

REVIEW ARTICLE

Application of acoustic resonators in photoacoustic trace gas analysis and metrology

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The application of different types of acoustic resonators such as pipes, cylinders, and spheres in photoacoustics is considered. This includes a discussion of the fundamental properties of these resonant cavities. Modulated and pulsed laser excitation of acoustic modes is discussed. The theoretical and practical aspects of high-*Q* and low-*Q* resonators and their integration into complete photoacoustic detection systems for trace gas monitoring and metrology are covered in detail. The characteristics of the available laser sources and the performance of the photoacoustic resonators, such as signal amplification, are discussed. Setup properties and noise features are considered in detail. This review is intended to give newcomers the information needed to design and construct state-of-the-art photoacoustic detectors for specific purposes such as trace gas analysis, spectroscopy, and metrology. © 2001 American Institute of Physics. [DOI: 10.1063/1.1353198]

I. INTRODUCTION

The photoacoustic (PA) effect in solids¹ was discovered by Bell in 1880. It was soon realized that the same effect exists in liquids and gases as well. Also in these first experiments, resonant amplification of the photoacoustic signal was discovered.² The possibility of using a cavity as an acoustic amplifier of the signal was very important for demonstrating the effect. However, due to the lack of proper instrumentation (such as light sources, microphones, and electronics), the PA effect was almost completely forgotten for more than half a century.

Finally, in 1938, Viengerov introduced a PA system based on a blackbody infrared source and a microphone for analysis of gas mixtures.³ In the 1960s, an important breakthrough was achieved by the first use of a laser light source in PA gas detection.⁴ Compared to conventional light sources, lasers have superior beam quality and spectral purity, and can provide high power radiation. Trace gas analysis was targeted first by the pioneering work of Kreuzer.⁵ A PA cell, operated in a resonant mode by tuning the laser modulation frequency to one of the acoustic resonances of the cylindrical gas cell, was introduced by Dewey *et al.*⁶ and by Kamm.⁷

In the 1970s and 1980s photoacoustic gas detection boomed. High sensitivities were achieved by PA systems using midinfrared gas lasers such as CO and CO₂ lasers.^{8–12} Because of their high output power in the watt range and their line tunability to strong fundamental vibrational transi-

tions, these lasers turned out to be ideal sources to push the sensitivity of PA gas detection into the ppb V (parts per billion volume) concentration range or even below. Initial results using line-tunable CO₂ and CO gas lasers, with modest power of about 1 W, were reported as early as 1972.¹³ In current state-of-the-art experiments CO₂ and CO lasers with much higher power (~ 10 W) are employed. The signal can be further enhanced by placing the PA cell in the optical cavity of the laser resonator, where a laser power of about 100 W can be reached (intracavity photoacoustic spectroscopy).¹¹ Although line-tunable CO₂ and CO gas lasers are relatively large, complex, expensive systems, they have already been used in mobile stations for *in situ* environmental gas detection.¹⁴

The outstanding features of the PA cell, most importantly its small size, its simplicity, and robustness, can only be fully exploited when it is combined with a suitable laser source. Therefore, recent progress made in the development of diode lasers has had an increasing influence on the application of compact PA gas analyzers.^{15,16} The currently available power of near infrared (NIR) diode lasers, operating near room temperature, is small compared with that of CO₂ and CO lasers, and therefore the sensitivity is limited mostly to ppm, or for certain gases to the sub-ppm range. However, they may offer an alternative solution where small size, reliability, low costs, and long lifetime are required. A special advantage of diode lasers is their electronic modulation feature, where both intensity and wavelength modulation are possible. Diode lasers are continuously tunable, but their tunability range is very limited (usually less than one wave

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number).¹⁷ A larger tunability range (20–50 nm) can be obtained with external cavity diode laser (ECDL) systems.^{18,19}

Beginning with the renaissance of photoacoustics around 1970, progress in this field always has been closely connected with the development of laser technology. A major impact on the field of trace gas detection can be expected from new extensively tunable solid-state laser systems working in the fundamental IR spectral region. In this respect the recent realization and further improvement of periodically poled lithium niobate (PPLN) optical parametric oscillators²⁰ (OPOs) and quantum cascade diode lasers²¹ could be an important breakthrough in the practical application of photoacoustic spectroscopy (PAS) in trace gas monitoring. These laser sources deliver continuous wave (cw) as well as pulsed broadly tunable radiation with reasonable power and bandwidth.

A crucial part of a PA gas detection setup is the cell in which the PA signal is generated and detected. The first “gas-microphone cells” were small cylindrical cavities with a transparent window.²² The microphone was connected to the cavity by a thin hole in one of the side walls of the cell. These PA sensors could be manufactured very easily; moreover, they were very cheap when miniature electret microphones were used. Since the PA signal is inversely proportional to the cell volume and the modulation frequency, high PA signal levels can be obtained by taking a small cell volume ($<10\text{ cm}^3$) and low modulation frequencies ($<100\text{ Hz}$). However, noise sources (intrinsic noise of the microphone, amplifier noise, external acoustic noise) show a characteristic $1/f$ frequency dependence, and therefore the signal-to-noise ratio (SNR) of such a gas-microphone cell is usually quite small. Moreover, light absorbed in the windows and in the wall material generates a coherent background signal, which is practically impossible to separate from the PA signal generated by the gas absorption itself. Therefore, small gas-microphone cells, which are still the most suitable PA detectors for solid and liquid samples, are hardly used in gas phase photoacoustics anymore.

The SNR of a PA cell can be increased by applying higher modulation frequencies (in the kHz region) and acoustic amplification of the PA signal. For this resonant PA cells operating on longitudinal, azimuthal, radial, or Helmholtz resonances have been developed.^{23–26} Furthermore, resonant cells can be designed for multipass or intracavity operation.^{11,12,27,28} The influence of the window signal has been minimized by introducing acoustic baffles²⁹ or by the development of a “windowless” cell.³⁰ Recently, a differential cell, specially designed to suppress flow and window noise, was introduced.¹⁷

In the following the requirements that need to be fulfilled by resonant PA cells in gas measurements will be discussed in detail, considering both theoretical and practical issues. First, the characteristics of the PA effect in gases will be briefly surveyed.

II. THE PHOTOACOUSTIC EFFECT IN GASES

The PA effect in gases can be divided into three main steps:¹⁵

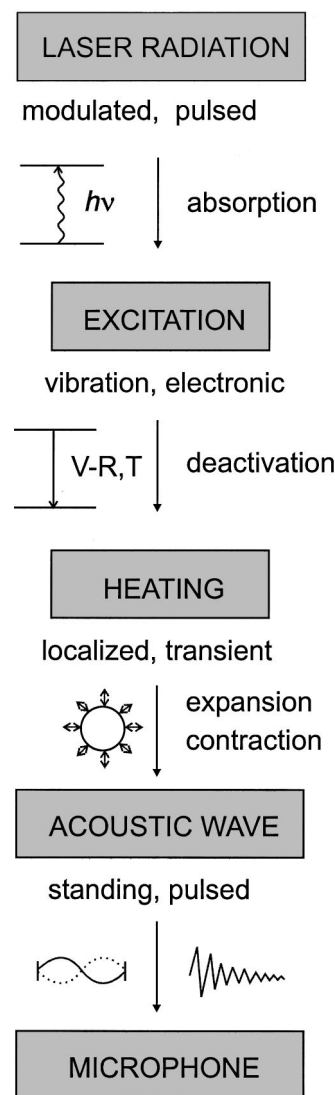


FIG. 1. Schematic of the physical processes occurring after optical excitation of molecules. Modulated or pulsed laser radiation leads to the population of rotational, vibrational, and electronic states. Collisional deactivation by $R-T$, $V-R$, T , and $E-V$, R , T processes leads to localized transient heating. The resulting expansion launches standing or pulsed acoustic waves, which are detected with a microphone.

- (1) localized heat release in the sample gas due to relaxation of absorbed light energy through molecular collisions;
- (2) acoustic and thermal wave generation due to localized transient heating and expansion;
- (3) detection of the acoustic signal in the PA cell with a microphone.

Molecular absorption of photons results in the excitation of molecular energy levels (rotational, vibrational, electronic). The excited state loses its energy by radiation processes, such as spontaneous or stimulated emission, and/or by collisional relaxation, in which the energy is transformed into translational energy. In the case of vibrational excitation, radiative emission and chemical reactions do not play an important role, because the radiative lifetimes of vibrational levels are long compared with the time needed for collisional deactivation at pressures used in photoacoustics ($\sim 1\text{ bar}$) and the photon energy is too small to induce

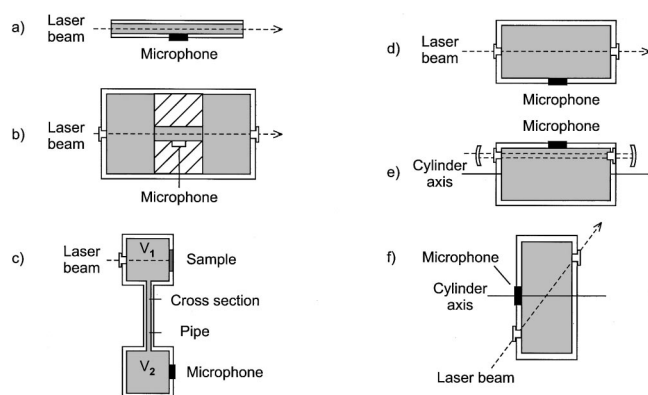


FIG. 2. Resonant acoustic cell designs. (a) Simple pipe (tube) for excitation of longitudinal modes, (b) pipe with two buffer volumes, (c) Helmholtz resonator with separate sample and detection chambers for solid samples, (d) coaxial excitation (e.g., of radial modes) in a cylinder, (e) asymmetric multipass arrangement for excitation of azimuthal modes in a cylinder, and (f) cylindrical cell suitable for excitation of the first radial mode with suppression of the window noise.

chemical reactions.^{31–33} Thus, in practice the absorbed energy is completely released as heat, appearing as translational (kinetic) energy of the gas molecules. The deposited heat power density is proportional to the absorption coefficient and the incident light intensity. A detailed schematic illustrating the series processes occurring during PA signal generation is presented in Fig. 1.

The laws of fluid mechanics and thermodynamics can be used to model the acoustic and thermal wave generation in gases.³⁴ The governing physical equations are the conservation laws for the energy, the momentum, the mass, and the thermodynamic equation of state. The physical quantities characterizing the acoustic and thermal processes are the temperature T , pressure p , density ρ , and the three components of the particle velocity vector $\mathbf{v}$. By eliminating the variables T , ρ , and $\mathbf{v}$ a linear wave equation can be derived for the sound pressure:

$$\partial_t^2 p(\mathbf{r}, t) - c^2 \nabla^2 p(\mathbf{r}, t) = (\sigma - 1) \partial_t H(\mathbf{r}, t), \quad (1)$$

where c , σ , and H are the sound velocity, the adiabatic coefficient of the gas, and the heat density deposited in the gas by light absorption, respectively.

This wave equation always has two independent solutions:³⁵ a weakly damped propagating acoustic wave with wavelengths in the centimeter range, and a heavily damped thermal wave. Since the latter wave has a very small wavelength (in the submillimeter region) and does not propagate beyond the distance of a few wavelengths, it can be observed only in the vicinity of the exciting light beam. Therefore, thermal and acoustic waves are separated in space and can be investigated independently.

Photoacoustic gas analysis is based on the detection of the acoustic signal. The source term of the acoustic wave equation is proportional to the deposited heat power density. The spatial size and shape of the source volume depend on the light-beam geometry and on the absorption length in the gas, while the time dependence of heat deposition is controlled by the time dependence of laser excitation. Thus, a laser pulse generates a heat pulse, which excites an acoustic

pulse,³³ while a modulated laser beam generates periodic sound due to the periodic localized heating of the gas.³⁶

The sound signal is generated in those locations, where light is absorbed, for example, by the species to be monitored. Interestingly, even the PA signal generated by a laser beam propagating in free air has been observed.³⁷ However, nearly all PA trace gas measurements are carried out in an enclosure, called a ‘‘PA cell’’ or ‘‘PA detector.’’ Both terms are used in the literature to describe the device in which the PA signal is generated and monitored. In the following the term PA resonator will be used for the cavity in which the resonant amplification of the PA signal takes place. The name PA cell is reserved for the entire acoustic unit, including the resonator, buffer volumes, acoustic filters, windows, gas inlets and outlets, and microphone(s). Finally, PA sensor or PA detector stands for a complete instrument, including PA cell(s), light source, gas handling system, and electronics used for gas detection.

From an acoustic point of view the PA cell is a linear acoustic system, which responds as a whole to the disturbance generated by light absorption. Since one of the most important parts of the PA cell is the acoustic resonator itself, its properties will be discussed first. The influences of the other parts of the PA cell are taken into account only as boundary conditions.

III. ACOUSTIC RESONATORS

The cylindrical acoustic waves generated by the absorption of a periodically modulated laser beam traveling through open air have a relatively small amplitude. However, when a gas sample is confined within a closed cell the amplitude may increase considerably because of the constructive interference caused by the boundaries. A simple acoustic resonator consists of a well defined regular cavity (ideally closed, but in reality equipped with one or more openings for the microphone and gas transport). Three types of acoustic resonators have found widespread use in PA detection: Helmholtz resonators, one-dimensional cylindrical resonators, and cavity resonators. Figure 2 displays a series of fundamental resonator types including a simple pipe or tube, a pipe with buffers, a Helmholtz resonator, and three different configurations used for laser excitation of specific modes in cylindrical resonators.³²

A. Helmholtz resonator

The Helmholtz resonator consists of a cavity and an adjoining neck, which opens to open air. It is the acoustic equivalent of a simple mechanical oscillator composed of a mass and a spring. The air in the cavity plays the role of the spring, while the air mass in the neck corresponds to the moving mass of the mechanical oscillator. When the air plug in the neck moves outward the pressure inside the cavity decreases, resulting in an inward-directed force, which tries to restore the original state. An oscillation will develop with the following resonance frequency:³⁵

$$f_0 = \frac{c}{2\pi} \sqrt{\frac{S}{Vl}}, \quad (2)$$

where c , S , V , and l are the sound velocity, the cross-sectional area of the neck, the volume of the cavity, and the length of the neck, respectively. The amplification at the resonance frequency depends on the losses (viscous and thermal losses at the wall of the neck and radiation losses through the opening) of the Helmholtz resonator.³⁵ The achievable amplification usually does not exceed a value of 10.

A Helmholtz resonator can be represented by an equivalent electric circuit using an analogy between acoustic and electric networks.³⁸ In this analogy the voltage and current correspond to sound pressure and volume flow (flow velocity times the cross-sectional area), respectively. The equivalent circuit of a Helmholtz resonator is a serially connected acoustic capacitance and inductance with $C_A = V/\rho c^2$ and $L_A = \rho l/S$. Since a PA cell has to be isolated against outside noise, such a simple cavity with a neck cannot be used as a PA cell. Therefore, the simplest, most practical applicable PA Helmholtz resonator consists of two cavities connected by a tube [see Fig. 2(c)]. In this case the volume V in Eq. (2) should be replaced by the effective volume defined as $V_{\text{eff}} = 1/(1/V_1 + 1/V_2)$.

Such coupled cavities have been used as PA cells,²⁵ especially for the measurement of solid-phase samples. However, since the optical window is situated directly on the walls of the resonator, the window signal and the PA signal due to gas absorption are generated in the same cavity, and cannot in practice be separated. The PA sensitivity achievable with Helmholtz resonators is relatively small,³⁹ and therefore they have not had widespread use in trace gas analysis.

B. One-dimensional acoustic resonator

If the cross-sectional dimensions of a resonator are much smaller than the acoustic wavelength, the excited sound field develops a spatial variation only along the length of the resonator, i.e., a one-dimensional acoustic field is generated. A narrow pipe (or tube) can be regarded as a one-dimensional acoustic resonator. A pressure wave propagating in the pipe will be reflected by an open/closed end with the opposite/same phase.³⁸ Through multiple reflections a standing wave will be formed. Therefore, open–open [see Fig. 2(a)] and closed–closed pipes should have resonances when the pipe length is equal to an integer multiple of the half wavelength, while an open–closed pipe should resonate when its length is equal to an odd integer multiple of the quarter wavelength. In reality the wavelengths at the resonances are somewhat larger.^{35,38} The corresponding resonance frequencies can be obtained from the following expressions:

$$f_n = \frac{nc}{2(l + \Delta l)} \quad n = 1, 2, 3, \dots, \quad (3)$$

$$f_{2m-1} = \frac{(2m-1)c}{4(l + \Delta l)} \quad m = 1, 2, 3, \dots,$$

where l is the length of the pipe. Here f_n corresponds to the open–open or closed–closed ends, while f_{2m-1} corresponds to the open–closed end. The quantity Δl is the so-called end correction, which should be added to the length of the pipe

for each open end.³⁵ The end correction for a closed end is naturally zero. Physically the end correction can be understood as an effect of the mismatch between the one-dimensional acoustic field inside the pipe and the three-dimensional field outside that is radiated by the open end.

The end correction can be approximated by the following expression: $\Delta l \cong 0.6r$, where r is the radius of the pipe. More precisely, the end correction decreases slightly with frequency,³⁵ therefore the resonance frequencies of an open pipe are not harmonically related but slightly stretched. On the other hand, the resonance frequencies of a closed–closed pipe are exact multiples of the fundamental frequency. The standing wave patterns are different in open–open and closed–closed pipes: the former has pressure nodes, the latter pressure antinodes at the ends.

Incompletely closed pipes or pipes with rounded horn-like openings naturally also have acoustic resonances, but the resonance conditions cannot be expressed in such simple forms as Eqs. (3). The end of a pipe that opens to a larger diameter volume [see Fig. 2(b)] behaves similarly to an ideal open end, while the properties of a closed pipe end with an opening having a much smaller diameter than the pipe itself are close to that of an ideal closed end. Pipe resonators have found widespread application in gas phase photoacoustics. Therefore, their properties will be discussed in more detail later.

C. Cavity resonators

If the dimensions of a cavity are comparable with the acoustic wavelength then several distinct resonances can be generated. The standing wave patterns and resonance frequencies depend on the shape and size of the cavity. Analytical expressions can be given only for certain regular shapes, such as spheres, cylinders, cubes, and rectangular prisms. Although spherical resonators have been used in photoacoustics,⁴⁰ the most frequently applied cavity resonator is the cylinder [see Figs. 2(d)–2(f)], with symmetry that coincides well with that of a laser beam propagating along the cylinder axis.^{33,36} The resonance frequencies of a lossless cylindrical resonator are as follows:

$$f_{jmq} = \frac{c}{2} \left[\left(\frac{\alpha_{jm}}{R} \right)^2 + \left(\frac{q}{L} \right)^2 \right]^{1/2}, \quad (4)$$

where R and L are the radius and length of the cylinder, the jmq indices (non-negative integers) refer to the eigenvalues of the radial, azimuthal, and longitudinal modes, respectively, and α_{jm} is the j th zero of the derivative of the m th Bessel function divided by π . The characteristic features of these different eigenmodes of a cylindrical resonator are illustrated in Fig. 3.

The properties of cavity resonators will be discussed in Sec. IV using a theoretical treatment discussed elsewhere.⁴¹ This treatment can be applied also to one-dimensional pipe resonators.

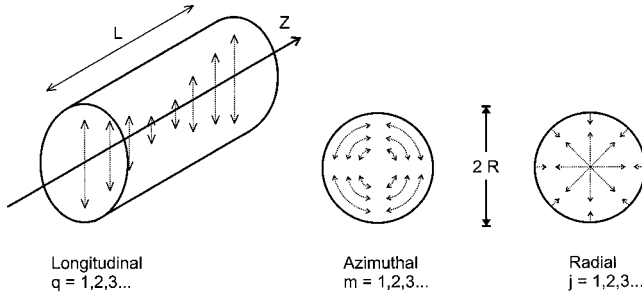


FIG. 3. Schematic of the acoustic longitudinal, azimuthal, and radial modes in a cylindrical resonator. Only oscillations at the resonant frequencies of these eigenmodes are amplified and they will significantly gain energy.

IV. PHOTOACOUSTIC SIGNAL IN A CAVITY RESONATOR

A. General theory

All cavities used as photoacoustic cells have acoustic resonances. The acoustic eigenmodes of a closed cavity are the solutions of the homogeneous wave equation:³⁵

$$\partial_t^2 p(\mathbf{r}, t) - c^2 \nabla^2 p(\mathbf{r}, t) = 0. \quad (5)$$

It can be shown that in the lossless case the solutions of the above equation are orthogonal.³⁵ In the case of an acoustic resonator with small openings the solutions can be written as a series expansion in the eigenfunctions of the closed lossless resonator. Indeed, small holes disturb the acoustic field distribution only slightly and can be considered as sources of loss of acoustic energy radiated out from the resonator. Thus, the solution of the inhomogeneous wave equation,³⁵ given in Eq. (1), can be written as^{33,41}

$$p(\mathbf{r}, t) = A_0(t) + \sum_n A_n(t) p_n(\mathbf{r}), \quad (6)$$

where A_n and p_n are the amplitude of the n th eigenmode component and the dimensionless eigenmode distribution, respectively.³³ Notice that the dimensions of A_0 and A_n are the same as those of the sound pressure p . As an example, the dimensionless eigenmode distribution function of a cylindrical resonator is given as

$$p_n(\mathbf{r}) = p_{jm q}(r, \varphi, z) = J_m(\pi \alpha_{jm}) \cos(m\varphi) \cos\left(q\pi \frac{z}{L}\right). \quad (7)$$

The meanings of the indices j , m , and q are explained above [see Eq. (4)]. The eigenmode index n used in Eq. (6) and in the following considerations represents a given ($jm q$) trial index group. The series expansion of Eq. (6) can be used for both pulsed and modulated excitation of acoustic resonances. In the modulated case the time dependence $\exp(i\omega t)$ can be assumed. Taking into account that $p_n(\mathbf{r})$ is a solution of the homogeneous wave equation, the following expression can be derived:

$$-\omega^2 A_0 + \sum_n (\omega_n^2 - \omega^2) A_n p_n(\mathbf{r}) = i\omega(\sigma - 1)H(\mathbf{r}). \quad (8)$$

The sound pressure amplitude A_0 can be determined by integrating the above equation over the volume of the reso-

nator, and taking into account the fact that the value of the volume integral of all p_n eigenmodes is zero:

$$A_0 = \frac{(\sigma - 1) \int H(\mathbf{r}) dV}{i\omega V_{\text{res}}}. \quad (9)$$

The A_n amplitude can be determined by multiplying Eq. (8) by $p_m(\mathbf{r})$ and integrating over the volume. Since the p_n and p_m eigenmodes are orthogonal, A_n can be expressed as

$$A_n = \frac{i\omega(\sigma - 1) \int H(\mathbf{r}) p_n(\mathbf{r}) dV}{\left(\omega_n^2 - \omega^2 + i\frac{\omega\omega_n}{Q_n}\right) \int |p_n(\mathbf{r})|^2 dV}. \quad (10)$$

In order to take into account in a formal way the effect of losses (see Sec. VIC) an additional term containing Q_n , the quality factor (Q factor) of the resonance, has been introduced in the denominator of Eq. (10). If the modulation frequency is equal to one of the acoustical eigenfrequencies of the cavity, the energy from many modulation cycles is accumulated in a standing wave and the system works as an acoustic amplifier. The final signal amplification is determined by the total losses of the resonator. After an initial transient state, during which energy is accumulated in a standing acoustic wave, a steady state is reached in which the energy lost per cycle by various dissipation processes is equal to the energy gained per cycle by the absorption of photons. At resonance the amplitude is Q_n times larger than the amplitude far from the resonance frequency, i.e., the amplification is equal to the value of the Q factor. The physical definition of the Q factor is

$$Q = \frac{2\pi \text{ accumulated energy}}{\text{energy lost over one period}}. \quad (11)$$

For high Q values another definition is used:

$$Q = \frac{f_0}{\Delta f}, \quad (12)$$

where f_0 and Δf are the resonance frequency and the half-width value of the resonance profile. The half width is measured between the points where the amplitude is a $1/\sqrt{2}$ value of the peak amplitude (half-maximum values of the intensity). Therefore, Δf is also called the full width at half maximum (FWHM).

Equations (9) and (10) can be written in a more familiar form which takes into consideration that the deposited heat density is equal to the product of the absorption coefficient and light intensity. The intensity can be written⁴² as follows:

$$I(\mathbf{r}) = W_L g(\mathbf{r}),$$

where W_L denotes the light power and $g(\mathbf{r})$ is the normalized intensity distribution. Its integral over the entire cross section of the beam is normalized to unity. Now, the sound pressure amplitudes can be written as follows:

$$A_0 = \frac{(\sigma - 1) \alpha L W_L}{i\omega V_{\text{res}}}, \quad (13)$$

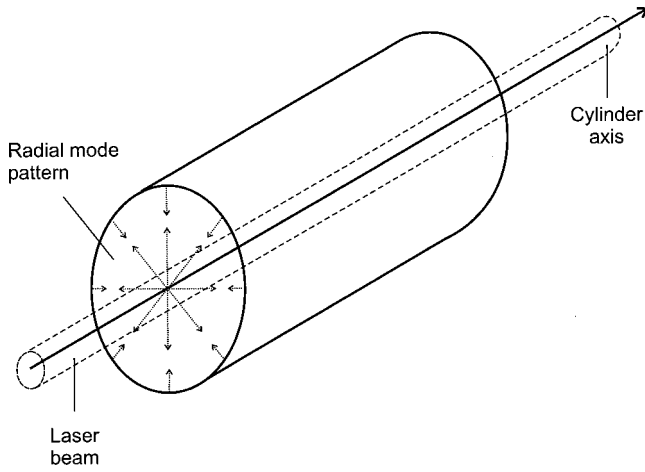


FIG. 4. Schematic of the spatial overlap of the cylindrical intensity distribution of the laser radiation propagating along the cylinder axis with the pressure distribution of the first radial mode. This configuration yields a large value of the corresponding overlap integral, and therefore efficient excitation.

$$A_n = \frac{i\omega}{\left(\omega_n^2 - \omega^2 + i\frac{\omega\omega_n}{Q_n}\right)} \frac{(\sigma-1)\alpha L W_L}{V_{\text{res}}} \frac{\frac{1}{L} \int g(\mathbf{r}) p_n(\mathbf{r}) dV}{\frac{1}{V_{\text{res}}} \int |p_n(\mathbf{r})|^2 dV}. \quad (14)$$

The amplitude of the oscillation (the PA signal) will be proportional to the absorption coefficient, the absorption length, and the light power, but inversely proportional to the modulation frequency and the cell volume. More precisely, the PA signal is inversely proportional to an effective cross section defined by V_{res}/L .

The last factor of Eq. (14), with the two integrals (in the following denoted by F_n), describes the effect of the spatial overlap between the propagating laser beam and the pressure distribution of the n th acoustic eigenmode of the resonator. The numerator, the so-called overlap integral, describes how effectively this n th eigenmode is excited by the spatial laser light distribution, while the denominator is a normalization factor of the n th eigenmode. Therefore, the dimensionless number F_n is called the “normalized overlap integral.” By proper choice of the light path the predominant excitation of a single resonance may be obtained, while the detection of unwanted resonances can be suppressed by making their overlap integrals zero. Figure 4 shows, as an example, the efficient excitation of a radial mode in a cylinder by the overlap of the cylindrical spatial intensity distribution of the laser beam propagating along the cylinder axis with the mode pattern of the first radial mode.

The measured PA signal depends also on the exact position of the microphone in the resonator. The signal detected by the microphone is proportional to the integral average of the pressure over the microphone membrane. Since mostly miniature microphones are applied in photoacoustics, the integral can be approximated by the value of the pressure amplitude at the microphone location. If the n th eigenmode is excited, and the microphone is located at the position $\mathbf{r}_M$, then the sound pressure at $\mathbf{r}_M$ can be written as

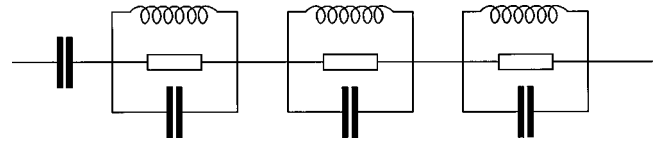


FIG. 5. Scheme of an electric network of serially connected parallel resonance circuits, where each acoustic eigenmode is modeled by a parallel resonance circuit and one capacitance which represents the nonresonant contribution to the acoustic signal.

$$p(\mathbf{r}_M, t) = \left[A_0 + \sum_n A_n p_n(\mathbf{r}_M) \right] e^{i\omega t}. \quad (15)$$

Substituting Eq. (14) into Eq. (15) enables the sound pressure as a function of the modulation frequency to be written as

$$p(\mathbf{r}_M, \omega) = \frac{(\sigma-1)L}{V_{\text{res}}} \left(\frac{1}{i\omega} + \sum_n \frac{i\omega F_n p_n(\mathbf{r}_M)}{\omega_n^2 - \omega^2 + i\frac{\omega\omega_n}{Q_n}} \right) \alpha W_L. \quad (16)$$

It can be seen from Eq. (16) that the suppression of unwanted resonance is possible also by placing the microphone in a node of this particular eigenmode. In this case the value of the corresponding eigenmode distribution function $p_n(\mathbf{r}_M)$ is zero.

Notice that the right-hand side of Eq. (16) can be written as the product of an acoustic impedance Z and a volume flow u :

$$p(\mathbf{r}_M, \omega) = Z(\mathbf{r}_M, \omega) u, \quad (17)$$

where

$$u = \frac{(\sigma-1)\alpha L W_L}{\rho c^2} \quad (18)$$

and

$$Z(\mathbf{r}_M, \omega) = \frac{\rho c^2}{i\omega V_{\text{res}}} + \sum_n \frac{i\omega \frac{\rho c^2 F_n p_n(\mathbf{r}_M)}{V_{\text{res}}}}{\omega_n^2 - \omega^2 + i\frac{\omega\omega_n}{Q_n}}, \quad (19)$$

which corresponds to an electric network of serially connected parallel resonance circuits and one capacitance as shown in Fig. 5. This means that each acoustic eigenmode can be modeled by a parallel resonance circuit, while the nonresonant part is represented by a capacitance. The PA source is described by a current source u , which does not depend on the frequency or the eigenmode distribution. It depends only on the quantity $\alpha L W_L$, which is the light power absorbed within the acoustic resonator.

The electric network described above can completely represent the properties of an acoustic cavity resonator. Such an electric network model has been used successfully for computer simulation of PA signal generation in cavity resonators.⁴³

B. Nonresonant cell and resonant cell, high- Q and low- Q resonators

In the photoacoustic literature the PA cells are often characterized as “nonresonant” or “resonant.” This terminology is misleading, because all PA cells can be operated at an acoustic resonance or far from their resonances. Thus, it is preferable to label the system according to the nonresonant or resonant mode of operation.

If the modulation frequency is much smaller than the lowest resonance frequency, the cell is operated in a nonresonant mode. In this case the sound wavelength is much larger than the cell dimensions, thus sound cannot propagate and standing waves cannot form. The average pressure in the cavity will oscillate with the modulation frequency. The photoacoustically generated pressure is given by the first term of the series presented in Eq. (6), thus the sound pressure is simply equal to A_0 in Eq. (6). Note that this term applies only for closed resonators, because in an open resonator the pressure change simply drives gas in or out until the equilibrium pressure is restored. If an open resonator is built into a closed PA cell, then the pressure generated by the PA effect will be distributed over the entire closed volume. Therefore, the total volume of the PA cell must be taken into account in Eq. (13), instead of the volume of the resonator.

For a small closed cell and low modulation frequencies the signal can be relatively large, as mentioned before. Unfortunately, the noise also increases with decreasing frequency and volume, which means that the SNR will usually decrease substantially. It should be noted that the PA signal has a 90° phase lag with respect to the light power.

For resonant operation the modulation frequency is tuned to one of the eigenresonances of the PA cell, i.e., $\omega = \omega_m$. As can be seen from Eq. (16) not only the m th but all eigenmodes of the acoustic resonator will be excited. The resonance amplitude is proportional to the Q factor Q_m , while the amplitudes of the other resonances are inversely proportional to the quantity $\omega_n^2 - \omega_m^2$. Therefore, distant resonances will not be excited as effectively. As was discussed previously, certain resonances can be suppressed since the overlap integral will be zero for special symmetry conditions, e.g., azimuthal modes cannot be excited if the cylindrical laser beam propagates exactly along the cylinder axis.

If the eigenresonances are well separated and the Q factor of the particular resonance to be used is large enough, the selected resonance can be excited much more effectively than the others. Therefore, the series expansion of the sound pressure in Eq. (6) can be approximated by one single term. In this “high- Q ” case the sound pressure amplitude $A(\mathbf{r}_M, \omega_n)$ of Eq. (16) is given by the resonance amplitude $A_n(\mathbf{r}_M, \omega_n)$ of the n th resonance by setting $\omega = \omega_n$ in Eq. (14):

$$A_n(\mathbf{r}_M, \omega_n) = \frac{(\sigma - 1)LF_n Q_n}{V_{\text{cell}} \omega_n} \alpha W_L. \quad (20)$$

If the Q factor of the selected resonance is not high enough, the contributions of the other resonances to the PA signal cannot be neglected, and the full expression of Eq. (16) has to be used (low- Q case):

$$p(\mathbf{r}_M, \omega_n) = \frac{(\sigma - 1)L}{V_{\text{res}}} \left(\frac{1}{i\omega_n} + \frac{F_n p_n(\mathbf{r}_M) Q_n}{\omega_n} + \sum_{j \neq n} \frac{i\omega_n F_j p_j(\mathbf{r}_M)}{\omega_j^2 - \omega_n^2 + i\frac{\omega_j \omega_n}{Q_j}} \right) \alpha W_L. \quad (21)$$

If $\omega_j/\omega_n > 1.2$ or $\omega_j \times \omega_n < 0.8$ and $Q_j > 20$, the imaginary parts in the denominators of the expression after the summation symbol can be neglected. In practical applications low-order eigenmodes are employed. Thus the ratio $\omega_j \times \omega_n$ will be larger than about 1.5, and therefore the ratio of the largest term behind the sum symbol to the second term, describing the selected resonance, will be smaller than $1/Q_j$. Since the other terms are much more separated, their contributions will be even smaller. For these reasons, $Q_j < 50$ may be regarded as a limit for the low- Q case.

Since the quantities in the prefactor to αW_L on the right-hand side of Eqs. (20) and (21) are independent of the light power and the absorption coefficient, these factors can be regarded as characteristic setup quantities for high- Q and low- Q PA resonators, respectively. Denoting this quantity by $C_n(\omega_n)$ the PA signal amplitude can be written as

$$A_n = C_n(\omega_n) \alpha W_L. \quad (22)$$

The quantity $C_n(\omega_n)$ describes the sensitivity of the PA resonator at a given resonance frequency. It is usually called the “cell constant” in the photoacoustic literature. The cell constant depends on the size of the resonator, the frequency, and the Q factor of the resonance selected for PA detection, however, it depends also on the spatial overlap of the laser beam and the standing acoustic wave pattern. Therefore, the name cell constant is misleading, because it characterizes the complete measurement arrangement (including the acoustic resonator with a selected resonance, microphone position, and laser beam profile with spatial location) rather than only the PA cell. Moreover, it depends on the frequency, and its value is different for the different eigenmodes. Therefore, it would be better to use the term “PA setup constant” instead of cell constant, despite the fact that the latter is already established in the literature. The setup constant of a high- Q acoustic resonator is a well-defined quantity [see Eq. (20)] that can be determined quite accurately by taking into account the geometrical dimensions, acoustic constants, beam parameters, and eigenmode distributions. On the other hand, the setup constant of a low- Q resonator is a complicated function of several eigenmodes [see Eq. (21)], and therefore it cannot be determined with sufficient accuracy by calculation. It has to be determined by photoacoustic calibration measurements using certified gas mixtures.

While in the overwhelming majority of photoacoustic papers excitation by modulated (periodic) radiation is applied it is interesting to consider also the response of an acoustic resonator to pulsed laser excitation.

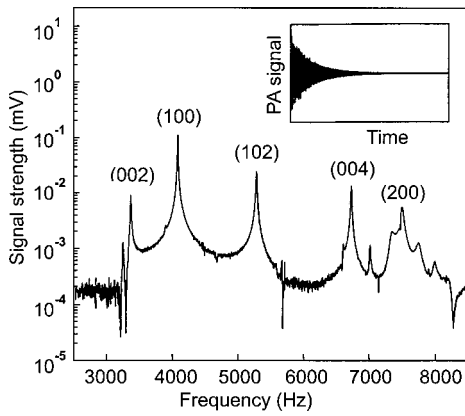


FIG. 6. Time dependent PA signal monitored with the microphone (inset) and the corresponding frequency spectrum of the cylindrical resonator showing the modes excited with a laser pulse.

C. Excitation of acoustic resonances with pulsed lasers

A resonator responds differently to pulsed and modulated disturbances. In pulsed excitation the absorption of photons ceases after the laser pulse terminates, but the relaxation processes will continue until full thermalization of the deposited energy is reached. Therefore, the heat pulse lasts somewhat longer than the light pulse. Nevertheless, the heat pulse may be regarded as a source of instantaneous acoustic excitation if the characteristic time of the acoustic processes under consideration is much longer. Since the acoustic response time is normally in the millisecond range (the lowest acoustic resonance of the PA cells used in practice is usually in the kilohertz range), while the pulse duration of most pulsed lasers employed is in the nanosecond range, the above condition is generally fulfilled. The short heat pulse acts as a broadband acoustic source, exciting all eigenmodes of the resonator simultaneously, similarly to a nonselective acoustic excitation process. The acoustic resonator responds to this sudden disturbance similarly to a ballistic pendulum or galvanometer reacting to a force or charge pulse: a sudden onset of acoustic oscillations is followed by a slow characteristic decay of their amplitudes. The amplitude of the very first oscillation period will be proportional to the released heat energy. Figure 6 shows an example of the excitation of cylindrical modes with a single laser pulse. The inset exhibits the decay of the photoacoustic signal measured in the time domain with the microphone. The corresponding frequency spectrum is obtained by Fourier transformation of the microphone signal and indicates the excitation of the longitudinal modes [(002) and (004)], the radial modes [(100) and (200)], and a combination mode (102) in the frequency range detected.

A short pulse excites a PA signal described by a series expansion of decaying sine functions having the following form:^{33,41}

$$p(t) = \sum_n A_n e^{-\beta_n t} \sin(\sqrt{\omega_n^2 - \beta_n^2} t) \\ = \sum_n A_n e^{-(\omega_n t / 2Q_n)} \sin\left(\sqrt{1 - \left(\frac{1}{2Q_n}\right)^2} \omega_n t\right). \quad (23)$$

For $Q > 5$ the term under the square root can be regarded as unity. The spectrum of the sum of the decaying sine functions is a sum of Lorentzian profiles:

$$p(\omega) = \sum_n \frac{A_n (\omega_n^2 / 4Q_n^2)}{(\omega - \omega_n)^2 + (\omega_n^2 / 4Q_n^2)}. \quad (24)$$

The amplitude A_n is given by

$$A_n = \frac{(\sigma - 1) L F_n P_n(\mathbf{r}_M)}{V_{\text{res}}} \alpha E_L, \quad (25)$$

where E_L denotes the laser pulse energy. This indicates that the amplitudes of the decaying sine functions do not depend on the Q factors of the resonances.^{33,41} The dependence on the location of the laser beam and the microphone position is the same as for the modulated case. When the frequency response of a resonator is measured by tuning the modulation frequency over a certain frequency range, a response given by Eq. (16) will be obtained. On the other hand, when the effect of a short pulse is analyzed by Fourier transformation of the time response a spectrum corresponding to Eq. (24) is found. Note that the frequency dependence of the resonance curve is different in these two cases. The properties of cylindrical resonators have been discussed in detail in previous papers^{33,41} and their application in pulsed photoacoustics was demonstrated in Ref. 44.

V. THEORETICAL DESCRIPTION OF ONE-DIMENSIONAL RESONATORS

A. General considerations

One-dimensional acoustic resonators can be described by two different methods. The first method is very similar to the treatment applied to cavity resonators earlier in Sec. IV A. In this case the eigensolutions of the lossless wave equation [see Eq. (5)] for the particular resonator have to be used in the series expansion of the sound pressure. That is, the $p_n(\mathbf{r})$ eigensolutions will be different for open–open, open–closed, and closed–closed pipes. The PA signal can be determined similarly, thus Eqs. (13) and (14) can be applied to calculate the sound pressure amplitude at the microphone position.

Although this method seems to be appropriate, it turns out that the basic assumptions of the method are not always justified for one-dimensional pipe resonators. For optimized cavity resonators the real solutions do not differ considerably from the eigensolutions of the lossless closed resonator. In this case the theoretical treatment of Sec. IV can be used. On the other hand, the frequency, Q factor, and mode shape of a pipe resonator depend strongly on the terminating impedances, which are functions of the sizes and shapes of the adjoining parts of the PA cell. Therefore, proper theoretical treatment should take into account the acoustic properties of the whole PA cell, not only those of the isolated resonator.

The second method is based on the formal analogy of the one-dimensional acoustic equations to the electromagnetic equations of a waveguide, such as a coaxial cable. The propagation of an acoustic wave in a pipe can then be described by a complex wave number, while the properties of the pipe are represented by a complex wave impedance. A

piece of pipe corresponds to an electric four-pole network, and arbitrary arrangements of pipes can be investigated by the well-known methods of electric network analysis and synthesis.

In the following, both methods will be described in more detail, and their advantages and disadvantages will be discussed.

B. Serial expansion of the PA signal for one-dimensional resonators

As mentioned already, the treatment described above can be applied to one-dimensional pipe resonators. The form of the eigensolutions in the ideal lossless case for a cylindrical pipe of length l can be given as follows:

open–open resonator:

$$p_n(x) = \sin\left(n\pi \frac{x + \Delta l_1}{l + \Delta l_1 + \Delta l_2}\right); \quad (26)$$

closed–closed resonator:

$$p_n(x) = \cos\left(n\pi \frac{x}{l}\right); \quad (27)$$

closed–open resonator:

$$p_{2m-1}(x) = \cos\left((2m-1)\frac{\pi}{2} \frac{x}{l + \Delta l_2}\right); \quad (28)$$

where $x=0$ and $x=l$ are the left and right ends of the pipe, respectively. The end corrections are denoted by Δl_1 and Δl_2 for the left and right open ends, respectively. The indices n and m are positive integers.

The PA signal generated by a laser beam propagating parallel to the axis of a pipe can be calculated by substituting the above eigensolutions into Eq. (14). If the light power is constant along the beam, i.e., the attenuation due to absorption is negligible (which is the usual case in trace gas detection), the overlap integral in the numerator of F_n will be proportional to the integral of the mode distribution $p_n(x)$ over the length of the pipe. The value of this integral can be given as follows for the three different cases:

open–open resonator:

$$\int_0^l p_n(x) dx = \frac{l + \Delta l_1 + \Delta l_2}{n\pi} \left[\cos\left(n\pi \frac{\Delta l_1}{l + \Delta l_1 + \Delta l_2}\right) - (-1)^n \cos\left(n\pi \frac{\Delta l_2}{l + \Delta l_1 + \Delta l_2}\right) \right]; \quad (29)$$

closed–closed resonator:

$$\int_0^l p_n(x) dx = 0; \quad (30)$$

closed–open resonator:

$$\int_0^l p_{2m-1}(x) dx = \frac{2(l + \Delta l_2)}{(2m-1)\pi} (-1)^m \times \cos\left((2m-1)\frac{\pi}{2} \frac{\Delta l_2}{l + \Delta l_2}\right). \quad (31)$$

The expressions show that under these conditions a PA signal cannot be excited in a closed–closed pipe, and only odd eigenmodes can be generated in a simple open pipe ($\Delta l_1 = \Delta l_2$). Moreover, the efficiency of excitation is inversely proportional to the eigenmode index n or $(2m-1)$. Therefore, in most cases the fundamental resonance of a pipe is used for photoacoustic detection.

Closed–closed pipes can also be employed, if the light path in the resonator is shorter than the length of the pipe. Let us assume that the light enters into the resonator at $x = x_1$ and leaves at $x = x_2$. In this case the overlap integral will be proportional to the following integral:

$$\int_{x_1}^{x_2} p_n(x) dx = \frac{l}{n\pi} \left[\sin\left(n\pi \frac{x_2}{l}\right) - (-1)^n \sin\left(n\pi \frac{x_1}{l}\right) \right]. \quad (32)$$

In the case of the ‘‘banana cell’’ described by Sigrist *et al.*⁴⁵ $n=2$, $x_1=l/4$, and $x_2=3l/4$, thus the absolute value of the integral is $1/\pi$, which is about half of the corresponding integral of an open–open pipe operating in the fundamental mode.

In practice, the resonant PA signal can be generated also in a closed pipe by a laser beam propagating along the axis of the pipe. However, this signal will no longer be proportional to the absorption coefficient. It may be excited either by background effects (for example, a window signal or PA signal caused by scattered light absorbed by the walls), or due to asymmetries of the acoustic properties of the resonator, or caused by attenuation of the radiation inside the resonator. In this last case the PA signal shows a quadratic dependence on the absorption coefficient.

C. Equivalent four-pole network of pipe resonators

The acoustic equations of a one-dimensional lossless system can be written as

$$\frac{\partial p}{\partial t} + \frac{\rho c^2}{S} \frac{\partial u}{\partial x} = 0, \quad (33)$$

$$\frac{\rho}{S} \frac{\partial u}{\partial t} + \frac{\partial p}{\partial x} = 0, \quad (34)$$

where S is the cross-sectional area of the pipe. These equations are very similar to the corresponding transmission line equations:

$$\frac{\partial U}{\partial t} + \frac{1}{C^*} \frac{\partial I}{\partial x} = 0, \quad (35)$$

$$L^* \frac{\partial I}{\partial t} + \frac{\partial U}{\partial x} = 0, \quad (36)$$

where L^* and C^* are the inductance and capacitance of unit length of the cable, respectively. Based on the similarity of the above pairs of equations sound propagation in pipes can be treated similarly to the propagation of electromagnetic waves in cables. The sound pressure p and volume velocity u correspond to the voltage U and current I , respectively. The acoustic inductance and capacitance of a pipe with unit length can be expressed as

$$L_{ac}^* = \frac{\rho}{S}, \quad C_{ac}^* = \frac{S}{\rho c^2}. \quad (37)$$

The wave impedance of the pipe can be defined the same as for electromagnetic waveguides:

$$Z_0 = \sqrt{\frac{L_{ac}^*}{C_{ac}^*}} = \frac{\rho c}{S}. \quad (38)$$

The solutions of the above equations are composed of a forward and a backward propagating wave:

$$p = (Ae^{-ikx} + Be^{ikx})e^{i\omega t}, \quad (39)$$

$$u = \frac{1}{Z_0}(Ae^{-ikx} - Be^{ikx})e^{i\omega t}, \quad (40)$$

where the wave number k is given as

$$k = \omega \sqrt{L_{ac}^* C_{ac}^*}. \quad (41)$$

The losses of the pipe can be taken into account by introducing loss terms into the above equations. In the case of electromagnetic waves the terms R^*I and G^*U are added to the first and second equations, respectively. These terms represent the ohmic resistance of unit length of the cable and the loss per unit length due to the conductance of the dielectric insulator of the cable. The wave number and the wave impedance will be complex, because $i\omega L^*$ and $i\omega C^*$ should be replaced by $i\omega L^* + R^*$ and $i\omega C^* + G^*$, respectively. Using a similar substitution in the acoustic equations the complex wave number and wave impedance can be expressed as

$$\gamma = \kappa + ik = \sqrt{(i\omega L_{ac}^* + R_{ac}^*)(i\omega C_{ac}^* + G_{ac}^*)}, \quad (42)$$

$$Z_0 = \sqrt{\frac{i\omega L_{ac}^* + R_{ac}^*}{i\omega C_{ac}^* + G_{ac}^*}}. \quad (43)$$

The dimensionless viscous and thermal loss factors can be written as follows:

$$\frac{R_{ac}^*}{\omega L_{ac}^*} = \frac{1}{r} \sqrt{\frac{2\nu}{\omega}}, \quad \frac{G_{ac}^*}{\omega C_{ac}^*} = (\sigma - 1) \frac{1}{r} \sqrt{\frac{2\mu}{\omega}}, \quad (44)$$

where ν , μ , and r are the kinematic viscosity and thermal diffusivity of the gas and the radius of the pipe, respectively.

Since other loss components may also be important, such as the volume losses in the pipe and the energy transferred to wall vibrations, the above expressions cannot determine the loss of the pipe accurately.

In the case of small losses their effect on the acoustic wave impedance can be neglected and the acoustic wave impedance can be approximated by the real quantity given in Eq. (38). In order to describe the attenuation of the acoustic wave during propagation the acoustic wave number, however, must be complex.

The relation between the input and output sound pressures and volume velocities for a pipe with uniform cross section can be represented by the impedance, admittance, and transfer (chain) matrices⁴⁶ as follows:

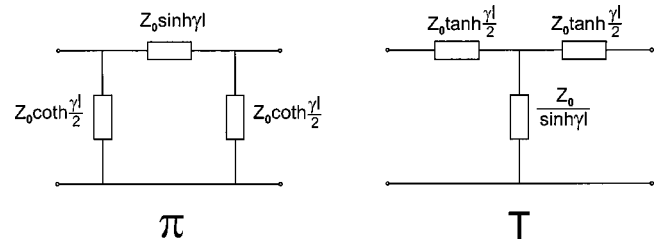


FIG. 7. Two equivalent electric circuits that can be used for a complete description of a pipe as an acoustic waveguide. The π network is better when the inputs of two or more pipes are connected in parallel, while the T-network representation is preferred for serially connected waveguides.

$$\begin{pmatrix} p_1 \\ p_2 \end{pmatrix} = \begin{pmatrix} Z_0 \coth \gamma l & \frac{Z_0}{\sinh \gamma l} \\ \frac{Z_0}{\sinh \gamma l} & Z_0 \coth \gamma l \end{pmatrix} \begin{pmatrix} u_1 \\ -u_2 \end{pmatrix}, \quad (45)$$

$$\begin{pmatrix} u_1 \\ -u_2 \end{pmatrix} = \begin{pmatrix} \frac{\coth \gamma l}{Z_0} & \frac{1}{Z_0 \sinh \gamma l} \\ \frac{1}{Z_0 \sinh \gamma l} & \frac{\coth \gamma l}{Z_0} \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \end{pmatrix}, \quad (46)$$

$$\begin{pmatrix} p_1 \\ u_1 \end{pmatrix} = \begin{pmatrix} \cosh \gamma l & Z_0 \sinh \gamma l \\ \frac{\sinh \gamma l}{Z_0} & \cosh \gamma l \end{pmatrix} \begin{pmatrix} p_2 \\ u_2 \end{pmatrix}, \quad (47)$$

where the indices 1 and 2 denote the input and output of the pipe, respectively. The direction of the volume flow was chosen in accordance with the convention of network theory, i.e., the impedance and admittance matrices are defined with flow directions into the pipe, while in the chain matrix the flow is directed inward at the input and outward at the output, allowing the connection of several four poles (pipes) in a chain. In this particular case, which is very important for practical applications, the chain matrix of the entire chain is given by the product of the chain matrices of the elements. On the other hand, impedance (admittance) matrices are preferred, if the inputs of two or more elements are connected in series (parallel).

The equivalent electric circuits (π and T networks) of a pipe with length l and cross section S can be seen in Fig. 7, where $Z_0 = \rho c / S$ is the wave impedance of the pipe. Both circuits can completely describe the pipe as an acoustic waveguide. The π network is preferred when the inputs of two or more pipes are connected in parallel, while a T network representation is better for serially connected waveguides.

If the acoustic four-pole network is terminated at the output by a load impedance Z_T , the remaining two pole can be represented by a single impedance, called input impedance. The input impedance of a pipe of length l terminated by Z_T can be determined from Eq. (47) as

$$Z_{in} = Z_0 \frac{Z_T \cosh \gamma l + Z_0 \sinh \gamma l}{Z_0 \cosh \gamma l + Z_T \sinh \gamma l}. \quad (48)$$

(Note that the input impedance of a pipe of arbitrary length terminated by Z_0 always equals Z_0 .) This expression is also

suitable for calculating the input impedance of a chain composed of pipes having different lengths and diameters. The input impedance of the last pipe should be calculated first, taking into account the terminating impedance at the end of this pipe. Then this value should be used as the terminating impedance to calculate the input impedance of the next to last pipe and so on. Thus, the input impedance of a chain containing an arbitrary number of pipe elements can be calculated by using a simple loop in a computer program. Similarly, the sound signal appearing at the output of the chain can be transformed into the input or vice versa.

The input impedances of an open ($Z_T=0$) and a closed ($Z_T=\infty$) pipe are given by $Z_{in}=Z_0 \tanh \gamma l$ and $Z_{in}=Z_0 \coth \gamma l$, respectively. Resonances occur when the value of the imaginary part of Z_{in} equals zero, i.e., at the roots of the functions $\tan kl$ and $\cot kl$, respectively. Since $k \equiv \omega/c$, the resonance frequencies for open and closed ends can be expressed as

$$f_n = n \frac{c}{2l}, \quad n=1,2,3,\dots, \quad (49)$$

$$f_{2m-1} = (2m-1) \frac{c}{4l}, \quad m=1,2,3,\dots$$

These expressions are similar to Eq. (3), but no end correction terms appear here.

According to Eq. (39) the sound field in the pipes is given as the sum of two counterpropagating plane waves. These waves can be regarded as an incident wave and a reflected one. The reflection coefficient can be defined as

$$R = \frac{Z_T - Z_0}{Z_T + Z_0}. \quad (50)$$

For an open end $Z_T \ll Z_0$, thus the reflection coefficient is $R \approx -1$, while for a closed end ($Z_T \gg Z_0$) the reflection coefficient is $R \approx +1$. This means that the sound pressure is reflected with the opposite phase from an open end and with the same phase from a closed end. The reflection coefficient at the boundary of two adjoining semi-infinite pipes can be written as

$$R = \frac{\frac{\rho c}{S_2} - \frac{\rho c}{S_1}}{\frac{\rho c}{S_2} + \frac{\rho c}{S_1}} = \frac{S_1 - S_2}{S_1 + S_2}, \quad (51)$$

which indicates that the sound is reflected by every sudden cross section change. If the acoustic resonator tube is placed between two wide cylinders (buffers), the sound field will be reflected back to the resonator very effectively.

Unfortunately, the one-dimensional model cannot describe three-dimensional effects, such as sound radiation by the pipe end into the buffer volume. Therefore, an end correction is not included in the distributed acoustic network model and resonance frequencies and reflection coefficients of the pipe cannot be determined accurately by this model. Better results can be obtained using the following correction impedance:³⁵

$$\Delta Z = \frac{\rho c}{S_{\text{opening}}} [\alpha(kr)^2 + i\beta(kr)], \quad (52)$$

where S_{opening} denotes the area of the actual opening at the pipe end (it may differ from the inner cross section S of the pipe), r is the equivalent radius of the pipe ($r=2 \times \text{volume/area}$ of the pipe wall for noncylindrical pipes), and $\alpha \approx 0.25$ and $\beta \approx 0.6$ are numerical parameters. Their values depend on the geometry of the pipe opening, but the values given above ensure sufficient accuracy in practical applications.

In this case the wave impedance $\rho c/S_2$ should be replaced by $\rho c/S_2 + \Delta Z$, or, more generally, ΔZ should be added to the terminating impedance Z_T . If S_2 increases, the impedance at the end of the pipe will approach ΔZ instead of zero.

Note that the one-dimensional model can be used only for frequencies below the cutoff frequency of the pipe, which is defined as the lowest transversal resonance frequency of the pipe. Its value for a pipe of radius r is defined by the expression³⁵

$$\frac{\omega_{\text{cutoff}}}{c} r = 1.84.$$

For a complex photoacoustic cell the equivalent radius of the buffer element with the largest cross section should be used to determine the cutoff frequency. One-dimensional modeling of the whole PA cell is possible only if the resonance frequency of the resonator is smaller than the cutoff frequency.

The main advantage of the application of the equivalent electric network is that PA signal generation can be quite easily included in the model. In this case a term describing the PA signal should be added to Eq. (33),

$$\frac{\partial p}{\partial t} + \frac{\rho c^2}{S} \frac{\partial u}{\partial x} = (\sigma - 1)H. \quad (53)$$

The PA signal in a pipe can be determined by solving Eqs. (34) and (53) simultaneously. This solution can then be used to determine the PA signal in a complex PA cell. The main steps of such a calculation can be explained with a model containing two pipe elements (pipe 1 and pipe 2) with different diameters. The goal is to determine the sound signal at the output of pipe 2. It is assumed that some kind of acoustic signal (e.g., external noise, window signal, etc.) is present in the input of pipe 1. This input signal (p_{11}) will be transformed to the output by the chain matrix of pipe 1. The next step is the calculation of the sound pressure (p_{12}) at the output of pipe 1 as the sum of two components, namely, the value of the solution of Eq. (53) at the output of pipe 1 and the transformed value of the input signal. Now p_{12} will be used as the input signal of pipe 2 and will be transformed to the output by the chain matrix of pipe 2. The resulting output pressure p_{22} will be obtained by adding the local value of the solution of Eq. (53) for pipe 2.

The above method can also be applied to determine the microphone signal in PA cells with complicated geometries. The calculation procedure should be started at the input(s) of the PA cell (window or gas inlet, or both) and should be

repeated until the microphone has arrived. The same procedure must be carried out for the other half of the PA cell, and both contributions should be added to obtain the PA signal at the microphone position.

It is beyond the scope of this review to give all details of such a calculation. In fact, it is more complicated than outlined above, because several sources (window absorption, external noise) and different losses have to be taken into consideration. However, the calculation can be easily performed on a PC. A PA signal calculation based on the electric circuit analogy was reported as early as 1990.¹⁰ Computer simulations of PA cells composed of pipe elements with different cross sections were introduced in 1992.⁴³

Although one-dimensional modeling of PA cells is very efficient and can be used for the analysis of complicated cell geometries, it is difficult to extract information on the sensitivity of different PA resonators, because the sensitivity cannot be expressed in closed analytical form. Therefore, the sensitivity of pipe resonators will be discussed and compared with other resonators by using the serial expansion model applied before to cavity resonators.

VI. SENSITIVITY OF RESONANT PHOTOACOUSTIC DETECTION

A. Setup constant

The PA amplitude generated in an acoustic resonator is given by Eqs. (13), (20), and (25) (the last applies to pulsed excitation). Although these expressions are valid in principle only for high- Q resonators, they may also be used to estimate the sensitivity of PA resonators with medium quality factors ($10 < Q < 50$). It turns out that the sound pressure is always proportional to the absorption coefficient α and the laser power W_L (or pulse energy E_L in pulsed photoacoustics), and it is inversely proportional to an effective cross section defined by the ratio V_{cell}/L . In the case of modulated PAS the signal is in addition inversely proportional to the modulation frequency and proportional to the Q factor of the resonance.

The sensitivity of a PA resonator to the pressure at the resonance frequency ω_n of the n th eigenmode can be represented by the setup constant $C_n(\omega_n)$ defined above:

$$C_n(\omega_n) = \frac{p(\omega_n)}{\alpha W_L} = \frac{(\sigma - 1) L F_n p_n(\mathbf{r}_M)}{V_{\text{cell}}} \frac{Q_n}{\omega_n}. \quad (54)$$

The units of C_n are given in Pa cm/W based on the usual dimensions of p , α , and W_L . When the spatial dimensions are specified in centimeters and the frequency in hertz, the setup constant (in units of Pa cm/W) can be calculated from the data of the resonator as follows:

$$C_n(\omega_n) \left[\frac{\text{Pa cm}}{\text{W}} \right] = 10^6 \frac{(\sigma - 1) L F_n p_n(\mathbf{r}_M)}{V_{\text{cell}} \Delta \omega_n}. \quad (55)$$

Here $\Delta \omega_n = \omega_n / Q_n$ is 2π times the half width (FWHM) of the resonance profile. Equation (55) clearly shows that the setup constant of an acoustic resonator depends critically on the effective resonator cross section and on the half width of the resonance. The values of F_n and $p_n(\mathbf{r}_M)$ are usually close to unity, and therefore the setup constant of a medium- Q

resonator with 1 cm² effective cross section and ~ 20 –50 Hz FWHM is expected to be in the 10³ Pa cm/W range, while a resonator optimized for high- Q performance (effective cross section ~ 80 cm², $Q \sim 1000$) has a setup constant of about 200 Pa cm/W.

The setup constant of the same eigenmode for pulsed excitation can be defined as

$$K_n = \frac{p}{\alpha E_L} = \frac{(\sigma - 1) L F_n p_n(\mathbf{r}_M)}{V_{\text{cell}}}. \quad (56)$$

The units of K_n are given in Pa cm/J. The setup constant of the same setup but for modulated excitation can be written as

$$C_n(\omega_n) = K_n \frac{Q_n}{\omega_n} = \frac{K_n}{\Delta \omega_n}. \quad (57)$$

The possibilities for improving the setup constant of acoustic resonators are limited. Let us consider Eq. (54) in more detail. The term $\sigma - 1$ depends only on the gas involved, which is normally air in trace gas measurements. Therefore, we find $\sigma - 1 = 0.4$. The factor F_n should be calculated for the specific arrangement, taking into account the location and intensity distribution of the laser beam and the mode pattern of the particular eigenmode selected for PA detection. This factor must be optimized, but the optimum values will be close to unity. The value of $p_n(\mathbf{r}_M)$ is unity, if the microphone is placed at the antinode of an eigenmode. This, of course, is not always possible, but a value in the range between 0.5 and 1 can usually be obtained. Thus, the only parameter that really can be changed in a larger range is the effective cross section of the cell. A reduction of the cell diameter will increase the setup constant. A lower limit is set by the diameter and divergence of the laser beam employed. The setup constant for modulated measurements is inversely proportional to the FWHM value of the resonance profile. Unfortunately, the half width cannot be reduced indefinitely, because it scales approximately with the surface-to-volume ratio of the resonator. As the cross section of the cell is reduced, the surface-to-volume ratio increases. Therefore, it is impossible to realize small cross sections and a small bandwidth (high Q) simultaneously. The smallest diameter used in practical PA systems is several millimeters, the largest about 10 cm.

If the eigenfrequencies and the acoustic eigenmode patterns can be calculated analytically, and the laser beam geometry is also known, K_n can be calculated fairly accurately. The determination of $C_n(\omega_n)$ requires the measurement of the FWHM of the acoustic resonance. This can be done by acoustic excitation. Thus, the setup constants of the frequently used acoustic resonator types can be determined without using calibrated gas mixtures and/or calibrated microphones for both pulsed and modulated excitation with this procedure.

Setup constants expressed in V cm/W units can be also found in the PA literature. In this case the setup constant C_n is multiplied by the responsivity of the microphone given in V/Pa units. However, this kind of setup constant, as a characteristic of the PA cell, can be used only if a calibrated microphone is available.

It can be stated that the PA resonators presently used by several research groups are close to optimal. Differences can be found; nevertheless, in the designs of the PA detectors and in the methods used for measuring the PA signal.

B. Noise

Noise plays an important role in all photoacoustic measurements and is of particular importance in the detection of ultralow gas concentrations, because the noise level limits the ultimate sensitivity. In the photoacoustic literature the detection level is usually defined by the SNR, where the noise is given by the microphone signal measured with the laser light blocked. However, when light hits the PA cell an additional background signal is generated which exists even when the absorbing species are not present in the detector. This background signal is often larger than the noise signal, and therefore the detection limit or sensitivity has to be defined by the signal-to-background ratio (SBR) in most experiments. Only the fluctuating part of the background should be considered in the SBR, because the constant part can be subtracted. Unfortunately, it is common practice to consider only the SNR. This procedure yields an extrapolated detection limit that may be considerably too small.

The noise level is determined by the microphone and the detection electronics employed. In addition external environmental noise sources may play an important role, for example, the laser used for excitation can disturb the photoacoustic measurement substantially.

The background signal is usually determined with a non-absorbing gas, such as nitrogen, in the PA detector. It is influenced by many system properties, such as the pointing stability, the divergence, and the diameter of the laser beam. Besides the quality of the laser source the construction of the PA cell is another important factor. For example, the cleanliness and optical absorption of the entrance and exit windows can dramatically influence the background signal. The diameter of a pipe resonator cannot be reduced too much, since it has to be selected according to the divergence of the laser beam to avoid scattering of laser light at the cell walls or even at the microphone. Impurities in the gas, which absorb the laser radiation, also make a contribution to the background signal. The background signal is expected to be much larger for pulsed laser excitation than for modulated operation.

Because of these dominating noise and background signals the ultimate theoretical noise limit, which is due to the pressure transducer and stems from the Brownian motion of the sample gas molecules, cannot be reached.

C. Loss mechanisms

The energy accumulation attainable in the standing wave of a resonant cavity is many times larger than the energy loss occurring during a single period of an acoustic oscillation. This acoustic amplification effect is limited, however, by various dissipation processes. The first detailed discussion of these dissipation effects observed in a closed cavity was given in Ref. 7. In order to compare theory and experiment the resonance frequency and half width were measured

and compared with model calculations. Good agreement was obtained for high quality spherical and cylindrical resonators.^{32,47}

The losses can be divided into surface effects and volumetric effects. The surface losses are due to the interaction of the standing wave with the internal resonator surface and may be subdivided into the following dissipation processes:

- (1) viscous and thermal dissipation inside the boundary layers at the smooth internal surfaces;
- (2) losses due to wave scattering at surface obstructions such as the gas inlet, microphone, and windows;
- (3) compliance of the chamber walls;
- (4) dissipation at the microphone diaphragm.

In a carefully designed high quality resonator, the contribution of the last three processes can be kept small. The main contribution is caused by the viscous and thermal boundary layer losses. Throughout the major portion of the resonator volume the expansion and contraction of the gas occur adiabatically. Near the walls, however, the process becomes isothermal. This leads to heat conduction within a transition region (thermal boundary layer), which is responsible for the thermal dissipation process. The viscous dissipation can be explained by the boundary conditions imposed by the walls. At the surface, the tangential component of the acoustic velocity is zero, whereas in the interior of the cavity, it is proportional to the gradient of the acoustic pressure. Thus, viscoelastic dissipation occurs in the transition region, which is called the viscous boundary layer.

In a spherical resonator no viscous surface losses appear for radial modes. This advantage and the favorable surface-to-volume ratio make the sphere a superior resonator compared to a cylinder. Very high Q factors (2000–10 000) can be achieved for carefully constructed spheres.^{48,49} Very good agreement with measured half widths of radial modes has been obtained by taking into account the thermal boundary losses and a small loss coming from free-space viscous and thermal dissipation. On the other hand, the description of laser excitation in a spherical resonator is more complicated than for one with cylindrical symmetry.⁴⁰

The volumetric or bulk losses are caused by processes that tend to establish equilibrium in the propagating wave.³⁵ These damping processes are

- (1) free space viscous and thermal losses,
- (2) relaxation effects,
- (3) diffusion effects,
- (4) radiation effects.

Friction due to compressional motion and transformation of organized energy into heat due to temperature gradients are responsible for the free-space viscous and thermal losses. These two processes are often called Stokes–Kirchhoff losses and play only a minor role compared to boundary layer losses. Diffusion effects are normally negligible, but molecular relaxation processes can make significant contributions in a limited pressure region which is given by the $p\tau$ value, where τ is the relaxation time. In this pressure region an accurate determination of the corresponding relaxation

time is possible from the resulting dispersion of the resonance frequency and the strong broadening of the acoustic resonance profile.⁵⁰

Radiation losses are negligible for completely closed cavity resonators because of the nearly perfect reflection of the sound at the walls. On the other hand, radiation losses through openings, for example, pipes connecting the resonator to buffer volumes, cannot be neglected. The radiation losses can be reduced by increasing the acoustic input impedance of the openings.³⁰ This is achieved by terminating the cavity resonator at the openings with acoustic band-stop filters, which prevent the sound from escaping from the resonator. In the case of one-dimensional acoustic resonators radiation is usually the dominating loss mechanism, which always has to be taken into account.

VII. OPTIMUM DESIGN OF RESONANT DETECTION SYSTEMS FOR TRACE GAS ANALYSIS

A. General requirements

In trace gas analysis usually small concentrations say below 100 ppm are detected. If it is assumed that absorption follows the Beer–Lambert law the light intensity decreases in the PA detector as $I = I_0 \exp(-\alpha x)$, where x is the optical path length. In the case of small absorption the fractional absorption in the detector is given as αL , where L is the length of the optical path within the detector. Taking into account typical values for the absorption coefficients of the species to be measured ($0.01\text{--}10\text{ cm}^{-1}$) and realistic diameters of the PA cells ($\sim 1\text{--}10\text{ cm}$), the fractional absorption is very small ($\sim 10^{-3}\text{--}10^{-7}$), which means less than 0.1% of the incident laser power. Often the windows of the PA detector and the adsorbates at their surfaces may absorb more light. Even the amount of light scattered by imperfections of the windows and by the inner walls of the detector because of low beam quality may exceed the amount absorbed by the species to be monitored. Therefore, a coherent background generated by window absorption and light scattering is always present in the PA detector. Effective suppression of this background is the most important requirement for a sensitive PA detector. As shown in Eqs. (13) and (14), the sound pressure generated by the modulated PA effect is proportional to the product of the absorption coefficient and the laser power. Since the power of the available laser sources is typically between 1 mW (diode lasers) and 1 W (CO_2 and CO lasers), the generated sound pressure is usually smaller than 1 Pa. In the case of NIR diode lasers, where overtones or combination bands are excited, the typical values are $10^{-3}\text{--}10^{-6}\text{ Pa}$. By considering that the average noise amplitude [root mean square (rms), broadband] in a laboratory corresponds to $10^{-3}\text{--}10^{-2}\text{ Pa}$, very good acoustic isolation of the PA cell is required.

The measurement of such small sound pressures requires high standards for the microphones such as high responsivity, low noise characteristics, and a small size (and for practical applications also a low price). Since the responsivity of condenser and electret microphones is about $10\text{--}100\text{ mV/Pa}$, PA signal levels in the nanovolt–microvolt range must be measured. Therefore, low noise microphones and micro-

phone preamplifiers are necessary and particular attention must be paid to the connections between the cell and preamplifier. Although high-quality condenser microphones offer the best noise performance, they are rarely used in photoacoustic gas detection because of their large size, lower robustness, and relatively high price. The most common microphones employed are miniature electret devices developed originally as hearing aids (for example, different types supplied by Knowles Electronics Inc. and Sennheiser GmbH).

The general requirements for PA detectors can be summarized as follows:

- (1) good background suppression;
- (2) good acoustic and vibrational isolation;
- (3) microphone with high responsivity;
- (4) low noise electronics;
- (5) good electronic isolation (no ground loops, proper shielding).

Since noise sources (intrinsic noise of the microphone, amplifier noise, external acoustic noise) have nearly a $1/f$ frequency dependence, low modulation frequencies should be avoided in PA trace detection. In order to minimize the noise, modulation frequencies in the $1\text{--}5\text{ kHz}$ frequency region are recommended. The signal loss due to the higher modulation frequency can be compensated for by using resonant cells with a reasonable Q factor.

PA detectors generally can be used for both modulated and pulsed excitation, but the requirements for optimal detection are different in the two cases. A comprehensive discussion of microphone selection criteria in conjunction with pulsed PAS can be found elsewhere.⁵¹

The sensitivity of the PA detector can be increased by employing a microphone array instead of one single microphone device. This configuration has been demonstrated as enhancing the detection sensitivity considerably.⁵²

B. Design principles of PA detectors

The main question to be answered before the most suitable design of a PA detector can be found is, *Which species have to be detected in which concentration range?* The next question is, *Which laser source is available to detect the given species in the given concentration region?*

To answer these questions laser sources and absorption bands of the species have to be selected. The product of the available laser power and the minimum measurable absorption coefficient can be used to represent the sensitivity of the PA detector. This quantity can be determined by using the value of the setup constant $C(\omega_n)$ given in Eq. (54):

$$\alpha_{\min} W_L = \frac{p_{\min}}{C(\omega_n)}, \quad (58)$$

where $p_{\min}$ is the minimum detectable PA signal. Assuming that the setup constant $C(\omega_n)$ of the resonator is already optimized, the easiest way to improve $\alpha_{\min}$ is to select a stronger laser line or a laser with higher power. If such a laser is not available, further improvement can be achieved only by pushing down the detection limit of the PA signal.

This can be done by using PA cells, microphones, and electronics designed for low noise performance and by applying more sophisticated data acquisition and evaluation techniques. The noise of the measurement can be reduced by using state-of-the-art (and therefore very expensive) lock-in amplifiers, and/or by using longer time averaging (the noise decreases with the square root of the averaging time), with the expense of longer measurement times. Effective noise reduction can be achieved also by analog/digital conversion synchronized to the modulation frequency.

The value of $p_{\min}$ can be determined by dividing the minimum detectable microphone signal $U_{\min}$ by the responsivity S_{mic} of the microphone. This means, the microphone responsivity must be known to estimate the absorption sensitivity of the PA detector. Therefore, it is recommended that one applies calibrated microphones for PA trace gas measurements. Then the PA sensitivity can be calculated as follows:

$$\alpha_{\min} W_L = \frac{U_{\min}}{C(\omega_n) S_{\text{mic}}} \quad (59)$$

The minimum detectable microphone signal $U_{\min}$ can be determined experimentally. Both, the background signal and the noise should be measured, and the larger one should be regarded as the detection limit at SNR=1 or SBR=1. A more realistic detection limit for gas detection can be defined as SNR=3 or SBR=3.

The value of $U_{\min}$ depends on several factors. In addition to the intrinsic noise of the microphone, preamplifier noise, gas flow noise, and acoustic and electronic noise from the environment, the background generated by the windows and scattered light may play an important role. The performance of the acoustic resonators applied in photoacoustics are almost optimal in many cases. On the other hand, however, noise and background levels of the PA detector could often be further decreased by proper detector design and sophisticated methods of data collection and processing. For example, the noise and background levels of a differential PA detector described previously¹⁷ are in the 100 nV–1 μ V range (for a 1 s time constant). These values can be reduced by an order of magnitude using state-of-the-art methods of measurement and data evaluation. If the average responsivity of 100 mV/Pa of the microphone is taken into account, the minimum detectable sound pressure $p_{\min}$ is about 10^{-5} – 10^{-7} Pa. With a setup constant of 1750 Pa cm/W the value of the minimum detectable absorption coefficient can be estimated as $\alpha_{\min} \approx 5 \times 10^{-9}$ – $5 \times 10^{-11}/W_L$. Assuming 10 mW modulated light power a minimum detectable absorption coefficient of $\alpha_{\min} \approx 5 \times 10^{-7}$ – 5×10^{-9} cm⁻¹ can be obtained. If fundamental vibration bands are excited (for example, of hydrocarbons in the 3 μ m range), sub-ppbV concentrations can be detected.

VIII. APPLICATION OF RESONATORS IN PHOTOACOUSTIC TRACE ANALYSIS

A. Complete photoacoustic gas detection system

The main parts of a complete photoacoustic system are shown schematically in Fig. 8. The laser radiation passes

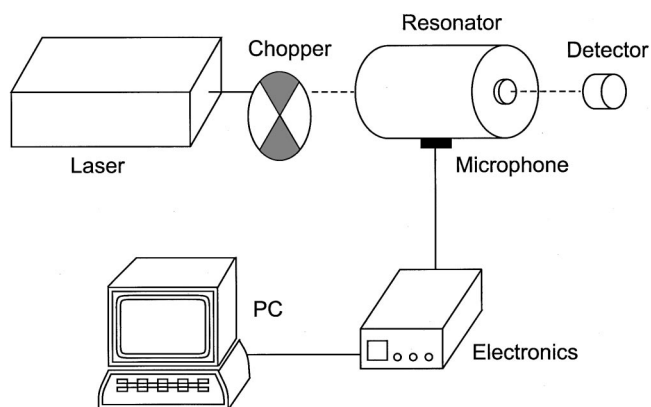


FIG. 8. Typical photoacoustic setup for modulated PA measurements. The cw laser radiation is chopped and transmitted through the cylindrical resonator to excite radial or longitudinal modes. The acoustic signal is measured with a microphone and processed by a lock-in amplifier and a PC.

through the PA cell and enters a power monitor. Continuous wave laser radiation is modulated by a mechanical chopper, an electro-optic device, or, as in the case of diode lasers, the diode current is modulated directly. Pulsed lasers can be used for broadband acoustic excitation. The excited sound waves are detected by an electret or condenser microphone with a responsivity in the 1–100 mV/Pa range. The microphone signal is measured by a lock-in amplifier or it is digitized and evaluated directly with a PC. In some cases a second, so-called “reference,” PA cell is used that contains a relatively high but known concentration of the gas component to be measured. The signal of this reference cell can be used for tuning the laser wavelength to the maximum of the absorption line. With this arrangement the effects of laser power fluctuations can be eliminated from the PA signal by measuring the ratio of the signals of the detection and reference cells.

The PA cell itself consists of windows, gas inlets and outlets, a microphone(s), and an acoustic resonator(s). Advanced PA cells also contain an acoustic filter to suppress the flow and window noise. Both high-Q and low-Q resonators can be applied. Since high-Q and low-Q resonators are used for quite different purposes, they will be treated separately.

B. High-Q resonators

Cavity resonators with cross-sectional dimensions in the range of several centimeters usually have high-Q eigenmodes. The value of the Q factor is normally around 100, but a value of $Q=1000$ has been reported⁴¹ for the first radial mode of a nearly perfect cylinder with carefully polished inner surfaces. As mentioned before, even higher Q factors can be realized with a spherical resonator (2000–10 000). Such devices have been used for acoustic precision measurements of the universal gas constant.^{48,49}

Since relaxation processes in the gas influence the acoustic losses and the sound velocity, the dispersion of the resonance frequency and the broadening of the half width of the resonance profile can be used for accurate measurements of vibrational and rotational relaxation times in the frequency domain.^{50,53} The same technique has been employed to study the chemical relaxation of systems such as $\text{N}_2\text{O}_4=2\text{NO}_2$,⁵⁴

the chemical relaxation of hydrogen bonds and the dynamics of hydrogen bond formation in dimeric formic acid,⁵⁵ and other aliphatic carboxylic acids⁵⁶ in the frequency domain.

High- Q acoustic resonators have also frequently been used for trace gas measurements. The first PA gas detectors investigated were simple cylinders equipped with windows and gas inlets and outlets. But windows attached directly to the cylinder surface produce a significant background signal. Therefore, more sophisticated PA detectors have been constructed recently. In these newer detectors the windows are separated from the resonator by pipes and/or buffer volumes (see Fig. 2). This solution was applied, for example, in the mobile CO₂ system.^{9,57}

Different configurations for laser excitation of cylindrical resonators have been applied in photoacoustic detection, for example, to excite the first (010) and second (020) azimuthal modes, the first radial mode (100), and the mixed radial-longitudinal (102) mode (see Fig. 3). Since the relatively large cylindrical cells have lower sensitivity, they were mostly used together with high-power gas lasers such as CO₂ lasers.

An open PA detector based on a cylindrical resonator combined with band-rejecting acoustic filters has been proposed.³⁰ Since the acoustic filters have excellent noise suppression around the selected resonance, the outside noise does not disturb the PA signal. This construction can also include windows,⁵⁸ because the background due to the windows can be efficiently eliminated by the filters.

A high Q factor can be achieved by keeping the losses of the resonant cavity low. All loss sources should be taken into consideration, including surface and volume losses, and losses through openings, microphones, and other sensors. Viscous and thermal losses at the walls can be decreased to some extent by using smooth well polished surfaces. Acoustic losses through openings can be minimized by using quarter-wavelength tubes to connect the resonator to external buffers.

In the case of very high Q factors ($Q > 500$) losses originating from the microphone can even influence the value of the Q factor.⁴¹ Therefore, miniature microphones with high acoustic impedance are strongly recommended for high- Q PA applications.

Unfortunately, high- Q resonators are very sensitive to temperature changes. Since the resonance frequency is proportional to the sound velocity [see Eq. (3)], the temperature dependence of the sound velocity is directly mirrored by the resonance frequency. The sound velocity of air has a temperature coefficient of about 0.18%/°C, thus a frequency shift $\delta f \approx 0.0018f_0 \times \Delta T$ is expected for a temperature change of ΔT °C. Therefore, a fixed modulation frequency may deviate by δf from the true resonance frequency. Then the PA signal will not be excited at the peak of the resonance, but slightly to one side. Since a detuning from the resonance peak by a quarter of the FWHM results in a $\sim 10\%$ drop of the PA signal, the detuning should be smaller than $f_0/4Q$ for $\pm 5\%$ signal stability. This stability can be ensured, if the condition $Q \times \Delta T \leq 138$ is fulfilled. The corresponding condition for PA signal stability of $\pm 1\%$ can be written as $Q \times \Delta T \leq 56$. These examples clearly show that

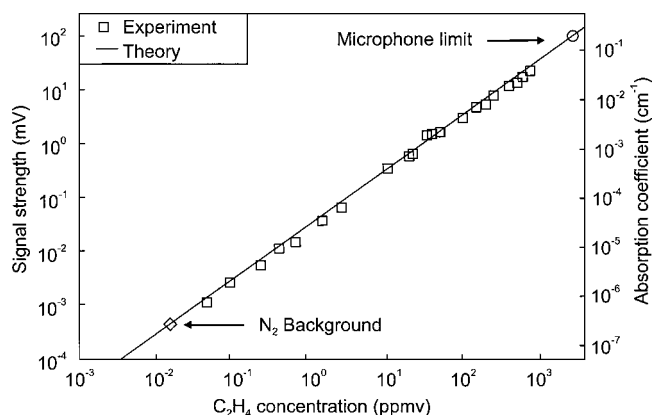


FIG. 9. Comparison of measured and calculated calibration curves. The open squares points give the PA signal strength observed for the 10P₁₄ line of the CO₂ laser and different C₂H₄ concentrations. The diamond marks the background signal in pure nitrogen and the open circles signal the maximum detectable signal. The line represents the calculated signal strength (calculation of the setup constant).

high- Q photoacoustic resonators are difficult to use in modulated photoacoustics without temperature stabilization or active tracking of the resonance to adjust the modulation frequency.

Several solutions to this problem have been reported. These include frequency scans of the modulation frequency over the acoustic resonance profile repeated at regular time intervals using PA^{18,57} or acoustic¹⁷ excitation. Monitoring the temperature and calculating the frequency shift by using the known temperature dependence of the sound velocity and setting the modulation frequency to the calculated new value at regular intervals are another possibility.¹⁰ Finally an active resonance tracking method based on an acoustic oscillator operating permanently on a higher eigenmode has been developed.⁵⁹ The last system also works well for sudden changes of temperature and/or gas composition.

The problem of the dependence of the resonance frequency on sound velocity can be elegantly circumvented by using broadband excitation with pulsed laser radiation. High- Q resonators are very well qualified for pulsed operation, because, as mentioned above, the light pulse excites a whole series of decaying sine signals. The Fourier spectrum of the time response is composed of several Lorentzian resonance curves, whose peaks correspond to the actual resonance frequencies, in agreement with the resonance spectra observed by point-by-point excitation in the frequency domain. Therefore, temperature shifts do not play a role in these pulsed measurements. It is also possible to design the resonator for a dominant mode by appropriate selection of the position of the laser beam and the location of the microphone at nodes of acoustic modes not to be detected. In the ideal case the PA signal is essentially a single decaying sine function which can be easily distinguished from noise and background signals.⁴¹

A high- Q resonator optimized for the detection of the first radial mode has been used for an absolute measurement of trace concentrations of ethylene.^{41,44} Since the PA signal did not depend on the Q factor of the resonance, the overlap integral K_n and the eigenmode distribution $p_n(\mathbf{r}_M)$ of Eq.

(56) could be calculated accurately from the dimensions of the resonator known with high accuracy. The calculation of the signal strength (setup constant) offers a new approach to determining absolute gas concentrations. The comparison of the measured PA signals of certified ethylene–nitrogen mixtures with the calculated values showed excellent agreement, as can be seen in Fig. 9. The calibration curve is obviously linear between the maximum signal detectable with the microphone used and the nitrogen background signal of 0.48 mV. It is also possible to determine the optical absorption coefficient of the absorbing species if the concentration is known, for example, by using a certified gas mixture.

In spite of these advantages, high- Q resonant PA detectors also have disadvantages if they are applied in trace gas analysis. The reasons for this are that their size is larger, their sensitivity lower, and their weight higher than that of the medium- and low- Q PA detectors.

C. Applications of medium- and low- Q resonators

Medium- and low- Q resonators are used frequently in PA detectors built for ultrasensitive trace gas monitoring. Mostly one-dimensional pipe resonators are applied with resonance frequencies in the 500 Hz–5 kHz region. The resonator itself is either a closed or an open pipe. Since an open pipe efficiently picks up and amplifies noise from the environment, it should be surrounded by an enclosure. In order to ensure high acoustic reflections at the pipe ends, a sudden change of the cross section is necessary. Therefore, the resonator pipe should open up into a larger volume or to buffers with a much larger cross section. Such “organ pipe” arrangements have found widespread use in photoacoustics.⁶⁰ The buffers can be optimized to minimize flow noise and/or window signals. An asymmetric buffer configuration has been tested and successfully applied for suppressing the window signals.⁴² More sophisticated PA detectors use adjoining acoustic filters for noise and background suppression;⁶¹ a true differential PA detector has been developed with two identical resonator pipes.¹⁷ This construction will be discussed in more detail below.

Due to their small size, medium- Q PA detectors are suitable also for intracavity operation. The best PA sensitivity, $\alpha_{\min} \approx 1.8 \times 10^{-10} \text{ cm}^{-1}$, reported to date has been achieved by an intracavity PA detector of organ pipe design. This value corresponds to 6 ppt V ethylene concentration in the given measurement setup.¹¹

PA detectors based on one-dimensional pipe resonators have been optimized for special purposes. A special “heat pipe” design has been used to investigate the PA signal of vapors originating from liquids with low volatility.⁶² Recently, a heatable PA detector has been applied for measuring pentachlorophenol (PCP) contamination of wood.⁶³ This detector was equipped with band-rejecting acoustic filters for additional noise suppression. The microphone was separated from the resonant cell by a 200 mm long thin stainless steel tube, thus allowing the PA cell to be heated up to 220 °C.

The operation of a multipass PA detector, based on an open acoustic resonator pipe, has been demonstrated recently.⁵⁷ The laser beam is reflected back and forth be-

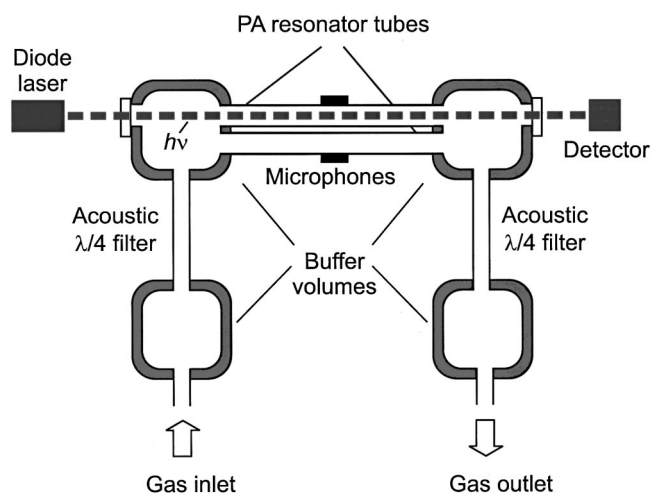


FIG. 10. Differential PA cell with two resonator tubes, buffer volumes, and $\lambda/4$ filters. Two resonant acoustic pipes (5.5 mm diam tubes) were placed between two acoustic filters. The two similar microphones were placed in the middle of each tube. The signal is amplified by a differential amplifier.

tween two mirrors placed outside the PA detector. The acoustic resonator of this detector was a broad pipe with a Q factor of $Q \approx 70$. In spite of the low sensitivity of the resonator itself, the overall sensitivity of the entire detector was $\alpha_{\min} \approx 2 \times 10^{-9} \text{ cm}^{-1}$ (corresponding to 70 ppt V ethylene concentration in the given measurement setup⁵⁷), due to the increased light absorption in the cell.

It should be mentioned that PA detectors can be used also at reduced pressures. Since the absorption coefficient increases (due to the decreasing pressure broadening effect) and the microphone responsivity and the Q factor of the acoustic resonance decrease, a sensitivity maximum can be found somewhere.⁶⁴ The exact pressure providing the maximum sensitivity depends on the properties of the microphone and on the excited molecular transition, thus no generally valid expression can be given for determining the maximum sensitivity. It should be mentioned that the above considerations are not valid for line tunable lasers. In that case the effective absorption coefficient may significantly decrease at reduced pressures because the overlap between the laser and absorption line may be degraded due to narrowing of the absorption line.

Open pipes were introduced for PA detection as early as 1977,²³ and the most sensitive PA detectors known today used are based on open resonant pipes.^{11,17} A closed pipe excited in its second resonance was introduced in 1987.⁴⁵ The banana cell (named after its shape) had two Brewster windows around the nodal points of the second longitudinal acoustic resonance. Similar cell construction was used recently for PA detection of aerosols.⁶⁵

D. Differential photoacoustic detector

The differential PA detector was specifically designed for fast time response, low acoustic and electric noise characteristics, and high sensitivity.¹⁷ In order to reduce the flow noise and external electromagnetic disturbances a fully symmetrical design was developed. Two acoustic resonators (5.5 mm diam tubes) were placed between two band-stop

acoustic filters as shown in Fig. 10. The gas flow passes through both tubes, producing about the same flow noise in both resonators. However, the laser light irradiates only one of them, thus the PA signal is generated in only one tube. Two microphones (Knowles EK 3029) are placed at the middle of each tube flush with the wall and their signal is amplified by a differential amplifier. The microphones have a so-called “ski-slope” frequency characteristic, with responsivity decreasing rapidly below 2 kHz. Thus, they are not sensitive to the dominant low-frequency part of the environmental noise. The selected pair of microphones has the same responsivity around the acoustic resonance frequency of the tubes of 4 kHz. Thus all noise components that are coherent in the two tubes are effectively suppressed. The microphones are isolated from the housing of the detector, which is connected electrically to the chassis of the amplifier through the screening of the cable. Three wires, including the common signal ground, connect the microphones to the amplifier. Thus, ground loops are completely avoided. Figure 10 presents a schematic of this optimized differential cell.

In order to keep the flow noise at a sufficiently low level, the flow must be in the laminar regime. Another practical requirement is the time response, which is determined by the exchange rate of the gas sample in the resonant cell. In addition, a delay occurs because the gas flows from the inlet to the resonant cell first through the acoustic filter. In the continuous flow mode a response time of <1 s and a delay of <10 s are possible. Taking into account the largest dimension and the limiting value of the Reynolds number ($Re \leq 2300$ for laminar flow) the flow velocity should not exceed 1.7 m/s. This value is far too large, since it would give a flow rate of about 4.8 l/min (large gas consumption). As an operating value a flow rate of up to 0.5 l/min has been used. With this value the maximum flow velocity was about 15 cm/s, the Reynolds number $Re < 200$, and the calculated response time $\tau < 0.7$ s. The response time determined from the rise time of the PA signal is larger because of mixing of the gas in the buffer volumes of the cell. Nevertheless, the measured response times are below 10 s for nonadsorbing gases. Adsorption at the walls of the PA cell may increase the response time significantly. The crucial problem of adsorption effects in photoacoustic detection is discussed in detail elsewhere.^{66–68} Note that the adsorption effect can be effectively reduced by using appropriate wall materials and elevated wall temperatures.⁶⁸

The photoacoustic sensitivity of the differential cell is about $\alpha_{\min} W_L = 1.0 \times 10^{-9} \text{ W cm}^{-1}$. The actual sensitivity depends on the instrumentation applied and the data evaluation method. The above value is the lower limit of the PA sensitivities of the differential cell obtained in measurements with methane, ethylene, and ammonia using a CO₂ laser, diode lasers, and an external cavity diode laser system. The sensitivity of the PA cell applied in the intracavity measurement in Ref. 11 was $\alpha_{\min} W_L = 1.8 \times 10^{-8} \text{ W cm}^{-1}$, much lower than that of the differential cell. Thus, the parts-per-trillion concentration sensitivity reported for ethylene was achieved mainly by the high intracavity power and the strong absorption of ethylene and not by an extremely sensitive cell. It is worth mentioning that the dynamic range of the PA

method is considerably reduced by intracavity operation. Optical saturation may occur for molecules with high absorption cross section¹¹ while uncontrollable signal changes may be obtained at higher overall absorption in the PA cell, because the loss of light intensity influences the gain of the laser. This effect may cause erroneous results when the sample concentration changes are large. Therefore, high sensitivity single- and multipass extracavity PA detectors offer a simpler alternative to intracavity devices.

E. Novel tunable light sources

While a state-of-the-art photoacoustic detector with an electret microphone and suitable electronics is relatively cheap, high power laser sources, such as CO₂ lasers, currently needed to reach the sub-ppb V range, make the setup too expensive and bulky for many practical applications. The more versatile single mode distributed feedback (DFB) or tunable ECDL diode lasers have, unfortunately, the disadvantage of low power and narrow spectral range, and the restriction that room temperature diodes emit in the NIR only. Thus, the availability of suitable laser sources plays a fundamental role for the further development of the field. They control the sensitivity (laser power), the selectivity (tuning range), and the practicability (ease of use, size, cost, and reliability) that can be achieved with the photoacoustic technique.

Compared to the previous situation in which the species to be detected were selected according to accidental coincidence of their resonances with available laser lines, the situation is changing gradually to the point where the species to be detected can be chosen according to scientific or practical interest and a suitable laser source with enough power and beam quality can be found for sensitive detection. Tunable solid-state laser devices especially may soon contribute to further development of the field. Since the power and tuning range of the currently available diode-laser sources, which are tunable in the fundamental IR spectral region (quantum cascade laser), are still limited, it is very important to choose the optimal design for the PA detector to reach state-of-the-art performance. The recent realization and further improvement of PPLN-OPO devices may provide an opportunity to realize widely tunable pulsed and modulated infrared radiation with high pulse energy or power. These devices will be more expensive but may find a niche, where high performance is needed.

ACKNOWLEDGMENTS

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