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Initial considerations on the relationship between the optical absorption and the thermal conductivity in dielectrics

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Abstract

The absorption of modulated or pulsed light leads to non-radiative processes that generate a photoacoustic (PA) wave. The standard model assumes that the amplitude of the PA wave is proportional to the optical absorption. In previous reports we have demonstrated experimentally and theoretically that from this proportionality: (1) one can obtain quantitative measurements of the optical properties of dielectric thin films and (2) that there may exist a relationship between the amplitude of the PA wave and the thermal conductivity of a given sample. Here we present analytic results that clearly show that the optical absorption and the thermal conductivity are coupled to the amplitude of the PA wave in the modulated regime and that this correlation holds for any type of macroscopic optical and thermal transparency. In particular, the present analysis shows that the product of the optical absorption and the thermal conductivity is related to the PA amplitude via a partition function.

1. Introduction

Photoacoustic (PA) absorption spectroscopy is extensively used in several scientific and technical fields. These range from applications in gases, condensed matter, laser control, colloidal materials and the so-called soft matter [1–6]. Most of the applications related to spectroscopic analysis are focused on either the study of optical properties or the determination of thermodynamic properties. Notably, over the last few years, PA-imaging applications have become of interest. The core of the PA phenomenon is the generation of wideband acoustic-like waves as a consequence of a process of absorption of radiation; the acoustic oscillation is induced in the sample by the interaction with a pulsed or modulated external light source. The range of frequencies of these waves can be from sound to ultrasound with this depending on the time frame of the excitation and on the thermoelastic properties of the medium. As long as the absorption of light is below the saturation limit, the amplitude of the induced sound-like wave is proportional to the amount of absorbed radiant energy. This is an empirical

result that has been experimentally verified and accepted by all present PA models [1–3, 5, 7–9]. However, as Haisch [10] pointed out, the extraction of quantitative information from the PA signals is a non-trivial task, with this being true for almost any PA application, and is particularly so for PA spectroscopy. In the PA field, the problem of extracting information has been solved on a case-by-case basis and this is a considerable limitation for the potential impact of the PA techniques. One of the main obstacles to achieving quantitative PA measurements is related to the lack of knowledge of the specific amount of energy that is transferred from the optical absorption process into measurable amounts of heat or work. In other words, we do not know the explicit analytic relationship between the optical absorption (optical resistance) and thermal conductivity (thermal resistance). The best we have is the experimental evidence that there exists a rule of proportionality between these resistances; see [11] and references above. Therefore, this implies the existence of a specific expression that relates the optical absorption (α) and the thermal conductivity (κ) with terms associated with a local change in temperature or

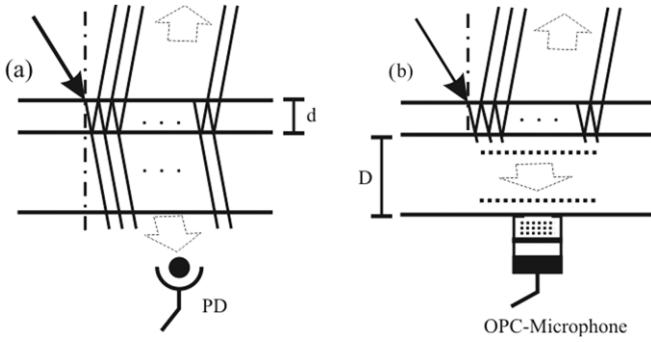


Figure 1. Schematics of the type of layered system we discuss in the main text. In (b) we picture the type of experimental detection we assume for our analysis, and (a) is the equivalent optical detection, and is displayed for the purpose of explanatory comparison alone.

pressure. Thus, this is an open problem which has yet to be solved.

In the present contribution we focus our attention on setting up conditions for finding a relationship of the type noted above. We start from a consideration of the analysis of solid dielectrics illuminated by low frequency modulated continuous light. Finally, we arrive at results from where one can infer the viability of the quantitative analysis. To do this, we analyse the product of the optical absorption and the thermal conductivity against all physically possible combinations between the macroscopic optical transparency and the thermal transparency. This product appears explicitly in almost the same functional form, in almost all the PA models. The actual meaning of this product embraces implications beyond the field of PA alone. We then discuss some aspects of such findings, with the starting point being the general expression used to represent a PA signal for CW-modulated illumination within the visible range.

For the present case, the modulation frequency is assumed to be in the range of 5 Hz to <100 Hz. Then we proceed to analyse, in a case by case manner, the corresponding particular boundary conditions and the material properties. From this we consider the optical absorption and its relationship with the thermal conductivity. The final step is to show the relationship between the rise in temperature within the interaction volume as a function of, among other parameters, the optical absorption and the thermal conductivity.

2. PA theory for modulated illumination

For simplicity and to aid with the analysis and the presentation of the results, we start from the analysis of a layered solid dielectric. See figure 1 for schematic guidance. The sample is a solid that is isotropic, homogeneous and in thermal equilibrium, as required by the standard experimental and theoretical PA model. This model refers to the measurement and analysis of sound-like signals induced in the sample as a result of the optical absorption of pulsed or modulated light, whose power is below the saturation limit. Since a fraction of this absorbed optical energy is transferred into the sample via non-radiative processes, there is a local increase in temperature together with a temporary pressure gradient. It should be noted

that these non-radiative processes are modulated by the spatial and temporal distribution of the illumination source. The time evolution of this gradient or burst of energy is expressed in terms of sound-like waves: the PA signals. These signals are recorded using a microphone or transducer directly attached to the sample (see figure 1). Experimentally, the amplitude of these PA signals is observed to be proportional to the optical absorption, and thus to the intensity of the radiant source.

In the standard PA model [3, 11, 12] the PA-amplitude output, which we call H_0 , is expressed in a general way through a *master* equation; which can be modified depending on the boundary conditions. This master expression includes the material properties and the instrumental and experimental set-up contributions (such as the frequency of modulation of the illumination, temperature, humidity and instrumental response). Once the experiment is set these contributions remain constant during the experimental process, thus there is no restriction to represent these contributions through a constant G_0 . We also recall that the general model assumes that, within a specific spectral distribution, the amplitude of the PA output is proportional to the intensity of illumination I_0 . Thus, the net PA-amplitude output is proportional to the product of these parameters, e.g. $H_0 \propto G_0 I_0$. Similarly, once the experimental conditions have been decided, the intensity of illumination at a given wavelength can be assumed constant. Therefore, one can obtain a normalized PA output, say H , by simply taking $H \propto H_0 / (G_0 I_0)$. In the rest of our analysis, for any reference to the PA output we mean the normalized H amplitude, expressed as

$$H = \frac{r}{r^2 - 1} \frac{2r - e^{-\alpha z_0} [(r + 1)e^{\sigma z_0} + (r - 1)e^{-\sigma z_0}]}{\sigma \kappa (e^{\sigma z_0} - e^{-\sigma z_0})}. \quad (1)$$

The details for the derivation of (1) can be found in the literature [2, 3, 11, 12]. This equation is presented in terms of the thickness of the sample z_0 (which is also constant for a given experiment; shown as d in figure 1), the thermal conductivity κ and a parameter r , which is the ratio of the optical absorption and the thermal diffusion coefficient, $\sigma = \sqrt{\pi f/a}$; where f is the frequency of modulation of the illumination and a is the thermal diffusivity, $a = \kappa/\rho c$. Here, ρ is the sample density and c is the specific heat at constant pressure [2, 6]. Then H has units of temperature divided by the flux of power per unit area, $K (W m^{-2})^{-1}$. Thus, physically H represents the rate of change in the local temperature as a result of the flux of energy from the non-radiative processes; these triggered within a volume of area A and length z_0 . Interestingly, these units are due to the product $\sigma \kappa$ in the denominator of (1). Whilst the remaining terms in (1) produce a dimensionless number that we label as ξ_0 . Therefore, (1) is rewritten as $H = \xi_0 / (\sigma \kappa)$. In the next step we multiply both sides of this expression by α . The result is that on the right-hand side we have the product $r \xi_0$, divided by the product of the optical absorption and the thermal conductivity. Therefore, by defining $\xi = r \xi_0$, which is also a dimensionless number, and after re-arranging terms we get

$$\kappa \alpha = \frac{\xi}{H}; \quad (2)$$

where

$$\xi = \frac{r^2}{r^2 - 1} \frac{2r - e^{-\alpha z_0} [(r + 1)e^{\sigma z_0} + (r - 1)e^{-\sigma z_0}]}{(e^{\sigma z_0} - e^{-\sigma z_0})}.$$

For given boundary conditions of a given sample, this ξ factor is a constant. Conversely, any change in the material or boundary conditions would imply a change in the value of ξ .

Thus, once the amplitude of the waves is normalized as indicated before, the PA amplitude will be expressed according to the many ways as (1) can be reduced; see section 3 for details. An important condition of H is that the optical properties of the sample, such as the reflectance, the optical scattering, the absorbance and the transmittance, are linear functions of the illumination wavelength. We recall that we assume we have a homogeneous and isotropic sample. For means of sensing the information, we assume that the sensor is a membrane microphone, such as that of the open photoacoustic cell (OPC) type [4, 13]. Since the absorbed radiant energy induces diffusive phenomena within the sample, then the modulation frequency of the incident illumination must be sufficiently low; this frequency would depend on the material properties. The specific details of these considerations can be found in [3, 13–15].

Note that in [11], we reported a relationship of the type represented by (2), along with the experimental support for this description. These results were obtained for only one specific set of boundary conditions. For this work we further investigate the relationship for the general case.

3. Different physical conditions

The various cases covered by the standard PA models are related to the different material properties and the boundary conditions associated with α and σ . This follows from the fact that they define the characteristic optical thickness (otherwise known as optical attenuation or optical length, $\mu_\alpha = 1/\alpha$) and the characteristic thermal thickness (the thermal attenuation or thermal diffusion length, $\mu_\sigma = 1/\sigma$), respectively. Therefore, the next stage is to describe the many possibilities in terms of the corresponding boundary conditions along with the respective expressions that are obtained from applying these conditions to equation (1). The analytic details can be found in [3, 5, 9, 12].

3.1. Optically thick (opaque) materials

A given material can be optically opaque (optically thick, $\mu_\alpha < 1$), implying that its transmittance is $T = \exp(-\alpha z_0) = 0$; and yet it can also be the following.

3.1.1. Thermally thin. This implies that $\mu_\sigma \gg z_0$ and $\mu_\sigma \gg \mu_\alpha$ or that $|r| \gg 1$ and thus $\exp(\pm\sigma z_0) \simeq 1 \pm \sigma z_0$; in this case (1) reduces to

$$H = \frac{1}{\sigma \kappa} \frac{1}{\sinh(\sigma z_0)}. \quad (3)$$

After multiplying both sides of (3) by α , and recalling the definition of r , the terms can be reorganized to give

$$\alpha \kappa = \frac{1}{H} \frac{r}{\sinh(\sigma z_0)}. \quad (4)$$

Since r and the \sinh are dimensionless, then as expected (4) has units of $(\text{W} (\text{m}^2 \text{K})^{-1})$.

3.1.2. Thermally thick. In this case $\mu_\sigma < z_0$ (or $1 < \sigma z_0$), having $|r| > 1$. Here we note that the hyperbolic ratio $1/(e^x - e^{-x})$ is $\text{csch}(x)$; which can be represented in terms of an asymptotic series expansion. Using such representation and the respective boundary conditions, (1) becomes

$$H = \frac{r}{(r^2 - 1)\sigma \kappa} e^{-\alpha z_0}. \quad (5)$$

After repeating the same procedure used for deriving (4) from (3), we get

$$\alpha \kappa = \frac{r^2}{r^2 - 1} \frac{e^{-\alpha z_0}}{H}. \quad (6)$$

3.1.3. Thermally very thick. This is where $\mu_\sigma \ll z_0$ (or more appropriately $1 \ll \sigma z_0$) and then $|r| < 1$. In this case, the argument of the hyperbolic function can be assumed to tend to infinite. With the help of the asymptotic representation introduced above, then (1) is reduced to

$$H = \frac{1}{r} \frac{e^{-\sigma z_0}}{\sigma \kappa}. \quad (7)$$

Again after multiplying both sides of equation (7) by α and reorganizing terms, we get

$$\alpha \kappa = \frac{e^{-\alpha z_0}}{H}. \quad (8)$$

It should be noted that (1) the general model only takes into account the thickness of the sample, (2) for the cases considered above, the optical absorption occurs within a volume of area A times a thickness z_1 , which may or may not be the same as the actual sample thickness, z_0 .

3.2. Optically thin (transparent) materials

Another set of possibilities arise for samples that are optically thin ($\mu_\alpha \gg 1$). This means that its transmittance is $T = \exp(-\alpha z_0) \neq 0$, and therefore, H depends on both the sample's optical properties and on the thermal properties. Again, an optically thin material can also be the following.

3.2.1. Thermally very thin. This is for $\mu_\sigma \gg z_0$ (with $|r| > 1$), then equation (1) reduces to

$$H = \frac{r}{r^2 - 1} \frac{\alpha z_0}{\sigma \kappa \sinh(\sigma z_0)}. \quad (9)$$

After using the same procedure as in the previous subsection and noting that at this scale $\sinh(\sigma z_0) \approx \sigma z_0 + \dots$, we get

$$\alpha \kappa = \frac{r^4}{(r^2 - 1)H}. \quad (10)$$

3.2.2. *Thermally thin.* In this case $\mu_\sigma > z_0$, and $|r| < 1$. Therefore, (1) is reduced to

$$H \cong r \frac{e^{-\alpha z_0}}{\sigma \kappa}; \quad (11)$$

and correspondingly

$$\alpha \kappa \cong r^2 \frac{e^{-\alpha z_0}}{H}. \quad (12)$$

3.2.3. *Thermally thick.* This case refers to $\mu_\sigma < z_0$ and $|r| \ll 1$, thus from (1) we get

$$H = r \frac{e^{-\alpha z_0}}{\sigma \kappa}; \quad (13)$$

from where we obtain

$$\alpha \kappa = r^2 \frac{e^{-\alpha z_0}}{H}. \quad (14)$$

In this way we verify that regardless of how the optical and thermal transparency combine, for each case one can derive an expression which equates with the product $\alpha \kappa$, and in general this is in terms of a dimensionless-type number, ξ , divided by the normalized PA amplitude H . This procedure describes in a fundamental way a new approach to the interpretation of the PA experimental data. Moreover, it provides a way to extend the theory, thus making more viable the quantitative analysis. As indicated above, in [11] we presented results related to this $\alpha \kappa$ product. At that time we considered that there was a possibility that this relationship could lead one to a Widenmann–Franz type law for dielectrics. The present results further support such an idea.

4. The product $\alpha \kappa$

In physical terms, the optical absorption coefficient can be seen as a measure of the coupling of each wavelength of the external field with the sample [16]. While within a solid, the transference (coupling) of this optical absorption to thermal energy depends on the sample's ability to conduct heat; and this can be quantified in terms of a flux of free energy [17]. This is explained in more detail in the rest of this section. The process of optical to thermal energy transference involves the generation of collective quanta of mechanical vibrations that are defined by the modes of lattice oscillation or lattice waves and can be observed as a spectrum of phononic oscillations; which at the low limit are sound waves [18, 19]. In this context, for dielectrics, it has been established that the efficiency of transference of the energy from optical to thermal is indicative of the strength of the interaction of the natural transverse lattice oscillation modes with each wavelength of the external illumination field (this is different from the case for metals where longitudinal waves are involved) [17, 18, 20]. This type of interaction signifies that for each illumination wavelength there exists a specific phonon spectral distribution response (or lattice wave distribution response). In other words, the non-radiative processes, in the sense we discuss here, will

occur when at a given wavelength the coupling of the external field with the solid results in inducing specific lattice-vibration modes. These vibrations are responsible for the transport of the energy flux represented by H , and thus is what determines the form of the non-radiative absorption spectra; as reported in [5, 11].

On the other hand, we recall that the thermal conductivity is directly related to the phonon mean free path (heat-carriers-free-path) which is determined by phonon–phonon scattering. At room temperature, an isotropic regular solid (crystalline) will have the highest thermal conductivity value when it is pure. Conversely, the thermal conductivity decreases with an increase in the impurities and/or the lattice defect density.

Thus, the product $\alpha \kappa$ can be seen as the measure of coherency between the external field and the induced thermal field as a result of the matching of the optical frequencies with the phonon mean-free-path distribution; or rather, the coupling between what can be described as the optical impedance to the thermal impedance. We recall that this product has units of $(\text{W}(\text{m}^2\text{K})^{-1})$. Therefore, this represents a flux of energy per unit time and unit of area, rated by the change in local temperature which only occurs during the presence of the external field (period of illumination). Therefore this flux, as described by this dimensional analysis, helps us to define $\alpha \kappa = z_1 \rho_w / T$, where ρ_w is the volumetric power density, $W/(Az_1)$; T is the temperature within the interaction volume. That is defined by the illumination area A and the interaction depth, z_1 , that is perpendicular to the surface where the external field is incident. Note that for an optical transmittance $T_{\text{opt}} = 0$, $z_1 \neq z_0$; while for $T_{\text{opt}} \neq 0$, $z_1 = z_0$ with consequences as described in section 3. Therefore, this volumetric power density can also be written in terms of the time variation of the volumetric energy density as

$$\rho_w = \frac{d\rho_e}{dt}. \quad (15)$$

After considering the $\alpha \kappa$ product, as expressed in the above paragraph, from (15) it is clear that

$$\frac{d\rho_e}{dt} = \frac{\alpha \kappa T}{z_1}. \quad (16)$$

The study of the type of interactions we describe here, related to the optical–thermal association and its significance, is not new; as can be seen in Fröhlich's theory of dielectrics [17]. The action of the external field on a dielectric, assuming one modulation period, is understood to be the amount of external work done on a constant volume, $V = Az_1$, of the solid. Since this work, on average, is periodic then it is applied in a cyclic reversible and isothermal way. It is of interest that the Fröhlich interpretation matches with the PA experimental and theoretical descriptions. In PA we assume that the sample is in thermal equilibrium with the environment and interacts with the external field in a reversible way. Therefore, it can be seen that ρ_e is the Helmholtz free energy density, F/V , with F being the Helmholtz free energy and V the volume within which the amount of work is done [17]. To the best of our knowledge, this is the first time this interpretation has been

proposed. Furthermore, we observe that this energy density is related to the partition function (Z) as

$$\rho_e = -k_B T \log(Z), \quad (17)$$

where k_B is Boltzmann's constant. Here T is the change in temperature within the interacting volume. The relevance of this formalism is that (1) we have a way to directly connect the description of the PA phenomenon with the statistical physics theory; (2) and therefore, we can connect the various microscopic phenomena with macroscopic observations; (3) additionally, once we know the partition function for a given sample one can obtain almost all the thermodynamic parameters and therefore a quantitative analysis is potentially available [1–3, 5, 7–9].

Once we have (17), the sample's internal temperature is the first parameter we can calculate,

$$T = \frac{z_1}{\kappa \alpha} \frac{d\rho_e}{dt}. \quad (18)$$

In our description, Z is related to the spectral distribution of the lattice-vibration modes produced by the absorption of radiation at a specific wavelength. Thus, because the optical absorption is a function of the wavelength one expects to get a different Z for each wavelength and therefore there will be a change in the thermal conductivity. The corresponding analytic description is complex and for the development of this study we use only the phenomenon seen in the experimental evidence [11]. In any case, it can be expected that the optical absorption, expressed as induced external work, would cause a change in the local temperature within the interaction volume and that this change is specific for each wavelength. This means that in the interaction of an external field with a solid, the amount of energy that is transferred from optical to thermal is characterized for each wavelength of illumination by a specific phonon distribution (the response to the illumination); and that response is an attribute of the material at that wavelength.

Now, by combining (15) and (17), we get

$$\frac{d\rho_e}{dt} = -k_B \left[\log(Z) \frac{dT}{dt} + T \frac{d \log(Z)}{dt} \right] = \frac{\kappa \alpha T}{z_1}. \quad (19)$$

On solving (19) two possible physical conditions become apparent: (1) when Z is time independent and (2) when Z is time dependent. We will now consider the significance of these cases. We recall that we assume a homogeneous and isotropic material, and that the frequency of modulation of the illumination is low. Thus, for the time dependent Z , we observe that if at the beginning of a period of illumination we consider an 'instant picture' of the phonon distribution (e.g. lattice-vibration modes) triggered by an external field, we would observe a Z_0 distribution of states. Then if at an arbitrary instant of time later we took a second picture we would observe that the distribution of states was essentially the same. This is because the interaction time scale is very short compared with the time scale for the transport and displacement of the phonon processes. This, combined with the condition that the number of oscillatory components involved is very large, implies that any effective change in the distribution of states will be within

the noise range of the average energy distribution due to the ambient temperature and thus undetectable [11, 17, 19]. Since in the right-hand side term within square brackets in (19), $d \log(Z)$ can be written as dZ/Z , then after substituting this, the resulting term will be zero. Thus, after arranging terms, we get

$$\frac{dT}{T} = -\frac{\kappa \alpha}{z_1 k_B \log(Z)} dt. \quad (20)$$

We solve this for a time, t , set within the time frame of illumination in a modulation period, t_0 . During this period, within the volume of interaction, the temperature changes from the initial value T_0 to a maximum $\delta T + T_0$. Thus, we solve (20) to get

$$\log \left(\frac{\delta T + T_0}{T_0} \right) = -\frac{\kappa \alpha}{k_B z_1 \log(Z)} t_0. \quad (21)$$

From here we obtain that the change in local temperature can be expressed as

$$\delta T = T_0 \left\{ -1 + \exp \left[-\frac{\kappa \alpha}{k_B z_1 \log(Z)} t_0 \right] \right\}. \quad (22)$$

This is the burst of temperature that is ultimately the engine for the wave that travels within the sample as a sound-like wave; i.e. the PA signal. Empirically, from the PA experimental evidence, we know that the local change in temperature is very small compared with the initial temperature: $T_0 \gg \delta T$. However, the caused effects are clearly measurable; as is done for the PA burst. Note that except for the partition function, all the other aspects contained in the PA models are discussed elsewhere in the PA literature (22) [5, 9, 11]. Thus, we explore some consequences of the introduction of this function. In this sense, if instead one chooses to solve (20) for Z , we start from (21) and take a series expansion of the exponential function and then we approximate this to first order since this is the most important contributing term at the $T_0 \gg \delta T$ regime. As a result we obtain that

$$\frac{\delta T}{T_0} = -\frac{\kappa \alpha}{k_B z_1 \log(Z)} t_0; \quad (23)$$

and after reorganizing terms and solving for Z , we get

$$Z = \exp \left(-\frac{T_0 \kappa \alpha}{\delta T k_B z_1} t_0 \right). \quad (24)$$

Let us define $\beta = 1/(\delta T k_B)$, and from (16) we find that, at each illumination wavelength, the term $T_0 \kappa \alpha t_0 / z_1$ represents the volumetric density of free energy within a single period of illumination. Thus, one can rewrite (24) as

$$Z = e^{-\beta \rho_e}; \quad (25)$$

recovering (17); which is the definition of Z at the $\delta T \rightarrow 0$ limit. This result implies that the temperature distribution is described by the canonical ensemble.

Now using equation (2) and substituting $\alpha \kappa$ in equation (24) by the ratio ξ/H we get an expression that is of the same analytic form as (25), albeit this corresponding to the PA phenomena. This function can be associated with a particular sample via the boundary conditions as

described in section 3. Hence, once we know the partition function associated with a sample, then in principle one knows everything about the sample; and one can derive all the observable physical quantities including, as we describe, the optical absorption. It should be noted that the inverse is also true for an optically thin sample: given the absorption spectrum, one can reconstruct the part of the partition function on which the optical absorption depends. However, if the sample is optically thick, then this inverse relationship is no longer unique: it is quite possible that two systems with different partition functions could possess the same optical absorption spectrum. As far as the current analysis goes, this is one of the possible limitations for the present results. However that is the subject of future analysis.

Let us assume we know all the terms in ρ_e , including the initial temperature and the amount of induced change in this temperature. Thus, in principle, as referred above, experimentally one can achieve a quantitative reconstruction of the portion of the partition function on which the optical absorption depends; i.e. the amount for which we can normalize the distribution of states at time to calculate e.g. the mean energy, the specific heat or other thermodynamic parameters.

The other variant that one can obtain from (19) is that for the partition function being time dependent. This situation arises when conditions are such that the interaction time and the decay times are similar, and the discreteness of the phase space is taken into account [21]. Such a possibility emerges e.g. for nano-samples (such as nano-particles, nano-films, and so on). The general feature is that the number of states contributing to the statistical distribution may become somehow limited and varying with time. Thus, we reorganize terms in (19) and correspondingly distribute $\log(Z)$, T , k_B and the time differential to obtain

$$\frac{dT}{T} + \frac{d \log(Z)}{\log(Z)} = -\frac{\kappa \alpha}{k_B z_1 \log(Z)} dt. \quad (26)$$

The PA experimental evidence indicates that if we illuminate the sample for a period of time, say t_0 , then within the interacting volume we will induce a change in local temperature. Going from initial T_0 to a final value $T = T_0 + \delta T$. Thus, we integrate (26) to get

$$\log\left(\frac{\delta T + T_0}{T_0}\right) = -\left[\frac{\kappa \alpha}{k_B z_1 \log(Z)} t_0 + \int \frac{d \log(Z)}{\log(Z)}\right]. \quad (27)$$

Since we want to solve for the temporal change in temperature, from (27) we obtain that

$$\delta T = T_0 \left\{ -1 + \exp\left[-\frac{\kappa \alpha}{k_B z_1 \log(Z)} t_0 \int \frac{d \log(Z)}{\log(Z)}\right] \right\}. \quad (28)$$

Here (28) is somewhat similar to (22), except for the extra term $\int d \log(Z)/\log(Z)$. Therefore, in this case any macroscopic temperature measurement would produce a noticeable bias temperature field resulting from the variations in the distribution of microstates. In this case, one is immediately tempted to ask: how measurable is the temperature variation? In fact, this will depend on how this

temperature variation compares with the fluctuation of the microstates. Further, recalling that Z is a quantity of statistical nature, the comparison should also be in statistical terms.

What is of interest is that in both regimes covered by (19), a flux of external energy in a confined volume of the sample provokes a local increase in temperature and that this is via non-radiative processes. This phenomenon is the engine that triggers an elasto-mechanical wave which travels within the sample as a sound-like wave; i.e. the photo-induced PA signal. The analysis for the short-time scale, τ_L , regime has not been included since it requires a specific and detailed analysis, in view of the fact that the theoretical set-up is different from the current one, τ_M . This is $\tau_M \gg \tau_L$, and different conditions arise.

5. Discussion of results

To date, neither experimentally nor theoretically is it possible to truly perform quantitative real-time PA measurements. The best we have is the deterministic process of backtracking the temporal evolution of a process such as the burst of energy occurring in the PA phenomenon. This study displays some aspects of this backtracking. In particular, this is related to describing how the absorbed and thermal energy evolve in time; this is made in terms of the PA-signal representations. From the set of expressions we obtain here, there seems to exist a way to perform an effective quantification of the transference of energy, from optical to thermal processes. As we describe, in the modulated illumination regime, the standard model provides us with conditions to obtain the product $\alpha\kappa$, which appears to be a consistent result for each case covered by such a model. Furthermore, this interpretation bring us to understand that once a dielectric sample is set to interact with a radiation external field, the sample's response to the field is in terms of how this field is coupled to local vibrational modes. If one takes into account the product $\alpha\kappa$, then one can estimate that a measure of such coupling is somehow proportional to the thermal conductivity. Then these conditions permit us to define a flux of energy in a similar way to that in fluids theory or to that described by an electric current. We recall that the current results correspond to the case for low frequency of modulation for the external field. However, the current results are hinting that a similar type of relationship for the short-time scale τ_L could exist, such as with the case for short laser pulses (>20 ns). Therefore, it would be very necessary to study and understand the implications on the existence of a more general relationship between α and κ , especially if we want to know which are the necessary and sufficient conditions for this relationship to exist. By now we consider that regardless of the time regime for the PA phenomena to occur, it is required to set up these common features: (1) a flux of external optical energy interacting within a portion of the local volume that provokes a local increase in temperature; (2) the so induced non-radiative processes would trigger an elasto-mechanical wave which travels within the sample as a sound-like wave [1, 9, 11]. This brings us to set the definition and actual physical meaning of the product we analyse in section 4. On the one hand, it is constructed from its interpretation as

proportional to a flux of radiative energy, which is the work that is made on a solid [17]. As a result we establish that the relationship between the optical absorption and the thermal conductivity is via a partition function.

6. Conclusions

So far the experimental and theoretical interpretations of the PA phenomenon have been well satisfied by a qualitative approach. For general applications one starts by defining the spatial volume within which the optical absorption takes place, and assumes this volume as a heat source q , regardless of the nature of the source. For practical applications related to condensed matter and gases, this is good enough. The existence of different models is a consequence of the many possible dynamics that the non-radiative process can follow due to many possibilities for boundary conditions and material properties. It should be noted that we have considered all the physically valid combinations between optical and thermal transparency, which occur for illumination at the low frequency modulation regime. There is evidence that at short-time scales similar types of results would be obtained. In itself this calls for defining a new set of phase space that equates with the Hamiltonian type of phase space derived from Liouville's theorem (conservation of energy [18, 19]). Our results demonstrate that for any type of sample the PA technique at low-modulation illumination mode, by now, can be used to obtain a complete set of the optical and thermal characteristics of the dielectric sample.

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