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THEORY OF SOLID-STATE PHOTOACOUSTIC-SIGNAL-SOURCE GENERATION VIA NON-RADIATIVE LATTICE PHONON-ASSISTED DE-EXCITATIONS

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The theory of the photoacoustic-signal-source generation upon light absorption by a crystalline solid is developed The model examines the physics of creation of a temperature- and time-dependent distributed heat source in the sample as a result of electron–phonon interactions followed by vibrational relaxation of the lattice The adiabatic Born–Oppenheimer (ABO) approximation and statistical thermal averages over phonon populations have been used to describe the rate of non-radiative de-excitation processes The theory provides expressions for the non-radiative decay rate and for the sample heating rate as functions of sample temperature Debye frequency, and energy level(s) of non-radiative state(s)

1. Introduction

Photoacoustic spectroscopy (PAS) of solid materials has recently emerged as a useful spectroscopic tool for the investigation of low [1–4] and high [5] temperature phenomena, non-radiative processes [1,6–8], and studies of crystalline disorders such as defects and impurities in semiconductors [9,10]. In these applications it has been noticed almost invariably [2,3] that the experimental data did not exhibit the simple temperature dependence which was expected from the Rosencwaig–Gersho (RG) model [11] Bechthold and Campagna [3] qualitatively attributed such departures from the RG theory to the temperature dependence of the velocity of sound in the coupling gas column, and to the temperature dependence of the viscosity and density of the transmitting gas. These authors also speculated on the possibility of contributions from the thermal properties of the sample to the temperature dependence of the photoacoustic signal. However, such contributions have not been considered in a theoretically rigorous fashion in the photoacoustic literature.

It is evident that the mechanisms of the photon energy conversion to thermal energy in the solid's excited-state manifold and the subsequent release of the heat into the solid followed by heat conduction processes will be responsible for the PAS signal origin. All information about the solid-state physics of the thermal response of the solid to the incident radiation is included in the heat release rate which acts as the heat source in the solid The magnitude, frequency response (frequency domain) or time-development (time domain), temperature, and position dependence in the material of the heat release rate are determined by the excited-state energy levels, populations, and non-radiative transition rates [1]. The photoacoustic signal as a function of the heating rate of the solid sample [11] carries valuable information about the excited-state manifold and is sensitive only to the non-radiative de-excitation channels and to the subsequent heat conduction processes in the solid.

While the photoacoustic-signal generation due to heat conduction processes is relatively well understood [11], no rigorous theoretical treatment of the heat-source generation which precedes thermal conduction in a solid has been attempted in the photoacoustic literature. The theoretical investigation of the physical processes which create the heat source responsible for the PAS signal from the solid is of fundamental importance to the interpretation of the signal in terms of such processes An understanding of factors

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contributing to the creation of a heat source in the solid is in turn crucial for assessing the relative importance of sample-related contributions in the overall thermal processes which generate the photoacoustic effect in solids A theoretical analysis of the non-radiative origins of PAS should provide a guide to some experimental areas of current interest, such as the determination of the energy levels of non-radiative states [9,10]; the study of defect states in crystalline solids [12]; and the measurement of non-radiative transition rates, lifetimes and quantum efficiencies.

In this work a single phonon-assisted optical-to-thermal energy conversion model is presented to account for the heat-source creation in a crystalline solid as the result of non-radiative de-excitation phenomena. It is subject to certain assumptions concerning the state of the optically excited solid and its vibrational spectrum, as well as the photon–electron and electron–phonon coupling This sample heating rate is determined as a statistically thermal average over phonon states and as a function of time-averaged populations of the excited-state manifold of the solid.

2. Theory

2 1. *The non-radiative transition rate*

In the present work the dynamics of the crystalline lattice on which a (assumed) monochromatic light beam impinges will be treated in the harmonic approximation. The atomic (or molecular) states of the lattice will be assumed to be adequately describable by the adiabatic Born–Oppenheimer (ABO) approximation [13–15] In the ABO approximation the nuclei are fixed at a single equilibrium position x, while the electron positions can be described by a set of independent coordinates r. The coupling term between electrons and the nuclear vibrational manifold is ignored [16]. The wavefunctions for the entire solid are thus given as products of an electronic and a vibrational wavefunction:

$$\psi_{\mathrm{ABO}}(x, r) = \phi(x, r)\chi(x). \tag{1.1}$$

Further, it is assumed that the Franck–Condon principle is generally valid, so that the electronic transition matrix element does not depend on the nuclear positions. A very useful consequence of this principle is the complete separation of radiative and radiationless transition matrix elements, so that the former enters the expressions for transition rates simply in the form of a multiplicative constant which is not directly measurable by the photoacoustic probe.

Lastly, it is reasonable to assume that the phonon system can attain thermal equilibrium internally in times short compared to the shortest radiative transition time. This assumption is especially true for long wavelength phonons which have mode densities similar to those of the incident photons In this case the ratio of non-radiative to radiative decay rates is on the order of $(c_\ell/c_s)^3 \approx 10^{16}$ [17]; c_ℓ and c_s are the speeds of light and sound, respectively, in a solid. As a consequence of fast thermalization, the phonon bath can be characterized by a well-defined thermodynamic temperature T at all times of experimental interest

The processes considered here include optical absorption of photons of a fixed frequency, excitation of the atomic lattice system, de-excitation, and return to the ground state via radiative, non-radiative, photochemical, etc. channels. In particular, we are interested in the non-radiative de-excitation process which involves emission of lattice phonons generating a heat source within the sample.

We are considering a system containing nuclear ion cores of mass M with coordinates x_n and electrons of mass m with coordinates r_i. The subscripts designate the positions of the nth atomic nucleus and ith electron, respectively. The hamiltonian for this system is

$$\mathcal{H} = \sum_n \left[-\frac{\hbar^2}{2M} \nabla_n^2 + \sum_{n>k} V_{\mathrm{I-I}}(x_n - x_k) \right]$$

$$+\sum_{i}\left[-\frac{\hbar^2}{2m}\nabla_i^2+\sum_{j>i}\left(\frac{e^2}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}\right)+\sum_{n}U_{e-I}(\boldsymbol{r}_i-\boldsymbol{x}_n)\right], \tag{1.2}$$

where V_{I-I} and U_{e-I} are the interaction potentials between two ion cores, and between an electron and an ion core, respectively.

At temperatures higher than 0 K, the vibrational-amplitude increase of the lattice ion cores due to energy absorption by the phonon ensemble is small for light intensities typically used in photoacoustic experiments. Typical temperature rises of sample surfaces excited by conventional arc-lamp sources, cw and pulsed lasers are on the order of 10^{-7}–10^{-3} °C [18]. For $\Delta T \ll T_0$, the mean-square displacement ratio of surface atoms is

$$\langle x^2(T_0+\Delta T)\rangle/\langle x^2(T_0)\rangle = 1+\Delta T/T_0, \tag{1.3}$$

for temperatures higher than the lattice Debye temperature. Eq. (1.3) indicates that at $(300+10^{-3})$ K the mean vibration amplitude of a surface atom is $(\Delta T/T_0)^{1/2} \approx 2\times10^{-3}$ times larger than that at 300 K, and 1.5×10^{-2} times larger than at 4 K

The above argument shows that a normal coordinate perturbation approach to the quantum-mechanical operator(s) responsible for non-radiative transition matrix elements is well justified Taylor expansions of the potential operators V_{I-I} and U_{e-I} can be obtained about the equilibrium position $\boldsymbol{R}_n$ of the ion cores The hamiltonian operator (1.2), is then separable into equilibrium and perturbation parts $\mathcal{H}^{(0)}$ and $\mathcal{H}'$, respectively:

$$\mathcal{H}_e^0=\sum_{i}\left[-\frac{\hbar^2}{2m}\nabla_i^2+\sum_{i>j}\left(\frac{e^2}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}\right)+\sum_{n}U_{e-I}(\boldsymbol{r}_i-\boldsymbol{R}_n)\right], \tag{1.4}$$

$$\mathcal{H}_I^{(0)}=\sum_{n}\left[-\frac{\hbar^2}{2M}\nabla_n^2+\sum_{n>k}V_{I-I}(\boldsymbol{R}_n-\boldsymbol{R}_k)\right], \tag{1.5}$$

$$\mathcal{H}'\equiv\sum_{n>k}\boldsymbol{A}_{nk}\cdot(\boldsymbol{u}_n-\boldsymbol{u}_k)+\sum_{i\,m}\boldsymbol{B}_{im}\cdot\boldsymbol{u}_m, \tag{1.6}$$

$\boldsymbol{u}_n=\boldsymbol{x}_n-\boldsymbol{R}_n$ is the atomic displacement vector of the nth ion.

In the harmonic approximation,

$$\boldsymbol{A}_{nk}=K_{nk}(\boldsymbol{R}_n-\boldsymbol{R}_k), \tag{1.7}$$

where K_{nk} has the units of the stiffness constant of an oscillator comprised of the nth and kth ion cores vibrating at a frequency ω_{nk}. If we choose a Coulomb-type of ion–electron interaction [19], then we can set in eq. (1.6):

$$\boldsymbol{B}_{im}=Ze^2\nabla_i(1/|\boldsymbol{r}_i-\boldsymbol{R}_m|),\quad Z \text{ is the nuclear charge.}$$

As a consequence of the Franck–Condon assumption the actual functional form of $\boldsymbol{B}_{im}$ does not affect the non-radiative transition matrix element. The coordinate-operator functions $\boldsymbol{u}_n-\boldsymbol{u}_k$ when statistically averaged over phonon populations and summed up over ion core positions can be shown to vanish. Therefore, the perturbation interaction hamiltonian of the system is given from eq (1.6) in the simplified form:

$$\mathcal{H}'=\sum_{m}\boldsymbol{B}_m\cdot\boldsymbol{u}_m, \tag{1.8}$$

where we assumed a one-electron system for convenience. The hamiltonian of eq. (1.8) is now treated as the perturbation which brings about the non-radiative decay of the excited state through the interaction $\boldsymbol{B}_m$ between the electronic and lattice coordinates at tempeatures higher than 0 K

The transition rate of the optically prepared state (I) to some final state (F) is given by [20]:

$$W_{\mathrm{I}\to\mathrm{F}} = (2\pi/h)|\langle n_{\mathrm{F}}, e_{\mathrm{F}}|\mathcal{H}'|n_{\mathrm{I}}, e_{\mathrm{I}}\rangle|^2\delta(E_{\mathrm{F}} - E_{\mathrm{I}} + \hbar\omega_{\mathrm{IF}}), \tag{1.9}$$

where $n_{\mathrm{I}}(n_{\mathrm{F}})$, $e_{\mathrm{I}}(e_{\mathrm{F}})$ are the initial (final) vibrational and electronic states, respectively. Eq (1.9) also allows for the possibility of vibrational excitation and decay without an electronic transition, depending on the perturbation hamiltonian $\mathcal{H}'$.

Upon substitution of the perturbation hamiltonian, eq (1.8), in eq. (1.9) we can write the transition matrix element

$$\mathfrak{M}_{\mathrm{IF}} = \langle n_{\mathrm{F}}, e_{\mathrm{F}}|\sum_m \boldsymbol{B}_m\cdot\boldsymbol{u}_m|n_{\mathrm{I}}, \mathrm{e}_{\mathrm{I}}\rangle, \tag{1.10}$$

where $\boldsymbol{u}_m$ is a Schrodinger position operator. The Franck–Condon principle and the adiabatic assumption permit separation of the electronic and vibrational parts

$$\mathfrak{M}_{\mathrm{IF}} = \sum_m \langle e_{\mathrm{F}}|\boldsymbol{B}_m|e_{\mathrm{I}}\rangle\cdot\langle n_{\mathrm{F}}|\boldsymbol{u}_m|n_{\mathrm{I}}\rangle. \tag{1.11}$$

To simplify eq. (1.11) further, we are assuming that [19]

$$|\boldsymbol{r}| \ll |\boldsymbol{R}_m|. \tag{1.12}$$

For Coulomb potentials:

$$\langle e_{\mathrm{F}}|\boldsymbol{B}_m|e_{\mathrm{I}}\rangle = Ze^2\langle e_{\mathrm{F}}|\nabla(1/|\boldsymbol{r} - \boldsymbol{R}_m|)|e_{\mathrm{I}}\rangle. \tag{1.13}$$

Under Coulomb conditions, as well as for shorter-range potentials the electronic contribution contains a factorable multiplicative constant, and the transition matrix element can be simplified

$$\mathfrak{M}_{\mathrm{IF}} = \langle e_{\mathrm{F}}|\boldsymbol{f}(r)|e_{\mathrm{I}}\rangle\cdot\sum_m \langle n_{\mathrm{F}}|\boldsymbol{u}_m|n_{\mathrm{I}}\rangle R_m^{-2n}, \tag{1.14}$$

where

$$\boldsymbol{f}(r) = Ze^2\int\phi_{\mathrm{F}}^*(\boldsymbol{r})(\nabla r)\,\phi_{\mathrm{I}}(\boldsymbol{r})\,\mathrm{d}^3r, \quad r = |\boldsymbol{r}|, \quad R_m = |\boldsymbol{R}_m|; \quad r \ll R_m,$$

and $n > 1$ indicates the power of a potential function of shorter range than the Coulomb type The non-radiative transition rate, thus becomes

$$W_{\mathrm{I}\to\mathrm{F}} = (2\pi/\hbar)|\langle e_{\mathrm{F}}|\boldsymbol{f}(r)|e_{\mathrm{I}}\rangle|^2\left|\sum_m \frac{1}{R_m^{2n}}\langle n_{\mathrm{F}}|\boldsymbol{u}_m|n_{\mathrm{I}}\rangle|\cos\psi_m\right|^2\delta(E_{\mathrm{F}} - E_{\mathrm{I}} + \hbar\omega_{\mathrm{IF}}). \tag{1.15}$$

ψ_m is the angle between the vectors $\boldsymbol{f}$ and $\boldsymbol{u}_m$. In most experimental cases, we do not know the exact initial state of the optically excited system. Therefore, we will average over the thermal equilibrium distributions of all phonon occupation levels in both the initial and the final states of the solid. We also take averages over $\cos^2\psi_m = 1/2$ and over the arbitrary nuclear equilibrium position vector magnitudes $R_m = \langle R_m\rangle \equiv R$. Indicating statistical thermal averages by $\langle\ \rangle_T$, we can write an expression for the average non-radiative transition rate from eq (1 15):

$$\langle W_{\mathrm{I}\to\mathrm{F}}(\omega_{\mathrm{IF}})\rangle_T = (\pi/\hbar)|\langle e_{\mathrm{F}}|\boldsymbol{f}'(r)|e_{\mathrm{I}}\rangle|^2\sum_{n_{\mathrm{I}}} P_{n_{\mathrm{I}}}\sum_{n_{\mathrm{F}}}|\langle n_{\mathrm{F}}|\sum_m \boldsymbol{u}_m|n_{\mathrm{I}}\rangle|^2\delta\left[\hbar\omega_{\mathrm{IF}} - \left(E_{n_{\mathrm{I}}} - E_{n_{\mathrm{F}}}\right)\right], \tag{1.16}$$

where now $f'(r)$ is a statistically averaged function of the equilibrium coordinates: $f'(r)=f(r)/R^{2n}$; E_{n_I}, E_{n_F} are the energies of phonons present at the initial and final states of the system, such that $E_{n_I} > E_{n_F}$; P_{n_I} is the probability distribution function of the initial state.

The time-evolution of the perturbation hamiltonian $\mathcal{H}'$ can be conveniently incorporated in the transition rate formalism using correlation functions (the time-integral representation [21]). This leads to a Fourier-transform function whose time dependence can then be handled by Heisenberg operator algebra for the phonon (boson) ensemble.

We introduce the Fourier transform pair:

$$\langle W_{I\to F}(\omega)\rangle_T=\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}G(t)\,dt \tag{1.17a}$$

and

$$G(t)=\int_{-\infty}^{\infty} e^{-i\omega t}\langle W_{I\to F}(\omega)\rangle_T\,d\omega. \tag{1.17b}$$

Substituting eq. (1.16) into eq (1.17b) and making use of the completeness property of the phonon eigenvector-operator set in Hilbert space $\{n_F\}$ and using statistical averages over phonon states n_I [21] we obtain.

$$G(t)=(\pi/\hbar^2)|\langle e_F|f'(r)|e_I\rangle|^2\sum_{m,j}\langle u_j(0)\cdot u_m(t)\rangle_T. \tag{1.18}$$

Insertion of eq. (1.18) into (1.17a) gives the time-integral representation of the statistically averaged non-radiative relaxation rate

$$\langle W_{I\to F}(\omega)\rangle_T=\left(|\langle e_F|f'(r)|e_I\rangle|^2/2\hbar^2\right)\int_{-\infty}^{\infty} e^{i\omega t}\sum_{m\ j}\langle u_j(0)\cdot u_m(t)\rangle_T\,dt. \tag{1.19}$$

The expression (1.19) may be evaluated using well-known expansions [21] for the operators $u_n(t)$. In these expansions, series of terms of operator products of the form $a_s a_s$ and $a_s^+ a_s^+$ have not been included because the time evolution of such products oscillates rapidly giving an average value of zero in the time scale of oscillation of the products $a_s a_s^+$ and $a_s^+ a_s$ [22,23]. The statistical thermal average of eq (1.19) can be obtained using phonon number operator average:

$$\langle n_s(k)\rangle_T=\{\exp[\hbar\omega_s(k)/k_BT]-1\}^{-1}. \tag{1.20}$$

The three-dimensional thermally averaged non-radiative transition rate can be obtained from eq (1.19) and the integral representation of the delta function, upon converting sums over phonon wavevectors k to integrals to facilitate computation:

$$\begin{aligned}\langle W_{I\to F}(\omega)\rangle_T=&\left(\pi\langle e_F|f'(r)|e_I\rangle^2/2\hbar M\right)\sum_{\alpha\ \beta\ s}\sum_{G_l}\left[e_\alpha^{(s)}(G_l)e_\beta^{(s)}(G_l)/\omega_s(G_l)\right]\\ &\times\{[\langle n_s(G_l)\rangle_T+1]\delta[\omega-\omega_s(G_l)]+\langle n_s(G_l)\rangle_T\delta[\omega+\omega_s(G_l)]\},\end{aligned} \tag{1.21}$$

where G are reciprocal lattice vectors, and $e_\alpha^{(s)}$, $e_\beta^{(s)}$ are lattice eigenvectors corresponding to branch α, β, respectively.

In eq. (1.21), the first term in the curly brackets describes single-phonon emission while the second term describes phonon absorption. From the energy conserving delta function in eq. (1.16) and for $\omega=\omega_{IF}$, we see that for the first term in the curly brackets.

$$\omega_{IF}=\omega_s(G_l)=(E_{n_I}-E_{n_F})/\hbar>0 \quad\text{or}\quad E_{n_I}>E_{n_F}. \tag{1.22}$$

This is consistent with the de-excitation assumption and indicates energy loss to the lattice through phonon emission The opposite occurs for the second term, since $\omega = \omega_{\mathrm{IF}} = -\omega_s(G_l)$, which results in $E_{n_{\mathrm{I}}} < E_{n_{\mathrm{F}}}$, i.e. a higher final state than the initially optically prepared state. This absorption term was introduced in the model through the coordinate vector expansions. Henceforth, it will be eliminated from this work, since we are considering the rate of non-radiative decay via phonon emission only. Under these conditions, a more restrictive form of eq (1.21) will be employed:

$$\langle W_{\mathrm{I}\stackrel{>}{\to}\mathrm{F}}(\omega_{\mathrm{IF}})\rangle_T = \left(\pi|\langle e_{\mathrm{F}}|f'(r)|e_{\mathrm{I}}\rangle|^2/2\hbar M\right) \times \sum_{\alpha,\beta}\sum_s\sum_{G_l}\left[e_\alpha^{(s)}(G_l)e_\beta^{(s)}(G_l)/\omega_s(G_l)\right]\left[\langle n_s(G_l)\rangle_T + 1\right]\delta\left[\omega_{\mathrm{IF}} - \omega_s(G_l)\right], \tag{1 23}$$

where the symbol I $\stackrel{>}{\to}$ F indicates the transition from state E_{I} to state E_{F}, such that $E_{\mathrm{I}} > E_{\mathrm{F}}$. Eq. (1.23) shows that non-zero non-radiative decay rates are the result of the following energy selection rule for allowed transitions: Energy conversion from the excited state into heat due to phonon emission during de-excitation can occur only when the energy difference $E_{n_{\mathrm{I}}} - E_{n_{\mathrm{F}}}$ is equal to a lattice vibrational energy $\hbar\omega_s(G_l)$, where $\omega_s(G_l)$ is a reciprocal lattice frequency. The selection rule

$$E_{n_{\mathrm{I}}} - E_{n_{\mathrm{I}}} = \hbar\omega_s(G_l), \tag{1.24}$$

is a function of the crystallographic structure of the solid sample This rule comprises a theoretical basis for the experimentally observed [10] relationship between photoacoustic signals and crystallographic nature of solid samples It is expected that eq. (1.24) will be useful in photoacoustic investigations of non-radiative states in solids.

It is convenient to use the continuous Debye model to obtain explicit expressions for $\langle W_{\mathrm{I}\stackrel{>}{\to}\mathrm{F}}\rangle_T$ in terms of measurable lattice quantities. We assume a continuous distribution of reciprocal lattice vectors [24]:

$$\sum_{G_l} \to \frac{1}{V}\int_0^{G_{\max}} \mathrm{d}^3G, \tag{1.25}$$

where $G_{\max}$ corresponds to the cutoff frequency ω_{D} of the lattice. Applying the transformation (1.25) to the rate (1.23), and using the completeness property of the lattice eigenvectors, we obtain

$$\langle W_{\mathrm{I}\stackrel{>}{\to}\mathrm{F}}(\omega_{\mathrm{IF}})\rangle_T = \frac{108\pi^4|\langle e_{\mathrm{F}}|f'(r)|e_{\mathrm{I}}\rangle|^2}{MV^2\hbar\omega_{\mathrm{D}}^3}\,\frac{\omega_{\mathrm{IF}}}{1-\exp(-\hbar\omega_{\mathrm{IF}}/k_{\mathrm{B}}T)}, \tag{1.26}$$

where we defined:

$$\hbar\omega_{\mathrm{IF}} \equiv \hbar^2|k_{\mathrm{IF}}|^2/2M \tag{1.27}$$

and

$$\langle n(\omega_{\mathrm{IF}})\rangle_T \equiv \langle n_s(k_{\mathrm{IF}})\rangle_T = \left[\exp(\hbar\omega_{\mathrm{IF}}/k_{\mathrm{B}}T) - 1\right]^{-1}. \tag{1.28}$$

Eq. (1.26) links the non-radiative transition probability from level (I) to level (F) to the Bose–Einstein distribution $\langle n(\omega_{\mathrm{IF}})\rangle_T$ for a one-phonon process between levels (I) and (F).

The present formalism predicts a constant term, in addition to the temperature-dependent Bose–Einstein term. The origin of this term has been identified [24] as due to spontaneous phonon emission phenomena. Eq (1.26) can be expressed in the form

$$\begin{aligned}\langle W_{\mathrm{I}\stackrel{>}{\to}\mathrm{F}}(\omega_{\mathrm{IF}})\rangle_T &= C\hbar\omega_{\mathrm{IF}}\{2[\langle n(\omega_{\mathrm{IF}})\rangle_T + 1/2] - \langle n(\omega_{\mathrm{IF}})\rangle_T\} \\ &= C(2\langle E_{\mathrm{IF}}\rangle - \langle E\rangle_{\mathrm{I}\stackrel{<}{\to}\mathrm{F}}),\end{aligned} \tag{1.29}$$

where C is a constant, $\langle E_{1F} \rangle$ is the average energy of a lattice-vibrational mode at a radian frequency ω_{1F} and $\langle E \rangle_{1 \leq F}$ is the energy consumed due to absorption of one phonon. The form of eq (1 29) is a result of our assumption of uncoupled harmonic oscillators in the solid matrix.

2 2 Excited state dynamics of heat-source generation in a solid

Non-radiative de-excitations in an optically excited solid followed by heat conduction processes are responsible for the temperature rise in the solid which generates the photoacoustic signal The temperature profile $T_s(\boldsymbol{r}, t)$ in the absorbing sample can be described by a heat-diffusion equation [18,26],

$$\nabla^2 T_s(\boldsymbol{r}, t) - \frac{1}{\alpha_s} \frac{\partial}{\partial t} T_s(\boldsymbol{r}, t) = -\frac{1}{k_s} \frac{\mathrm{d}}{\mathrm{d}t} H(\boldsymbol{r}, t), \tag{2.1}$$

where α_s, k_s are the thermal diffusivity and thermal conductivity of the sample, and $H(\boldsymbol{r}, t)$ is the total heating rate (erg $\mathrm{cm}^{-3}\ \mathrm{s}^{-1}$) which acts as a time-dependent distributed heat source In the present work, $H(\boldsymbol{r}, t)$ is assumed to be a cosinusoidal function of time at the modulation frequency ω_0 of the incident light beam An extension to time-domain excitations is straightforward [1]

The heating rate of the solid can be determined from consideration of all energy levels (I, J) to (from) which non-radiative transitions occur. For the decay $I \rightarrow J$ $(E_I > E_J)$, the net rate of heat production is [1],

$$\mathrm{d}h_{IJ}(\boldsymbol{r}, t)/\mathrm{d}t = (E_I - E_J)\left[N_I(\boldsymbol{r}, t) W_{I \geq J} - N_J(\boldsymbol{r}, t) W_{J \geq I}\right], \tag{2.2}$$

where N_I, N_J are the instantaneous population densities of levels (I, J) at a depth $\boldsymbol{r}$ in the solid immediately after the optical excitation. The total rate of heat production in the sample is

$$\mathrm{d}H(\boldsymbol{r}, t)/\mathrm{d}t = \sum_{I>J} \mathrm{d}h_{IJ}(\boldsymbol{r}, t)/\mathrm{d}t = 2 \sum_{I>J} E_{IJ} N_I(\boldsymbol{r}, t) W_{I \geq J}; \quad E_{IJ} = E_I - E_J > 0. \tag{2 3}$$

Hunter et al. [27] have used the gas-phase equivalent expressions to eq (2.3) to describe gas molecule de-excitations following harmonic optical pumping and modulation of the excited state populations. For a frequency-domain solid-state photoacoustic experiment the time dependence of the Ith excited state population will be the real part of the expression,

$$N_I(\boldsymbol{r}, t) = \tfrac{1}{2} N_I^{(0)}(\boldsymbol{r})\left[1 + \exp(\mathrm{i}\omega_0 t)\right]. \tag{2 4}$$

The modulation frequency ω_0 is assumed to be much lower than the rate of approach to thermodynamic equilibrium by the phonon populations. Murphy and Aamodt [1], Rosencwaig and Hildum [28], and Powell and co-workers [7,29] have applied expressions similar to eq (2.3) to the study of the PAS signal from specific impurity systems whose excited-state manifolds were known. In general, however, only statistical thermal averages of all excited-state contributions to the sample heat source are meaningful for the purpose of PAS signal analysis. Taking the thermal average of eq. (2 3), we can express the experimentally detectable heating rate $\dot{H}_{\mathrm{exp}}$

$$\dot{H}_{\mathrm{exp}}(\boldsymbol{r}, t) = \langle \mathrm{d}H(\boldsymbol{r}, t)/\mathrm{d}t \rangle_T = 2\hbar \langle \sum_{I>J} \omega_{IJ} N_I(\boldsymbol{r}, t) W_{I \geq J} \rangle_T. \tag{2.5}$$

Using the definition of thermal averages [21], we can show that

$$\dot{H}_{\mathrm{exp}} = 2\hbar \sum_{I>J} \langle \omega_{IJ} N_I(\boldsymbol{r}, t) W_{I \geq J} \rangle_T. \tag{2.6}$$

The term ω_{IJ} in the brackets is a constant and therefore it can be pulled out of the thermal averaging operation. For a general K-level system N_1 may be calculated from the dynamic equation of level (I) [30]

and from eq (2 4)

$$\mathrm{d}N_I(\boldsymbol{r},t)/\mathrm{d}t=\left[\sum_{m,K}(R_m)_{K\to I}N_K(\boldsymbol{r},t)\right]-N_I(\boldsymbol{r},t)\left[\sum_{m,K}(R_m)_{I\to K}\right]$$
$$=\tfrac{1}{2}\mathrm{i}\omega_0 N_I^{(0)}(\boldsymbol{r})\exp(\mathrm{i}\omega_0 t). \tag{2.7}$$

$(R_m)_{K\to I}$ is the mth type of transition rate (e.g. radiative, non-radiative, intersystem crossing, etc.) from level (K) to level (I).

Defining the total relaxation time constant from level (I) as

$$\tau_I\equiv\left[\sum_{m,K}(R_m)_{I\to K}\right]^{-1}, \tag{2.8}$$

we find

$$N_I^{(0)}(\boldsymbol{r})=\tau_I\left[\sum_{m,K}(R_m)_{K\to I}N_K^{(0)}(\boldsymbol{r})\right]/(1+\mathrm{i}\omega_0\tau_I) \tag{2.9}$$

From eqs. (2 4) and (2 9), we find the following expression for the time evolution of the average number density of states at level (I):

$$\bar{N}_I(\boldsymbol{r},t)=\tfrac{1}{2}\bar{N}_I^{(0)}(\boldsymbol{r})\{[1+\exp(\mathrm{i}\omega_0 t)]/(1+\mathrm{i}\omega_0\tau_I)\}, \tag{2.10}$$

where

$$\bar{N}_I^{(0)}(\boldsymbol{r})\equiv\sum_{m,K}(R_m)_{K\to I}N_K^{(0)}(\boldsymbol{r})/\sum_{m,K}(R_m)_{I\to K}. \tag{2.11}$$

Now, $N_I(\boldsymbol{r},t)$ can be pulled out of the $\langle\ \rangle_T$ brackets in eq. (2.6) and can be replaced by eq. (2.10), since it does not depend on thermal averaging,

$$\dot{H}_{\mathrm{exp}}(\boldsymbol{r},t)=\hbar[1+\exp(\mathrm{i}\omega_0 t)]\sum_{I>J}\sum\left[\omega_{IJ}\bar{N}_I^{(0)}(\boldsymbol{r})/(1+\mathrm{i}\omega_0\tau_I)\right]\langle W_{I\geq J}(\omega_{IJ})\rangle_T. \tag{2.12}$$

Eq. (2 12) is a general expression for the experimentally measurable heat-release rate in a frequency-domain photoacoustic experiment. Upon consideration of the expression (1.26) for the non-radiative decay rate, it becomes apparent that $\dot{H}_{\mathrm{exp}}$ generally depends on T: the higher the temperature of the solid, the larger the thermally averaged $\langle W\rangle_T$ and the faster the heat release rate. The occurrence of larger non-radiative transition rates at higher temperatures (i.e. shorter non-radiative lifetimes) predicted by eq. (1.26) has been previously observed (e.g. Le Si Dang et al. [25]). Physically, the faster heat-release rate at higher temperatures is the result of the presence of a statistically larger number of lattice phonons due to the Bose–Einstein distribution at all energy levels. These phonons assist in carrying through the non-radiative transitions more efficiently than at low temperatures, thereby shortening the lifetime of the transition. In the next section, we shall consider some special cases of eq. (2.12) which are of interest to experimentalists, namely heating rates of solids excited to a single and multiple energy level, and the production of the photoacoustic signal from a two-level solid at room temperature.

2 3. Special cases and discussion

The equation for the distribution of the optical energy upon excitation of a solid by radiation of wavelength λ and intensity $I_0(\lambda,\boldsymbol{r},t)$ (W/cm²) is

$$\sigma(\lambda)I_0(\lambda,\boldsymbol{r},t)N_0=N_I(\boldsymbol{r},t)\sum_{m,K}(R_m)_{I\to K}, \tag{3.1}$$

where N_0 is the ground-state population, N_I is the population of the (assumed) single level of excitation (I), and $\sigma(\lambda)$ is the absorption cross section for transitions excited by light of wavelength λ. σ is given in terms of the optical absorption coefficient $\beta(\lambda)$:

$$\sigma(\lambda) = \beta(\lambda)/N_0. \tag{3.2}$$

Eqs (3.1) and (3.2) give the following expression for the average number density of states

$$\bar{N}_I^{(0)}(\boldsymbol{r}) = \beta(\lambda) I_0(\lambda, \boldsymbol{r}) / \sum_{m\,k} (R_m)_{I \to k}, \tag{3.3}$$

where a consinusoidal dependence on time was assumed for $I_0(\lambda, \boldsymbol{r}, t)$. I_0 is usually [11] taken to satisfy the Beer–Lambert law

$$I_0(\lambda, \boldsymbol{r}) = I_0(\lambda) \exp[-\beta(\lambda)|\boldsymbol{r}|]. \tag{3.4}$$

(i) We shall now examine the temperature dependence of $\dot{H}_{\text{exp}}$ in the single and multiple excitation cases. For optical excitation to multiple levels, eq. (2.5) can be written using eq. (1.26) for the non-radiative transition rate

$$\langle \mathrm{d}H(\boldsymbol{r}, t, T)/\mathrm{d}t \rangle_T = A[1 + \exp(\mathrm{i}\omega_0 t)] \sum_I [\bar{N}_I^{(0)}(\boldsymbol{r})/(1 + \mathrm{i}\omega_0 \tau_I)] Q_I(T), \tag{3.5}$$

where

$$A \equiv (108\pi^4/MV^2\omega_\mathrm{D}^3)|\langle e_\mathrm{F}|f'(\boldsymbol{r})|e_1\rangle|^2, \tag{3.6}$$

and

$$Q_I(T) = \sum_J \omega_{IJ}^2/[1 - \exp(-\hbar\omega_{IJ}/k_\mathrm{B}T)]. \tag{3.7}$$

In order to calculate the summation in eq. (3.7), it is convenient to work in the continuous Debye limit of lattice frequencies. Taking the density of modes

$$g(\omega_J)\,\mathrm{d}\omega_J = (18\pi n/\omega_\mathrm{D}^3)\,\omega_J^2\,\mathrm{d}\omega_J \equiv B\omega_J^2\,\mathrm{d}\omega_J \tag{3.8}$$

(n is the number of atoms in the solid) and transforming the sum of eq. (3.7) into an integral, we get:

$$Q_I(T) = B\int_0^{\omega_\mathrm{M}} \omega_J^2 \omega_{IJ}^2\,\mathrm{d}\omega_J/[1 - \exp(-\hbar\omega_{IJ}/k_\mathrm{B}T)], \tag{3.9}$$

where

$$\begin{aligned} \omega_\mathrm{M} \equiv (\omega_J)_\mathrm{Max} &= \omega_I; \quad && \omega_I < \omega_\mathrm{D}; \\ &= \omega_\mathrm{D}; && \omega_I \geqslant \omega_\mathrm{D}. \end{aligned} \tag{3.10}$$

The term $\omega_{IJ}^2/[1 - \exp(-\hbar\omega_{IJ}/k_\mathrm{B}T)]$ in the integrand of eq. (3.9) and in summation of eq. (3.7) is a measure of the density of occupied states at temperature T when spontaneous non-radiative decay processes are present in addition to induced non-radiative transitions. For optical upward transitions, the energy of the excited state (I) is usually much larger than $\hbar\omega_\mathrm{D}$ due to the photon frequencies which are much higher than those of lattice phonons. Therefore, we will henceforth set $\omega_\mathrm{M} = \omega_\mathrm{D}$ in eq. (3.9).

At low temperatures,

$$Q_I(T) \approx B\int_0^{\omega_\mathrm{D}} \omega_J^2 \omega_{IJ}^2\,\mathrm{d}\omega_J \approx \tfrac{1}{3} B\omega_I^2 \omega_\mathrm{D}^3, \tag{3.11}$$

for $\omega_l \gg \omega_D$. Inserting eq. (3.11) into eq (3.5), we find

$$\langle \mathrm{d}H(\boldsymbol{r}, t, T)/\mathrm{d}t \rangle_{T \ll \hbar\omega_D/k_B} = \tfrac{1}{3}AB\omega_D^3[1 + \exp(\mathrm{i}\omega_0 t)] \sum_l \frac{\overline{N}_l^{(0)}(\boldsymbol{r})\omega_l^2}{1 + \mathrm{i}\omega_0\tau_l}. \tag{3.12}$$

Eq. (3.12) is independent of temperature. In this limit the RG theory [11] of the photoacoustic effect is rigorously valid

At high temperatures eq (3.7) gives

$$Q_l(T) = B(k_B T/\hbar) \int_0^{\omega_M} \omega_j^2 \omega_{lj} \, \mathrm{d}\omega_j \approx \tfrac{1}{3} B\omega_D^3 (k_B T/\hbar)\omega_l, \tag{3.13}$$

for $\omega_l \gg \omega_D$. Now, eq. (3.5) yields

$$\langle \mathrm{d}H(\boldsymbol{r}, t, T)/\mathrm{d}t \rangle_{T \gg \hbar\omega_D/k_B} = \tfrac{1}{3}AB\omega_D^3[1 + \exp(\mathrm{i}\omega_0 t)](k_B T/\hbar) \sum_l \frac{\overline{N}_l^{(0)}(\boldsymbol{r})\omega_l}{1 + \mathrm{i}\omega_0\tau_l}. \tag{3.14}$$

Eq (3 14) indicates that at high temperatures, the heat-release rate is proportional to T in the continuous Debye approximation.

If there are only two discrete energy levels $|0\rangle$ and $|1\rangle$ in the solid and absorption occurs due to the 0 → 1 transition, eq (3.5) gives

$$\begin{aligned}\langle \mathrm{d}H(\boldsymbol{r}, t, T)/\mathrm{d}t \rangle_T &= A\overline{N}_1(\boldsymbol{r}, t)\{\omega_{10}^2/[1 - \exp(-\hbar\omega_{10}/k_B T)]\} \\ &= A\overline{N}_0^{(0)}(\boldsymbol{r})[R_{0\to 1}/(R_{1\to 0} + \mathrm{i}\omega_0)][1 + \exp(\mathrm{i}\omega_0 t)]\{\omega_{10}^2/[1 - \exp(-\hbar\omega_{10}/k_B T)]\},\end{aligned} \tag{3.15}$$

where R is the total transition rate At low temperatures, eq. (3.15) is independent of T and proportional to ω_{10}^2, while at high temperatures it is linear in T and ω_{10}. These characteristics of the two-level solid are similar to those obtained for the continuous solid.

(ii) The theoretical development in this work has given a method for analyzing the photoacoustic signal as a direct measure of the heating rate of the solid sample. Once the $\dot{H}_{\mathrm{exp}}(\boldsymbol{r}, t, T)$ is known, a standard approach to the calculation of the PAS signal can be applied [11,26] via the heat-diffusion equation, eq (2.1). The model presented here demonstrates the possibility of a sample-related temperature-dependent heat source in the range of room/high temperatures and/or small photon energies, especially in the infrared, i.e. for $\hbar\omega_P < k_B T = 0.026$ eV at $T = 300$ K, and for most phonon energies up to $\hbar\omega_D$. The Rosencwaig–Gersho explicit formalism [11] hinges on assuming a heat source independent of T. The present work shows that for the simple case of vibrationally harmonic solid and a single phonon de-excitation mechanism, the linear heat-diffusion equation (2.1) must be replaced in general by a non-linear equation of the form

$$\nabla^2 T_s(\boldsymbol{r}, t) - \frac{1}{\alpha_s}\frac{\partial}{\partial t} T_s(\boldsymbol{r}, t) = f(T_s, \boldsymbol{r}, t), \tag{3.16}$$

which in its general form can only be solved by special approximate methods [31]. Only at very low temperatures or in solids with large energy level spacings is the forcing function f in eq. (3.16) independent of T, and the RG formalism strictly valid. Under these circumstances, the apparent disagreement between temperature-dependent experimental PAS data [2,3] and the T^{-1} dependence predicted by the RG model is not surprising. For the usual one-dimensional sample geometries [11,26] and assuming a two-level solid at room temperature, eq. (3.16) can be written as

$$\frac{\partial^2}{\partial x^2} T_s(x, t) - \frac{1}{\alpha_s}\frac{\partial}{\partial t} T_s(x, t) = -A_{\mathrm{eff}} \exp[-\beta(\lambda)|x|][1 + \exp(\mathrm{i}\omega_0 t)] T_s(x, t), \tag{3.17}$$

where

$$A_{\mathrm{eff}} \equiv [\beta(\lambda) I_0(\lambda)/2k_s]\eta_{\mathrm{eff}}, \tag{3.18}$$

and η_{eff} is the effective quantum efficiency of the non-radiative transition from level $|1\rangle$ to level $|0\rangle$:

$$\eta_{\mathrm{eff}} \equiv A k_B(\omega_{10}\tau_1)/\hbar(1 + \mathrm{i}\omega_{10}\tau_1), \tag{3.19}$$

A is given by eq. (3.6).

Considering only the AC component of eq (3.17) which is responsible for the generation of the photoacoustic effect [11] we can write

$$\mathrm{d}^2T(x)/\mathrm{d}x^2 + \{A_{\mathrm{eff}} \exp[-\beta|x|] - \mathrm{i}\omega_0/\alpha_s\}T(x) = 0, \tag{3.20}$$

where it was assumed

$$T_s(x, t) = T(x) \exp(\mathrm{i}\omega_0 t)$$

The general solution of eq. (3.20) can be expressed as follows:

$$\begin{aligned} T(x) = {} & U\left[1 + (A_{\mathrm{eff}}/\beta) \sum_{n=1}^{\infty} \frac{\mathrm{e}^{-n\beta x}}{n(n\beta - 2\sigma_s)}\right] \exp(\sigma_s x) \\ & + V\left[1 + (A_{\mathrm{eff}}/\beta) \sum_{n=1}^{\infty} \frac{\mathrm{e}^{-n\beta x}}{n(n\beta + 2\sigma_s)}\right] \exp(-\sigma_s x), \end{aligned} \tag{3.21}$$

where U, V are complex-valued constants, and

$$\sigma_s = (\mathrm{i}\omega_0/\alpha_s)^{1/2}. \tag{3.22}$$

Eq. (3.21) reduces to the RG model expression, eq. (4b) of ref. [11] for temperature-independent non-radiative transition rates.

The PAS signal which is predicted using eq. (3.21) and eq. (15) of ref. [11], is larger than that predicted by the temperature-independent heat-source term of the RG model at all solid temperatures $T_s \gg \hbar\omega_D/k_B$, owing to the contributions of the summations multiplying the A_{eff} terms Qualitatively, this behavior which results from the modification of the RG theory is consistent with the gentler than T^{-1} fall-off of PAS signal ($\propto T^{-1/2}$) observed by Kuhnert and Helbig [2] at room temperature. However, exact predictions of the temperature behavior of the PAS signal cannot be obtained unless the exact three-dimensional equation (3.16) is numerically solved. Numerical solutions will be presented in a future publication.

The present theory is rigorously valid for cases where the thermal disturbance of the solid due to non-radiative de-excitations from an optically excited level is both fast and small compared to the disturbance due to its exposure to the ambient temperature bath. Two- and more-phonon processes have not been considered here and are assumed to have negligible effects in the radiationless transition rate. In the special case of a single optically prepared state (I), this work provides a generalization of specialized heating rate expressions derived previously (eqs (1) of ref. [26]). This can be seen, if eq. (2 12) is written in the form

$$\dot{H}_{\mathrm{exp}}(\lambda, \boldsymbol{r}, t, T) = \tfrac{1}{2} I_0(\lambda)\beta(\lambda) \exp[-\beta(\lambda)|\boldsymbol{r}|]\{[1 + \exp(\mathrm{i}\omega_0 t)]/(1 + \mathrm{i}\omega_0\tau_I)\} \sum_{\mathrm{all}\,J} \langle\eta_{IJ}\rangle_T E_{IJ}, \tag{3.23}$$

where $\langle\eta_{IJ}\rangle_T$ is the thermally averaged absolute quantum efficiency of the non-radiative transition between levels (I) and (J), defined by

$$\langle\eta_{IJ}\rangle_T \equiv \langle W_{I \gtrsim J}\rangle_T / \sum_{m,K} (R_m)_{I \to K}. \tag{3.24}$$

The summation is over all levels (K) to which any transition from level (I) can occur, such that $\hbar\omega_{IK} > 0$.

The present theory accounts for the effects of the crystallographic structure of the lattice on the heat-source generation, via the selection rule, eq. (1.24) for allowed non-radiative transitions.

The calculation of the Debye frequency of the sample from the PAS signal via eqs (3.5) and (3.21) is rather difficult due to the general lack of reliable absolute PAS amplitude data and the indeterminacy of the electronic matrix element $\langle e_{\Gamma}|f'(r)|e_{1}\rangle$. However, relative amplitude and phase data as functions of the temperature T should, in principle, give information about the energy gap $\hbar\omega_{I}$ between the excited state and the ground state to which it is coupled non-radiatively, as shown by eqs. (3.18)–(3 21).

3. Conclusions

A quantum-mechanical theory of the creation of a heat source in a crystalline solid upon optical excitation has been developed using a single-phonon coupling mechanism to the vibrational spectrum of the solid Explicit expressions for the non-radiative transition rate and the heat-release rate in the solid were obtained These expressions led to solid temperature profiles qualitatively consistent with PAS trends in published experimental data [2], assuming a simple two-level solid The generality of the quantum-mechanical normal-coordinate perturbation approach to non-radiative de-excitation employed in this work shows that the origin of the optically created heat source in a solid is independent of the photoacoustic effect which ensues, as would be expected intuitively. Therefore, the heat-source-generation theory may also be applied to the study of calorimetric absorption spectroscopy [32] (CAS) and photothermal deflection spectroscopy [18] (PDS) It is particularly suited for the analysis of the PAS signal obtained from a piezoelectric transducer, since this technique depends directly on the vibrational excitation energy of the solid resulting from the coupling of optical energy to the phonon spectrum of the lattice [33].

The present formalism may be extended in a straightforward manner to include contributions to the heating rate of a solid with lattice defects by redefinition of the interaction hamiltonian of eq. (1.8) in terms of local strain operators [21]. Other non-radiative processes which have been investigated experimentally with photoacoustics and are amenable to extensions/modifications of the present theory include de-excitations of ions [6,7] and molecules [34] in host crystal matrices and solutions; defect states [9,10,12]; and electron–phonon interactions [35] in semiconductors Temperature-dependent phase transitions [36], photovoltaic energy conversion [37], laser annealing PAS studies [38], and photoacoustic detection of magnetic phenomena (e.g electron paramagnetic resonance (EPR) [39]) could also be examined theoretically with the present approach using appropriate hamiltonian operators

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