Resonance-enhanced low-pressure optoacoustic cell

M. Hartemink and H. P. Godfried

Nederlands Centrum voor Laser Research B.V., Postbus 2662, 7500 CR Enschede, The Netherlands

(Received 3 January 1992; accepted for publication 12 March 1992)

A low-pressure optoacoustic cell is described that can be used to lock the emission frequency of a laser. A model is developed which describes the low-pressure behavior of the optoacoustic cell as a function of cell dimensions, gas properties, and operating pressure. Resonant optoacoustic cells are predicted to improve the acoustic signal levels significantly. Experiments were carried out with a cell filled with CF_4 . The model was found to accurately predict resonator quality, resonance frequency, and acoustic response for pressures ranging from 0.1 to 3.0 kPa. At these low pressures acoustic attenuation processes, slow vibration to translation (VT) relaxation and diffusion to the cell wall strongly influence the acoustic behavior of the cell. Using the relaxation time of the ν_4 vibrational mode of CF_4 as a fitting parameter its value was determined to be three times slower than VT relaxation from the ν_2 level. The experimental values for the response were predicted by the model with an error of less than 10% in the whole pressure range. Predictions for the optoacoustic signal for different resonator dimensions were also confirmed. Model predictions for the optoacoustic signal for mixtures of gases and the influence of the temperature are also given. Especially the option of cooling the gas seems to be attractive for the case of CF_4 .

I. INTRODUCTION

The optoacoustic effect is the conversion of light energy into pressure waves by absorption in a medium. The effect can be simply obtained by chopping the incident radiation, producing heat and pressure waves at the chopping frequency. The pressure wave, the amplitude of which is proportional to the absorption, can be measured by a sensitive microphone inserted in the absorption cell in which the wave is generated. The optoacoustic cell geometry ensures that the acoustics are well defined. The cell shields the microphone from the surroundings and it allows regulation of the cell contents. Although calorimetric measurements of inorganic and biological materials have also been reported¹ optoacoustic cells were mainly investigated because of their importance for high sensitivity pollution monitoring.²⁻⁵ Initially blackbody infrared sources were used but these were soon superseded by infrared lasers because of their high spectral brightness. Unlike the main constituents of air (N_2, O_2) a great many air pollutants have absorption features in the infrared. To increase the sensitivity cells were sometimes designed acting as an acoustic resonator, leading to detection levels much better than 1 ppb for a variety of gases. At the same time the theoretical description of acoustic behavior as outlined by Morse and Ingard⁶ was further developed, and applied successfully to predict the performance of optoacoustic cells at atmospheric pressure.^{1,2,4,7,8}

Optoacoustic cells have also been used for frequency locking of laser emission frequencies to the absorption lines in many gases.⁹⁻¹¹ This application is particularly important in optically pumped gas lasers when frequency selectivity or output stability requirements are high (e.g., optically pumped CH_3OH FIR lasers for electron density measurements in fusion devices⁹). Contrary to the experiments for detection of air pollution where the absorption lines are pressure broadened and the insensitivity to a shift

in laser frequency is seen as an advantage, the optoacoustic cell has now to be operated at low pressures where line widths are much smaller to allow frequency stabilization to absorption line center. A consequence of low-pressure operation is the reduced signal strength. Consequently the experimenter usually makes a trade-off between signal strength and absorption line width. At these low pressures the theoretical description of the acoustic behavior of the cell is altered, compared to the atmospheric behavior of the optoacoustic cell. Although some low-pressure experiments have been reported^{12,13} we feel that the experimental conditions in the measurements were not well defined, e.g., acoustic coupling to the surrounding containers could not be neglected. Moreover, no attempt was made to compare the experimental results with some theory, so that the results cannot be transferred to other cells of different design or when using different gases. For spectroscopic measurements where line broadening needed to be eliminated, experiments were done at low pressures by Olafsson.¹⁴ Approximate expressions were given for the quality factors in this low-pressure regime. However no model was given to predict the performance of such a resonator as a function of pressure. In this article we develop a model for the optoacoustic cell, incorporating corrections for low gas pressures. Results from this model and a simple analytical model which does not incorporate the low-pressure corrections were compared with measurements on a longitudinal optoacoustic cell. The excellent quantitative agreement between the model calculations and measurements allows us to optimize the response of the optoacoustic cell and thereby improve the emission frequency locking stability.

II. EXPERIMENTAL SETUP

The design of the optoacoustic cell is shown in Fig. 1. The cell is made up of a cylindrical resonator tube which is in open connection with two buffer volumes of much larger

FIG. 1. Optoacoustic cell cross section.

diameter. The threaded ends of the resonator tube are screwed in circular disks fitted with O rings along the perimeter, pinning the resonator firmly in the cylindrical cell. Similar disks are used to hold the 1-in.-diam, AR-coated ZnSe windows of the cell, sealing each end of the cell. Buffer rings serve as spacers between windows and the resonator tube. Gas is fed into the cell through an entrance chamber which is connected to the buffer volumes and the resonator volume by two holes of 6-mm diameter in the disks holding the resonator. In the center of the cell a cover flange is fitted to allow replacement of resonator tube or microphone.

The inner wall of the brass resonator tube was polished to reduce acoustic losses. Half way the length of the tube a small hole of 1.5-mm diameter was drilled for the microphone. The microphone was glued in a brass holder which fits a counter piece fixed on the resonator tube. In this way the rigidity of the microphone connection to the tube was improved. Leaks around the tightly fitted microphone were further reduced by applying silicone rubber between holder and counter piece. For all measurements we used buffer volumes with a length of 85 mm and a resonator tube of 10-mm diameter and 170-mm length unless indicated otherwise.

A schematic of the experimental setup is shown in Fig. 2. The 4-W cw CO₂ laser was tuned to the 9R(12) line and was locked to the $R^+(29)A_1^+ + E^0 + F_1^{14}$ absorption feature of the CF₄ gas using a second optoacoustic cell, a configuration described in more detail in Ref. 15. The output beam was amplitude modulated by a variable chopper with a frequency range of 10–1800 Hz. The chopped beam was passed through the optoacoustic cell and the pump power was measured behind the exit window by a power meter. The signal of the Knowles EK-3024 microphone was monitored on the oscilloscope and fed into a lock-in amplifier referenced to the chopper frequency. Varying the chopper frequency the response of the cell could be measured at different CF₄ gas pressures. CF₄ pressure in the cell was monitored with a Barocell with a resolution of 0.2 Pa.

Alternatively a TEA CO₂ laser could be used, tuned to the 9R(12) line and kept in the single-frequency fundamental mode by an intracavity cw section and the use of intracavity diaphragms. With this configuration we were

FIG. 2. Experimental setup. Radiation from either a cw CO₂ laser or a hybrid TEA CO₂ laser can be injected into the optoacoustic cell.

able to determine the impulse response of the optoacoustic cell.

Since the optoacoustic cell could not be cooled down, an indication of the temperature effects was obtained in experiments with another CF₄ gas cell. The 2.78-m-long cell which could be cooled down, with a cold section of 2.10 m, was used as a “nonresonant” optoacoustic cell with the microphone situated in the gas inlet which is kept at room temperature.

III. THEORY

A. Simple model

The optoacoustic cell can be seen as a wide tube with a constriction in the form of the smaller diameter resonator tube. If the wavelength of the acoustic wave is much larger than the dimensions of the cross section of the tube its acoustic behavior can be represented by an electric equivalent model.^{4,6,16} This is discussed in the next section. If we consider the system as a Helmholtz resonator a simple expression follows for the pressure response p at the resonance frequency f_0 .⁴ We assume that a laser beam of power W_L is partly absorbed by the gas with absorption coefficient α (per unit length) but that the length l' of the resonator is such that $\alpha l' \ll 1$, resulting in uniform power deposition in the cell. The pressure response p can then be written as

$$p = F(f_0) \alpha W_L \quad (1)$$

where F is a cell constant which only depends on the gas properties and resonator dimensions. The cell constant can be expressed in terms of resonator tube volume and length, V and l , specific heat ratio γ and resonator quality Q .⁴

$$F(f_0) = \frac{(\gamma - 1) l Q G}{j 2 \pi f_0 V} \quad (2)$$

The factor G is a geometrical factor which is of order 1. The quality Q is the ratio of the energy stored in the acoustic wave and the resonator energy losses per cycle. The resonance frequency f_0 is approximately given by

$f_0 = (v/2l)$ with v the speed of sound. If we denote the resonator tube cross section by S and the inner radius of the resonator tube by r , the resonator quality factor for the limiting case when $d_v, d_h \ll r$ is given by [see Eq. (14b)]

$$Q = \frac{2S}{2\pi[d_v + (\gamma - 1)d_h]}. \quad (3)$$

The quantities

$$d_v = \left(\frac{2\eta}{\rho\omega} \right)^{1/2}, \quad (4a)$$

$$d_h = \left(\frac{2\kappa}{\rho\omega C_p} \right)^{1/2}, \quad (4b)$$

are the thicknesses of the viscous boundary layer and the thermal boundary layer, respectively. In the expression for d_v we find the viscosity η , the gas density ρ , and the chopper angular frequency $\omega = 2\pi f$. In the formula for d_h the thermal conductivity κ and the specific heat at constant pressure C_p appear. The thermal boundary layer is the region in the acoustic resonator where the expansion of the gas is no longer adiabatic but will be approximately isothermal due to heat conduction to the cell walls resulting in thermal losses. We assume that the heat capacity of the wall is much larger than that of the gas. In the viscous boundary layer the tangent gas velocity drops to zero, causing losses in a layer of thickness d_v . The quality factor is thus seen to be proportional to the ratio of the tube cross section to that of the annulus in which the acoustic losses occur.

For a quantitative analysis of the optoacoustic cell response we use a one-dimensional transmission line theory. Using this analysis a value for the geometric factor G can be derived but also corrections can be introduced to the quality factor, [Eq. (3)] for a more accurate description of the gas behavior for pressures below 1 kPa, where d_v, d_h are no longer $\ll r$.

B. Optoacoustic signal generation by infrared absorption

Heat deposition in a gas can induce temperature and pressure changes, leading to the formation of acoustic waves. The pressure changes are caused by the conversion of the absorbed energy, stored in the form of vibrational motion, in translational motion. If other relaxation processes as diffusion and radiative decay by spontaneous emission are much slower than the vibrational to translation relaxation all the absorbed energy will be converted into heat. Assuming that there are no viscosity losses or heat conduction losses, Morse⁶ derives the following differential equation for the pressure change p in the presence of a heat source H per unit volume per unit time

$$\nabla^2 p - \frac{1}{v^2} \frac{\partial^2 p}{\partial t^2} = -\frac{(\gamma - 1)}{v^2} \frac{\partial H}{\partial t}. \quad (5)$$

If all the absorbed power is converted into heat we can write down an expression for the power deposition per unit length. For a laser beam modulated at angular frequency ω we find

$$H(r, t) = \frac{W_L \alpha e^{j\omega t}}{S}, \quad (6)$$

where W_L is the power of the laser and α the absorption coefficient per unit length. With the assumption that the heat deposition is uniform over the whole volume resulting in a uniform pressure in the tube, a simple solution for the pressure changes generated is then

$$p(t) = \frac{(\gamma - 1) W_L \alpha e^{j\omega t}}{j\omega S}. \quad (7)$$

To describe the transmission of an acoustic wave through a tube we have to account for the losses at the boundaries and in the gas itself. The basic theory of such a description can be found in Ref. 6 and was extended by Bernegger and Sigrist⁴ to include a matrix formalism. First we will write down the equations describing the acoustic behavior to show the analogy with the electric transmission line, then we will include the matrix formalism which allows us to calculate the optoacoustic signal at any position in the cell at an arbitrary frequency.

C. Acoustic transmission line

To include the losses for the acoustic wave in a tube, we will turn to the first-order equation of motion for a plane acoustic wave, in terms of the pressure change p and fluid velocity u :⁶

$$\frac{\partial p}{\partial x} = -\rho \frac{\partial u}{\partial t}, \quad (8a)$$

$$\kappa \frac{\partial p}{\partial t} = -\frac{\partial u}{\partial x}, \quad (8b)$$

where κ is the adiabatic compressibility of the gas $\kappa = 1/\rho v^2$. These equations are equivalent to differential equation [Eq. (5)] in the absence of a heat source, as can be seen by taking the gradient with respect to x of Eq. (8a) and the time derivative of Eq. (8b).

To describe the acoustic wave propagation in a tube of small cross section we assume that the heat conduction and viscosity losses in the gas itself are small. The expressions for acoustic losses in the gas itself can be derived by applying the Navier-Stokes equation that describe a viscous compressible fluid and continuity equations for the mass and heat flows. For CF_4 even at pressures as low as 100 Pa the total losses are less than 1%/m and depend inversely on the pressure.^{6,14} On the other hand the constraints imposed on the acoustic waves by the boundary conditions are such that thermal losses $\mathcal{L}_h$ and viscosity losses $\mathcal{L}_v$ occur in boundary layers near the wall.⁶ They are given by

$$\mathcal{L}_v = \frac{1}{2} \rho \omega d_v D |u|^2, \quad (9a)$$

$$\mathcal{L}_h = \frac{(\gamma - 1) \omega}{2 \rho v^2} d_h D |p|^2, \quad (9b)$$

TABLE I. Circuit elements for the acoustic transmission line.

Simple expression	Benade correction factor (Ref. 17)	
$L_a = \frac{\rho}{S}$	$1 + \frac{d_v}{r}$	
$C_a = \frac{S}{\rho v^2}$	$1 + (\gamma - 1) \frac{d_h}{r}$	
$G_a = \frac{(\gamma - 1)\omega d_h D}{2\rho v^2}$	$f_G(r_v)^a$	$\left(r_v = \frac{\sqrt{2}r}{d_v}\right)$
$R_a = \frac{\rho\omega d_v D}{2S^2}$	$f_R(r_h)^a$	$\left(r_h = \frac{\sqrt{2}r}{d_h}\right)$

^aThe factors f_G and f_R can be found in Table II as a function of parameter r_v and r_h respectively.

with $D = 2\pi r$ the perimeter of the resonator tube.

The presence of the walls of the tubes necessitates a modification of Eq. (8a) for the pressure gradient. We have to add a term on the right-hand side to account for the acoustic resistance per unit length caused by the viscosity, obstructing fluid movement and causing pressure to build up. Using the time dependence for u , following from Eq. (7), Eq. (8a) is modified to

$$\frac{\partial p}{\partial x} = - \left(j\omega \frac{\rho}{S} + \frac{\rho\omega d_v D}{2S^2} \right) Su. \quad (10)$$

Next we consider the fluid velocity gradient along the tube. We take into account the thermal losses in the boundary layer and the generation of heat by the infrared absorption. Writing the latter as a source I_0 per unit length and using the time dependence for p [Eq. (7)] we rewrite this as

$$\frac{\partial(Su)}{\partial x} = - \left(\frac{j\omega S}{\rho v^2} + \frac{(\gamma - 1)\omega d_h D}{2\rho v^2} \right) p + I_0. \quad (11)$$

The explicit form for the source $I_0 = (Su)'_0$ can be found by combining the expression for the heat-induced pressure changes [Eq. (7)] and corresponding fluid velocity [Eq. (8b)].

$$\left(\frac{\partial(Su)}{\partial x} \right)_0 = (Su)'_0 = I_0 = \frac{(\gamma - 1)W_L \alpha e^{j\omega t}}{\rho v^2}. \quad (12)$$

The formal equivalence with electric transmission line theory was shown in Ref. 6. If the tube has cross-sectional area S , the total volume flux of the fluid Su can be seen as the analog of electric current I and the pressure p as the analog of the voltage U . We get expressions for the acoustic inductance L_a , acoustic capacitance C_a , the impedance R_a , caused by the viscosity losses, and the admittance G_a caused by heat conduction to the wall (see also Ref. 17). All quantities are expressed per unit length and listed in Table I.

If the acoustic wave is attenuated by other additional processes these can also be included in the model through an extra acoustic resistance R_s in series with the resistance R_a in the transmission line model. We assume that the attenuation is described by an absorption coefficient α per

FIG. 3. Transmission line with characteristic impedances and current (heat) source I_0 per unit length.

unit length for the acoustic power P_a . The appropriate expression for the acoustic resistance R_s is

$$R_s = \frac{\rho v}{S} \alpha. \quad (13)$$

Writing $R_a = R_v + R_s$ we find for the quality factor Q , the ratio of energy stored in the acoustic wave and the average power dissipated in each period

$$\frac{1}{Q} = \frac{\frac{1}{2}R_a |Su|^2 + \frac{1}{2}G_a |P|^2}{\frac{1}{2}\omega L_a |Su|^2 + \frac{1}{2}\omega C_a |P|^2}. \quad (14a)$$

If only viscosity and heat losses are present, this reduces to

$$Q = \frac{2S}{D[d_v + (\gamma - 1)d_h]}. \quad (14b)$$

If we substitute the expressions for the acoustic circuit elements (Table I) into Eqs. (10), (11) and also include other loss mechanisms described by the series resistance R_s , we find

$$\frac{\partial p}{\partial x} = - (j\omega L_a + R_a) Su, \quad (15a)$$

$$\frac{\partial(Su)}{\partial x} = - (j\omega C_a + G_a) p + I_0. \quad (15b)$$

We will now consider the one-dimensional electric transmission line shown in Fig. 3. The voltage $U(x)$ and current $I(x)$ are functions of the position x and the relevant differential equations are

$$\frac{dU}{dx} = -ZI, \quad (16a)$$

$$\frac{dI}{dx} = -YU + I_0, \quad (16b)$$

where $Z = R + j\omega L$ and $Y = G + j\omega C$ are the impedance and admittance per unit length of the transmission line. I_0 is a current source, also expressed per unit length. With our identification of p as the acoustic analog of the voltage U and the fluid flux (Su) as the analog of the current I we see that the equations describing the electric transmission line [Eq. (16)] have the same form as those for the acoustic wave propagation in a tube [Eq. (15)]. General solutions of the differential equations [Eq. (16)] are

$$I(x) = Ae^{\beta x} + Be^{-\beta x}, \quad (17a)$$

$$U(x) = \frac{I_0}{Y} - Z_c(Ae^{\beta x} - Be^{-\beta x}), \quad (17b)$$

with propagation constant $\beta = (ZY)^{1/2}$ and characteristic impedance of the transmission line $Z_c = (Z/Y)^{1/2}$. The coefficients A and B are integration constants determined by the boundary conditions.

D. Matrix formalism

We can now apply transmission line theory to the optoacoustic cell.^{4,7,8} In particular we can use the theory to calculate the response of a cell consisting of a finite number of sections with different diameter, parallel tubes, etc. Therefore we divide the cell in a finite number N of tube elements with length l_i , radius r_i etc. and apply transmission line theory to each of these sections. Each element i ($i=1..N$) can then be described as a four-terminal port in the equivalent electric circuit with boundary conditions

$$I_i(x_i=0) = I_{i-1}(x_{i-1}=l_{i-1})$$

and

$$U_i(x_i=0) = U_{i-1}(x_{i-1}=l_{i-1}).$$

Using Eqs. (17a) and (17b) the network response can be described by the matrix equation for the coefficients A and B of adjacent four-terminal ports.

$$\begin{pmatrix} A_i \\ B_i \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix}_i \begin{pmatrix} A_{i-1} \\ B_{i-1} \end{pmatrix} + \begin{pmatrix} V_1 \\ V_2 \end{pmatrix}_i, \quad (18)$$

with the matrices M_i and vectors V_i , the latter containing the sources. By iteration of Eq. (18) we can find a relation between (A_1, B_1) and (A_N, B_N) . Two more equations are provided by the boundary conditions at the cell windows. In our case we are taking the impedance for the cell's windows, the terminal impedance, as infinitely large. This implies that the current at the windows must be zero. This in turn means that we assume the windows to be very stiff.

E. Low-pressure corrections

1. Small resonator tube diameter

The expressions for the circuit elements given in Table I are only valid under the condition that the tube radius r is much larger than the thicknesses of the thermal and viscous boundary layers. For small tube diameters and for low pressures of the working gas this is usually not the case and corrections as described by Benade¹⁷ have to be made. Benade numerically calculated low-pressure correction factors and in addition derived analytical expressions for the circuit elements in the limiting cases of the tube diameter being either much larger or much smaller than the boundary layer thicknesses.

Benade shows that in the large tube approximation for the resistance R_v already deviates from the numerical calculations by $\sim 5\%$ when $r_v = \sqrt{2}r/d_v = 50$. While the actual resistance R_v is underestimated by the analytical expression in Table I, the admittance G on the other hand is overestimated (by about 3.5% for $r_v=20$). Values for L and C are more accurate if we include analytic correction factors

TABLE II. Correction factors for the transmission line model of the optoacoustic cell for low pressures (cf. Ref. 17). f_R —correction for the resistance R ; f_G —correction for the admittance G .

$r_{v,h}$	f_R	f_G
1	5.665	0.086
1.5	3.789	0.261
2	2.868	0.488
2.5	2.342	0.665
3	2.009	0.764
3.5	1.796	0.806
4	1.654	0.825
5	1.494	0.853
7.5	1.312	0.901
10	1.234	0.931
20	1.106	0.965
50	1.054	0.986
100	1.00	1.00

(Table I), for values $r_{v,h} > 5$. Residual deviations then are always smaller than 2%. To extend the use of the model a computed¹⁷ table of correction factors f_R for the resistance R_v and f_G for the admittance (Table II) was used for values of $r_{h,v}$ smaller than 100. Where necessary linear interpolation was applied to find factors f_R and f_G for values of $r_{h,v}$ not given in Table II.

2. Conversion efficiency of the absorbed radiation

Another important effect which has to be taken into account at low pressures is the reduction of the conversion efficiency of absorbed laser power into acoustic power. This reduction is due to a slowdown of the vibration to translation (VT) relaxation of the excited vibrational levels. Lowering the gas pressure one finds that on the one hand only part of the absorbed energy is released as heat at the modulation frequency of the chopper; on the other hand diffusional relaxation of the excited molecules to the cell wall becomes increasingly important.

The $\nu_2 + \nu_4$ combination vibration relaxes very rapidly by collisions with ground state molecules. This results in either one molecule with a single ν_2 vibration and one with a single ν_4 vibration or a transition to the ν_1 vibrational state since in CF_4 the ν_1 vibration is quasi-resonant ($\Delta E \approx 150 \text{ cm}^{-1}$) with the $\nu_2 + \nu_4$ vibration. For the latter process, however, not only two vibrational quanta have to be exchanged upon a collision with a molecule in the ground state but also the energy difference ΔE must be accommodated in the kinetic and rotational energies of the collision partners. We therefore think that the resonant transfer of just one quantum from $\nu_2 + \nu_4$ excited molecules will dominate. In terms of the original absorbed energy a fraction $f_2=41\%$ is resident in the ν_2 vibrational states and $f_4=59\%$ in ν_4 vibrational states. Assuming that the inter-vibrational relaxation $\nu_4 \rightarrow \nu_2$ is absent the conversion efficiency for each vibration can be described separately. The total conversion efficiency can then be found by multiplying the individual efficiencies η_i ($i=2,4$) by the corresponding fractions f_i and summing

$$\eta_{\text{tot}} = f_2\eta_2 + f_4\eta_4. \quad (19)$$

Diffusional relaxation to the cell wall becomes faster when lowering the pressure. The relaxation time τ_{diff} depends linearly on pressure while the VT relaxation time τ_i has an inverse dependence. The reduced conversion efficiency $\eta_{\text{VT}}(\tau_i)$ can be found by considering the transition rates and is written in terms of the relaxation times

$$\eta_{\text{VT}}(\tau_i) = \frac{\tau_{\text{diff}}}{\tau_{\text{diff}} + \tau_i}. \quad (20)$$

The conversion efficiency is still further reduced if the VT relaxation time is long compared to the oscillation period of the acoustic wave. When light is absorbed in the gas, the amount of heat released in the gas by VT relaxation will grow to its steady-state value in the response time τ_i . When the light is shut-off an exponentially decaying heat input will be present. The slow relaxation effectively acts as a low pass filter in the conversion of the absorbed energy into heat. Hence the reduction in efficiency at the acoustic angular frequency ω is given by the usual expression for a low pass filter

$$\eta_p(\omega, \tau_i) = \frac{1}{(1 + \omega^2 \tau_i^2)}. \quad (21)$$

The conversion efficiency for a single ν_i vibration is thus given by

$$\eta_i = \eta_{\text{VT}}(\tau_i) \eta_p(\omega, \tau_i). \quad (22)$$

Only considering the two lowest lying vibrations, ν_2 and ν_4 , we find for the total efficiency [Eq. (19)]

$$\eta_{\text{tot}} = f_2 \eta_{\text{VT}}(\tau_2) \eta_p(\omega, \tau_2) + f_4 \eta_{\text{VT}}(\tau_4) \eta_p(\omega, \tau_4). \quad (23)$$

Multiplying the expression for the heat source [Eq. (12)] with the efficiency η_{tot} thus corrects for both the influence of diffusion and the slow VT relaxation.

3. Acoustic attenuation

When applying equilibrium thermodynamics it is implicitly assumed that temperature is changed slowly enough so that the equilibrium distributions over the internal molecular states can be reached through relaxation processes. For translational and rotational motion this is indeed the case; for the vibrational modes, however, the VT relaxation times can be of the order of ms. The inverse of this relaxation time falls well in the acoustic frequency range. This leads to attenuation near resonance and to dispersion of the acoustic velocity v $[(\gamma R_g T/M)^{1/2}]$, resulting in an increased velocity of sound above the resonance frequency.

The contributions to the attenuation due to the different vibrations ν_i ($i=1,2,3,4$ in CF_4) can be calculated by considering each vibrational contribution separately. The specific heat at constant volume C_v has contributions from the attenuating vibration, C_v^i , and from rotation, translation, and other vibrations, C_v^{oi}

$$C_v = C_v^{\text{oi}} + C_v^i. \quad (24)$$

The absorption coefficient for the power of the pressure wave at acoustic angular frequency ω due to vibration ν_i is given by¹⁸

$$\alpha_i = \frac{R_g C_v^i \omega^2 \tau_i}{v \{ C_v (C_v + R_g) + [C_v^{\text{oi}} (C_v^{\text{oi}} + R_g)] (\omega \tau_i)^2 \}}. \quad (25)$$

Differentiating Eq. (25) with respect to frequency the maximum absorption is found to occur at the acoustic angular frequency

$$\omega_i = \frac{1}{\tau_i} \left(\frac{C_v (C_v + R_g)}{C_v^{\text{oi}} (C_v^{\text{oi}} + R_g)} \right)^{1/2}. \quad (26)$$

The absorption coefficients for the attenuation due to the different vibrational relaxations can be included in the transmission line model by calculating the acoustic resistances R_s^i [Eq. (13)] corresponding to the different absorption coefficients α_i . The resistances are then added to the acoustic resistance R_v for the viscosity losses to give a correct description of the resonator response.

F. Frequency response and resonator quality

If the gas properties, resonator dimensions, and the pump laser power are known, the acoustic response at the microphone position can be calculated at an arbitrary frequency. The matrix formalism was used in a computer program to calculate the response of our optoacoustic cell as a function of frequency. The quality factor Q of the resonator was determined from the full width half maximum (FWHM) band width of the response

$$Q = \sqrt{3} \frac{f_0}{\Delta f_{1/2}}, \quad (27)$$

or by taking the half power points $Q = f_0 / \Delta f$.

The maximum response occurs at the resonance frequency f_0 , which can also be approximately calculated by using the resonance condition of the equivalent RCL-circuit $2\pi f_0 = (L/C)^{1/2}$ giving current resonance. For low quality resonators the voltage resonance frequency will deviate considerably from the current resonance

$$f_0^2 = f_Q^2 \left(1 - \frac{1}{2Q^2} \right). \quad (28)$$

IV. MODEL PREDICTIONS

A. Qualitative picture

If the gas molecules in the optoacoustic cell are assumed to interact via a Lennard-Jones potential, Eqs. (1)–(4) can be recast in a more compact form. For Lennard-Jones gases the Prandtl number ($\equiv \eta C_p / \kappa$) is a constant, equal to 2/3. This can be substituted in the expression for the quality factor Q [Eq. (3)]. The ideal gas expression for the velocity of sound, $v = (\gamma R_g T/M)^{1/2}$, with universal gas constant R_g , temperature T , and molar mass M may also be used to rewrite the resonance frequency condition $\omega_0 = \pi v / l$. Combining Eqs. (1)–(4) the pressure response p_{resp} is written as

$$p_{\text{resp}} = \frac{G}{(\pi^2 R_g)^{3/4}} \frac{(\gamma-1)M^{3/4}}{\gamma^{1/4} [1 + \sqrt{3/2}(\gamma-1)] \sqrt{2\eta(T)} T^{3/4}} \times \frac{\sqrt{l}}{r} \sqrt{\rho\alpha(p,T)} W_L. \quad (29)$$

Therefore gases with large molecular weight M , large specific heat ratio γ , and small viscosity η will show relatively large signals. The resonator tube should be long and narrow. Increasing the pressure will be beneficial for the response. Lowering the gas temperature will generally lead to a larger specific heat ratio and a lower viscosity. Cooling the gas at constant pressure will therefore be beneficial for the acoustic response unless the absorption decreases significantly.

B. Pressure dependence

The acoustic response in a room-temperature optoacoustic cell as a function of CF_4 gas pressure was calculated. Values for gas density ρ , sound velocity v , viscosity η , thermal conductivity κ , specific heat C_p , and specific heat ratio γ were taken from experimental data found in Ref. 19. First the values for the circuit elements from Table I were used without corrections. From this the geometrical factor G was determined by comparison of the computed results with the response of the resonator predicted by the simple model [Eq. (1)]. For our system we found $G=1.20$.

The resonator response with no corrections applied is given as a function of the gas pressure in the optoacoustic cell by the short dashed curve in Fig. 4(a). Calculations using the correction factors from Tables I and II are indicated by the long dashed curve. Including the attenuation losses and the conversion efficiency the response is further reduced as indicated by the dash-dotted curve. For the latter curve we assumed that the VT relaxation times for the ν_4 and ν_2 vibrational levels are equal: $\tau_4=\tau_2$. Since the energy content of the ν_4 vibration is larger than that of the ν_2 vibration, the corresponding relaxation is expected to be slower. In Table III the calculated pressure response is given with the relaxation time τ_4 as a parameter. In Fig. 4(a) the response is also plotted in the case that $\tau_4=3\tau_2$ (solid line). In Table III the response was also calculated including the ν_1 and ν_2 vibrations in the model, assuming a relaxation time of 100 ms Pa for the VT relaxation. The corresponding reduction in the response was found to be less than 3%. The experimental values (+) are also shown and will be discussed in the section on results.

The predictions for the resonator quality factor are shown in Fig. 4(b). Without the corrections the short dashed curve is found while with the corrections of Benade the predicted values are reduced, giving the long dashed curve. Just as for the pressure response the model predictions are given including the corrections for acoustic attenuation and conversion efficiency assuming $\tau_4=\tau_2$ (dash-dotted curve) and $\tau_4=3\tau_2$ (solid curve). The latter corrections give a drop in resonator quality ranging from less than 10% at 3 kPa to more than 30% at 100 Pa. The pressure dependence of the resonator quality approximately shows the expected $\sqrt{p}$ dependence. In view of these

FIG. 4. (a) Pressure dependence of optoacoustic signal amplitude at room temperature. Solid curve gives the model predictions while experimental data are indicated by (+). Also shown are results of calculations without any corrections (short dashes) and with the Benade corrections only (long dashes). When Benade corrections and the effects of acoustic attenuation and reduced conversion efficiency are included the dash dotted and solid curves result. For the dash-dotted curve we assumed that the VT relaxation of the ν_4 level was the same as for the lower lying ν_2 level. The solid curve is obtained using the relaxation time of the ν_4 level as a fitting parameter. (b) Idem for pressure dependence of resonator quality. (c) Idem for pressure dependence of optoacoustic resonance frequency.

theoretical results resonance enhancement is predicted for all pressures of the operating range of the microphone (> 30 Pa) with quality factors dropping to approximately 1 for the lowest pressures.

Predictions for the resonance frequency, including all corrections and assuming $\tau_4=3\tau_2$, are described by the solid curve in Fig. 4(c). The solid curve is almost the same as the dash-dotted curve (including all corrections but assuming $\tau_4=\tau_2$) and the long dashed curve (only Benade corrections). For the resonance frequency the corrections of Benade are the most important. Only at the lowest pressures a further drop in resonance frequency below the Benade corrections is found due to the drop in resonator quality. The short dashed line shows the high pressure limit $f_0=527$ Hz. It should be noted that the models prediction for the resonance frequency $f_0=525$ Hz at atmospheric pressures. Without corrections the short dashed curve is found for the resonance frequency in the whole pressure range.

TABLE III. Measured and calculated pressure response of the optoacoustic cell.

Gas pressure p (kPa)	Measured response p^m (Pa)	Calculated response for different relaxation times					
		Relaxation time τ_4 ($\tau_2=26$ ms Pa)					$\tau_1=100$ ms Pa $\tau_2=100$ ms Pa $\tau_4=\tau_2=26$ ms Pa
		τ_2	$2\tau_2$	$3\tau_2$	$4\tau_2$	$5\tau_2$	
0.13	0.5	0.63	0.49	0.40	0.36	0.31	0.61
0.27	1.55	2.07	1.86	1.64	1.50	1.39	2.01
0.40	2.84	3.65	3.42	3.15	2.96	2.79	3.55
0.52	4.3	5.35	5.11	4.82	4.60	4.39	5.21
0.67	5.7	6.90	6.66	6.37	6.14	5.92	6.79
1.07	11.3	11.80	11.6	11.2	11.0	10.8	11.6
1.33	14.1	15.3	15.0	14.7	14.3	14.2	15.0
2.00	23.5	22.9	22.6	22.2	21.9	21.7	22.5
2.67	30.0	30.1	29.7	29.2	28.9	28.5	29.6

C. Temperature dependence

In order to calculate the response of the cell as a function of temperature CF_4 gas properties given in Table IV were used. It is noted that these values are calculated on the basis of elementary gas kinetic theory and are in excellent agreement with the experimental data¹⁹ where available. The frequency response for our optoacoustic cell was calculated for different temperatures at a pressure of 266 Pa only applying the corrections of Benade (Fig. 5). A dramatic increase is seen in the signal strength when the temperature is lowered. The predicted increase of the response is a factor 28 when cooling down from 293 to 110 K. The resonance frequency is seen to shift to lower frequencies due to the decreasing velocity of the acoustic waves. In the response at 110 K another resonance peak is seen to appear which is a harmonic of the resonance frequency also satisfying the boundary conditions. The small kink between the harmonic and the fundamental resonance peak is due to a change in the standing wave pattern.

It is noted here that similar temperature effects can be expected for other gases. In fact a large increase in the optoacoustic signal is always found except when the absorption of the gas shows a strong decrease when lowering

the temperature. It is noted that at a fixed acoustic frequency the maximum absorption shifts to higher pressures.

D. Gas mixtures

When taking the different thermodynamic properties of various gases into account some of these gases seem very suitable for use in a resonant optoacoustic cell. The resonator response per unit absorbed power can easily be calculated to allow comparison between different gases. Gas properties, quality factors, and response values for a variety of gases at a pressure of 400 Pa, and a temperature of 273 K are shown in Table V.

The differences seem to suggest that optoacoustic signals may be enhanced by addition of a suitable buffer gas. In order to look into this possibility the mixture rules in Ref. 18 were used to predict the viscosity of a mixture of two gases. The thermal conductivity was approximated using the Prandtl number in the same way as described in Sec. III A. For four different mixtures of CF_4 the cell response per unit of absorbed power was calculated as a function of the fraction of the buffer gas in a mixture with CF_4 at a pressure of 267 Pa and a temperature of 273 K (Fig. 6). For CF_4 the addition of Xe is seen to be benefi-

TABLE IV. CF_4 gas properties. Calculated values and values taken from literature (Ref. 19) in parentheses.

T (K)	Atmospheric density ρ (kg/m ³)	Viscosity $\eta 10^5$ (Ns/m ²)	Diffusion coeff. D (N/s)	Specific heat C (J/kg/K)	ratio γ	Heat conductivity $\kappa 10^2$ (W/m/K)	Absorption coeff.		Relaxation times	
							low press. $\alpha 10^3$ (1/m/Pa)	0.27 kPa α (1/m)	VV $\tau_{ov} 10^3$ (s Pa)	VV $\tau_v 10^3$ (s Pa)
100	10.59	0.58	0.070	394	1.31	0.323	5.5	0.75	2.67	115
120	8.82	0.70	0.102	402	1.30	0.397	5.0	0.71	3.60	104
150	7.06	0.87	0.161	456	1.26	0.557	3.6	0.59	4.92	87
180	5.88	1.04	0.230	492	1.24	0.717	2.5	0.47	6.53	70
200	5.29	1.15	0.283	539	1.21	0.859	2.0	0.39	7.50	58
230	4.60	1.31	0.369	576	1.20	1.05	1.5		9.24	43.5
250	4.24	1.41	0.427	608	1.18	1.17	1.2	0.25	10.6	35.6
273	3.88 (3.88)	1.52 (1.61)	0.519	656	1.17	1.37 (1.51)	1.0	0.20	11.7	28.9
288	(3.68)	(1.68)				(1.63)	0.8		12.6	26.3
293	3.61	1.62 (1.71)	0.596	685	1.16	1.52 (1.67)	0.7	0.16	12.9	25.9
298	3.56	1.65	0.611	691 (706)	1.16		0.7		13.2	25.5
300	3.53	1.66	0.620	695	1.16	1.58	0.7	0.15	13.3	25.5
323	3.28	1.78 (1.85)	0.697	714	1.15	1.73 (1.90)	0.5	—	14.8	—
373	2.84	1.99 (2.07)	0.902	780	1.14	2.11 (2.28)	0.3	—	18.0	—

FIG. 5. Temperature dependence of the optoacoustic signal amplitude for a CF_4 gas pressure of 0.27 kPa.

cial; adding lighter gases like air and especially H_2 has a detrimental effect on the response. Addition of Ar does not have much effect on the response, although the predicted resonator quality (not shown) decreases.

E. Optoacoustic cell dimensions

The response of the cell can be enhanced by a well designed optoacoustic cell. It is very important to keep the

FIG. 6. Predicted pressure response per unit absorbed power per unit length as a function of buffer gas fraction for mixtures of CF_4 and Xe (---), CF_4 and Ar (---), CF_4 and N_2 (---), CF_4 and H_2 (—).

resonator tube radius small and the length of the tube large, because of the $l^{1/2}/r$ dependence for the response [Eq. (29) and Ref. 4]. At high pressures of the active gas two major constraints limit the resonator tube length and diameter. One constraint is the divergence of the laser beam, determined by the beam confocal parameter. The divergence is given by the confocal parameter $z_0 = \pi w_0^2 / \lambda$ of the laser beam which gives the distance z_0 , where the beam size increases by a factor $\sqrt{2}$ from its focal point

TABLE V. Properties of different gases at 273 K and optoacoustic response at 400-Pa pressure (resonator length 170 mm).

Gas	Molar mass M (g)	Viscosity η (10^{-5} Pa s/m)	Heat conduct. κ (10^{-2} W/mK)	Spec heat C_p (J/KgK)	Prandtl No.	Res. freq. f_0 (Hz)	Quality Q	Response (Pa/W)
CF_4	88	1.61	1.51	651	0.69	511	5.2	17.4
Air	29	1.71	2.40	1000	0.71	971	3.3	13.6
H_2	2	0.84	17.40	14300	0.69	3724	2.3	2.6
Helium	4	1.86	14.40	5100	0.66	2857	1.6	3.8
Neon	20	2.97	4.60	1030	0.67	1270	1.9	9.8
Argon	40	2.10	1.60	520	0.68	905	2.7	20.0
Krypton	84	2.33	0.87	250	0.67	630	3.0	33.7
Xenon	131	2.10	0.52	159	0.64	500	3.6	48.6
Methane	16	1.02	3.00	2210	0.75	1269	3.9	9.6
Ethane	30	0.85	1.80	1720	0.81	894	5.3	13.2
Propane	44	0.76	1.50	1530	0.78	711	6.6	12.2
Butane	56	0.71	1.37	1530	0.79	622	7.4	12.1
Octane	114	0.67	1.30	1658	0.86	426	9.5	11.3
SO_2	64	1.16	0.84	640	0.88	625	5.4	23.5
CO_2	44	1.39	1.40	820	0.81	765	4.3	17.7
SF_6	146	1.42	1.21	668	0.78	383	6.7	15.9
Freon-12	121	1.20	0.85	600	0.85	431	6.7	22.1
Ethanol	26	0.94	1.85	1701	0.86	965	4.8	11.8
Ethyn	46	1.08	1.30	1438	1.19	698	5.7	11.5
UF_6	353	1.67	0.61	384	1.06	244	7.9	21.4

diameter $2w_0$. Another constraint is that saturation effects of the absorbing gas must be absent; otherwise focusing the beam to a smaller diameter will lead to a decrease in absorbed power.

In addition to the above, the thermal and viscous boundary layer thicknesses have to be smaller than the resonator tube diameter since otherwise acoustic waves will be severely attenuated. For high pressures this is always the case. However, in the low-pressure regime these requirements put further constraints on the minimum resonator tube diameter.

For the resonance frequency the length of the resonator tube is the most important parameter. If pressure and temperature of the gas are fixed the resonance frequency is essentially set. Fine tuning can still be achieved by varying the buffer lengths. Decreasing the buffer lengths the resonance frequency shifts to higher frequencies. Larger buffer lengths have the opposite effect. The pressure amplitude changes very little unless the buffer length is either reduced to lengths smaller than $l/10$ or larger than l . The buffer diameter may also be varied: keeping the buffer diameter a factor three (or more) larger than the resonator tube diameter one has the case of an open resonator. Decreasing the buffer diameter a reduced pressure response is predicted and a decrease in resonance frequency. This is caused by increased resonator losses, since the impedance of the buffer volume is better matched to that of the resonator tube. A detailed analysis of the effects of buffer length and diameter on resonator quality, response, and resonance frequency at atmospheric pressures was given by Harren¹⁶ for a similar design of the cell. Predictions of their model were confirmed experimentally.

V. RESULTS

A. Pressure dependence

Using the setup with the cw CO₂ laser the frequency dependence of the resonator response was found to be accurately predicted by the model for high pressures (> 2 kPa). In Fig. 7 the frequency response of the pressure amplitude is shown for cell pressures of (a) 0.27 kPa and (b) 2.7 kPa. At a pressure of 2.7 kPa the model describes the measurements (+) well if only the Benade corrections are included (long dashes). Including the attenuation losses and the reduction in conversion efficiency (dash-dotted curve) results in a small improvement. At a pressure of 0.27 kPa the influence of the Benade corrections (long dashes), giving a frequency shift of the response curve, is clearly seen. Acoustic attenuation (dotted curve) and the reduction in conversion efficiency (dash-dotted curve) strongly affect the amplitude of the response. To model the pressure response as a function of pressure in the presence of acoustic wave attenuation and a reduced conversion efficiency we first assumed that the VT relaxation rates of the lower lying vibrational levels are equal $\tau_4 = \tau_2$. Both the predicted response [Fig. 4(a)] and resonator quality factor [Fig. 4(b)] then are in reasonable quantitative agreement with the measurements over the pressure range in the experiments (dash-dotted curves). However,

FIG. 7. Experimental data (+) and calculated frequency response (—) for a CF₄ pressure of (a) 0.27 kPa and (b) 2.7 kPa at room temperature. For the explanation for the different curves, see Fig. 4. In addition the curve for Benade corrections and only acoustic attenuation (dotted curve) is drawn.

as discussed earlier, VT relaxation from the ν_4 level is expected to be slower than from the ν_2 level. This is confirmed by the model predictions using $\tau_4 = 3\tau_2$, which give an improved fit to the experimental data (solid curve). The deviations of the model prediction from the experimentally measured values for the response are less than 10% in the whole pressure range. At the same time the frequency dependence of the response and the resonator quality are also accurately predicted. From these results we conclude that the VT relaxation time of the ν_4 vibrational level in CF₄ is approximately given by $\tau_4 \approx 3\tau_2$.

Experimental results for the resonance frequency are shown in Fig. 4(c). The predictions for the resonance frequency (solid curve) are in error by about 2% with the measured values in the pressure range of 0.13–2.7 kPa. The shift in resonance frequency is mainly due to the Benade corrections. In view of the accuracy of the literature values for the CF₄ gas properties, the predictions for the resonance frequency are excellent.

The impulse response of the optoacoustic cell [Fig. 8(a)] was also measured, using the setup with the TEA CO₂ laser. The system clearly behaves as a damped oscil-

FIG. 8. (a) Impulse response of the optoacoustic cell, using a hybrid TEA CO₂ laser. CF₄ pressure is 0.53 kPa. (b) Fourier transform of the impulse response. Measurements of the frequency response at 0.53 kPa using a chopped cw CO₂ laser are indicated by +.

lator, set in motion by the absorption of the pulse energy. The damped oscillation in the time domain can be related to the frequency response by taking the Fourier transform. The corresponding frequency response at 0.53 kPa is shown by the solid curve in Fig. 8(b). Since the absorbed energy is not known the peak value was scaled to the peak of the pressure amplitudes measured in the chopped cw CO₂ experiments. The frequency response derived from the pulsed measurements confirmed the response as measured with the cw laser (+) over the whole frequency range. The small oscillations below 100 Hz are not significant since total measurement time used for calculating the Fourier transform was only 20 ms.

B. Temperature dependence

In our design of the optoacoustic cell no provision was made for cooling down the cell. In order to investigate the temperature effects a 2.80-m-long gas cell was used with a 2.10-m-long cold section which could be cooled using a nitrogen gas flow. The gas inlet was placed at one of the room-temperature sides of the cell. No attempt was made to model the acoustical behavior. Response values were measured using a Knowles EK-3024 microphone placed in

FIG. 9. Temperature dependence of the optoacoustic response of a 2.80-m-long absorption cell. The response at 293 K (+), 142 K (●), and 110 K (▲) is shown.

the gas inlet close to the volume where absorption takes place. Measurements were taken at a pressure of 267 Pa in a frequency range of 7–700 Hz. In Fig. 9 the resulting signal amplitude at 293 K (+), 142 K (●), and 110 K (▲) is shown. The signal around 7 Hz is increased by a factor 9 even though only 75% of the absorbing length is cooled down. Taking into account that the cell is long, not satisfying the condition $\alpha l \ll 1$, the actual increase for a well designed system might be even larger. Note that some resonance occurs around 45 Hz while at 110 K a second peak around 90 Hz is observed. The resonant behavior of the cell might be caused by the existence of a cold section with a much higher gas density of approximately 210-cm length ($v \approx 100$ m/s) giving rise to Helmholtz-type oscillations. Alternatively the gas inlet with tubing to the manometer, gas valves and small cavities near the electrical feed-through also present possibilities for resonant behavior. However at room temperature the frequency response does not show resonant peaks. Although we did not attempt to relate the increase of the acoustic signal with model predictions, these results show that cooling down the gas of an optoacoustic resonator can be an effective way to improve the signal amplitude.

C. Gas mixtures

The effects of adding air to the CF₄ gas were studied. Because of the narrow constrictions in the resonator at least 12 h were needed to obtain a homogeneous mixture. Several homogeneous mixtures at high pressure were made and pressure was changed by pumping part of the mixture away. Since vacuum pumps are notorious for their selective pumping of certain gas species from mixtures, the pressure was lowered by sealing off a small portion of the gas from the optoacoustic cell by closing a valve and then evacuating that small part of the optoacoustic volume. The pressure is then reduced by closing off the pump and opening the valve.

In this way the frequency response of several CF₄-air mixtures was measured. From these experiments resonator quality [Fig. 10(a)] and the pressure response at resonance

FIG. 10. (a) Quality factor and (b) pressure response of the optoacoustic cell for different mixtures of CF₄ and air as a function of total gas pressure. Results are given for pure CF₄ (+), and CF₄-air mixtures containing 33% (Δ), 50% (○), and 67% (□) air. In (a), model predictions for mixture quality are also shown. The calculated curve for pure air is also shown (—). This could not be measured because of the absence of absorption.

[Fig. 10(b)] were determined. The quality of the resonator was measured for pure CF₄ (+) and CF₄-air mixtures containing 33% (Δ), 50% (○), and 67% (□) air. Also shown is the quality factor for those mixtures predicted by the model, with Benade corrections only. The other corrections were not applied. Instead the predictions for the mixtures were reduced by 13%, a value suggested by the difference in pure CF₄ between the model prediction with Benade corrections only and the measurements. The solid curve is the prediction for pure air. The mixture quality is seen to exhibit the predicted behavior as a function of pressure and fraction CF₄ in the mixture. The pressure response showed a strong dependence on the fraction CF₄ [Fig. 10(b)].

In another experiment with an atmospheric mixture of air with 133-Pa CF₄ a resonator quality $Q=48 \pm 3$ was measured and a resonance frequency of 966 Hz, which agrees well with the predicted quality $Q=50$ at a resonance frequency of 961 Hz. Due to the low fraction of CF₄ the latter prediction is the same as for pure air.

Although the response of pure CF₄ is always higher than in the case of a mixture at the same pressure it must be realized that for frequency locking purposes the combination of pressure response and linewidth is to be optimized. Therefore comparisons should be made on the basis of the pressure response at equal linewidth. Here we only show that the quality of a mixture exhibits the behavior predicted by the model. If the absorbing gas has a low molecular weight the addition of a small amount of heavy buffer gas will be beneficial for the resonator quality. If line-broadening effects are small, an enhanced response can be expected.

D. Optoacoustic cell dimensions

From the model predictions one of the most important parameters in the cell design to improve the resonator response was found to be the resonator tube radius. Changing the buffer length and diameter is not predicted to im-

FIG. 11. (a) Quality factor and (b) pressure response of the optoacoustic resonator as a function of resonator tube diameter. Model predictions for a CF₄ gas pressure of 0.27 kPa (---), 0.53 kPa (—), and 1.3 kPa (—) are shown, experimental results for those pressures are indicated by (●) for 0.27 kPa, (▲) for 0.53 kPa, and (+) for 1.3 kPa.

prove the response significantly and may serve to fine tune the resonance frequency. The 10-mm-diam resonator tube was replaced by one of 14-mm-diam of equal length. The experimental data for response and quality factor are given in Fig. 11 for pressures of 0.27 kPa (●), 0.40 kPa (▲), and 1.33 kPa (+). It should be noted that the experiments with different diameters were not obtained with the same microphone since the microphone used for the measurements for the 10-mm tube broke down. We think however that the present results confirm the model predictions that reducing the tube diameter will be beneficial for the acoustic response of the cell.

VI. OPTIMUM CELL DESIGN

Finally we want to address the question how to design an optimum cell for frequency locking of a (pump) laser. It is important to realize that the quantity to optimize is the signal-to-noise ratio of the optoacoustic cell pressure response. In most experiments the chopping frequency can be stabilized well enough to give negligible amplitude and phase fluctuations. Also as we have seen the cell quality factor is reduced at low pressures. In the preceding sections we have treated the influence of the cell geometry, externally controllable parameters such as chopping frequency, gas pressure and temperature, and mixture concentrations and of intrinsic gas properties on the resonance frequency, cell response, and quality factor. The outcome of the optimization procedure will in addition be determined by the acceptable frequency noise of the laser to be stabilized, its free-running frequency and amplitude stability, the level of acoustic noise and other experiment specific quantities. The current model allows such an optimization to be made.

¹A. Nordhaus and J. Pelzi, Appl. Phys. **25**, 221 (1981).

²E. Kritchman, S. Shtrickman, and M. Slatkine, J. Opt. Soc. Am. **68**, 1257 (1978).

³P. L. Meyer and M. W. Sigrist, Rev. Sci. Instrum. **61**, 1779 (1990).

⁴S. Bernegger and M. W. Sigrist, Appl. Phys. B **44**, 125 (1987).

⁵R. A. Rooth, A. J. L. Verhage, and C. W. Wouters, Appl. Opt. **29**, 3643 (1990).

- ⁶P. M. Morse and K. U. Ingard, *Theoretical Acoustics* (McGraw-Hill, New York, 1968).
- ⁷M. Fiedler and P. Hess, in *Photo-acoustic, Photothermal and Photochemical Processes in Gases*, edited by P. Hess (Springer, Berlin, 1989), Topics Curr. Phys., Vol. 46, Ch. 5.
- ⁸S. Bernegger and M. W. Sigrist, *Infrared Phys.* **30**, 375 (1990).
- ⁹J. Heppner, G. O. Weiss, and P. Plainchamp, *Opt. Commun.* **23**, 381 (1977).
- ¹⁰D. T. Hodges, J. R. Tucker, and T. S. Hartwick, *Infrared Phys.* **16**, 175 (1976).
- ¹¹P. F. Gascoyne and M. N. Rutt, *J. Phys. E* **16**, 31 (1983).
- ¹²T. L. Wallace and C. A. Ventrice, *Rev. Sci. Instrum.* **60**, 3074 (1989).
- ¹³J. R. Fishback, M. Azar, and C. A. Ventrice, *Rev. Sci. Instrum.* **59**, 238 (1988).
- ¹⁴A. Olafsson, Ph.D. thesis, Univ. of Copenhagen, Copenhagen, Denmark, 1990.
- ¹⁵M. Hartemink and H. P. Godfried, *IEEE J. Quantum Electron.* **28**, 272 (1992).
- ¹⁶F. Harren, Ph.D. thesis, Katholieke Universiteit Nijmegen, Nijmegen, the Netherlands, 1988.
- ¹⁷A. H. Benade, *J. Acoust. Soc. Am.* **44**, 616 (1968).
- ¹⁸J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1967).
- ¹⁹*Encyclopie des Gaz*, edited by L'Air Liquide, Division Scientifique (Elsevier, Amsterdam, 1976), p. 215 ff.