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Non-Resonant Optoacoustic Signal
on Pressure and Buffer Gases

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THE DEPENDENCE OF ACOUSTICALLY NON-RESONANT
OPTOACOUSTIC SIGNAL ON PRESSURE AND BUFFER GASES

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ABSTRACT

The dependence of an acoustically non-resonant signal on the buffer gas, pressure, and microphone response is presented. We extend the theoretical treatment of Kerr and Atwood to account for the strength of the observed signal. Considerations for detector optimization are discussed.

The growing interest in optoacoustic spectroscopy has created the need for a better understanding of the processes involved in the generation of the observed signal. In particular, it is important to consider the role of the buffer gas and its thermodynamic and transport properties, to examine the dependence of the optoacoustic signal on pressure, and to include the microphone response and the detector geometry in the analysis. Molecular relaxations and energy transfer among the molecules involved should be taken into account in the case of the acoustically resonant detector since the typical time scales at which these processes occur are comparable to the modulation frequencies of the exciting light (≥ 1 kHz). On the other hand, in the acoustically non-resonant case, bulk properties of gases constitute the dominant factors in determining the behavior of the detector. We report here on the dependence of the non-resonant signal on pressure and on a wide range of buffer gas thermodynamic properties. The microphone response is taken into account for the first time. Our findings for the acoustically resonant case have been reported earlier [1].

The thermodynamic solid gas theory of Kerr and Atwood [2] provides a suitable starting point to analyze the optoacoustic signal strength. A weakly absorbing gas confined to a cylindrical cell is excited by radiation passing through on axis. This axial heating results in a negligible gas flow [$\Delta T(r=0) < 10^{-2}^{\circ}\text{C}$], so that we may view the gas as a solid, determine the temperature everywhere in the cylinder and find the consequent local pressure rise, and then calculate the equilibrium pressure when the gas is allowed to shift. The temperature redistribution in the ensuing gas flow is of second order. A step rise in the onset of heating will cause

a time-dependent pressure rise given by

$$p(t) = \beta(P_0) \frac{W}{L} \frac{P_0}{4\pi \bar{\kappa} T} \left\{ \sum_m D_m(b) \exp\left(-\bar{\alpha} \xi_m^2 \frac{t}{a^2}\right) \right\} \quad (1)$$

where W/L is the power incident per unit length (z -axis dependence is ignored), $\beta(P_0)$ is the fraction of W/L absorbed, P_0 and T are the equilibrium pressure and temperature within the cell, respectively,

a is the radius of the cell, and ξ_m is the m th root of the zeroeth order Bessel function $J_0(\xi) = 0$. In our case, $\bar{\kappa}$ is the effective thermal conductivity and $\bar{\alpha}$ is the effective thermal diffusivity of the mixture. $D_m(b)$ are numerically calculated coefficients which depend on b , the ratio of the Gaussian beam waist to cell radius (0.189 in our case). The D_m are difficult to calculate for small values of b due to round-off error, but may be verified with the relation [3]

$$\sum_m D_m(b) = 1 - b^2 + \frac{b^2 - \frac{1}{2b^2}}{e^{1/b^2}}$$

Since in practice, the exciting light is approximately square-wave modulated, we may, from Eq. (1), determine the first harmonic lock-in amplifier output as

$$V = S(P_0, \bar{\gamma}, T) \beta(P_0) \frac{W}{L} \frac{P_0}{4\pi \bar{\kappa} T} \left\{ \sum_m \frac{D_m e^{i\theta_m}}{\sqrt{1 + \frac{\omega^2 a^4}{\bar{\alpha}^2 \xi_m^4}}} \right\} \quad (2)$$

where $S(P_0, \bar{\gamma}, T)$ is the sensitivity of the microphone, and $\tan \theta_m = (\omega a^2 / \bar{\alpha} \xi_m^2)^{-1}$. The explicit dependence of the microphone sensitivity on

P_o , $\bar{\gamma}$, and T is given by [4]

$$S(P_o, \bar{\gamma}, T) = S_{\text{rated}} \frac{1 + B}{1 + B \frac{P_o \bar{\gamma} T_{\text{STP}}}{P_{\text{atm}} \gamma_{\text{air}} T}} \quad (3)$$

where $B \cong 1$, $\bar{\gamma} = (\bar{C}_v + R)/\bar{C}_v$; $\bar{C}_v = x_i C_{pi} + (1 - x_i) C_{pj} - R$, and x_i is the molar fraction of i , the optically absorbing gas; the buffer gas is denoted by j . Equation (3) indicates that the microphone sensitivity increases as the pressure decreases.

Most simple schemes for computing the thermal conductivity of a mixture are susceptible to large errors when nearly equal amounts of gas are present (around 15 to 40 torr in our experiment). Mason and Saxena [5] describe a tractable method to calculate the thermal conductivity of a gas mixture which is accurate to a few percent for the mixtures used in our case. The thermal diffusivity can then be calculated by a simple extension. For a two-gas mixture,

$$\bar{\kappa} = \frac{\kappa_i}{1 + \phi_{ij} \frac{1 - x_i}{x_i}} + \frac{\kappa_j}{1 + \phi_{ji} \frac{x_i}{1 - x_i}}$$

$$\phi_{ij} = \frac{1.065}{2\sqrt{2}} \left(1 + \frac{M_i}{M_j}\right)^{-\frac{1}{2}} \left\{1 + \left(\frac{\kappa_i^0}{\kappa_j^0}\right)^{\frac{1}{2}} \left(\frac{M_i}{M_j}\right)^{\frac{1}{4}}\right\}^2$$

where M_i is the molecular weight of the i^{th} species and

$\kappa_i^0 = \kappa_i / (0.115 + 0.354(\gamma/\gamma - 1))$ is the thermal conductivity with the internal degrees of freedom frozen out; x_i is the molar fraction of

the i^{th} species. The diffusivity is then

$$\bar{\alpha} = \frac{\alpha_i}{1 + \phi_{ij} \frac{1-x_i}{x_i}} + \frac{\alpha_j}{1 + \phi_{ji} \frac{x_i}{1-x_i}}$$

For a pure gas ($\bar{\alpha} \rightarrow \alpha$, $\bar{\kappa} \rightarrow \kappa$), and in the limit $\omega^2 a^4 / \bar{\alpha}^2 \xi_1^4 \gg 1$, the result presented here is equivalent to that of Parker and Ritke [6], except for the microphone dependence which we include for the first time. Thus at high pressures their result has the same parameter dependence as the one presented here, while at low pressures not all of their assumptions hold. In particular, one does not have an indication as to the position of the peak of the curves generated by Eq. (2).

In Figs. 1 and 2 we give graphic representations of the theoretical predictions of Eq. (2) for representative buffer gases. A few comments on the figures are in order:

- 1) The initial rise is due to increasing P_0 , and in the case of the heavy gases, is also due to decreasing $\bar{\kappa}$.
- 2) The low-pressure "dip" found in the H_2 curve at low modulation frequencies is due to increasing $\bar{\kappa}$ until P_0 dominates.
- 3) The term $\omega^2 a^4 / \bar{\alpha}^2 \xi_1^4$ becomes much greater than 1 near the peak of each curve, allowing the $1/P_0$ dependence of the diffusivity to cancel the leading P_0 factor and limits any further increase in signal.
- 4) The high-pressure fall-off is due to a decreasing power absorption, $\beta(P_0)$, and a decreasing microphone sensitivity.

- 5) The relative signal strength at 760 torr will have a dependence of roughly $1/C_{vj}$.

The experimental configuration is shown in Fig. 3. A partial pressure of 10 torr CH_4 (the optically absorbing species) was maintained throughout the experiment. The 3.39μ line from a He-Ne laser served as the exciting light. The CH_4 relaxation time has been shown to be less than 0.2 msec for our case [7], too short to be noticed here. The thermodynamic properties of the cell were varied by the substitution of the following buffer gases: He, Ne, Ar, Kr, Xe, H_2 , CO, CO_2 , N_2O , and SF_6 . An external mixing chamber was used to ensure rapid and full gas mixing. Frequency and power fluctuations of the laser output proved to be the limiting factor in the data analysis.

The detector consisted of a 6-cm long cylindrical brass cell, 0.9-cm in diameter. Two Knowles Electronics miniature electric microphones (model BT-1759) were placed at the front end and one was placed at the rear. Except for the confirmation of the first longitudinal resonance in SF_6 around 1000 Hz, little difference existed between microphones, and a single microphone was used throughout.

The 3.39μ output of the He-Ne laser lies in *near* coincidence with the ν_3 absorption band of CH_4 [8]; consequently, the power absorbed first rose, then fell with increasing pressure as the CH_4 line was broadened into the laser line. Since our laser operated in a multimode fashion, and due to the overlapping absorption lines at high pressure, it was judged appropriate to simply determine the pressure dependence of $\beta(P_0)$ from difference measurements with the power meter behind the cell. As expected, each buffer gas has a slightly different dependence due to

differing molecular weights and sizes, as the curves in Fig. 4 indicate.

Typical experimental results are compared with theory in Figs. 1 and 2. The dependence of the optoacoustic signal on pressure for various buffer gases is in good quantitative agreement with the theoretical predictions of Eq. (2). We find that D_1 alone does not adequately describe the pressure dependence of the signal, particularly for low pressures, and that the number of terms required increases for gases of low molecular weights. Ten terms were used in our case. As anticipated, the signal strength is strongly influenced by the heat capacity of the gases involved. The many internal degrees of freedom associated with a large heat capacity, as in the case of SF_6 , compete for the exciting energy, thus depressing the optoacoustic signal. On the other hand, the noble gases produce the largest signals. Those gases with large thermal diffusivities yield their largest signals at higher pressures than those with smaller diffusivities.

The frequency dependence of the signal is clearly demonstrated by the set of curves for H_2 shown in Fig. 2. The dominance of the second term under the radical of Eq. (2) begins at lower P_0 with greater ω . The complicated pressure dependence of the $\bar{\alpha}$ in the radical, together with the leading P_0 term, then eliminate the dip found at lower ω . He shows no dip even at the lowest frequency; however, a small dip is expected to appear in a cell of smaller radius. One may also note that the overall peak height increases with decreasing ω , due to the ω dependence under the radical. Furthermore, due to the P_0 dependence of the diffusivity, the peak will shift towards lower pressure with increasing frequency.

There do exist some discrepancies between the theory and the

experimental results. The turn-over points tend to be shifted lower or higher in pressure than predicted, depending on whether the buffer thermal conductivity is lower or higher than that of the absorbing gas. Secondly, the actual curves tend to fall off with increasing pressure more than the theory predicts, particularly for CO , CO_2 , N_2 , N_2O , and H_2 . The differences, although not large, are most likely a result of a combination of factors. The effective thermal conductivity, for example, should remain constant when CH_4 is added to CH_4 . The Mason and Saxena method instead indicates a 3% variation, which is significant in our case. The diffusivity will suffer a similar difficulty. Since 50 to 90% of the incident power was absorbed in the experiment (Fig. 4), the z -dependence may improve the accuracy of the model slightly, but a more gas-dependent mechanism is a likelier cause for error. Also, the adequacy of Eq. (3) in describing the microphone sensitivity has not been experimentally verified. Finally, we use a multimode laser with no attempt made to stabilize its frequency, leading to fluctuations in the power absorbed at low pressures.

A practical consequence of our results is that if one were to optimize the S/N of an acoustically non-resonant detector, the following should be taken into account: The second term under the radical in Eq. (2) must be kept on the order of one or smaller for as high a pressure as possible. Since α is proportional to $\kappa/(P_0 \cdot C_V)$, the first term eventually drops out, the P_0 dependence cancels, the κ dependence cancels, and the signal becomes proportional to $1/C_V$. Until this happens, however, the signal rises with pressure. Ideally then, one requires a small κ and a large α in the buffer gas. Both this and the high-pressure dependence

mentioned above point to as small a C_v as possible, indicating the selection of a noble gas. Within the noble gases, the choice is not as clear in general. Argon worked well, and this may be due to the near match in diffusivity with the absorber. In particular, we find that a higher signal may be obtained with an absorber-buffer mixture than with any amount of absorber alone.

One may also moderate the increase of the second term under the radical by varying the other factors. One should use as low a modulation frequency as possible, although the $1/f$ noise of the electronics limits the benefits of this approach. A reduction in the cell's radius would be particularly effective since this enters as a factor to the fourth power. Here, too, a trade-off exists as the D_m falls with increasing b . In front of the brackets we find that reducing the temperature enhances the signal as well as (within limits) lowering the electrical noise.

In conclusion, we have demonstrated that a small-radius, non-resonant optoacoustic detector operating at low frequencies has a S/N ratio that compares well to the acoustically resonant case. It generates its largest signal at low pressure whereas the resonant detector operates best at high pressures [9]. Low pressure operation has the advantage of better spectroscopic line resolution and lower background signal [9]. The non-resonant signal, furthermore, is relatively independent of molecular relaxation times and viscosity effects, unlike the resonant signal. Advantages of such a detector include compactness and flexibility, since it lacks the restriction of a particular resonant frequency.

Many of the advantages of the optoacoustic technique are shared by

the two types of detectors. For example, our findings point to the optoacoustic detector's potential as a quick means to determine the thermal conductivity and diffusivity of an optically non-absorbing gas or gas mixture. One may non-invasively study chemical reactions by monitoring the thermal conductivity and power absorbed. One may also invasively investigate laser-induced photophysical and photochemical processes.

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3. Note that several values of D_m given in Table 2 of Ref. [2] are incorrect. The corrected values are:

$D_2(0.25) = 0.0868$	$D_1(0.20) = -1.0458$
$D_2(0.20) = 0.1036$	$D_3(0.20) = -0.0215$
$D_4(0.20) = 0.0052$	$D_5(0.20) = -0.0013$
$D_6(0.20) = 0.0003$	$D_7(0.20) = -0.0001$
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FIGURE CAPTIONS

Fig. 1. Optoacoustic signal as a function of pressure for representative buffer gases. Solid lines are the theoretical predictions of Eq. (2). Modulation frequency is 50 Hz. κ and C_v were obtained chiefly from "Thermophysical Properties of Matter," Vols. 3 and 6, Y.Y.Touloukian, P.E.Liley and S.C.Saxena, editors [Plenum Press, N.Y., 1970)]; and C.Y.Ho, R.W.Powell, and P.E.Liley, J. Phys. Chem. Ref. Data 3, Suppl. 1 (1974). Vertical axis in arbitrary units.

Fig. 2. Optoacoustic signal as a function of modulation frequency for H_2 . Solid lines are the theoretical predictions of Eq. (2). Vertical axis in arbitrary units.

Fig. 3. Schematic of the experimental configuration.

Fig. 4. Percent of power absorbed as a function of pressure for the buffer gases of Figs. 1 and 2.

Fig. (1)

XBL 789-2688

XBL 789-2690

Fig. (2)

Fig. (3)

XBL 789-2691

XBL 789-2689

Fig. (4)

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