Calculation of Vibrational Relaxation Times in Multi-component Excitable Gases

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

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I. INTRODUCTION

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

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

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Calculation of Vibrational Relaxation Times-·-Ke-Sheng Zhang et al.

II. OVERVIEW FOR A SINGLE-RELAXATION PROCESS

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

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

(1)

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

$$dE(T_{\text{vib}})/dt = -[E(T_{\text{vib}}) - E(T)]/\tau.$$  

(2)

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

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

1. Thermodynamic Energy Change of the Gas Mixture

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

$$dQ = dE^t + dE^v = C_{\text{V}} dT + \sum_{j=1}^{N} a_j C_j^{\text{vib}} dT_{\text{vib}}^j = C_{\text{V}}^{\text{eff}}dT,$$

(3)

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