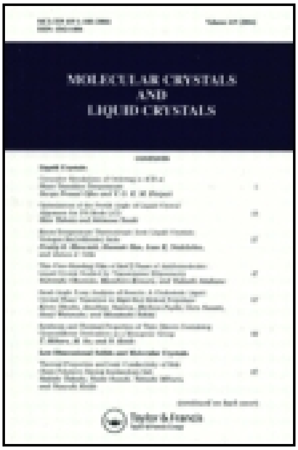

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Some Recent Results in Single Molecule Spectroscopy

M. Orrit [a], J. Bernard [a], L. Fleury [a] & R. Brown [a]

[a] Centre de Physique Moléculaire Optique et Hertzienne, CNRS et Université Bordeaux I, 351, Cours de la Libération, 33405, Talence, France

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SOME RECENT RESULTS IN SINGLE MOLECULE SPECTROSCOPY

M. ORRIT, J. BERNARD, L. FLEURY and R. BROWN
Centre de Physique Moléculaire Optique et Hertzienne, CNRS et Université
Bordeaux I, 351, Cours de la Libération 33405 Talence (France).

Abstract Fluorescence excitation spectra of small and dilute samples show the spectrally resolved lines of single solute molecules. The narrow lines can be used as probes of the low-temperature motion of the matrix around the molecule, or as probes of intramolecular transitions between electronic levels. In particular, electron spin resonance of a single molecule can be observed.

Keywords: single molecule spectroscopy, zero-phonon line

I- INTRODUCTION

The ever increasing integration of electronic circuits has led researchers to imagine devices working at the nanometer or molecular scale, a concept known as molecular electronics[1]. Obviously, although many steps will be required before this ambitious goal can be reached, the most fundamental of them are better control and knowledge of matter at the molecular level.

Today, several methods have been developed to observe matter at the molecular level, i.e. to study single quantum systems such as atoms, ions and molecules. The studies of single atoms or ions isolated in vacuum have started many years ago, first on atoms in beams[2], then on atomic ions confined in electromagnetic traps[3]. For the last ten years or so, the scanning tunneling and related microscopes are providing clear pictures of solid surfaces showing individual atoms and molecules[4], so giving us new insights into surface physics and chemistry, and making a whole new class of nanophysics experiments thinkable. More recently, single dye molecules were detected in liquid solutions at room temperature[6,7], an important milestone in biophysics. Nearly at the same time, spectroscopic studies were started on single impurity molecules in molecular solids at helium temperature[8,9]. The present paper concerns the latest results of our group in the latter field of single molecule spectroscopy.

At low temperature, the fixed matrix configuration around each molecule determines the frequency of its narrow optical zero-phonon line (at zero temperature, the natural linewidth is typically 10^{-3} cm^{-1}). In a macroscopic sample, the overlapping of the many individual lines lead to a broad and structureless band. This so-called inhomogeneous broadening is of the order of a few cm^{-1} in a well ordered crystal, and of 10^3 cm^{-1} in an amorphous matrix. The study of single impurity molecules in a transparent solid matrix is based on the spectral selection by a narrow exciting laser of a single molecular line in the inhomogeneous absorption band of a small and dilute sample. If the number of impurities in the sample is less than the ratio of inhomogeneous broadening to homogeneous width, the lines of single molecules will be spectrally resolved from each other. The only difficulty then is to separate the weak molecular signal from the background due to the much more numerous matrix molecules.

The detection method giving the best results so far is fluorescence excitation, in which the laser is scanned across the inhomogeneous band of the sample. Whenever the resonance frequency of a particular molecule is reached, fluorescence photons are emitted, which can be separated from stray exciting photons by filters, and counted by a sensitive detector. A description of our setup for the study of single molecules can be found in refs.[9,10]. The fluorescence signal from a single molecule also carries important information which remains hidden in conventional experiments done on populations of independent molecules. The time-distribution of the emitted photons bears the signature of all processes affecting the absorption-emission process, for example intramolecular transitions between levels, external perturbations or matrix dynamics (see section II). The time-distribution of the detected photons is best characterized by its correlation function, which can be measured by a digital correlator.

The present paper focuses on two recent experiments performed on single molecules. Section II is about the study of single localized matrix regions responsible for relaxation at low temperature (the so-called TLS's) and in section III, we consider the detection of electron spin resonance of a single molecule by means of its fluorescence signal.

II- PROBING THE LOW-TEMPERATURE DYNAMICS OF DISORDERED SOLIDS

Amorphous materials (glasses) are metastable systems at low temperature, which can present many different configurations with comparable free energy[11]. Even at helium temperature, tunneling can occur between nearly degenerate configurations. Since the parameters of the tunnel barriers are broadly distributed, glass dynamics at low temperature are spread over many timescales. In a given time scale and for a given localized region of the glass, jumping will be more frequent between two particular configurations, which behave as an effective two-level system (TLS). Many of the anomalous (with respect to crystals) properties of glasses at low temperatures can be successfully modeled by suitable distributions of TLS's. Being very narrow, single molecule lines are sensitive to motion in their neigborhood, even to the subtle changes involved in TLS tunneling, which will cause shifts of the line frequency.

If the density of TLS in the glass is not too high, we may consider a simple model in which any single molecule is coupled with at most one single TLS. The frequency of the exciting laser being tuned to the maximum of the molecule's line, jumps of the TLS will shift the single molecule line out of and back into resonance with the laser. Therefore, large fluctuations of the fluorescence intensity are expected, which should appear on the intensity correlation function. As the TLS tunnels between two configurations, the molecular frequency accompanies it in its slow motion, giving rise to two distinct lines in the excitation spectrum. A simple calculation shows that the fluorescence correlation function should have the same characteristic time for excitation of the two lines, though with different contrast.

Single molecule lines can be observed in polyethylene doped with absorbing terrylene impurities[12]. For 70 to 80 % of the lines studied, the correlation function presented no particular feature in the time window accessible to our correlator (from 1 μs to several minutes). For the rest, however, a wide variety of correlation patterns were observed[13,14]. The most common occurence was a single-exponential correlation decay, but two or more could also be obtained. We attribute each exponential component of the decay to coupling of the molecule to a particular TLS in its environment. This attribution could be confirmed in a few cases, where the two lines (corresponding to the two configurations of the TLS) could be identified in the same laser scan. In those cases, we could check that the correlation decay time is indeed the same for both lines, and that

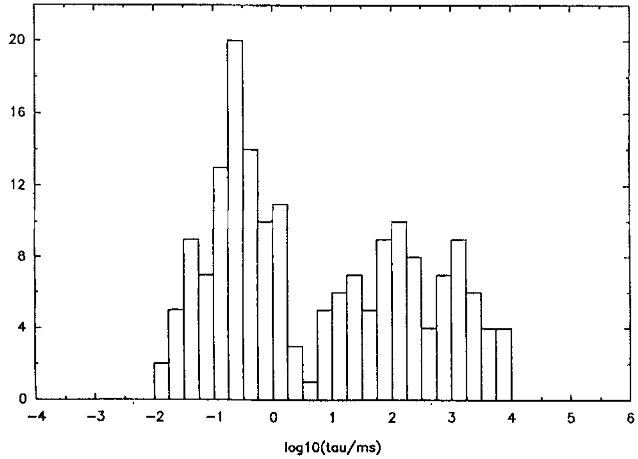

Figure 1 : Histogramme of the jumping rates of 179 single TLS's measured in the correlation functions of fluorescence from single terrylene molecules at 1.8 K. Note the logarithmic scale. The cutoffs at short and long times are due to experimental limitations.

the contrast of the correlation varies inversely with the intensity of the lines, as expected from the simple model.

Whenever a single exponential decay was identified, the characteristic jumping time of a TLS was deduced. The examination of some 200 TLS's measured at 1.8 K led to the histogram of rates presented in Fig1. As expected from the general arguments given above, the distribution of rates is very broad and actually extends beyond our experimental window, which is responsible for the cutoffs at 10 μs and at 10 s. However, in the range of rates investigated, there seems to be a variation of the rate distribution which is larger than can be accounted for by statistical fluctuations. In particular, a gap appears around a few ms. So far, we have no explanation for this hole, which does not seem to be an experimental artefact. We must note, however, that a similar gap appears in a study by stimulated photon echoes of the phase II of ethanol[15].

Once a particular TLS has been identified in the correlation function of a single molecule, its jumping rate can be studied as a function of external parameters, like laser intensity and temperature. The intensity dependence of the jump rate showed that jumps can be spontaneous as well as photo-induced. However, since large irreversible jumps tend to occur at high laser power, this study was difficult. Hereafter, we concentrate on the temperature dependence.

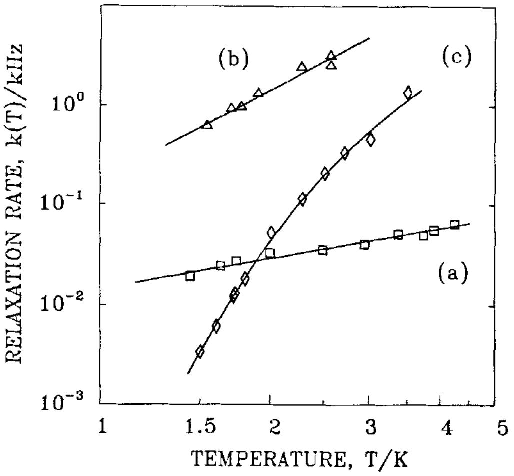

Figure 2 : Temperature dependences of the jumping rates of three TLS's. The most common occurence is a nearly linear dependence (a), attributed to tunneling assisted by one acoustical phonon. In some cases, a cubic temperature dependence is found (b), corresponding to tunneling assisted by the absorption of one, and the emission of another phonon. Finally, in one case, the temperature dependence could be well fitted by an Arrhenius law (c).

The jumping rates of several TLS's were studied in the range from 1.4 to 4.5 K. Some results are presented in Fig2, for three TLS's in the vicinity of three different single terrylene molecules. In five cases, the rate dependence on temperature could be fairly well fitted by a power law, with exponent 1 (3 cases) or 3 (2 cases). These power laws are expected for a TLS coupled linearly to acoustic phonons, when tunneling is assisted by one or two phonons, respectively, and for temperatures larger than the energy difference between the wells. In one other case, an Arrhenius behavior was obtained (with activation temperature about 15 K), where the jump rate changed by a factor larger than 500 between 1.4 and 3 K. An activated law immediately suggests to us classical barrier crossing. However, the oscillation period in this case should be as long as 10^{-6} s, which is much larger than the period expected in one of the wells of a TLS. Two alternative explanations involve tunneling:

i) tunneling could be much more probable in the first excited state than in the ground state of the potential well of the TLS. In this case, the activation energy would be the excitation quantum.

ii) slow matrix modes such as acoustic phonons could relax around the tunneling particle in each of the wells of the TLS. This distortion of slow modes would forbid direct transitions between the relaxed wells (much in the same way as phonon relaxation traps an electron in a polaron). Tunneling would thus first require removal of the stabilization energy, an activated process[16].

This study shows the sensitivity of single molecule lines to subtle changes in matrix regions that are probably several nm away from the molecule. By observing a small region around the probe molecule, the averagings involved in conventional studies are by-passed, which allows theoretical models to be tested more readily.

III- OPTICALLY DETECTED ELECTRON-SPIN RESONANCE OF A SINGLE MOLECULE

Nuclear and paramagnetic resonances are of primary importance in chemistry and biology because the spin resonance frequencies are signatures of the molecular structure, and in medicine where NMR allows non-destructive imaging of living tissues. It is therefore interesting to inquire about the ultimate sensitivity of these techniques. The experiments presented here deal with the electron spin resonance of the single electron pair of a single pentacene (Pc) molecule in a p-terphenyl (pTP) crystal. Our experiments were done in collaboration with Prof. Ch. von Borczyskowski and J. Wrachtrup from the Free University in Berlin[17]. Similar experiments were done simultaneously and independently by Köhler et al.[18].

Pentacene in para-terphenyl crystal (Pc/pTP) has been studied by several spectroscopic methods[19]. The Pc molecules can occupy four inequivalent sites in the pTP crystal, giving four lines, of which only the two lower energy ones are of use for single molecule studies. The triplet yield of these two sites are low (about 0.5 %), and the triplet lifetime is rather short (50 μs), so some millions of photons can be absorbed per second and per molecule when the triplet is fully saturated, giving enough signal counts for detection and study of single Pc molecules.

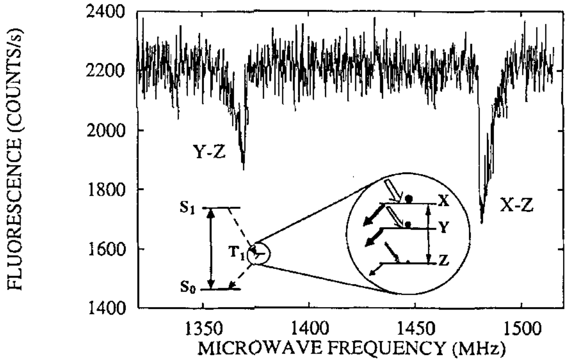

Figure 3 : Electron spin resonance spectrum of a single Pc molecule in a pTP crystal, measured by the variations of fluorescence intensity. The two lines correspond to X-Z and to Y-Z transitions. Their asymmetrical shape is due to coupling to nuclear spins within the molecule. The level diagram shows the principle of the detection, based on a population change of the triplet sublevels.

Pc/pTP is the first system in which single molecule detection has been demonstrated[8,9]. Single Pc molecules can be used to probe the crystal dynamics, much as was done in polyethylene (see section I), but here, we discuss only the time-correlated properties of fluorescence from single Pc molecules. The time distribution of the fluorescence photons carry information about the transitions between electronic levels in the Pc molecule (relaxation between vibrational levels is too short to measure by this method). For instance, photon antibunching was demonstrated recently[20] on a single Pc molecule; this quantum phenomenon arises from the restoring time needed by the molecule to get excited again by the laser after an emission event took place. On the longer timescale of microseconds, fluorescence photons are bunched in packets[9]. Bunching is due to ISC transitions of the Pc molecule into and out of the triplet manifold : starting from the ground state, the laser induces bright fluorescence, until (about once in 200 times) the molecule crosses over to the triplet. There, the molecule no longer absorbs until it crosses back to the ground singlet, where the whole cycle starts again. Packets of fluorescence photons are thus separated by dark intervals. Photon bunching is nicely demonstrated by correlation of the fluorescence photons[10]. The study of the correlation function as a function of exciting intensity determines the ISC rates of population and decay of the triplet, taken as a single sublevel for simplicity. We found different ISC rates for different Pc molecules, which correspond to slight distortions of the molecule by the disordered pTP crystal matrix.

However, the three sublevels of the triplet have different energies (because of electron-electron spin interaction) and different rates of population and decay (see the level diagram of Fig3). Therefore, if we apply a microwave in resonance with the transition between two sublevels, we can modify the populations of these sublevels, and consequently the average triplet lifetime. Thus, the average fluorescence intensity will be altered by the microwave, which allows the detection of magnetic resonance on a single molecule.

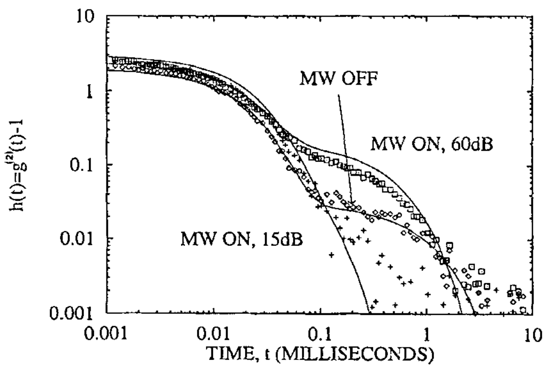

Figure 4 : Fluorescence correlation functions of a single Pc molecule under saturating optical irradiation and different microwave excitations. Note the double logarithmic scale. The function without microwave (empty diamonds) presents the bunching due to ISC and a weak but significant tail at longer times due to transitions toward the Z level. For low microwave power (60 dB, empty squares), the tail grows because the Z population increases; but for large power (15 dB, crosses), the spin state precesses between X and Z, and no population can build up in the Z level. The solid lines are fits using optical and magnetic Bloch equations.

The fluorescence intensity as a function of microwave frequency (Fig3) shows two of the three expected transitions (the last one, weaker than the noise, could not be detected). The assignement of the transitions follows the work of Schmidt's group on a related system[21]. The shape of the magnetic lines, obviously asymmetrical, is determined by the coupling of the electron spin to proton spins in the molecule. We measured the fluorescence correlation function on the same single Pc molecule for different microwave power levels (Fig4). In agreement with the model, the contrast of the correlation increases when the microwave is applied on the X-Z transition, because dark intervals lengthen. However, the most striking feature of these correlation functions is the appearance of an important correlation tail, decaying after 1 μs. This tail, though weak, is present without microwave. It increases, then decreases when the microwave power is raised. This complex behavior is satisfactorily reproduced by a model including optical and magnetic Bloch equations[22], and may be qualitatively understood as follows. The tail is thought to arise from a small population of the long-lived Z level. A moderate amount of microwave increases the Z population and therefore the correlation tail, but a high microwave power builds a coherent state precessing between X and Z, which decays quickly and does not give rise to any long-lived tail.

CONCLUSION

The results presented here show the variety of experiments that can be undertaken on single molecules[23,24]. We think that this type of spectroscopy has a great potential for fundamental studies of dynamics and structure at the nanoscopic level : both the molecule itself and the surrounding matrix can be studied in this way. In the future development of single molecule spectroscopy, it will be important to extend the number of host-guest systems and to improve the space and time-resolution of the method.

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