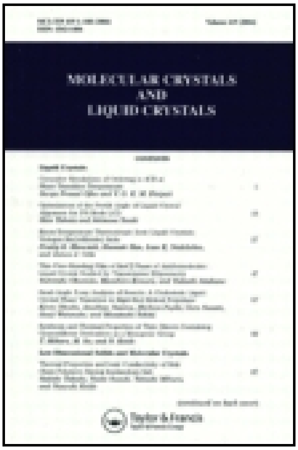

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STOCHASTIC MODEL DESCRIPTION OF SINGLE MOLECULE SPECTROSCOPY

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Abstract We calculate the optical line shape of a single molecule in a solid matrix taking into account its relaxation and the interaction with the host. Under the influence of the environment, described by an ensemble of TLSs, the optical transition frequency of the guest molecule is time dependent. Its dynamics is simulated by dichotomic stochastic processes.

INTRODUCTION

Optical spectroscopy of single molecules (SMD) in condensed matter[1,2] is a new technique which allows to get information on the structure and the dynamics of the host matrix. With SMD it is possible to observe various new phenomena such as spectral diffusion in crystals and disordered materials[3], e.g. polymers and glasses, and recently magnetic resonance[4] of a single molecular spin was observed. The first system was investigated using absorption spectroscopy. Because of the better signal-to-noise ratio fluorescence excitation technique is used now. The experimental results show a time dependent position of the resonance line which can be understood invoking the interaction of the guest molecule with two-level-systems (TLSs) of the matrix. Discontinuos and quasicontinuos as well as a systematic shift of the optical line ("jumps", "wandering" and "creeping") is observed.

We calculate[5] the optical line shape of the guest molecule taking into account the time dependence of the transition frequency caused by the noise of the TLSs in the environment. The dynamics of the TLSs is described by stationary dichotomic Markov processes. Simulations of such processes show that the experimental results are described by a variation of the number of the coupled TLSs and their initial state.

THEORY

Optical line shape

In this section we determine the optical line shape, i.e. the mean absorbed power, of a guest molecule interacting with the TLSs of its environment and with a heat bath. The guest molecule is modelled by its ground state $|g\rangle$, the optical excited state $|e\rangle$ and the transition frequency ω_i. The external electrical field couples to the transition dipole moment of this molecule. The equation of motion for the density operator $\tilde{\sigma}(t)$, without any noise, in a rotating frame, and using the rotating wave approximation, reads:

$$\frac{d}{dt}\tilde{\sigma}(t) = -i\tilde{L}\tilde{\sigma}(t) = -i \begin{pmatrix} -i\Gamma_g & +i\Gamma_e & +\frac{\Omega}{2} & -\frac{\Omega}{2} \\ +i\Gamma_g & -i\Gamma_e & -\frac{\Omega}{2} & +\frac{\Omega}{2} \\ +\frac{\Omega}{2} & -\frac{\Omega}{2} & +\Delta - i\gamma_2 & 0 \\ -\frac{\Omega}{2} & +\frac{\Omega}{2} & 0 & -\Delta - i\gamma_2 \end{pmatrix} \tilde{\sigma}(t)$$

$\tilde{L}$ is the Liouville operator, $\Delta = \eta - \omega_i$ the detuning frequency, $\Omega = 2E\mu/\hbar$ the Rabi frequency, μ the transition dipole moment of the molecule, E the amplitude and η the frequency of the external field. Γ_g, Γ_e and γ_2 are relaxation constants.

This equation is solved using the Laplace transformation method. In the time domain the density operator is given by:

$$\tilde{\sigma}(t) = U_\Delta(t)\tilde{\sigma}(t=0)$$

$U_\Delta(t)$ is the time domain transform of the matrix $U_\Delta(z) = (z + i\tilde{L})^{-1}$.

The transition energy of the molecule is modulated by the noise $w(t)$ caused by the TLSs of the environment. Fig.1 shows a typical realization of the noise.

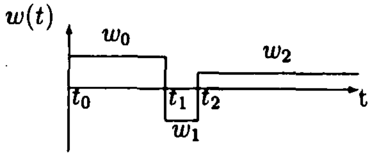

FIGURE 1 Realization of the noise $w(t)$

$\{w_k\}$ are the frequency values of the noise, and $\{t_k\}$ the jumping times. In the time intervals between two jumps the density operator is given by:

$$\begin{aligned} t_0 &\leq t < t_1 : \tilde{\sigma}(t) &&= U_{\Delta - w_0}(t - t_0)\tilde{\sigma}(t_0) \\ t_1 &\leq t : \quad \tilde{\sigma}(t) &&= U_{\Delta - w_1}(t - t_1)\tilde{\sigma}(t_1) = \\ & &&= U_{\Delta - w_1}(t - t_1)U_{\Delta - w_0}(t_1 - t_0)\tilde{\sigma}(t_0) \end{aligned}$$

etc.

To calculate the mean absorbed power, we take into account the stationary as well as the transitory states. It is given by:

$$\overline{W}_T(t) = 2\eta E n \mu Im \tilde{\sigma}_{eg}(t)$$

n is the density of the molecules. In stationary state, i.e. for $t \rightarrow \infty$, $Im\tilde{\sigma}_{eg}(t)$ describes a homogeneous Lorentzian line (with saturation broadening).

Stochastic description of the dynamics of the TLSs

The environment of the molecule is described as an ensemble of TLSs. Similar to the theory of Reilly and Skinner[6] the TLS l creates die noise $w_l(t, r) = \xi_l(t)a_l(r)$ to the transition frequency of the guest molecule. $\xi_l(t) = \begin{pmatrix} +1 \\ -1 \end{pmatrix}$ determines the instantaneous state of the TLS. Assuming dipole–dipole interaction between the guest molecule and the TLS the amplitude of the noise is proportional to r^{-3}. Here $\vec{r}$ describes the distance between guest molecule and the TLS l. Since the TLSs are independent the total noise is a superposition of the individual contributions. The transition frequency of the molecule can be written as: $\omega(t) = \omega_i + w(t, \{\vec{r}\})$, $(w(t, \{\vec{r}\}) = \sum_{l=1}^{N} w_l(t, \vec{r}))$.

The dynamics of a TLS is taken to be stochastic. The TLS jumps between its two energy states (E_1, E_2) with the transition rates k_u (up) und k_d (down). We simulate the noise of the TLS by a stationary dichotomic Markov process. The random variable can have the two values $w_1 = -a$ und $w_2 = +a$, where a is the amplitude of the noise from above. The transition matrix P is a 2×2-matrix with the parameters α and β; $\alpha, \beta \in (0, 1)$. The jumping times $\{t_k\}$ are determined by a Poisson process. Thus the time intervals $\{\Delta t_k\}$ between two jumps are independent and identically distributed with the density $\Phi(\Delta t_k) = \lambda exp(-\lambda \Delta t_k)$. The relations between the transition rates k_u, k_d and the parameters α und β are given by: $\alpha = \frac{k_u}{\lambda}, \beta = \frac{k_d}{\lambda}$. They determine the equilibrium distribution for the two TLS states.

We describe the spatial dependence of the noise amplitudes by the following model: The TLSs are distributed homogeneously in space with density ϱ. We divide the space around the guest molecule into spherical shells, where all TLSs of the same shell create the same noise amplitude. The thickness of the shell is determined by the relation of the amplitude at the surfaces of the shells.

The simulation parameters are summarized in Table 1.

TABLE 1 Parameters of the simulations

Parameter	$T = 1.5K$	$T = 4.0K$
$k_u^{(1)}[10^{-4}s^{-1}]$	13.3	67.4
$k_d^{(1)}[10^{-4}s^{-1}]$	76.5	130.0
$k_u^{(2)}[10^{-4}s^{-1}]$	1.0	-
$k_d^{(2)}[10^{-4}s^{-1}]$	5.6	-
$\lambda[10^{-3}s^{-1}]$	20.0	20.0
$\Omega[10^{6}s^{-1}]$	1.2	1.2
$\gamma_1[10^{6}s^{-1}]$	7.6	7.6
$\varrho[10^{-7}\mathring{A}^{-3}]$	1	1

$\gamma_1 = \Gamma_g + \Gamma_e$; $k^{(1)}$ and $k^{(2)}$ describe two different kinds of TLSs; the values of $k^{(1)}$ are taken from Ph. D. Reilly and J. L. Skinner[6].

RESULTS

Discret frequency jumps are caused by the interaction of only a few TLSs with the guest molecule. Fig.2 und Fig.3 show the $Im\tilde{\sigma}_{eg}(t)$ of the molecule coupled to a single TLS for the temperatures $T_1 = 1.5K$ and $T_2 = 4.0K$. With increasing temperature the TLS jumps more often to higher frequencies. The transitory states have a very short life time as compared to the time intervals between jumps and can therefore be neglected.

The coupling of many identical TLSs in equilibrium gives rise to the "wandering" of the optical line. Fig.4 and Fig.5 represent the simulation of the noise of 263 identical TLSs with a distribution of the distance from the guest molecule for two different temperatures. Raising the temperature from $T_1 = 1.5K$ to $T_2 = 4.0K$ increases the spectral diffusion rate und range.

Fig.6 shows the noise of the transition frequencies created by two kinds of TLSs with different transition rates. Initially the TLS were not in equilibrium; the approach to equilibrium gives rise to a creeping of the frequency. The time constant of the creeping is determined by the TLSs with the smaller transition rates. Im summary, this simple model of coupling of a guest molecule to TLSs gives a qualitative description of the dynamics of the optical line observed in single molecule spectroscopy.

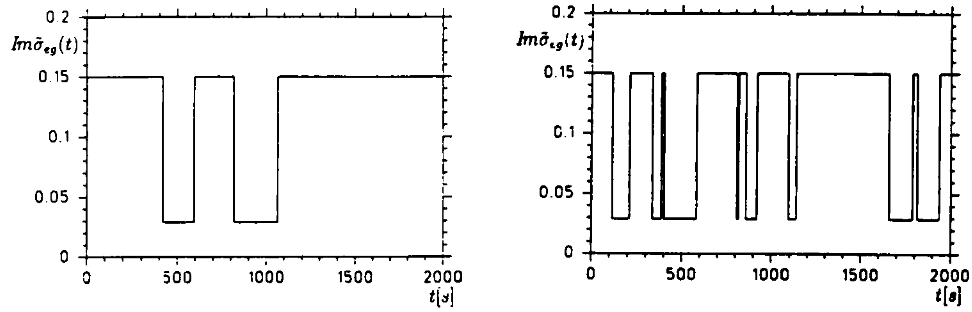

FIGURE 2 $Im\tilde{\sigma}_{eg}(t)$ for the coupling of one TLS$^{(1)}$ with noise amplitude $a = 4$ ($\eta = \omega_i - a$), $T = 1.5K$ (left), $T = 4.0K$ (right)

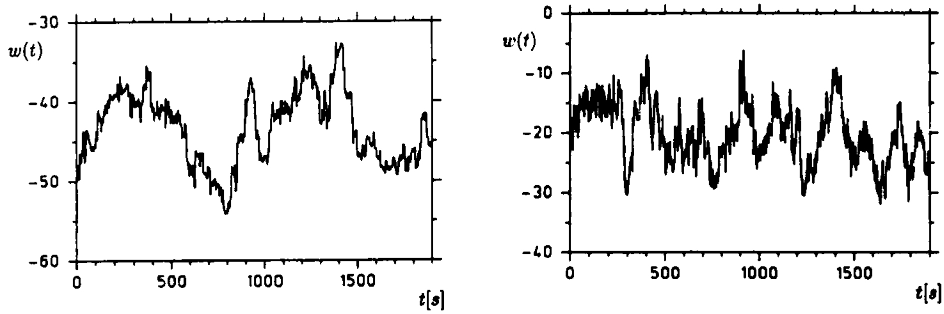

FIGURE 3 Noise $w(t)$ of 263 TLSs$^{(1)}$ in equilibrium, $T = 1.5K$ (left), $T = 4.0K$ (right)

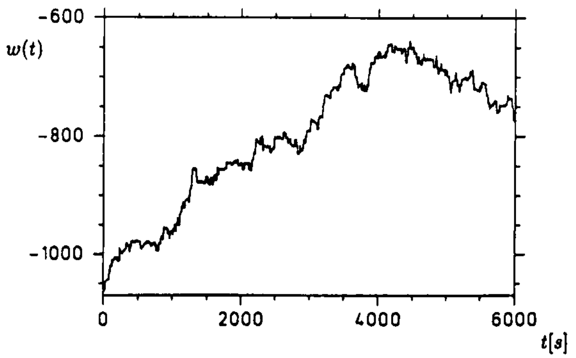

FIGURE 4 Noise $w(t)$ of 263 TLSs$^{(1)}$ and 200 TLSs$^{(2)}$ in non-equilibrium, $T = 1.5K$

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