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Decoupling Multiple Rotational Relaxations of Hydrogen to Detect Gas Mixtures

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ABSTRACT Decoupling multiple acoustic relaxations in multi-component gas mixtures is an effective method to acquire acoustic relaxation characteristic of gas molecules, which can be used to determine gas composition. However, decoupling multiple rotational relaxations of hydrogen still remains challenge. In this paper, we present the decoupling model of hydrogen and decouple the multiple rotational relaxation into the group of single-relaxation ones. Based on this model, the whole rotational relaxation process of hydrogen can be simplified as a few decoupled single rotational relaxation processes. The decoupled results of the effective specific heat, the absorption spectrum and the acoustic velocity dispersion agree with the experimental data, which validates our decoupling model. Furthermore, the proposed decoupling rotational relaxation model can be combined with the existing decoupling vibration model to detect gas mixture. Applications in the detection of gas mixtures including N_2 , CO_2 , O_2 and H_2 are provided. Compared with existing gas sensing method ignoring rotational relaxation, our detection result of gas mixtures $H_2 - O_2 - H_2O$ is more convincing since the proposed decoupling model contains significant rotational relaxation of hydrogen. Therefore, the proposed decoupling model not only reveals the mechanism of multiple rotational relaxations of hydrogen, but also provides the new method to detect hydrogen gas mixtures.

INDEX TERMS Acoustic absorption, vibrational relaxation, decoupling model, multiple rotational relaxation.

I. INTRODUCTION

Acoustic relaxation of gases is an effective way to detect the gas compositions [1]–[3] and calculate relaxation contributions [4], [5]. Compared with the traditional methods [6]–[8], acoustic relaxation method has advantages such as simple, low-cost, no calibration and without preprocessing [9]–[12]. Over the decade years, there are many literatures based on acoustic relaxation to detect gas mixtures [1], [13]–[16]. According to Dain and Lueptow's molecular acoustic pyramid [1], sensing gas mixtures is an inverse problem from the top to the base, which means acoustic relaxation properties of gas molecules can be obtained by a decoupling model.

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Acoustic relaxation of gas mixtures results from the energy exchange between external (translation) and internal (rotation and vibration) degrees of freedom of gas molecules [17], [18]. Based on different sources of internal energy exchange, there are two categories of molecular relaxation theory: molecular vibration relaxation and molecular rotation relaxation [18]. In the vibrational relaxation theory, for most gases, molecular vibration relaxation dominates the whole molecular relaxational processes. Based on the existing theoretical models and experimental data for vibrational relaxation in many publications, some decoupling vibrational relaxation theories have been presented. For example, Bauer *et al.* [19] and Shields [20] both provided phenomenological decoupling theories for pure gases or binary gas mixtures. Zhang *et al.* [21] decoupled a multimode vibrational relaxation process of gas mixtures into

the single-relaxation processes. The existing works above are effective to analyze the multi-vibrational relaxation processes and detect most gases such as CO_2 , O_2 , N_2 , CL_2 and CH_4 . However, they just focused on the vibrational relaxation of gas mixtures and cannot be applied to detect gases with significant rotational relaxations.

In the rotational relaxation theory, for hydrogen, rotational relaxation plays a major role in acoustic relaxation processes while vibrational relaxation is negligible. Rhodes [22] proposed that para-hydrogen has two significant rotational relaxations at environment temperatures based on the measurement of acoustic velocity. Bauer and Bass [23] determined rotational energy transfer rates by acoustic measurements and calculated the absorption and velocity dispersion of normal hydrogen. Montero and Pérez-Ríos [24] presented the formulation of the rotational relaxation time by solving the close-coupling Schrödinger equations. These literatures provide effective ways to calculate acoustic characteristic of rotational relaxation of hydrogen. However, studies of decoupling rotational relaxation of hydrogen and exploring its relaxation mechanism are lacking. In this paper we propose a decoupling rotational relaxation model and it can be used to simplify the model and sense hydrogen gas mixtures, which is a necessary supplement to the existing decoupling model of multimode vibrational relaxation.

The following paper is organized as follows. In Section 2, we decouple a multiple process of rotational relaxation into the group of single-relaxation processes. In Section 3, the relaxational curves given by the proposed decoupling model are compared with the experimental data and the whole rotational relaxation process of hydrogen can be simplified as a few decoupled single ones. In Section 4, the total decoupling model of gas mixtures are obtained based on the combination of our decoupling rotational relaxation model and the existing model of decoupling vibrational relaxation [21]. Applications of detecting gas mixtures of $H_2 - N_2$, $H_2 - CO_2$ and $H_2 - O_2 - H_2O$ is given. In Section 5, we conclude the paper.

II. DECOUPLING MODEL OF MULTIPLE ROTATION RELAXATION FOR HYDROGEN

A. ROTATIONAL RELAXATION OF HYDROGEN

During acoustic relaxation processes of gas mixtures, the effective specific heat reflects the macroscopic footprint of molecular relaxation. For most gases, the contribution of internal degrees of freedom to the specific heat is almost entirely attributed to molecular vibrational relaxation [18]. And rotational relaxation is usually classified as the translation [21]. However, molecular relaxation of hydrogen is not the same as most gases with significant vibrational relaxations. Molecular weight of hydrogen is the lightest one among gases, which results in the moment of inertia of hydrogen smaller than those of other gases [18]. Consequently, the rotational energy of hydrogen jumps larger and the rotational relaxation takes longer time. On the contrary, the vibrational specific heat of hydrogen is so small that

TABLE 1. Molecular number proportion and rotational energy of pH_2 and oH_2 at 300 K.

Hydrogen gas level	Proportion of total % [30]	Energy [17]
pH_2 $J=0$	51.4	$0 \leftrightarrow 2 = 353$
pH_2 $J=2$	47.0	$2 \leftrightarrow 4 = 826$
pH_2 $J=4$	1.60	$4 \leftrightarrow 6 = 1294$
oH_2 $J=1$	87.8	$1 \leftrightarrow 3 = 586$
oH_2 $J=3$	12.1	$3 \leftrightarrow 5 = 1062$
oH_2 $J=5$	0.10	$5 \leftrightarrow 7 = 1530$

the contribution to relaxation can be ignored around ambient temperature. Thus, for hydrogen gas, the whole specific heat almost comes from the contribution of the rotational relaxation [25]–[27].

The so-called normal hydrogen (H_2) consists of 25% para-hydrogen (pH_2) with even-numbered rotational levels and 75% ortho-hydrogen (oH_2) with odd-numbered levels at room temperature [28]. The proportion ratio of molecular number of pH_2 between the $J = 6$ level and the $J = 0$ level is 10^{-4} , so the molecular number of the $J = 6$ level is so small that can be ignored [29]. The proportion ratio of molecular number of pH_2 between the $J = 4$ level and the $J = 2$ level is less than 0.018. In fact, approximately half of pH_2 would be in the $J = 0$ and the other in the $J = 2$ level while almost 90% oH_2 would be in the $J = 1$ level at the temperature of 300 K [17]. Table 1 displays that the molecular proportion and energy exchange between rotational energy levels for H_2 , pH_2 and oH_2 . The energies between rotational levels $0 \leftrightarrow 2$, $2 \leftrightarrow 4$ and $4 \leftrightarrow 6$ are 353 cm^{-1} , 826 cm^{-1} and 1294 cm^{-1} respectively, they rise with the increase of the energy level J . The population of molecular number of the rotational levels $J = 4$ in pH_2 and $J = 5$ in oH_2 are 1.6% and 0.1% respectively [30], which means their relaxation contributions to the specific heat are very small. Therefore, both $0 \leftrightarrow 2$, $2 \leftrightarrow 4$ transitions in pH_2 and $1 \leftrightarrow 3$, $3 \leftrightarrow 5$ transitions in oH_2 are important in rotational relaxation processes of H_2 . We mainly discuss the effects of above rotational energy levels on hydrogen relaxation in this paper.

B. EFFECTIVE ISOBARIC SPECIFIC HEAT OF HYDROGEN

According to the definition of enthalpy and the amagat's law, the enthalpy H of an ideal gas mixture is

$$H = H_1 + H_2 + \dots + H_n. \quad (1)$$

It can be seen from (1) that the enthalpy can be linearly superposed. Thus, the enthalpy of hydrogen can be given by

$$H = H_t + H_r + H_v, \quad (2)$$

where H_t , H_r and H_v represent transitional, rotational and vibrational enthalpies of hydrogen respectively. Derived by temperature T , (2) can be rewritten as:

$$dH = C_p^t dT + C_p^r dT_r + C_p^v dT_v, \quad (3)$$

where C_p^t , C_p^r and C_p^v denote transitional, rotational and vibrational specific heat of hydrogen respectively; T is the

translational temperature. C_p^t is defined as [31]

$$C_p^t = E_J dN_J / dT_r, \quad J=0, 1, 2, 3, \dots, N, \quad (4)$$

where N_J and E_J are the molecular number and the energy of the rotational level J in the equilibrium respectively. The rotational energy is calculated from $E_J = J(J + 1)h^2 / (8\pi^2 \mu r_e^2)$. h is the Planck's constant; $\mu = m_1 m_2 / (m_1 + m_2)$ is the reduced mass of the collision pair; m_1 and m_2 are the molecular weights; r_e is the distance between two atoms. According to (3) and the definition of isobaric specific heat $dH = C_p dT$, the effective isobaric specific heat C_p^{eff} can be expressed as:

$$C_p^{\text{eff}} = C_p^t + C_p^r \frac{dT_r}{dT} + C_p^v \frac{dT_v}{dT}, \quad (5)$$

In (5) the translational specific heat of hydrogen C_p^t is affected by the molecular symmetry. Hydrogen is the linear molecule and has 3 translations, so $C_p^t = 3/2R$. The specific heat of vibrational relaxation is far less than that of rotational relaxation around room temperature and can be negligible [18]. oH_2 and pH_2 have different rotational degrees of freedom while their translational temperatures can be regarded as the same [24]. Substituting (4) into (5), the effective isobaric specific heat of a single rotational relaxation process is expressed as:

$$C_p^{\text{eff}} = C_p^t + \frac{E_J dN_J}{dT}, \quad J=0, 1, 2, 3, \dots, N. \quad (6)$$

Clearly, the effective isobaric specific heat is mainly determined by the ratio between the molecular number of the rotational energy level N_J and temperature in (6). Analogous to vibrational mode, the effective isobaric specific heat of a multiple rotational relaxation process becomes:

$$C_p^{\text{eff}} = C_p^t + \sum_{J=0}^N b_J \frac{E_J dN_J}{dT}, \quad J = 0, 1, 2, \dots, N. \quad (7)$$

where b_J represents the molar fraction of the rotational energy level. It can be seen that the value of C_p^{eff} mostly depends on the second part of (7).

C. DECOUPLED EXPRESSION OF EFFECTIVE SPECIFIC HEAT OF HYDROGEN

Similar to vibrational energy transfer of gases, the rotational energy transfer results in the fluctuation ratio between the molecular number of the rotational levels and the temperature of degrees of freedom. Thus the calculation of dN_J/dT is the key to decouple the rotational relaxation for hydrogen. Suppose there are two rotational energy levels I and J , which corresponds to different rotational energies in pH_2, H_2 or oH_2 . The rotational relaxation equation is defined as [31]

$$\frac{dN_J}{dt} = \sum_{J=0; J \neq I}^N k_{IJ} N_I - k_{JI} N_J, \quad I, J=0, 1, 2, \dots, N \quad (8)$$

where N_I and N_J are the molecular numbers of rotational energy levels I and J ; k_{IJ} and k_{JI} are the energy transition probabilities of rotation relaxation from I to J and from

J to I , respectively. The energy transition probability between rotational energy levels I and J is obtained as [32]

$$k_{IJ} = N_0 (\pi \sigma^2 p) (8KT / \pi \mu)^{1/2} \exp \frac{\alpha^2 (E_I - E_J)}{KT}, \quad (9)$$

where p is the pressure and $I, J = 0, 1, 2, \dots, N$. σ represents the hard-sphere diameter of hydrogen molecule (the rotation is regarded as a rigid hard ball); N_0 and K are Avogadro constant and Boltzmann constant respectively; α represents an adjustable proportional constant. k_{IJ} is in units of per second per molecule. $E_I - E_J$ denotes the difference between the I and J rotational energy levels.

In acoustic relaxation field with small wave disturbances, the temperature T and the molecular number of rotational energy level N_J vary periodically with time t during the rotational relaxation. It also means that both $T - T_0$ and $N_J - N_J^0$ are proportional to $e^{i\omega t}$. Inserting $T = T_0 + \Delta T e^{i\omega t}$ and $N_J = N_J^0 + \Delta N_J e^{i\omega t}$ into (8) and deriving it by time and temperature, the algebraic rotational relaxation equation can be expressed as:

$$\left(i\omega + \sum_J k_{IJ} \right) \frac{dN_I}{dT} - \sum_J k_{JI} \frac{dN_J}{dT} = \mathbf{D}, \quad (10)$$

where $\mathbf{D} = \frac{N_I}{KT^2} \sum_J k_{IJ} (E_I - E_J)$ and $I, J = 0, 1, 2, \dots, N$. For simplicity, (10) can be rewritten in a matrix form as

$$(\mathbf{B} + i\omega \mathbf{I}) \mathbf{x} = \mathbf{D}, \quad (11)$$

where \mathbf{I} represents the identity matrix and ω is the angular frequency; $\mathbf{x}_J = dN_J/dT$. $\mathbf{B}_{IJ} = k_{IJ}$, $\mathbf{B}_{JI} = -k_{JI}$ are the rotational energy transition rate matrixes. In most cases \mathbf{B} can be diagnosed as $\mathbf{B} = \mathbf{V} \Lambda \mathbf{V}^{-1}$. Λ , \mathbf{V} and \mathbf{V}^{-1} is the eigenvalue matrix, the eigenvector matrix and the inverse matrix of \mathbf{B} respectively. Substituting $\mathbf{I} = \mathbf{V} \mathbf{V}^{-1}$ into (11), x_J is

$$x_J = \sum_{n=0}^N \frac{V_{Jn} d'_n}{(1 + i\omega \lambda_n^{-1})}, \quad (12)$$

where V_{Jn} and d'_J are the entries of matrices \mathbf{V} and $\Lambda^{-1} \mathbf{V}^{-1} \mathbf{D}$ respectively; λ_n is the eigenvalue value of B . Substituting (12) into (7) and the effective isobaric specific heat of hydrogen becomes:

$$C_p^{\text{eff}} = C_p^t + \sum_{n=0}^N \frac{d'_n \sum_{J=0}^N b_J E_J V_{Jn}}{(1 + i\omega \lambda_n^{-1})}, \quad (13)$$

where $J, n = 0, 1, 2, \dots, N$. By setting $\tau_n = \lambda_n^{-1}$ and $C_n^{\text{rot}*} = d'_n \sum_{J=0}^N b_J E_J V_{Jn}$, the expression of multiple rotational relaxation process containing N single rotational relaxation processes is:

$$C_p^{\text{eff}} = C_p^t + \sum_{n=0}^N \frac{C_n^{\text{rot}*}}{(1 + i\omega \tau_n)}, \quad n = 0, 1, 2, \dots, N. \quad (14)$$

(14) is the decoupled expression of the isobaric specific heat of hydrogen, which is composed of N single rotational relaxation processes. Each of $C_n^{\text{rot}*}$ includes a part of the effective isobaric specific heat of all the rotational energy levels which are caused by the rotational-rotational energy coupling. τ_n is the corresponding relaxation time, which comes from the reciprocal of the eigenvalue of the energy-transition-rate matrix B . $b_J E_J$ is the contribution of the J th decoupled process to the effective isobaric specific heat. Similar to the decoupled vibrational relaxation expression [21], the rotational-rotational energy coupling strongly influences the relaxational characteristic such as the relaxation strength and the relaxation time [17], [18], [33].

D. ACOUSTIC ABSORPTION SPECTRUM AND VELOCITY DISPERSION BASED ON DECOUPLING MODEL

The effective isobaric specific heat is determined by the compositions of gases in the acoustic relaxation [34]. During acoustic propagation of gas mixtures, the complex effective wave number k_e is a function of the effective isobaric specific heat C_p^{eff} , which can be expressed as:

$$k_e = \sqrt{\frac{\rho_0 C_p^{\text{eff}} - R}{P_0 C_p^{\text{eff}}}} = \frac{\omega}{V(\omega)} - i\alpha_r(\omega). \quad (15)$$

where ρ_0 and P_0 are the density and the pressure in the equilibrium state respectively. The real and imaginary parts of k_e yield acoustic velocity $V(\omega)$ and relaxation absorption $\alpha_r(\omega)$ respectively. $\alpha_r(\omega)$ is conventionally represented by the dimensionless absorption coefficient $\alpha_r(\omega)\lambda$, where λ is the acoustic wavelength.

$$V(\omega) = 1/\text{Re}(k_e^{-1}), \quad (16)$$

$$\alpha_r(\omega)\lambda = -2\pi \cdot \text{Im}(k_e^{-1})/\text{Re}(k_e^{-1}). \quad (17)$$

C_p^{eff} of (15) also can be expressed as $C_p^{\text{eff}} = x(\omega) - iy(\omega)$, where $x(\omega)$ and $y(\omega)$ are

$$x(\omega) = C_p^t + \sum_{n=0}^N \frac{C_n^{\text{rot}*}}{1 + (\omega\tau_n)^2}, \quad (18)$$

$$y(\omega) = \sum_{n=0}^N \frac{\omega\tau_n C_n^{\text{rot}*}}{1 + (\omega\tau_n)^2}. \quad (19)$$

III. SIMULATIONS OF THE DECOUPLING MODEL OF HYDROGEN

In order to verify our decoupling rotational model, H_2 and pH_2 are firstly considered in this section. Absorption spectrum, rotational isobaric specific heat and velocity dispersion can be displayed as the frequency-pressure ratio f/p on a logarithmic scale since the relaxation frequency is inversely proportional to the ambient pressure. Fig. 1 shows predictions by the proposed decoupling model of H_2 are compared with the experimental data. On the one hand, the solid curve in Fig. 1(a) displays the specific heat curve by the proposed decoupling model agrees with the experimental data (circles)

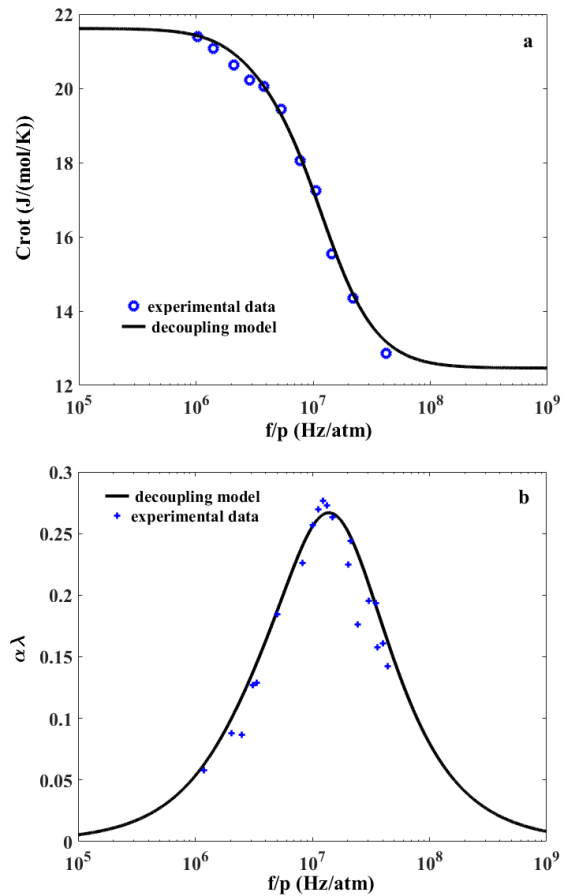


FIGURE 1. (a) Comparison of the isobaric specific heat curve by the decoupling model with experiment data from Takayanagi [29] for pH_2 at 298.4 K;(b) Comparisons of the acoustic absorption spectrum curve by the decoupling model with experiment data from Winter [35] for H_2 at 295 K.

from Takayanagi [29] for pH_2 at the temperature of 298.4 K. For comparison, the experimental data from Takayanagi [29] has a unit conversion from $cal \cdot mol^{-1}$ to $J \cdot mol^{-1} \cdot K^{-1}$ by multiplying 4.16. The effective specific heat of gas mixtures traces molecular relaxation processes and defines the absorption spectra and velocity dispersion. On the other hand, Fig. 1(b) shows comparison of the acoustic absorption spectrum of H_2 by our work with experimental data (circles) from Winter [35]. The absorption spectral peak is 0.2702 and the corresponding relaxation frequency is 1.36×10^7 Hz/atm. The curves of isobaric specific heat and acoustic absorption spectrum both are in good agreement with the experimental data, which valid our decoupling model of hydrogen from two aspects.

To further verify our decoupling model, decoupled results of acoustic velocity dispersion for hydrogen are considered. As shown in Fig. 2(a), the predicted curve (black) by the decoupling model matches experimental data from Winter [35], which again confirm the validity of our decoupling model. Curves of acoustic velocity dispersion in Fig. 2(b) are obtained from the four decoupled single rotational relaxation processes which include $0 \leftrightarrow 2$, $2 \leftrightarrow 4$ transitions of para-hydrogen and $1 \leftrightarrow 3$, $3 \leftrightarrow 5$ transitions

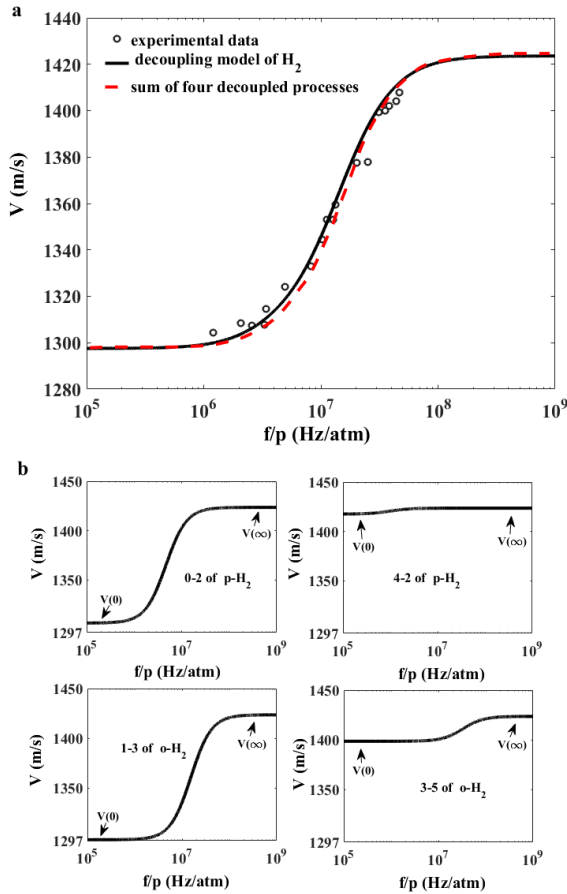


FIGURE 2. (a) Curves of acoustic velocity dispersion are compared with experimental data from Winter [35] at 295 K; (b) Curves of acoustic velocity dispersion of four decoupled processes for H_2 , their sum is the red curve in Fig. 2(a).

of ortho-hydrogen. The red curve of Fig. 2(a) is the sum of the four decoupled single curves in Fig. 2(b). The red curve agrees with the black curve predicted by the decoupling model, which demonstrates that only a few decoupled single rotational relaxation processes of hydrogen have remarkable contribution to the whole rotational relaxation process and others can be neglected. This conclusion is consistent with the analysis of Rhodes [22] and Takayanagi [29]. Furthermore, the difference of $V(\infty) - V(0)$ for acoustic velocity dispersion reflects the relaxation strength, which results from energy consumption of the entire molecular relaxation. For example, for pH_2 , the difference of $V(\infty) - V(0)$ from $0 \leftrightarrow 2$ transition is larger than one from $2 \leftrightarrow 4$ transition. This means the relaxation strength of $0 \leftrightarrow 2$ transition in the relaxation processes of pH_2 is bigger than that of $2 \leftrightarrow 4$. The trends of the differences of $V(\infty) - V(0)$ from $1 \leftrightarrow 3$ transition and $3 \leftrightarrow 5$ transition are the same. Consequently, the whole rotational relaxation process of the decoupling model for normal hydrogen can be simplified as $0 \leftrightarrow 2$, $2 \leftrightarrow 4$ transitions from p- H_2 and $1 \leftrightarrow 3$, $3 \leftrightarrow 5$ transitions from o- H_2 . Among the four decoupled processes, $0 \leftrightarrow 2$ of transition from para-hydrogen and $1 \leftrightarrow 3$ transition from ortho-hydrogen play the key role.

In summary, a decoupling rotational model of hydrogen is proposed. Similar to the decoupling vibrational model [21], the multimode rotational relaxation process of hydrogen is the sum of the decoupled single ones. It can be simplified as the four rotational relaxation processes. The black solid curves of acoustic absorption spectrum and velocity dispersion in Figs. 1(a) and 2(b) are calculated by our decoupling model for the same normal hydrogen under the same condition. Both of them result from the same specific heat of molecular relaxation. The decoupled results of the effective isobaric specific heat, absorption spectrum and velocity dispersion agree with the experiment data well at different temperatures, which demonstrates the reliability of our decoupling model. In addition, the relaxation frequency of hydrogen is more than 1 MHz/atm where the relaxation absorption becomes so small that be submerged into the large amplitude classical absorption. As a result, the relaxation absorption coefficient is hardly acquired. Therefore, to our knowledge, using acoustic velocity dispersion by our decoupling model to detect hydrogen is a better method in the high frequency-pressure range for molecular relaxation.

IV. THE COMBINED DECOUPLING MODEL OF ROTATION AND VIBRATION

The decoupling model not only provides the deep insight into the mechanism of molecular rotational relaxation for hydrogen, but also can be combined with the existing vibrational decoupling model to detect gas mixtures. A vibrational relaxation process of gases (except hydrogen) is independent of a rotational relaxation process of hydrogen [36]. Combining the proposed decoupling rotational model of hydrogen and the existing decoupling vibrational model [21], the decoupled expression of the specific heat of hydrogen gas mixtures can be expressed as:

$$C_p^{A, \text{eff}} = g_1 C_p^{\text{eff}} + g_2 \left(C_p^\infty + \sum_{m=1}^M \frac{C_m^{\text{vib}^*}}{(1+i\omega\tau_m)} \right), \quad (20)$$

where g_1 is the fraction of hydrogen and $g_1 + g_2 = 1$. The content of the first parenthesis is the decoupled isobaric specific heat of hydrogen C_p^{eff} . The content of the second parenthesis is the decoupled isobaric specific heat for gas mixtures except hydrogen (for more details refer to [21]). C_p^∞ is the external specific heat of gas mixtures except hydrogen. $C_m^{\text{vib}^*}$ is the specific heat of decoupled vibrational relaxation process and τ_m is the corresponding relaxation time. Instead of C_p^{eff} , $C_p^{A, \text{eff}}$ is substituted into (15), (16) and (17), acoustic velocity dispersion and absorption spectrum of hydrogen gas mixtures can be calculated. Obviously, in (20) a multiple relaxation process of hydrogen gas mixture is linear combination of rotational and vibrational relaxational processes. There are some differences between the decoupled rotational and vibrational relaxational processes. Vibrational relaxation results from the fluctuation between the vibrational degrees of freedom and temperature. Differently, hydrogen relaxation results from the fluctuation between the molecular number of energy level

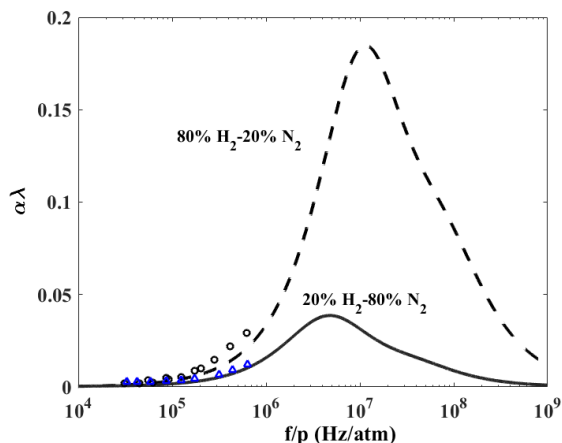


FIGURE 3. Comparisons of the decoupled results of acoustic absorption spectrum with experimental data for gas mixtures 20% $H_2 - 80\%N_2$ and 80% $H_2 - 20\%N_2$ at 298.6 K and 297.8 K.

and temperature. $y_j = dT_j^{vib}/dT$ in Zhang et al. [21] and $x_j = dN_j/dT$ in this paper both relate the microscopic molecular relaxation processes to the macroscopic effective specific heat of gas mixture.

To validate the combined decoupling model above, we consider the first example that hydrogen is mixed with gases including one vibrational relaxation process such as N_2 . Fig. 3 displays that the predictions of acoustic absorption spectrum by the combined decoupling model for gas mixture $H_2 - N_2$ are compared with the experimental data from Ejakov et al. [11] at the temperatures of 298.6 K and 297.8 K respectively. For simplicity, the values of experimental data larger than zero are given in Fig. 3. The predicted absorption spectrum by the decoupling model is consistent with the experimental data at low values of f/p . Due to the limit of measurement capability, there is no experimental data from Ejakov et al. [11] at moderate and high values of f/p . Nevertheless, the predicted absorption spectrum covers the frequency-pressure range where the experimental device fails to measure. With the concentration of H_2 adding from 20% to 80%, the spectral peak increases about from 0.04 to 0.18 in Fig. 3. The acoustic absorption spectrum are strongly determined by the composition of $H_2 - N_2$. The above quantitative acoustic relaxation absorption spectrum [1] can be used to identify the composition of $H_2 - N_2$.

To further validate the combined decoupling model, next example is considered that the hydrogen gas mixtures contain multiple vibrational and rotational relaxation processes. Gas mixtures of $H_2 - CO_2$ combine the relaxation characteristics of CO_2 and H_2 at different concentrations. Fig. 4 displays the predicted results of acoustic velocity dispersion by the proposed decoupling model. The decoupled values of acoustic velocity dispersion for $H_2 - CO_2$ are squared to be compared with the square values of the experiment data from Behnen et al. [36]. As shown in Fig. 4, acoustic velocity dispersion of 2% $H_2 - 98\%CO_2$ coincides with experimental data well at the temperature 303.15 K. To insight into the

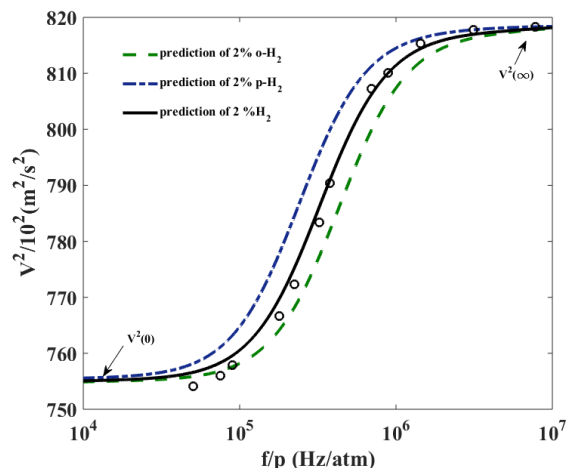


FIGURE 4. Comparisons of the predicted acoustic velocity dispersion by our decoupling model with experimental data for 2% $H_2 - 8\%CO_2$ at $T = 303.15$ K.

TABLE 2. Decoupled results of gas mixture 2% $H_2 - 98\%CO_2$ in Fig. 4.

Number	Process	$C_p^* (Jmol^{-1}K^{-1})$	τ/s
1	R-R	0.0123	2.05×10^{-8}
2	R-R	0.0076	3.02×10^{-9}
3	R-R	0.158	3.37×10^{-8}
4	R-R	0.0015	1.27×10^{-9}
5	V-V	7.385	3.65×10^{-6}
6	V-V	6.7×10^{-8}	1.3×10^{-6}
7	V-V	0.3943	2.2×10^{-4}

mechanism of molecular relaxation, the effective specific heat and the corresponding relaxation time by the combined decoupling model are shown in Table 2 for gas mixture 2% $H_2-98\% CO_2$ (the solid curve in Fig. 4) at the temperature 303.15 K. There are seven decoupled processes composed of three vibrational relaxation processes and four rotational ones for $H_2 - CO_2$. The corresponding isobaric specific heats of the decoupled processes is 0.0123, 0.0076, 0.158, 0.0015, 7.385, 6.7×10^{-8} and 0.3943 $Jmol^{-1}K^{-1}$. The biggest effective specific heat of 98% CO_2 is 7.385 $Jmol^{-1}K^{-1}$ with the significant relaxation time 3.65×10^{-6} . Small additions of 2% H_2 have small specific heat, which means that it has weak contribution to the whole relaxation process.

In addition, the decoupling model predict acoustic velocity dispersion of 2% $pH_2 - 98\%CO_2$ and 2% $oH_2 - 98\%CO_2$. Acoustic velocity dispersion reflects the characteristics of the spin isomers for pH_2 , oH_2 and H_2 [37]. To our knowledge, there is few experimental data of acoustic velocity for $oH_2 - CO_2$ and $pH_2 - CO_2$. Our combined decoupling model predicts their velocity dispersions over the frequency-pressure range where the experiments have not been performed. To detect gas mixtures, traditional methods [38], [39] are based on a relationship that acoustic velocity is nearly proportional to average molecular weights of gas mixtures. However, for gas mixtures $pH_2 - CO_2$, $H_2 - CO_2$ and $oH_2 - CO_2$, traditional methods are invalid since their same molecular weights are same. Differently, our

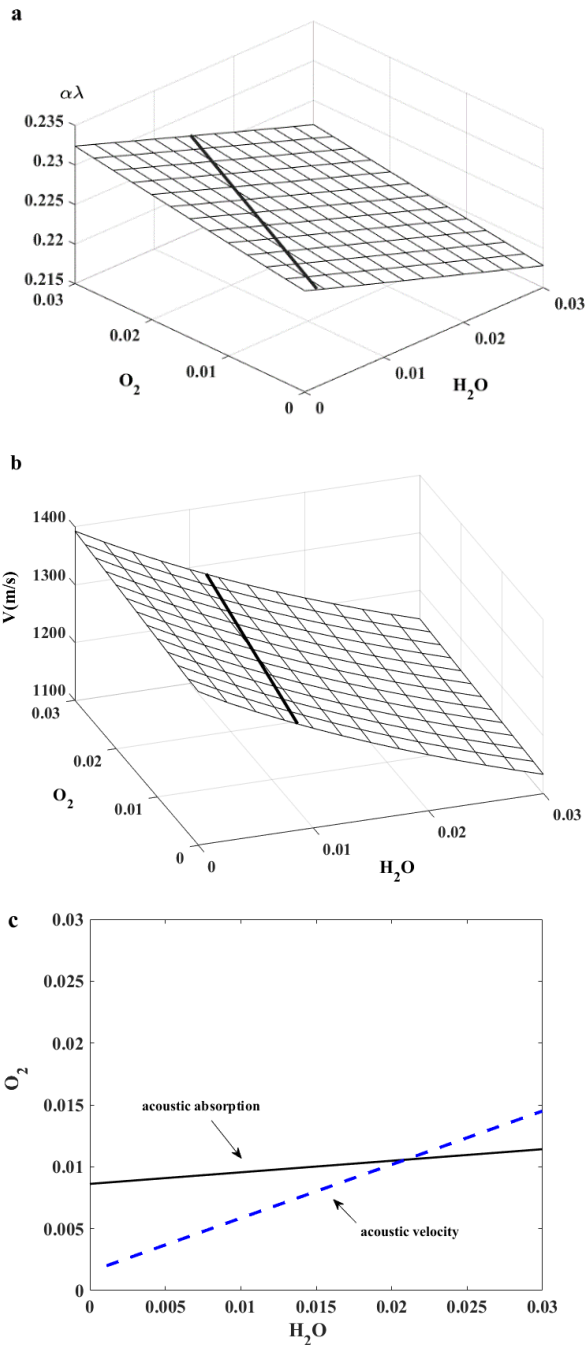


FIGURE 5. Variations of acoustic property with different concentrations of $O_2 - H_2O$ by our work. (a) acoustic relaxational absorption; (b) acoustic velocity; (c) Intersection of two curves from Figs. 5(a) and 5(b) determines the composition of gas mixtures.

combined decoupling model can predict acoustic velocity and the relaxation frequency. For example, the relaxation frequencies of $2\%pH_2 - 98\%CO_2$, $2\%H_2 - 98\%CO_2$ and $2\%oH_2 - 98\%CO_2$ are $2.41 \times 10^5 Hz/atm$, $3.28 \times 10^5 Hz/atm$ and $4.43 \times 10^5 Hz/atm$ from left to right at the same square value of acoustic velocity $786.7 m^2/s^2$ respectively. Gas mixtures of $2\%pH_2 - 98\%CO_2$, $2\%H_2 - 98\%CO_2$ and $2\%oH_2 - 98\%CO_2$ can be identified based on different relaxation frequencies.

The following example is considered that a three-component mixture of $H_2 - O_2 - H_2O$ from the oxygen generation system which may be expected in the spacecraft station module atmosphere [40]. In this system, H_2 and O_2 are produced by electrolyzing water. Phillips *et al.* [10] extracted the composition of gas mixtures $H_2 - O_2 - H_2O$ based on the prediction of the theoretical relaxation model. However, Phillips *et al.* [10] only consider the vibrational relaxation processes of hydrogen and ignore its dominant rotational relaxation. In this section, the same mixture of $H_2 - O_2 - H_2O$ is detected by our decoupling model containing rotational relaxation of H_2 in the same ambient condition. It is assumed that the concentration of hydrogen retains at the fixed 97% and the remaining 3% is sum of the concentration of oxygen and water vapor.

Duo to the explosive danger of H_2 mixing with O_2 , to our knowledge, there is no experimental data of acoustic relaxation for $H_2 - O_2 - H_2O$ up until now. We only compare our simulation results with Phillips's ones. As displayed in Figs. 5(a) and 5(b), the dimensionless absorption coefficient $\alpha\lambda$ is about from 0.215 to 0.235 while $\alpha\lambda$ from Phillips [10] ranges from 0.03×10^{-4} to 1.5×10^{-4} . Acoustic velocity by our decoupling model is about from 1100 m/s to 1400 m/s while that of Phillips [10] ranges from 1000 m/s to 1300 m/s. Whether theoretical model consider the rotational relaxation of hydrogen causes above big difference. Two surfaces that acoustic absorption and acoustic velocity vary with different composition of gas mixtures $H_2 - O_2 - H_2O$ are constructed at the frequency of 10 MHz/atm respectively. Two solid curves on the surfaces are the horizontal slices through the absorption and velocity at their measured values respectively. Along the solid curves of Figs. 5(a) and 5(b), any concentration of gas mixtures $H_2 - O_2 - H_2O$ has the same values of acoustic absorption and velocity respectively. Suppose that the absorption 0.227 and the velocity 1284 m/s are measured in a host gas H_2 containing uncertain concentration of O_2 and H_2O . One slice curve from the absorption surface and the other curve from the acoustic velocity surface intersect at a point. The location of the intersection determines the unknown gas mixtures is $1\%O_2 - 2\%H_2O - 97\%H_2$. Therefore, on the basis of our combined decoupling model, the three-component mixtures including hydrogen can be detected by jointly measuring absorption and acoustic velocity.

V. CONCLUSION

In this paper, a decoupling model of hydrogen is proposed and its multiple rotational relaxation process can be decoupled into the single ones. As a result, it can be simplified as four rotational relaxation processes, $0 \leftrightarrow 2, 2 \leftrightarrow 4$ processes from para-hydrogen and $1 \leftrightarrow 3, 3 \leftrightarrow 5$ processes from ortho-hydrogen. Simulation results indicate that the predicted curves of effective specific heat, acoustic absorption spectra and velocity dispersion match the experimental data, which validates our decoupling model. Furthermore, the difference and similarity between rotational and vibrational relaxation

processes are pointed out. Vibrational relaxation results from the fluctuation ratio between each vibrational relaxation process and the temperature while rotational relaxation is from the fluctuation ratio between the molecular number of rotational level and the temperature. Both of vibration and rotational relaxation are multi-mode relaxation process and can be expressed as the sum of single relaxation processes. The proposed decoupling model from a microscopic angle provides an insight into the mechanism of rotational relaxation of H_2 . It is necessary supplement to the existing decoupling model of multi-mode vibrational relaxation.

In addition, the decoupling rotational relaxation model can be combined with our previous decoupling vibrational relaxation model [21] to detect gas mixtures. Based on quantitative acoustic absorption spectrum and velocity dispersion obtained by our combined model, the compositions of binary gas mixtures such as $H_2 - N_2$, $CO_2 - pH_2$ or oH_2 and $CO_2 - H_2$ can be detected. For the three-component mixtures of $H_2 - O_2 - H_2O$, compared with Phillips *et al.*'s detection method based on vibrational model [10], our detection result based on rotational and vibrational model is more convincing since our model contains the rotational relaxation of hydrogen. Thus the decoupling model provides new way to detect hydrogen gas mixtures.

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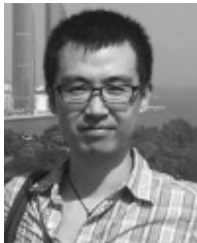
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