

## Probing Individual Two-Level Systems in a Polymer by Correlation of Single Molecule Fluorescence

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We have measured the autocorrelation of the fluorescence of single aromatic molecules in polyethylene at  $T \approx 2$  K. Intensity fluctuations are caused by frequency jumps when two-level systems (TLS's) change states. Individual TLS's can be probed with minimal recourse to theory and no assumptions about the distribution of TLS parameters. Besides providing a simple confirmation of the tunneling theory of TLS's, this new method, by eliminating statistical uncertainties, proves that while some TLS's may be stable for several hours others are modified by transitions of their neighbors. Tunneling times of individual TLS's are measured directly. Their temperature dependences reveal three types of TLS-phonon coupling, of which one is new.

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Single molecule spectroscopy is a new field in which sharp resonances of single impurity molecules are resolved in the broad, inhomogeneous band of very dilute and small samples. The first absorption spectra of single molecules, recorded by Moerner and Kador [1], were barely above the noise. Introduction of fluorescence excitation by two of us [2] opened the way to many experiments by dramatically improving the signal to noise ratio. The main results in the first system studied, pentacene in *p*-terphenyl crystals, were the following [3]: observation of the line shape of one molecule, its temperature dependence, optical saturation, spectral diffusion caused by defects, and the Stark effect. Since then, polyethylene doped with perylene [4] or terrylene [5], as below, was also studied. The line shapes of single molecules, photoinduced spectral jumps, and the Stark effect were observed in this polymer.

But the temporal distribution of fluorescence photons also contains a wealth of information. Correlation of the emission of single molecules is one of their hallmarks, whereas in usual systems the effect is smothered by the emission of many independent sources. In our first paper [2], we demonstrated photon bunching caused by inter-system crossing, an effect we later used to obtain the crossing rates [6]. Experiments by Basché and Moerner [7] nicely confirmed photon antibunching at times of the order of the Rabi period of the molecule in the laser field. Recent work [6,8] led us to expect the method could be used to measure the dynamics of the matrix at low temperatures.

Several properties of amorphous materials differ strongly at low temperatures from those of crystals. The specific heat, the thermal conductivity, and the attenuation of ultrasound waves in glasses indicate the presence, beside acoustic phonons, of other low energy excitations [9]. In the late 70's and 80's, many papers were devoted to optical transitions in crystals and glasses [10–12]. Lately, new work using time-resolved persistent spectral hole burning [13,14] or photon echoes [15] displayed the

broad time range covered by dynamical processes in glasses. We usually think of a glass as a solid prepared in one of the multitude of secondary minima of the complex, multidimensional intermolecular potential. Phillips [16] and Anderson, Halperin, and Varma [17] suggested that the anomalous excitations of glasses are tunneling jumps of two-level systems (TLS's) in double well features of the potential, each associated with two metastable configurations of an atom or group of atoms. While twenty years of effort have confirmed the broad lines of the tunneling model and much has been learned from the above methods, we should like to describe a new experimental method, removing all statistical effects, which has potential for all of the questions for which interpretation of bulk measurements is complicated by the presence of an ensemble [18,19].

Consider then the autocorrelation function of pairs of fluorescence photons separated by delay  $\tau$ ,

$$g^{(2)}(\tau) = \langle I(t+\tau)I(t) \rangle / \langle I(t) \rangle^2, \quad (1)$$

where the temporal average should be taken over an interval much longer than all the fluctuations of the source. Deviation of  $g^{(2)}(\tau)$  from unity depends on the typical amplitude and duration of changes in the counting rate  $I(t)$ . If we tune a high resolution laser to the sharp line (here, 40 to 200 MHz wide at 2 K) of a single molecule, subsequent changes of the molecular resonance frequency are the main cause of intensity fluctuations in our solid system. For single molecules in liquids, other effects are important [20]. Such jumps of the lines of single molecules, reported in [2], were later assigned to spectral diffusion [3], i.e., shifts of the resonance caused by relaxation of the matrix. We call these jumps "slow" below, because they have time constants of at least seconds and may occur only once during a recording. The experiments measure intensity fluctuations caused by faster jumps. The jumps, spontaneous or photoinduced, may be due to intrinsic TLS's in the polymer or to extrinsic ones accompanying insertion of the fluorescent probe.

Suppose a molecule is coupled to just one TLS, which may pass from well 1(2) to well 2(1) by tunneling or classical activation with rate  $k_2(k_1)$ . Let  $\nu_1$  and  $\nu_2$  be the resonance frequencies of the molecules corresponding to configurations  $q_1$  and  $q_2$  of the environment, and  $I_1$  and  $I_2$  be the corresponding fluorescence intensities for some fixed laser frequency  $\nu_L$ , usually  $\nu_1$  or  $\nu_2$ ; see Fig. 1. Then from a simple kinetic scheme we have

$$g^{(2)}(\tau) = 1 + C \exp[-(k_1 + k_2)\tau]. \quad (2)$$

The contrast,  $C = k_1 k_2 (I_1 - I_2)^2 / (k_1 I_1 + k_2 I_2)^2$ , reduces to  $k_1/k_2$  for tuning to  $\nu_2$  and well separated lines (vanishing  $I_1$  at  $\nu_L = \nu_2$ ). If  $k_1 \neq k_2$ , tuning to the weaker line should give the stronger contrast (short bright intervals).

Terrylene is a heavier analog of perylene (Fig. 2), absorbing around 570 nm in polyethylene. Reference [6] describes the experimental details. The small volume of sample required for detecting single molecules was obtained by sticking a flake of polyethylene doped with a trace of terrylene on the end of a monomode optical fiber. Fluorescence excited by a continuous wave laser was collected with a parabolic mirror of large numerical aperture. The photomultiplier was protected from laser light by a red pass filter (Schott RG610) or a holographic filter (Kaiser Notch 577), which gave better throughput and a lower background. Most measurements were therefore made at 577 nm, in the middle of the red wing of the inhomogeneous excitation band of terrylene. The pulses from the amplifier-discriminator were passed to a correlator (ALV model 5000). The logarithmic spacing of the sampling times of the ALV5000 allows measurement of the correlation in one run, from 200 ns to tens of seconds, depending on accumulation time, a strong point when we are studying the dynamics of a glass with relaxation rates spread over many decades.

We first swept the laser over 30 GHz portions of the inhomogeneous absorption band (FWHM  $\approx 500 \text{ cm}^{-1}$ ),

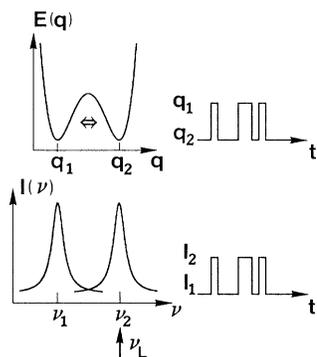


FIG. 1. Left: Double well potential of a TLS, with the absorption spectrum of the molecule when the particle sits in either well. Right: As the TLS jumps from one well to the other, the resonance frequency of the molecule also jumps from  $\nu_1$  to  $\nu_2$ . At fixed laser frequency  $\nu_L$ , the fluorescence intensity fluctuates at the TLS rate.

and picked one of the stronger of the (usually less than 5) single molecule resonances in such a spectrum. On tuning the laser to the peak of most of the lines, we obtained flat correlation functions, with contrast less than the noise between 200 ns and 10 s, although the correlation sometimes rose below  $2 \mu\text{s}$ , perhaps a sign of bunching caused by intersystem crossing [6]. Some (10–20)% of the molecules had clearly decaying correlation, implying reversible spectral jumps, within the time range of the correlator. Correlation was observed over all accessible time scales. Shorter and longer ones probably exist, too.

Figure 2 shows some of the simpler shapes of the correlation functions from these 100 or so molecules. Clearly, there is a wide variety of environments and couplings in this disordered system. Because of the logarithmic time axis, the exponential expected for coupling to one TLS appears as a single step, like the fit of Eq. (2) to decay curve *a*. Two or more exponential steps, as in curve *b*, may arise from coupling to several TLS's. Continuous drop of the correlation, like curve *c* [here close to a logarithmic decay,  $g^{(2)}(\tau) \approx \text{const}_1 - \text{const}_2 \ln(\tau)$ ], could have two explanations: coupling to many different TLS's or coupling to one TLS, itself changing on all time scales. Exponential steps sometimes appeared superimposed on a logarithmic decay. Some molecules had quite different correlation functions before and after a single spectral jump, due to a "slow" TLS. This confirms coupling between TLS's, e.g., the relaxation time changes because of the change of the fast TLS's splitting and tunneling matrix elements in the new strain field of the "slow" TLS. These effects appear to have been envisaged previously mainly for the dephasing of TLS's [21]. They can modify both the shape of the correlation function and its con-

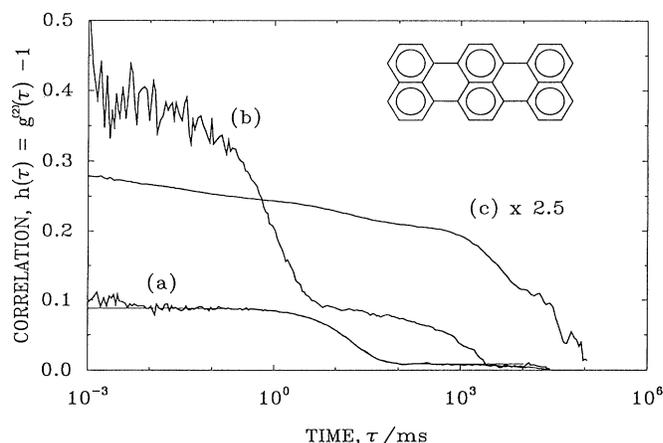


FIG. 2. Three examples of correlation functions of single terrylene molecules at 1.7 K. Curve *a* is perfectly fitted between  $10^{-3}$  and  $10^4$  ms by a single exponential (smooth curve). Curve *b* presents two exponential steps. Curve *c* presents a nearly logarithmic decay of the correlation between  $10^{-3}$  and  $10^3$  ms. These curves may be interpreted as the interaction of the molecule with one, two, or many TLS's.

trast. Correlation functions are reproducible only if all transition times are short compared to the integration time.

Testing for photoinduced jumps by looking at the power dependence of the correlation functions was very difficult, because we usually lost the molecular resonances after a large, irreversible spectral jump at high power, a kind of hole burning [3]. However, the relaxation rates of two stable molecules showed spontaneous jumps at low power and a faster, photoinduced process at higher power, with saturation behavior similar to that in Ref. [6]. These results will be developed elsewhere [22]. Photoinduced jumps are not necessarily due to extrinsic TLS's. Strain and heating around the probe molecule may perturb intrinsic TLS's, too. Molecules below were studied at low power, so we assume only spontaneous jumps occurred.

We supposed above that a molecule coupled to one TLS has two resonances. The second resonance was not usually identified, since it could be any one of the lines in the sweep of the laser, or even outside the scan range. Occasionally we discovered it, when two lines jumped together to new positions with the same spacing, in a slow spectral jump. Both peaks had the same exponential step in their correlations, confirming the identification; cf. Fig. 3. One pair jumped back and forth 5 times in an hour or so, with the same correlation function, showing the stability of the TLS over this time. We usually discovered the other peaks too late, when two or even four lines disappeared together. The weaker line in Fig. 3 produces the stronger contrast and the expression for the contrast is verified after correction for the background. This appears to be the first time one TLS has been isolated and studied

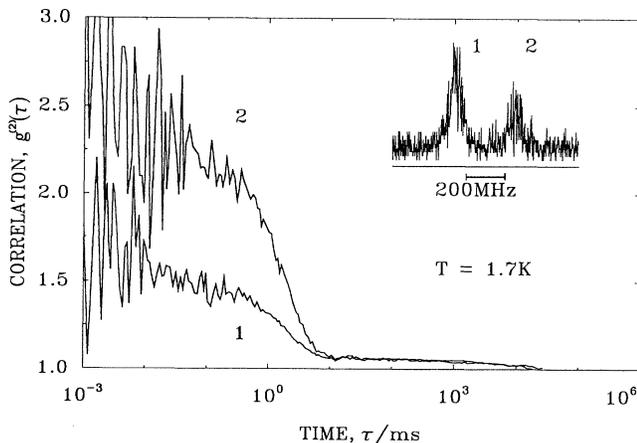


FIG. 3. An example of a molecule with two excitation peaks, shown in the inset spectrum. The correlation functions of the two peaks have the same exponential decay within noise. Their contrasts are in the ratio expected from the simple model given in the text: The weak peak gives the larger correlation. Such observations strongly support assignment of the correlation to interaction with a single TLS.

in a glass.

Next, we measured the temperature dependence of the correlation functions of molecules showing a single, well-defined step. The steps were well fitted by monoexponentials, from which we deduced the rate  $k(T) = k_1 + k_2$ , assuming coupling to one TLS. The rate usually varied by a factor of less than 100 between 1.4 and 4.5 K, the highest temperature we could confidently reach with an acceptable risk of losing the line in a large, irreversible frequency jump. The range of the rates for different molecules was  $10^1 - 10^4 \text{ s}^{-1}$ .

Observation of slow rates with weak temperature dependences is incompatible with crossing the TLS barriers by classical activation, for which we should have  $k(T) \approx \omega_0 \exp(-\Delta/k_B T)$ , where the expected oscillation frequency in either well is  $\omega_0 \approx 10^{13} \text{ s}^{-1}$ . Then the barrier height  $\Delta$  has to be large for  $k(T)$  to be small, but the temperature dependence would then be much too fast. Note, however, that the prefactor might be much smaller than  $\omega_0$ , if the barrier was a distant saddle, approached by a tortuous path over the potential surface.

In fact, we observed power laws  $k(T) \approx T^\eta$ , with  $\eta = 1$  (3 times) or  $\eta = 3$  (twice). Figure 4 shows examples. The scatter of  $k(T)$  was sometimes large with no clear law, perhaps because the TLS was unstable. Now a simple model of tunneling of TLS's assisted by acoustic phonons, predicts a rate  $k(T) \propto \coth(\Delta E/k_B T)$  for a one-phonon process between levels split by  $\Delta E$ . This reduces to  $k(T) \propto T$  if  $\Delta E < k_B T$ . A two-phonon Raman process yields  $k(T) \propto T^3$ , again if the mismatch is smaller than  $k_B T$ . Clear experimental confirmation of two-phonon coupling seems to have been difficult up to now [19,21].

We once obtained activation,  $k(T) \propto \exp(-T_0/T)$

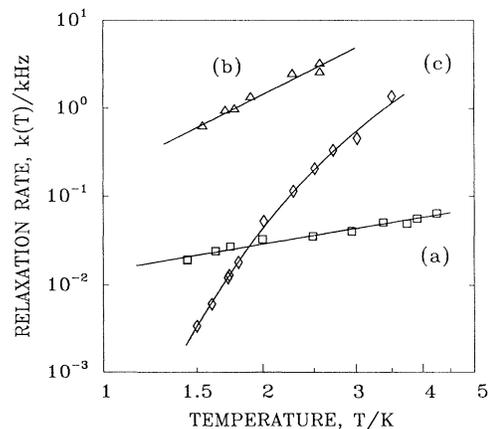


FIG. 4. Three examples of temperature dependences of the jumping rate of single TLS's, derived from the correlation functions of different single molecules. Note the log-log scales. The straight lines (a) and (b) represent  $T$  and  $T^3$  dependences. These laws are expected for tunneling between quasidegenerate TLS levels, assisted by one or two acoustic phonons, respectively. The curve is a fit to the data of molecule (c) by an Arrhenius law:  $\exp(-T_0/T)$ , with  $T_0 = 15 \text{ K}$ .

with  $T_0 \approx 15$  K, molecule (c) of Fig. 4. But we feel this too is explained by tunneling, because the prefactor is too small for classical activation. According to Kagan's theory of tunneling [23], activation may be necessary to compensate a polaronlike stabilization of the TLS, which does not follow it adiabatically during tunneling. This new law would then imply strong TLS-phonon coupling.

In conclusion, direct measurement of TLS properties such as the temperature dependence of jump rates, with minimal recourse to models, should be useful in improving the theory of TLS dynamics, which is still subject to debate [18], e.g., regarding the strength of TLS-phonon coupling. This coupling is exhibited simply, underlining the presence of several mechanisms in one sample under the same conditions, whereas most models assume only one mechanism [9,19]. Evidence from hole burning, for example, is less conclusive [19] because of ensemble averaging. Further, one of the mechanisms above appears to be previously unobserved. Again, study of individual TLS's proves the stability of some of them over several hours, whereas bulk measurements cannot exclude the possibility of constantly changing TLS's within a stable distribution. Modification of some TLS's by one another is also revealed directly. Finally, because working with single TLS's eliminates all averaging, it should be a useful step toward a new method of identifying tunneling degrees of freedom.

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