Line Broadening and Line Shifts in One- and Two-Photon Single-Molecule Spectra

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The temperature and laser-power dependent $S_1 \leftarrow S_0$ spectra of single diphenyloctatetraene molecules in *n*-tetradecane are investigated using one- and two-photon excitation at cryogenic temperatures. Under one-photon excitation, the single-molecule transitions shift to lower frequencies and the line widths increase with increasing temperature while the line shapes are independent of the laser power up to spectral saturation. The experimental data are consistent with the model of thermal activation of a single local phonon. Under two-photon excitation, the transitions shift linearly to lower frequencies with increasing laser power while the lines broaden only weakly. These results are discussed in terms of laser-induced ac-Stark shifts and matrix dynamics. In particular, a bottleneck effect in the thermalization of nonequilibrium phonons is supposed to play an essential role in the observed broadening and shifts. The comparison of one- and two-photon excitation spectra provides information about the processes that govern the two-photon spectra.

1. Introduction

Single-molecule spectroscopy is a rapidly growing and diversifying field and several techniques have been applied to detect single molecules in different environments. Fluorescence excitation spectroscopy has been shown to provide a very sensitive method to investigate the optical properties of single molecules (SMs) under various conditions.[1−4]

The line shapes of single molecules are determined by intrinsic and matrix induced effects. The intrinsic effects are present for the molecules in the vacuum while the matrix induced effects are due to the interaction of the molecule with its environment. The transition frequency of a SM can be given as the sum of a static ω_0 (on the time scale of the experiment) and dynamic component ω' . ω_0 includes the molecular vacuum transition frequency and the static solvent shift. Because of lattice inhomogeneities, ω_0 changes from molecule to molecule which gives rise to the inhomogeneous broadening. Line narrowing techniques, such as spectral hole burning, can remove the inhomogeneous broadening.[5−7] Fluctuations in the transition frequencies result from dynamical processes in the molecule's environment. In the past, ω' was assumed identical for each chromophore, and accordingly, the effect of broadening was termed homogeneous line broadening. Single-molecule spectroscopy has established that not only ω_0 but also ω' changes from molecule to molecule so that each molecule has its own characteristic dynamic line shape.[8−15]

The dopant chromophores located substitutionally in the lattice give rise to low-frequency local vibrations which foremost influence the line shapes at temperatures below 10 K. Hesselink and Wiersma[16] investigated the dephasing of photon echoes for mixed molecular crystals of pentacene in naphthalene and *p*-terphenyl in the range of 4.5−20 K. The comparison of the echo signals of protonated and perdeuterated pentacene in naphthalene revealed that the dephasing is dominated by a librational local modes. A librational mode was also identified for tetracene in *p*-terphenyl by Kryschi et al.[17] Voelker et al. studied the temperature dependent shape of photochemically burned spectral holes for free-base porphin in *n*-octane crystals between 1.7 and 4 K.[18] Their analysis showed that the frequencies of the spectral holes shift and the widths increase according to activation laws with identical activation energies indicating the coupling of the chromophore to a single local phonon. An example was also reported by Dicker et al.[19] Most of the investigations based on SM techniques have concentrated merely on the line widths[20−25] and only very few studies have so far taken advantage of the SM resolution to investigate the temperature dependence of both, frequency shifts and line broadenings.[26,27]

Recently, the spectra of single diphenyloctatetraene (DPOT) molecules in *n*-tetradecane (TD) matrices were studied using two-photon (TP) excitation.[28] This technique allows for the investigation of nonlinear optical phenomena in single quantum systems and provides good sensitivity at low background. In particular, the SM lines were observed to shift linearly to lower frequencies with increasing laser power while the broadening was weak.[29] These observations were explained by an ac-Stark effect and by a temperature increase of the matrix induced by the laser irradiation. However, it has remained ambiguous to which extent the optical ac-Stark effect contributes to the shift and whether other mechanisms of the matrix dynamics could lead to SM frequency shifts. For example, using the intensity-time-frequency correlation (ITFC) technique an accelerated spectral diffusion in TP excitation spectra was identified.[30] One way to settle these questions is to use one-photon (OP) excitation. In this case, very little energy is dissipated into the lattice and thermal effects can be studied in the absence of laser-induced heating.

In this paper, we report on the temperature-dependent line shapes of single DPOT molecules in TD Shpol'skii matrices under OP excitation at cryogenic temperatures. These results are then used for the interpretation of previously measured SM TP excitation spectra.

2. Experimental Section

Shpol'skii samples of TD doped with about 10^{-5} M DPOT were produced by fast cooling of a thin layer of liquid solution

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that was sandwiched between two microscope coverslips. The OP transition from the 1^1A_g ground (S_0) to the 2^1A_g lowest excited singlet (S_1) state of DPOT is forbidden by parity. It becomes weakly allowed when the crystal field induces a symmetry breaking which can be described as a vibronic coupling between the S_1 and the nearby ^1B_u state.[31,32] Here we investigate the zero-phonon transition of single DPOT molecules at the noncentrosymmetric Shpol'skii site I with $\lambda = 444.0$ nm using OP and TP excitation. The experimental setup has been presented in refs 33 and 34.

For the temperature-dependent measurements, the samples were mounted in a He-flow cryostat (Janis SVT-200) and the sample temperature was regulated between 1.8 and 7 K with a temperature controller (LakeShore 330). For OP excitation, the beam of the single-mode Ti:sapphire laser emitting at 888.4 nm was frequency doubled and scanned over the molecular resonance, while detecting the red-shifted fluorescence. The laser intensity was kept below the saturation intensity of about 1 W/cm^2 to avoid saturation broadening. At such intensities and an excitation spot of 2−4 μm diameter the laser-induced heating was negligible. The power released to the matrix was 10^6−10^7 times smaller in OP if compared to TP excitation experiments. An accurate control of the laser frequency was achieved using a home-built temperature stabilized reference cavity with a free spectral range of 163 MHz and a finesse of 9. The long-term frequency drift of this cavity was 0.02 (±0.02) MHz/h, measured for 9 h. The frequency fluctuations on short time scales were 2.7 MHz. The spectra were corrected with respect to the cavity transmission fringes.

3. Results

3.1. One-Photon Excitation. Using OP excitation fluorescence spectroscopy, line widths and frequency shifts of several individual molecules were measured in the temperature range of 1.8−6.6 K. For the two temperatures, 1.8 and 5.15 K, the spectra of molecules E−H are displayed in Figure 1. The changes of line widths and shifts are clearly visible if the two spectra are compared. The lines of the two molecules F and G, close to each other in frequency, could not be resolved anymore at 6.6 K.

For the interpretation of the observed broadening and line shifts we consider the model of a single local mode for which the broadening $\Delta\Gamma$ and line shift $\Delta\nu$ are[35−38]

$$\Delta\Gamma = \Gamma - \Gamma_0 = \beta_\Gamma W\tau \tag{1}$$

$$\Delta\nu = \nu - \nu_0 = \beta_\nu W\tau \tag{2}$$

where Γ_0 and ν_0 are the line width and frequency at zero temperature, W is the excitation rate of the upper phonon state, and τ is the lifetime of this state.

The constants are

$$\beta_\Gamma = 2\tau\delta\left(\frac{\delta/2\pi}{1+\tau^2\delta^2}\right),\quad \beta_\nu = \left(\frac{\delta/2\pi}{1+\tau^2\delta^2}\right) \tag{3}$$

where δ is the difference in the electronic transition energy upon the local mode excitation. In thermal equilbrium, $W\tau = \exp(-E_a/kT)$ so that line widths and shifts results from the activation laws

$$\Delta\Gamma = \beta_\Gamma \exp(-E_a/kT) \tag{4}$$

$$\Delta\nu = \beta_\nu \exp(-E_a/kT) \tag{5}$$

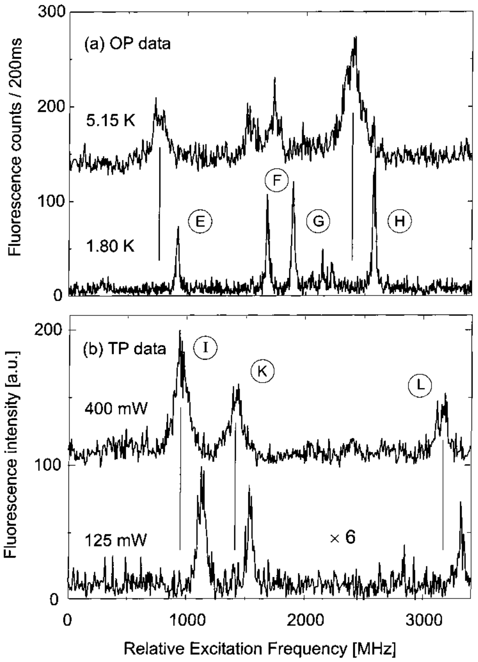

Figure 1. Excitation fluorescence spectra of DPOT in TD. (a) OP excitation spectrum of DPOT molecules E−H in TD at 1.8 and 5.15 K (trace shifted for clarity) recorded at a laser wavelength of 444.2 nm. (b) TP excitation spectrum of molecules I,K, and L taken from ref 28. The spectra were recorded at 1.8 K and a laser wavelength of 888.3 nm for excitation powers of 125 and 400 mW (trace shifted for clarity).

where E_a denotes the activation energy equal to the energy $\hbar\omega_{LP}$ of the local phonon. Note that Γ and ν are in units of Hz, whereas δ is in units of rad s^{-1}. As a characteristic quantity for the discrimination between the different processes we consider the ratio

$$\frac{\Delta\Gamma}{\Delta\nu} = \frac{\beta_\Gamma}{\beta_\nu} = 2\tau\delta \tag{6}$$

which does not depend on temperature.

Within the model of a single local mode, the zero-phonon line (ZPL) consists, in addition to the conventionel Lorentzian, of a dispersive component and a sideband.[39] The relative amplitude of the dispersive component was estimated to be smaller than 2% and is thus below the noise level of the present data. The latter holds also for the sideband. Therefore, simple Lorentzians were fitted to the experimental SM spectra to dermine line widths and frequencies for all temperatures. The differences $\Delta\Gamma(T)$ and $\Delta\nu(T)$ were then fitted to the activation laws, eqs 4 and 5; the parameters are listed in Table 1. For molecule D the line widths and line shifts are shown in Figure 2 together with the fits. For all molecules there was no significant variation of the line frequencies and line widths below 3 K. Therefore, we set Γ_0 and ν_0 equal to the average of the values between 1.8 and 2.5 K. Good agreement with the activation laws was obtained at lower temperatures, at temperatures above 6 K there are significant deviations. These deviations are more pronounced for the broadening than for the shift. Thus, bulk phonons may be the reason for the deviations because they lead to a broadening that grows faster than the shift with increasing temperature.[40] The activation energies of the 9 molecules in Table 1 are between 14 and 19 cm^{-1} and the lifetimes within 1−3 ps. Similar results were observed for octatetraene in *n*-hexane.[41] The width-to-shift ratios are in the range of $0.4 < |\Delta\Gamma/\Delta\nu| < 1.0$.

TABLE 1: Line width, Activation Energies, and Related Parameters of Single DPOT Molecules in TD Obtained from the Temperature Dependent OP Excitation Spectra: The Ensemble Values Determined from the SFS Investigations Are Also Presented.

molecule	Γ_0 [MHz]	E_a/hc [cm^{-1}]	β_Γ [GHz]	β_ν [GHz]	(β_Γ/β_ν)	$(\delta/2\pi)$ [GHz]	τ [ps]
A	27.5	17.2	11.8	−31.4	0.38	−32.5	0.9
B	18.0	17.9	24.1	−25.3	0.96	−31.0	2.5
C	35.0	17.3	15.7	−24.4	0.64	−26.9	1.9
D	58.5	14.6	13.5	−18.0	0.76	−20.5	2.9
E	25.7	18.9	18.6	−34.8	0.54	−37.3	1.1
F	22.2	17.0	9.4	−20.2	0.48	−21.3	1.8
G	26.6	15.9	7.0	−15.8	0.44	−16.6	2.1
H	29.2	16.7	11.0	−21.1	0.56	−22.5	1.8
J	32.0	18.9	13.6	−34.2	0.40	−35.5	0.9
average	30.5	17.2	14	−25	0.57	−27	1.7
SFS[a]	25.0	20.7	16.8	−38	0.44	−40	0.9
SFS[b]	26.0	19.7	15.0	−42	0.36	−43	0.7

[a] Same sample. [b] Different sample.

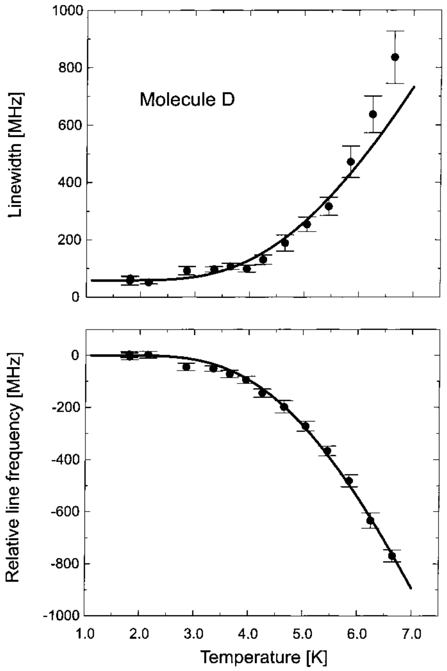

Figure 2. Temperature-dependent line width and frequency shifts of molecule D. The solid lines are the fits to eqs 4 and 5. The parameters are given in Table 1.

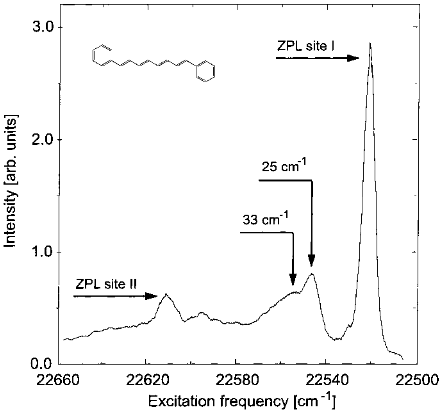

Figure 3. TP excitation spectrum of the $S_1 - S_0$ transition of DPOT in TD at 1.8 K. The 0−0 zero-phonon line (ZPL) at 22521 cm^{-1} (444.0 nm) results from a noncentrosymmetric site (site I) and the ZPL at 22625 cm^{-1} from a centrosymmetric site (site II), respectively. Note that the frequency scale corresponds to twice the laser frequency in the case of TP excitation.

To compare SM with ensemble data, we investigated the statistical fine structure (SFS) of OP excitation spectra.[34,42] From the autocorrelation function of the spectra we determined the ensemble line width for each temperature and from the cross-correlation function calculated from spectra at different temperatures we determined the temperature-dependent frequency shifts of the ensemble. The results obtained from two different samples are also given in Table 1. A reasonable agreement between the SM and the SFS data is observed. We thus conclude that the molecules A−J form a representative set.

To relate the fitted activation energies to observed local phonon modes, we consider the TP excitation spectrum of DPOT in TD at 1.8 K shown in Figure 3. The 0−0 ZPL at 22521 cm^{-1} is assigned to a chromophore located at the noncentrosymmetric site I. This line was also observed under OP excitation.[33] The line at around 22625 cm^{-1} (442.1 nm) is the ZPL of DPOT located at the centro-symmetric site II and is absent in OP excitation spectra. Here we report exclusively on spectra assigned to site I. Two peaks at 25 and 33 cm^{-1} are clearly resolved in the phonon band of the ZPL of site I. Both frequencies are larger than the local mode frequencies obtained from the activation laws. We argue that local vibrations crucial for the broadening and shift need not necessarily be strongly active modes in allowed electronic transitions. In a hole-burning study of phthalocyanine doped TD, Rebane et al.[43] reported that the phonon frequency obtained from the sideband was about twice the activation frequency determined from the temperature dependent line broadening. It was concluded that the local mode detected in the sideband was totally symmetric while the mode of the activation process was nontotally symmetric. Using the same argument, we conclude that the local modes responsible for the activation behavior of the line widths and shifts are of low symmetry.

The measured line widths are now compared with the lifetime limited value. The lifetime was determined from the decay of the $S_1 \rightarrow S_0$ fluorescence of DPOT in TD at 1.8 K. The measurements yielded 11.0(5) ns corresponding to an homogeneous line width of 14.5 MHz. This value, although measured for the bulk, is considered as a lower limit for the line width of the individual chromophores. Only very few of the measured line widths are close to the limiting value of 14.5 MHz, most of the measurements exceed this value typically by 5−20 MHz. We speculate that the origin of the additional broadening is spectral diffusion caused by TLS dynamics.

3.2. Two-Photon Excitation. We first review previous TP-excitation investigations of DPOT in TD.[29] The SM lines shift linearly to lower frequencies with increasing laser power. In the range of 125−400 mW the slopes are 500−800 MHz/W. The broadening was much less affected and a line width increase of 30−140 MHz/W was reported. It was concluded that a smaller part of the shift is due to the ac-Stark effect, while the major contribution is due to a laser-induced heating of the matrix.[29]

For two different laser powers the TP excitation spectra are shown in Figure 1b so that the temperature dependence of OP excitation spectra can be compared with the power dependence of TP excitation spectra. At 125 mW the lines in the TP spectra are broader than the lines in the OP spectra at 1.8 K by approximately a factor of 2. This results from the TLS dynamics induced by the irradiated laser power.[30] The line shifts observed in the OP spectra, when the temperature is increased from 1.8 to 5.1 K, are approximately equal to the line shifts observed in the TP spectra, when the power is increased from 125 to 400 mW. The corresponding broadening, however, is much smaller in the TP spectra than in the OP spectra.

Considering molecule E in Figure 1a as an example, the line width increases by 110 MHz and the frequency shifts by −175 MHz upon a temperature change from 1.8 to 5.15 K. The corresponding width-to-shift ratio is $|\Delta\Gamma/\Delta\nu|_{\mathrm{OP}} \simeq 0.6$. This compares with a line broadening of $\Delta\Gamma \simeq 50$ MHz and a shift of $\Delta\nu \simeq -160$ MHz observed for molecules I, K, and L in Figure 1b upon a laser power increase from 125 to 400 mW. The broadening of $\Delta\Gamma \simeq 50$ MHz results from matrix dynamics and saturation.[28] Accounting for an optical saturation broadening of at least 35 MHz, the remaining broadening is $\Delta\Gamma \lesssim 15$ MHz which yields a width-to-shift ratio of $|\Delta\Gamma/\Delta\nu|_{\mathrm{TP}} \lesssim 0.1$. Thus, $|\Delta\Gamma/\Delta\nu|$ ratio is at least 5 times larger for OP excitation than for TP excitation.

The value of $|\Delta\Gamma/\Delta\nu|_{\mathrm{TP}} \lesssim 0.1$ is supported by the TP−SFS analysis. From the auto- and cross-correlation function of the SFS data we observed that upon an increase of the laser power from 70 to 340 mW the lines shift to lower frequencies by approximately 44 MHz and broaden by less than 9 MHz. The increase in width and shift is significantly smaller for the SFS than for the SM technique because an average is taken over the spatially inhomogeneous laser field in the illuminated spot by the SFS technique. Accordingly, the average laser field is considerably smaller than the field at the center of the spot relevant for the SM detection. The ratio of $|\Delta\Gamma/\Delta\nu|_{\mathrm{TP-SFS}} = 9/44 \simeq 0.2$ is an upper limit, because part of the 9 MHz broadening is caused by power-broadening. Concluding, the TP−SFS data confirm that in TP excitation spectra the width-to-shift ratio is $\lesssim 0.1$.

4. Discussion

In this Section we address the question whether the frequency shifts observed in TP-excitation spectra are light shifts or thermal effects.

4.1. ac-Stark Effect. The ac-Stark effect is primarily an intrinsic property of the molecule.[44,45] The SM frequency shifts due to the nonlinear interaction between molecule and laser field. To lowest order of approximation the ac-shift of the molecule in the vacuum is given by

$$\Delta\nu_{\mathrm{Stark}} = -\frac{1}{4h}\mathbf{F}\Delta\alpha\mathbf{F} \tag{7}$$

where $\Delta\alpha$ is the difference between the dynamic polarizability tensors of the excited and ground states at the laser frequency ν_{L}, $\mathbf{F}$ is the laser electric field amplitude at the location of the molecule, and h is Planck's constant. The ac-Stark effect causes exclusively a light shift and does not give rise to a line broadening.

For DPOT the strong transition dipole moments are aligned parallel to the long axis of the molecule,[46] and therefore only the component of the polarizability tensor parallel to the long axis is considered. We thus write for the molecule in the solid

$$\Delta\nu_{\mathrm{Stark}} = -\frac{1}{2hc\epsilon_0}R^2L^2\cos^2\beta\,\Delta\alpha(\nu_{\mathrm{L}})I \tag{8}$$

where c is the speed of light, ϵ_0 is the vacuum permittivity, and $\cos\beta$ is the direction cosine of the field polarization relative to the molecular axis. I is the laser intensity at the location of the molecule in the absence of the dielectric matrix (in units of $\mathrm{Wm^{-2}}$). In eq 8 we have also considered dielectric field corrections: $R = 2/(n + 1)$ accounts for the reflection of the incident field on the sample surface and $L = (n^2 + 1)/3$ is the Lorentz field correction, where n is the refractive index. The dynamic polarizabilities of the ground and excited state are

$$\alpha_{\mathrm{g}}(\nu_{\mathrm{L}}) = 2\sum_i |\langle g|\mu|i\rangle|^2 \frac{E_i}{E_i^2 - (h\nu_{\mathrm{L}})^2} \tag{9}$$

$$\alpha_{\mathrm{e}}(\nu_{\mathrm{L}}) = 2\sum_i |\langle e|\mu|i\rangle|^2 \frac{E_i - E_e}{(E_i - E_e)^2 - (h\nu_{\mathrm{L}})^2} \tag{10}$$

where the sums run over all states i with energy E_i and wave function $|i\rangle$. μ is the electric dipole moment operator. For resonant TP excitation $2h\nu_{\mathrm{L}} = E_e$.

We are not aware of detailed ab initio calculations of the first few electronically excited states and of corresponding transition moments that would allow for a reliable calculation of the dynamic polarizabilities. For an estimate we therefore consider the dc-polarizabilities parallel to the long molecular axis[47,48] $\alpha_{\mathrm{g}}^{\mathrm{dc}} = 100 \times 10^{-40}\,\mathrm{CV^{-1}m^2}$ and $\alpha_{\mathrm{e}}^{\mathrm{dc}} = 165 \times 10^{-40}\,\mathrm{CV^{-1}m^2}$, yielding $\Delta\alpha^{\mathrm{dc}} = 65 \times 10^{-40}\,\mathrm{CV^{-1}m^2}$. Taking into account the laser spot size of 2 μm diameter, the angle β of approximately 60°,[34] and the refractive index of $n \simeq 1.45$, we get $\Delta\nu/\Delta P \simeq -180$ MHz/W. This value is significantly smaller than the observed value of $\Delta\nu/\Delta P \simeq -(500-1000)$ MHz/W. From eqs 9 and 10 it follows that the ac values are larger than the dc values in general so that one might expect that $\Delta\alpha^{\mathrm{ac}} > \Delta\alpha^{\mathrm{dc}}$. However, a substantial contribution to the polarizabilities is from the second electronically excited-state $|i\rangle = |\mathrm{S}_2\rangle$ at 24 390 cm^{-1}. This state contributes with a negative sign to the sum in eq 10 so that the dc value could also be larger than the ac value. Furthermore, the S_1 and S_2 states are close to each other, so that the matrix distortion of the molecule induces a strong interaction between these states. This renders the calculation of the dc-polarizabilities of the two states complicated.[48] We conclude that from the available data the observed shifts might be attributed without contradiction solely to an ac-Stark effect.

4.2. Matrix Dynamics. One part of the laser power is absorbed by the host molecules and dissipated into the lattice. This became evident from the observed boiling of the liquid helium at the film surface setting on at a laser power of 500 mW. The question thus arises whether the absorption and release of energy leads to highly nonequilibrium conditions and to a significant heating of the laser spot.

At temperatures as low as a few kelvins, the relaxation and thermalization of the absorbed energy is a complicated process. The molecular vibrational energy is released to lattice vibrations at nonthermal energies which give rise to pumping of phonon modes that otherwise would have negligible probability of population by thermal activation. The elastic and inelastic scattering probabilities and the mean free paths of the phonons

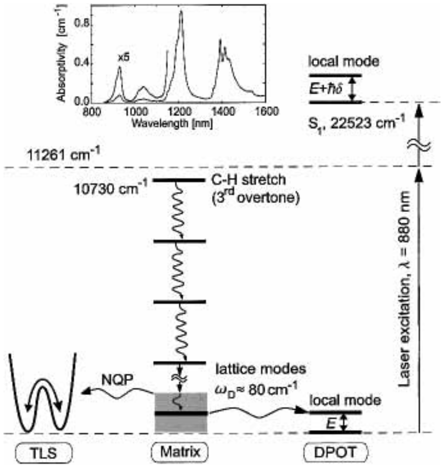

Figure 4. Scheme of the processes relevant for the laser irradiation at 888 nm. The third overtone of the C−H stretching vibration of the matrix molecules is pumped. NQPs are generated by vibrational relaxation, propagate and interact with TLSs. The chromophore DPOT is optically cycled between the S_0 ground and the S_1 excited state by TP laser excitation. The excitation and deexcitation of the local modes lead to a broadening and to line shifts. The inset shows the absorption spectrum of TD at room temperature.

depend on their frequencies.[49] Thus, the heat transport takes place ballistically and diffusionally through the micro crystallites. At the crystallite surfaces the heat transport is governed by the resistance of the heat transfer to the reservoir. The microcrystallite structure was detected using a microscope under white light illumination. The size of the crystallites was typically 10−30 μm.

A scenario of relaxation and associated phonon mediated processes is schematically shown in Figure 4. The IR irradiation is weakly absorbed by the 3rd overtone of the C−H stretching mode at 10 730 cm^{-1} of the matrix molecules. The absorption coefficient can be estimated from the absorption spectrum which was recorded at room temperature and is presented in the inset of Figure 4. At 888 nm the absorptivity is 0.008 cm^{-1} corresponding to an absorption coefficient of $\epsilon = 0.017$ cm^{-1}. Accordingly, the excitation rate of the matrix molecules is about 3 kHz at a laser intensity of 12 MW/cm^2 at the center of the laser-light focus. The vibrational energy is released by an unspecified relaxation path including molecular internal and lattice vibrations. Because multiphonon transitions play presumably a dominant role in the relaxation, the pumping of acoustic phonons takes place primarily at higher phonon frequencies below the Debye frequency ω_D, giving rise to nonequilibrium phonons (NQP).[49] The dissipation of energy by the host molecules may be compared with the energy dissipation by the single molecule resonant with the laser. An upper limit of the SM dissipation rate is determined by the lifetime of the S_1 state of 11 ns, corresponding to a rate of $\simeq 10^8$ s^{-1}. This compares with the excitation rate of $\simeq$3 kHz per host molecule times 10^{10}, the number of host molecules in the excited volume of $\simeq$ 4 μm^3. Thus, the SM absorption does not significantly contribute to the energy dissipation.

We now estimate the matrix heating under TP excitation on the basis of the OP excitation data. Assuming that in TP excitation spectra the broadening of 15 MHz owing to a power increase from 125 to 400 mW results solely from the heating, a temperature increase from 1.8 to 3.5 K is calculated using eq 4 and the averaged parameters of Table 1. At temperatures below 10 K the phonon mean free path is expected to be larger than the size of the micro crystallite. In such a case the temperature within the crystallites is governed exclusively by the heat transfer resistance at the crystal boundaries, also called Kapitza resistance.[50,51] This resistance was used to estimate the effective temperature $T_{\rm eff}$ in the crystal, $T_{\rm eff}^{\ 4} = T_{\rm b}^{\ 4} + \Lambda P$, where $T_{\rm b}$ is the temperature of the bath and Λ is a constant. If $T_{\rm eff}$ is inserted into eq 5, a nonlinear behavior of the frequency shift follows.[29] Evidently, on a small scale of power variation a quasi-linear dependence of the line shift results. From these considerations and from Λ adjusted to the data a heating of the irradiated crystallite by 1−2 K is feasible. On the basis of OP data the heating from 1.8 to 3.5 K is associated with a line shift of $\Delta\nu = -30$ MHz, that is −110 MHz/W, 1 order of magnitude smaller than the observed value. This result indicates that the shifts observed in TP-excitation spectra do not result from laser-induced matrix heating.

Since the IR energy is absorbed by the host molecules, high energy molecular vibrations and NQPs are generated everywhere in the laser spot which may interfere with chromophores and TLSs before thermalization. Such a process was documented for DPOT in TD by the ITFC technique.[30] It has been shown that the broadening in TP spectra increases with the frequency-scan time which is a signature of spectral diffusion. Because the line widths, recorded in the limit of fast scans in TP spectra, are equal to the ones of OP spectra, a significant matrix heating can be ruled out up to a power of 140 mW, at which the ITFC study was carried out. Thus, the remarkable conclusion follows that the spectral diffusion observed for slow scans, has to be assigned to TLSs triggered by NQPs. Because of the random distribution of the TLSs the spectral diffusion varies from molecule to molecule. In fact, 2−3 times less SMs were detected in TP than in OP spectra.[52] This was explained by spectral diffusion so strong that the majority of the molecules was no longer detectable.

Because a large amount of energy is released in a small volume, the laser spot represents a system far from equilibrium. We thus speculate that NQPs, which trigger the TLSs, may also pump higher frequency local modes. Our discussion is based on the following scaling laws valid for the Debye model:[53] $\tau_{\rm p} \sim \omega^{-5}$ for the phonon lifetime,$\tau_{\rm s} \sim \omega^{-4}$ for the elastic phonon scattering time, $l \simeq s\tau_{\rm s} \sim \omega^{-4}$ for the mean-free path, $D = l^2/\tau_{\rm s} \sim \omega^{-4}$ for the diffusion coefficient, $L \simeq \sqrt{D\tau_{\rm p}} \sim \omega^{-9/2}$ for the diffusion length, and $V_{\rm d} \sim \omega^{-27/2}$ for the diffusion volume, where s denotes the sound velocity. The large exponents indicate that the situation may change completely if the phonon frequency is altered. Above a critical phonon frequency $\omega_{\rm c}$ the diffusion length is expected to be smaller than the spot size. Thus, for frequencies $\omega > \omega_{\rm c}$ the propagating phonons do not escape from the excitation volume before decay and the pumping and relaxation mechanisms can be assumed to be homogeneous in space. Below $\omega_{\rm c}$ the diffusion length and the mean free path become much larger than the spot size. Correspondingly, the energy is carried efficiently out of the laser spot by phonons of frequencies below $\omega_{\rm c}$. This transport is limited primarily by the micro crystallite surfaces. Therefore, the critical frequency $\omega_{\rm c}$ acts as a *bottleneck* in the state occupancy of phonons in the laser spot.[54−56]

The energy of 10^4 cm^{-1} absorbed at a rate of 3 kHz per molecule, mentioned above, corresponds to a power of $\dot{Q}/hc \simeq 3 \times 10^7$ cm^{-1}s^{-1} per molecule. The absorbed energy is quickly released into propagating lattice vibrations. To estimate the NQP population, we make the following assumptions. (i) All phonon modes with $\omega_c < \omega < \omega_D$ are equally pumped. (ii) Phonons decay spontaneously into two phonons of equal frequency. Thus, for $2\omega_{\rm c} \geq \omega_{\rm D}$ only one generation of phonons has to be considered. The estimates, calculated below, do not significantly change, when these assumptions are modified, for instance when the pumping of phonons is restricted to frequencies close to ω_D and the first relaxation generation is considered in detail. From the balance between pumping and decay, the phonon occupancy obeys the scaling law $n_\mathrm{NQP} \sim \tau_p \sim \omega^{-5}$. Below ω_c the probability of the NQPs to remain in the laser spot scales as $1/V_d \sim \omega^{27/2}$. Therefore, the occupancy of phonons in the laser spot is assumed to follow the scaling law $n_\mathrm{NQP} \sim \omega^{\zeta}$, $\omega < \omega_\mathrm{c}$, $\zeta \simeq 5.5$, where the phonon density of states and the conservation of energy is taken into account. From the heat capacity measurements of TD we estimate the Debye frequency $\omega_D/2\pi c \simeq 80$ cm^{-1} and for the critical frequency we chose $\omega_c/2\pi c \simeq 35$ cm^{-1} based on the peaks in the phonon band in Figure 2. This value is slightly below $\omega_D/2$; nevertheless, we consider only one generation of the phonon relaxation.

We next estimate the phonon lifetime from the expression[57]

$$\tau_\mathrm{p} = \frac{128\rho s_\mathrm{L}^5}{h\phi^2}\left(1 + 2\left(\frac{s_\mathrm{L}}{s_\mathrm{T}}\right)^3\right)\omega_\mathrm{NQP}^{-5} \tag{11}$$

where s_L and s_T are the longitudinal and transverse sound velocities. ρ is the mass density and ϕ is the anharmonicity parameter. With $s_\mathrm{L} = 2900$ m s^{-1}, $s_\mathrm{L}/s_\mathrm{T} \simeq 2$, $0.5 < \phi < 2$, and $\rho = 762$ kg m^{-3}, we obtain $\tau_\mathrm{p}(\omega_\mathrm{c}) = 10-100$ ns. We are now able to normalize the occupancy $n_\mathrm{NQP} = N\omega^{-5}$ by equating the total pumping and the energy release integrated over all modes

$$\dot{Q} = \int_{\omega_\mathrm{c}}^{\omega_\mathrm{D}} n_\mathrm{NQP}(\omega)\, \tau_\mathrm{p}^{-1}(\omega)\, \hbar\omega\, \rho\omega\, \mathrm{d}\omega \tag{12}$$

where $\rho_\omega = 9\, N_\mathrm{M}\omega_\mathrm{D}{}^{-3}\omega^2$ denotes the density of phonon states, here considered for one molecule, $N_\mathrm{M} = 1$. We obtain $n_\mathrm{NQP}(\omega_\mathrm{c}) = 0.001-0.01$. These estimates are presumably lower limits because of the above assumptions concerning the pumping and single generation. We thus take $n_\mathrm{NQP}(\omega_\mathrm{c}) = 0.01$ as our estimate. This value is large if compared to the corresponding values at thermal conditions. A temperature of $T \simeq 11$ K is required for $n_\mathrm{NQP}(\omega_\mathrm{c}) = 0.01$ by thermal activation which demonstrates that NQPs may give rise to strong effects. The phonon-occupation $n_\mathrm{NQP} \simeq 0.01$ is small if compared with the limit required to establish a hot spot in the sense of Levinson.[53,54] Therefore, a hot spot is unlikely to be generated.

We estimate the frequency shift due to the nonequilibrium conditions by adopting the principle of equipartition of energy between resonant states. For a local mode with frequency $\omega_\mathrm{LP} = \omega_\mathrm{c}$, the detailed balance is $W\,\tau = n_\mathrm{NQP}(\omega_\mathrm{c}) \simeq 0.01$. Using the average β_ν value of Table 1, we obtain $\Delta\nu \simeq -250$ MHz. With respect to the uncertainties in the derivation, this estimate is in a reasonable agreement with the observed values of 160−320 MHz at 400 mW.

The broadening induced by NQPs is estimated from the scaling law $\tau \sim \omega_\mathrm{LP}^{-2}$.[58] Thus, $|\Delta\Gamma/\Delta\nu| \sim \omega_\mathrm{LP}^{-2}$, which shows that the motional narrowing becomes more effective with increasing local mode frequency. At $\omega_\mathrm{LP} \simeq \omega_\mathrm{c}$ we calculate a width-to-shift ratio of $|\Delta\Gamma/\Delta\nu| \simeq 0.1$, compatible with the data of TP excitation. Although we are not able to provide accurate estimates, we conclude that the observed line widths and shifts can be explained solely by NQPs.

To justify the bottleneck model we also estimate the phonon diffusion length at ω_c. For this purpose the mean-free path is needed, a quantity difficult to estimate because it depends on lattice imperfections and umklapp processes.[59−61] There are no data available for TD; we thus consider other organic solids. Interestingly, very low values are found for the heat conductivity when compared with data typical for insulators.[62] Conversely, the sound velocities show a regular behavior which indicates that there are small mean-free paths in these solids. For instance, for naphthalene at the relevant temperature of $T \simeq \hbar\omega_\mathrm{c}/3k_\mathrm{B} \simeq 17$ K,[59] the heat conductivity is $\kappa = {}^1\!/_3 Cs\bar{l} \simeq 5$ W m^{-1} K^{-1} [63] and the heat capacity per unit volume is $C = 4.5 \times 10^4$ J m^{-3} K^{-1}.[64] With the sound velocity of $s \simeq 2900$ m s^{-1} [65], we calculate a mean free path of $\bar{l} = 3\kappa/(Cs) \simeq 0.1$ μm. Taking this value for the mean-free path l of TD at ω_c we estimate a scattering time of $\tau_\mathrm{s} \simeq 30$ ps. The results obtained on the basis of naphthalene are consistent with values determined for anthracene[66] and polyethylene.[67,68] The scattering time of $\tau_\mathrm{s} \simeq 30$ ps is much smaller than the corresponding phonon lifetime of $\tau_\mathrm{p} = 10-100$ ns. Thus, the above considered equipartition of energies between NQPs and local modes is justified. With the estimated mean free path, the diffusion length is $L = \sqrt{ls\tau_p} \simeq 1-5$ μm which is of the order of the spot size. This result supports the choice of $\omega_\mathrm{c}/2\pi c = 35$ cm^{-1} as the critical frequency.

5. Conclusions

OP excitation spectra of the S_1-S_0 transition of single DPOT molecules in TD have been investigated as a function of the sample temperature between 1.8 and 6.6 K. With increasing temperature, the SM lines were observed to broaden and to shift to lower frequencies, both according to an activation law with the same activation energy of about 17 cm^{-1}. The line width-to-shift ratio $|\Delta\Gamma/\Delta\nu|$ was smaller than unity in all cases and typically 0.5. This behavior is characteristic for coupling of the optical transition to a single local phonon in the intermediate to fast exchange regime. Between 1.8 and 2.5 K the molecules showed a constant line broadening exceeding the lifetime limited value typically by 5−20 MHz. This was attributed to saturated TLS dynamics.

The temperature dependence of the OP data was then compared with the power dependence of SM TP data. While in OP excitation spectra the temperature dependent widths and shifts were obseved to obey activation laws, in TP excitation spectra a strictly linear dependence of the line shifts on the laser power and a weak broadening were observed. A possible explanation of the latter observations is given by the ac-Stark effect which leads to a linear dependence of the shift on the laser power and to no broadening. The shifts estimated from dc-polarizabilities, however, were significantly smaller than the observed values.

Matrix dynamics were also considered for the interpretation of the TP data. We found that NQPs play an important role. They accelerate the TLS dynamics which lead to a spectral diffusion as detected by the intensity−time-frequency-correlation technique. Therefore, the lines are significantly broader at the lowest laser power applied in TP excitation spectra when compared to corresponding lines in OP excitation spectra at the same temperature.

We considered the laser spot as a system far from equilibrium. Because of the dramatic change of the heat transport properties with frequency, a bottleneck in the phonon occupancy arises when the phonon diffusion length becomes smaller than the laser spot with increasing phonon frequency. Rough estimates indicate that NQPs may contribute substantially to line shifts while the corresponding broadening remains small.

We conjectured that the mean free paths of low-frequency phonons above the thermalization is larger than the size of the matrix microcrystallites so that the energy is transported ballistically. Therefore, the laser-induced heating of the micro crystallite is governed by the thermal transfer resistance at the crystallite surfaces. The observed boiling of the liquid helium at the film surface confirmed a heating of the crystallites at very large laser powers. Estimates showed that a weak broadening and small line shifts by heating of the sample are feasible.

This study of the temperature dependent SM OP excitation spectra has led to an improved understanding of the SM TP excitation spectra. Nevertheless, further studies are required to shed light on the aforementioned points. By the variation of the chromophores and matrices and by using two lasers for independent matrix and SM excitation, the contributions of the ac-Stark effect, spectral diffusion, NQPs, and matrix heating could decisively be disentangled.

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