

# Short tutorial on photoacoustic trace gas detection

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## 1 Introduction

This is a short introduction to the photoacoustic detection of trace gas molecules. It describes the most relevant and basic equations, some experimental issues, and gives relevant references. First an introduction is given into photoacoustic signal generation and phase sensitive detection. Next, the photoacoustic background signals and the acoustic resonator quality factor are discussed. This is followed by a discussion of the effects of molecular relaxation.

## Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
<b>2</b>	<b>Gas phase photoacoustics</b>	<b>2</b>
<b>3</b>	<b>Phase sensitive detection</b>	<b>3</b>
<b>4</b>	<b>Photoacoustic background signals</b>	<b>3</b>
<b>5</b>	<b>Acoustic resonator quality factor</b>	<b>3</b>
<b>6</b>	<b>Molecular relaxation</b>	<b>5</b>
<b>7</b>	<b>Effect of finite relaxation speed</b>	<b>5</b>

## 2 Gas phase photoacoustics

Photoacoustic spectroscopy is based on the following principle [1]: the absorption of light excites a molecule into a higher energy state. Due to collisions with the surrounding gas molecules part of the energy of the excited molecule is relaxed and transferred into translational energy of the collision partner. The increase of translational energy is equivalent to an increase of the temperature of the gas. As the absorbed energy is modulated in time (either by amplitude modulation or wavelength modulation over an absorption line), the temperature is adiabatically transformed into a pressure wave, which is detected with a microphone.

Consider a laser beam with power  $P_{laser}$  incident on a gas with a density  $N$  and molecules with an absorption cross section  $\sigma$ ; then for small absorbed fractions, the amount of energy absorbed  $W$  in a path length  $\Delta x$  and a time  $\Delta t$  is

$$\Delta W = N\sigma\Delta x P_{laser}\Delta t \quad (1)$$

This amount of energy is dissipated over all the  $N$  molecules in the photoacoustic volume  $V$ , leading to a temperature increase (assuming three internal degrees of freedom) of

$$\Delta T = \frac{\Delta W}{\frac{3}{2}kNV} \quad (2)$$

the induced pressure increase can be derived using the ideal gas law  $\Delta pV = (NV)k\Delta T$ , with  $NV$  the total amount of molecules in the volume  $V$

$$\Delta p = \frac{2\Delta W}{3V} = \frac{N\sigma\Delta x}{3V} 2P_{laser}\Delta t \quad (3)$$

Here it is assumed that the time  $\Delta t$  is still sufficiently small such that no heat transport to the walls of the cavity takes place (adiabatic approximation). Taking a time modulated laser beam with frequency  $f = 1/\Delta t$  and a sample volume  $V = A\Delta x$  for a cylinder with cross sectional area  $A$  we arrive at the equation for the electrical signal strength  $S$  (in Volts)

$$S_{meas} = kG \frac{2QN\sigma P_{laser}}{3Af} (1 - \eta) \quad (4)$$

with  $\eta$  the luminescence quantum efficiency,  $Q$  the acoustic quality factor of the cylindrical gas enclosure that amplifies the pressure increase (see section 5),  $k$  the microphone sensitivity (pressure to volts), and  $G$  a geometrical factor that describes the overlap of the laser beam with the excited acoustic mode [2]. The detection limit is set by  $S_{meas} = N$  the noise level. The main advantage of photoacoustics trace gas detection is the signal amplitude scaling with laser power and the background free measurement (i.e. no absorption results in no signal).

### 3 Phase sensitive detection

In general photoacoustic signal detection is performed by amplitude modulation of the intensity of the light beam at acoustic frequencies, hence its name. The generated photoacoustic signal is composed of both a signal and a background at the modulation frequency with in addition a random noise background [3]. Both the signal and the background have a particular phase and magnitude relative to the modulation frequency and should be added vectorially when the signal magnitude is measured.

$$S_{meas} = \sqrt{(\vec{S} + \vec{B})^2 + N^2} \quad (5)$$

with  $\vec{S}$  the photoacoustic signal,  $\vec{B}$  the background signal, and  $N$  the random noise signal. After some basic trigonometry

$$S_{meas} = \sqrt{S^2 + 2SB\cos(\theta_{PA} - \theta_{BG}) + B^2 + N^2} \quad (6)$$

with  $\theta_{PA}$  the photoacoustic phase angle and  $\theta_{BG}$  the background phase angle. Since the signal  $S$  is linear with the gas concentration, a quadratic dependence of measured signal versus concentration is obtained. If, on the other hand, the in-phase signal is measured, the background vector is projected to the signal phase and added to the random noise. The result is a linear dependence of measured signal versus concentration.

### 4 Photoacoustic background signals

Photoacoustic background signals are generated due to heating of the solid enclosing the resonator. This heat is dissipated in a thin gas layer on top of the solid that subsequently expands. The theory of photoacoustic signal generation with solids has been extensively described by the Rosencwaig-Gersho theory [4]. It describes the photoacoustic signal generation due to an absorbing layer on top of a transparent backing layer. Later it has been extended [5] to treat the effect of absorbing coatings on top of absorbing layers. The latter theory shows that photoacoustic background signals can be reduced by a factor  $e^{-\sigma_{coating}d}$ , with  $d$  the thickness of the coating and  $\sigma$  a measure being proportional to the thermal diffusion coefficient. Consequently, for materials with low thermal conductivity the photoacoustic background signal may be significantly reduced (compared to a metal for example).

### 5 Acoustic resonator quality factor

The quality factor of an acoustic resonator is determined by volume and wall losses of the gas inside the resonator [6] (for a good introduction into acoustics see Kinsler [7]). Following Moloney, we add the wall and radiation quality factors resulting in  $Q^{-1} = Q_{wall}^{-1} + Q_{rad}^{-1}$ . Since the quality factor depends on radius and

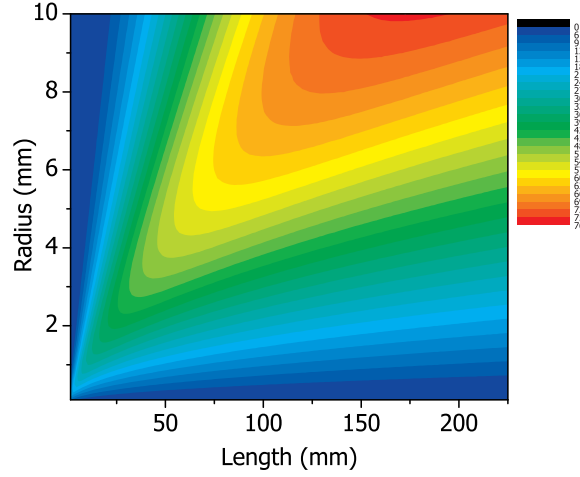


Figure 1: Acoustic resonator quality factor as a function of length and radius of a cylindrical cavity.

length and the resonance frequency on length (neglecting end effects) the quality factor can be calculated for  $N_2$  (see Table 1 for the relevant physical parameters of  $N_2$ ) as a function of resonator dimensions, see Fig. 1. At a constant resonator length the resonator quality factor has a maximum. At smaller radii, walls losses start to dominate, while at larger radii radiation losses start to dominate.

property	value	unit
speed of sound	334	$\text{ms}^{-1}$
density	1.25	$\text{kg m}^{-3}$
viscosity	$17 \cdot 10^{-6}$	$\text{Pa s}$
$C_p$	1040	$\text{J kg}^{-1} \text{m}^{-3}$
$C_v$	743	$\text{J kg}^{-1} \text{m}^{-3}$
$\kappa$	0.024	$\text{W m}^{-1} \text{K}^{-1}$

Table 1: Physical properties of nitrogen at 273 K

## 6 Molecular relaxation

Molecular relaxation takes place due to collisions in the gas. The total number of collisions  $Z$  of a single molecule with the other gas molecules is

$$Z = \langle v_{rel} \rangle \pi d^2 \frac{N}{V} \quad (7)$$

with  $\langle v_{rel} \rangle$  the relative molecular speed, which is  $\sqrt{2}$  times the molecular speed  $v = \sqrt{8kT/\pi m}$  for a molecule with mass  $m$  at temperature  $T$ . The collision cross section  $d$  is of the order of a few Ångström which means that at atmospheric pressures the collision rate is of the order of a few Gigahertz. Consequently, the relaxation of the molecule caused by collisions can be extremely fast. On the other hand, collision partners can trap the excitation energy in an excited state thus causing a significant slowdown of the relaxation speed.

## 7 Effect of finite relaxation speed

In the definition of signal amplitude in Eq. 4 an infinitely fast relaxation speed was assumed. A finite relaxation rate  $W = 1/\tau$  can lead to a decrease of the signal amplitude if the relaxation rate is of the same order of magnitude as the modulation frequency  $\omega$ . The signal decrease is described by [8]

$$S_{meas} = \frac{S}{\sqrt{1 + (\omega\tau)^2}} \quad (8)$$

which leads to a shift  $\theta$  of the photoacoustic signal relative to the phase of the laser intensity modulation

$$\theta = \arctan(\omega\tau) \quad (9)$$

The signal drop due to finite relaxation speed also can be calculated from a simple model. Assume a two-level system  $N_0$  and  $N_1$  where there is an excitation rate  $R$  and a relaxation rate  $W = 1/\tau$  the the rate equation model is

$$\frac{dN_1}{dt} = RN_0 - (R + W)N_1 \quad (10)$$

The general time-dependent solution is

$$N_1(t) = \frac{RN_0}{R + W} + \left( N_1(0) - \frac{RN_0}{R + W} \right) e^{-(R+W)t} \quad (11)$$

If the excitation rate is modulated at frequency  $f$  then after a time  $T' = 1/2f$  of excitation and a time  $T'$  of decay, the excited fraction  $N_2$  should be again at the same level. Consequently, solving

$$N_1(0) = \left( \frac{RN}{R + W} + \left( N_1(0) - \frac{RN}{R + W} \right) e^{-(R+W)T'} \right) e^{-WT'} \quad (12)$$

Results in a modulation frequency dependent excited state population

$$N_{1,max} = \frac{RN}{R+W} \left( \frac{e^{-(R+W)T'} - 1}{e^{-(R+2W)T'} - 1} \right) \quad (13)$$

$$N_{1,min} = \frac{RN}{R+W} \left( \frac{e^{-(R+2W)T'} - e^{-WT'}}{1 - e^{-(R+2W)T'}} \right) \quad (14)$$

Equations 11 and 13 fully define the temporal evolution of the excited state population. Figure 2 shows the temporal evolution for various decay rates relative to the modulation frequency of 1000 Hz (1 ms period). As can be observed, the amplitude of the modulation decreases with decreasing relaxation rate. The

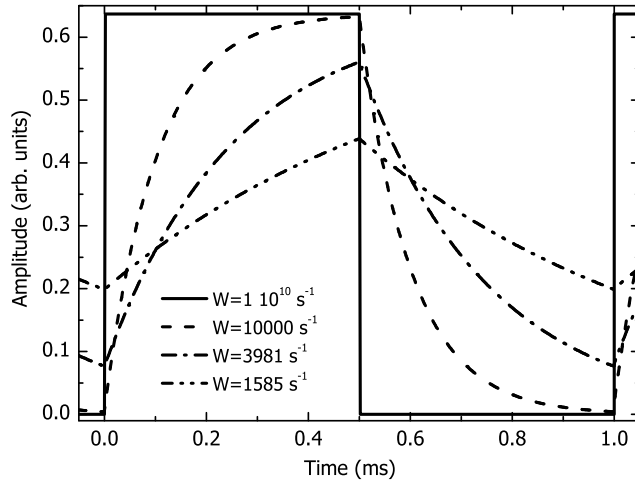


Figure 2: Calculated signal time traces for a square wave modulated pump (1000 Hz) for various decay rates. Note that both the upper and lower excited state population are decreasing and increasing, respectively. This leads to a signal decrease and phase delay for decreasing decay rates.

photoacoustic signal amplitude per unit volume is related to the excited state population of Eq. 11 by [9]

$$P(t) = P_0 + \frac{2}{3} E \frac{1}{\tau_c} e^{-t/\tau_T} \int_0^t N_1 e^{t'/\tau_T} dt' \quad (15)$$

where  $\tau_T$  describes the thermal decay transient effects and  $\tau_c$  the collisional relaxation time. It leads to a constant pressure increase in combination with a pressure modulation. Typically, only the modulation term is measured using

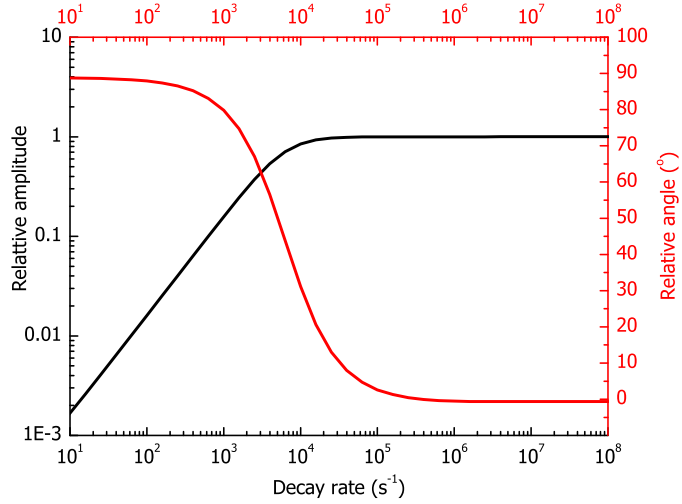


Figure 3: Signal and phase delay of the time traces shown in Fig. 2 determined from their Fourier transforms.

lock in amplification rejecting all transient effects (this is equivalent to setting  $\tau_T = \infty$  and taking it out of the integral). Consequently, the photoacoustic signal is proportional to the integral of the excited state population. Since the excited state can be described by a sinusoidal varying population, the signal is also proportional to  $N_1$ . Consequently, the signal amplitude is proportional to the Fourier component at frequency  $\omega$ , which is given by Eq. 8. It is also calculated from the time traces shown in Fig 2 and is shown in Fig. 3 given the same result. Experimental work on photoacoustic relaxation rate enhancement is presented in Refs. [10] and [11].

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