Time-dependent single molecule spectral lines

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A general conceptual problem of time-dependent single molecule spectra is discussed theoretically in the framework of recently developed intensity-time-frequency correlation spectroscopy. It is shown that the new method is closely related to a ''gedanken'' three-pulse photon echo experiment done on an ensemble of identical molecules interacting with statistically identical microscopic environments. The correlation function is an integral transform (under certain conditions a Fourier transform) of the echo amplitude as a function of the delay between the first and the second pulses.

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A common characteristic feature of single molecules, single quantum dots, or any other single quantum systems (later on all are referred to as SMs) is that each successive spectral measurement performed on the same SM can reveal a new ''spectrum'' even when the macroscopic conditions do not change.[1,2] In mathematics, such time-dependent spectra are called joint time-frequency distributions.[3] The spectral dynamics result from fluctuations of the microscopic surroundings of each SM. These surroundings are sometimes simulated by a set of two-level systems (TLSs) interacting with a phonon bath.[4,5] Each TLS is characterized by two parameters, the energy splitting E and the sum of downward and upward TLS flip rates K. The interaction between a SM and a TLS leads to a SM resonance frequency shift $2v$ when the TLS flips. These flips are random and are not correlated with flips of other TLSs. Thus the resonance frequency becomes a stochastic function of time.[6] This effect is called spectral diffusion (SD). For a bulk sample SD also leads to time-dependent line shapes, and time-frequency distributions in bulk materials have been studied intensively for more than 20 years.[7,8] Different from nonreproducible SM spectra, a time-frequency distribution for an ensemble of molecules is a reproducible macroscopic characteristic.

It is important to emphasize that time and frequency obey the uncertainty principle and one can speak about time-dependent ''spectra'' only when the measuring procedure is exactly described. There are few methods for measuring time-dependent spectra of ensembles. These are two- and three-pulse photon echo[9–11] and ''hole burning.''[12]

Hole burning makes little sense for SMs. Hahn-echo-type experiments, which are limited by the lifetime of the exited state, can be done even on a SM,[13] but classical two-and three-pulse echoes require an ensemble. Strictly speaking, neither experimental methods nor even a consistent theoretical description for time-dependent reproducible spectral distributions for single molecules have existed. Only recently, a new approach called intensity-time-frequency correlation (ITFC) was suggested and demonstrated experimentally.[14]

ITFC spectroscopy works in three steps: (a) N laser scans over the same spectral region are acquired and the SM luminescence intensity as a function of the laser frequency is measured, (b) a correlation function is calculated for each scan, and (c) these functions are averaged:

$$S_{\text{ITFC}}(\omega',\Delta) \cong \lim_{N\to\infty} \frac{1}{N} \sum_{k=1}^{N} \int_0^{\omega_0} I_k(\omega) I_k^\Delta(\omega+\omega') d\omega,$$

(1)

where $I_k(\omega)$ is the kth single scan spectrum and $I_k^\Delta(\omega)$ is the $(k+p)$th scan starting with a time delay Δ with respect to $I_k(\omega)$. $\Delta=0$ corresponds to an autocorrelation. The laser frequency $\omega(t)=rt$, where r is the frequency scan rate. Throughout the paper t is the time measured from the beginning of the corresponding scan. The frequency scan interval ω_0 is chosen such that during the experiment the SM luminescence intensity is negligible outside of the scan range. This also implies that $\Delta \gg T_1$ if $\Delta \neq 0$, where T_1 is the lifetime of the excited state. In any case, the integration limits can be set to $+\infty$ and $-\infty$.

A remarkable difference can easily be seen between $I_k(\omega)$ and $S_{\text{ITFC}}(\omega',\Delta)$. Though all I_k are different because the microscopic environment changes during each scan, ITFC is a reproducible characteristic for each molecule, which depends only on the scan rate and Δ. Geva and Skinner[15] have already calculated reproducible time-dependent spectra of SMs subject to spectral diffusion, simply ignoring TLSs with flip times longer than a measuring time τ_m but allowing the SMs to interact with the laser light for an infinitely long time. Thus, to calculate a spectrum for the SM, they could apply the fluctuation-dissipation theorem[16] and a theory developed by Kubo and Anderson.[16–18] Though such an approach is self-contradictory, this does not lead to big errors when a SM interacts with a large number of TLSs and when the parameters for those TLSs have very broad and flat distributions, which was actually indirectly assumed in Ref. 15. But the fluctuation-dissipation theorem approach does not work at all, for example, if a SM interacts with TLSs all having the same flipping rate. In this case, Ref. 15 predicts two line shapes: one for $\tau_m K > 1$ and one for $\tau_m K \leq 1$. But actually a gradual line-shape evolution should be observed when τ_m changes. It is Eq. (1) which provides a rigorous definition for a SM line-shape evolution.

Another fundamental question is the relation between the ITFC method and the methods developed for bulk samples. According to an abstract mathematical theory, all time-frequency distributions are connected to each other.[3] Of course, such distributions for individual molecules are not
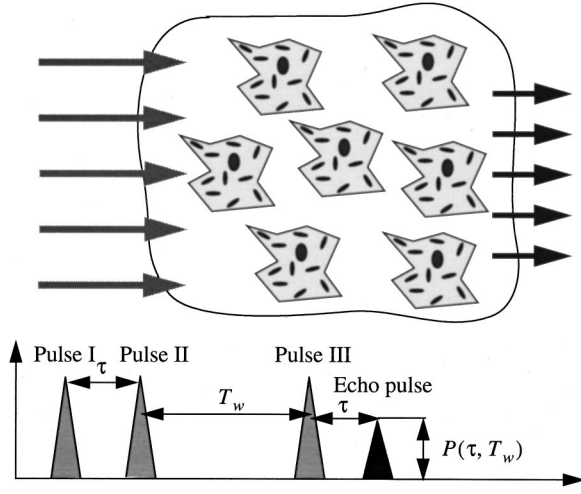
FIG. 1. A ''gedanken'' three-pulse photon echo experiment. The sample consists of molecules (shown as large ellipses) having statistically identical microscopic environments, i.e., interacting with identical sets of TLSs (black bars). Flips of TLSs are not correlated. The echo amplitude is a function of the two time delays τ, T_w, and parameters of all TLSs.

accessible after ensemble averaging so only a ''gedanken'' experiment like that shown in Fig. 1 and ITFC measurements must be related.

In the present paper, a general theory for the ITFC spectra is developed. We treat a SM as a two-level atom, whose behavior is described by a density matrix ρ. The probability for the atom to emit a spontaneous photon at a time t is then proportional to the density matrix element $\rho_{22}(t)$ and Eq. (1) becomes

$$S_{\mathrm{ITFC}}(\omega',\Delta) \sim \left\langle \int_{-\infty}^{\infty} \rho_{22}(t)\rho_{22}^{\Delta}(t+\theta)dt \right\rangle, \qquad (2)$$

where index 2 indicates the exited state of the SM, $\theta = \omega' r^{-1}$, and the time evolution of the density matrix is described by the optical Bloch equations:

$$\dot{\rho}_{12} = [i\omega(t) - i\vartheta(t) - \gamma]\rho_{12} + i\Omega(\rho_{22} - \rho_{11}), \qquad (3)$$

$$\dot{\rho}_{22} = -2\gamma\rho_{22} + i\Omega(\rho_{12} - \rho_{21}), \qquad (4)$$

where the SM transition frequency $\vartheta(t)$ is an arbitrary stationary stochastic function of time, Ω is the Rabi frequency which is proportional to the amplitude of the laser light, and $2\gamma = 1/T_1$. The particular form of $\vartheta(t)$ assumed in the TLS model is not essential for most of the following discussion. $\langle\ \rangle$ in Eq. (2) means an average over all possible realizations of the stochastic function $\vartheta(t)$. At low laser power $\rho_{11}\approx1$, $\rho_{22}\approx0$, and hence $\dot{\rho}_{12} = [i\omega(t) - i\vartheta(t) - \gamma]\rho_{12} - i\Omega$. In this case, the solution of linear Eqs. (3), (4) is straightforward.

Since in Eq. (2) $\rho_{12}(0) = \rho_{22}(0) = 0$, $\rho_{22}(t)$ can be written in the following form:

$$\rho_{22}(t) = 2\Omega^2 \,\mathrm{Re}\left[\int_0^t e^{-2\gamma t'} \int_0^{t-t'} e^{-\gamma t''} \right.$$
$$\left. \times \exp\left(i\int_{-t'-t''}^{-t'} [\omega(t+u) - \vartheta(t+u)]du \right) dt''dt' \right]. \qquad (5)$$

If $\Delta \neq 0$, then $\rho_{12}^{\Delta}(0) = \rho_{22}^{\Delta}(0) = 0$. If $\Delta = 0$, we should take into account that when emitting a photon at time t, the SM jumps to the ground state and hence $\rho_{12}^{\Delta}(t) = \rho_{22}^{\Delta}(t) = 0$. A general expression for $\rho_{22}^{\Delta}(t+\theta)$ is

$$\rho_{22}^{\Delta}(t+\theta) = 2\Omega^2 \,\mathrm{Re}\left[\int_0^{\chi} e^{-2\gamma\tau'} \int_0^{\chi-\tau'} e^{-\gamma\tau''} \right.$$
$$\times \exp\left(i\int_{-\tau'-\tau'}^{-\tau'} [\omega(t+\theta+u) \right.$$
$$\left. \left. - \vartheta(t+\theta+u+\Delta)]du \right) d\tau''d\tau' \right], \qquad (6)$$

where $\chi = t + \theta$ if $\Delta \neq 0$ and $\chi = \theta$ otherwise.

Each of the scans starts far from the resonance and takes a time much longer than T_1. This means that $\rho_{22}(t)$ is different from zero only when $\gamma t \gg 1$ and hence, due to $\exp(-2\gamma t')$ and $\exp(-\gamma t'')$ factors in the integrated function in Eq. (5), the upper limits of the integrals over dt', dt'' can be set to infinity. If $\Delta \neq 0$, this can be done also in Eq. (6) for integrals over $d\tau'$ and $d\tau''$. If $\Delta = 0$, the approximation is valid only if $\gamma\theta \gg 1$. When $\gamma\theta < 1$, a dip of width $\omega_d' < r/\gamma$ in the frequency domain corresponds to the well-known photon antibunching effect.[19] For simplicity, this effect is not considered here and all limits are assumed to be ∞.

From Eqs. (5) and (6) it follows that

$$\int_{-\infty}^{\infty} \langle \rho_{22}(t)\rho_{22}^{\Delta}(t+\theta) \rangle dt = 2\Omega^4[\mathrm{Re}(A^-) + \mathrm{Re}(A^+)], \qquad (7)$$

where, substituting $\omega = rt$, $A^{\pm}$ reads

$$A^{\pm} = \int_{-\infty}^{\infty}\int_0^{\infty}\int_0^{\infty}\int_0^{\infty}\int_0^{\infty} e^{-2\gamma(t'+\tau')}e^{-\gamma(t''+\tau'')}$$
$$\times e^{irt(t''\pm\tau'')}e^{i\lambda^{\pm}r}\left\langle \exp\left(-i\int_{-t'-t''}^{-t'} \vartheta(t+u)du \right.\right.$$
$$\left.\left. \mp i\int_{-\tau'-\tau'}^{-\tau'} \vartheta(t+\theta+u+\Delta)du \right) \right\rangle dV. \qquad (8)$$

Here $\lambda^{\pm} = -t't'' \mp \tau'\tau'' \pm \theta\tau'' - (t''^2 \pm \tau''^2)/2$ and dV stands for $dt''dt'd\tau'd\tau''dt$. Since $\vartheta(t')$ is a function whose average is independent of a time shift t, integration over dt gives a δ function $\delta(r(t'' \pm \tau''))$. Because t'', $\tau'' > 0$, $A^+ = 0$. Further, since t', τ' are on the order of $\gamma^{-1} \ll (\theta + \Delta)$, the average over possible trajectories in Eq. (8) depends very little on the time shifts t' and τ'. If this dependence is neglected, the integration over dt'', dt', and $d\tau'$ is straightforward and leads to the following expressions for $S_{\mathrm{ITFC}}(\omega',\Delta)$:

$$S_{\text{ITFC}}(\omega',\Delta) \sim \frac{\Omega^4}{4\pi r\gamma^2} \text{Re}\Bigg[\int_0^\infty e^{-i\omega'\tau''} \frac{e^{-2\gamma\tau''}}{1+(T_1 r\tau'')^2}$$

$$\times \Bigg\langle \exp\Bigg(-i\int_0^{\tau''}\vartheta(u)du$$

$$+ i\int_{\theta+\Delta+\tau''}^{\theta+\Delta+2\tau''}\vartheta(u)du \Bigg)\Bigg\rangle d\tau'' \Bigg] \qquad (9)$$

or

$$S_{\text{ITFC}}(\omega',\Delta) \sim \text{Re}\Bigg(\int_0^\infty \frac{e^{-i\omega'\tau}}{1+(T_1 r\tau)^2} P(\tau,T_w)d\tau \Bigg), \quad (10)$$

where $T_w = \theta+\Delta = \omega' r^{-1}+\Delta$ and $P(\tau,T_w)$ is explicitly the three-pulse photon echo amplitude[20] measured in the ''gedanken'' experiment shown in Fig. 1. If $T_1^2 r \ll 1$ (slow scan) and $\Delta \gg \omega' r^{-1}$ (unless $\Delta = 0$, $\Delta \gg \omega_0 r^{-1} \gg \omega' r^{-1}$) $S_{\text{ITFC}}(\omega',\Delta)$ is simply a Fourier transform of $P(\tau,\Delta)$.

Starting with a paper by Klauder and Anderson,[20] averages like that in Eq. (9) have been calculated many times for ensembles of two-level atoms (spins) interacting with an ensemble of TLSs.[21–23] A significant difference between an ensemble and a SM is that we do not need to average over distributions of the TLS parameters E, v, and K because the SM interacts only with a specific environment. For each molecule $\vartheta(t) = \Sigma_m v_m \xi_m(t)$, where $\xi_m(t)$ are stochastic functions equal to 1 or -1. The index m refers to the mth TLS. Using a quantity

$$F_m(\tau) = 4v_m^2 \frac{|\sin(Y_m\tau)|^2}{|Y_m|^2} \text{sech}\Bigg(\frac{E_m}{2k_B T}\Bigg)^2 e^{-K_m\tau}, \quad (11)$$

where T is a temperature, k_B is Boltzmann's constant, and $Y^2 = v^2 - K^2/4 + ivK\tanh[E/(2k_B T)]$, the average can be written in the following form:[23]

$$\Bigg\langle \exp\Bigg(-i\int_0^\tau \vartheta(t')dt' + i\int_{T_w+\tau}^{T_w+2\tau}\vartheta(t')dt' \Bigg)\Bigg\rangle$$

$$= \prod_m \Bigg\{ 1 - 2K_m\int_0^\tau F_m(\tau')d\tau' - (1-e^{-K_m T_w})F_m(\tau)\Bigg\}. \qquad (12)$$

When averaged over many molecules,[14] an ITFC is equivalent to a three-pulse photon echo performed on those molecules. In this case molecular individuality is lost but such an averaged ITFC would be a complementary method to the conventional photon echo technique because it can be done on photo stable molecules with negligible yield into a metastable (triplet) state. Such molecules are most suitable for a single molecule experiment while two- and three-pulse photon echos work in this case only if all delays are smaller than T_1.

In this paper a rigorous theory of time-dependent single molecule spectral lines has been developed. A remarkable analogy between ITFC and three-pulse photon echos is shown. It turns out that three-pulse photon echo experiments are not exclusively for ensembles but in an equivalent way can be done on a single molecule and hence all the ideas developed for echo experiments are applicable to single molecules. This opens up the whole temporal range accessible in bulk measurements to single molecule spectral dynamics studies. Though until now most of single molecule spectroscopy has been done at low temperatures, investigations can be extended to room temperature and even to biologically relevant systems (see Ref. 24 as an example). In such systems much of the dynamics takes place on time scales from nanoseconds to seconds, where the ITFC technique can be used to gain insight into the physics underlying biochemical process.

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