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Assessment of the lifetime resolution limits in time-resolved photoacoustic calorimetry vs transducer frequencies: setting the stage for picosecond resolution

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Abstract. Time-resolved photoacoustic calorimetry (PAC) gives access to lifetimes and energy fractions of reaction intermediates by deconvolution of the photoacoustic wave of a sample (E-wave) with that of the instrumental response (T-wave). The ability to discriminate between short lifetimes increases with transducer frequencies employed to detect the PAC waves. We investigate the lifetime resolution limits of PAC as a function of the transducer frequencies using the instrumental response obtained with the photoacoustic reference 2-hydroxybenzophenone in toluene or acetonitrile. The instrumental response was obtained for a set of transducers with central frequencies ranging from 0.5 MHz up to 225 MHz. The simulated dependence of the lifetime resolution with the transducer frequencies was anchored on experimental data obtained for the singlet state of naphthalene with a 2.25 MHz transducer. The shortest lifetime resolved with the 2.25 MHz transducer was 19 ns and our modelling of the transducer responses indicates that sub-nanosecond lifetimes of photoacoustic transients can be resolved with transducers of central frequencies above 100 MHz.

1 Introduction

A chromophore absorbing a short laser pulse releases a heat pulse when that chromophore undergoes radiationless transitions. This heat pulse produces a thermoelastic expansion of the medium that, if confined in time and space, launches a photoacoustic wave. Time-resolved photoacoustic calorimetry (PAC) is based on the detection of photoacoustic waves using ultrasonic transducers. PAC is often the technique of choice to measure transient volume/enthalpy changes of short-lived intermediates, and their corresponding lifetimes, due to radiationless processes subsequent to electronic excitation by a short laser pulse.¹⁻³ Such measurements require the deconvolution of the sample signal, named $E(t)$ wave, from the instrumental response, named $T(t)$ wave, which is obtained in an independent measurement using the same conditions but employing a photoacoustic reference.⁴⁻⁵ A photoacoustic reference absorbs the same laser energy as the sample but converts it in a heat pulse within the laser pulse duration. In these conditions, the photoacoustic reference provides the $T(t)$ wave required for the deconvolution. PAC has been particularly useful for the characterization of radiationless processes common in photophysics and for the measurement of the enthalpies of photoinduced reactions taking place in the nano and microsecond timescales.⁶⁻⁹

There are essentially two approaches to detected PAC waves: the wave is detected perpendicularly to the laser beam,³ or the wave is detected collinearly with the laser beam and in this case the detector is protected from the laser by a mirror. In the latter case, often described as the “front-face” PAC cell,¹⁰ the homogeneously irradiated volume expands in phase and a pressure wave propagates through the mirror to the detector. The time resolution of the “front-face” PAC cell is limited by the response of the detector when the mirror is highly reflective at the laser wavelength (>99.9% reflection) and sufficiently thin to minimize the distortion of the photoacoustic wave due to differential absorption of its frequency components.¹⁰ This work explores the limits of the time resolution of PAC experiments with the “front-face” cell, establishing a relation between the resonance frequencies of the transducers that can be used as detectors and the lifetimes of the heat decays that may occur in the samples.

The front-face design of PAC cells has resolved transient decays with 2 to 10 nanosecond lifetimes, which

are the shortest-lived transients measured with PAC.¹¹ Theoretical and practical arguments have been presented to suggest that PAC cannot attain a sub-nanosecond time resolution.^{11,12} However, the continued interest in ultrafast processes, namely involving optically silent intermediates such as those taking place in solar cells,¹³ and the remarkable advances of photoacoustic tomography (PAT) in medical imaging,¹⁴ that may evolve to time-resolved PAT, motivated a re-investigation of the presumed time-resolution limits of this technique. We take advantage of the use of 2-hydroxybenzophenone (HBP) as PAC reference, which has negligible fluorescence and a singlet lifetime shorter than 10 ps in non-hydrogen bonding solvents,¹⁵ and of a 30 ps laser pulse, to insure that the $T(t)$ wave duration is only limited by the frequencies of the transducers employed in this work, which range from 0.5 to 225 MHz. Moreover, we use the convolution of these experimental $T(t)$ waves with theoretical heat functions $H(t)$ of various lifetimes to obtain calculated $E(t)$ waves

$$E(t) = T(t) \otimes H(t) \quad (1)$$

and obtain a criterion to establish the time resolution of PAC in the basis of the phase shift differences between $T(t)$ and $E(t)$ waves. The dependence of the PAC shortest and longest lifetime resolution limits on the transducer central frequency was predicted based on the experimental limits obtained with the transducer of 2.25 MHz.

2 Theory

The photochemical scheme representing the kinetics of two consecutive first-order reactions processes is represented as:



The transient concentrations of the reactant and consecutive intermediate species are given by the set of differential equations:

$$-\frac{d[A]}{dt} = k_1[A] \quad (2)$$

$$-\frac{d[B]}{dt} = -k_1[A] + k_2[B] \quad (3)$$

which have the following solutions^{16,17}

$$[A] = [A]_0 \exp(-k_1 t) \quad (4)$$

$$[B] = [A]_0 \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (5)$$

where k_n is the reciprocal of the reactant or intermediate lifetime ($k_n = \frac{1}{\tau_n}$).

Heat depositions H_n in the medium may be described in terms of their rates ν_n , which are proportional to the concentrations of each species with k_n as the corresponding rate constants.

$$\nu_A = \frac{dH_A}{dt} = k_1[A] = \phi_1 k_1 \exp(-k_1 t) \quad (6)$$

$$\nu_B = \frac{dH_B}{dt} = k_2[B] = \phi_2 \frac{k_1 k_2}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (7)$$

Where ϕ_n are the non-radiative fractions of energy deposited in the medium.¹⁶ The number of exponentials depends on the number of species that can be assessed, typically PAC analysis can resolve three species or a three states decaying model.

PAC gives lifetimes and energies of transient species by comparing the photoacoustic wave generated by the heat deposition with a reference, which consist of a compound that loses all the absorbed energy in a lifetime faster than the instrumental response of the transducer. The instrumental function $T(t)$ can be appropriately described using only three frequencies (f) of the transducer, as shown in previous work,¹⁶ using the function:

$$T(t) = \frac{(t_0 - t)}{Y_0} \left[\exp\left(\frac{(t_0 - t)}{w_1}\right) \sin(f_1(t + \theta_1)) + \exp\left(\frac{(t_0 - t)}{w_2}\right) \sin(f_2(t + \theta_2)) + \exp\left(\frac{(t_0 - t)}{w_3}\right) \sin(f_3(t + \theta_3)) \right] \quad (8)$$

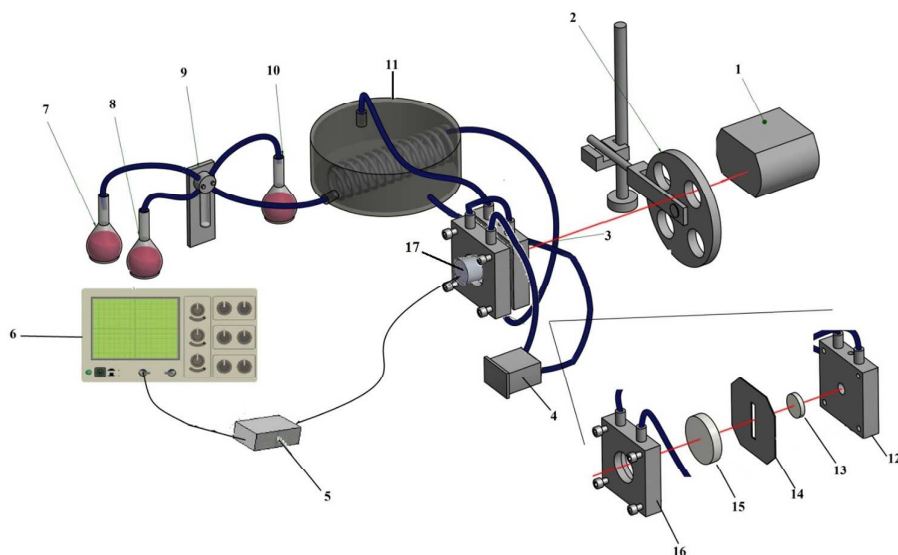
Where t_0 is related to the time delay from the triggering of the oscilloscope and sets the function to zero when $t=t_0$. The parameter Y_0 is related with the rise time of the wave, w is the damping time of the transducer and θ is the phase. Thus, using the instrumental response of the set-up and a kinetic model to describe the decays of the transient species, the sample wave $E(t)$, can be obtained by the convolution expressed by Eq. (1). The software¹⁸ based on the equations above allows for the analysis of the sample wave using a given

instrumental wave for a kinetic model up to three lifetimes and three energy decays.

3. Experimental

Time-resolved PAC measurements were performed in a homemade apparatus following the front-face irradiation design described by Arnaut *et al*¹⁰ using the 3rd and 4th harmonic (355 and 266 nm) of a Nd:YAG laser with 30 ps pulse width. Scheme 1 presents the components necessary to perform a PAC experiment. The homemade photoacoustic cell, labelled number 3 in the scheme 1, is composed of metal structure (numbers 12, 16 in the expanded view) that holds a quartz window (13) pressed against a dielectric mirror (15), where a transducer (17) is coupled. A copper foil (14) between the front window and the back mirror determines the optical path, which is 0.1 mm in our work. This cell allows the solution to flow from the bottom to the top. The expanded view of the cell is given in the inset above the cell. The solutions are flown using a pump (9) Kloehn Co. LTD, 55022, controlled by computer, with three syringes (7, 8, 10) for inserting solvent, sample and reference solution and one channel to flow the solutions to the PAC cell. A chamber (11) connected to a thermal bath (4) linked to the front and rear metal structures (12, 16) allows for the control of the temperature. A set of neutral filters (2) is used to run the experiments with four different intensities of the laser (1) beam, avoiding bi-photonic effects.

Scheme 1: Photoacoustic cell and apparatus available in the Coimbra Laser Lab.



A complete set of experiments, including 4 repetitions for each solution and four variations in laser intensity, takes ca. 30 min to run in this setup. A user-friendly software is available online free of charge.¹⁸ PAC with this setup is a straightforward and reliable technique.

The transducers used to obtain the photoacoustic waves in this work have central frequencies at 0.5, 1.0, 2.25, 10, 15, 20, 100 and 225 MHz. All acoustic detectors were contact transducers (Panametrics), except the 10 MHz that is an immersion transducer. All signals were pre-amplified (5) with an ultrasonic amplifier Panametrics model 5676 or MITEQ model AU-1565. The data were collected in the oscilloscope Tektronix model DPO7254 (6).

The photoacoustic reference 2-hydroxybenzophenone (HBP, Aldrich) was used without further purification in toluene and acetonitrile (Aldrich and Fisher). The data were analysed with the software developed by the authors¹⁶ and available online.¹⁸ In order to determine the lower lifetime resolution limit we used the well-known compounds 9-cyanoanthracene, carbazole and naphthalene (all from Aldrich) in toluene or acetonitrile, which have lifetimes of 12 ns,¹⁹ 15 ns,¹⁹ both in inert atmosphere N₂, and 18 ns²⁰ (air saturated), respectively.

4. Results and discussion

In order to determine the limits of the lifetime resolution as a function of the transducer frequency, we selected the transducer of 2.25 MHz that is largely used in our lab. The upper lifetime limit of 1 μ s was taken from various data published by our group.^{16,21} The lower lifetime limit was determined by running experiments with compounds with well known S₁ state lifetimes. The compounds tested and their lifetimes were: 9-cyanoanthracene, carbazole and naphthalene. In all cases, the photoacoustic reference was HBP and the $E(t)$ and $T(t)$ waves were collected and deconvoluted to determine the lifetime of the singlet S₁ state using two or three decay lifetimes (τ_1 , τ_2 , τ_3), depending on the excited states lifetime of each compound, and their respective energy fractions (ϕ_1 , ϕ_2 , ϕ_3). In all cases only the τ_1 parameter was fixed at the laser pulse width of 30 ps. When the transducer is able to separate the first internal conversion decay ($S_n(E_{hv})-S_1$),

which occurs in a lifetime τ_1 much faster than transducer resolution, from the lifetime τ_2 of the S_1 state, the energy of the S_1 state can be determined from:

$$E_{S_1} = E_{hv}(1 - \phi_1) \quad (9)$$

where E_{hv} is the energy of the photons in the laser pulse.

The first attempt to separate the formation of the S_1 state from the decay of the S_1 state employed 9-cyanoanthracene in toluene excited at 355 nm ($E_{hv}=337$ kJ/mol) in inert atmosphere (N_2). The data were analysed considering two decays (in N_2 atmosphere, the triplet state lifetime is beyond the resolution of the 2.25 MHz transducer, i.e. $\tau_3 \gg 1\mu s$). The formation of the S_1 state from the initially prepared Franck-Condon state $S_n(E_{hv})$ was assigned a lifetime τ_1 identical to the laser time profile, $\tau_1 = 30$ ps. The S_1 state lifetime and S_1 energy of 9-cyanoanthracene are known: $\tau_2 = 12$ ns¹⁸ and $E_{S_1} = 297$ kJ/mol.¹⁸ The lifetime obtained by PAC was 32 ± 3 ns, which is an unacceptable overestimate of the S_1 state lifetime. Although this transducer cannot resolve the 12 ns lifetime, the energy obtained for the S_1 state was 283 ± 9 kJ/mol ($\phi_1 = 0.16 \pm 0.01$), which is close to the spectroscopic value 297 kJ/mol. Another attempt was made with carbazole in N_2 -saturated acetonitrile, with excitation at 266 nm ($E_{hv}=450$ kJ/mol). The analysis was made as above. In this case, the lifetime obtained by PAC was 317 ± 69 ns and the energy of the S_1 state was 306 ± 19 kJ/mol ($\phi_1 = 0.32 \pm 0.02$). The spectroscopic energy of the carbazole S_1 state is 347 kJ/mol¹⁹ and its lifetime is 15 ns.¹⁹ Again, the discrepancy between the lifetime measured for carbazole and the actual S_1 state lifetime is unacceptable. This large discrepancy may be related to the large excess of energy used in the excitation of this system (≈ 100 kJ/mol), but nevertheless we must conclude that the 2.25 MHz transducer was unable separate τ_1 from τ_2 in this system.

The criterion to establish the time resolution of the 2.25 MHz transducer was the ability of the fitting to converge to physically meaningful values of the adjustable parameters. This was achieved experimentally with naphthalene in acetonitrile with excitation at 266 nm in air-saturated atmosphere. Naphthalene excited states decaying in air-saturated acetonitrile follow the three states model with the first lifetime τ_1 shorter than transducer resolution (laser pulse profile fixed in 30 ps), the second lifetime τ_2 related with the S_1 state

lifetime with 18 ns,²⁰ the third related to the triplet lifetime. The fitting was made with five free parameters: ϕ_1 , ϕ_2 , ϕ_3 and τ_2 and τ_3 . The PAC experiment gave $\tau_2 = 20 \pm 1$ ns, which is in very good agreement with the 18 ns of the S_1 state lifetime reported in air-saturated acetonitrile.²⁰ The energy of the S_1 state was 393 ± 63 kJ/mol ($\phi_1 = 0.12 \pm 0.02$), which is also in agreement with the value of the literature of 384 kJ/mol.²⁰ The lifetime τ_3 is the triplet lifetime of naphthalene. The value obtained by PAC, $\tau_3 = 203 \pm 6$ ns, is consistent with triplet state lifetimes of aromatic hydrocarbons in air-saturated solutions. Thus, the naphthalene S_1 state lifetime set the lower limit of 20 ± 1 ns for the transducer with central frequency of 2.25 MHz. These results are summarized in the table 1.

Table 1: S_1 state lifetime τ_2 and energy comparison between PAC and literature values.

	PAC		Literature	
	τ_2 / ns	E_{S1} / kJ/mol	τ_2 / ns	E_{S1} / kJ/mol
9-cyanoanthracene	32 ± 3	283 ± 9	12	297
Carbazole	317 ± 69	306 ± 19	15	347
Naphthalene	20 ± 1	393 ± 63	18	384

Once the experimental limit was determined for the transducer with $f = 2.25$ MHz, the next step was to relate it with the difference between a sample wave $E(t)$ having τ_2 much shorter than the transducer resolution, and sample waves with increasing values of τ_2 . The reference $T(t)$ wave was obtained experimentally for the transducer of 2.25 MHz and fitted with equation (8). The simulated sample $E(t)$ waves were obtained with a bi-exponential kinetic model $H(t)$ using the software described earlier¹⁸ and typical fractions of energy released ($\phi_1 = 0.5$ and $\phi_2 = 0.1$). The procedure to find the time resolution limits of a transducer with a known $T(t)$ wave involves several steps. First we simulate a sample wave with $\tau_2 \approx \tau_1$, which corresponds to zero shift between the $T(t)$ and the sample wave, and name this sample wave $E(t_0)$. $E(t_0)$ differs from $T(t)$ only because the values of ϕ_1 and ϕ_2 do not add up to unity. Next we increase the value of τ_2 to a higher lifetime, calculate a new $E(t)$ wave and obtain the difference between this new sample wave

and that with $\tau_2 \approx \tau_1$, i.e., $\Delta(t) = E(t_0) - E(t)$. Then, we repeat this procedure with increasing values of τ_2 to obtain a series of $\Delta(t)$ difference waves. The procedure is stopped when two successive $\Delta(t)$ difference waves are very similar, which means that the transducer is no longer responding to the increase in τ_2 . This value of τ_2 is the upper limit of measurable lifetime with this transducer (fig. 1). The values of the maxima of the function $\Delta(t) = E(t_0) - E(t)$ are represented in figure 2 for a dense series of τ_2 values, after normalization for the highest value found in the series, using the $T(t)$ wave of the 2.25 MHz transducer. Using different values of ϕ_1 and ϕ_2 did not change the picture presented in fig. 2.

Given the method to estimate the lifetime limits of the 2.25 MHz transducer, we run experiments with HBP using transducers with $f = 1, 10, 100$ and 225 MHz to obtain the instrumental wave $T(t)$ of these transducers. Figure 3 presents the instrumental responses and their simulations with equation 8. The frequencies obtained in the fitting of the $T(t)$ wave of the transducers employed in this study are collected in Table 1. The method to obtain the experimental limits was then applied to these transducers and a sigmoidal dependence was observed for all of them, as shown in fig. 2 for $f = 0.5$ MHz and $f = 100$ MHz. The similarity of the sigmoidal curves suggests that upper and lower lifetime resolution limits should be related to the maxima of the $\Delta(t)$ function much in the same way as the lifetime limits obtained for the 2.25 MHz transducer. Thus, the lifetime resolutions for each transducer were determined assuming the same thresholds as those experimentally obtained for the 2.25 MHz transducer. The lifetime limits presented in Table 2 were calculated from the experimental $T(t)$ for all transducers according to figure 2. Such limits are related with the frequencies of the transducers: higher frequency transducers can resolve shorter lifetimes. Apparently, the shortest lifetime that can be obtained with a 225 MHz transducer is ca. 900 ps. However, the frequencies measured for this transducer are anomalous because of the attenuation of high frequencies by the materials separating the source of the photoacoustic wave from the transducer, namely the 1 cm thick quartz mirror. Figure 4 presents a linear relation between the lower lifetime and the inverse of the transducer frequency, using the highest frequency f_3 of table 1, $\tau = 0.13/f$.

Table 2. Lifetime resolution limits in function of transducers frequencies, nominal and obtained from the fitting.

Central Frequency (MHz)	f_1 (MHz)	f_2 (MHz)	f_3 (MHz)	Lower (ns)	Upper (ns)
0.5	0.17	0.54	0.95	142.0	13,677
1.0	0.4	1.2	1.3	82.0	8,299
2.25	1.5	2.5	4.0	18.5	1000
10*	7.0	8.9	10.9	5.0	129
15	1.6	7.2	15	13.8	1400
20	0.2	17.2	19.2	6.3	689
100	38.1	97.3	104.8	1.0	112
225	26.2	40.3	119.0	0.9	126

* Immersion transducer

Figure 5 presents the Fast Fourier Transforms (FFT) of the experimental $T(t)$ waves in Figure 3 and of the transducer of 225MHz. The frequencies distribution is consistent with that obtained in the fitting of the transducers responses and presented in Table 2. Moreover, the central frequencies agree with those reported by the manufacturer, except for the 225 MHz transducer. The FFT and the fitting of the 225 MHz transducer response show that the frequency components above 130 MHz are not present in the signal detected in PAC. We assign the absence of frequency components higher than 130 MHz to their strong attenuation in the medium where the photoacoustic wave propagates. The PAC cell used in this work uses a 1 cm thick mirror in the back of the cell to protect the transducer from the laser beam and to reflect it back into the sample. The relatively long distance that the ultrasound must travel in the quartz mirror and the stronger ultrasound attenuation at higher frequencies filters the high frequencies of the ultrasound and imposes an instrumental limit on the time resolution of PAC with the “front face” cell. This limitation may be overcome using thinner back mirrors. In theory, using the relation presented above between lifetimes and transducer frequencies, a 225 MHz transducer should be able to resolve 600 ps decays.

Conclusions

We established a criterion and a method to assess the dependence of the lifetime resolution of the PAC technique in the front-face cell configuration on the transducer frequencies. Based on the lifetime resolution

limits obtained experimentally with the transducer of 2.25 MHz, we determined the lifetime resolution limits for a set of transducers with frequencies from 0.5 MHz up to 225 MHz measuring the instrumental response of each of them experimentally and simulating the response in function of the lifetime decay in a two species kinetic model. We demonstrated that is feasible to resolve sub-nanosecond lifetimes using transducers with $f > 100$ MHz. Practical applications of picosecond PAC require an experimental setup with a short distance (< 2 mm) between the source of the PAC signal and its detection with ultrasonic transducers.

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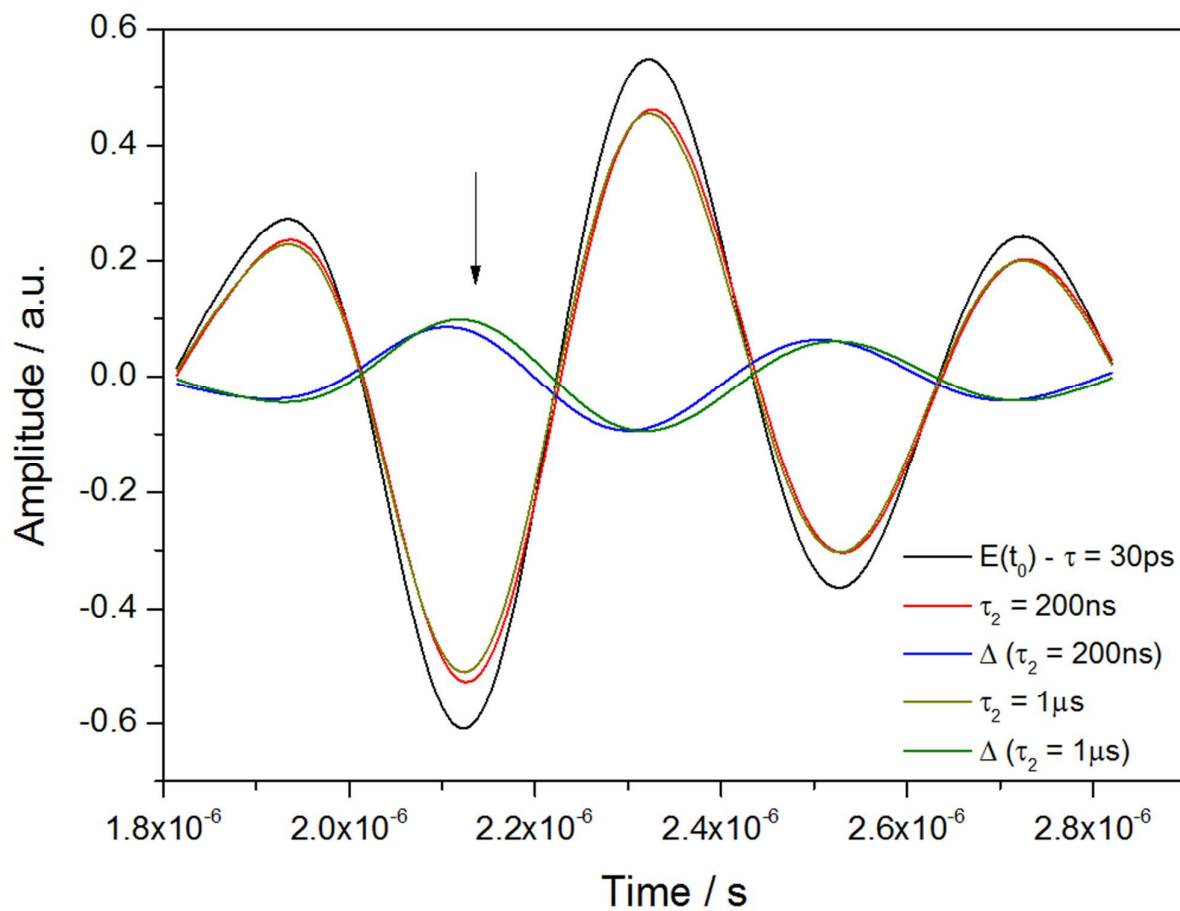


Figure 1. Values of the difference $\Delta(t) = E(t_0) - E(t)$ for $\tau_2 = 200$ ns and $\tau_2 = 1$ μs . The arrow indicates the peak used in the figure 2.

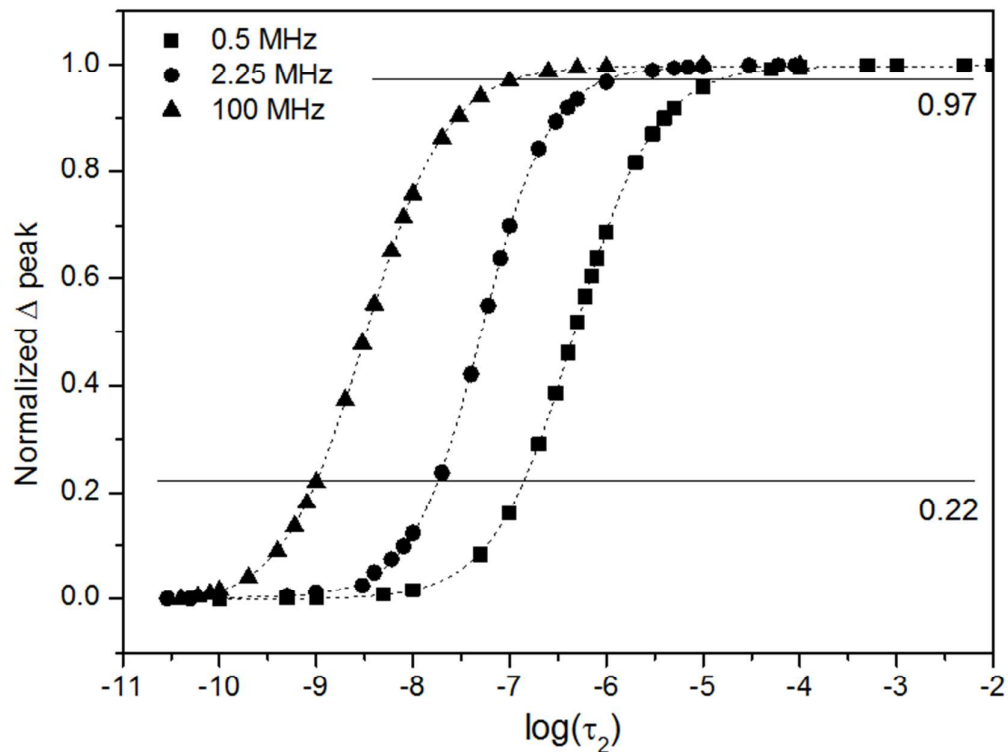


Figure 2: Normalized Δ peak values as a function of the logarithm of τ_2 for the 0.5, 2.25 and 100 MHz transducers. The dotted line represents the sigmoidal curve fitting. Lifetime limits of 20 ns = 0.22 and 1 μ s = 0.97.

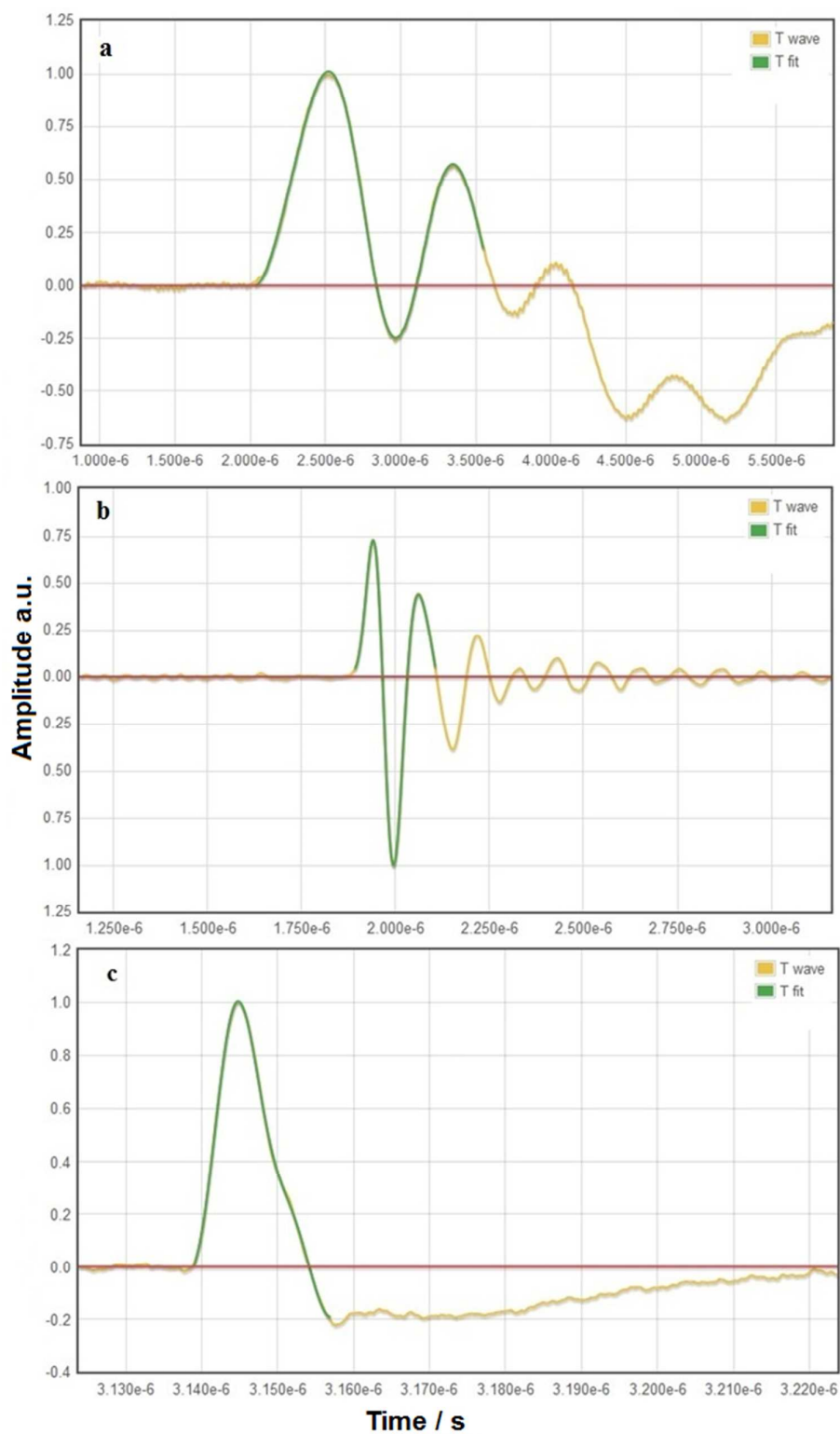


Figure 3. Instrumental T(t) waves (yellow) and respective fittings (green) obtained with the (a) 1 MHz, (b) 10 MHz and (c) 100 MHz transducers. Images from the software¹⁷ for PAC analysis.

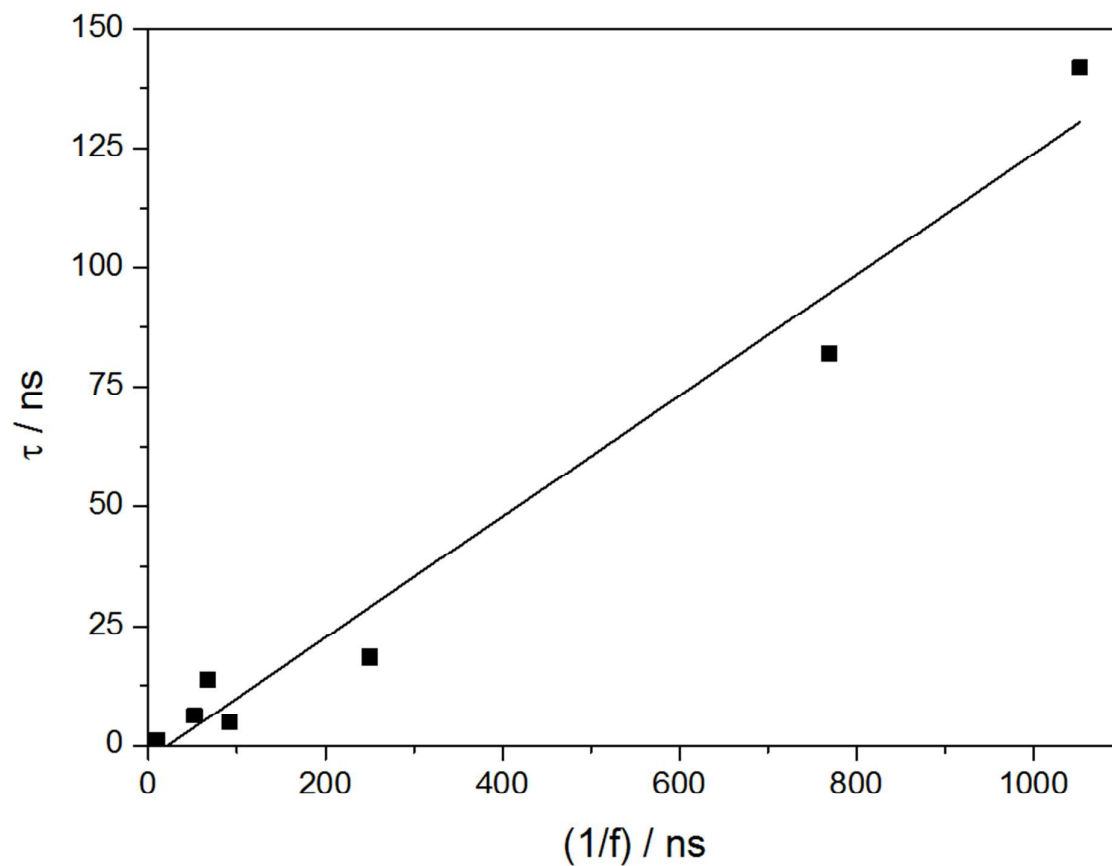


Figure 4: Linear relation between the lifetime resolution and the inverse of the transducer frequency, showing that approximately $\tau = (1/f) * 0.13$.

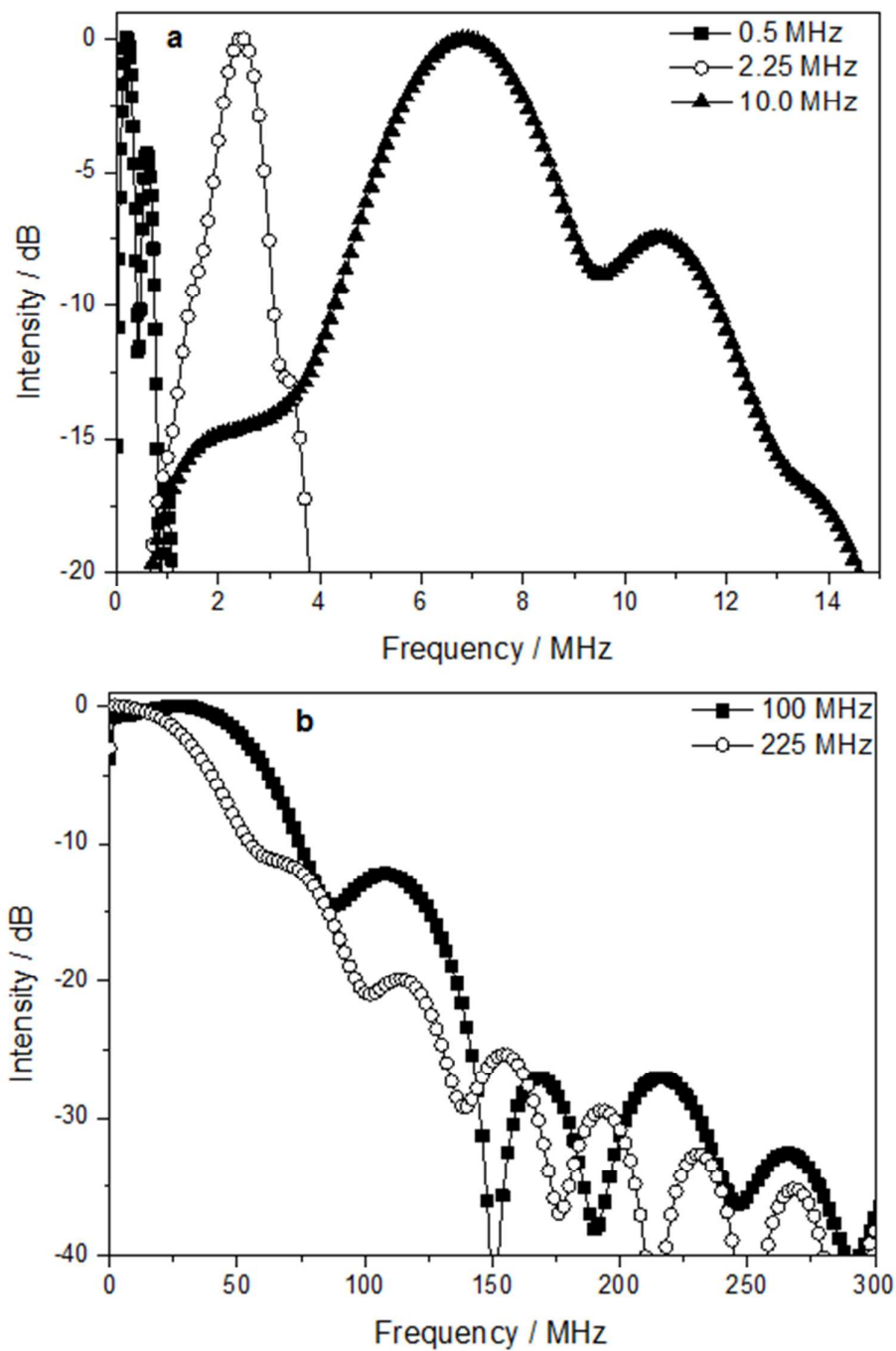
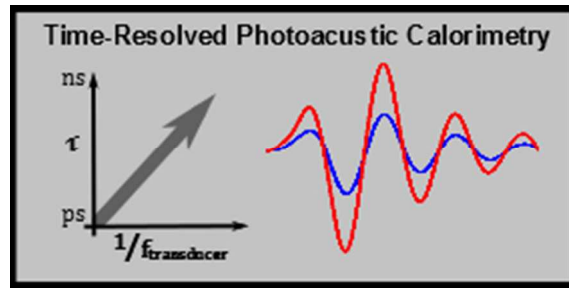


Figure 5: Frequency spectra obtained via Fast Fourier Transform (FFT) of the instrumental waves for (a) low frequency transducers and (b) high frequency transducers.



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