

## 12. Spectral diffusion

### 12.1. Spectral diffusion, Two-Level Systems

Until now, we have supposed that the optical transition frequency of each single molecule is a constant (except when we considered its variation under external fields). However, under the influence of a number of microscopic processes, the line of a single molecule can wander in the spectrum (in analogy with molecular diffusion, one calls that wandering spectral diffusion). This diffusion can be as simple as jumping between two positions, or have much more complex forms, and present widely different timescales. It is important to realize that spectral diffusion implies that the fluctuations are slow enough. The Fourier relation between frequency and time indicates that, to have a meaning, frequency changes have to be larger than the inverse of the time on which they occur. In particular, if a modulation of the transition frequency is too fast, it becomes “motionally narrowed”, i.e. it does not lead to any significant broadening. This is in particular the case in magnetic resonance at room temperature. The spectral diffusion we consider here will be slower than nanoseconds and concerns frequency excursions larger than or comparable to the homogeneous bandwidth.

Spectral diffusion is on the one hand an ‘enemy’ in single-molecule studies, because it limits the time the resonance between laser and molecule can be kept, on the other hand, it is a very powerful tool to probe the dynamics of the surrounding matrix. The main causes of spectral diffusion are transitions of the host-guest system between different possible ground states. Most of these transitions are rather modest in terms of atomic rearrangements, which means that they are most of the time reversible (cf. non-photochemical hole-burning; rearrangements involving the breaking of chemical bonds are irreversible and often lead to bleaching of the guest). Such transitions between ground states can be thermally induced (i.e. proceed by classical thermal activation, or by thermally assisted tunneling), photo-induced, i.e. depend on the laser energy absorbed by the guest, or arise from other sources such as applied electric fields and currents, for example. In the latter case, spectral diffusion follows from rearrangements of local charges under the influence of the applied electric field or current.

Spectral diffusion is a common phenomenon in glassy and disordered systems. Early observations of glasses at low temperatures indicated the presence of additional

degrees of freedom, as compared to crystals with similar compositions. This additional motion leads to higher specific heat, enhanced ultrasound attenuation, and various other anomalies. It was soon realized that not all of these degrees of freedom are harmonic oscillators, i.e., that some of them can be saturated, at high microwave or acoustic power.

A simple phenomenological model, the standard two-level system (TLS) model, was very successful to understand those saturable anomalies. In the complex potential landscape of a glass (in the multidimensional space of atom coordinates), tunneling may occur between nearby pairs of minima. Transitions between these pairs of states lead to additional dynamics at low temperatures. Because a glass is disordered, the TLS parameters are distributed. The exponential dependence of tunneling on distance and energy gives rise to a broad distribution of the logarithms of tunneling matrix elements. A convenient parametrization of the model gives a good description of glass anomalies at temperatures lower than a few Kelvin.

## 12.2. Hole-burning and optical single-molecule experiments

Optical observations of impurities in glasses by hole-burning and photon echoes also show evidence for spectral diffusion. The hole width is often much larger than the lifetime limit would require, and this was attributed to the slow relaxation of TLS's between burning and reading the hole. While these studies supported the TLS model, they left many questions open. For example :

- how « real » are TLS's ? Isn't glass relaxation a random walk between many minima, with no special role of pairs of minima (the TLS's)?
- the model's distributions of asymmetries and barrier heights were drawn from reasonable assumptions, but how do they compare to experimental data ?
- are TLS's individually identifiable (like spins), or are they so strongly coupled, that a transition of one affects the others ?
- what is the average « lifetime » of a TLS ?
- what is the nature of TLS's, how many atoms on average are involved in their transitions?

The observations of single molecule in glasses have actually started to bring answers to these old questions, although much remains to be done. Hereafter, we review a few experiments and summarize the main conclusions.

A striking feature of TLS's is that their concentration in glasses is almost independent of the chemical nature of the glass. At a few Kelvin, it turns out that a single probe molecule has less than one TLS in its immediate neighborhood, where coupling is strong enough to give rise to a detectable splitting of the optical line. It must be stressed that the sharp zero-phonon line is very sensitive to changes in the environment. For example, motion of an electron by only 0.1 nm creates a change in electric field that can shift a single-molecule line by its width at a distance of 10 nm. Elastic deformations due to the transition of two-level systems can be felt at comparable distances.

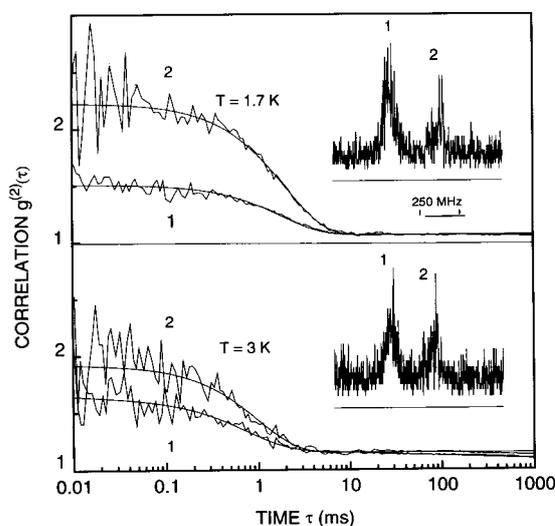


Figure 12.1 : Top : Spectrum and correlation function of a single terrylene molecule in polyethylene. The molecule is coupled to a single TLS, which gives rise to a splitting of the spectrum. The jumps of the TLS lead to correlation with contrast inversely proportional to the intensity of the line. At higher temperature (bottom), the line intensities and correlation contrasts tend to equalize [L. Fleury et al., *J. Lumin.* 56 (1993) 15].

We now discuss the influence of a single TLS on a single molecule line. A slow recording of the spectrum will show two lines, corresponding to the spectral positions of the line in either state of the TLS (see Figure 12.1). If the laser is tuned to one of these lines, the signal will display a characteristic blinking, which can be analyzed via the on- and off-times, or via the correlation function. Figure 12.1 shows the correlation functions recorded on the two spectral positions. They show the same mono-exponential rate (the sum of the two jump rates in the TLS), and contrasts which are inversely proportional to the intensity of the line (after background correction).

The correlation due to the single TLS is studied at two temperatures (Fig. 12.1). At the higher temperature, the intensities of the two lines (proportional to the occupation probabilities), as well as the contrasts, tend to equalize, and the rates shorten. If  $I_1$  and  $I_2$  are the fluorescence intensities when the TLS is in state 1 or 2 respectively, with  $k_1$  and  $k_2$  the rates of jumping from 1 to 2 and from 2 to 1, respectively, the correlation function is given by:

$$g^{(2)}(\tau) = 1 + k_1 k_2 \left( \frac{I_1 - I_2}{k_1 I_2 + k_2 I_1} \right)^2 \exp[-(k_1 + k_2)\tau]$$

By following the jump rate as a function of temperature, one finds different possible variations (in a temperature range limited by spectral jumps on the high temperature side): linear or cubic temperature dependences, and activated laws. In all these cases, including the last one, tunneling is found to play a central role in the TLS jump.

In the foregoing discussion, we have supposed that the jumps of the TLS are caused only by thermal fluctuations, and that the single-molecule line only probes the jumps. In many cases, however, the jump rate increases markedly with laser intensity (three cases can be found: the rate can be independent of light intensity, proportional to light intensity, or the sum of a constant plus a light-induced rate). This phenomenon is called light-induced spectral diffusion in bulk samples, and leads to (non-permanent) non-photochemical hole-burning.

The standard TLS model considers the TLS's as randomly distributed spins in the material. Indeed, some molecules are strongly coupled to two or three TLS's, giving rise to 4 or 8 lines in their spectra. However, when studying large numbers of molecules, deviations from the behavior expected for pure TLS are often found. For example, 3-levels systems occur in small proportions (which is not too surprising if one thinks of the potential landscape model). Sometimes, intensity distributions between the two lines caused by a first TLS change suddenly after a jump of a second TLS, indicating coupling between them. Some single molecule lines creep in the spectrum, a behavior which cannot be understood within the standard TLS model. The overall agreement with the TLS model is rather good, but only for ensembles of many molecules, because the deviating behaviors tend to cancel one another in the averages.

### 12.3. Identified mechanisms in p-terphenyl crystals

Here, we discuss in somewhat more detail the mechanism of jumps where it is better known, in the case of the molecular crystal p-terphenyl as a matrix. Figure 12.2 shows the chemical structure of p-terphenyl and of terrylene, and the crystal structure at low temperature. Terrylene is one of the two guests studied as single molecules so far, the other one being pentacene. P-terphenyl is a flexible molecule, where the central ring can rotate with respect to the two outer ones (in the crystal structure the outer rings remain parallel to one another). The planar structure of the molecule is unfavorable because of steric hindrance, and each molecule adopts one of two tilted conformations of its central ring, with opposite tilts.

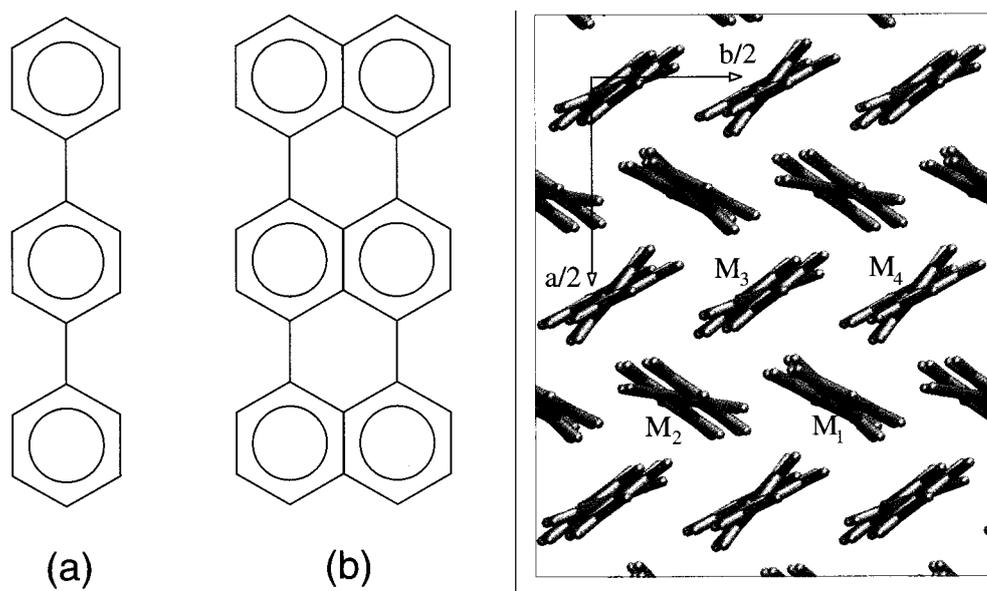


Figure 12.2 : Chemical structures of p-terphenyl (a) and of one of its single-molecule guests, terrylene (b). Crystal structure of the low-temperature phase of p-terphenyl. Note that the four molecules in the unit cell (labeled  $M_1$  to  $M_4$ ) all have different distortions, leading to four spectroscopic sites upon substitution, see Fig.12.3 (from [P. Bordat and R. Brown, Chem. Phys. Lett. 331 (2000) 439].

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In the high temperature (monoclinic) phase, the two positions are equally populated by thermal fluctuations, and there are two molecules in the unit cell, related by a mirror symmetry. Below about 190 K, a phase transition takes leads to a new structure (triclinic) with 4 non-equivalent molecules in the unit cell, with 4 different tilts. Guest molecules replacing a p-terphenyl molecule have thus 4 possible environments, giving

rise to 4 spectroscopic sites in inhomogeneous optical spectra (Fig. 12.3). This situation is observed with pentacene as well as with terrylene guests.

Seen from a given single molecule, the symmetry of the high-temperature phase can be broken in four different ways upon the phase transition, giving rise to four different kinds of domains. By analogy with ferromagnetism, the new phase is called ferro-elastic.

As in ferromagnetism, the (Weiss) domains are separated by borders called walls. The molecules in walls can't decide to which domain they want to belong, therefore the two tilt positions are nearly equivalent for them. These central rings can thus flip, even at low temperatures. This flipping was shown to be the origin for the spectral diffusion of single pentacene molecules in p-terphenyl crystals (Fig. 12.4).

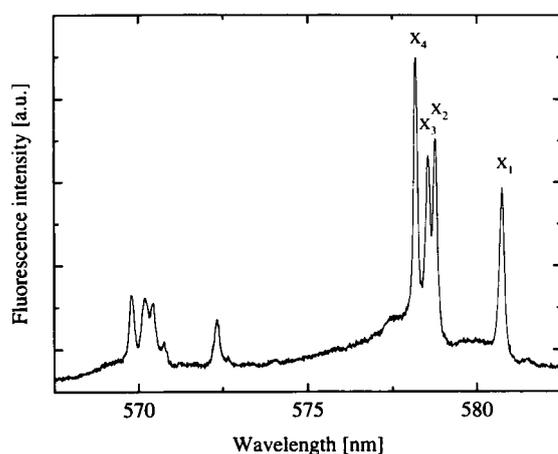


Figure 12.3 : Bulk fluorescence excitation spectrum of terrylene in p-terphenyl, showing the four spectroscopic sites [S. Kummer, Th. Basché, C. Bräuchle, *Chem. Phys. Lett.* 229 (1994) 309 ; copyright 1994 with permission from Elsevier].

Terrylene can be embedded as a guest in a p-terphenyl crystal. In the high-quality crystals studied by Basché and his group, no spectral diffusion was detected, probably because no domain walls were present. However, photo-induced spectral jumps were found for two of the sites, and were studied in great detail for site X<sub>1</sub> (the low-energy one). The mechanism of this spectral jump has been elucidated thanks to molecular dynamics simulations. It turns out that the phenyl ring of a second neighbor of the guest can flip, shifting the line by about 800 GHz. The Stark effect shows that the central symmetry of the photoproduct has been destroyed. Because two different host molecules can flip, the Stark effect of the photoproduct can present two opposite

signs. The molecular model is in full agreement with these observations. This is the first clear identification of a mechanism of non-photochemical hole-burning.

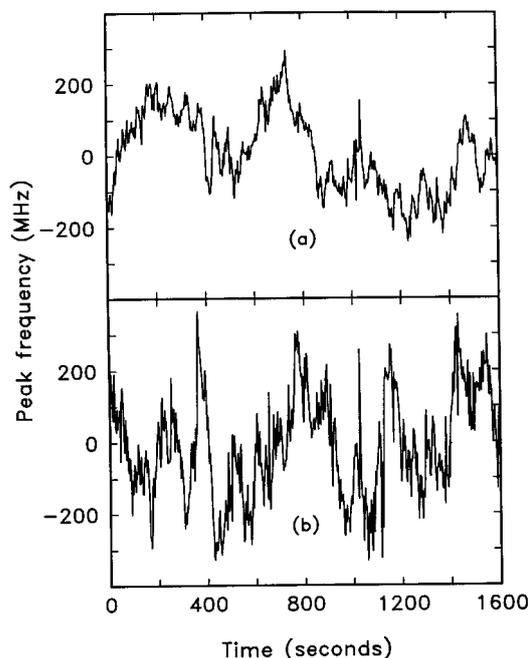


Figure 12.4 : Spectral diffusion of a single pentacene molecule in a *p*-terphenyl crystal at two temperatures, 1.5 K (a) and 4 K (b) [W.P. Ambrose, Th. Basché, and W. E. Moerner, *J. Chem. Phys.* 95 (1991) 7150 ; Copyright 1991, American Institute of Physics].

#### 12.4. Other sources of spectral diffusion

Even at low temperature, many more kinds of motion can be responsible for spectral diffusion. To cite a few examples : tunneling of methyl groups, or of other light particles. Charges (electrons and holes) are particularly light, and can tunnel easily. For example, dynamics of the protein backbone holding a bacterial antenna complex together (see next lecture) give rise to spectral diffusion of the exciton lines. At higher temperatures, the number of possible rearrangements leading to spectral diffusion increases quickly. The lines broaden, but the sizes and rates of the jumps increase too, so that spectral diffusion can also be observed at higher temperature, albeit with a lower resolution and on a wider frequency domain.

*Exercise 12.1:* Use the formalism of Anderson's matrix (see Abragam, the Principles of Magnetism) to study the transition from spectral diffusion to motional narrowing for a single molecule coupled to a single two-level system.

Exercise 12.2: Prove the above expression of the correlation function for an emitter jumping between two values of the intensity  $I_1$  and  $I_2$  with rates  $k_1$  and  $k_2$ .