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# Methodical studies on the time resolution of photoacoustic calorimetry

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**Abstract**

A front face illumination set-up and transducers of resonance frequencies between 5 and 100 MHz have been used to explore the lower limit of the time resolution of photoacoustic measurements. A monoexponential test system could be followed quantitatively down to a minimum time constant of 2.5 ns. It was found possible to determine quantitatively a biexponential test system by convolution with five free fit parameters, as long as both slow time constants are in the transducer bandwidth and differ by at least a factor of four. Generally, a reduction in temporal bandwidth and sensitivity is observed on increasing the resonance frequency of the transducer. © 1997 Elsevier Science S.A. All rights reserved.

*Keywords:* Biexponential decay; Monoexponential decay; Photoacoustic calorimetry; Time resolution

## 1. Introduction

Photoacoustic calorimetry (PAC) allows the direct investigation of radiationless processes in the deactivation cascade. It is a valuable method complementing luminescence spectroscopy. The quantitative determination of the amplitude and temporal behaviour of acoustic waves leads to information on the efficiencies, energetics and reaction volumes [1–4]. However, time-resolved measurements of the enthalpy and volume changes have only been taken within a rather restricted time range. The deactivation of most electronically excited molecules occurs in few nanoseconds. Therefore, the extension of the time resolution of PAC to this time scale and the investigation of the possibility of separating consecutive radiationless decays is of great interest.

## 2. Experimental details

Benzophenone (BP, Aldrich 99+%), *cis*-1-phenyl-1-cylohexene (cPCH, Aldrich 95%), acetonitrile (ACN, Aldrich, 99.5%), cyclohexane (CHX, Aldrich 99+%), and KI (Janssen, puriss.) were used as recieved. *o*-Hydroxybenzophenone (HBP, Aldrich, 99%) was crystallized twice from ethanol, and water was doubly distilled. Absorption spectra were recorded on a Hewlett Packard HP 8452A diode array spectrometer. Sample and reference (HBP) solutions were optically matched at the excitation wavelength 337 nm. PAC measurements were performed using a set-up described earlier [5,6]. Briefly, we used the output of a MSC 1600 $N_2$ laser from LTB for excitation (pulse width 0.5 ns, pulse energy 0.7 mJ). The PAC cell is a copy of the front face illumination cell described by Melton and co-workers [7,8]. Its design allows better time resolution compared to the conventional right angle spectroscopic set-up. The distance between the front and rear quartz discs is 0.26 mm. The rear quartz disc is coated on the solution side surface by a dielectric layer with maximum reflectance at 337 nm. The acoustic signals were detected by ceramic transducers pressed against the back side of the rear quartz disc. The thickness of the rear quartz disc of 15 mm is sufficient to decouple the electrical perturbation signals almost completely from the acoustic signals by the sound travel time. Transducers of different resonance frequency (Panametrics A109S (5 MHz), A113R (15 MHz), V213-BA-RM (30 MHz), V2054-BA (100MHz)) were used. The signals were amplified when necessary by an Ortec 9306 1GHz preamplifier and fed to a Tektronix TDS 620A storage oscilloscope with a minimum time resolution of 0.1 ns/channel. Experiments were performed at room temperature with deoxygenated solutions under an Ar atmosphere. Acoustic signals were averaged over 100 laser shots. For each measurement, the laser pulse energy dependence was examined. Only energy linear results were employed. Convolution programs were kindly supplied by Professors R.A. Caldwell and L.A. Melton, University of Texas at Dal-

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las, and by Professor J. Rudzki-Small, Eastern Washington University at Cheney.

## 3. Results and discussion

### 3.1. Time-resolved monoexponential decay

After photoexcitation of a molecule, radiationless deactivation processes very rapidly convert energy into heat. If, in the deactivation cascade, a transient is formed which decays much slower than the rest of the excited species and which can be monitored time-resolved by PAC, a formally biexponential heat release function $H(t)$ is required for evaluation [9]:

$$H(t) = (f_1/\tau_1)\exp(-t/\tau_1) + f_2/\times(\tau_2-\tau_1)\,[\exp(-t/\tau_2)-\exp(-t/\tau_1)] \qquad (1a)$$

$$H(t) = f_1'/\tau_1 \exp(-t/\tau_1) + f_2'/\tau_2 \exp(-t/\tau_2) \qquad (1b)$$

$$f_1' = f_1 + f_2\tau_1/(\tau_1-\tau_2) \qquad (1c)$$

$$f_2' = f_2\tau_2/(\tau_2-\tau_1) \qquad (1d)$$

$\tau_1$ is the time constant and $f_1$ is the fraction of excitation energy released in the very fast relaxation processes, which are only integrally determined by PAC. $\tau_2$ and $f_2$ are the respective parameters of the slow relaxation process. As long as $\tau_1 \ll \tau_2$, the apparent heat fractions are given by $f_1' = f_1$ and $f_2' = f_2$.

In a theoretical analysis of the photoacoustic diagnostics of fast photoinduced processes, it was shown by Puchenko that PAC set-ups with "in line" front face illumination (FFI) allow much better time resolution than PAC set-ups in conventional "right angle" arrangement [10]. It was estimated that for a non-resonant broad frequency response piezoelectric film detector the upper frequency limit in the FFI set-up is $f_{up} = 25$ MHz. Therefore, the lower limit of time resolution for a slow relaxation process as opposed to very fast relaxation with a time constant of $\tau_1 \leq 0.1$ ns for a non-resonant detector is given by $0.1/f_{up} \approx 3$ ns [10,11]. However, this estimate only holds true for a signal-to-noise ratio of about 100, for complete radiationless decay, i.e. $f_2 = 1 - f_1$ and $f_2/f_1 \approx 3$. In fact, the smallest lifetime measurable by PAC depends on the absolute values of $f_1$ and $f_2$, as well as on $f_2/f_1$ [10]. It can be seen from Eq. (1b) that for very small values of $f_1$ or $f_2$, one of the two exponentials becomes very small compared with the second, leading to large uncertainties in the evalation and thus to a deterioration of the time resolution. Since the values of $f_1$ and $f_2$ depend on the products of efficiency and the reaction heat of the considered radiationless processes, the lower limit of time resolution for a given set-up is not an absolute number but depends on the system being investigated.

The quenching of the lowest excited triplet state $T_1$ of BP by KI is a well known test system for the quality of time-resolved PAC measurements [12,13]. After excitation of BP by laser photons of molar energy $E_L$, the $T_1$ state of energy $E_T$ is populated very rapidly, with a time constant $\tau_1 < 0.1$ ns and an efficiency of unity. The fraction of heat evolved in this intramolecular relaxation process, which cannot be temporally resolved by PAC (fast heat), is $f_1 = (E_L - E_T)/E_L$. Quenching by KI deactivates $T_1$ with a time constant $\tau_2 = (k_q[\mathrm{KI}])^{-1}$, where $k_q$ is the rate constant of $T_1$ state quenching. By changing the concentration [KI], $\tau_2$ can be varied in a controlled manner. This intermolecular deactivation step, which releases the fraction of slow heat $f_2 = E_T/E_L$, can be monitored time-resolved by PAC. Although only one decay process ($\tau_2$, $f_2$) is determined time-resolved, the formally two-fold exponential heat release function of Eqs. (1a), (1b), (1c) and (1d) is required for evaluation.

If the absorbance in the FFI PAC cell is smaller than 0.2 on the optical path of 2 · 0.26 mm, then the excitation occurs almost homogeneously and the volume expands almost in phase during the time of about 2 ps that the light needs to cross the cell [7]. Under these conditions, which have been used in the present study, the possible lower limit of the time resolution does not depend on the acoustic transient time. Since the laser pulse width is only 0.5 ns, the lower limit of the time resolution should be determined mainly by the transducer resonance frequency for the given test system. We have used different transducers to study the influence of the resonance frequency on the temporal resolution. Fig. 1 shows the acoustic signals $S(t)$ of the sample and $R(t)$ of the reference recorded with the 30 MHz transducer, as well as the fit $F(t)$ obtained by the Rudzki-Small program with a formally biexponential decay. With one fixed ($\tau_1 = 0.1$ ns) and three free fit parameters ($f_1$, $f_2$ and $\tau_2$), the correct determination of $f_1$, $f_2$ and $\tau_2$ was even possible at $\tau_2 = 2.5$ ns. The same results were obtained with the convolution program of Melton and co-workers. On the left side of Table 1 are listed the values of the fit parameters as a function of [KI] resulting from the 30 MHz experiments. Increasing the quencher concentration from [KI] = 0.125 to 0.250 M (KI was added in equal amounts to solutions of BP and of the reference HBP in order to keep the thermoelastic properties and velocity of sound the same in the sample and reference) resulted in $\tau_2 = 1.2$ ns; however, incorrect values of $f_1$ and $f_2$ were obtained. Obviously, for this set-up and test system the lower limit of time resolution is reached at about 2 ns with a resonant detector. Up to now, the best time resolution has been achieved by Melton and co-workers with a FFI set-up and a home-built non-resonant PAC detector based on a piezoelectric film as active element. These authors obtained for the same test system in a convolution with three free fit parameters a lower limiting value of $\tau_2 = 5$ ns [13]. These results are in accordance with the estimate of about 3 ns theoretically derived by Puchenkov [10].

The temporal bandwidth for time-resolved measurements is only small with the 30 MHz transducer. Above $\tau_2 = 40$ ns, the fraction $f_2$ of slow heat was undercalculated by the convolution program. However, the fraction $f_1$ of fast heat was correct even without added quencher. From the average

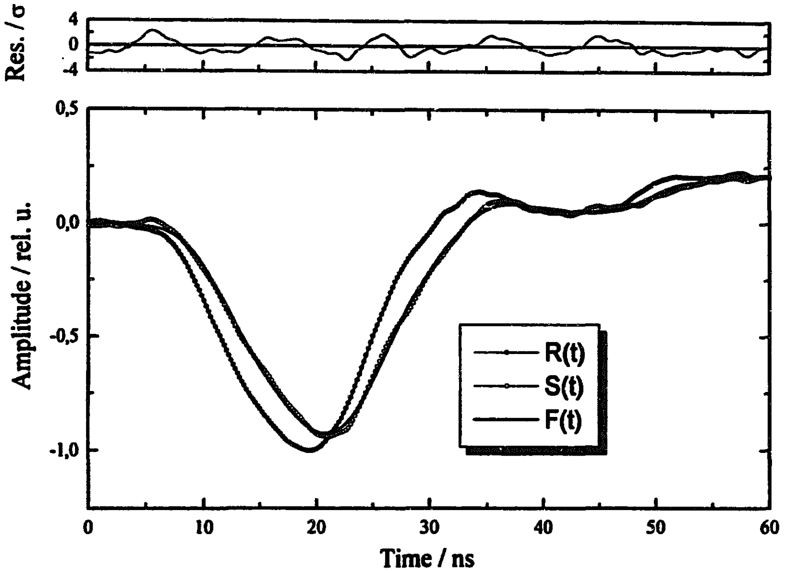

Fig. 1. Acoustic waves $S(t)$ and $R(t)$ of sample BP/KI and reference HBP in ACN/water (4/1) recorded with the 30 MHz transducer. $S(t)$ and $R(t)$ are averages over 100 laser shots. $F(t)$ is the fitted wave, $\tau_2 = 2.5$ ns. The upper display gives the residuals in units of standard deviation $\sigma$ of $S(t)$ from $F(t)$. The vibration of the residuals ( ≈ 100 MHz) is caused by electrical perturbations of the acoustic signals.

$0.192 \pm 0.015$ of all the values of $f_1$, we calculate using $E_L = 354.7$ kJ mol$^{-1}$ the triplet state energy of BP in ACN/water (4/1) as $E_T = 286.7 \pm 5.2$ kJ mol$^{-1}$ in comparison to the literature value of $E_T = 287.4$ kJ mol$^{-1}$ in ACN/water (9/1) [13]. If the result $f_1 = 0.229$ ([KI] = 0.050 M) which deviates distinctly from the rest of the $f_1$ values is omitted, $f_1 = 0.188 \pm 0.010$ and $E_T = 287.9 \pm 3.4$ kJ mol$^{-1}$ are obtained as mean values. Considering only the $T_1$-lifetimes, we note that values of $\tau_2$ are realistic up to 130 ns, indicating that for determinations of time constants the limits of time resolution are wider than for determinations of heat fractions. A plot of $\tau_2^{-1}$ versus [KI] is linear and passes through the origin. The slope is the quenching constant $k_q = (3.23 \pm 0.04) \times 10^9$ M$^{-1}$ s$^{-1}$, which is smaller than the literature values $4.0 \times 10^9$ M$^{-1}$ s$^{-1}$ in ACN/water (9/1) [13] and $7 \times 10^9$ M$^{-1}$ s$^{-1}$ in pure ACN [12]. Obviously, $k_q$ decreases with increasing water content of ACN.

Similar results, which are listed on the right side of Table 1, have been observed in [KI]-dependent experiments with the 15 MHz transducer. The upper limit for accurate values of $f_1$, $f_2$ and $\tau_2$ was reached at $\tau_2 = 143$ ns. However, $T_1$-lifetimes were realistic up to $\tau_2 = 272$ ns, confirming the findings with the 30 MHz transducer that the limits of time resolution are wider for accurate values of the time constant than for accurate values of the heat fractions. The lower limit of time resolution was reached in the three parameter fits at $\tau_2 = 3.9$ ns. The corresponding Stern–Volmer plot is linear. As mean values, we obtained $f_1 = 0.193 \pm 0.007$, $E_T = 286.2 \pm 2.5$ kJ mol$^{-1}$ and $k_q = (3.13 \pm 0.07) \times 10^9$ M$^{-1}$ s$^{-1}$. Accurate values of $f_1$, $f_2$ and $\tau_2$ were found with the 5 MHz transducer in the range 12 ns $\leq \tau_2 \leq$ 400 ns. Thus, the upper and lower limits of time resolution and consequently the temporal bandwidth vary approximately reciprocally with the resonance frequency. The dynamic range of time-resolved measurements

Table 1

Values of fit parameters obtained for the BP/KI test system with the Rudzki-Small program; $\tau_1 = 0.1$ ns, and $\tau_2$, $f_1$ and $f_2$ as fit parameters

| [KI] ($10^{-2}$ M) | $\tau_2{}^{a}$ (ns) | $f_1{}^{a}$ | $f_2{}^{a}$ | $\Sigma f^{a}$ | $\tau_2{}^{b}$ (ns) | $f_1{}^{b}$ | $f_2{}^{b}$ | $\Sigma f^{b}$ |
|---|---|---|---|---|---|---|---|---|
| 0.0 | | 0.180 | | | | 0.188 | | |
| 0.1 | 148 | 0.175 | 0.554 | 0.729 | 272 | 0.185 | 0.718 | 0.903 |
| 0.2 | 130 | 0.173 | 0.736 | 0.909 | 143 | 0.185 | 0.787 | 0.972 |
| 0.4 | 70.4 | 0.183 | 0.733 | 0.916 | 66.6 | 0.203 | 0.764 | 0.967 |
| 0.8 | 37.6 | 0.188 | 0.798 | 0.986 | 36.2 | 0.194 | 0.783 | 0.977 |
| 1.6 | 22.0 | 0.196 | 0.804 | 1.000 | 18.6 | 0.196 | 0.790 | 0.986 |
| 2.5 | 12.0 | 0.194 | 0.789 | 0.983 | 11.8 | 0.204 | 0.784 | 0.988 |
| 3.5 | 8.3 | 0.203 | 0.764 | 0.972 | 8.2 | 0.193 | 0.808 | 1.001 |
| 5.0 | 6.5 | 0.229 | 0.756 | 0.985 | 6.8 | 0.186 | 0.812 | 0.998 |
| 6.5 | 4.6 | 0.193 | 0.788 | 0.981 | 4.9 | 0.198 | 0.800 | 0.998 |
| 8.0 | 3.8 | 0.189 | 0.799 | 0.988 | 3.9 | 0.188 | 0.800 | 0.988 |
| 12.5 | 2.5 | 0.193 | 0.790 | 0.983 | 2.6 | 0.314 | 0.708 | 1.022 |
| 25.0 | 1.2 | 0.336 | 0.680 | 1.016 | 1.6 | 0.391 | 0.630 | 1.021 |

[a] 30 MHz transducer.

[b] 15 MHz transducer.

defined as the ratio of the respective limiting time constants remains almost constant for the transducers investigated with values of 20 (30 MHz), 35 (15 MHz) and 33 (5 MHz). However, the sensitivity of the PAC measurements decreases strongly with increasing resonance frequency.

Experiments with the 100 MHz transducer led only to very noisy signals, which could not be evaluated quantitatively. The damping of the acoustic signal grows strongly in the high frequency range. As a matter of fact, preliminary experiments with a 1 GHz acoustic lens demonstrated an enormous damping of the acoustic signals in aqueous solution. In organic solvents, the damping is even stronger. Therefore, these results led to the conclusion that the lower limit of time resolution of about 2 ns is general applicable to time-resolved PAC measurements with a FFI cell.

### *3.2. Time-resolved biexponential decay*

With a set-up of suitable time resolution, it is possible to extend PAC measurements to electronically excited systems using two consecutive radiationless decays with different time constants $\tau_2$ and $\tau_3$. This problem was studied systematically by Rudzki-Small et al., who investigated triplet–triplet energy transfer (TTET) from BP($T_1$) to 2,5-dimethyl-2,4-hexadiene (DMH) in ACN [9]. DMH($T_1$) decays with the lifetime $\tau_3 = 44$ ns, distinctly different from the [DMH]-dependent TTET time constant $\tau_2$ which varied from 71 to 1500 ns. Nevertheless, successful fits with a formally three-fold exponential heat release function ($\tau_1, f_1, \tau_2, f_2, \tau_3, f_3$) could only be performed if three of the six fit parameters ($\tau_1 = 0.1$ ns, $\tau_3, f_3$) were fixed. Thus, only the first of both slow heat release processes could quantitatively be evaluated. This result can be understood on the basis of the above-described experiments. Because of the reciprocal relation between the resonance frequency of the transducer and the lower limit of time resolution, the latter is estimated to lie at about 60 ns from the experiments of Rudzki-Small et al. with the 1 MHz transducer, indicating why the faster heat release could not be determined time-resolved.

The TTET from BP to DMH in acetonitrile was also studied by Puchenkov and Malkin [11] using a FFI PAC set-up. Again, successful fits with a formally three-fold exponential heat release function could only be performed if three of the six fit parameters ($\tau_1 = 0.1$ ns, $f_1$, $\tau_3$) were fixed. Nevertheless, the results obtained appear unrealistic. The rate constant of energy transfer is calculated from their values of $\tau_2$ by a Stern–Volmer plot as $k_{ET} = (2.1 \pm 0.3) \times 10^{10}\ M^{-1}\ s^{-1}$. This value is far too large for a diffusion controlled reaction and distinctly surmounts the realistic value of $k_{ET} = 7.7 \times 10^9$ $M^{-1}\ s^{-1}$ given by Rudzki-Small et al. [9]. The reason for the deviation is not known. One possible factor was the choice of an unsuitable [DMH] range only allowing for values of $\tau_2$ ranging from 10 to 169 ns, which are not far enough apart from $\tau_3 = 44$ ns (vide infra).

The only researchers to report the successful determination of a time-resolved biexponential decay by PAC with five free fit parameters were Goodman et al. [14], who investigated TTET from $T_1$(BP) to cPCH by means of a slow transducer. According to the scheme of Fig. 2, the heat released in the first fast relaxation step to BP($T_1$) is given by $f_1 = (E_L - E_T^{BP})/E_L$. The time constant $\tau_2$ of TTET varies with [cPCH]. Keeping [cPCH] $\geq 10^{-3}$ M ensures complete deactivation of BP($T_1$) by diffusion controlled TTET. The first fraction of slow heat is thus given by $f_2 = (E_T^{BP} - E_T^{cPCH})/E_L$. Goodman et al. chose [cPCH] = 0.1 M. In this way, they obtained the sum $f_1 + f_2 = 0.36 \pm 0.04$ as the fraction of fast heat in their experiments in CHX. cPCH($T_1$) forms the ground state of the trans isomer tPCH with quantum yield $\phi_{ct}$ and decays in competition to ground state cPCH with quantum yield $1 - \phi_{ct}$. The energy difference between tPCH and cPCH is $E_{tPCH}$. Therefore, the second fraction of slow heat is $f_3 = (E_T^{cPCH} - \phi_{ct} E^{tPCH})/E_L$. Time-resolved measurement of this decay was made by Goodman et al., who determined $f_3 = 0.44 \pm 0.04$ and $\tau_3 = 66 \pm 8$ ns. tPCH is only metastable and goes back to cPCH. The isomerization is much slower and was the second time-resolved relaxation process to be monitored by Goodman et al. Values of $f_4 = 0.20 \pm 0.03$ and $\tau_4 = 9.4 \pm 2.5$ μs were obtained. Thus, a quantitative separation of two slow heat release processes, whose time constants differ by a factor of 150, could be achieved by means of a slow transducer of about 0.25 MHz resonance frequency (estimated from the halfwidth of the first acoustic halfwave of about 2 μs compared with the respective value of 90 ns for a 5 MHz transducer). Obviously, their transducer had a particularly wide band responsivity, even allowing determination of the relatively fast 66 ns decay.

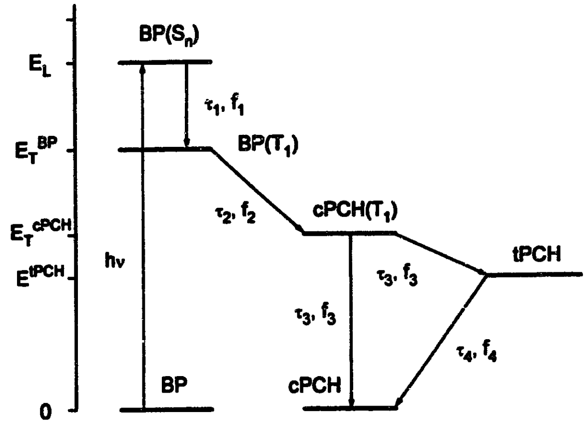

Fig. 2. Energy level scheme for the sequential radiationless decays in the system BP/cPCH.

It was of interest to find the limits of the time constants within which separate determination of the fractions $f_1$, $f_2$ and $f_3$ is possible. Therefore, tuning of $\tau_2$ was required. [cPCH] was varied between $5.7 \times 10^{-3}$ and $4.0 \times 10^{-2}$ M. Experiments with the 5 MHz transducer did not result in correct determination of $f_1$, $f_2$ and $f_3$. Presumably, the response of the 5 MHz transducer is too slow for a quantitative separation of two decays with $\tau_2 < \tau_3 \approx 70$ ns, although a single exponential decay with $\tau_2 = 12$ ns could be resolved with this detector. The PAC waves recorded with the 15 MHz transducer were

Table 2
Values of fit parameters obtained for the BP/cPCH test system with the Rudzki-Small program; $\tau_1 = 0.1$ ns, 15 MHz transducer

| [cPCH] ($10^{-3}$ M) | $\tau_2$ (ns) | $\tau_3$ (ns) | $f_1$ | $f_2$ | $f_3$ | $\Sigma f$ |
|---|---|---|---|---|---|---|
| 15 | 42.0 | 79.5 | 0.212 | 0.337 | 0.241 | 0.790 |
| 17 | 18.4 | 68.3 | 0.213 | 0.173 | 0.359 | 0.745 |
| 18 | 14.4 | 77.8 | 0.190 | 0.167 | 0.429 | 0.786 |
| 20 | 13.6 | 70.3 | 0.207 | 0.156 | 0.386 | 0.749 |
| 22 | 12.8 | 68.7 | 0.204 | 0.152 | 0.407 | 0.763 |
| 25 | 12.2 | 73.5 | 0.208 | 0.164 | 0.397 | 0.769 |
| 29 | 9.6 | 72.5 | 0.201 | 0.152 | 0.418 | 0.771 |
| 33 | 8.3 | 73.2 | 0.193 | 0.156 | 0.430 | 0.779 |
| 40 | 7.2 | 75.7 | 0.193 | 0.157 | 0.440 | 0.790 |

first evaluated with the convolution program of Rudzki-Small et al. [9]. The acoustic waves $S(t)$ are fitted by convolutions of $R(t)$ with the heat release function $H(t)$:

$$H(t) = f_1'/\tau_1 \exp(-t/\tau_1) + f_2'/\tau_2 \exp(-t/\tau_2) + f_3'/\tau_3 \exp(-t/\tau_3) \quad (2a)$$

$$f_1' = f_1 + f_2\tau_1/(\tau_1-\tau_2) + f_3\tau_1^2/(\tau_1-\tau_2)/(\tau_1-\tau_3) \quad (2b)$$

$$f_2' = f_2\tau_2/(\tau_2-\tau_1) + f_3\tau_2^2/(\tau_2-\tau_1)/(\tau_2-\tau_3) \quad (2c)$$

$$f_3' = f_3\tau_3^2/(\tau_1-\tau_3)/(\tau_2-\tau_3) \quad (2d)$$

The fit parameters $f_1'$, $f_2'$ and $f_3'$ depend on the true heat fractions and the time constants $\tau_1$, $\tau_2$ and $\tau_3$, which also have to be fitted. Therefore, they cannot be set constant, even if the true heat fractions $f_1$, $f_2$ and $f_3$ are known. Only if the condition $\tau_1 \ll \tau_2$, $\tau_3$ holds true is Eq. (2b) replaced by $f_1' = f_1$. The evaluation was carried out with $\tau_1 = 0.1$ ns and five free fit parameters: $\tau_2$, $\tau_3$, $f_1'$, $f_2'$ and $f_3'$. From the results and Eqs. (2b)–(2d), values of $f_1$, $f_2$ and $f_3$ have been calculated which are given in Table 2. Inspection of the data demonstrates that both radiationless decays are well separated for $7.2 \le \tau_2 \le 18.4$ ns. Separation is also achieved for [cPCH] = 0.015 M: however, the value of $\tau_2$ is found to be too large. Omitting the data for this concentration, we obtain as mean values $f_1 = 0.201 \pm 0.008$, $f_2 = 0.160 \pm 0.007$, $f_3 = 0.408 \pm 0.025$ and $\tau_3 = 72 \pm 3$ ns. The sum $f_1 + f_2 = 0.361 \pm 0.015$, $f_3$ and the decay time $\tau_3$ agree very well with the literature data (see above). From the value of $f_1$, we obtain for BP in CHX $E_T = 283.3 \pm 2.8$ kJ mol$^{-1}$ compared with $287.9 \pm 3.4$ kJ mol$^{-1}$ in acetonitrile/water (4/1). Since the triplet is of $n\pi^*$ configuration, a hypsochromic shift of $T_1$ is actually expected. The sum $f_1 + f_2$ yields $E_T^{\mathrm{cPCH}} = 227 \pm 5$ kJ mol$^{-1}$ in agreement with the literature value $227 \pm 14$ kJ mol$^{-1}$ [14]. Since the value of $\phi_{ct}$ for CHX is not known, calculation of $E^{\mathrm{tPCH}}$ is prevented [14]. The quantitative separation of two fast radiationless decays is achieved as long as $\tau_3/\tau_2 \ge 4$. From a plot of $\tau_2^{-1}$ versus [cPCH] we obtain for the rate constant of the diffusion controlled TTET $k_{ET} = (3.6 \pm 0.3) \times 10^9$ M$^{-1}$ s$^{-1}$. This result gives good agreement with the value $k_{ET} = 5.0 \times 10^9$ M$^{-1}$ s$^{-1}$ determined for the diffusion controlled TTET from thioxanthone to cPCH in benzene [15], if the different viscosities of benzene (0.62 cP) and CHX (1.02 cP) are considered.

The same acoustic waves have been evaluated with the convolution program of Melton et al., which uses Eq. (3) for the heat release function [7]:

$$\begin{aligned} H(t) = {} & (f_1/\tau_1) \exp(-t/\tau_1) + f_2/(\tau_2-\tau_1) \\ & \times [\exp(-t/\tau_2) - \exp(-t/\tau_1)] + f_3/(\tau_1-\tau_3)/ \\ & \times (\tau_1-\tau_2)/(\tau_2-\tau_3)[\tau_1(\tau_2-\tau_3)\exp(-t/\tau_1) \\ & - \tau_2(\tau_1-\tau_3)\exp(-t/\tau_2) + \tau_3(\tau_1-\tau_2) \\ & \times \exp(-t/\tau_3)] \end{aligned} \quad (3)$$

Probably because of the sum of six exponentials, the Melton program is distinctly slower than that of Rudzki-Small et al., which further profits from the use of refined algorithms developed originally for single photon counting software [9]. However, the Melton program allows known fractions of the heat constant to be set. This can be a great advantage if thermodynamic information about the system under investigation is already to hand. Of course, this procedure ignores the risk of overlooking photoinduced volume changes, which could also contribute to the amplitudes of the photoacoustic waves, particularly in aqueous systems where thermal induced volume changes are relatively small because of the low thermal expansion coefficient of water. Therefore, it is only recommended to set constant calculated values of $f$ if photoinduced structural volume changes or electrostriction effects can be excluded. With $\tau_1 = 0.1$ ns and five free fit parameters, no separation of decays was possible. Obviously, the program of Rudzki-Small et al. is superior under such conditions. However, setting $f_1 = 0.201$, $f_2 = 0.160$ and $\tau_1 = 0.1$ ns, the program converges with three free fit parameters: $\tau_2$, $\tau_3$, and $f_3$. The resulting data, which are listed in Table 3, reveal that for [cPCH] $\ge 0.025$ M the values of $\tau_3$ and $f_3$ are significantly larger than the corresponding averages of the rest of the data. Actually, for these concentrations the

Table 3
Values of fit parameters obtained for the BP/cPCH test system with the Melton program; $\tau_1 = 0.1$ ns, $f_1 = 0.201$, and $f_2 = 0.160$, 15 MHz transducer

| [cPCH] ($10^{-3}$ M) | $\tau_2$ (ns) | $\tau_3$ (ns) | $f_3$ |
|---|---|---|---|
| 5.7 | 38.6 | 71.5 | 0.440 |
| 6.7 | 35.1 | 66.3 | 0.385 |
| 8.0 | 30.1 | 69.0 | 0.393 |
| 9.5 | 26.4 | 71.5 | 0.431 |
| 12 | 22.8 | 71.0 | 0.382 |
| 15 | 17.8 | 74.6 | 0.418 |
| 17 | 15.7 | 74.2 | 0.403 |
| 18 | 14.9 | 76.7 | 0.420 |
| 20 | 14.1 | 71.7 | 0.401 |
| 22 | 13.1 | 70.6 | 0.418 |
| 25 | 11.4 | 77.7 | 0.435 |
| 29 | 10.3 | 78.0 | 0.433 |
| 33 | 9.3 | 77.3 | 0.429 |
| 40 | 8.0 | 79.3 | 0.440 |

values of $\tau_2^{-1}$ level off moderately from the straight line in the Stern–Volmer plot. From the results for [cPCH] < 0.025 M, we obtain with the mean values $\tau_3 = 72 \pm 3$ ns, $f_3 = 0.410 \pm 0.020$ and $k_{ET} = (3.2 \pm 0.1) \times 10^9$ M$^{-1}$ s$^{-1}$, which are practically the same as in the evaluation with the Rudzki-Small program. However, separation of both slow decays is achieved even for $\tau_3/\tau_2 \approx 2$. This is a remarkable result, but it should be kept in mind that of course less parameters are extracted from the acoustic waves. The possibility of setting known values of $f$ constant in the evaluation procedure is sometimes a great advantage, and makes the program of Melton et al. an interesting and valuable complement to the Rudzki-Small program. However, it should be noted that in the mean time a more developed version of the Rudzki-Small program has become commercially available (Sound Analysis 3000 version 13.1, Quantum Nothwest, P.O. Box 30430, Spokane, WA 99223-3007, USA) which is able to fit a consecutive model with fixed values of $f$ and to combine the advantages of the two programs investigated in this study.

## 4. Conclusions

It has been shown that the lower limit of the time resolution of PAC measurements of a single exponential decay lies at about 2 ns with a front face illumination cell. Thus, caloric measurements of excited states with lifetimes > 2 ns are possible if the respective fraction of heat released is not too small ($f_2 > 0.3$). Actually, this set-up has already been used successfully for a PAC study of the equilibrium between the local excited singlet state and the charge transfer singlet state of 9,9-bianthryl [16]. Investigation of the biexponential radiationless decays demonstrates that separation of sequential decays by PAC measurements with a single transducer is usually expected if the time constants $\tau_2$ and $\tau_3$ differ by a factor of at least four, if both time constants are within the transducer bandwidth and if the apparent fractions of slow heat are non-negligible ($f_1', f_2' > 0.2$). Generally, a reduction in temporal bandwidth and sensitivity is observed on increasing the resonance frequency of the transducer.

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