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## Application of the thermal wave resonator to the measurement of the thermal diffusivity of gas mixtures

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A gas analyzer device based on thermal wave interference in a cavity is presented. The thermal diffusivity of CO<sub>2</sub>-air mixtures as a function of the relative concentration is measured. It is demonstrated that different concentrations of CO<sub>2</sub> in air can be detected with accuracy using the described experimental device. The results presented here open the possibility to perform routine measurements of thermal diffusivity of binary gas mixtures and using this parameter to monitor the relative gas concentration. © 2001 American Institute of Physics. [DOI: 10.1063/1.1334622]

We report about the use of a recent developed photothermal technique for measurements of the thermal properties of gas mixtures. The proposed technique, henceforth denoted as thermal wave resonator (TWR), is based upon the concept of thermal wave interference first discussed by Bennett and Patty,<sup>1</sup> and more recently explored by Shen and Mandelis.<sup>2</sup> We demonstrate how the TWR detection can be used for investigating the thermal properties of gas mixtures. This is carried out using binary CO<sub>2</sub>-air mixtures with varying concentrations as a test sample. Using the logarithm mixing model for the thermal properties of a two-phase system, the thermal diffusivity dependence on the CO<sub>2</sub> concentration is adequately described at the same time that the thermal properties of the individual constituents are accurately determined.

Our experimental setup, described in detail in Ref. 3, consists on a closed cell, adequately adapted for gas exchange and control of ambient parameters, in which the TWR is enclosed. The TWR cavity of variable length  $L$ , containing the gas under investigation, is formed between a thin (15  $\mu\text{m}$  thick) Al foil and a pyroelectric sensor (25  $\mu\text{m}$  thick polyvinylidene difluoride (PVDF) film with Al metalized surfaces). The 5 mm diam Al foil and PVDF sensor, were both cut from commercial sheets. The light beam from a 20 mW He-Ne laser (Meredith Instruments), modulated at the frequency  $f = \omega/2\pi = 10\text{ Hz}$  by means of a mechanical chopper (Model 650 EG&G), is conveniently expanded and impinges uniformly on the black painted outer surface of the

Al foil, which acts as a light absorber. Following the absorption of the modulated light beam, the Al foil temperature fluctuates periodically at the modulation frequency of the incident beam thereby launching a thermal wave into the gas filled cell. The thermal waves, thus generated, propagate back and forth between the Al foil and the pyroelectric sensor separated by a distance  $L$ . On striking the gas-Al and gas-sensor boundaries, the thermal waves are partially reflected, and interference between the reflected and incident wave trains will set in. The temperature rise at the pyroelectric surface, which results from the superposition of all arriving waves, is probed using a lock-in amplifier (model 5210 EG&G) interfaced to a personal computer. As discussed in Refs. 2 and 3, the method consists in measuring the temperature fluctuation at the pyroelectric sensor as a function of the gas layer thickness. To this end, the pyroelectric sensor is assembled on a micrometer stage coupled to a computer controlled stepping motor so that the cavity length can be varied. For a step resolution of 5  $\mu\text{m}$ , the time required for the scanning of a 5 mm long cavity is roughly 4 min.

The temperature rise at the sensor surface can be written as:<sup>2,3</sup>

$$T(L) = \frac{T_0 \exp(-qL)}{1 - \gamma \exp(-2qL)}, \quad (1)$$

where  $T_0$  is the gas temperature at the Al foil internal surface,  $q = (i\omega/\alpha_g)^{1/2}$ ,  $\alpha_g$  is the gas thermal diffusivity,  $i = (-1)^{1/2}$  and  $\gamma = R_{gA}R_{gP}$ . The parameters  $R_{gA}$  and  $R_{gP}$  are the reflection coefficients for plane thermal waves propagating through a gas medium (denoted by  $g$ ) at the boundary with the media  $A$  (corresponding to the Al foil) and  $P$  (cor-

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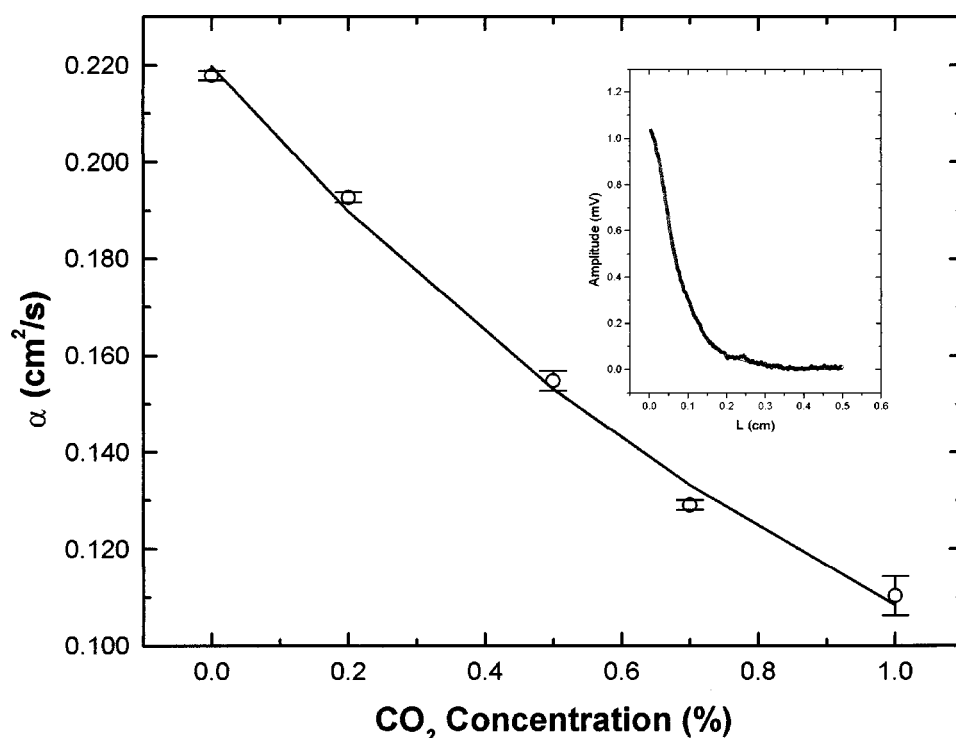


FIG. 1. Thermal diffusivity as a function of  $\text{CO}_2$  concentration in dry air. The solid curve represents the result of the data fitting to Eq. (5). Inset: Amplitude of the TWR signal for a dry air sample containing 50% in volume of  $\text{CO}_2$ , as a function of the gas layer thickness. The solid curve represents the result of the data fitting to Eq. (2).

responding to the PVDF sensor), respectively. They are written as  $R_{gA} = (1 - b_{gA}) / (1 + b_{gA})$  and  $R_{gP} = (1 - b_{gP}) / (1 + b_{gP})$ , where  $b_{gA} = \varepsilon_A / \varepsilon_g$ ,  $b_{gP} = \varepsilon_A / \varepsilon_g$  and  $\varepsilon$  represent the thermal effusivity. The thermal diffusivity and the thermal effusivity are related to the thermal conductivity,  $\kappa$ , specific heat,  $c$ , and mass density,  $\rho$ , by  $\alpha = \kappa / \rho c$  and  $\varepsilon = (\kappa \rho c)^{1/2}$ . The temperature rise given by Eq. (1) induces an electric field between the two opposite surfaces of the PVDF sensor. The resulting voltage  $V$  is given by a complex function

$$V = V_0 \langle T_p \rangle, \quad (2)$$

where  $V_0$  is a complex function containing the frequency dependence of the pyroelectric sensor signal and geometrical parameters characterizing the detection system, and  $\langle T_p \rangle$  is the average temperature rise of the pyroelectric sensor, proportional to  $T(L)$ . From the resulting dependence of the pyroelectric signal on the cavity length, the thermal diffusivity is obtained from the fit of the experimental data to the theoretical model.

We have performed a series of measurements with different  $\text{CO}_2$ -air mixtures at ambient temperature ( $21^\circ\text{C}$ ) and pressure (76.7 mm Hg) using a gas calibration and supplier system. The relative humidity in the laboratory was 65%. The mixtures were prepared by mixing synthetic air (20%  $\text{O}_2$  and 80%  $\text{N}_2$ ) and  $\text{CO}_2$  (99.99%) using electronic mass flow controllers (5850S from Brooks Instruments) throughout a buffer cell. The absolute concentration in volume of  $\text{CO}_2$  in air, for each sample, was set adjusting the relative fluxes for each component and measuring the  $\text{CO}_2$  concentration using an infrared gas analyzer (URAS 14 from Hartmann and Braun).

In Fig. 1, we present the plot of the measured thermal diffusivities as a function of the  $\text{CO}_2$  concentration. The inset in Fig. 1 shows a typical cavity thickness dependence of the

TWR signal amplitude for an air sample containing 50%  $\text{CO}_2$ . The solid curve corresponds to the signal amplitude data fitting to Eq. (2). The value we got from the data fitting procedure for the thermal diffusivity was  $\alpha = 0.155 \pm 0.002 \text{ cm}^2/\text{s}$ . The same procedure was applied to all other sample investigated. The reproducibility of our experimental results was checked by carrying out a series of, at least, five experimental runs for each gas mixture. In particular, we note that the values we got for the thermal diffusivities of pure air and  $\text{CO}_2$ , namely,  $0.218 \text{ cm}^2/\text{s}$  and  $0.110 \text{ cm}^2/\text{s}$ , are in very good agreement with their room temperature values reported in the literature,<sup>4,5</sup> that is, 0.221 and 0.106, respectively. To understand the observed dependence of the thermal diffusivity of the air: $\text{CO}_2$  mixture as a function of the  $\text{CO}_2$  concentration, we resort to the kinetic theory of multicomponent gas mixtures.<sup>6</sup> The rigorous result of this theory is quite complex and has been experimentally verified only in the cases of dilute binary and ternary mixtures of some noble gases.<sup>7</sup> Due to the complexity of the theoretical expression for the thermal conductivity predicted by the kinetic theory, empirical expressions are often used to analyze the experimental data. Among these, the most widely used are the so-called geometric mean model<sup>7</sup> and the logarithm mixing<sup>8</sup> for the thermal conductivity. As discussed in Ref. 8, the geometric mean model corresponds, in general, to the case of maximum effective conductivity of a mixture, whereas, the logarithm mixing is more adequate for a random distribution of a two-phase system. We can readily express the thermal diffusivity of the binary gas mixture in terms of the thermal properties of the constituents gases combining the effective thermal conductivity with the expression for the heat capacity per unit volume for the binary mixture, namely,

$$\rho c = (\rho c)_{\text{air}}[(1-x) + (\rho c)_{\text{CO}_2}]x, \quad (3)$$

where  $x$  denotes the  $\text{CO}_2$  concentration. We have used both models outlined above to analyze our thermal diffusivity data and found that the logarithm mixing gives us the best fit to the data. In this model, the thermal conductivity for the binary mixture is written as

$$\kappa = \kappa_{\text{air}}^{(1-x)} (\kappa_{\text{CO}_2})^x. \quad (4)$$

From Eqs. (3) and (4) and using  $\alpha = \kappa/\rho c$ , the thermal diffusivity of the air: $\text{CO}_2$  mixture reduces to

$$\alpha = \alpha_{\text{air}} \left( \frac{\lambda^x}{[1 + (\chi - 1)(x)]} \right), \quad (5)$$

where we have introduced the parameters  $\lambda$  and  $\chi$  defined as

$$\lambda = \frac{\kappa_{\text{CO}_2}}{\kappa_{\text{air}}}, \quad \chi = \frac{(\rho c)_{\text{CO}_2}}{(\rho c)_{\text{air}}}. \quad (6)$$

This model is strictly valid for a two-component gas mixture. To apply it to the case of air: $\text{CO}_2$  mixtures, we assume that air (a multicomponent gas) may be treated as a single component gas. This assumption seems to be reasonable since the air thermal properties<sup>9</sup> are essentially dominated by those of  $\text{N}_2$  ( $\alpha_{\text{N}_2} = 0.223 \text{ cm}^2/\text{s}$ ,  $\kappa_{\text{N}_2} = 0.26 \text{ mW/cm K}$ ,  $\alpha_{\text{air}} = 0.224 \text{ cm}^2/\text{s}$ ,  $\kappa_{\text{air}} = 0.262 \text{ mW/cm K}$ ). The solid line in Fig. 1 represents the result of our data fitting to Eq. (5), in which we have left  $\alpha_{\text{air}}$ ,  $\lambda$ , and  $\chi$  as adjustable parameters. The results we got for these parameters were:  $\alpha_{\text{air}} = 0.22 \text{ cm}^2/\text{s}$ ,  $\lambda = 0.636$ , and  $\chi = 1.29$  within a 1.6% error. Using the room temperature values reported in the literature,<sup>5</sup>  $\lambda$  and  $\chi$  are estimated to be 0.632 and 1.32, respectively, which compares quite well with the values we have obtained from the data fitting using the logarithm mixing model for the thermal conductivity.

These results suggest that the proposed TWR may indeed become a quite useful technique for the investigation of the thermal properties of gas mixtures. As demonstrated, it provides us with a simple means of measuring the thermal

diffusivity of a gas mixture from which the thermal properties of the constituent gases can be estimated. Furthermore, we note that the TWR technique is quite sensitive to changes in the  $\text{CO}_2$  concentration. For instance, using the values of  $\lambda$  and  $\chi$  as obtained from the data fitting, and taking into account that the average experimental error in the thermal diffusivity is of the order 1.36%, Eq. (5) tells us that the determined thermal diffusivity is sensitive to changes in the  $\text{CO}_2$  concentration of the order of 1.6% with the present TWR configuration. Testing different cell configurations and heating sources can further improve the sensitiveness of the TWR technique. For example, as the heat source does not need to be an Al foil heated by a laser beam. Another light source of reduced dimensions such as a light emitting diode, diode laser, or a filament lamp can be employed instead of a He-Ne laser or it can be replaced by a radiator driven by an oscillating voltage, so that a, low cost, compact equipment can be devised.

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<sup>1</sup>C. A. Bennett and R. R. Patty, *Appl. Opt.* **21**, 49 (1982).

<sup>2</sup>J. Shen and A. Mandelis, *Rev. Sci. Instrum.* **66**, 4999 (1995).

<sup>3</sup>J. A. P. Lima, E. Marín, M. G. da Silva, M. S. Stethel, D. F. Takeuti, S. L. Cardoso, C. N. Gatts, H. Vargas, C. E. Rezende, and L. C. M. Miranda, *Rev. Sci. Instrum.* (in press).

<sup>4</sup>S. Whitaker, *Elementary Heat Transfer Analysis* (Pergamon, New York, 1976).

<sup>5</sup>Y. S. Touloukian, R. W. Powell, Y. C. Ho, and M. C. Nocalasu, *Thermal Diffusivity* (Plenum, New York, 1973).

<sup>6</sup>J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964).

<sup>7</sup>B. N. Srivastava and S. C. Saxena, *J. Chem. Phys.* **27**, 583 (1957).

<sup>8</sup>R. P. Tye, *Thermal Conductivity* (Academic, New York, 1969), Vol. 1.

<sup>9</sup>*Handbook of Chemistry and Physics*, edited by D. R. Lide, 78th ed. (Chemical Rubber Corp., New York, 1997).