Light Induced Single Molecule Frequency Shift

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A light induced frequency shift of the 0-0 line was measured in two-photon excitation spectra of single diphenyloctatetraene molecules doped in a crystal matrix. The shifts were proportional to the laser power with a slope of about 600 MHz/W when the laser beam of about 300 mW power was focused to a diameter of 2 μm. Significantly, the observed line broadenings were an order of magnitude smaller than the shifts. The effect is ascribed mainly to a "fast" energy exchange between a local vibration and thermal phonons created by the third harmonic C-H band absorption in the matrix, and partially to an ac Stark shift. [S0031-9007(96)02047-9]

Two-photon single molecule spectroscopy (SMS) in solids [1], a further development of the SMS technique providing observations of very fine effects without ensemble averaging [2], opened new possibilities for high resolution spectroscopy on a single quantum system (SQS). Precise control of interactions between a SQS and external fields is required for many potential applications of SQSs, e.g., quantum computation [3]. In this paper, a particular type of such interaction has been studied. We report on a light induced resonance frequency shift (LIFS) on the order of 200 MHz, of all-trans-1,8-diphenyloctatetraene (DPOT) in *n*-tetradecane (TD) [4].

The experimental setup has already been described [1]. The sample was immersed in a superfluid He bath. The purely electronic $1\,^1A_g \rightarrow 2\,^1A_g$ zero-phonon line of DPOT at 444 nm was excited by two photons with a wavelength at 888 nm when laser light with a power of a few hundred mW was focused onto a spot of 2 μm diameter. The luminescence emitted by DPOT was recorded as a function of the laser frequency detuning. All spectra were measured at a bath temperature of 1.8 K when the laser spot was placed far from the edges of a single TD microcrystal. The sizes of the crystals in the polycrystalline Shpol'skii sample were on the order of 40 × 10 μm with a thickness of 10–20 μm.

Two scans taken at different laser powers (Fig. 1) on the red wing of the inhomogeneous band show a significant LIFS of about 170 MHz for 3 single molecules (SMs). It is remarkable that the broadening of these lines was only 50 MHz. Methodical LIFS investigations have been performed for 11 SMs. To avoid a systematic error due to the laser frequency drift, the laser power was alternated between high and low levels several times (Fig. 2). For all molecules, the frequency shift could be satisfactorily fit to a linear function of the power. The average shift coefficient for the investigated molecules was −600 MHz/W. In contrast to the line frequencies, the linewidths were almost insensitive to the laser power though they were 2−3 times larger than under one-photon excitation [5]. A small broadening was observed at

powers above 250 mW, but this can be explained by saturation due to the triplet bottleneck [1]. To exclude saturation broadening only linewidths measured at powers below 250 mW have been taken into account. In this region, the broadening was at least 5 times smaller than the line shift (see Table I). In addition to this systematic and continuous line shift, discrete spectral jumps were observed (Fig. 3). Such jumps of a SM line frequency in a Shpol'skii matrix were reported in [6]. The laser power dependence of the jump rate was not studied in this work. For some molecules, this rate was so high that the contribution to the regular power shift could not be evaluated. Such molecules are not included in Table I where the data are summarized.

A resonance frequency shift $\Delta\nu$ is an intrinsic property of two-photon excitation (TPE) [7]. It is caused by
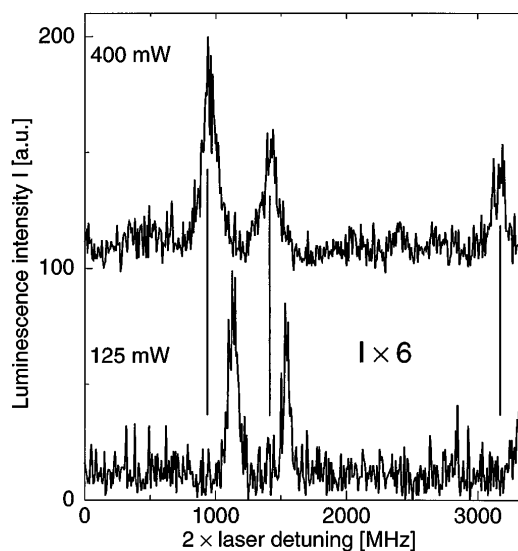

FIG. 1. TPE spectra of three SMs (molecules 6, 7, and 8 in Table I) measured at 400 and 125 mW laser power. There is a significant power dependent shift for the molecular resonance frequencies. The excitation wavelength was 888.3 nm. The horizontal axis scale is twice the laser frequency scale.
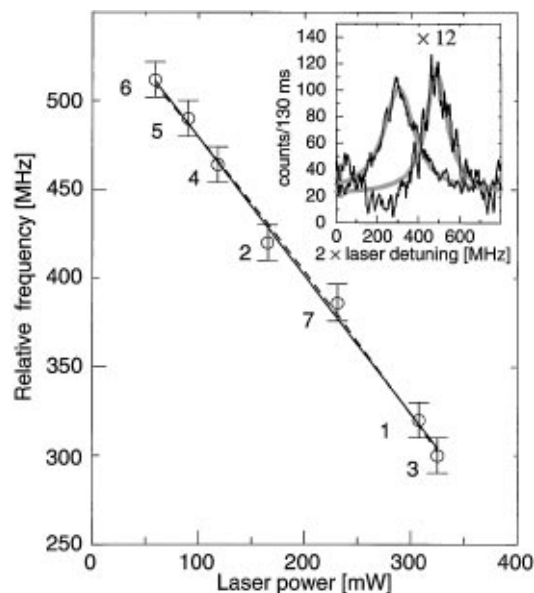
FIG. 2. Line shift power dependence observed for a SM (molecule 1 in Table I). The circles are the experimental data. The numbers near the data points show the order they were measured. The solid line is a linear fit. The dashed line is a fit to Eq. (2). The inset shows the SM line measured at 320 mW (left) and 90 mW (right) with Lorentzian fits.

the quadratic optical Stark shift and equals $-\Delta\alpha\Phi^2/4$, where $\Delta\alpha = \alpha_g - \alpha_e$ is the difference between the ground and excited state polarizabilities, and Φ is the ac electric field amplitude in the focus of the laser beam. For DPOT, $\Delta\alpha_z = 6.5 \times 10^{-39}$ C V^{-1} m^2 and $\Delta\alpha_x \approx \Delta\alpha_y \approx 0$ (z along the long axis of a DPOT molecule),

TABLE I. Power dependence of the line frequency and the linewidth for 11 SMs. The excitation power was changed within the range 60–400 mW. Γ_0 is the low power limit of the linewidth. In SMS it is difficult to avoid a selection when only the strongest SM lines are measured. One has to be careful when extrapolating SM data to the ensemble average.

Molecule	Line shift [MHz/W]	Γ_0 [MHz] (linear fit)	Line broadening [MHz/W]
1	-800 ± 25	120 ± 40	150 ± 160
2	-600 ± 120	60 ± 30[a]	$\ldots$[a]
3	-900 ± 300	80 ± 30[a]	$\ldots$
4	-520 ± 80	50 ± 20	30 ± 50
5	-600 ± 45	55 ± 15	60 ± 60
6	-630 ± 90	63 ± 6	30 ± 40
7	-500 ± 80	60 ± 18	60 ± 60
8	-600 ± 60	36 ± 18	160 ± 100
9	-580 ± 80	55 ± 25	70 ± 120
10	-600 ± 50	100 ± 50[a]	$\ldots$[a]
11	-680 ± 80	140 ± 40[a]	$\ldots$[a]

[a]The linewidth fluctuations from scan to scan (probably due to small frequency jumps when taking spectra) have not allowed us to estimate the line broadening and Γ_0. The mean value of Γ and its standard deviation (measured at low power) is given instead of Γ_0.

measured at room temperature [8]. Taking into account the laser spot size and the Lorentz local field correction factor of 1.4, the quadratic Stark shift in the center of the Gaussian laser beam is estimated to be about -500 MHz/W for the electric field parallel to the z axis, i.e., it is the upper limit for the Stark shift. On the other hand, considering only the closest ^1B_u intermediate state [4], independent of the electric field direction $\Delta\nu^2 \approx R_{\mathrm{ex}}\Gamma(\langle e|r^2|e\rangle - \langle g|r^2|g\rangle)^2/(\langle e|r^2|g\rangle^2 C_{\mathrm{FC}})$, where almost equal energy denominators are cancelled, R_{ex} is the TPE rate, Γ the SM linewidth "g" and "e" designate the electronic wave function in the ground and the excited states, and r is the electron coordinate. Comparing to a similar expression for atoms [7], there is an additional coefficient C_{FC} equaling the relative intensity of the purely electronic line in the luminescence spectrum. For DPOT in TD, $C_{\mathrm{FC}} = 0.04$ [5]. For two neighboring molecular states having identical symmetry, one can assume $\langle e|r^2|e\rangle \approx \langle g|r^2|g\rangle \approx \langle e|r^2|g\rangle$ and estimate the line shift as $|\Delta\nu| < [R_{\mathrm{det}}\Gamma/(A_{\mathrm{tot}}\eta C_{\mathrm{FC}})]^{1/2} \approx 50$ MHz, where $\Gamma \approx 100$ MHz, $R_{\mathrm{det}} \approx 1$ kHz is the photomultiplier count rate (at 300 mW laser power), $A_{\mathrm{tot}} \approx 0.01$ the total collection efficiency, $\eta \approx 0.1$ the luminescence quantum yield of DPOT [1]. The resulting maximal coefficient of 165 MHz/W is 3 times smaller than in the case when the electric field vector is parallel to the z axis indicating a tilt of the axis with respect to the polarization plane of the laser beam. A tilt of this order was observed for
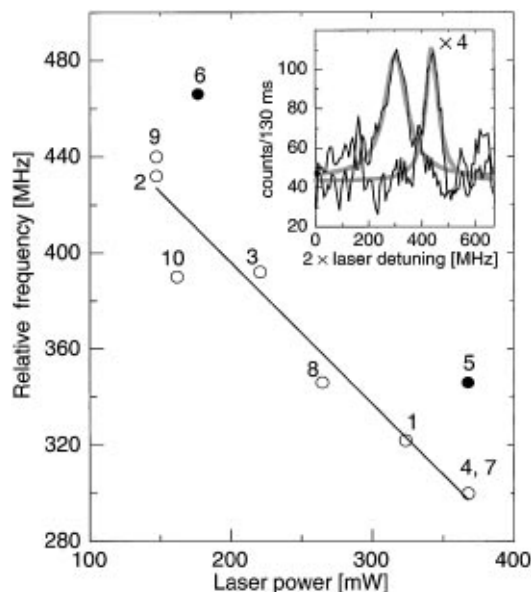

FIG. 3. Line shift power dependence (opened circles) observed for a SM (molecule 5 in Table I). The numbers have the same meaning as in Fig. 2. The filled circles represent a discrete jump in the resonance frequency (circles 5 and 6), then the molecule returned to the original state (circle 7 coincides with 4). The line shows a linear fit to the experimental power dependence. Inset shows the SM spectral line measured at 360 mW (left) and 150 mW (right) with Lorentzian fits.

terrylene in a *n*-hexadecane matrix [9] where the same sample preparation technique and sample orientation were used.

The electrostriction effect [10], a field-induced density increase of the medium in order to minimize the free energy of the system, may lead to a redshift of about 10 MHz/W of the SM frequency analogous to the usual redshift caused by the external pressure increase [11] (for the 2 μm laser spot size, the electrostrictive pressure coefficient is of about 1 kPa W^{-1}).

The optical rectification effect [10] may cause a dc electric field proportional to the laser power if the inversion symmetry of a TD crystal is broken around a DPOT impurity molecule. A typical nonlinear susceptibility is $(10^{-1}-10^{-12})$ mV^{-1}. The corresponding dc electric field is 2–20 V cm^{-1} W^{-1} for the actual beam diameter. Since the permanent dipole moment difference between the ground and excited electronic states of DPOT is about 1 D [8], a line shift on the order of 10 MHz/W is expected due to a linear Stark effect.

Thus all considered nonlinear optical effects combined can contribute to the line shift coefficient less than 200 MHz/W, i.e., about 30% of the observed value.

Next, thermal heating effects from the powerful laser irradiation necessary for TPE are considered. It is important to note that heating is strongly localized to the excited volume inside the TD microcrystal and cannot be measured directly. The average temperature increase in the cryostat was negligible (<0.05 K). A peculiarity of the heat transfer in superfluid He is the He film boiling at high heat flux [12]. In our experiments, such a regime, which disable measurements, was observed at laser powers higher than 400–500 mW. Although the spectra were measured at powers below 400 mW, the He film boiling shows that heating must be taken into account.

Temperature induced frequency shifts, observed in Shpol'skii matrices using hole burning [13] and for single terrylene molecules in *p*-terphenyl [14], were explained within the framework of the "exchange model." In this model [15], a guest molecule can be excited to a local vibrational sublevel with width γ and energy E, due to the interaction with the phonon bath. The vibrational frequency is $(E + \Delta)/h$ if the molecule is electronically excited, where h is Planck's constant. Under these assumptions, the temperature induced broadening and shift are

$$\Gamma(T) - \Gamma_0 = \frac{2c\Delta(\Delta/\gamma)}{1 + (\Delta/\gamma)^2} \frac{\exp(E/T)}{[\exp(E/T) - 1]^2}, \quad (1)$$

and

$$\nu(T) - \nu_0 = \frac{c\Delta}{1 + (\Delta/\gamma)^2} \frac{1}{[\exp(E/T) - 1]}, \quad (2)$$

where T is the temperature in units of cm^{-1}, ν the line frequency in Hz, Γ the SM linewidth in Hz, and c the speed of light. We assume first that the temperature increase is proportional to the laser power P, i.e.,

$T = T_b + \beta P$, where T_b is the temperature of the He bath. Thus (1) and (2) have four parameters Δ, γ, E, and β. In our experiments, the line broadening was at least 5 times smaller than the line shift. Although this is quite unusual, it is consistent with the "fast exchange" condition $|\Delta/\gamma| \ll 1$. Later on only (2) will be analyzed. The 3 parameters Δ, E, β could be varied in a wide range yielding no significant disagreement with the experimental data. Therefore, an independent estimate for the coefficient β was obtained.

An absorption spectrum measured at room temperature showed that the main reason for thermal heating is infrared absorption by the third harmonic of the C-H vibration in the matrix [16], having an absorption coefficient of $\varepsilon = 1.7 \times 10^{-2}$ cm^{-1} at 888 nm. The corresponding absorption rate per TD molecule is about 300 s^{-1} at 10 MW/cm^2 laser power, or at least 10^4 excitations during the accumulation of a spectrum. Strong excitation of the C-H vibration near a DPOT molecule may trigger spectral diffusion (SD) [17]. Infrared light absorption induced SD was observed in [18], being already saturated after a few excitations of a fundamental vibration. Because of the big number of C-H excitations, the SD in our sample can be saturated as well, yielding no linewidth power dependence. The SD could explain the difference between SM linewidths observed under one- and two-photon excitation. After a few ps, the C-H band energy is transformed into acoustic phonons and the further evolution depends on the heat transfer processes. If the thermal conductivity coefficient k is independent of the temperature, the steady state temperature increase in the excited volume is approximately $\varepsilon P/k$. At low temperature the coefficient k is unknown for TD and may be estimated only very roughly as $k = CV_s l_p$, where C is the specific heat per unit volume ($\approx 10^{-4}$ J K^{-1} cm^{-3} at 1.8 K [19]), v_s is the sound velocity ($\approx 2 \times 10^5$ cm/s), and l_p the phonon mean free path (at liquid He temperature we will take half of the microcrystal thickness s for the estimate, $s = 10^{-3}$ cm). In this case, $k = 10^{-2}$ W K^{-1} cm^{-1} and $\beta = \varepsilon/k = 1.7$ W^{-1} K = 1.2 W^{-1} cm^{-1}. In Fig. 2, an example of a least squares fit of Eq. (2) with fixed β is shown. The estimated values $\Delta \approx -0.7$ cm^{-1} and $E \approx 7$ cm^{-1} have a reasonable order of magnitude [13], but even for fixed β the parameters could be varied within quite a broad range.

The nonlinear Kapitza resistance [20] and a temperature dependent thermal conductivity lead to a nonlinear relation between T and P. Because of the Kapitza resistance, the temperature in a solid near an interface with liquid He, T_i, and the He bath temperature T_b are related by the equation $T_i^4 - T_b^4 = \chi q$, where q is the heat flux through the surface, and χ is a coefficient. The acoustic impedance theory provides an estimate, which usually exceeds the experimental values by an order of magnitude, of $\chi \ll 6.2 \times 10^{-7}$ [W^{-1} g^{-1} cm] $\Theta^3 M \approx 25$ cm^{-2} W^{-1}, where Θ is the Debye temperature of

the solid (≈ 60 cm^{-1} for TD), and M is its molar mass (198 g/mol). In the steady state case, $q = \zeta P$, where as an estimate $\zeta \approx (\varepsilon s)/s^2 \approx 20$ cm^{-2}. The film boiling was observed at $P \approx 500$ mW or at a heat flux of $\zeta \times 0.5 W = 10$ W cm^{-2}. This is in reasonable agreement with the critical flux of around 10 W cm^{-2} at $T_b = 1.9$ K reported in literature [12]. At very low temperature, the thermal conductivity is proportional to the specific heat, i.e., to T^3. In this case, $T^4 - T_\infty^4 \approx \varepsilon P T_\infty^3 / k_\infty$ yields the steady state temperature T in the excited volume, where $T_\infty \approx T_i$ is the temperature far from the laser spot and k_∞ is the thermal conductivity at $T = T_\infty$. Hence $T^4 - T_b^4 \approx (\varepsilon T_\infty^3 / k_\infty + \chi \zeta) P \equiv \Lambda P$, where $\Lambda \ll 500$ cm^{-4} W^{-1}. Using this for T, Eq. (2) can be fit to the experimental data with the following parameters: $E \approx 10$ cm^{-1}, $\Delta \approx -0.7$ cm^{-1}, $\Lambda \approx 70$ cm^{-4} W^{-1}. The fit is indistinguishable from the dashed line in Fig. 2.

At low temperature when $T \ll \Theta$, the interaction with acoustic phonons [21] may also cause the line shift $\nu(T) - \nu_0 = c \xi (\pi^4/15) \times (T/\Theta)^4$, where ξ is the electron-phonon coupling constant, which is around 10 cm^{-1} [22]. If $T^4 - T_b^4 \approx \Lambda P$, a linear LIFS is expected, but the observed slope of 600 MHz/W leads to the nonrealistic conclusion that $\Lambda \approx 4 \times 10^3$ cm^{-4} W^{-1}.

A linear line shift may be caused by thermal expansion. The expansion coefficient at low temperature is proportional to T^3 [23] and hence the crystal volume increase is proportional to $T^4 - T_b^4$. The thermal expansion coefficient is very small at 1.8 K (2×10^{-8} K^{-1} estimated with the Grüneisen formula [23]) and one could expect a blue line shift of about 2 MHz/W.

Thus, after many nonlinear optical and thermal effects have been considered, we come to the conclusion that the LIFS observed in SM TPE spectra can be described and understood within the framework of C-H band excitations followed by energy exchange between acoustic phonons and a local vibration in the "DPOT-TD" system. An optical ac Stark effect can contribute up to 30% to the observed LIFS.

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[16] The sample was a sandwich with two microscope cover glasses and the TD crystal. The cover glass thickness was 150 μm, and its absorption was less than 8×10^{-4} cm^{-1} at 888 nm. The crystal had many cracks and a rough surface, so the thermal contact between the glass and TD must be very poor. Additionally, all cracks and gaps between glass and TD are to be filled with superfluid He improving thermal isolation of a single microcrystal from glass. The observed film boiling could start on the TD-He or the glass-He interface as well.

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