

Photoacoustic studies of non-radiative relaxation of excited states in melanin

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Abstract. Photoacoustic measurements made at various chopping frequencies on dense aqueous melanin suspensions have revealed a significant dependence upon pH and redox state. It is shown that such behaviour, differing from the simple predictions of the Rosencwaig-Gersho theory, can be explained in terms of finite carrier diffusion and recombination times. The implications of these findings with respect to the amorphous semiconductor model proposed to describe the dynamic role of epidermal melanin are discussed. From the experimental data, values of physical parameters were calculated which allow a qualitative correlation between chemical states and electronic behaviour and, consequently, some aspects of the molecular biology of the melanosome, founded on a rigorous base.

Key words: Melanin, photoacoustics, electron relaxation

1. Introduction

Although different physiological roles have been suggested for the class of pigments collectively called melanins, depending upon their anatomical location in the organism, the most relevant one is the photoprotective function performed in the human body by epidermal melanin granules. However, despite a lot of experimental effort in this direction in the past twenty years, the understanding of the primary photoprocesses in the light excited melanin molecules is still unsatisfactory, mainly with respect to the events immediately following the electronic excitation, including both thermal relaxation and possible formation of triplet states.

The role of transient free radicals and the consequent modifications of the molecule (including interactions with oxygen) was exhaustively investigated and threw some light on this de-excitation channel (Chedekel 1982). In contrast, electronic relaxations via direct interaction with molecular vibration has received rather little interest, despite the suggestion, due to McGinness et al. (McGinness 1972; McGinness et al. 1974) that the molecular biology of the melanosome could be based on the amorphous semiconductor properties of melanin. As a consequence, electronic band structure (Crippa et al. 1978; Strzelecka 1982; Galvão and Caldas 1988) and electron-phonon interaction (McGinness and Proctor 1973) become central features in this subject.

The present work describes the applications of such ideas to a photoacoustic (PA) study of melanin under various conditions of pH and oxidation. This approach is based on the following assumptions:

- the bulk of the energy absorbed by melanin is released in radiation-less transitions as heat, so rendering PA spectroscopy particularly useful in the study these processes. The very weak fluorescence emission (Kozi-kowski et al. 1984) and the low yield of photochemical products (Felix et al. 1978) are assumed to be unimportant in the present analysis;
- the theoretical treatment of the PA effect in semiconductors has been recently extended to take into account finite carrier diffusion and recombination times (Miranda 1982). With the hypothesis that the melanosome behaves as some kind of "solid state" device at the cellular level, such parameters are essential to characterize the dynamic role of epidermal melanin;
- melanins are redox polymers containing high concentrations of o-quinone and o-hydroquinone groups and therefore show a pH dependent redox equilibrium. This effect is well known in the case of simple quinones and was discussed in several classical papers (Michaelis and Schubert 1938; Vetter 1952). We have

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studied the consequences of the possible redistribution of conjugated double bonds by investigating the effect of mild reduction at various pH values on the PA response in order to correlate variations of the extension of electronic delocalization with differences in carrier diffusion and recombination. In such a way we try to connect chemical properties with a physical description of the electronic behaviour.

2. Experimental methods

Materials

Synthetic melanin was obtained by auto oxidation of l-dopa(1-3,4-dihydroxyphenylalanine) in water at pH 9. After 48 h, the resulting black suspension was divided into three lots and the pH of each one was regulated with HCl and KOH to values of 3, 7 and 12 respectively. By incomplete evaporation at 50°C, dense samples of concentrated melanin were prepared and used immediately for the experiments. Reduced specimens were obtained by adding a slight excess of sodium dithionite.

All these manipulations were performed in air. As reported previously (McGinnes et al. 1979), a strong effect on the titration curves of melanins due to the absorption of CO₂ is observed at high pH. Measurements are in progress to evaluate the possible contribution of this reaction to our results.

Experimental apparatus

PA measurements were performed with an EG & G PARC cell model 6003 equipped with the preamplifier model 6005. The light source was an Ar laser (Spectra Physics mod. 2020) used in single line mode, with the power kept at about 600 mw. The blue ($\lambda=488$ nm) and the green ($\lambda=514.5$ nm) lines were used. The beam was modulated with an EG & G PARC model 192 variable frequency chopper in the range 40–350 Hz. These limits are dependent on the geometrical characteristics of the cell and were chosen in order to avoid: *a*) saturation of the signal due to 3 D effects (at low frequency) and *b*) deviation caused by Helmholtz resonances (at high frequency). This range was selected after previous measurements on black carbon samples, used also to test the linear response of the apparatus.

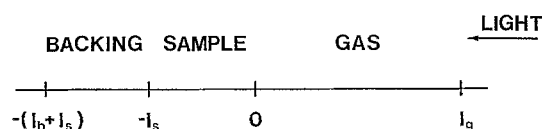


Fig. 1. Schematic geometrical configuration of a gas-microphone PA cell

The PA signal was revealed by a two phase digital lock-in amplifier (EG & G PARC model 5206). The control of the various experimental parameters and the data acquisition and elaboration were performed with a Commodore Amiga 1000 personal computer.

3. Theory

It has been established that the generation of the photo-acoustic signal may be calculated within the framework of a one dimensional heat diffusion theory (Rosencwaig and Gersho (R & G) 1976). The R & G theory assumes that the absorption of light by the valence electrons is immediately followed by non-radiative relaxations with yield 1. The fundamental parameters involved in this treatment are summarized in Table 1, together with the values used for melanin and air. Figure 1 shows a schematic of the geometrical configuration of the cell.

Assuming that the sample has an electronic energy band structure, the heat power density may be assumed to be proportional to the time derivative of the electron excess density in conduction band, $n(x, t)$:

$$Q_s(x, t) = \varepsilon h \nu \frac{\partial n(x, t)}{\partial t}. \quad (1)$$

$h \nu$ is the energy absorbed from the exciting field and $\varepsilon = \frac{\tau}{\tau + \tau_{ph}}$, where τ is the electron hole recombination time and τ_{ph} is the electron phonon collision time. Since $\tau_{ph} \ll \tau$, we have $\varepsilon \approx 1$.

With the previous assumptions we can write:

$$\frac{\partial n(x, t)}{\partial t} = \frac{\beta I_0}{h \nu} \exp \beta x \exp i \omega t \quad (2)$$

where $f = \omega/2\pi$ is the chopping frequency, ν is the frequency of the incident light and β is the absorption

Table 1. Fundamental parameters. The subscript $i=s, g$ and b denotes respectively sample, gas and backing parameters

	Melanin	Air
l = sample length (cm)	≈ 0.1	–
k_i = thermal conductivity (cal/cm s °C)	$1.5 \cdot 10^{-3}$	$5.7 \cdot 10^{-5}$
ρ_i = density (g/cm ³)	1.5	$1.29 \cdot 10^{-3}$
C_i = specific heat (cal/g °C)	0.61	0.24
$\alpha_i = k_i/\rho_i C_i$ = thermal diffusivity (cm ² /s)	$1.6 \cdot 10^{-3}$	0.19
$a_i = (\omega/2\alpha_i)^{1/2}$ = thermal diffusion coefficient (cm ⁻¹)	–	–
$\mu_i = 1/a_i$ = thermal diffusion length (cm)	–	–
β = optical absorption coefficient (cm ⁻¹)	–	–
$\mu_g = 1/\beta$ = optical penetration depth (cm)	–	–
D = carrier diffusion coefficient (cm/s)	–	–
I_0 = intensity of incident light (erg/scm ²)	–	–