

## Electronic Energy Relaxation and Transition Frequency Jumps of Single Molecules at 30 mK

Taras Plakhotnik\* and Elizabeth A. Donley

*Physical Chemistry Laboratory, Swiss Federal Institute of Technology, ETH Zentrum,  
CH-8092, Zurich, Switzerland*

Boris M. Kharlamov

*Institute of Spectroscopy, RAS, 142190 Troitsk, Moscow region, Russia*

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Transition frequency jumps for single terylene molecules in a polyethylene matrix caused by resonant laser irradiation are investigated at 30 mK. These jumps are not accompanied by substantial sample heating. A model for the effect is proposed, based on the interaction of tunneling two-level systems (TLSs) surrounding the single molecule with high-energy nonthermal phonons emitted by the molecule during electronic energy relaxation. The radius of the effective interaction volume is estimated to be  $r_m \approx 12.5$  nm, and the interaction cross section for nonequilibrium phonon-TLS scattering is estimated as  $\sim 10^{-22}$  cm<sup>2</sup>.

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The low-temperature properties of glasses have strong anomalies as compared to crystals [1–3]. These anomalies are successfully described by the tunneling two-level system (TLS) model, which assumes the existence of a special kind of local low-energy excitations with a very broad distribution of energies and relaxation rates. Phonon assisted TLS dynamics is thought to be responsible for many anomalous properties of glasses at low temperatures and has been the subject of extensive investigation by various methods for almost 30 years. One tool used for the investigation of these dynamics is optical spectroscopy, in particular, photon echo, hole burning, and single-molecule spectroscopy (SMS) (see reviews [4–13]). All of these methods use a chromophore impurity as a probe whose resonance frequency is subject to spectral diffusion (SD) because of interactions between the probe and TLSs. In principle, impurities can disturb the matrix structure, but there is no indication that impurities at low and moderate concentrations affect the TLS density. An increase of the rate of SD has been detected in samples only at chromophore concentrations above  $10^{-2}$  mol/l [14]. Another expected effect of impurity molecules on their local environments could arise from light absorbed by the chromophore. Through subsequent decay processes the absorbed energy is inevitably partially converted to high-energy phonons, which spread into the surrounding space, exciting TLSs and finally decaying into thermal equilibrium phonons. TLS excitation via high-energy phonons was suggested in [14] as a reason for a specific SD time dependence in highly concentrated samples, but no direct evidence for this effect was obtained. The advantage of SMS in measurements of such a kind is that one and the same molecule serves as a phonon generator and as a probe. Therefore, the measurements can be carried out at a low concentration of chromophores, which does not

disturb the structure of the matrix. The present work is a first attempt at direct investigation of the influence of high-energy phonons emitted by impurity molecules on their local environments.

Experiments were performed on the sample used in previous works [15,16]. The sample has a sandwich structure. A thin layer (about 1  $\mu$ m thick) of polyethylene (PE) doped with terylene at a concentration of  $\sim 10^{-6}$  M was put between two undoped PE layers that were about 10  $\mu$ m thick. That protected the chromophore molecule properties from the influence of surface effects. Single-molecule spectra have been measured with an optical <sup>3</sup>He/<sup>4</sup>He dilution refrigerator (a detailed description of the cryostat can be found in [17]). The sample was mounted onto a spherical mirror objective and immersed directly into the <sup>3</sup>He/<sup>4</sup>He mixture. A Coherent CR-899 dye laser containing Rhodamine 6G dye was used for fluorescence excitation at wavelengths between 572 and 574 nm. The laser intensity was about 10 mW/cm<sup>2</sup>. The laser frequency jitter was  $\approx 1$  MHz on the time scale of the linewidth measurements. The estimated long-time laser frequency drift (LFD) was about 4 MHz/10 min [18(a)].

The spectra were measured using the SM microscopy setup described previously [19]. Fluorescence excitation spectra were extracted from digitized fluorescence images of the sample that were collected at an excitation frequency scan covering a range of 2 GHz with 2 MHz steps. The data accumulation time for each frequency point was in the range 0.2–0.7 s. The random errors (RE) in the measurement of the SM absorption line frequency caused by the signal noise and LFD was estimated as about 6 MHz [18].

The goal of the experiments was to measure and analyze SM frequency jumps resulting from a change of state of the TLSs surrounding the SM. The measurement

procedure was the following: two consecutive data cubes (data files with fluorescence intensity as a function of two spatial coordinates and excitation frequency) were measured and the spectral positions of the SMs in two scans were compared. 953 jumps were found in 24 pairs of 12 min scans. 356 jumps were detected in 4 min scans. The histogram of jump probability versus jump size is shown in Fig. 1 for the slower scans. While the central part of the distribution can be explained by RE, the quantity of longer frequency jumps is far larger than the amount expected to arise from SD at 30 mK. The temperature dependence of the mean SM linewidth was measured for the same sample in [15,16]. It can be described in the temperature region from 30 mK to 1.8 K by the formula  $\langle \Gamma \rangle = \Gamma_0 + bT$ , where  $\Gamma_0 \approx 41.7(3)$  MHz is the linewidth at  $T = 0$  and  $b \approx 35.2(8)$  MHz/K characterizes the temperature broadening of the chromophore absorption line [15,16]. Thus, the average chromophore frequency jump due to the interaction with the equilibrium phonon bath at 30 mK is  $\approx 1$  MHz. The equilibrium spectral jump distribution is expected to be Lorentzian [20], which has about 1.5% of its intensity in the wings with frequencies above 20 MHz. In the data presented in Fig. 1, 13% of the jumps are larger than 20 MHz, which rules out equilibrium SD as their cause. The assumption that the jumps arise from heating of the local volume near the chromophore by phonons emitted at a decay of the excited state can also be ruled out. For the case of sample heating by the excitation laser, the temperature dependence of the chromophore absorption linewidth would be strongly nonlinear and its limit at  $T = 0$  would be larger than the radiative one. But the above value of  $\Gamma_0$  is in good agreement with earlier results of lifetime measurements [21].

A model explaining the excess TLS jumps is suggested below. Consider a single molecule absorbing photons at a high rate (a typical rate in our experiment is  $10^6$  photons/s when the laser is resonant with the absorption line of a molecule). About 30% of the absorbed energy is transformed into high-energy phonons during the energy relaxation, resulting in a phonon emission power of  $\Phi \approx 10^9$  cm<sup>-1</sup>/s. The absence of heating means that emitted phonons escape in a ballistic or quasiballistic manner to somewhere far away from the chromophore before being thermalized. However, high-energy phonons can also excite nearby TLSs. The excitation mechanism in this case should be excitation of TLSs via resonant absorption or a Raman-type process. The scheme for such excitations is

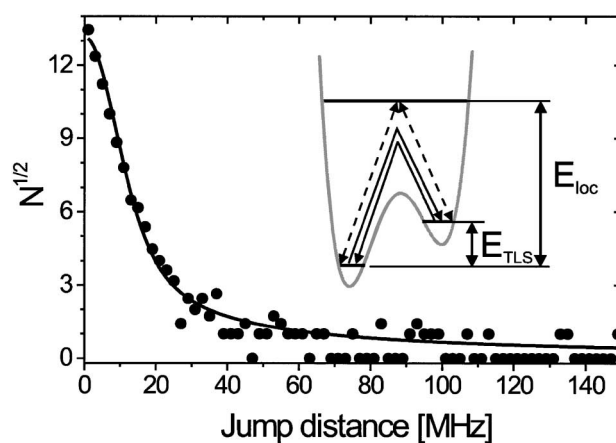


FIG. 1. The distribution of SM frequency jumps extracted from two consecutive scans of 12 min duration (see text). The solid line is a fit to Eq. (3). The square root of the number of frequency jumps is used to emphasize the low probability events. The data are presented in this form for better comparison of the experiment to the fit curve in the long jump region. The inset shows a scheme of energy transitions in a DWP due to the interaction with high-energy phonons. The dashed arrows represent the resonant absorption and emission of phonons by a high-energy level in the DWP. The solid arrows designate the Raman-type process.

shown as an inset in Fig. 1. It is based on a soft potential model approach (see reviews [22,23] and the references therein). The probability for a TLS flip via interactions with high-energy phonons is independent of the TLS relaxation rate and should be comparable for slow and fast relaxing TLS, but only “slow” TLSs with relaxation times longer than 12 min can cause jumps contributing to the histogram in Fig. 1.

High-energy phonons created by chromophore excitation undergo a rapid frequency down-conversion [24]. Each generation of phonons has an average frequency of about half of that of the previous generation and propagates through a volume roughly 3 orders of magnitude larger than the previous generation (for details, see [24]). Assuming that the interaction between local modes of the corresponding double-well potential (DWP) and phonons is proportional to the cube of the phonon frequency [25], we conclude that the interaction region has rather sharp spherical boundaries characterized by a radius  $r_m$  and that it is enough to consider only one active phonon generation with a characteristic frequency  $\omega_{ph}$ .

The distribution of the SM frequencies in the simplest case of a single TLS jump can be expressed as

$$P_{\nu,1}(\nu) = \iiint_0^{r_m} P_{\vartheta,\mu}(\vartheta, \mu) P_r(r) \delta(\mu \vartheta r^{-3} - \nu) d\vartheta d\mu dr. \quad (1)$$

Here  $P_{\vartheta,\mu}$  is the distribution function for the orientational factor and the chromophore–TLS coupling constant  $\mu$ . The orientational factor we take to have the form  $\vartheta = \cos\theta$ , where  $\theta$  is the angle between the TLS and the chromophore dipole moments. Assuming the dipole moments of all chromophores are the same,  $\mu$  reflects

the distribution of TLS dipole moments.  $P_r(r) = 3r^2 r_m^{-3}$  is the spatial TLS distribution around the chromophore and  $\delta$  is a delta function. Assuming  $-1 < \vartheta < 1$ ,  $0 < \mu < \mu_m$ , and  $P_{\vartheta,\mu}(\vartheta, \mu) = \frac{1}{2} \cdot \mu_m^{-1}$  [26] the analytical expression

$$P_{\nu,1}(\nu) = \begin{cases} \frac{r_m^3}{8\mu_m} \left(1 - 2\ln\left[\frac{|\nu|r_m^3}{\mu_m}\right]\right) & \text{if } |\nu| \leq \frac{\mu_m}{r_m^3} \\ \frac{\mu_m}{8r_m^3\nu^2} & \text{if } |\nu| \geq \frac{\mu_m}{r_m^3} \end{cases} \quad (2)$$

can be found. The characteristic parameter of the distribution is the ratio of the interaction volume to the maximum interaction constant,  $r_m^3/\mu_m$ . The complete distribution should also include molecules whose transition frequencies did not jump and molecules that had more than one jumped TLS in their active volume. The distribution function for molecules not undergoing jumps is  $P_{\nu,0}(\nu) = \delta(\nu)$ . To get the function  $P_{\nu,n}(\nu)$  that describes the distribution of the SM frequencies if exactly  $n$  TLS jumps occurred, one should calculate  $P_{\nu,1}(\nu) * P_{\nu,1}(\nu) * P_{\nu,1}(\nu) * \dots$ , where the convolution is repeated  $n - 1$  times. Convolving the complete distribution with the distribution of random errors in frequency measurement  $G(\nu)$  (it was approximated by Gaussian) we come to an expression that can be compared to the experimental data:

$$P_{\text{fit}}(\nu) = \int d\nu' G(\nu') \sum_n B_n(\aleph) P_{\nu,n}(\nu - \nu'). \quad (3)$$

The weight factors  $B_n(\aleph) = \aleph^n \exp(-\aleph)/n!$  are the probabilities that exactly  $n$  TLS jumps happened in the active volume. This probability follows a Poisson distribution characterized by the mean number of TLS jumps  $\aleph$ .

A representative experimental data set (based on 12 min scans) was fitted with the function (3). The fit parameters are  $r_m^3/\mu_m$  and  $\aleph$ . The standard deviation  $w$  of the frequency error distribution was fixed at  $w = 6$  MHz [18]. The weighted least squares fit gives  $r_m^3/\mu_m = 0.09(2)$  MHz $^{-1}$  and  $\aleph = 2.1(5)$ . The result of the fit is shown in Fig. 1.

$r_m$  and the concentration of slow TLSs in polyethylene  $c_{\text{TLS}}$  cannot be estimated only on the basis of optical measurements (see below), but the number of slow TLSs inside the interaction volume can be determined given two optically measurable parameters:  $\alpha_1 = r_m^3/\mu_m$  and  $\alpha_2 = \langle\mu\rangle c_{\text{TLS}} = \mu_m c_{\text{TLS}}/2 \approx 50$  MHz.  $\alpha_2$  was calculated using the data reported in [16] and the standard distribution function of the relaxation times [1–3]. An unknown upper limit for the relaxation times we have set at  $10^7$  s, but  $\alpha_2$  depends only logarithmically on this limit. The number of TLSs in the interaction volume is  $N_{\text{TLS}} = 4/3\pi r_m^3 c_{\text{TLS}} = 4/3\pi\mu_m\alpha_1 c_{\text{TLS}}$ . Deriving  $c_{\text{TLS}}$  from the expression for  $\alpha_2$  we find  $N_{\text{TLS}} = 8/3\pi\alpha_1\alpha_2 \approx 40$ . For an estimation of  $r_m$  the value of the coupling constant  $\mu$  is necessary. Unfortunately, optical measurements provide only the product  $\mu c_{\text{TLS}}$ . However, the value of  $c_{\text{TLS}}$  can be estimated on the basis of specific heat data [27]. Following this procedure a value of  $\langle\mu\rangle \approx 11$  GHz  $\cdot$  nm $^3$  was obtained in [16], resulting in  $r_m \approx 12.5$  nm. This estimation for  $r_m$  has a weak cubic root dependence on  $\mu$  and other parameters.

The number of frequency jumps should decrease with decreasing laser fluence (scan time in the present experiment). That can be checked by comparing the relative amount of long frequency jumps in experiments with 4 and 12 min scans. The contribution of frequency jitter falls with a good precision to zero for  $\nu > 30$  MHz. All frequency changes above this value should be caused by phonon-assisted TLS jumps. The difference in the scan time in two scans is a factor of 3. But the difference in average fluence per molecule is smaller, because the shorter scan also decreases the signal-to-noise ratio and only molecules with higher emittivity appear in the statistics. About twice as many molecules could be identified in 12 min scans than in 4 min ones. Taking this into account, the average amount of energy absorbed by each molecule in 12 min scans can be roughly estimated as about 2 times higher than for 4 min scans. The experimental values are  $N_{\nu>30}/N_{\text{tot}} \approx 8\%$  for 12 min scans and  $N_{\nu>30}/N_{\text{tot}} \approx 4\%$  for 4 min scans, which qualitatively agree with the model.

Let us estimate the probability of TLS interaction with high-energy phonons for diffusive phonon motion. The radius of the volume populated by the active generation of high-energy phonons can be approximated as  $r_m = \sqrt{Dt_{\text{dec}}}$ , where  $D$  is the phonon diffusion constant and  $t_{\text{dec}}$  is the lifetime of the active generation. The phonon concentration  $n$  can be estimated, by comparison of the generation rate of phonons  $Q = \Phi/(\hbar\omega_{\text{ph}})$  with their decay rate  $Q = \frac{4\pi}{3}r_m^3 n t_{\text{dec}}^{-1} = \frac{4\pi}{3}r_m D n$ . For the sake of simplicity, we assume that phonons fill the active volume homogeneously. The probability for phonon interaction with a DWP in the active volume is  $p = ns\sigma$ , where  $s \approx 2000$  m/s is the speed of sound and  $\sigma$  is the interaction cross section between phonons and TLSs. The total rate  $A = \aleph/t_s$  of TLS flips, where  $t_s \approx 4$  s is the typical SM line scan time, equals the product of  $p$  and the number of TLSs in the active volume. Solving for  $\sigma$  we obtain

$$\sigma = \frac{4\pi A r_m D}{Q s N_{\text{TLS}}}. \quad (4)$$

According to [28], the average diffusivity in PE is approximately inversely proportional to the temperature and decreases from  $D \approx 0.1$  to  $D \approx 0.01$  cm $^2$ /s for a temperature increase from about 5 to 100 K. The phonon generation rate is also inversely proportional to the phonon energy and thus  $D/Q$  is practically independent of  $\omega_{\text{ph}}$ . For our estimation we took the diffusivity of active phonon generation  $D \approx 0.02$  cm $^2$ /s for phonons with energy on the order of 10 cm $^{-1}$ . Putting all numbers in Eq. (4) we obtain  $\sigma \approx 10^{-22}$  cm $^2$ . It is interesting to compare this estimation with an estimation of absorption cross section by a resonant two-level absorber. This cross section is of the order of  $10^{-12}$  cm $^2$  (see, for example, [29]). But if the interaction cross section of high-energy phonons with DWPs would be as high as  $10^{-12}$  cm $^2$ , high-resolution optical measurements would be impossible in glasses at low temperatures not only for the case of SMS, but also for photon

echo and hole burning experiments due to a huge amount of light induced SD. Zero phonon lines of molecules would be smeared by this effect. But, as follows from our analysis, the interaction of “hot” phonons with DWPs is more typical for the two-phonon (Raman-type) processes.

Measurements of SM frequency jumps caused by resonant laser irradiation reveal the peculiarities of characterizing the interaction of TLSs with phonons emitted by a chromophore, which can be summarized as follows. (i) The intense irradiation of a SM by laser light does not cause observable heating of the chromophore environment even at 30 mK. (ii) The interaction of nonthermalized high-energy phonons with TLSs is realized via high-energy states in a DWP, for which the lowest state is a TLS. The probability of TLS excitation by high-energy phonons within the framework of the model has no significant dependence on the TLS relaxation rate. (iii) The interaction zone is rather compact. The radius of the interaction sphere estimated from the experimental data is  $\approx 12.5$  nm. (iv) The rate of frequency jumps for a SM via this interaction corresponds to the interaction cross section of  $\approx 10^{-22}$  cm<sup>2</sup>. Therefore, the influence of chromophore excitation on the TLS dynamics is usually rather weak. The final two points are especially interesting and give valuable and somewhat surprising quantitative information concerning the TLS-phonon and the TLS-chromophore interactions. It is clear now that the mechanism proposed in [14] for light-induced nonequilibrium SD in highly concentrated samples due to TLS charging during hole burning requires orders of magnitude higher irradiation fluences than used in hole burning experiments. It looks more probable that the nonequilibrium SD is caused by the same mechanism which is proposed in [14] to explain why “old” holes are broadened when “new” ones are burned. The tautomerization of a chromophore molecule changes the local electric field and/or the strain field. This creates a nonequilibrium state in the TLS ensemble interacting with nonburned molecules.

The data on frequency jumps for SMs under laser irradiation can be consistently explained by the present model. In particular, the apparent contradiction between the low-temperature line broadening and large SM frequency jumps is removed. Further investigations of SM jump distributions can bring new information about DWP high-energy structure and their density of states, high-energy phonon propagation, and frequency evolution.

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\*To whom correspondence should be addressed.

Email address: taras@phys.chem.ethz.ch

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