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RESEARCH ARTICLE OPEN

Photo-Acoustic Linear and Circular Dichroism

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An instrument for measurement of photo-acoustic linear dichroism (PALD) using continuously modulated light polarization is presented. It allows direct detection of differential heat dissipation, for orthogonal light polarizations, in a macroscopically oriented sample in contact with a piezo-electric transducer. PALD in combination with ordinary linear dichroism (LD) from transmission measurement of linearly polarized light, is suggested as a tool for studying de-excitation mechanisms in ordered systems. PALD also extends LD applications to turbid and semi-opaque samples. Preliminary results indicate that the probability of radiation-less dissipation in aromatic dye molecules macroscopically aligned in a stretched poly(vinyl alcohol)matrix depend on the orientation of the molecular frame relative to the polymer chains, which can provide information about perturbation and heat transfer mechanisms in an anisotropic environment. The possibility of measuring photo-acoustic circular dichroism (PACD) is also briefly discussed with applications to turbid or strain-birefringent samples, for example, for comparison of conformation between liquid and crystalline powder samples.

Dedicated to Professor Josef Michl on his 80th birthday and in memory of our friends, polarized spectroscopy pioneer Professor Erik W. Thulstrup, and electronics genius Mr Simon Danielsson, who all three contributed in different ways to this study.

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I. INTRODUCTION

I will here report on some experiments I should have reported long ago, but the days have slipped by and the weeks and now 42 years have passed. Unfortunately, this means that results that were considered preliminary at the time when obtained will remain preliminary since the equipment is long gone, having been a victim of ferocious department heads who think all old equipment must be destroyed to make room for more modern-looking equipment. Despite the long time that has elapsed, however, the instrument design, electronics and signal-to-noise performance make the technique interesting and compatible also today, and should be applicable in various contexts of photo-activation energy transfer. One application, of emerging importance, is to assess the energy transfer mechanisms of matrix-bound molecules in solar energy harvesting devices.

The idea of the photoacoustic spectroscopy goes back one and a half century to Alexander Graham Bell who invented the 'spectrophone' as an analytical tool for measuring light absorption of both transparent as well as opaque materials.[1]In all experiments, reported so far to the best of my knowledge, periodically interrupted or single-pulsed light is incident on the absorbing sample which is in contact with a microphone or some other pressure-sensitive transducer. The amount of thermally deexcited energy is then detected from the amplitude of the pressure oscillations occurring at the light-chopping beat frequency: in Bell's case the chopper was the needle-holder of his wife's sewing machine and the acoustic detection was a rubber tubing between a soot-covered glass funnel containing air and his ear (a humming sound to be heard). By way of contrast, the experiment I report on here is based on a constant-intensity light beam with modulated polarization and a phase-sensitive detection of dissipation anisotropy. Despite the elapse of time, and interesting novel developments in the field of photoacoustic spectroscopy, there are still advantages that can make our device worth considering even today.

The fundamentals of photoacoustic spectroscopy were reported almost50 years ago by Rosenczwaig[2,3] in terms of a general theoretical framework for applications to gas as well as liquid and solid samples. More recent applications include analytical cavity-enhanced laser detection,[4] chirality and circular dichroism detection in materials,[5,6] and several examples of tomographic applications in material science and in medicine.[7-10] The applications of PALD could complement those described by Josef Michl and Erik Thulstrup in their great textbook on spectroscopy with polarized light for studying solute alignment by photoselection, liquid crystals, polymers, and membranes.[11]

II. MATERIALS & METHODS

The piezoelectric transducer was a $BaTiO_3$ cylindrical disc, diameter 19 mm, height 7 mm, a gift from Josef Michl when I visited him in 1978 in his laboratory at the Chemistry Department of the University of Utah in Salt Lake City. Josef Michl and Erik Thulstrup had been pursuing some photo-acoustic experiments with similar transducers, using chopped light, but were annoyed by an inconvenient acoustic noise sensitivity, a special challenge when students were playing football in the hallway.

In order to increase the pressure sensitivity by decreasing the surface area to fit the sample size and focused optical aperture, the disc was cut with a diamond saw to final dimensions 5 mm x 6 mm (height still 7 mm). This tablet was mounted between aluminum foils (serving as electrodes) in an IR cell holder, pressed between two 7 mm thick isotropic silica windows with the rear aluminum foil serving as back mirror, in immediate contact with the sample, a 0.05 mm thick stretched poly(vinyl alcohol) film containing 9-aminoacridine.The 9-amino acridinium chloride was commercial *pro analysi* grade and oriented PVA samples were prepared as described elsewhere.[12,13] Absorbance measured with unpolarized light was at maximum ca 0.3 for the 0-0 transition at 428 nm. By trial and error we found that an optimal sound-damping effect was obtained with 5 mm thick lead plate, welded into an air-tight cubic box with ca 15 cm sides in which both sample and pre-amplifier were contained.

The principles of the instrument are shown in Figure 1. As a light source, and including a lock-in amplification system, a JASCO J-40 spectro-polarimeter was used and modified as follows. Its 450 W Xe arc lamp provided after passage through a double polarizing quartz prism monochromator an intense monochromatic beam, which was focused by a silica lens, f = 10 cm, on to the sample PVA film with an effective final illumination aperture of ca 2 mm x 5 mm at a monochromator slit opening 0.5 mm and 6 mm x 5 mm at a wide open slit 5 mm.

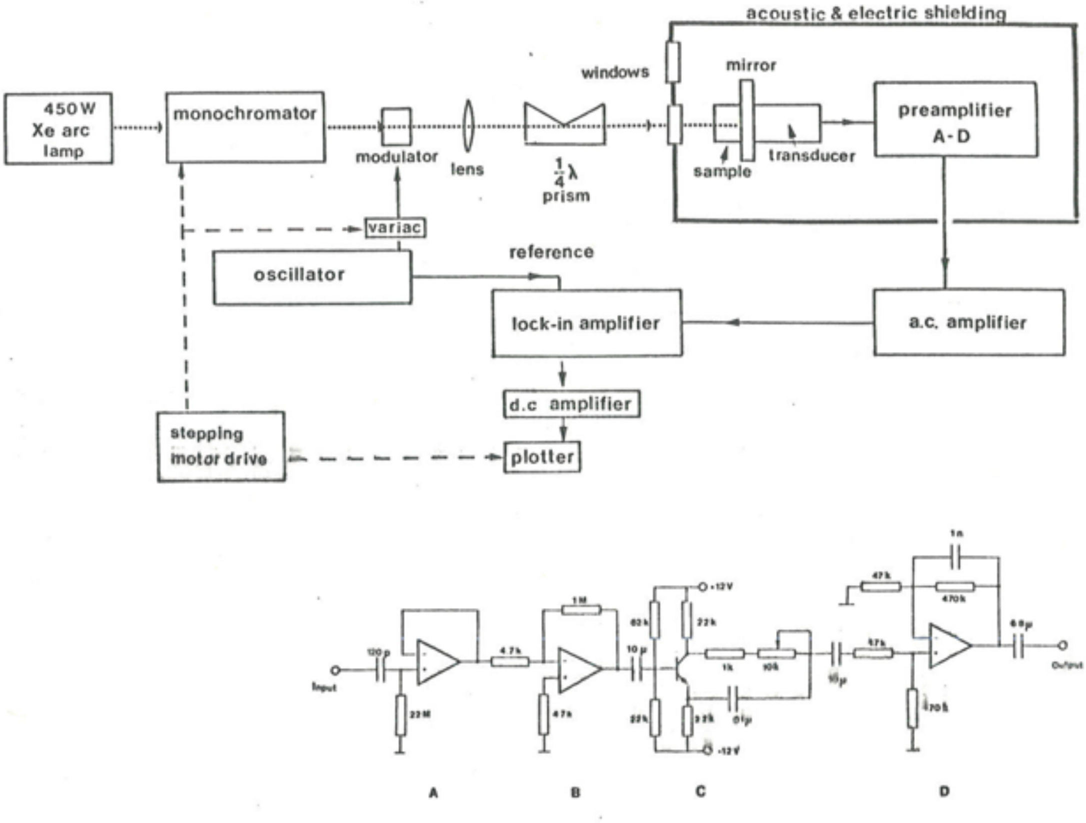

FIG 1

Figure 1. Instrument principles. The beam from the J-40 is focused through a fused-silica window on the sample film in mechanical contact with the $BaTiO_3$piezoelectric transducer screwed tight together in an IR cell holder. The pre-amplifier (scheme shown) and sample set-up were all contained inside an acoustic and electric

shielding, a cubic box made of lead. A more sophisticated pre-amplifier (see Supplementary Information) was found to give a significantly improved signal to noise signal.

The modulator is a Pockels cell producing circularly polarized light, or rather a beam with continuously modulated polarization resulting from a sinusoidal alternating voltage at 370 Hz on the Pockels cell, and a Variac coupled to the monochromator drive to produce a constant-amplitude electric birefringence of quarter-wave retardation giving an optimized Bessel coefficient J_1in the Fourier expansion of the CD signal to be recorded (see below). An achromatic quarter-wave device (Oxley prism of fused Suprasil)[14]oriented at 45° from horizontal direction converted the circular polarization to linear ditto with principal axes vertical and horizontal. The conversion of a CD instrument to LD measurement has been described and analyzed in detail using Stokes-Mueller algebra.[14,15]

The pressure signal from the $BaTiO_3$ transducer was fed into a pre-amplifier as shown in the figure. Mr Simon Danielsson constructed a second pre-amplifier (see Supplementary Information) with much improved performance and lower noise level having a band-pass tuned to 370 Hz, which increased the signal-to-noise ratio by almost an order of magnitude, typically reading out LD with a noise equal to about 10^{-5} absorbance units in the high intensity Xe arc region 400-550 nm, and 10^{-4} or worse in other regions. The lead chamber made the system apparently both acoustically and electrically (Faraday cage) isolated. The LD signal was calibrated as described elsewhere.[16]

The effect of phase-modulation is as follows. The signal from the transducer (and pre-amplifier) is a sinusoidal weak (mA) alternating current in phase with the sinusoidal modulation voltage on the Pockels cell, or to be more exact with an effective time delay ρas a result of the thermal relaxation and finite lifetime of the excited molecule. In contrast to normal CD instruments where the DC current is also recorded, and CD evaluated as an <AC>/DC current ratio, with our set-up we may only record the AC component:

$$I_{\omega t} = K \sin [\delta_0 \sin \omega(t-\rho)]\, e^{-\varepsilon Cd}\, \mathrm{PALD} \qquad (1)$$

assuming a small absorbance A= εCd and a small PALD = A(par)-A(perp) with A(par) and A(perp) denoting the absorbances measured with polarization parallel and perpendicular to the principal sample axis, respectively. Here K is a constant, ε molar extinction coefficient, C concentration, and d path length. A Fourier series expansion:
$\sin [\delta_0 \sin \omega(t-\rho)] = 2J_1(\delta_0) \sin \omega(t-\rho) + 2J_3(\delta_0) \sin 3\omega(t-\rho)$ + higher order terms,
with ω signal optimized at $J_1(\delta_0) = 0.58$ at $\delta_0=1.8$, we get in case retardation ρ may be assumed small (with ns excited molecular lifetimes, we have $\rho<10^{-8}$ sec, and thus negligible at 370 Hz modulation frequency):

$$\langle I_\omega \rangle = K' e^{-\varepsilon Cd}\, \mathrm{PALD} \qquad (2)$$

with $K'= 2J_1(\delta_0)$ from which expression the PALD is evaluated. Note that birefringence modulation optimizing the J_1 term corresponds to traditional detection of circular dichroism, at frequency ω, as a result from the quarter-wave effect changing the polarization of light from circular to linear.

III. RESULTS AND DISCUSSION

We will follow standard notations of polarized light spectroscopy.[11,13] The transmission LD of the film was -0.050±0.005 absorbance units at the absorption maximum at 400 nm (0-1 transition) as measured on a Cary spectrophotometer equipped with Glan polarizers in the two channels. The 'reduced' LD is defined as[13]
$LD^r = 3[A(par) – A(perp)]/[A(par)+2A(perp)]$,
with A(par) and A(perp) denoting the absorbances measured with polarization parallel and perpendicular to the film's stretch direction, respectively. LD^r= -0.11 ± 0.03 for the 380-440 nm band (a purely y-polarized A_1->B_1 transition)[12] and +0.95±0.07 for the 250-270 nm (a purely z-polarized A_1->A_1)[12] transition, with z denoting the longaxis and y the short in-plane axis of the acridinium molecular frame. This means that the orientation of the acridinium molecule with long-axis parallel to the stretch direction is not perfect, but only some 30%:

S_{zz}= 0.95/3 = +0.32
S_{yy}=-0.11/3= - 0.04
S_{xx}=-0.32+0.04 =-0.28
obtained from $\Sigma S_{ii} = 0$.

Order parameters S_{ii} for molecular symmetry axes i=x,y,z defined as usual.[11,13]

That $S_{yy}>S_{xx}$ is consistent with the preference of the in-plane short-axis to align parallel with the poly(vinyl alcohol) chains, and the normal x perpendicular to the chains, i.e. the 9-aminoacridinium does not exhibit a rod-like orientation distribution but rather, as expected, that of a rectangular sandwich.

The photo-acoustic LD (PALD) spectrum is characterized by a perfectly flat base-line LD=0±10^{-5}over the entire wavelength region 230-

650 nm tested in absence of sample. Also, with sample, the baseline is completely flat outside the absorption region. This is consistent with considerably less sensitivity of the piezoelectric detector than a photomultiplier to the polarization state of light (an effect likely due to strain birefringence in the photomultiplier windows or to metallic reflections in the grid material in the PM tube). This constant background of the PALD instrument facilitated greatly the analysis of the spectral shape of the sample absorption bands. The spectral shape of PALD was found almost identical to the transmission LD spectrum, as expected, and the PALD sensitivity was high compared to the two-spectra measured LD, with a typical noise level of $\pm 10^{-5}$ absorbance units in the region 400-500 nm and $\pm 10^{-4}$ in other regions with less intense Xe radiation. The instrument response was tested using an aluminum foil sooted in a candle flame, as sample, and calibrated using a tilted fused silica slide,[16] put into the beam preceeding the sample, outside the lead house, which when rotated 90° showed a perfectly symmetric (opposite sign) PALD signal varying with wavelength in the expected manner.[16,11]

The shape of PALD of the oriented 9-aminoacridinium sample followed the absorbance profile yielding, like the transmission LD,[12] a constant reduced dichroism. However, a slight deviation (by some 10%) in the positive direction was seen at long wavelength, in the tail of the 0-0 transition. A possible source of this deviation could be a stronger fluorescence quantum yield via the 0-0 channel, than the 0-1 and 0-2 transitions, and/or to that a fraction of poorly oriented acridinium molecules having their short in-plane axes parallel with the poly(vinyl alcohol) chains display a stimulated degree of dissipation (positive PALD) due to contact with the matrix for the y-polarized transition. An observation in support of the latter hypothesis was that the deviation tended to be smaller the better the orientation in a range of PVA films stretched uniaxially 200-500%.

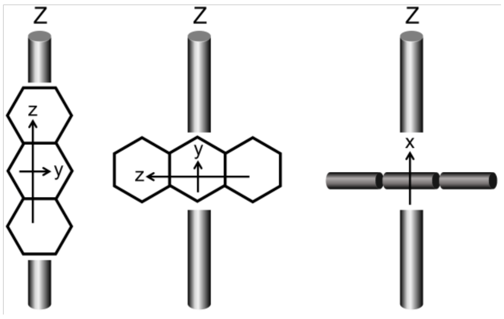

Figure 2. The three principal orientations of the acridinium skeleton relative to the PVA chains corresponding to S_{zz} =1 (left), S_{yy} =1 (middle), S_{xx} =1 (right). $S_{ii} = (3\langle\cos^2 (iZ) - 1\rangle/2$ with (iZ) being the angle between molecular axis i and matrix axis Z. LD shows that the true orientation distribution in the stretched PVA matrix corresponds to $S_{zz} = +0.32$, $S_{yy} = -0.04$, $S_{xx} = -0.28$, i.e. that the long axis z prefers to align parallel with the polymer chains (about 55%) as does the y axis (about 30%) while the x axis avoids this orientation (only about 15 %).

An interesting possibility that we shall briefly consider is to use the PALD instrument for measurement of photo-acoustic circular dichroism (PACD). It could be valuable on one hand for correlating conformations between solution and crystal states[17] (when a crystal structure may be available) or for studying crystal-stabilized chiral molecules[18] on the other – in both cases exploiting, for example, pressed KBr discs in which decreased transparency and strain birefringence provide challenges to normal CD measurement.

Many attempts to measure circular dichroism in the solid state or on other non-isotropic systems have failed because of artifacts due to linear birefringence (LB) that tends to mix circular and linear dichroism, the latter generally two or three orders of magnitude bigger than the circular dichroism. With the present measurement technique, with a polarization modulator and a lock-in amplified detection, we have shown how the apparent CD contains LD impurities according to the expression:[19]

$$CD_{app} = CD + LD \cos 2\beta_0 \sin\kappa + (1/6)\,[CB\ LD\ LB - CD\ LB^2\,] + \text{higher-order terms.} \qquad (3)$$

Here κ is the effective static birefringence of optical elements of the system between (and including) the polarization modulator and the sample with a principal axis orientation, in a plane perpendicular to the light propagation direction, defined by the angle β_0 . CB and LB denote circular birefringence (i.e. optical activity) and linear birefringence, respectively. All parameters can be considered to vary with wavelength. It is often assumed in the literature that artifacts in the CD spectra of anisotropic samples may average out by sampling over different angles, γ, of orientation of the sample in a plane perpendicular to the propagation direction. That assumption may be justified as the second term,

$$\langle LD \cos 2(\beta_0+\gamma) \sin\kappa \rangle_\gamma = 0 \qquad (4)$$

will vanish when averaged over all orientations γ. However, in the third term, CB LD LB does not generally average out (LD and LB as mentioned usually being two or three orders of magnitude bigger than the CD) and hence generally provides a serious challenge. Finally, CD being a tensor will depend or orientation so <CD(γ)> might be not trivial to interpret.

ACKNOWLEDGEMENT

I am grateful to Josef Michl for many years of inspiration in polarized light spectroscopy. The present report is based on experiments I made after returning from a very inspiring week in Salt Lake City in late September 1978. The weather was a beautiful sunny, hot Indian summer but I was told that in exactly three days a serious snow storm was expected, something I first thought was a joke. However, the town changed completely over a night with a near 1 m thick snow cover coming down. Together with the Michl children I built a big snowman – about 3 m high – as it happened just outside the family's garage. The children of course did not allow it be destroyed but Josef wrote to me by April the following spring: 'your snowman has eventually melted and we were allowed to take out the car'.

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Supplementary Information

Improved pre-amplifier tuned for 370 Hz detection of PALD. Options: T= piezoelectric transducer, M=gas microphone

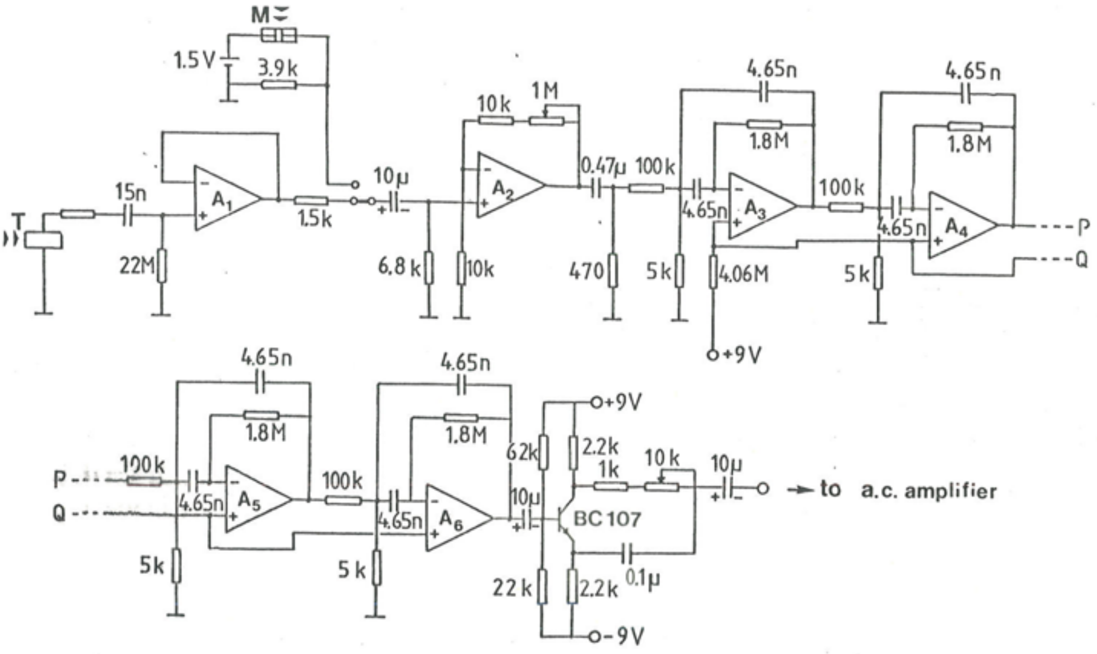

FIG 2

Bengt Nordén. "Photo-Acoustic Linear and Circular Dichroism Technique." *International Journal of Engineering Research and Applications (IJERA)*, vol.10 (10), 2020, pp 10-15.