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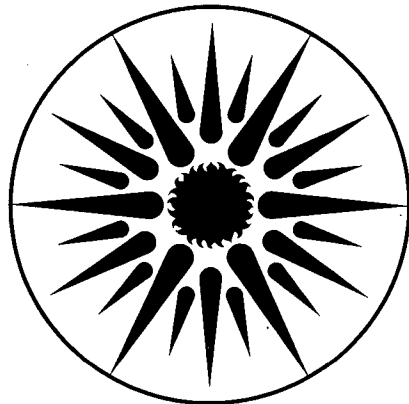
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PHOTOACOUSTIC SPECTROSCOPY

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NEW THEORETICAL ASPECTS OF RESONANT PHOTOACOUSTIC SPECTROSCOPY*

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ABSTRACT

We derive the surface Q for an arbitrary mode, compare azimuthal to radial mode signal, discuss cell size considerations, and compare to nonresonant PAS.

* Work supported by the Director, Office of Energy Research Physical and Technological Reference Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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In addition to its longstanding application to measurement of weak absorption in gases, the resonant spectrophone has more recently been applied to measurement of thermophysical and relaxation properties of gases.¹ In such measurements, the primary information sought is not the absorption coefficient of the gas, but the frequency and quality factor of a cavity resonance. In a carefully constructed spectrophone, classical viscous and thermal boundary layer effects account for most of the losses responsible for the Q , and also contribute a small downward frequency shift.² Thus far, a theoretical expression for the surface losses was available only for purely radial modes.³ However, it would be desirable to have an expression applicable to a mode having arbitrary mode indices, since then information could be gained from a wider variety of resonances. For example, measurements of quality factors for different types of modes of the same resonator could yield both the thermal conductivity and the viscosity of a gas, whereas using only radial modes, one would have to measure Q 's of two or more cells with different length/radius ratios to obtain the same information. Also, the use of azimuthal resonances in trace gas detection has been introduced,^{4,5} and it would be useful to be able to calculate the Q 's of such resonances in order to estimate the signals obtainable.

We have obtained the following theoretical expression for the surface viscous and thermal contribution to the Q :

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$$\frac{1}{Q_{mnq}^{(surf)}} = \frac{2}{(1+\delta_{0q})L} \left\{ (\gamma-1)d_h \left[1 + \frac{L}{R} \frac{(1+\delta_{0q})}{2\left(1 - \frac{m^2}{\pi^2\alpha_{mn}^2}\right)} \right] + d_v \left[\frac{1 - \left(\frac{1+\delta_{0q}}{2}\right)\frac{L}{R}}{1 + \frac{q^2R^2}{\alpha_{mn}^2L^2}} + \frac{L}{R} \frac{(1+\delta_{0q})}{2\left(1 - \frac{m^2}{\pi^2\alpha_{mn}^2}\right)} \right] \right\} \quad (1)$$

where m , n , and q are, respectively, the azimuthal, radial, and longitudinal mode indices, L is the chamber length, R is its radius, γ is the specific heat ratio, δ_{0q} is the Kronecker delta, α_{mn} is the n 'th zero of $dJ_m(\pi\alpha)/d\alpha$, and d_h and d_v are, respectively, the thermal and viscous boundary layer thicknesses, given by $d_h = d_v/\sqrt{Pr} = (2\kappa/\omega\rho_0C_p)^{1/2}$, and where κ is the thermal conductivity, ρ_0 is the density, C_p the specific heat at constant pressure (per unit mass), $Pr = \mu C_p/\kappa$ is the Prandtl number, and μ is the coefficient of shear viscosity. The overall Q is obtained from $1/Q = \Sigma 1/Q_{mnq}^{(i)}$, where the summation index i runs over all the different loss mechanisms enumerated by Kamm,³ but the classical surface loss given by Equation (1) will generally be dominant as long as strong relaxation effects or scattering from major cavity imperfections are not present. Accompanying the broadening of the resonance, there will also be a frequency shift due to the boundary layers given by:

$$\delta\omega = -\omega_{mnq}/2Q_{mnq}^{(surf)} \quad (2)$$

where the minus sign indicates that this is a downward shift.

We have not done an exhaustive experimental test of Equation (1), but have compared it to some data for noble gases obtained with the spectrophone described by Johnson *et al.*² and found that, as in the case of purely radial modes,² it accounts for about 95% of the experimentally observed losses for low-order resonances, but a decreasing percentage for higher-order resonances.

Based on Kreuzer's analysis,⁶ if we assume the beam diameter is small compared to the acoustical wavelength, we find that the rms pressure amplitude p'_{010} obtained at resonance for the first radial mode in the usual radial mode excitation geometry is given by:

$$p'_{010} = \frac{(\gamma-1)\alpha W Q_{010}}{\pi^2\alpha_{01} c R |J_0(\pi\alpha_{01})|} \quad (3)$$

where α is the absorption coefficient, W is the rms value of the first harmonic component of the chopped beam power, and c is the sound velocity. For a geometry such as that used by Poizat and Atkinson,⁵ exciting the first azimuthal resonance, the maximum rms pressure amplitude p'_{100} obtainable (for a single pass) is:

$$p'_{100} = \frac{2(\gamma-1)\alpha W Q_{100}}{\pi^2 \alpha_{10} c R \left(1 - \frac{1}{\pi^2 \alpha_{10}^2}\right)} \quad (4)$$

The ratio of pressure amplitudes obtainable for the azimuthal and radial modes is then:

$$\frac{\text{AZIMUTHAL}}{\text{RADIAL}} = \frac{p'_{100}}{p'_{010}} = \frac{2\alpha_{01} \left| J_0(\pi\alpha_{01}) \right| Q_{100}}{\alpha_{10} \left(1 - \frac{1}{\pi^2 \alpha_{10}^2}\right) Q_{010}} = 2.38 \frac{Q_{100}}{Q_{010}} \quad (5)$$

The Q values used in this equation should be overall quality factors, containing contributions from all the loss mechanisms. However, we can make an estimate by assuming that the classical surface losses are dominant and using Equation (1) for the Q values. We then obtain:

$$\frac{p'_{100}}{p'_{010}} = \frac{1.65}{1 + \frac{0.418(L/R)[(\gamma-1)+\sqrt{Pr}]}{(\gamma-1)(1+\frac{L}{R}) + \sqrt{Pr}}} \quad (6)$$

For the experiment of Poizat & Atkinson,⁵ Equation (6) is not really applicable because the surface viscous and thermal losses are not dominant; their experimental Q_{100} is only about half that predicted by Equation (1). However, since they did not specify Q_{010} , we cannot use Equation (5). Equation (6) would predict a ratio of 0.85 for the azimuthal/radial signal ratio for their cell, whereas they observed a ratio of about 3.3. Since their radial resonance occurred above 20 kHz, it is likely that the high frequency rolloff of the microphone decreased the signal for that mode relative to the 10 kHz azimuthal resonance. The signal for the azimuthal resonance, however, is at least comparable to (theoretically) or greater than (experimentally) the radial mode signal for the same cell. The azimuthal mode has the advantage of a lower Q , so that the signal is more stable with respect to chopping frequency fluctuations, temperature drift, and small variations in gas composition.

If one inserts into Equations (3) and (4) the theoretical expressions for the surface Q 's of the appropriate modes from Equation (1), one obtains the overall dependence of the photoacoustic signal amplitude on cell dimensions L and R . In both cases (radial

and azimuthal modes) one finds that if the ratio L/R is held constant, the signal goes as $R^{-1/2}$ for all R , while if L is held constant, the pressure amplitude goes as $R^{-1/2}$ for $R \ll L$, and as $R^{-3/2}$ for $R \gg L$, with a gradual transition in between. Of course, for both theoretical and practical reasons the $R^{-1/2}$ behavior does not persist as $R \rightarrow 0$, but nevertheless, this suggests that the cell radius should be as small as possible. This is usually limited by the available means of chopping the light, and may also be limited by the collisional deactivation time of the absorbing molecules. Since the azimuthal mode has a resonant frequency less than half that of the radial mode, it allows a smaller cell radius for a given maximum available chopping frequency. In the case where signal varies as $R^{-1/2}$, the Q for either type of mode goes as $R^{+1/2}$, so that reducing the radius reduces the Q , and hence improves the stability.

It is sometimes asserted that use of a resonant spectrophone is pointless because one can obtain more signal from a small-diameter nonresonant spectrophone excited at the same frequency (where presumably the noise level is comparable). We find theoretically that at atmospheric pressure, the nonresonant cell diameters necessary to accomplish this become impractically small for resonant cell diameters of a few centimeters or smaller. However, at high frequencies, noise is generally white, and one can increase the nonresonant cell signal without a corresponding noise increase by simply going to lower frequency. Under virtually no circumstances can the signal in a resonant cell be as high as the signal for a nonresonant cell in its low frequency limit, but of course, the noise at such low frequencies is much higher. Numerous other practical considerations must be taken into account in the choice between resonant and nonresonant PAS.

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