}}^* dT^{\text{vib}} = C_P^\infty dT$ . Thus,  $\left(\frac{\partial T}{\partial T^{\text{vib}}}\right)_{PS} = \left(\frac{dT}{dT^{\text{vib}}}\right)_{PS} = -C_{\text{vib}}^*/C_P^\infty$  and  $\left(\frac{\partial\rho}{\partial T^{\text{vib}}}\right)_{PS} = \left(\frac{\partial T}{\partial T^{\text{vib}}}\right)_{PS} \left(\frac{\partial\rho}{\partial T}\right)_{PS} = -\frac{C_{\text{vib}}^*}{C_P^\infty} \left(\frac{\partial\rho}{\partial T}\right)_{PS}$ . Based on the state equation of a gas  $PV = nRT$  ( $n$  is the number of moles in the gas), i.e.,  $\rho = PM/(nRT)$  ( $M$  is the molar mass of gas),  $\left(\frac{\partial\rho}{\partial T}\right)_{PS} = -\frac{PM}{nRT^2} = -\frac{\rho}{T}$ , so  $\left(\frac{\partial\rho}{\partial T^{\text{vib}}}\right)_{PS} = \frac{C_{\text{vib}}^*}{C_P^\infty} \frac{\rho}{T}$ . Then, from Eqs. (4) and (5), the normalized acoustic relaxation equation of gas density is given as:

$$\frac{1}{\rho} \frac{\rho - \rho_0}{(P - P_0)} = \frac{1}{\rho} \left(\frac{\partial\rho}{\partial P}\right)_{ST^{\text{vib}}} + \frac{RC_{\text{vib}}^*}{PC_P^0 C_P^\infty} \frac{1}{(1 + i\omega\tau_{PS})}. \tag{6}$$

### 3 Analytical relationship between acoustic relaxational absorption and speed dispersion

1. Effective coefficient of compressibility

The sound speed reflects the compressibility of a medium due to sound propagation. The sound speed in a fluid is determined by the Newton–Laplace equation  $c = \sqrt{\left(\frac{\partial P}{\partial\rho}\right)_s} = \sqrt{\frac{1}{\rho\kappa_s}}$ , where  $\kappa_s$  is the coefficient of compressibility under an adiabatic condition [26]:

$$\kappa_s = -\frac{1}{\rho} \left(\frac{\partial\rho}{\partial P}\right)_s = -\frac{1}{V} \left(\frac{dV}{dP}\right)_s = (\rho c^2)^{-1}. \tag{7}$$

Furthermore, combining the state equation of a gas under an adiabatic condition  $PV^\gamma = \text{const}$  (where  $\gamma$  is the molar heat ratio of the gas) and the state equation of a gas  $PV = nRT$  together, one can obtain other expressions of  $\kappa_s$ :

$$\kappa_s = -\frac{1}{V} \left(\frac{dV}{dP}\right)_s = \frac{1}{\gamma P}. \tag{8}$$

According to the definition of  $\kappa_s$  in Eq. (7) (i.e.,  $\kappa_s = -\frac{1}{\rho} \left(\frac{\partial\rho}{\partial P}\right)_s$ ), Eq. (6) can be rewritten as:

$$\kappa_s^{\text{eff}} = \kappa_s^\infty + \frac{RC_{\text{vib}}^*}{PC_P^0 C_P^\infty} \frac{1}{(1 + i\omega\tau_{PS})}, \tag{9}$$

where  $\kappa_s^{\text{eff}} = \frac{\rho - \rho_0}{\rho(P - P_0)}$  is the effective coefficient of compressibility of an excitable gas under an adiabatic condition due to an acoustic disturbance;  $\kappa_s^\infty = \frac{1}{\rho} \left(\frac{\partial\rho}{\partial P}\right)_{ST^{\text{vib}}}$ , where the superscript  $\infty$  in  $\kappa_s^\infty$  represents the adiabatic coefficient of compressibility as the sound frequency satisfies  $\omega\tau \rightarrow \infty$ . As  $\omega\tau \rightarrow \infty$ , the gas begins to expand before the energy of the external DOF can come into the

internal DOF in the compression period, and the energy of the external DOF fails to have enough time to enter the internal DOF, causing  $T^{\text{vib}}$  to remain unchanged for this case. Hence,  $\kappa_S^\infty$  is equivalent to the adiabatic coefficient of compressibility when  $T^{\text{vib}}$  remains unchanged. Furthermore, because no energy exchange takes place between external and internal DOF,  $C_{\text{vib}}^*$  becomes zero to make the molar heat ratio  $\gamma^\infty = C_P^\infty/C_V^\infty$ . Therefore, from Eq. (8), one gets:

$$\kappa_S^\infty = \frac{1}{P} C_V^\infty / C_P^\infty. \quad (10)$$

Consider the other extreme case, i.e.,  $\omega\tau \rightarrow 0$ . The internal state will always be in equilibrium with the external states; then, the molar heat ratio becomes  $\gamma^0 = C_P^0/C_V^0$ . Thus, combining Eq. (8) with Eq. (10), we find that the coefficient of compressibility when  $\omega\tau \rightarrow 0$  is:

$$\kappa_S^0 = \frac{1}{P} C_V^0 / C_P^0 = \kappa_S^\infty \frac{C_V^0 C_P^\infty}{C_P^0 C_V^\infty}. \quad (11)$$

From Eq. (10),  $P^{-1} = \kappa_S^\infty C_P^\infty / C_V^\infty$ , which can be substituted into Eq. (9) to get:

$$\kappa_S^{\text{eff}} = \kappa_S^\infty \left( 1 + \frac{RC_{\text{vib}}^*}{C_P^0 C_V^\infty} \frac{1}{1 + i\omega\tau_{PS}} \right). \quad (12)$$

Moreover, considering Eqs. (11) and (12) together, we, respectively, obtain the normalized high-frequency and low-frequency effective coefficients of compressibility as:

$$\frac{\kappa_S^{\text{eff}}}{\kappa_S^\infty} = \frac{C_V^0 C_P^\infty}{C_P^0 C_V^\infty} \left[ \frac{1 + \omega^2 \tau_{PS} \tau_{VS}}{1 + (\omega\tau_{PS})^2} - i \frac{\omega(\tau_{PS} - \tau_{VS})}{1 + (\omega\tau_{PS})^2} \right],$$

$$\frac{\kappa_S^{\text{eff}}}{\kappa_S^0} = \frac{1 + \omega^2 \tau_{PS} \tau_{VS}}{1 + (\omega\tau_{PS})^2} - i \frac{\omega(\tau_{PS} - \tau_{VS})}{1 + (\omega\tau_{PS})^2}. \quad (13)$$

## 2. Acoustic relaxational absorption and speed dispersion

Equation (7) can be extended to the situation when there is an acoustic relaxation process [23]:

$$\kappa_S^{\text{eff}} = \frac{1}{\rho[\tilde{c}(\omega)]^2}, \quad (14)$$

where  $\tilde{c}(\omega)$  is an effective thermodynamic speed. The propagation of sound can be described using an effective wavenumber  $\tilde{k}(\omega)$  while  $\tilde{k}(\omega)$  is composed of the frequency-dependent phase speed dispersion  $c(\omega)$  and

relaxational absorption  $\alpha(\omega)$ , namely  $\tilde{k}(\omega) = \frac{\omega}{\tilde{c}(\omega)} = \frac{\omega}{c(\omega)} - i\alpha(\omega)$  [24]. Hence, from Eq. (14), one has:

$$[\tilde{k}(\omega)]^2 = \omega^2 \rho \kappa_S^{\text{eff}} = \left[ \frac{\omega}{c(\omega)} \right]^2 - [\alpha(\omega)]^2 - i2\omega \frac{\alpha(\omega)}{c(\omega)}. \quad (15)$$

### 1) Analytical relationship based on the low-frequency sound speed

When  $\omega\tau \rightarrow 0$ , the minimum of sound speed dispersion or the low-frequency sound speed  $c_0$  is achieved [5, 19]. Then, the low-frequency coefficient of compressibility is  $\kappa_S^0 = (\rho c_0^2)^{-1}$  based on Eq. (7). Substituting  $\rho = (\kappa_S^0 c_0^2)^{-1}$  into Eq. (15) and with aid of the normalized low-frequency coefficient of compressibility in Eq. (13), we get:

$$\frac{\kappa_S^{\text{eff}}}{\kappa_S^0} = \frac{1 + \omega^2 \tau_{PS} \tau_{VS}}{1 + (\omega\tau_{PS})^2} - i \frac{\omega(\tau_{PS} - \tau_{VS})}{1 + (\omega\tau_{PS})^2}$$

$$= \frac{c_0^2}{[c(\omega)]^2} - \frac{[\alpha(\omega)]^2 c_0^2}{\omega^2} - i2 \frac{\alpha(\omega) c_0^2}{\omega c(\omega)}. \quad (16)$$

Making the real parts of Eq. (16) equal yields  $\frac{1 + \omega^2 \tau_{PS} \tau_{VS}}{1 + (\omega\tau_{PS})^2} = \frac{c_0^2}{[c(\omega)]^2} - \frac{[\alpha(\omega)]^2 c_0^2}{\omega^2}$ . Because the value of the sound speed is mainly determined by the molecular mass of a gas rather than its molecular relaxation [19],  $c_0/c(\omega) \approx 1$ . In most cases, there is  $[\alpha(\omega)]^2 c_0^2 / \omega^2 \ll 1$ , we therefore obtain the sound speed dispersion from Eq. (16) as:

$$[c(\omega)]^2 = \frac{1 + (\omega\tau_{PS})^2}{1 + \omega^2 \tau_{PS} \tau_{VS}} c_0^2. \quad (17)$$

Now, by letting the imaginary parts of Eq. (16) be equal and with the aid of Eq. (17), we obtain the analytical relationship between the dimensionless sound relaxational absorption  $\mu(\omega) = \alpha(\omega)\lambda$  (where  $\lambda = 2\pi c(\omega)/\omega$  is the wavelength) and the sound speed dispersion based on the low-frequency sound speed as:

$$\mu(\omega) = \frac{[c(\omega)]^2}{c_0^2} \pi \frac{\omega(\tau_{PS} - \tau_{VS})}{1 + (\omega\tau_{PS})^2}. \quad (18)$$

### 2) Analytical relationship based on the high-frequency sound speed

When  $\omega\tau \rightarrow \infty$ , the maximum sound speed dispersion or the high-frequency sound speed  $c_\infty$  is obtained [5], so from Eq. (7), the high-frequency coefficient of compressibility is  $\kappa_S^\infty = (\rho c_\infty^2)^{-1}$ . Substituting  $\rho = (\kappa_S^\infty c_\infty^2)^{-1}$  into Eq. (15) with the aid of the normalized high-fre-

quency coefficient of compressibility in Eq. (13), we have:

$$\begin{aligned} \frac{\kappa_S^{\text{eff}}}{\kappa_S^\infty} &= \frac{C_V^0 C_P^\infty}{C_P^0 C_V^\infty} \left[ \frac{1 + \omega^2 \tau_{PS} \tau_{VS}}{1 + (\omega \tau_{PS})^2} - i \frac{\omega(\tau_{PS} - \tau_{VS})}{1 + (\omega \tau_{PS})^2} \right] \\ &= \frac{c_\infty^2}{[c(\omega)]^2} - \frac{[\alpha(\omega)]^2 c_\infty^2}{\omega^2} - i2 \frac{\alpha(\omega) c_\infty^2}{\omega c(\omega)}. \end{aligned} \tag{19}$$

Similarly, making the real parts of Eq. (19) equal produces another expression for the sound speed dispersion:

$$[c(\omega)]^2 = \left[ \frac{C_P^0 C_V^\infty}{C_V^0 C_P^\infty} + \left( 1 - \frac{C_P^0 C_V^\infty}{C_V^0 C_P^\infty} \right) \frac{\omega^2 \tau_{PS} \tau_{VS}}{1 + \omega^2 \tau_{PS} \tau_{VS}} \right] c_\infty^2. \tag{20}$$

Then, by letting the imaginary parts Eq. (19) be equal and with the help of Eq. (20), we obtain the analytical relationship between acoustic relaxational absorption and speed dispersion based on the high-frequency sound speed:

$$\mu(\omega) = \frac{[c(\omega)]^2}{c_\infty^2} \pi \frac{C_V^0 C_P^\infty}{C_P^0 C_V^\infty} \frac{\omega(\tau_{PS} - \tau_{VS})}{1 + (\omega \tau_{PS})^2}. \tag{21}$$

Here, we are more concerned about the analytical relationship between  $\mu(\omega)$  and  $c(\omega)$  rather than between  $\alpha(\omega)$  and  $c(\omega)$ . The frequency-dependent  $\mu(\omega)$  (i.e.,  $\alpha(\omega)\lambda(\omega)$ ) is composed of the relaxational absorption of sound waves with different frequencies after propagating a distance corresponding to their wavelength. When the propagation distance is one wavelength, all sound waves with different frequencies have only completed a compression and expansion process, and the acoustic excitation energy retained in the vibration mode has only completed a thermal relaxation process. However, only when the acoustic change period is close to the relaxation time of gas molecules, will the significant acoustic relaxation absorption occur, and the closer the two are, the stronger the absorption will be [18, 27]. This feature causes sound waves with different frequencies to have different strengths of relaxational absorption in excitable gases, resulting in the appearance of an absorption peak for  $\mu(\omega)$ . Thus, measuring the absorption peak for  $\mu(\omega)$  can be used to study the characteristics of molecular relaxation in a gas [27, 28]. Furthermore, because  $\mu(\omega) = \alpha(\omega)\lambda(\omega) = 2\pi\alpha(\omega)c(\omega)/\omega$ , from the analytic relationship between  $\mu(\omega)$  and  $c(\omega)$  (Eqs. 18 and 21), we easily obtain the analytic relationship between  $\alpha(\omega)$  and  $c(\omega)$ :

$$\alpha(\omega) = \frac{\omega\mu(\omega)}{2\pi c(\omega)} = \frac{c(\omega)}{2c_\infty^2} \frac{\omega^2(\tau_{PS} - \tau_{VS})}{1 + (\omega\tau_{PS})^2} = \frac{c(\omega)}{2c_\infty^2} \frac{C_V^0 C_P^\infty}{C_P^0 C_V^\infty} \frac{\omega^2(\tau_{PS} - \tau_{VS})}{1 + (\omega\tau_{PS})^2}. \tag{22}$$

As a consequence, based on Eqs. (18), (21), and (22), we clearly know that these two basic acoustic parameters of acoustic speed dispersion and relaxational absorption in excitable gases have an analytical relationship and can be converted one to the other. Therefore, sound speed and sound absorption cannot be used together to detect excitable gases as two independent acoustic parameters.

### 4 Analytical analysis and simulation results

#### 1. Analytical analysis for acoustic relaxational absorption and speed dispersion

First, we analyze the molecular information carried by sound relaxational absorption and sound speed dispersion. Substituting Eq. (17) into Eq. (18), we obtain a more concise expression for sound relaxational absorption based on the low-frequency sound speed:

$$\mu(\omega) = \pi \frac{\omega(\tau_{PS} - \tau_{VS})}{1 + \omega^2 \tau_{VS} \tau_{PS}}. \tag{23}$$

From Eq. (23), clearly, the sound relaxational absorption can only provide information on relaxation times  $\tau_{PS}$  and  $\tau_{VS}$ . However, using Eqs. (17) and (20), we find that the sound speed dispersion  $c(\omega)$  not only contains information on  $\tau_{PS}$  and  $\tau_{VS}$ , but also contains information on the minimum of the sound speed dispersion or the low-frequency sound speed  $c_0^2$  and the maximum of the sound speed dispersion or the high-frequency sound speed  $c_\infty^2$ . Furthermore, the analytical expressions for  $c_0^2$  and  $c_\infty^2$  are [19]:

$$c_0^2 = (P_0/\rho_0)/[1 + R/(C_V^\infty + C_{\text{vib}}^*)], \quad c_\infty^2 = (P_0/\rho_0)/(1 + R/C_V^\infty). \tag{24}$$

From Eq. (24), on one hand, comparing the sound relaxational absorption, the sound speed dispersion provides extra information such as the equilibrium density  $\rho_0$  and the equilibrium pressure  $P_0$ . On the other hand,  $C_V^\infty$  in Eq. (24) provides information on the molecular geometric structure (for linear molecules,  $C_V^\infty = 5R/2$ ; for nonlinear molecules,  $C_V^\infty = 3R$ ) [24], and  $C_{\text{vib}}^*$  includes information on the vibrational frequency of the normal vibration modes of gas molecules [5].

As a result, sound speed dispersion contains all the information provided by sound relaxational absorption, as well as additional information such as the equilibrium pressure and density. Also, getting other essential information on the gas molecule, such as the molecular geometric structure and the vibrational frequency of the normal vibration modes, is easier. More importantly, in an actual acoustic measurement, the measured sound attenuation includes losses due to viscosity and thermal

conductivity, losses due to diffusion in gas mixtures, losses due to diffraction of sound sources, and losses due to molecular energy relaxation [29, 30]. Thus, the measurement error for the sound relaxational absorption can reach more than 40% [31], while that of the sound speed can be less than 0.01% [16]. Consequently, compared with sound relaxational absorption, sound speed dispersion is more appropriate for obtaining information on gas molecules and has greater advantages in gas detection.

Second, we focus on analyzing the characteristic points in the curves of acoustic relaxational absorption and speed dispersion. A molecular relaxation process of relaxing gases is characterized by its relaxation time and relaxation strength [23]. They determine the position of the maximum sound absorption along the abscissa and the height of the maximum relaxational absorption, respectively [30]. Thus, measuring the maximum point of the frequency-dependent relaxational absorption has potential applications in gas qualitative and quantitative detection [6, 30, 32].

If we let  $\varepsilon = 1 - \tau_{VS}/\tau_{PS}$ , then Eq. (23) can be rewritten as:

$$\mu(\omega) = \pi\varepsilon \frac{\omega\tau_{PS}}{1 + \omega^2(1 - \varepsilon)\tau_{PS}^2}. \quad (25)$$

By Eq. (25), when  $\omega = \omega_{\text{relx}} = 1/\sqrt{\tau_{VS}\tau_{PS}} = 1/\tau_{PS}\sqrt{(1 - \varepsilon)}$ ,  $\mu(\omega)$  reaches to the maximum  $\mu_m = \pi\varepsilon/2\sqrt{(1 - \varepsilon)} \approx \pi\varepsilon/2$ , because  $\varepsilon \ll 1$ ; hence,  $\omega_{\text{relx}}$  is called the relaxation frequency [21]. Because the maximum absorption  $\mu_m$  is determined by  $\varepsilon$ ,  $\varepsilon$  is defined as the relaxation strength [23]. Then, Eq. (21) can also be rewritten to get a more concise expression for sound relaxational absorption based on the high-frequency sound speed:

$$\mu(\omega) = \frac{1}{(1 - \varepsilon)} \pi \frac{[c(\omega)]^2}{c_\infty^2} \frac{\omega\varepsilon\tau_{PS}}{1 + (\omega\tau_{PS})^2}. \quad (26)$$

Furthermore, from Eq. (17), the frequency-dependent dispersion curve  $[c(\omega)]^2$  is concave when  $\omega \in (0, 1/\sqrt{\tau_{VS}\tau_{PS}}]$  and convex when

$\omega \in (1/\sqrt{\tau_{VS}\tau_{PS}}, +\infty)$ . Therefore, the inflection frequency of sound speed dispersion  $\omega_{\text{inflec}}$  is the same as the relaxation frequency of sound relaxational absorption  $\omega_{\text{relx}}$ . Substituting  $\omega = \omega_{\text{relx}} = 1/\sqrt{\tau_{VS}\tau_{PS}}$  into Eqs. (17) and (20) with the aid of  $\tau_{VS}/\tau_{PS} = C_P^0 C_V^\infty / C_V^0 C_P^\infty$  and  $\varepsilon = 1 - \tau_{VS}/\tau_{PS}$ , we get:

$$c^2(\omega_{\text{relx}}) = \frac{2 - \varepsilon}{2(1 - \varepsilon)} c_0^2 = \frac{2 - \varepsilon}{2} c_\infty^2, \quad (27)$$

By Eq. (27), the sound speed dispersion at  $\omega_{\text{inflec}}$  or  $\omega_{\text{relx}}$  is:

$$c^2(\omega_{\text{inflec}}) = c^2(\omega_{\text{relx}}) = (c_0^2 + c_\infty^2)/2, \quad (28)$$

and

$$\varepsilon = 1 - c_0^2/c_\infty^2, \quad \tau_{VS}/\tau_{PS} = c_0^2/c_\infty^2. \quad (29)$$

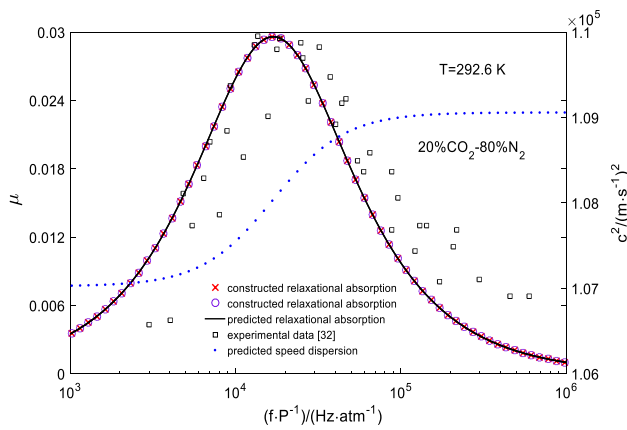
Moreover, Eq. (25) can be rewritten in the form of  $\mu(\omega) = \mu_m \frac{\omega/\omega_{\text{relx}}}{1 + \omega^2/\omega_{\text{relx}}^2}$ ; thus, the relaxational absorption is determined by just two characteristic values: the maximum absorption  $\mu_m$  and the relaxation frequency  $\omega_{\text{relx}}$ . This is the reason we were able to reconstruct the frequency-dependent sound relaxational absorption from  $\mu_m$  and  $\omega_{\text{relx}}$  in our previous work [30]. On one hand, Eq. (28) shows that  $\omega_{\text{relx}}$  is as the same as the inflection frequency  $\omega_{\text{inflec}}$  of sound speed dispersion. On the other hand, according to Eq. (29), the ratio of  $c_\infty^2$  to  $c_0^2$  not only reflects the ratio of different types of relaxation times  $\tau_{PS}$  and  $\tau_{VS}$ , but also determines the magnitude of the absorption strength  $\varepsilon$  or the maximum absorption  $\mu_m = \pi\varepsilon/2\sqrt{(1 - \varepsilon)}$ . Therefore, sound relaxational absorption can be constructed from sound speed dispersion.

- Using sound speed dispersion to construct sound relaxational absorption

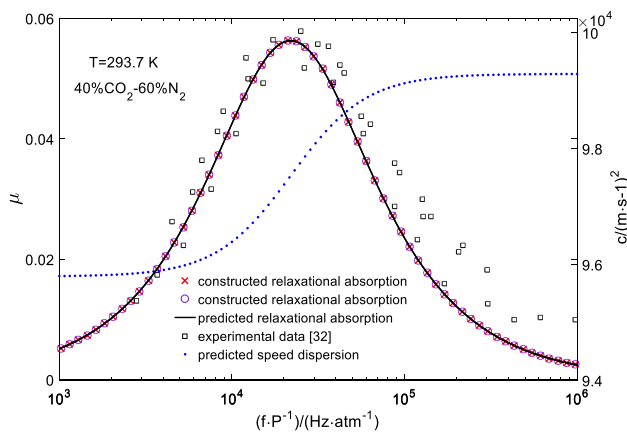
Now, we will do numerical simulations for mixtures of  $\text{N}_2\text{-CO}_2$  and  $\text{N}_2\text{-CH}_4$  at room temperature to verify that sound relaxational absorption can be constructed from sound speed dispersion. Table 1 gives the corresponding values of two types of relaxation times  $\tau_{PS}$  and  $\tau_{VS}$  (selected from Table 2 in Ref. [25]), and the high-

**Table 1** Adiabatic constant pressure relaxation time  $\tau_{PS}$ , adiabatic constant volume relaxation time  $\tau_{VS}$ , low-frequency sound speed  $c_0^2$ , high-frequency sound speed  $c_\infty^2$ , and relaxation strength  $\varepsilon$  for  $\text{CO}_2\text{-N}_2$  and  $\text{CH}_4\text{-N}_2$  mixtures at a temperature around room temperature ( $P = 1$  atm)

Gas	$T$ (K)	$\tau_{PS}$ (s) [25]	$\tau_{VS}$ (s) [25]	$c_0^2$ (m s <sup>-1</sup> ) <sup>2</sup>	$c_\infty^2$ (m s <sup>-1</sup> ) <sup>2</sup>	$\varepsilon$
20% $\text{CO}_2\text{-80}\%$ $\text{N}_2$	292.6	$9.508 \times 10^{-5}$	$9.330 \times 10^{-5}$	$1.0702 \times 10^5$	$1.0907 \times 10^5$	$1.866 \times 10^{-2}$
40% $\text{CO}_2\text{-60}\%$ $\text{N}_2$	293.7	$7.391 \times 10^{-5}$	$7.130 \times 10^{-5}$	$9.580 \times 10^4$	$9.929 \times 10^4$	$3.521 \times 10^{-2}$
20% $\text{CH}_4\text{-80}\%$ $\text{N}_2$	293.2	$4.720 \times 10^{-6}$	$4.695 \times 10^{-6}$	$1.310 \times 10^5$	$1.3178 \times 10^5$	$5.441 \times 10^{-3}$
40% $\text{CH}_4\text{-60}\%$ $\text{N}_2$	293.0	$3.309 \times 10^{-6}$	$3.276 \times 10^{-6}$	$1.422 \times 10^5$	$1.437 \times 10^5$	$9.901 \times 10^{-3}$



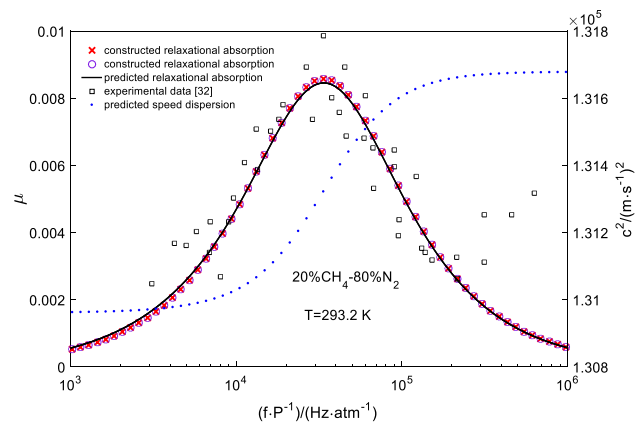
**Fig. 1** Sound relaxational absorption constructed from sound speed dispersion for the 20%CO<sub>2</sub>–80%N<sub>2</sub> mixture. Crosses are based on the high-frequency sound speed, while circles are based on the low-frequency sound speed



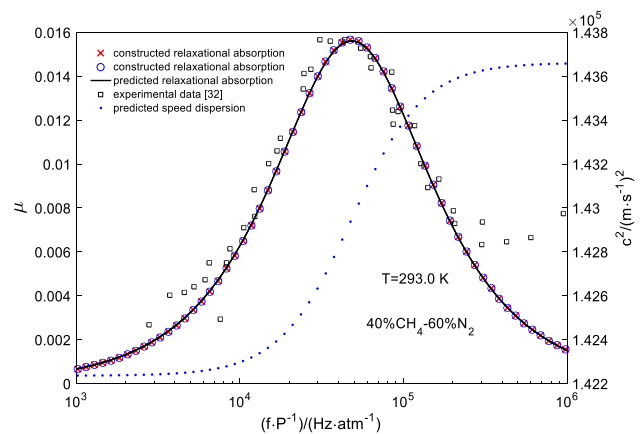
**Fig. 2** Sound relaxational absorption constructed from sound speed dispersion for the 40%CO<sub>2</sub>–60%N<sub>2</sub> mixture. Crosses are based on the high-frequency sound speed, while circles are based on the low-frequency sound speed

frequency and the low-frequency sound speeds (calculated using our prediction model [21]) for the mixtures. Although the number of single-relaxation processes would be the same as the number of the vibrational modes, only the primary relaxation process has significant relaxation strength to cause an obvious acoustic absorption peak as measured by the experiments involving the most excitable gases [1, 22]. Thus, the values of the relaxation times in Table 1 are actually for the primary relaxation processes in excitable gases.

Figures 1, 2, 3 and 4 show the acoustic relaxational absorption constructed from acoustic speed dispersion for the gas mixtures by using the parameters in Table 1 with Eqs. (18) and (26). Because a lowering of the ambient pressure is equivalent to a raising of the sound fre-



**Fig. 3** Sound relaxational absorption constructed from sound speed dispersion for the 20%CH<sub>4</sub>–80%N<sub>2</sub> mixture. Crosses are based on the high-frequency sound speed, while circles are based on the low-frequency sound speed



**Fig. 4** Sound relaxational absorption constructed from sound speed dispersion for the 40%CH<sub>4</sub>–60%N<sub>2</sub> mixture. Crosses are based on the high-frequency sound speed, while circles are based on the low-frequency sound speed

quency and vice versa, the acoustic relaxational absorption and speed dispersion are plotted as functions of the frequency divided by the pressure,  $f/P$ . First, we calculate the sound speed dispersion curves (points) by using our prediction model [21]. Then, we use those speed dispersion curves and the corresponding parameters in Table 1 to construct the sound relaxational absorption based on the low-frequency sound speed (i.e., calculated by Eq. (18), “circles”) and the high-frequency sound speed (i.e., calculated using Eq. (26), “crosses”). A comparison among the two constructed relaxational absorption, the one calculated using our prediction model (solid line) and the experimental data [29] (squares), demonstrates that (1) the two constructed absorption using the sound speed dispersion based on Eqs. (18) and

(26) completely overlaps for all gas mixtures in Table 1, verifying that the analytical relationships based on the low-frequency sound speed and on the high-frequency sound speed are equivalent; (2) the two constructed relaxational absorption curves overlap the one calculated using the prediction model [21] and are consistent with the experimental data [29] (the amplitudes of constructed curves are slightly smaller than the experimental data over values of  $f/P > 10^6$  Hz atm<sup>-1</sup>, because we omit the classical absorption during calculation); (3) the inflection frequency of sound speed dispersion is consistent with the relaxation frequency of relaxational absorption; (4)  $\pi/2$  times the relaxation strength  $\epsilon = 1 - c_0^2/c_\infty^2$  is equal to the maximum absorption  $\mu_m$ , e.g., for 20%CO<sub>2</sub>-80%N<sub>2</sub> in Table 1, we can calculate  $\pi\epsilon/2 \approx 2.931 \times 10^{-2}$  from the corresponding relaxation strength, which is the same as the value of the maximum absorption in Fig. 1. These simulation results verify that the maximum absorption and the relaxation frequency can be accurately obtained from the sound speed dispersion and confirm that the sound relaxational absorption can be constructed using the sound speed dispersion. Consequently, sound relaxational absorption and sound speed dispersion can be converted into each other analytically, so they are not two independent acoustic parameters for gas sensing.

## 5 Conclusion

In this paper, we employ the connection between the effective coefficient of compressibility and the effective wave-number to study the relationship between sound relaxational absorption and sound speed dispersion in excitable gases. We obtained the analytical relationship between them from the low-frequency and high-frequency speeds respectively. The comparison and simulation results in the gas mixtures of 20%CO<sub>2</sub>-80%N<sub>2</sub>, 40%CO<sub>2</sub>-60%N<sub>2</sub>, 20%CH<sub>4</sub>-80%N<sub>2</sub>, and 40%CH<sub>4</sub>-60%N<sub>2</sub> prove that sound relaxational absorption can be constructed using sound speed dispersion and that they cannot be used as two independent acoustic parameters for gas sensing. Based on the analytical relationship between them, we demonstrate that (1) the inflection frequency of sound speed dispersion is equal to the relaxation frequency of sound relaxational absorption and the ratio of the high-frequency sound speed and the low-frequency sound speed determines the relaxation strength and the maximum of sound relaxational absorption; (2) the sound speed dispersion cannot only provide information of the adiabatic constant pressure relaxation time and the adiabatic constant volume relaxation time given by relaxational absorption, but also extra information, such as the gas equilibrium pressure and density, and information on the molecular geometric

structure and the frequency of the normal modes of vibration can be extracted more easily. Furthermore, compared with sound relaxational absorption, sound speed dispersion has a much lower measurement error in practice. Thus, sound speed dispersion is more applicable for gas sensing than sound relaxational absorption.

The analysis of the analytical relationship between acoustic relaxational absorption and speed dispersion in this paper is based on the derivation of an acoustic single-relaxation process. However, for multi-component excitable gases with multiple vibration modes, the acoustic multi-relaxation process is the sum of its decoupled single-relaxation processes with different relaxation times [21] and the sound multi-relaxation relaxational absorption is the sum of the relaxational absorption due to each decoupled single-relaxation process [22]. Therefore, the conclusions of this paper are suitable for the analysis of the relationship between sound speed dispersion and sound relaxational absorption caused by a multi-relaxation process in multi-component excitable gases. Overall, this paper provides better theoretical basis for further work on how to use sound speed dispersion for gas sensing.

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