

Synthesizing Primary Molecular Relaxation Processes in Excitable Gases Using a Two-Frequency Reconstructive Algorithm

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Identifying molecular relaxation processes in excitable gases remains challenging. An algorithm that reconstructs the primary relaxation processes is presented. Based on measurements of acoustic attenuation and sound speed at two frequencies, it synthesizes the entire frequency dependence of the complex effective specific heat of the gas, which is the macroscopic “footprint” of relaxation effects. The algorithm is based on the fact that for a simple relaxation process, such as occurs in many polyatomic gases at temperatures around 300 K, the effective specific heat traces a semicircle in the complex plane as a function of frequency. Knowing the high-frequency or instantaneous value of the specific heat provides the capability to not only sense the presence, but also infer the nature and, for mixtures of unlike-symmetry molecules, the concentration of foreign molecules leaking in a host gas.

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Measuring the frequency-dependent acoustic attenuation and sound speed is a powerful method to characterize molecular relaxation in polyatomic gases [1]. Since relaxation times vary inversely with the ambient pressure, traditional methods use one (or a few) frequencies and vary the pressure over a wide range in order to obtain a broad frequency-pressure ratio range that covers the main relaxation processes. This requires many measurements at several frequencies and many pressures. Furthermore, oftentimes the pressures that are necessary are so small that the received signals are buried in noise or so large that the nonideality of the gas must be considered. If detection time is critical, as in the case of a gas monitor based on molecular relaxation, one cannot afford to wait until the sensing volume is evacuated and refilled to obtain the needed pressure range, nor can one rely solely on a few data points to measure the full range of values needed to reconstruct the main relaxation process, especially when the nature of foreign molecular species is desired.

In this Letter, we present a unique approach whereby, *at a single pressure*, a minimum of two operating frequencies can be used to “reconstruct” or “synthesize” the full frequency dependence of the main relaxation process involving the operating frequencies, and, for sensing applications, infer the molecular nature and concentration of contaminant gases in a host gaseous environment.

In polyatomic gases, the acoustic attenuation results from a classical contribution, α_c , due to viscosity, heat conduction, and diffusion (for mixtures), and a nonclassical contribution, α_m , associated with molecular relaxation processes. The speed of sound becomes dispersive in the presence of molecular relaxation. In the study of relaxation phenomena, the classical contribution to the attenuation can be omitted without loss of generality. Thus, acoustic propagation in excitable gases can be described in terms of an effective wave number [2] formed from the frequency-dependent phase speed $c(\omega)$ and relaxational attenuation

$\alpha_m(\omega)$:

$$\tilde{k}(\omega) = \frac{\omega}{c(\omega)} - i\alpha_m(\omega) = \frac{\omega}{\tilde{c}(\omega)} \quad (1)$$

The irreversibilities associated with internal relaxation can be described by the *effective* isochoric and isobaric molar specific heats, $C_V^{\text{eff}}(\omega)$ and $C_P^{\text{eff}}(\omega)$, representing the macroscopic “footprint” of the inability of the internal degrees of freedom to follow the external (acoustic) temperature fluctuations. The molar specific heats are related by $C_P^{\text{eff}}(\omega) - C_V^{\text{eff}}(\omega) = R$, where $R = 8.314 \text{ J/mol K}$ is the universal gas constant. To introduce the effective specific heat explicitly, we resort to an effective specific heat ratio [3], $\gamma^{\text{eff}}(\omega) \equiv C_P^{\text{eff}}(\omega)/C_V^{\text{eff}}(\omega)$, which allows the expression of the square of the effective wave number via an effective thermodynamic speed $\tilde{c}(\omega) = \sqrt{(p_0/\rho_0)} \tilde{c}^{\text{eff}}(\omega)$ as

$$\tilde{k}^2(\omega) = \frac{\omega^2}{\tilde{c}^2(\omega)} = \omega^2 \frac{\rho_0}{p_0} \frac{C_V^{\text{eff}}(\omega)}{C_V^{\text{eff}}(\omega) + R} \quad (2)$$

where ρ_0 and p_0 are the equilibrium density and pressure, respectively. Squaring Eq. (1) and using the last equality in Eq. (2), C_V^{eff} is found as

$$C_V^{\text{eff}} = \frac{R p_0}{\rho_0 c^2} \left(1 - \frac{\alpha_m^2 c^2}{\omega^2} - 2i \frac{\alpha_m c}{\omega} \right) \left[1 - \frac{p_0}{\rho_0 c^2} \left(1 - \frac{\alpha_m^2 c^2}{\omega^2} - 2i \frac{\alpha_m c}{\omega} \right) \right]^{-1} \quad (3)$$

It is bounded by a low-frequency (static) limit, $C_V^0 = \lim_{\omega \rightarrow 0} C_V^{\text{eff}}(\omega)$, and a high-frequency (instantaneous) limit, $C_V^\infty = \lim_{\omega \rightarrow \infty} C_V^{\text{eff}}(\omega)$. The difference between the two limiting values represents the contribution of the relaxing internal degrees of freedom of the molecules, $C^{\text{int}} = C_V^0 - C_V^\infty$ [4]. An effective-heat-based analysis offers di-

rect access to the effect of the relaxing internal degrees of freedom as well as to C_V^∞ , which depends on molecular symmetry. For most simple molecules (except H_2) around room temperature, molecular rotation is in thermal equilibrium with molecular translation. Molecular vibration, on the other hand, has large quantum level spacings and longer relaxation times. This makes the vibrational degrees of freedom unable to follow the external temperature fluctuations. Thus, at room temperature, the internal contribution to the molar specific heat is almost entirely due to the vibrational modes, $C^{\text{int}} = C^{\text{vib}}$.

Consider a relaxation process characterized by a relaxation time τ . The effective isochoric specific heat using C^{vib} for C^{int} is given by [5]

$$C_V^{\text{eff}}(\omega) = C_V^\infty + \frac{C^{\text{vib}}}{1 + i\omega\tau} = C_V^\infty + C^{\text{vib}} \frac{1 - i\omega\tau}{1 + (\omega\tau)^2} \quad (4)$$

For simplicity, we write $C_V^{\text{eff}}(\omega) = x(\omega) + iy(\omega)$. The acoustic losses due to molecular relaxation are the largest when $\omega\tau = 1$ (i.e., the acoustic period is commensurate with the relaxation time), so $y_{\text{max}} = -C^{\text{vib}}/2$. In the complex plane, $C_V^{\text{eff}}(\omega)$ moves from C_V^0 to C_V^∞ along a semicircular locus of radius $r \equiv C^{\text{vib}}/2$ and centered on the point $x_0 \equiv C_V^\infty + C^{\text{vib}}/2$, as shown in Fig. 1, according to Eq. (4). The frequency at which $x = x_0$ and $y = -r$ is the *effective relaxation frequency*, satisfying $f_{\text{relax}} = \omega_{\text{relax}}/2\pi = 1/(2\pi\tau)$.

If the speed of sound c and the nonclassical attenuation α_m are known at a minimum of two angular frequencies, ω_a and ω_b , along with the ambient parameters p_0 and ρ_0 , the effective isochoric specific heats $C_V^{\text{eff}}(\omega_a)$ and $C_V^{\text{eff}}(\omega_b)$ can be formed according to Eq. (3). In the complex plane, the semicircle passing through these points and whose center lies on the $y = 0$ axis is unique. Reconstructing it based on the two measurements (at ω_a and ω_b) provides access to the vibrational contribution to the effective spe-

cific heat, characterized by the relaxation frequency f_{relax} . From Fig. 1, by virtue of the Pythagorean theorem, it is easy to show that the center x_0 and radius r are

$$x_0 \equiv C_V^\infty + \frac{C^{\text{vib}}}{2} = \frac{x_b^2 - x_a^2 + y_b^2 - y_a^2}{2(x_b - x_a)} \quad (5a)$$

and

$$r \equiv \frac{C^{\text{vib}}}{2} = \sqrt{x_a^2 + y_a^2 + x_0(x_0 - 2x_a)} \quad (5b)$$

where (x_a, x_b) and (y_a, y_b) are the real and imaginary parts, respectively, of $C_V^{\text{eff}}(\omega_a)$ and $C_V^{\text{eff}}(\omega_b)$. Equations (5) give direct access to $C^{\text{vib}} = 2r$ and $C_V^\infty = x_0 - r$. The latter is linked to the symmetry (or geometry) of the molecules. Using the real part of the second equality of Eq. (4) evaluated at $\omega_a = 2\pi f_a$ and the first equalities of Eqs. (5), the relaxation time is

$$\tau = \frac{1}{\omega_a} \sqrt{\frac{C^{\text{vib}}}{x_a - C_V^\infty} - 1} = \frac{1}{\omega_a} \sqrt{\frac{2r}{x_a - (x_0 - r)} - 1}. \quad (6)$$

The semicircular locus of $C_V^{\text{eff}}(\omega)$ around ω_{relax} can be synthesized from the data at frequencies ω_a and ω_b by using Eq. (4) with C_V^∞ , C^{vib} , and τ calculated in terms of x_0 and r [Eqs. (5) and (6)].

If there is a contaminant gas present in the host gas at a molar fraction ξ , then the molar-weighted instantaneous and static specific heats of the mixture are

$$C_V^\infty = (1 - \xi)C_{V,1}^\infty + \xi C_{V,2}^\infty = x_0 - r, \quad (7a)$$

$$C_V^0 = (1 - \xi)C_{V,1}^0 + \xi C_{V,2}^0 = x_0 + r, \quad (7b)$$

where $C_{V,1}^\infty$, $C_{V,1}^0$, $C_{V,2}^\infty$, and $C_{V,2}^0$ are the instantaneous and static specific heats of the base gas (subscript 1) and contaminant (subscript 2). Around room temperature, the translational and rotational degrees of freedom of most polyatomic molecules are in equilibrium such that $C_{V,1}^\infty$

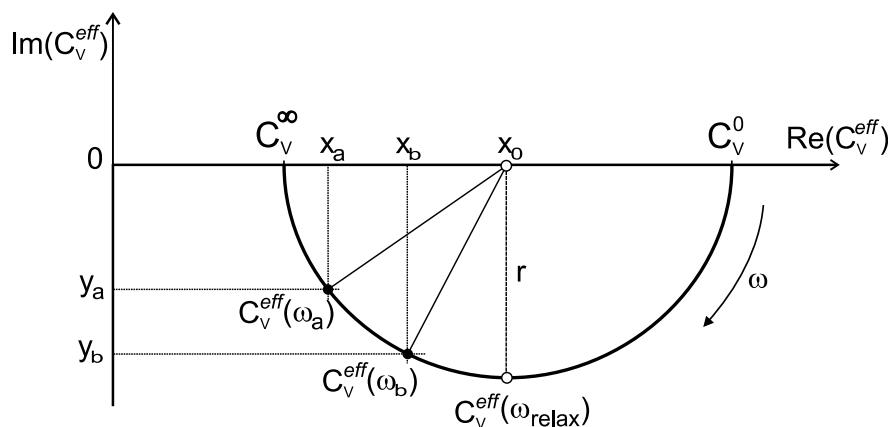


FIG. 1. Complex plot of the semicircular locus of the effective specific heat $C_V^{\text{eff}}(\omega)$ for a single relaxation time, passing through $C_V^{\text{eff}}(\omega_a)$ and $C_V^{\text{eff}}(\omega_b)$. By calculating the radius r and center x_0 from the real (x_a, x_b) and imaginary (y_a, y_b) parts, one can reconstruct the semicircle and determine the effective relaxation frequency ω_{relax} . The arrow indicates increasing frequency.

and $C_{V,2}^\infty$ are either $5R/2$ (diatomic and linear molecules) or $3R$ (nonlinear molecules). If the geometries of the base and the unknown molecules are different such that $C_{V,2}^\infty \neq C_{V,1}^\infty$, which we call a *heterosymmetric* mixture, then Eq. (7a) can be used to estimate the fraction ξ of the contaminant molecules. Thus, in terms of x_0 and r , and the known quantities $C_{V,1}^\infty$ and $C_{V,2}^\infty$, the unknown contaminant fraction is

$$\xi = \frac{(x_0 - r) - C_{V,1}^\infty}{C_{V,2}^\infty - C_{V,1}^\infty}. \quad (8)$$

If the two species have the same symmetry, forming a *homosymmetric* mixture, then $C_{V,2}^\infty = C_{V,1}^\infty = C_V^\infty$ and the contaminant fraction cannot be found directly from Eq. (7a).

As an example of how the reconstructive algorithm might be used in practical sensing applications, consider a device operating at $f_a = 215$ kHz and $f_b = 92$ kHz that monitors a known base atmosphere of N_2 gas at 300 K and atmospheric pressure, which is characterized by extremely weak vibrational relaxation at a very low frequency (~ 0.01 Hz). Thus, at the two frequencies of interest, the attenuation due to molecular relaxation is negligible ($\alpha_m \approx 8 \times 10^{-9} \text{ m}^{-1}$), and the sound speed is $c = 353.07 \text{ m/s}$. Assume that an unknown gas leaks in and the device measures the sound speeds $c(\omega_a) = 356.40 \text{ m/s}$ and $c(\omega_b) = 356.38 \text{ m/s}$ and attenuation coefficients $\alpha_m(\omega_a) = 0.3102 \text{ m}^{-1}$ and $\alpha_m(\omega_b) = 0.2972 \text{ m}^{-1}$. Using the effective specific heats at the two frequencies, $C_V^{\text{eff}}(\omega_a) = 20.992 - i0.012 \text{ J/mol K}$ and $C_V^{\text{eff}}(\omega_b) = 21.001 - i0.027 \text{ J/mol K}$, obtained from Eq. (3), the relaxation time is $\tau = 7.428 \mu\text{s}$ from Eqs. (5) and (6), corresponding to an effective relaxation frequency $f_{\text{relax}} = 21.426 \text{ kHz}$.

The semicircular locus of the new mixture can be “reconstructed” from the initial data at two frequencies. Figure 2 shows the complex plots of $C_V^{\text{eff}}(\omega)$ for pure N_2 (curve 1, known *a priori*) and for the mixture of N_2 with the

unknown gas (curve 2, reconstructed). The striking features of the curves in Fig. 2 are the quite different values of the radius r and the center x_0 , the latter resulting in the real-axis offset. The difference in radius shows that the overall relaxational contribution C^{vib} is considerably larger for the mixture than for pure nitrogen, which means that the vibrational level spacing of the foreign species must be smaller than that of N_2 . From the large difference in x_0 , one infers that the mixture has $C_V^\infty > 5R/2$, thereby eliminating diatomic and linear molecules as candidates for the contaminant species. These arguments, and the larger sound speed in the presence of the foreign gas, restrict the nature of the unknown species to lighter, nonlinear polyatomic molecules ($C_V^\infty = 3R$) with smaller vibrational quanta (and possibly higher vibrational amplitudes) than those of N_2 . For this example, $C_{V,1}^\infty = 5R/2$, $C_{V,2}^\infty = 3R$, $C_V^\infty = x_0 - r \approx 20.993 \text{ J/mol K}$, and $C^{\text{vib}} = 2r \approx 0.123 \text{ J/mol K}$. From Eq. (8), the molar fraction of the unknown species is $\xi \approx 0.0498$ or 4.98%.

It is now possible to synthesize the effective specific heat $C_V^{\text{eff}}(\omega)$ of the mixture using Eq. (4) using the values for τ , C^{vib} , and C_V^∞ . The measured ambient ρ_0/p_0 ratio and $C_V^{\text{eff}}(\omega)$ can then be used to form an effective wave number according to Eq. (2), from which the sound speed and normalized attenuation frequency dependence can be extracted using Eq. (1). Figure 3 shows the reconstructed effective specific heat (identical to curve 2 in Fig. 2), sound speed, and normalized attenuation, for the mixture of N_2 with the foreign gas—in this case, 5% molar fraction of methane (CH_4). The dashed lines represent the “real” behavior of the mixture (95% N_2 and 5% CH_4 , molar fractions) as predicted by the physical theoretical model [6,7]. The reconstructive algorithm predicts the main effective relaxation frequency to be 21.426 kHz, which is within 0.14% of the value 21.456 kHz predicted by the theoretical model. A weaker secondary relaxation process occurs at 790 Hz. The algorithm identifies only the relaxation process that involves the two measured frequencies used to reconstruct the curve, hence the discrepancy between the

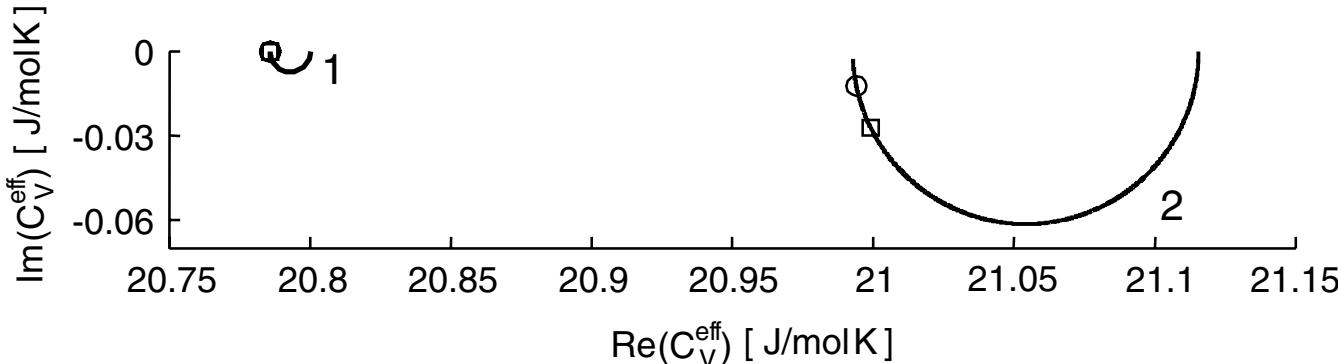


FIG. 2. Complex-plane representations of the effective specific heats of pure N_2 gas (curve 1) and of the mixture of N_2 with an unknown species (curve 2). Symbols: \circ , value at $f_a = 215$ kHz; \square , value at $f_b = 92$ kHz.

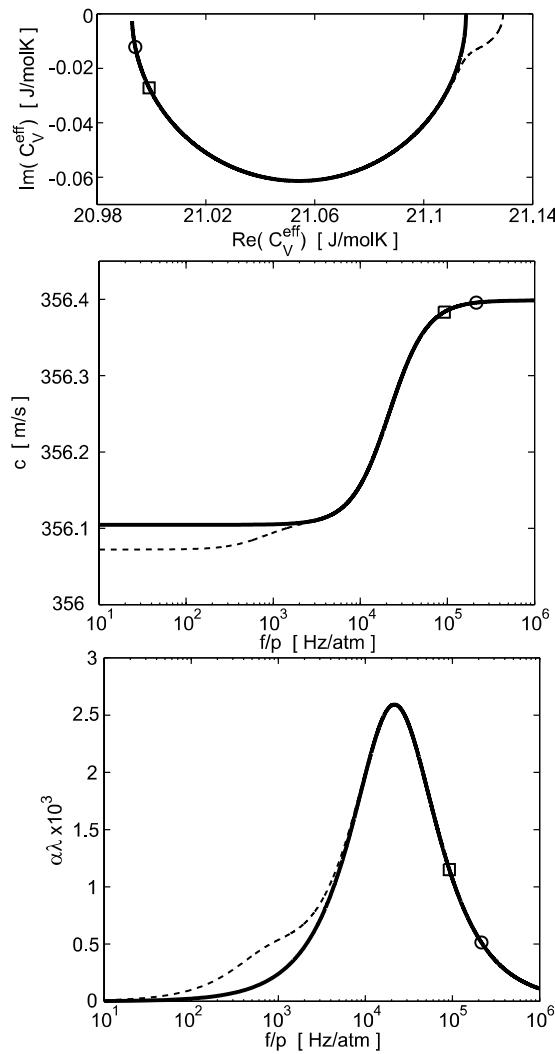


FIG. 3. Reconstructed or synthesized frequency-dependence for C_V^{eff} (top), sound speed (middle), and normalized attenuation (bottom) for a 95%N₂-5%CH₄ mixture (molar fractions). Solid curve, reconstructive algorithm; dashed curve, exact theory (Ref. [6]). Symbols: \circ , values at $f_a = 215$ kHz; \square , values at $f_b = 92$ kHz. The reconstructive algorithm captures the main relaxation event at 21.456 kHz.

reconstructed and the predicted curves. Using the initial information at the two frequencies of 215 and 92 kHz, the

algorithm accurately captures the principal relaxation event (the solid curves in Fig. 3), which can help pinpoint the nature of the unknown molecules as discussed above. Any measurement error will of course propagate up the thread of the algorithm to the reconstructed effective wave number. These errors could be minimized by adding one or more operating frequencies. For instance, for the mixture we considered, a 5% error in the measured attenuation at f_a and f_b leads to 15% and 11% errors in the reconstructed $\alpha\lambda$ peak magnitude and in f_{relax} , respectively. By adding a third measurement at 22 kHz, these errors fall, respectively, to <1% and 3%.

In summary, we present an algorithm whereby with measurements at only two acoustic frequencies one can reconstruct the effective specific heat of an excitable gas mixture and extract the characteristics of the main relaxation mechanisms, which can provide clues to the nature of the molecular species present in the mixture. As a bonus, the composition of a binary heterosymmetric mixture can be inferred from the data at only two frequencies via the instantaneous specific heats [Eq. (8)]. The line of thought of the algorithm is not restricted to gases: with appropriate modifications, it could be extended to include relaxation phenomena in liquids, solids, and maybe even soft matter.

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