

## 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 a disadvantage in single-molecule studies, because it limits the time the laser can be kept in resonance with the molecule, but 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. We have seen similar slight rearrangements in 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), or they can be photo-induced, and in that case are most often caused by excitation of the very guest molecule under study. They can also 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 various anomalies of glasses, in particular a higher specific heat, enhanced ultrasound attenuation, and slow relaxation towards thermal equilibrium. It was soon realized that a large part of these additional degrees of freedom are no 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. A complex potential landscape of a glass can be represented in the multidimensional space of the coordinates of the composing atoms. Transitions of the system may occur between nearby pairs of minima, through classical activation or through quantum tunneling. Transitions between these pairs of states lead to additional dynamics at low temperatures. Because a glass is disordered, the TLS barrier parameters (shape, height and width) are distributed. The exponential dependences of tunneling on distance and height, and of activation on barrier height give rise to a broad distribution of the logarithms of tunneling matrix elements or of the activation rates. A convenient parametrization of the TLS model with a broad distribution of rates on a logarithmic scale 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.

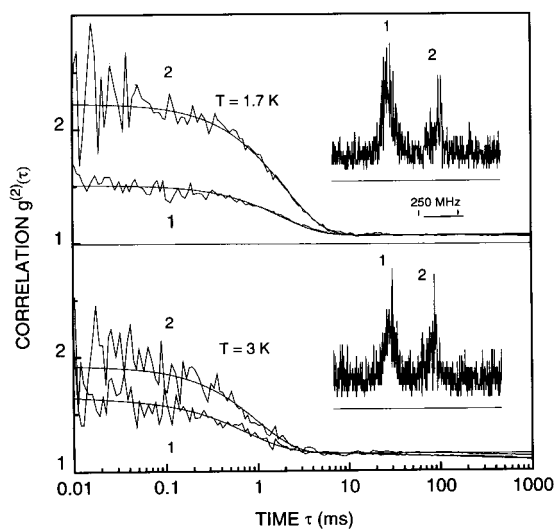


Figure 12.1 : Top : Spectrum and correlation function of a single terrylene molecule in polyethylene. The molecule is coupled to a single TLS, which gives rise to a splitting of the spectrum. The jumps of the TLS lead to correlation with contrast inversely proportional to the intensity of the line. At 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-photochemical hole-burning in large ensembles of molecules.

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 between hydrogen atoms in neighbor rings, and each molecule adopts one of two tilted conformations of its central ring, with opposite tilts. 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 leads to a new structure (triclinic) with 4 non-equivalent molecules in the unit cell, with 4 different tilts of their central phenyl ring. 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.

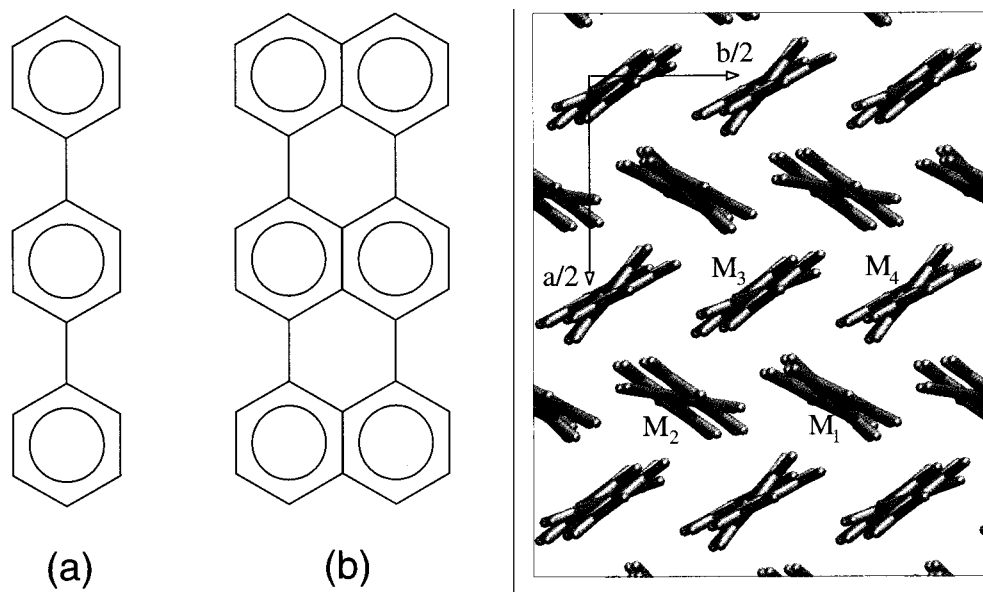


Figure 12.2 : Chemical structures of *p*-terphenyl (a) and of one of its single-molecule guests, terylene (b). Crystal structure of the low-temperature phase of *p*-terphenyl. Note that the four molecules in the unit cell (labeled  $M_1$  to  $M_4$ ) all have different distortions, leading to four spectroscopic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

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 domain 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).

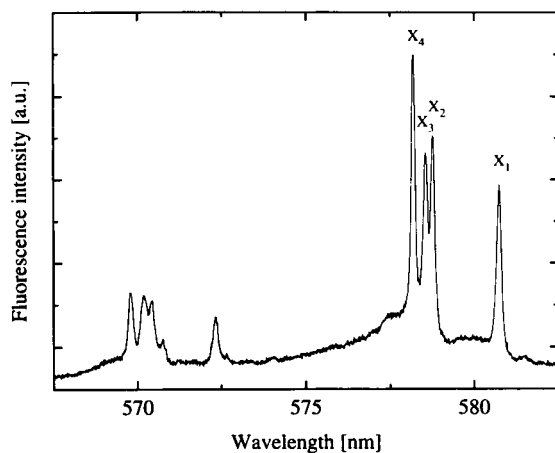


Figure 12.3 : Bulk fluorescence excitation spectrum of terylene in *p*-terphenyl, showing the four spectroscopic sites [S. Kummer, Th. Basché, C. Bräuchle, *Chem. Phys. Lett.* **229** (1994) 309 ; copyright 1994 with permission from Elsevier].

Terylene 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 had been broken. 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.

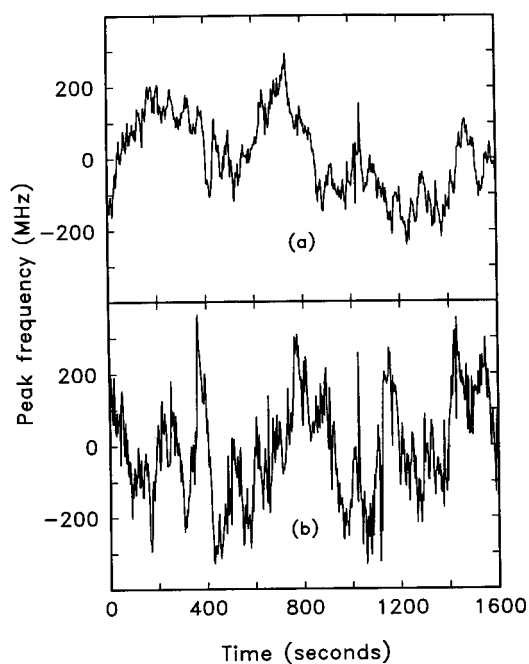


Figure 12.4 : Spectral diffusion of a single pentacene molecule in a *p*-terphenyl crystal at two temperatures, 1.5 K (a) and 4 K (b) [W.P. Ambrose, Th. Basché, and W. E. Moerner, *J. Chem. Phys.* **95** (1991) 7150 ; Copyright 1991, American Institute of Physics].

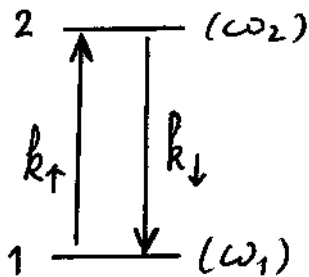
#### 12.4. Other sources of spectral diffusion

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: Decoherence and spectral diffusion

An optical two-level system is coupled to another two-level system, which we call the 'nuclear' two-level system. We suppose the nuclear system switches at random between levels (1) and (2) under the influence of thermal fluctuations, with rates  $k_{\uparrow}$  and  $k_{\downarrow}$ , and according to the level diagram below:



As the nuclear two-level system switches as a random telegraph, it modulates the optical frequency of the electronic two-level system, between two values,  $\omega_1$  and  $\omega_2$ . We neglect any back action of the optical system on the nuclear one, supposed to be macroscopic and classical.

One can show that, under these conditions, the optical absorption lineshape is related to the Fourier transform of the following time average:

$$G(t) = \left\langle \exp \left[ -\frac{i}{\hbar} \int_0^t \Delta(t') dt' \right] \right\rangle,$$

where  $\Delta(t)$  is the instantaneous deviation of the optical frequency from its time average.

i) Explain the physical meaning of the integral, and that of the complex exponential. The bracket indicates a time average which can be seen as an ensemble average over many different realizations of the random function  $\Delta(t)$ .

Discuss the condition for the time average of a single system to be equivalent to the ensemble average over many similar, but uncorrelated systems.

It can be shown (see e. g., Abragam, Principles of Magnetic Resonance) that the lineshape can be expressed under the following form:

$$I(\omega) \propto \text{Im} \int_0^{\infty} G(t) e^{i\omega t} dt = \text{Re} \left\langle 1 \left| \frac{1}{\omega - \Omega - iK} \right| g(0) \right\rangle,$$

where  $\langle 1 | = (1 \ 1)$ ,  $|g(0)\rangle = \frac{1}{k_{\uparrow} + k_{\downarrow}} \begin{pmatrix} k_{\downarrow} \\ k_{\uparrow} \end{pmatrix}$ , and

$$\Omega + iK = \begin{pmatrix} \omega_1 - ik_{\uparrow} & ik_{\downarrow} \\ ik_{\uparrow} & \omega_2 - ik_{\downarrow} \end{pmatrix} \text{ is a } 2 \times 2 \text{ matrix involving the optical frequencies and}$$

the switching rates between the nuclear system's levels.

ii) Express the absorption spectrum as

$$I(\omega) = \text{Re} \left\{ \frac{1}{\Delta} \left[ \omega - \frac{k_{\downarrow} \omega_2 + k_{\uparrow} \omega_1}{k_{\uparrow} + k_{\downarrow}} + i(k_{\uparrow} + k_{\downarrow}) \right] \right\}$$

with  $\Delta = (\omega - \omega_1 + ik_{\uparrow})(\omega - \omega_2 + ik_{\downarrow}) + k_{\uparrow}k_{\downarrow}$ .

iii) we first examine the high-temperature limit, for which  $k_{\uparrow} \approx k_{\downarrow} = k$ ; we call

$\bar{\omega} = \frac{\omega_1 + \omega_2}{2}$ , and  $\Delta\omega = \omega_2 - \omega_1$ . Use the above expression to derive the absorption spectrum as:

$$I(\omega) = \frac{\omega - \bar{\omega} + 2ik}{(\omega - \bar{\omega} + ik)^2 + k^2 - \Delta\omega^2 / 4}.$$

Consider first the limiting cases of slow modulation  $k \ll \frac{\Delta\omega}{2}$ . Show that the

spectrum exhibits two lines corresponding to the two states of the nuclear two-level system. What are their linewidths and the physical interpretation?

For fast modulation,  $k \gg \frac{\Delta\omega}{2}$ , show that the spectrum now presents a single line at

the average frequency  $\bar{\omega}$ , with a linewidth  $\frac{\Delta\omega^2}{4k}$ , which decreases when the jump

rate increases. This regime is called motional narrowing.

iv) We now turn to low temperatures:  $k_{\uparrow} \ll k_{\downarrow}$ . Only consider the line

corresponding to the longest dwell time, i.e. for frequency  $\omega_1$ . Deduce from the

zeroes of the above determinant that the position and linewidth  $\gamma$  of that line obey:

$$\omega \approx \omega_1 - ik_{\uparrow} - \frac{k_{\downarrow}k_{\uparrow}}{-\Delta\omega + ik_{\downarrow}}, \quad \gamma = k_{\uparrow} \frac{\Delta\omega^2}{\Delta\omega^2 + k_{\downarrow}^2}.$$

In the limit of slow modulation, we again find a line at about  $\omega_1$  with width  $2k_{\uparrow}$ , and

in the limit of fast modulation, a line narrowed by motion, with width  $2k_{\uparrow} \left( \frac{\Delta\omega}{k_{\downarrow}} \right)^2$ .

In the slow modulation case, conclude that the line is slowly jumping or drifting in the spectrum. This limit is called *spectral diffusion*.

In the quick modulation case, as the coherence has no time to follow the fast modulation of the frequency, conclude that each change in frequency produces a small, random phase shift of the coherence. The addition of all these phase shifts leads to a loss of coherence, leading to *decoherence* (or *dephasing*).

Exercise 12.2: Consider a two-level system performing transitions between the two levels through absorption and emission of phonons. At temperatures  $T$  much lower than the Debye temperature, only acoustic phonons need be considered.

i) At the lowest order in perturbation theory, and with linear coupling to phonons, transitions are caused by the absorption and emission of a single phonon. Show that, as long as the energy splitting of the TLS is much less than  $k_B T$ , the transition rate scales as  $T$ .

ii) For very small energy splitting, it may be more favorable to interact with two phonons, in a so-called Raman process, where one phonon is absorbed and another one is emitted. Apply perturbation theory at the lowest order with linear coupling to the phonons, and show that the transition rate will now scale as  $T^3$ .

iii) We now assume that the coupling to phonons is quadratic, i.e., we expand the TLS potential to second order in the phonon coordinate and neglect the contribution of the linear coupling term. Show that in that case the jump rate scales as  $T^7$ .