TRANSIENT VIBRATIONAL GRATING SCATTERING

D.P. WITEKAMP, Koos DUPPEN and Douwe A. WIEPSMA
Picosecond Laser and Spectroscopy Laboratory, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Received 18 July 1983; in final form 15 September 1983

A new method for measuring vibrational lifetimes in the solid state is demonstrated in a dilute mixed molecular crystal. Using a picosecond light pulse at $\omega_1$ and simultaneous crossed pulses at $\omega_2$, a vibrational population grating at $\omega_1 - \omega_2$ is prepared. The decay of this grating is followed by measuring at variable delay the Bragg-angle diffraction of a probe pulse, resonant with an optical transition.

1. Introduction

The phenomena of diffraction from transient, light-induced, spatial modulations in optical properties has been widely applied in recent years to study relaxation processes in condensed phases. Applications to the relaxation of various molecular and bulk properties are discussed in recent reviews [1–5]. Here we demonstrate the extension of such transient grating spectroscopy to the study of vibrational lifetimes, presenting low-temperature results on the 756 cm$^{-1}$ mode of pentacene present as a dilute guest in single crystals of naphthalene.

Fig. 1 shows the spatial arrangement of the laser beams, the sample, and two lenses. Four parallel optical pulses of 6 ps duration enter the figure from the right propagating in the z direction. Their points of intersection with 15 cm focal-length lenses before and after the sample are indicated by the labeled circles. Pulses 1, 2 and 2' at frequencies $\omega_1$, $\omega_2$ and $\omega_2'$, respectively, are time coincident. They are followed after a variable delay $t$ by a probe pulse of frequency $\omega_1$ which is labelled 1'.

Together, the preparation fields at $\omega_1$ and $\omega_2$ cause a Raman transition from the pentacene ground state $|a\rangle$ to a ground-state vibration $|b\rangle$ located at the transition frequency $\omega_{ba} = \omega_1 - \omega_2$. The spatial modulation in $I(\omega_2)$, due to the crossed beams, is thus transferred to the populations of these states. The population grating in $\rho_{bb}$ is sketched within the (exaggerated) sample volume of fig. 1 as a function of both $y$ and $z$.

Fig. 2 shows the relationships of the applied frequencies to the molecular energy levels. Besides the Raman resonance $\omega_{ba} = \omega_1 - \omega_2$, there are also near-resonances $\omega_1 = \omega_{cb} - \Delta$ and $\omega_2 = \omega_{cb} - \Delta$ involving the origin of $S_1$ labeled as $|c\rangle$. These enhance the Raman transition probability. In the probe process there is an exact resonance $\omega_1 = \omega_{ab}$ and again the
Fig. 2. Relationship of the applied pulse frequencies to the molecular energy levels. Crossed preparation pulses at $\omega_2$ lead to a grating which scatters the probe pulse at $\omega_1$ at a similar angle. For the experiments reported $\Delta = 9$ cm$^{-1}$.

near-resonance $\omega_1 = \omega_{ab} - \Delta$. The same four-level scheme and applied frequencies have been used to describe both frequency [6,7] and time [8,10] domain coherent, anti-Stokes, Raman scattering (CARS) experiments on similar systems.

From this energy-level diagram, it is clear that the laser-induced grating of the vibrational population difference $\rho_{bb} - \rho_{aa}$ leads to a similar grating in the $S_1 \leftrightarrow S_0$ population differences and thus to a grating in the electronic polarization involving $|a\rangle$ or $|b\rangle$. This polarization leads to the most efficient diffraction when the angle between the probe pulse wave vector $k_1$ and its projection in the $x$-$z$ plane is at the Bragg value $\theta_0$ satisfying

$$\sin \theta_0 = \pi/\Lambda k_1,$$

where $\Lambda = 2\pi/|k_2 - k_3|$. The probe pulse at $\omega_1 = \omega_{ab}$ thus leads to a diffracted beam in the direction $k'_1 = (k_2 - k_3)$ (dotted line in fig. 1), the intensity of which is a measure of the population gratings remaining at time $t$.

2. Results

2.1. Experimental

The experimental apparatus is identical to that described earlier for delayed CARS experiments on the same system [9,10], except for the arrangement of beams in space (fig. 1). The sample was a $\approx 0.5$ mm thick single crystal of naphthalene doped with pentacene at a concentration of $10^{-5}$ M/M. The beams enter the $ab$ face of the crystal and are polarized along $x$, which corresponds to the crystal $a$ axis. The applied frequencies are $\omega_1/2\pi c = 16577$ cm$^{-1}$ ($6030.9$ Å) and $\omega_2/2\pi c = 15821$ cm$^{-1}$ ($6319.1$ Å). The state $|b\rangle$ is the 756 cm$^{-1}$ ground-state vibration of pentacene while $|d\rangle$ is the 747 cm$^{-1}$ vibration of $S_1$. The offset $\Delta$ in fig. 2 is $9$ cm$^{-1}$.

All pulses have an intensity fwhm of $6$ ps. Pulses 2 and $2'$ have energies of $1.0 \times 10^{-6}$ J. The probe pulse $1'$ is $0.2 \times 10^{-6}$ J while pulse 1 is varied below $0.9 \times 10^{-6}$ J. The spot diameters in the sample are $\approx 100$ µm.

The diffracted light at $\omega_1$ is filtered spatially and with a monochromator. The repetition rate is $10$ s$^{-1}$ and the delay of the probe pulse is slowly scanned while averaging the photomultiplier output with a boxcar integrator with an effective time constant of several seconds. The sample temperature is $4.2$ K.

2.2. Grating decay

Fig. 3 shows the diffracted fluence at $\omega_1$ as a function of the delay $t$ of the probe pulse for two different intensities of the $\omega_1$ pump-pulse energy. At $t < 0$ there is a finite signal of which $\approx 90\%$ depends on the probe pulse and the remainder on the $\omega_1$ preparation pulse. These signal levels are unaffected by blocking one or both $\omega_2$ beams. This stray light is minimized by moving the sample to those spots at which the transmitted beams are least aberrated.

As the probe pulse begins to overlap with the preparation pulses there is an increase in the diffracted light, a partial dip centered at $t = 0$ and a recovery followed by a monotonic decay to an asymptotic level. This long-lived asymptote expressed as a fraction of the maximum scattering increases from $30\%$ in fig. 3a to $60\%$ in fig. 3b with a doubling of the intensity of the $\omega_1$ preparation pulse. In addition, the maximum moves to finite delay. When either or both of the $\omega_2$ pulses are blocked, the signal returns to the stray-light level observed at $t < 0$.

2.3. Fluorescence

With the same irradiation sequence, the incoherent
3. Theory

3.1. Grating kinetics

A doubly rotating frame density operator formalism for the calculation of the coherences and populations resulting from the preparation pulses at \( \omega_1 \) and \( \omega_2 \) has been given elsewhere [9]. Here we relate the kinetics in the dark of the populations \( \rho_{ii} \) after such preparation to the transient grating amplitudes detected by the scattering of the probe pulse. The model for low-temperature vibrational relaxation is expressed by the rate equations

\[
\begin{align*}
\dot{\rho}_{aa} &= T^{-1}_{1b} \rho_{bb}, \\
\dot{\rho}_{bb} &= -T^{-1}_{1b} \rho_{bb}, \\
\dot{\rho}_{cc} &= T^{-1}_{1d} \rho_{dd}, \\
\dot{\rho}_{dd} &= -T^{-1}_{1d} \rho_{dd}.
\end{align*}
\]

These state that population in \( \mid d \rangle \) relaxes into \( \mid c \rangle \) with an exponential decay time \( T_{1d} \) and similarly population in \( \mid b \rangle \) relaxes into \( \mid a \rangle \) with a time \( T_{1b} \). Electronic decay processes responsible for the 19.5 ns lifetime of \( \mid c \rangle \) [11] are negligible on the picosecond timescale of the current observations.

As sketched in fig. 2, \( \omega_1 = \omega_{db} = \omega_{ca} - \Delta \). Since both the Rabi frequency and the spectral width of the probe pulse will be a significant fraction of \( \Delta \), the contributions of both the \( \mid d \rangle \leftrightarrow \mid b \rangle \) and \( \mid c \rangle \leftrightarrow \mid a \rangle \) resonances will be considered in the scattering of \( \omega_1 \). The other electronic transitions are off-resonance by the much larger vibrational energy and so do not contribute to the diffraction.

At a given position in the sample, the polarization induced by the probe pulse will depend on the population differences \( \rho_{dd} - \rho_{bb} \) and \( \rho_{cc} - \rho_{aa} \). The diffracted field (section 3.2) will be assumed to be proportional to the differences \( \Delta_{db} \) and \( \Delta_{ca} \) in these quantities between a crest and a trough of \( I(\omega_2) \) at the beam center. Since the populations \( \rho_{bb} \) and \( \rho_{dd} \) require \( \omega_2 \) in order to be excited, they are zero at the troughs. The prepared population \( \rho_{cc} \) will be taken as identical at peak and trough, consistent with the observation that the fluorescence of the sample was not measurably dependent on \( I(\omega_2) \). Solving eq. (2) and incorporating these assumptions, the crest-to-trough differences are found to be

emission from \( \mid c \rangle \) to the ground-state vibrations at \( \approx 1370 \text{ cm}^{-1} \) was observed. To within the observational sensitivity of 10%, this is independent of both the probe-pulse delay and of the presence or absence of the \( \omega_2 \) beams.

Fig. 3. Decay of gratings induced at two different intensities of the \( \omega_1 \) preparation pulse as measured by Bragg scattering of the delayed probe pulse. In (a) the \( \omega_1 \) preparation pulse is 0.45 \( \mu \)J. The solid curve is a simulation according to eq. (4) with \( s = 2.35, \phi_\theta = \pi, \rho_{dd}(\tau) = 0.016, \rho_{bb}(\tau) = 0.037, \rho_{cc}/\rho_{ca} = 2.45, T_{1d} = 33 \text{ ps} \) and \( T_{1b} = 51 \text{ ps} \). For the dashed curve the parameters are the same except that \( \rho_{dd}(\tau) = 0.05 \) and \( \rho_{bb}(\tau) = 0.035 \). In (b) the \( \omega_1 \) pulse is 0.9 \( \mu \)J. The detection sensitivity was lowered between the scans. The solid curve has the same parameters as the corresponding curve in (a) except \( \rho_{dd}(\tau) = 0.05 \) and \( \rho_{bb}(\tau) = 0.066 \). The dashed curve uses these same initial populations and is otherwise analogous to the dashed curve of (a).
\[ \Delta_{db}(t) = \rho_{dd}^c(\tau) \exp(-t/T_{1d}) - \rho_{bb}^c(\tau) \exp(-t/T_{1b}). \quad (3a) \]
\[ \Delta_{ca}(t) = 2\rho_{db}^c(\tau) - \rho_{dd}^c(\tau) \exp(-t/T_{1d}) \\
+ \rho_{bb}^c(\tau) \exp(-t/T_{1b}). \quad (3b) \]

where the initial condition \( \rho^c(\tau) \) is the density operator at a crest of \( I(\omega_2) \) at the end of the preparation period of duration \( \tau \).

### 3.2. The diffracted beam

The scattering of the probe pulse by the population gratings may be described as Bragg diffraction of light by a thick, sinusoidal hologram grating. The steady-state low-power theory of such diffraction is well known \([12,13]\). In this limit, the sample is characterized by the periodic modulation of its absorption coefficient (amplitude or absorption grating) and of the real part of the refractive index (phase grating). For a grating with wave vector perpendicular to the traversed sample faces, the intensity of the light diffracted at the Bragg angle is a sum of a contribution from each of these gratings.

For the present experimental situation, where the probe pulse is far shorter than the relaxation times of the levels responsible for the optical grating, the existing theories are not directly applicable. In lieu of a full treatment of the coherent propagation problem, we propose here a simple model for the scattered signal which retains some physical features of the steady-state coupled-wave theory \([12,13]\) and in addition incorporates the stray light observed experimentally. The signal flux is taken to be of the form

\[ \Phi(t) = s + \exp(i\phi_g) [c_{db}\Delta_{db}(t) + ic_{ca}\Delta_{ca}(t)]. \quad (4) \]

The first term represents the stray-light field. Its phase is, without loss of generality, taken as zero. The overall phase \( \phi_g \) of the grating terms with respect to the stray light is then a fitting parameter. The real parameters \( c_{db} \) and \( c_{ca} \) characterize the scattering effectiveness for a certain probe pulse of the gratings \( \Delta_{db} \) and \( \Delta_{ca} \), respectively. Since the contribution of a transition to the phase grating vanishes at exact resonance \([14-16]\), \( \Delta_{db} \) contributes only to the amplitude grating and has a real coefficient in eq. \((4)\). On the other hand, the \( \omega_{ca} \) transition is off resonance by \( 9 \text{ cm}^{-1} \), which exceeds both the spectral width and Rabi frequency of the probe pulse. Thus \( \Delta_{ca} \) will contribute almost exclusively to the phase grating and its coefficient in eq. \((4)\) is taken as imaginary.

An assumption implicit in eq. \((4)\) is that the stray-light field is coincident in time with the grating scattering and that the grating phase \( \phi_g \) is constant over the several-minute scan of the delay table. A much smaller contribution to the stray-light flux at the detector is due to the \( \omega_1 \) preparation pulse. Since this contribution is not simultaneous with the scattering of the probe pulse at finite delay, it was simply subtracted and does not appear in eq. \((4)\).

### 3.3. Simulations

The solid lines in fig. 3 are simulations according to eq. \((4)\). The parameters used are given in the caption. The excited-state vibrational lifetime, \( T_{1d} = 33 \text{ ps} \), is already known from stimulated echo experiments on the \( 1d) \leftrightarrow 1a) \) transition \([11]\). The ground-state vibrational lifetime used is \( T_{1b} = 51 \text{ ps} \). This is one half of the \( T_2 \) measured previously \([9]\) by delayed CARS for the \( 1b) \leftrightarrow 1a) \) transition. This relationship holds if there is no pure dephasing contribution to \( T_2 \) at this low temperature. The magnitude of the probe-pulse stray light \( s^2 \) is measurable, since this is the only signal when the \( \omega_1 \) preparation pulse is blocked.

This still leaves the parameters \( c_{db}, c_{ca}, \phi_g, \rho_{dd}^c(\tau) \) and \( \rho_{bb}^c(\tau) \) to be determined by simulation. The search is further constrained since the ratio \( c_{db}/c_{ca} \) of the scattering amplitudes is independent of preparation. The individual values were allowed to vary between the two scans in order to accommodate changes in the photomultiplier voltage and monochromator slit width. The phase angle \( \phi_g \) associated with the stray light was set to \( 180^\circ \) for both scans. Values up to \( 45^\circ \) away also gave plausible fits with the same \( T_{1b} \) and \( T_{1d} \), but with some adjustment of other parameters. Values around \( \phi_g = 0 \) led to a local minimum at finite delay which is inconsistent with the data. Another constraint for simulation of fig. 3b is that when the maximum diffraction is at finite delay, this delay and the ratio \( T_{1b}/T_{1d} \) uniquely fixes the ratio \( \rho_{dd}^c(\tau)/\rho_{bb}^c(\tau) \).

The dashed curves of fig. 3 are similar, but for these it was assumed that \( \phi_g \) is similar, "but" for the time scale of the boxcar integration.
4. Discussion

The details of the simulations must be considered tentative in view of the multidimensional parameter space and limited data, which does not allow a full exploration of the range of behavior predicted by eq. (4). While a more complete study is planned, this is not considered worthwhile with the present experimental arrangement, because of the signal-to-noise ratio currently attainable. The noise in fig. 3 is due overwhelmingly to instabilities in the pulses. This is not surprising because of the highly non-linear nature of the phenomenon: the lowest-order response involving the Raman population of \( |b\rangle \) and the subsequent scattering is expected to have a power dependence \( \Phi \alpha \Omega(\omega_1) \Omega(\omega_2) \Omega(\omega_1') \). Thus, it is even more susceptible to laser-power fluctuations than the conventional phenomena of non-linear optics described by the third-order susceptibility \( \chi^{(3)} \) [17]. In addition, fluctuations in \( \phi_g \) may be a source of noise.

We are currently modifying the apparatus to allow the recording and computer storage of all beam energies for each shot. This will eliminate noise due to energy fluctuations and facilitate intensity-dependent studies. Another useful modification would be to put one of the \( \omega_2 \) beams through an acousto-optic modulator so that it can be phase shifted. This modulates \( \phi_g \) and will allow an assessment of its stability. Also it may allow the phase-independent, \( \cos \phi_g \) and \( \sin \phi_g \) terms of eq. (4) to be measured separately.

Nevertheless, even these preliminary results are of interest. They demonstrate the potential of grating scattering for the measurement of vibrational \( T_1 \) in dilute crystals. The failure to observe any dependence of the fluorescence on probe-pulse delay or on \( f(\omega_2) \) shows that the technique can work in the near-resonance regime, where the occupation of the excited manifold via \( |b\rangle \) is small relative to the one-photon process from \( |a\rangle \). The advantage of the grating diffraction experiment over this fluorescence measurement or any absorbance technique is the relatively high ratio of signal to background at the detector.

The signals of fig. 3 are consistent with the assumption made in the fitting procedure that the previously observed \( T_2^{2b} = 101 \pm 5 \) ps [9,10] is lifetime limited. A value of \( T_{1b} \) up to \( \approx 80 \) ps cannot be ruled out within this model, especially when the fluctuation of the phase angle \( \phi_g \) is taken to be rapid compared to the boxcar integration time. A very likely explanation for a decay component of this order involves the presence of a bottleneck state in the vibrational decay that retards the recovery of \( |a\rangle \) slightly with respect to the decay of \( |b\rangle \). This is a subject of continuing investigation.

The theory presented here does not apply to the region around \( t = 0 \) where the preparation and probe pulses overlap, and this data was excluded from the simulations. A simple explanation of the dip at \( t = 0 \) is that the temporal overlap and interference of the beams 1 and 1' superimposes a second grating with an \( x \)-axis wave vector onto the \( y \)-axis grating due to beams 2 and 2' (see fig. 1). Not surprisingly, this attenuates the effectiveness of scattering in the direction of observation.

The long-lived component of the signal decay is interpreted as being due to excitation of \( |d\rangle \) during the preparation process. This population corresponds to the constant term \( 2p_{dd}(t) \) in \( \Delta_{ca}(t) \) [eq. (3)]. It becomes trapped in \( |c\rangle \) leading to a grating contribution, which presumably would vanish with the fluorescence lifetime. Though in the four-level model only the \( \omega_{ca} \) transition is responsible for this long-lived diffraction, a contribution from absorption from \( |c\rangle \) to some higher excited state cannot be ruled out presently.

Also associated with excitation of \( |d\rangle \) is the shift of the maximum to finite delay at the higher preparation power. The decay of \( |d\rangle \) into \( |c\rangle \) at short times increases the polarizability due to the partially bleached \( \omega_{db} \) transition and decreases that due to the \( \omega_{ca} \) transition. Both changes increase the contrast between crest and trough and thus increase the diffraction.

In transient grating studies of electronic relaxation, heating effects are often encountered which lead to long-lived components in the decay [1--5]. Such an effect seems unlikely here. The experimental observations demand that any energy deposition mechanism invoked to explain the signal must depend on the simultaneous presence of \( \omega_1 \) and \( \omega_2 \) during pumping. The two-photon (Raman) population of \( |b\rangle \) and the subsequent population of \( |d\rangle \) by a third photon are the only obvious candidates for such an absorption process. On the time scale of the experiments, either absorption process contributes at most a vibrational quantum to the lattice since relaxation of \( |c\rangle \) occurs on the far longer time scale of the fluorescence decay.
Any change in the scattering properties of the lattice upon absorbing these quanta should be insignificant relative to the near-resonant changes of the four-level system which is losing them.

Acknowledgement

The investigations were supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

References