

## Time Resolved Single Molecule Spectroscopy

Taras Plakhotnik and Daniel Walser

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

(Received 25 August 1997)

A new method based on the calculation of autocorrelation functions for spectra measured at a high acquisition rate is developed to study spectral dynamics of single molecules. The technique allows for spectroscopy with time resolutions down to the luminescence lifetime. The method is used to study spectral diffusion in two-photon excitation spectra of diphenyloctatetraene molecules doped in an *n*-tetradecane crystal matrix. The diffusion is light induced, and is absent in one-photon excitation spectra. It has a "steplike" time behavior, different from gradual diffusion observed in glasses. [S0031-9007(98)05986-9]

PACS numbers: 78.55.Kz, 33.70.Jg, 63.20.Mt

Experiments with single quantum systems are on the frontier of modern physics and chemistry. Differently from single ions and atoms trapped in electromagnetic fields [1], rapidly developing single molecule (SM) studies in solids [2–4] allow for investigations of both light-matter interactions and solid state dynamics. The SM technique provides a deeper understanding of the basic phenomena underlying all bulk properties and seems to have no limitations in combining with other methods. Single molecule electron spin [5,6] and nuclear spin spectroscopy [7], conventional [8] and near-field microscopy [9,10], and SM Raman spectroscopy [11,12] have already been demonstrated.

Time resolution in SM spectroscopy is also desirable, for example, to study SM interactions with an environment which cause time dependent resonance frequency changes or so-called spectral diffusion (SD). According to the two-level systems (TLSs) model, which was suggested for amorphous solids [13,14] to explain their acoustic and thermodynamic properties, expanded later to include optical phenomena [15], and confirmed in many experiments [16,17], the environment is imitated by a set of TLSs with flip rates distributed from microhertz to gigahertz. A study of fast dynamics requires high time resolution, but it has been considered impossible to implement high time resolution spectroscopy for SMs so far, because the number of detected photons emitted by a SM is small and to first approximation fluctuates according to a Poisson distribution. Even when the exciting laser power saturates the transition and the emission rate is at maximum, a SM signal rarely reaches  $10^5$  counts/s (a strong emitter is terylene [18]). To measure the SM linewidth, the laser intensity should be well below the saturation value. So, only  $10^4$  counts/s are detected. To determine the line shape, the recording time should be on the order of 10 ms in the best case. For molecules with 100 times lower emission rate [pentacene, diphenyloctatetraene (DPOT), and many others], this time can be as long as a few seconds. A conventional photon correlation technique [19,20] allows one to gain insight into fast SM dynamics but does not provide spectral information.

In this paper, a new approach to SM spectroscopy is reported which pushes the time resolution far below one second, even for molecules with poor emission rates. This technique, which we call intensity-time-frequency correlation (ITFC) SM spectroscopy, can yield microsecond or even better time resolution with an intrinsic theoretical limit at the luminescence lifetime. The ITFC technique is used for studying dynamics in two-photon excitation (TPE) spectra of DPOT molecules in an *n*-tetradecane matrix [21], where a significant difference between the linewidths in one-photon excitation (OPE) and TPE spectra was observed and tentatively explained by SD induced by the powerful laser illumination required for TPE [22,23]. This explanation agrees with the significant line broadening observed for OPE data in the presence of infrared illumination [24].

ITFC spectroscopy works as follows. Instead of recording one spectrum with an accumulation time long enough to have the required signal/noise ratio,  $N$  very fast scans over the same spectral region are acquired. Each of them is a SM spectrum with a high time resolution but very small signal/noise ratio. When this ratio is improved by summing up many scans, the time resolution is lost. Summation yields a SM line broadened by spectral dynamics that occur on time scales shorter than the recording time of all traces. To improve the signal/noise ratio preserving the time resolution, autocorrelation functions (ACFs) are calculated for each scan, and then these functions are averaged. We define

$$\begin{aligned} \text{ITFC}(\omega') &\equiv \langle \text{ACF}(\omega') \rangle \equiv \frac{1}{N} \sum_{k=1}^N I_k(\omega') \star I_k(\omega') \\ &\equiv \frac{1}{N} \sum_{k=1}^N \int_{-\omega_0/2}^{\omega_0/2} I_k(\omega) I_k(\omega + \omega') d\omega, \quad (1) \end{aligned}$$

where  $I_k(\omega)$  is the  $k$ th single scan spectrum. The frequency scan interval  $\omega_0$  is chosen such that during the experiment the line intensity is negligible outside the scan range. In this case, the integration limits can be set to  $+\infty$  and  $-\infty$ . ACFs, though quite noisy in this case, have the important peculiarity that their maximum is always at the origin independent of the frequency position of the SM

line in a trace. Even if the molecular frequency “jumps” to a new position from scan to scan, the ACFs will “ignore” these jumps and only faster dynamics will define the shapes of the ACFs. Hence, averaging ACFs preserves the time resolution [25]. If  $\text{ITFC}(\omega')$  is significantly different from zero only for  $0 < \omega' < \omega'_{\max} < \omega_0$  (see Fig. 1, more details of the computer simulations are later in the text), this indicates that a part of the scan interval  $\omega_0$  consists of no signal and  $\omega_0$  can be narrowed without losing the “jumping” molecule. Thus,  $\omega'_{\max}/r$ , where  $r$  is the frequency scan rate, can be defined as the time resolution, no matter how large  $\omega_0$  is. The average cross correlation  $(N - p)^{-1} \sum_{k=1}^{N-p} I_k(\omega') \star I_{k+p}(\omega')$  yields  $\text{ITFC}_p(\omega')$ , whose time resolution is  $p\omega_0/r$ . Thus, different time resolutions can be obtained from a single set of scans. Generally, SM line shapes may be very complex functions [26] which cannot be described by a single, well-defined parameter such as a linewidth or  $\omega'_{\max}$ . Such non-Lorentzian lines can be approximately characterized by fitting a Lorentzian whose width depends on the scan rate (time resolution).

The signal/noise ratio of  $\text{ITFC}(\omega')$  is smaller than for an ACF calculated after summing up all traces.  $\{\sum I_k(\omega')\} \star \{\sum I_j(\omega')\} = \sum \{I_k(\omega') \star I_j(\omega')\}$  yields all  $N^2$  possible autocorrelations and cross correlations of individual traces and hence  $N^{-1}$  noise reduction in comparison with a single scan ACF. In the case of ITFC only  $N$  ACFs are summed and the noise reduction is  $N^{-1/2}$ .

In SM excitation spectra,  $I_k$  are proportional to the population of the excited state. This population is a solution of the optical Bloch equations when the molecular resonance frequency  $\vartheta$  and the laser frequency  $\omega$  are functions of time (see, e.g., [27]).  $\omega(t) = -\omega_0/2 + rt$

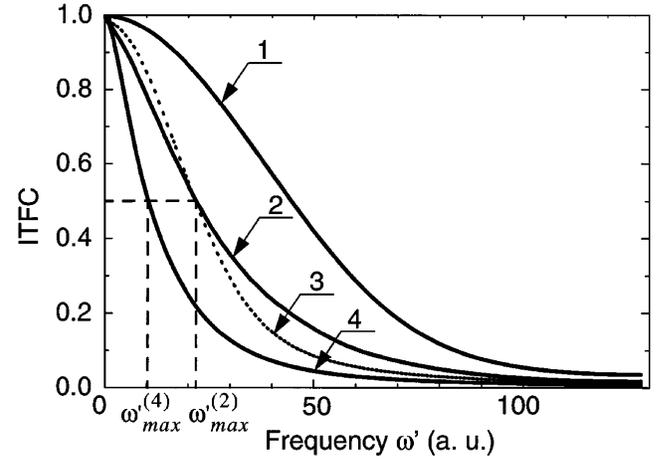


FIG. 1. Numerical simulations of the ITFC. A SM ( $\Gamma = 5$ ) interacts with 12 TLSs. The parameters are as follows:  $\Delta\vartheta = \{3, 4, 5, 6, 8, 10, 11, 12, 16, 20, 22, 23\}$  and  $\tau = \{0.05, 0.15, 0.1, 0.25, 25, 75, 45, 35, 125, 38, 40, 100\}$ , respectively.  $\omega_0 = 256$ . ITFC calculated for the scan rate  $r = 0.005/1$  (frequency units/time units) is the long time limit for the SD (curve 1). Curve 2 represents the ITFC for  $r = 1/1$ , curve 3 was obtained for the same scan rate but with TLSs having correlation times  $\tau_m > 1$  switched off. Curve 4 simulates a very fast scan with  $r = 500/1$ . For curves 2 and 4, the time resolution equals  $\omega'_{\max}/r$  (22 and 0.02, respectively) but not  $\omega_0/r$  (256 and 0.5).

and  $\vartheta(t)$  is a stochastic function. We will consider an approximation, which is valid if the time between frequency jumps and  $1/rT_1$ , the time to scan the frequency interval  $1/T_1$ , are both longer than  $T_1$ , the lifetime of the optical transition. In this case,  $\vartheta(t)$  and  $\omega(t)$  are slowly varying parameters, and one can use the steady state population of the excited state, which is a Lorentzian function of  $\omega(t) - \vartheta(t)$ . Thus

$$\text{ITFC}(\omega') = \left\langle \int_{-\infty}^{\infty} \left[ \left[ \omega - \vartheta\left(\frac{\omega}{r}\right) \right]^2 + \Gamma^2 \right]^{-1} \left[ \left[ \omega + \omega' - \vartheta\left(\frac{\omega + \omega'}{r}\right) \right]^2 + \Gamma^2 \right]^{-1} d\omega \right\rangle, \quad (2)$$

where  $\Gamma \geq (2T_1)^{-1}$  approximately includes dephasing (if any) on time scales shorter than  $T_1$  [28].  $\omega/r$  is a time, and  $N\omega_0/r$  is the total recording time.  $\vartheta(t) = \sum_m \zeta_m(t)$ , where  $\zeta_m(t)$  are stochastic functions describing temporal frequency changes. The functions  $\zeta_m(t)$  can be divided into two groups with correlation times shorter and longer than  $\omega_0/r$ , the time to scan one trace. When evaluating the integral in (2), only  $\zeta_m(t)$  with correlation times shorter than  $\omega_0/r$  are significant. Functions with long correlation times can be replaced by a constant which will not affect the integral when its limits are  $+\infty$  and  $-\infty$ . If all  $\zeta_m(t)$  have long correlation times, the integral is a Lorentzian with a width of  $4\Gamma$ , as if there were no spectral dynamics.

Results of numerical simulations are shown in Fig. 1. We assumed  $\zeta_m(t) = \Delta\vartheta_m \xi_m(t)$ , where  $\xi_m(t)$  are stochastic functions equal to 1 or  $-1$  with correlation times

$\tau_m$ . This model corresponds to a SM interacting with a set of TLSs.  $|2\Delta\vartheta_m|$  is the frequency shift of the SM line, when the  $m$ th TLS flips between the two states. Here, for simplicity, the “up” and “down” transition rates are equal for each TLS (high temperature limit). The comparison of curves 2 and 3 with curve 1 shows that scanning at the rate  $1/1$  removes contributions from slow TLSs. Curve 4, where  $\omega_{\max}^{(4)} = 2\Gamma = 10$ , shows that the  $2\Gamma$  limit for the observed linewidth was achieved for the fastest scan. At this scan rate, the ITFC has a Lorentzian shape. This is not generally true for relatively slow scans where the ACF shape depends on the properties of the functions  $\zeta_m(t)$ .

Not only SD can contribute to the ITFC spectra. Similarly to the conventional correlation technique, photon bunching due to shelving of a SM in a long-lived triplet state can be seen in ITFC data. If the laser power  $P$  is

much smaller than the saturation power  $P_s$ , a small additional contribution  $\sim(P/P_s)\exp(-\omega'/T_{tr}r)$  in the case of OPE [20] and  $\sim(P/P_s)^2\exp(-\omega'/T_{tr}r)$  for TPE, where  $T_{tr}$  is the triplet lifetime, appears. For the time resolution and intensities we used in the experiment described below, the photon bunching effect was negligible.

We applied the ITFC technique to study SD in the Shpol'skii system DPOT-tetradecane [29]. Curve (a) in Fig. 2 shows a TPE spectrum of DPOT ( $1^1A_g \rightarrow 2^1A_g$  transition at 444.0 nm) measured in the center of the inhomogeneous band using a single mode cw Ti:sapphire laser emitting at 888 nm. The light of 140 mW power was focused onto a spot approximately 3  $\mu\text{m}$  in diameter. The sample was immersed in superfluid He at 1.8 K. The intensity of the weak one-photon emission was measured as a function of the laser frequency. Experimental and spectroscopic details are described in [21,23]. The spectral feature at 3030 MHz represents a SM line with a width of about 60 MHz, a typical linewidth in TPE spectra [21]. This linewidth is more than twice the average linewidth of 26 MHz measured in SM OPE spectra [23]. In the ITFC spectrum with a time resolution of about 40 ms (inset in Fig. 2), significant line narrowing down to 28 MHz is observed. This time resolution can only be achieved using the ITFC technique. The SM line cannot be seen on the single scan (b).

The data points in Fig. 3 represent the linewidths averaged over about ten molecules, whose resonance frequencies are in the 3.7 GHz total scan range, as a function of the time resolution. To get this average, the ACF can be calculated for the whole 3.7 GHz trace at once. On a logarithmic scale, the observed linewidth dependence appears as a step function. It indicates that, in contrast to glasses, the distribution of TLSs in the DPOT-tetradecane system is remarkably different from the one assumed in the standard TLS model. Figure 3 shows that there is no SD on the time scales  $10^{-3}$ – $10^{-2}$  s and 10–200 s, where the linewidth remains almost constant (31 and 65 MHz, respectively). These values are still broadened by 3–5 MHz due to a small remaining saturation of the optical transition [21]. Thus, the linewidth is 26–28 MHz on a short time scale, in agreement with OPE data. OPE spectra do not show spectral dynamics in the time range  $10^{-3}$ – $10^2$  s. This confirms that the difference between the SM linewidths in OPE and TPE spectra is caused by SD induced by the strong illumination at 888 nm, a hypothesis discussed in [22,23]. The dependence of the SD on the IR power was not studied in this work. First, the intensity under TPE depends on the square of the IR power, and it was difficult to vary the power in a broad range. Second, the observed SD significantly varies from molecule to molecule, but additional frequency jumps of 0.1–10 GHz occurring on the time scale of  $10^3$ – $10^4$  s have disabled covering the whole time range presented in Fig. 3 by observing the same SM. Such jumps have been observed under both

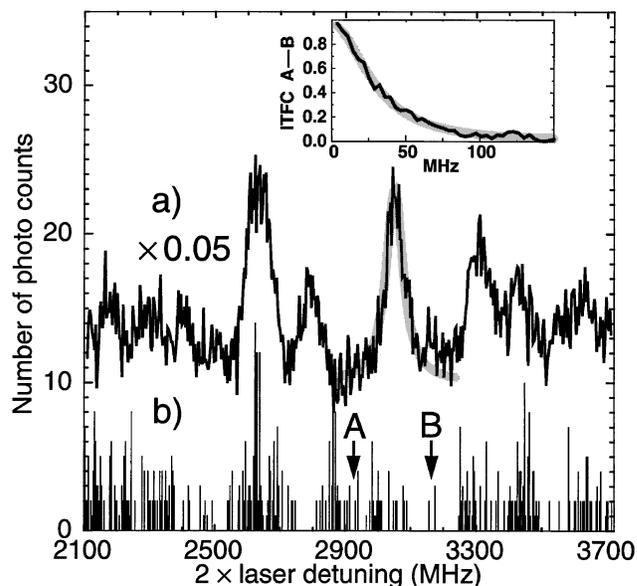


FIG. 2. (a) A two-photon excitation spectrum obtained by averaging 200 single scans recorded with frequency steps of 3.6 MHz and 5 ms accumulation time at each frequency position. The spectrum has a time resolution  $\sim 500$  s. (b) Example of a single scan. The SM line at 3030 MHz has a count rate of about 1.3 counts/trace in the maximum. In spectrum (a), the line has a width of 62 MHz (the thick grey line is a Lorentzian fit). The inset shows the average over 200 ACFs of single scans, calculated for the spectral region between arrows A and B. The decay of the ITFC corresponds to a linewidth of 28 MHz (a Lorentzian fit is shown).

OPE and TPE and have already been reported for other Shpol'skii systems [31]. Because of these dynamics and conventional photobleaching, the molecular ensemble under study usually changes after one or two hours, even if the spectral range and the laser beam position are

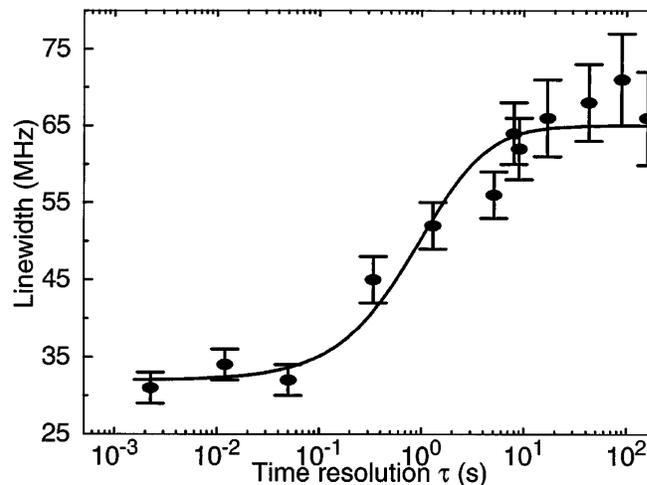


FIG. 3. Time dependence of the linewidth (half width at half maximum of the ITFC) in TPE spectra. Each data point represents the average linewidth of 10 SMs. The solid line  $31 \text{ MHz} + 33 \text{ MHz} \times [1 - 1/(1 + 0.5 \text{ Hz} \times \tau)^2]$  is a least squares fit with the trial function from Ref. [30].

preserved. For this reason, only the average linewidth of 10 molecules is shown in Fig. 3. It must be emphasized that this averaging is not related to the ITFC method itself, which allows the study of SMs provided that they are photostable.

Recently, light induced SD has been observed in spectral hole-burning experiments on dye doped polymethylmethacrylate and was explained by interaction of probe molecules with water molecules embedded in the polymer and flipping between two states under IR illumination. For those TLSs, a narrow distribution of the flip rates has been assumed, and an approximate relation  $\Delta\Gamma = A[1 - 1/(1 + \Lambda\tau)^2]$  describing the line broadening  $\Delta\Gamma$  was deduced [30]. In this equation,  $A$  describes the interaction between a probe molecule and TLSs, and  $\Lambda$  approximately equals the TLSs flip rate. A fit to this equation is shown in Fig. 3. The fit yields a TLS flip rate of 0.5 Hz. This number should be considered as a rough estimate.

We presented the new ITFC technique for SM spectroscopy. Its application for the investigation of SD in TPE spectra of DPOT in tetradecane revealed a narrow distribution for the diffusion rates. The SD is induced by the IR illumination and its absence in OPE spectra accounts for the difference between SM linewidths in OPE and TPE spectra. The technique can be widely applied to examine spectral dynamics on time scales from microseconds to hours—to check the standard TLS model in glasses on the SM level, to study SD due to flipping nuclear spins which broaden resonance lines in single electron spin magnetic resonance spectroscopy [7], or to investigate light induced SD in single nanocrystallite quantum dot spectra [32].

Careful proofreading by Elizabeth Donley, fruitful discussions with Felix Graf, and the continuing interest and support of Professor Urs P. Wild are gratefully acknowledged. This work was financially supported by the ETH Zürich.

[1] W. M. Itano, J. C. Bergquist, and D. J. Wineland, *Science* **237**, 612 (1987); H. Walther, *Aust. J. Phys.* **46**, 37 (1993).  
 [2] W. E. Moerner and L. Kador, *Phys. Rev. Lett.* **62**, 2535 (1989).  
 [3] M. Orrit and J. Bernard, *Phys. Rev. Lett.* **65**, 2716 (1990).  
 [4] T. Plakhotnik, E. A. Donley, and U. P. Wild, *Annu. Rev. Phys. Chem.* **48**, 181 (1997).  
 [5] J. Köhler, J. A. J. M. Disselhorst, M. C. J. M. Donckers, E. J. J. Groenen, J. Schmidt, and W. E. Moerner, *Nature (London)* **363**, 242 (1993).  
 [6] J. Wrachtrup, C. von Borczyskowski, J. Bernard, M. Orrit, and R. Brown, *Nature (London)* **363**, 244 (1993).  
 [7] J. Wrachtrup, A. Gruber, L. Fleury, and C. von Borczyskowski, *Chem. Phys. Lett.* **267**, 179 (1997).  
 [8] F. Güttler, T. Irrgartinger, T. Plakhotnik, A. Renn, and U. P. Wild, *Chem. Phys. Lett.* **217**, 393 (1994).

[9] E. Betzig and R. J. Chichester, *Science* **262**, 1422 (1993).  
 [10] W. E. Moerner, T. Plakhotnik, T. Irrgartinger, U. P. Wild, D. W. Pohl, and B. Hecht, *Phys. Rev. Lett.* **73**, 2764 (1994).  
 [11] K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. R. Dasari, and M. S. Feld, *Phys. Rev. Lett.* **78**, 1667 (1997).  
 [12] S. Nie and S. R. Emory, *Science* **275**, 1102 (1997).  
 [13] P. W. Anderson, B. I. Halperin, and C. M. Varma, *Philos. Mag.* **25**, 1 (1972).  
 [14] W. A. Phillips, *J. Low Temp. Phys.* **7**, 351 (1972).  
 [15] T. L. Reinecke, *Solid State Commun.* **32**, 1103 (1979).  
 [16] W. A. Phillips, *Rep. Prog. Phys.* **50**, 1657 (1987).  
 [17] L. R. Narasimhan, K. A. Littau, D. W. Pack, Y. S. Bai, A. Elschner, and M. D. Fayer, *Chem. Rev.* **90**, 439 (1990).  
 [18] P. Tchénio, A. B. Myers, and W. E. Moerner, *J. Lumin.* **56**, 1 (1993).  
 [19] A. Zumbusch, L. Fleury, R. Brown, J. Bernard, and M. Orrit, *Phys. Rev. Lett.* **70**, 3584 (1993).  
 [20] J. Bernard, L. Fleury, H. Talon, and M. Orrit, *J. Chem. Phys.* **98**, 850 (1992).  
 [21] T. Plakhotnik, D. Walser, M. Pirotta, A. Renn, and U. P. Wild, *Science* **271**, 1703 (1996).  
 [22] T. Plakhotnik, D. Walser, A. Renn, and U. P. Wild, *Phys. Rev. Lett.* **77**, 5365 (1996).  
 [23] D. Walser, T. Plakhotnik, A. Renn, and U. P. Wild, *Chem. Phys. Lett.* **270**, 16 (1997).  
 [24] T. Plakhotnik, D. Walser, A. Renn, and U. P. Wild, *J. Lumin.* **72–74**, 22 (1997).  
 [25] This averaging presupposes no significant time irreversible changes in the sample.  
 [26] E. Geva and J. L. Skinner, *J. Phys. Chem. B* **101**, 8920 (1997).  
 [27] R. G. DeVoe, A. Wokaun, S. C. Rand, and R. G. Brewer, *Phys. Rev. B* **23**, 3125 (1981).  
 [28] In a different approach, the Fourier transform of a dipole moment autocorrelation function is calculated. In this approach, there are no restrictions on fast TLS relaxation rates, but TLSs with relaxation times longer than a time resolution do not contribute at all [26].  
 [29] L. A. Nakhimovsky, M. Lamotte, and J. Jousot-Dubien, *Handbook of Low Temperature Electronic Spectra of Polycyclic Aromatic Hydrocarbons* (Elsevier, Amsterdam, 1989).  
 [30] K. Barth and W. Richter, *Mol. Cryst. Liq. Cryst.* **283**, 225 (1996). The authors assume that each TLS gives the same contribution to the broadening (ensembles of TLSs interacting with each dye molecule are statistically identical) and neglect SD during “burning” and “reading” times. In this case, ensemble (hole-burning) and time (SM spectra) averages of the transition frequency are equivalent.  
 [31] W. E. Moerner, T. Plakhotnik, T. Irrgartinger, M. Croci, V. Palm, and U. P. Wild, *J. Phys. Chem.* **98**, 7382 (1994).  
 [32] S. A. Empedocles, D. J. Norris, and M. G. Bawendi, *Phys. Rev. Lett.* **77**, 3873 (1996).