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Probing local currents in semiconductors with single molecules

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The narrow zero-phonon lines of single molecules at low temperatures can be used as sensitive probes for slow dynamical processes in solids at nanometer scales. Here we propose to probe electric conduction in semiconductors. In poorly conducting samples of ZnO, we found that only a small fraction of the molecules react to electric currents, but these reactions can be very strong, leading to line broadening or to changes in the fluorescence autocorrelation function. Even for moderate applied voltages, we found a few ‘‘hot spots’’ pointing to a strong spatial concentration of joule heating in areas less than 100 nm in size. A single molecule can therefore act as a nanothermometer. In more conducting samples of indium-tin oxide, we found even more surprising effects. For most molecules, we observed large shifts of the molecular lines under static voltages. The shift does not arise from a conventional Stark effect and cannot be attributed to lattice heating because the lines do not broaden, even for the highest voltages we used. We propose that the shift is caused by a change of polarizability of the semiconductor on application of a current, possibly related to hot carriers. When we applied ac currents to the sample, we observed clear resonant structures at very low frequencies, between 100 Hz and a few MHz. The resonance spectra were completely different for different molecules in the same laser spot of less than 1 micrometer in radius. We also observed autooscillations of the molecular transition frequency when a dc voltage was applied to the semiconductor film, with a clear threshold and oscillation frequencies lower than 100 kHz. The interpretation of these effects is still open, but we think that the molecules are very close to the semiconductor surface, making image effects quite strong. The surprising resonating systems we discovered could be related to recharging waves, whose existence was predicted theoretically some 30 years ago in compensated semiconductors.

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I. INTRODUCTION

Nanoscience and nanotechnology need ever smaller and faster devices to acquire, store, and process ever larger amounts of information. Building and integrating smaller and smaller components is a fascinating technological challenge, whose ultimate limits are set only by the finite sizes of atoms and molecules. Whereas the basic physical laws governing the interactions of electrons and nuclei are known in principle, the complex interplay of their collective properties with quantum-mechanical effects remains difficult to predict and analyze. Indeed, many of the spectacular effects found in solid state physics were first observed before they could be interpreted and fully understood. Yet, quantum and collective effects will certainly play a crucial part in the functioning of future nanometric components, and harnessing them may lead to completely new operating principles. To achieve this goal, we need tools and instruments to manipulate, observe, and measure matter at nanometer scales.[1] An example of a simple nano-instrument might be a well-known, reproducible nanoobject, which could be placed in the vicinity of the device under study. By measuring the perturbations exerted by the device on the nanoinstrument, we would obtain information about the device's workings. Any well-defined nanoobject, a single nanocrystal, a self-assembled quantum dot, a nanotube, or, as proposed here, an organic molecule, could serve as a nanoinstrument. Single nanoobjects can be seen as the starting points to devise the intruments and sensors we need to explore the nanoworld. In the present work, the nanoobjects will have a fixed position with respect to the device of interest, but eventually the idea is to place these instruments at arbitrary positions with respect to the nanostructure of interest, moving them for example by means of a sharp tip.

The optical spectroscopy and microscopy of single molecules has expanded spectacularly in the past years, and may soon become a current technique in physical chemistry and biophysics.[2,3] The simple idea on which the present work is based is to use single organic molecules to probe the transport of charge carriers in a conducting material at nanometer scales. Single fluorescent molecules have a number of advantages. They can be isolated by purely optical means and observed with an excellent signal-to-noise ratio. Selecting a single molecule removes all the averaging effects of conventional ensemble experiments, and directly reveals static and dynamic fluctuations of the molecule itself or of its close environment. When a molecule is included in a suitable matrix at liquid helium temperatures, its sharp zero-phonon line is extremely sensitive to external perturbations, as can be readily estimated. With the known Stark effect coefficients of single molecules, a change of 1 D(3.3×10^{-30} Cm) in a dipole moment lying 10 nm away causes an observed shift of the order of the linewidth of the probe molecule (typically 10^{-3} cm^{-1} or 100 neV). The ionization of an electron donor in an insulating medium could be felt at a distance of 200 nm. By following a molecule's transition frequency as a function of time, i.e., by following the comparatively slow frequency jumps and drifts of the single molecule line, one can probe the local processes occurring in the molecular environment. This can be done either by recording many consecutive spectra[4] or by means of a correlation function of the fluorescence intensity.[5] A number of applications of single molecule spectroscopy to the investigation of dynamical processes in solids can already be found in the literature. Single pentacene molecules have been used to probe the dynamics of the domain walls between two ferroelastic domains in a molecular crystal of *p*-terphenyl.[4,6] The two-state behavior observed in the optical spectra has been ascribed to flipping of the inner phenyl ring of host molecules between two positions. More recently, a similar mechanism in the local environment of another probe molecule (terrylene) has been shown to be responsible for persistent spectral hole burning.[7,8] The low-temperature dynamics of amorphous systems is modelled by a sea of tunnelling systems (TLS's), whose jumps are activated by thermal phonons. By selecting single molecules, it is possible to detect and study single TLS's in polymers,[5,9] and to test the basic hypotheses of the standard TLS model.[10] Single molecules are also sensitive to electronic degrees of freedom. A recent work focused on spectral diffusion induced by the migration of triplet excitons in the environment of single molecules.[11] The time-dependence of spectral diffusion showed that the migrating excitons were funnelled to the vicinity of the probe molecule by perturbed neighbor host molecules. The investigation of electron transfer processes with single molecules has not been restricted to cryogenic conditions. Single cresyl violet molecules adsorbed on the surface of a semiconductor (indium-tin oxide, ITO) at room temperature showed different rates of electron transfer to the ITO substrate.[12] Each single molecule presented a single-exponential decay, with a wide distribution of rates for the ensemble. Luminescent nanocrystals are also sensitive to the electric fields created by localized charges in their neighborhood.[13] The strong fluctuations of their luminescence, called blinking, which are hallmarks of single-particle experiments,[14] have been attributed to the transfer of charge carriers from the active core of the dot to its mantle or to its immediate environment.

The experiments reported here are a first step towards the design and development of new nanoinstruments to sense electrical observables at small distances. In the present work, we only wish to demonstrate the feasibility of this idea, and to show that single organic molecules can indeed probe local electrical processes. We used rather crude experimental procedures, and we prepared the samples ourselves with a sputtering apparatus and standard techniques such as spin-coating. Although there is still much room for improvement in the quality and reproducibility of these samples, we report several new and unexpected effects of the interaction between the molecule and the conducting material. The results presented here raise many questions and require much further experimental and theoretical work, but we think that they demonstrate that the realization of devices to monitor electronic processes in individual nanostructures is within reach of today's techniques.

The paper is set up as follows. In Sec. II, we describe our experimental procedures. The macroscopic characterization of the semiconductor layers are described and discussed in Sec. III. Section IV is devoted to a description of the results of our single molecule studies. These results are discussed and possible interpretations are suggested in Sec. V.

II. EXPERIMENT

Two types of semiconductor films were prepared by sputtering, either zinc oxide (ZnO) or indium-tin oxide doped with germanium (ITGO, with the molar ratios 97% In_2O_3, 2.5% SnO_2, and 0.5% GeO_2), from the respective cathode materials. The Ar pressure, voltage, and substrate temperature were determined in earlier studies[15] so as to optimize the conductivity of thin films for uses as transparent electrodes. The resulting deposition speed varied between 0.02 and 0.2 nm/s. The 10 to 100 nm thick films used in the present work were deposited on a glass substrate.

The bulk electrical properties of the sputtered material were determined previously at room temperature.[16–18] For ZnO,[16,17] the resistivity depended strongly on the residual oxygen pressure in the vacuum chamber and varied between 4×10^{-3} and 10 Ω cm, corresponding to a degenerate to nondegenerate semiconductor, showing metallic to insulating behavior at liquid helium temperatures. The resistance of the nondegenerate samples increased by several orders of magnitude upon cooling.

Bulk ITGO layers prepared from the same cathode material had a resistivity of $2.27\times10^{-4}\ \Omega$ cm, corresponding to a carrier density of $5\times10^{20}\,\mathrm{cm}^{-3}$, and to a mobility of 55 cm^2/Vs.[18] For this highly degenerate material, the resistance of the layers we prepared did not change by more than 10% upon cooling to liquid helium temperature. Knowing the thickness of our deposited film, we could calculate its resistance from the bulk resistivity, and compare it to the measured resistance value. This measured value was about 3 times larger than the theoretical estimate. This result is consistent with a moderate disorder in the layer, which could be represented as interconnected grains or islands. Scanning electron microscope images of the layers did not show any significant structure at a low resolution of 100 nm, apart from a few larger defects. We also recorded atomic force images of the layer with an AFM (see Fig. 1). The images show a marked grain structure, with a typical grain size comparable to the thickness of the layer, about 10–30 nm for the films used in the present work. Some control measurements on even better conductors were done on metallic films. We chose chromium because it yields thin conducting layers without islands already for thicknesses as small as 10–20 nm. The resistance of a square sample of our Cr layer was 2.7 kΩ.

In the ideal experiment, the zero-phonon line of a single molecule should probe electrical processes in the underlying conducting layer. Therefore, the sensitivity of the molecule will be directly proportional to the sharpness of its optical absorption line. In room temperature experiments, where optical lines are very broad anyway, it is possible to adsorb organic molecules directly onto the surface of the semiconductor.[12] However, if we want sharp zero phonon lines at cryogenic temperatures, we need a rigid matrix to hold the organic molecules in place after optical excitation.[19] We employed two procedures to deposit molecular layers on top of the semiconductor films. In the first procedure, which we used mainly for ZnO films, we spin-coated a thin polyisobutylene (PIB) layer with a low concentration (about

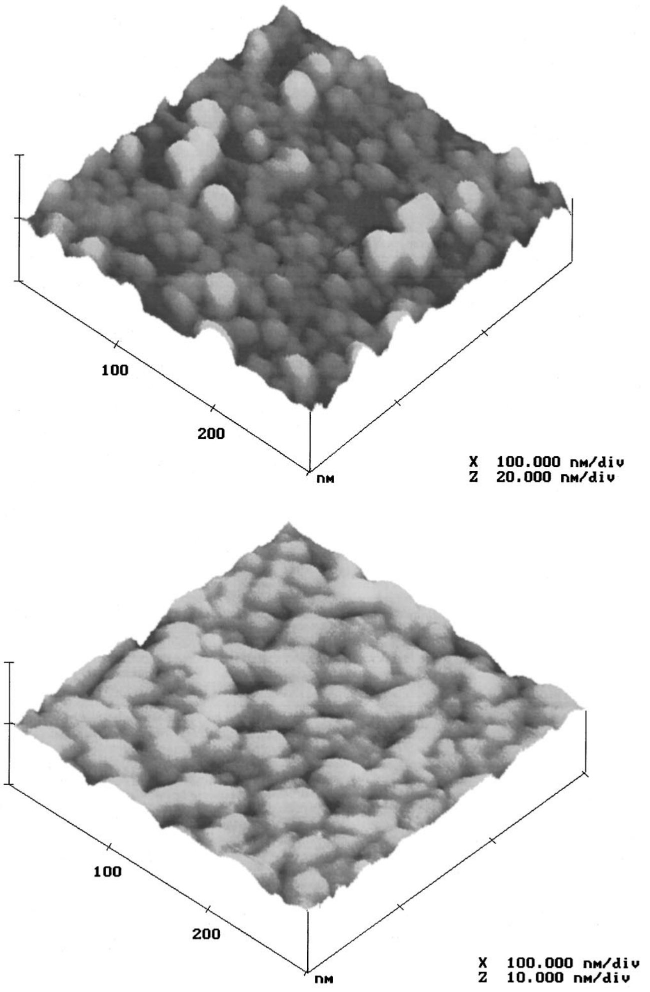

FIG. 1. Images of the surfaces of two of our ITGO films recorded with an atomic force microscope. The upper image is from a 10–20 nm film, the lower one from a 50 nm film. Note the grain structure and the merging of the grains when the layer thickens.

10^{-5} g/g) of terrylene (Tr) or tetra-tert-butyl-terrylene (TBT).[20] In the second procedure, mainly used for ITGO films, we started by spreading a droplet of a dilute toluene solution of the probe aromatic molecules Tr or TBT, on the clean semiconductor surface. After the toluene had evaporated, we spread a small quantity of liquid hexadecane (HD) on the surface and let it evaporate for several minutes to reduce its thickness to some extent. This second procedure had the advantage of a much better spectral stability of the single molecule lines in the crystalline Shpol'skii matrix,[21,22] but had the drawback that the average distance from the molecule to the semiconductor was not controlled. Nevertheless, on the basis of our results, we think that a large fraction of the molecules (at least some 50%) remained stuck to the semiconductor surface or located at a very short distance from it. This uncertainty, and the lack of reproducibility of the spatial distribution of the molecules from sample to sample will have to be kept in mind when interpreting the data. Shortly after preparation, the hexadecane samples were placed in the cryostat and cooled to prevent further evaporation. The polymer samples could be kept at room temperature for long times. The final layout of the samples is sketched schematically in Fig. 2.

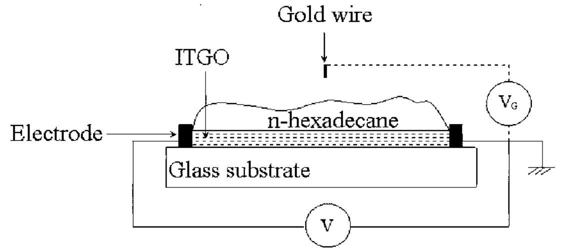

FIG. 2. Schematic layout of our sample, with the glass substrate, the thin conducting film of ZnO or ITGO, and the matrix layer containing the probe molecules (here hexadecane). A current can be established in the film by means of a voltage V connected by ohmic contacts with silver lacker (electrodes). In some experiments, we applied a much stronger voltage V_G with a gold electrode, leading to a strong electric field perpendicular to the film; of course, no current flowed perpendicular to the film.

The samples of coated films (2×2 mm^2) were fitted with two silver-lacker electrodes providing ohmic contacts for macroscopic resistance measurements and for application of dc or ac voltages to the film. To apply electric fields perpendicular to the film (which we did for complementary experiments on the ITGO layers), we added a third electrode, either on the opposite side of the glass substrate (i.e., below the layer), or as a thin wire above the layer (see Fig. 2). Only in the latter kind of cell did a significant electric field apply to all the molecules. In the former geometry, the electric field was very efficiently screened by the highly conducting ITGO layer, so that its effect was unnoticeable in most of the molecules.

All of the results presented here were obtained in a pumped superfluid helium bath to minimize heating effects. The nominal cryostat temperature, measured by a Ge resistor, was kept in the range 1.6–2.5 K for all the measurements. Most often, it was stabilized at 1.8 ± 0.05 K.

The optical setup was basically the one described in earlier publications on single molecule spectroscopy from our group.[3] Here, we used the confocal arrangement based on the high-quality concave parabolic mirror of Ref. 23. The exciting light was focused by the mirror, which also collected the fluorescence light in the inverse pathway. This mirror has the advantages of being perfectly achromatic and of having a wide collection angle, but its surface quality is limited by machining defects. The point spread function (i.e., the optimal spot size obtained upon focusing a beam parallel to the optical axis) was about one to two microns in width. The molecules were excited in their 0-0 band (about 575 nm) by means of a tunable single-frequency laser (Coherent Radiation CR699-21). The exciting light was removed from the detection path by colored glass filters (Schott, RG610). The fluorescence photons were detected with a photoncounting avalanche photodiode (SPCM-AQ-131) and fed into an acquisition card (model Accuspec from Canberra). A typical fluorescence signal from a single terrylene molecule with this setup yielded about 100 000 cps close to the saturation, which enabled accurate measurements of the line shape and line shifts on a time scale of seconds or shorter. No spatial images were recorded, but the exciting spot could be moved manually across the surface, so as to illuminate a fresh region of the sample. Single molecule signals were recorded as excitation spectra, i.e., the absorption lines were observed by monitoring the fluorescence intensity as a function of the frequency of the exciting laser, for various applied dc voltages. By recording many excitation spectra repeatedly, we obtained spectral trails of the molecules,[4,10] which allowed us to follow the spectral diffusion of the molecule with a time resolution of about 1 s, or to record the influence of external parameters such as the amplitude of the dc voltage applied to the layer, or the frequency of an ac voltage of constant amplitude. Finally, we could also measure the correlation function of the fluorescence intensity for a fixed laser frequency and a fixed applied dc voltage. The correlation function keeps track of the fluctuations of the fluorescence intensity, usually caused by fluctuations in the molecular frequency with respect to the fixed frequency of the exciting laser.[5]

III. ELECTRICAL CHARACTERIZATION OF THE CONDUCTING LAYERS

We measured the resistance of ZnO films as a function of temperature between 1.7 K and room temperature, which allowed us to distinguish between degenerate and nondegenerate materials. For nondegenerate samples in the temperature range 1.4–2.1 K, the resistance followed a Mott law, characteristic of variable range hopping in a disordered material.[24]

In view of the surprising results reported in Sec. IV, we investigated the macroscopic electrical properties of our ITGO layers in more detail. The dc conductivity of the samples seemed to follow Ohm's law in the range of voltages we used for the optical experiments, 0–10 V. However, on closer inspection, we found a significant variation of the resistance with the applied voltage at all temperatures, including in superfluid helium. This effect cannot be attributed to lattice heating by joule dissipation (see discussion below). It is well known in other materials and has been ascribed to the heating of charge carriers by the applied electric field.[25,26] Because the electron-phonon coupling becomes very inefficient for low excess energies of electrons and at low temperatures, electrons can be significantly warmer than the lattice or the bath of acoustic phonons. The electron-phonon relaxation rate increases very steeply with electron temperature (as the fifth power of temperature, according to Ref. 27). Therefore, the temperature difference between hot carriers and lattice is limited, but it can easily reach 10 K for an applied electric field of 10 kV/m. The relative resistance changes for such fields are about 0.1%.

The behavior of the ac conductivity as a function of frequency was quite smooth and only showed a slight decrease of the impedance at higher frequencies, for a constant voltage amplitude. This observation is rather common in disordered layers and is usually attributed to capacitive effects in the network of conducting grains or islands.

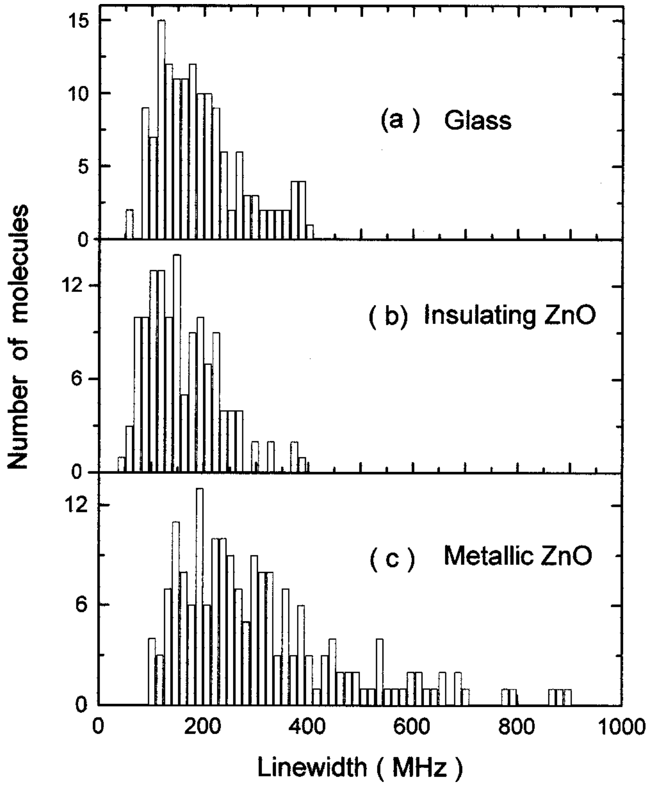

FIG. 3. Histogrammes of the linewidths of single TBT molecules in a 10 nm PIB film deposited on three different substrates. The single molecule lines are about twice broader on average on the metallic ZnO film.

IV. RESULTS

A. Experiments on ZnO

We started our experiments with poorly conducting films of ZnO, expecting to find hopping transport at a local scale. For these experiments, we prepared 100 nm thick ZnO films, on top of which we spin-coated a 10 nm thick layer of PIB doped with TBT at low concentration. We prepared two kinds of samples, either with nondegenerate ZnO films (insulating, resistance of a square larger than a GΩ at 1.8 K), or with highly conducting ZnO films (resistance of a square of a few kΩ at 1.8 K). We used a spin-coated layer on glass as a blank sample. The broad inhomogeneous absorption band of the three samples deduced from the spectral positions of a hundred single molecules was roughly the same within experimental and statistical inaccuracies.

In a first attempt to detect additional dynamics induced by charge transport in the semiconductor layer, we measured histogrammes of the linewidths of single molecules. The linewidths are known to be sensitive to the dynamical degrees of freedom still active at the temperature of the experiment.[9,22] Figures 3(a)–3(c) compares these histogrammes for the glass, the insulating ZnO and the metallic ZnO samples. As could be expected, there is no essential difference between the insulating ZnO and glass. The metallic ZnO sample, however, shows significantly broader single molecules lines, the average width being about twice as large as in the sample on glass. One could think of fluorescence

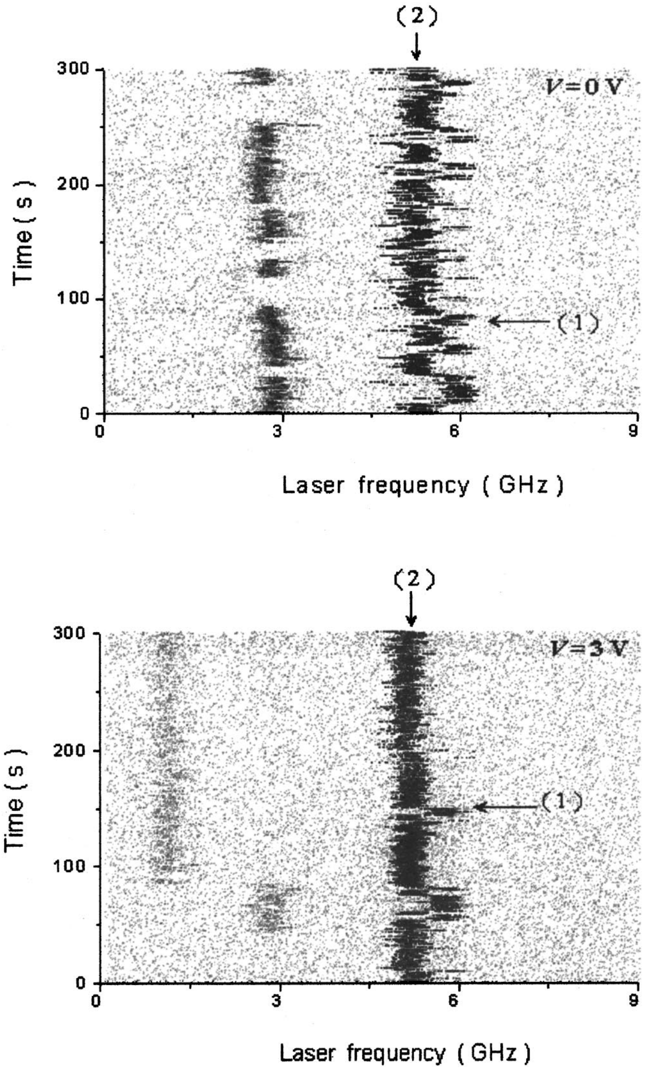

FIG. 4. Dependence on voltage of the spectral trail of a single molecule on a metallic ZnO film. A two-level system is active at $V=0$ (top trail) and is responsible for the spectral jumps. At $V=3$ V (bottom trail), it is nearly frozen in one of its wells.

quenching as a possible cause for this broadening. Quenching could result from the creation of electron-hole pairs in the conducting layer. However, metallic ZnO is transparent in the visible (gap energy 3.5 eV), and we did not find any difference in the average fluorescence intensity of single molecules for the three samples. We also detected single molecules on thin Cr films, which are much more efficient fluorescence quenchers than metallic ZnO. Therefore, we do not think that fluorescence quenching is the source of this added broadening. We attribute the difference in histogrammes to perturbations of the molecules by the additional degrees of freedom in metallic ZnO, probably by thermally induced movements of charge carriers.

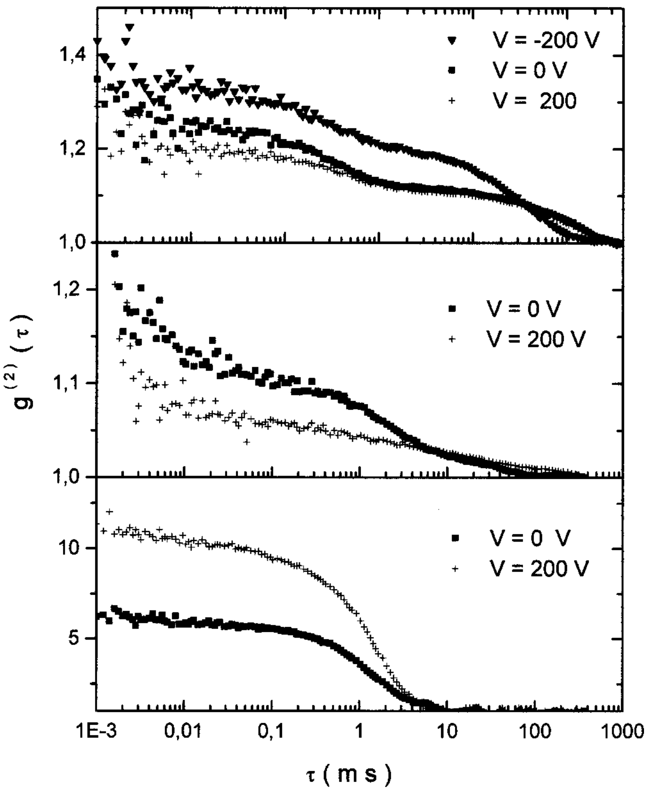

FIG. 5. Examples of changes of the intensity correlation functions of the fluorescence of single molecules under an applied field. Such strong changes never occur for the ranges of fields used here when the molecules are embedded in the bulk of an insulating matrix. These changes can be attributed to fluctuations of the molecular frequency induced or altered by dynamical conduction processes in the film.

We then studied single molecules with a variable applied electric field to search for individual two-level systems (TLS's) or other degrees of freedom influenced or activated by an applied field. Earlier studies of single Tr molecules in polyethylene did not show any significant electric field effects on most of the usual TLS's for the range of fields investigated (less than 10 MV/m). To look for these effects in our thin films on ZnO, we monitored the spectral trails of single molecules under various dc fields. The cases of significant variations of the spectrum by the electric field were rather rare (less than 10%). Figure 4 presents one example where the spectral trail of a single molecule depends on the applied dc voltage. The jumps to spectral position (1) are seen to be much less frequent under an applied voltage of 3 V. Another way to keep track of fast spectral jumps is to record the autocorrelation function of the fluorescence for a fixed frequency of the exciting laser.[5] A few examples of changes of the correlation function are presented in Fig. 5. Figure 5(a) shows a change in contrast of the correlation, which may be attributed to a change in asymmetry of the TLS responsible for the fluctuation. In Fig. 5, the correlation time is changed, an occurrence which was only observed upon temperature changes in Ref. 5. Figure 5 shows a complete change of shape of the correlation, from single-exponential without voltage to multiexponential or logarithmic for high voltage. This could be explained by the activation of many tunneling systems with a range of jumping times, as would be the case for charge transport. However, in our experiments, such events were too rare (10%) to study systematically.

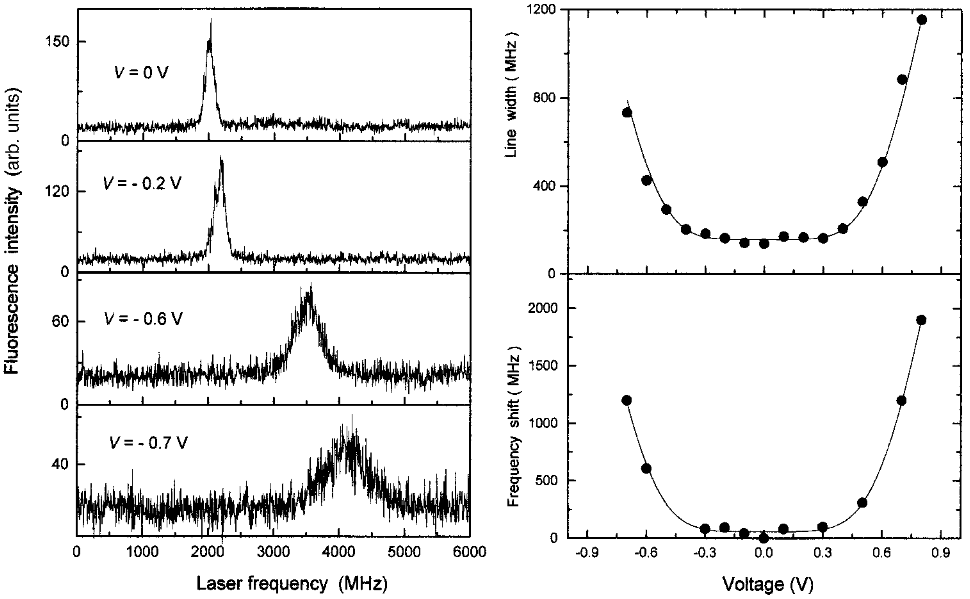

FIG. 6. Broadening and shift of the line of a single molecule close to a metallic ZnO film as functions of an applied voltage. The smooth lines are fits with a simple model, where the temperature is raised by joule dissipation in the film. Such plots are observed for very few molecules only, and are a proof that a significant part of the joule heat is dissipated in a few small "hot spots."

In the last kind of experiment, we followed the line shape of single molecules under various voltages applied, as is done in Stark effect experiments.[28–30] Figure 6 presents single molecule spectra showing a strong broadening and shift for voltages lower than 1 V (corresponding to a field of 500 V/m). The broadening and the shift suddenly increase for voltages larger than 0.3 V with a behavior which seems exponentially activated if the temperature increase is proportional to the square of the applied voltage (Fig. 6). We attribute the broadening and the shift to a local temperature increase induced by the current. The total power dissipated in the ZnO film is of about 3 mW. Only less than 1–2% of the molecules showed any broadening for such voltages. This shows that the joule power is dissipated in a very inhomogeneous way, with a few hot spots here and there, and comparatively larger cool areas where most molecules are situated. The linewidth can be related directly to a temperature by means of the thermally induced broadening of the line.[20] Therefore, here, a single molecule acts as a very local thermometer. The mechanism of the shift is less clear, and will be discussed in Sec. V. We encountered only 2 molecules close to hot spots in the same laser spot where over 100 molecules were investigated. This indicates that the area responsible for the hot spot must be smaller than about 100 nm in diameter.

B. Experiments on ITGO

The results on ZnO showed the extreme inhomogeneity of electron transport in this disordered semiconductor. On insulating films, we could not find any molecule which reacted to the weak current, although strong effects should have been seen for the few molecules close to the conduction paths postulated in Mott's theory. On metallic films, on the other hand, we saw that only a few molecules showed strong effects (such as hot spots), and therefore that the charge transport was still inhomogeneous. Trying to separate the part of the effects due to homogeneous conduction in the bulk of a material from those due to localized conducting paths, we decided to use much thinner layers of a much more conducting material, ITGO, which is often used for transparent electrodes. We did not expect any dramatic influence of a homogeneous current on single molecules, but to our big surprise, we found the novel effects described below. The ITGO films used in this part had thicknesses ranging between 10 and 20 nm. They were covered by about a micron of hexadecane matrix in which Tr or TBT molecules had been dissolved.

1. dc experiments

The lines of single Tr and TBT molecules on the thin ITGO films were easy to detect. About 70% of the molecules showed strong shifts when moderate dc voltages of less than 10 V were applied to the film (fields lower than 5000 V/m). We think that those molecules were close to the semiconductor surface, and attribute the other, nonshifting lines to molecules having diffused in the bulk of the hexadecane layer

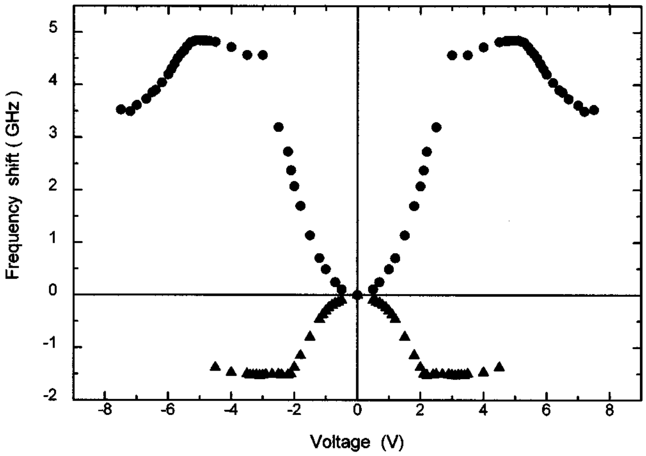

FIG. 7. Examples of the shift for two single molecule lines when a dc voltage is applied to an ITGO film. Note the different possible signs of the effect, its magnitude, and the presence of a threshold, beyond which a new regime is found.

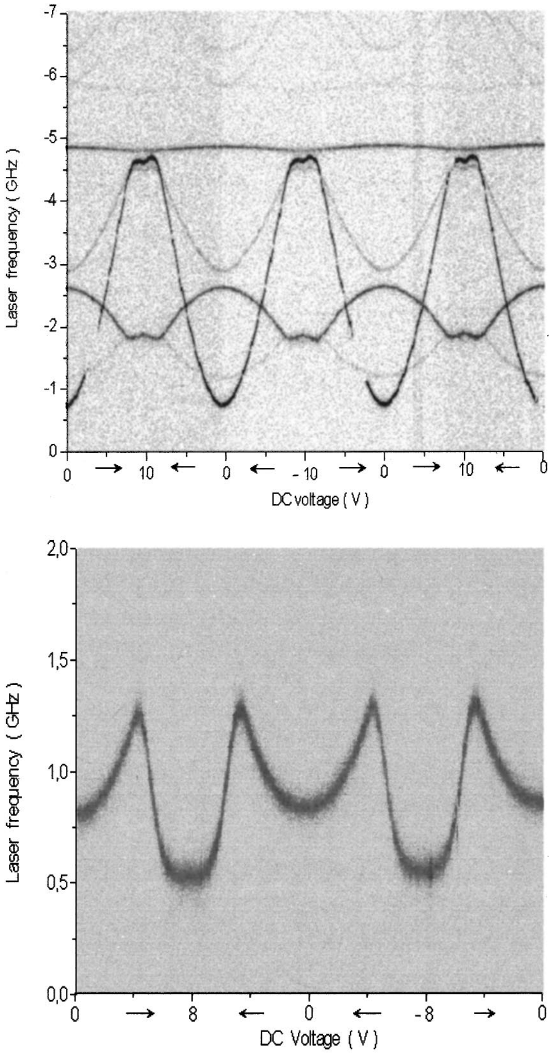

FIG. 8. Spectral trails as functions of the applied voltage for a few other molecules. Note that the lines shift without significant broadening, which proves that the lattice remains cold, although a significant power is dissipated in the film. In the top trails, most of the molecules shift to the red, with variable coefficients. The bottom trail shows a molecule whose blue shift decreases again, and even changes sign after the voltage threshold (about 5 V).

during the preparation. For most of the “shifting” molecules, the order of the shift was about 0.1 to 10 GHz for 10 V. The shift was nearly quadratic in voltage for low voltage, and could either be to the red (in about 3 out of 4 cases) or to the blue (1 out of 4). Figures 7 and 8 show several examples of shifts of single molecules, either plotted as functions of the applied voltage V, or recorded as “spectral trails,”[10] as a function of voltage. These trails are series of successive spectra where the intensity is coded by levels of gray. In the case of the trails of Fig. 8, the voltage varied like a sawtooth as a function of time, which allowed us to test the reproducibility of the shift by comparing several scans. The examples highlighted in Fig. 7 are quite typical and we will describe them in detail. The shift of the line is roughly proportional to V^2 for voltages lower than a few V. Then, a threshold is reached, and in a rather abrupt way, a transition to a new regime takes place, in which the shift may still increase, or decrease, and sometimes even change sign. It is worth noting that shift curves are different for each individual molecule we studied. Note also that the magnitude of the shift is about 1000 times larger than the usual linear or quadratic Stark effects observed for the same molecules in insulating matrices.[30] We could not measure any linear component to this shift. Within our experimental accuracy, the quadratic component was always dominant, even for very low fields. A very important feature, and a striking difference from the molecule of Fig. 6 on ZnO, is the absence of any significant broadening of the line for voltages below the threshold, and even above threshold for a large fraction of the molecules. If we consider the zero-phonon lines of our molecules as local thermometers, as in the case of ZnO, we see that they did not indicate any change in lattice temperature (within a few K, since the linewidth increases very slowly with temperature below 4 K). On some shift curves, we notice slope changes for well-defined voltages, which could perhaps indicate other thresholds. For example, in some cases, above a second threshold V_1 somewhat higher than the first one, the trail becomes very noisy, and the molecule eventually disappears (i.e., undergoes a large spectral jump, which shifts it irreversibly out of the scanning range of the laser) if the voltage is further increased. The threshold value was often the same for molecules in the same laser spot, one to two microns in size (see Fig. 8), but varied when the spot was moved by a few

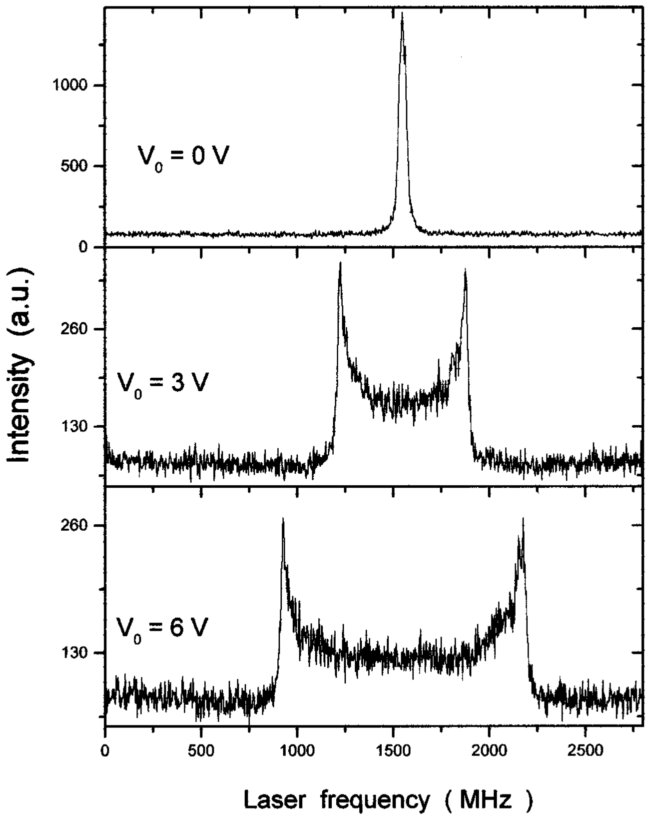

FIG. 9. “Cat’s ears,” i.e., shape of a single Tr molecule line in hexadecane on an ITGO film, when an ac voltage is applied to the semiconductor for three different amplitudes of the voltage at the same frequency.

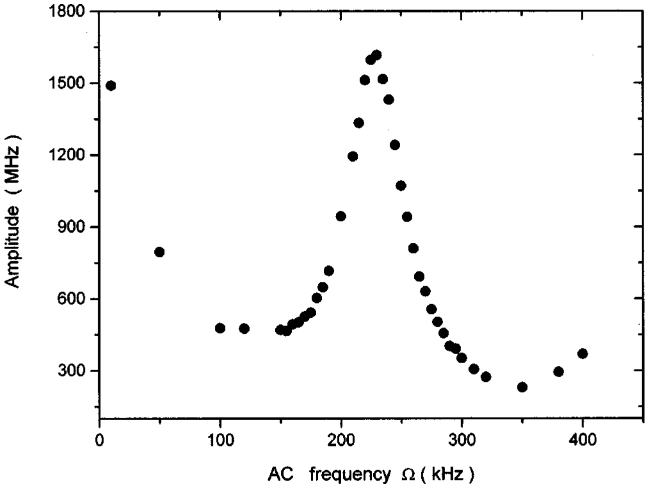

FIG. 10. Plot of the splitting of the "cat's ears" for a given voltage amplitude of 1 V and as a function of the ac frequency. The initial decrease of the effect for frequencies lower than 50 kHz is followed by a resonant structure with a roughly Lorentzian shape. A further structure occurs above 400 kHz (not shown on the plot).

microns across the sample. This may indicate that the phenomena responsible for the thresholds are located in regions of about one to a few micrometers in diameter.

In order to check for electric field effects, we applied electric fields perpendicular to the film. Invariably, the field had to be much larger to measure shifts, and the shifts were linear, as in other Shpol'skii matrices[30] and other molecular crystals,[28] with no measurable quadratic component for the fields applied (of the order of 1 MV/m). This confirms that the large shifts observed when the field is applied parallel to the layer are connected to the current in the layer rather than to the field itself. Because the quadratic shifts reminded us of a joule effect of the dissipated power, and although no broadening was measurable, we tried to check for thermal effects by changing the resistance of the film, either by changing its geometry, or its conductivity. Such changes should have altered the production and transport of heat and therefore the temperature reached. In spite of the difficulty of comparing different molecules in different samples, no statistically significant difference was found from sample to sample, which points to a purely local effect rather than to a global effect felt locally, such as a heating of the whole sample.

2. ac experiments

Trying to elucidate the origin of the large dc shifts, we investigated the spectra of single molecules under an applied ac voltage. For practical reasons, the frequencies we could reach were limited to less than 15 MHz. The idea was to try and find whether slow processes were involved in the unknown mechanism relating voltage to shift. When a weak ac-voltage $V_0 \cos \omega t$ is applied at a low frequency to a single molecule with a quadratic shift in voltage, the line shifts sinusoidally at the second harmonic of the applied frequency. The resulting spectrum, which we dubbed "cat's ears," has two intense structures corresponding to voltages 0 and $\pm V_0$ with a minimum inbetween. This typical profile of a $(1-x^2)^{-1/2}$ function is shown in Fig. 9 for various voltages at the same frequency. The splittings induced by the ac voltage were measured as the spectral distance between the "ears" as a function of the applied frequency, for a constant voltage amplitude. This splitting only gives the amplitude (or modulus) of the effect. We did not attempt to measure its phase.

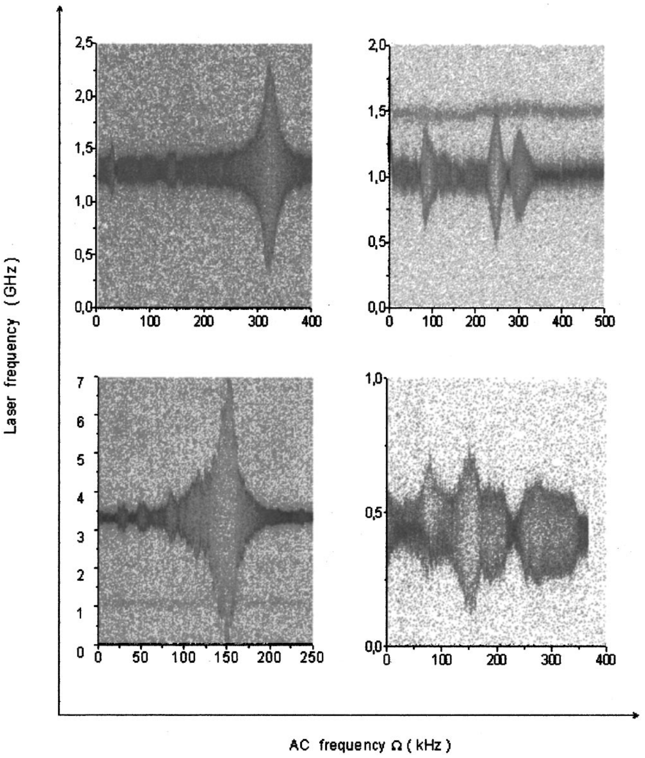

FIG. 11. Four further examples of the resonance curves (see Fig. 10) for four single molecules in hexadecane on an ITGO film, presented as spectral trails as functions of the ac voltage frequency. Note the wide range of resonance frequencies, widths, and shapes observed for different molecules. All these different behaviors are observed in the same focal spot of the laser, about 1 micron in size, which shows that the domains responsible for the resonances are 100 nm in diameter or less.

We did not expect any significant amplitude change for low frequencies (less than a few MHz) because we thought the charge carriers in the semiconductor would respond almost instantaneously to the applied field. Quite unexpectedly, we observed very strong variations of the shift amplitude, in general for frequencies lower than 1 MHz, including distinct Lorentzian resonances. Figure 10 shows the typical response curve of a single molecule. The shift first decreases for frequencies lower than 50 kHz, then increases to resonate at about 230 kHz and decreases again at higher frequencies. The width of the resonance is about 30 kHz. A few other examples are shown as spectral trails in Fig. 11. The spectra are now plotted successively as the ac frequency is varied. These response curves can show either no resonance, or one, two or more, or even totally confused patterns. Two resonances sometimes appear to interfere, or to give rise to beat-like patterns. Often, additional structures can be seen at frequencies lower than the main resonance. The most striking feature of these response curves is that they depend entirely (via their frequency, width, amplitude, the number of the structures, etc.) on the particular molecule under study. Within the same laser spot of a diameter of one to two microns, we never found two resonances to have the same frequency or shape, even after studying tens of molecules. This important point shows that the interacting molecule-semiconductor systems producing this response must be very local, with sizes probably well below 100 nm. We also found that the resonances depend on the preparation of the samples. In one case, we observed the usual dc shifts, but the response curves of all molecules were uniformly decreasing with frequency (usually by a factor 2 for about 100 kHz), with no resonance for frequencies below a few MHz. This might indicate the sensitivity of these resonances to the precise distance or contact between molecules and semiconductor, which may depend on the preparation of the sample.

3. Spontaneous oscillations under dc voltage

Although the macroscopic current-voltage characteristics we measured on our samples were nearly compatible with Ohm's law, apart from the slight change of the resistance with the applied voltage, we may expect the conduction process on smaller scales to be highly nonlinear for high enough voltages. The molecule-semiconductor systems discussed in the previous section behave like oscillators, i.e., they respond like damped oscillators to a sinusoidal excitation. When driven by a nonlinear process, even under dc voltages, such oscillators can be expected to give rise to auto-oscillations. We indeed found several examples of such self-oscillations at high enough voltages. Figure 12 shows the dc shift of a molecule, presented in the form of a spectral trail as a function of dc voltage. Beyond the first threshold at 5.5 V, the shift suddenly rises, then appears to saturate, while the spectral shape changes dramatically, showing distinct ripples. We dubbed such patterns "tire tracks." The ripples are not an intrinsic spectral feature of the line. They depend on the scanning rate of the laser. One of the spectra can be fitted with a simple simulation of a Lorentzian line whose center frequency oscillates periodically in the spectrum. Fitting the oscillations' parameters on the experimental spectrum, we found a frequency of about 100 Hz. Let us stress again that the frequency of the line oscillates although only a purely dc voltage is applied to the sample. We also found the signatures of faster oscillations in the intensity autocorrelation function. Since the molecule moves in and out of resonance with the laser, the intensity is modulated at the oscillation frequency or at its second harmonic, depending on the average spectral position of the molecule with respect to the exciting laser. Figure 13 shows an example of a correlation function below and above a given voltage which was a threshold for the auto-oscillation. This threshold was clearly higher than the first one observed in the dc-shift characteristic. A natural question arising from the oscillations of the correlation function is that of their quality factor. In Fig. 13, the oscillations appear severely damped, but this is mainly due to the pseudologarithmic scale and to the numerical treatment of the data to obtain the correlation function. The frequency of the self-oscillations sometimes corresponded to the resonances in the ac-shift response, but not always. We also found molecules oscillating simultaneously with two distinct frequencies.

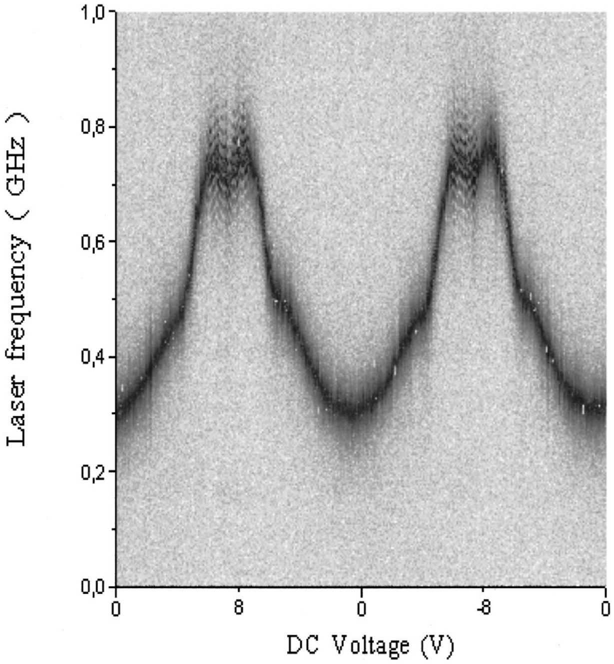

FIG. 12. The dc voltage dependence of the spectrum of a single TBT molecule on ITGO. After a first, then a second threshold, the trail appears to become "spotty." These spots may be attributed to spontaneous oscillations of the transition frequency of the single molecule in and out of resonance with the laser. The oscillation frequency is about 100 Hz in the present case.

V. DISCUSSION

Since the discovery of single molecule lines, they have been exposed to various external field effects. The position of the zero-phonon line of a single molecule is known to be sensitive to electric fields,[28–30] to hydrostatic pressure[31,32] or more generally to mechanical stress. Magnetic field shifts are usually negligible for singlet states but they were already measured by hole burning on ring-shaped molecules.[33] The frequencies of single molecules are also sensitive to changes of dielectric permittivity in their environment. For example, the frequency of a spectral hole (corresponding to a large number of single molecules, all with the same transition frequency) burned in a surface monolayer containing dye molecules shifts when the sample is immersed into superfluid helium.[34] The change in permittivity across the interface modifies the images of all charges, including the molecular static and transition dipoles, and the other charged molecules in their surroundings. The optical transition is shifted by the interaction of the molecular electronic cloud with the modified images. This shift, which includes van der Waals forces among other effects, may be seen as caused by the collective response of the remote electrons in the helium bath to the oscillations of the optical electron of the molecule. In the following, after eliminating the other possible mechanisms,

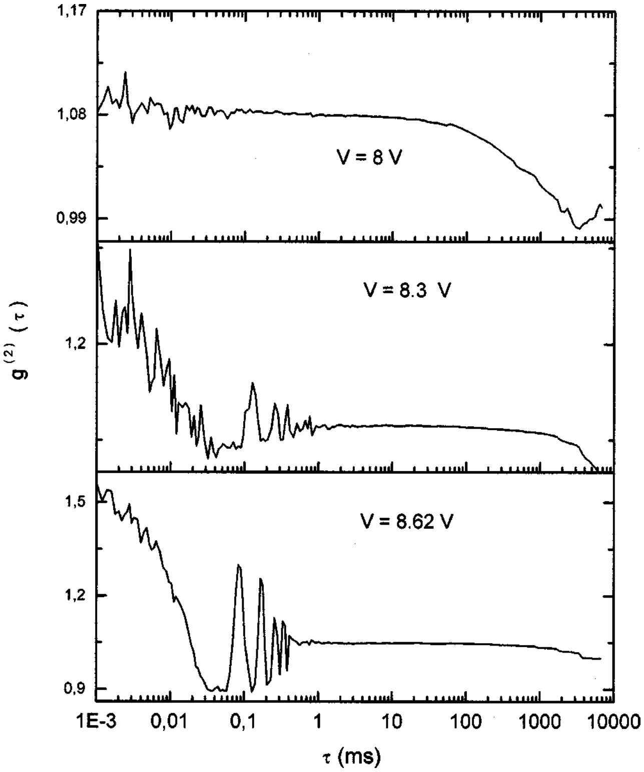

FIG. 13. Autooscillation of a single molecule line on ITGO with an applied dc voltage. The oscillation appears above a given voltage threshold (8.3 V in the present case), and is detected in the fluorescence autocorrelation function. The periodic oscillatory feature around 0.1 ms is distorted by the logarithmic time scale of the plot.

we argue that this latter effect is responsible for the large dc shift we observed.

Let us first consider the ‘‘normal’’ Stark effect, due to the direct interaction of the applied field with the static dipole moments and polarizabilities in the ground and excited electronic states.[30] The observed shift is too large for a quadratic Stark effect, which would require an enhancement of the local field by a factor 1000. On the one hand, such a high enhancement factor is very unlikely in a conducting medium prone to screening, on the other hand, it should be spatially concentrated by the same factor 1000, since the total potential drop is fixed. The fact that a large part of the molecules in many samples show strong dc shifts effectively eliminates the Stark effect as a possible explanation. We may also add that the Stark effect should have a dominant linear component for low fields (as observed for Tr or TBT in hexadecane[30]), which was never observed as long as the field was applied within the layer, and that blue shifts are not compatible with the normal polarizability change of terrylene molecules.[35]

One can also think of mechanical or pressure effects induced by the electric field. Similarly, the order of magnitude of pressure shifts shows that electrostriction leads to shifts generally comparable to or smaller than the quadratic polarizability.[30]

A second possible explanation coming to mind are thermal effects, which could lead to mechanical dilations or phonon shifts.[36] The Joule power dissipated in our millimetric sample is far from negligible, up to about 100 mW. However, several arguments, as follows, lead us to reject changes of the lattice temperature as possible causes of the observed shifts.

The effective changes of the lattice temperature cannot be larger than a few K, because no line broadening is observed, even above the thresholds. Thermal expansion is very weak at such low temperatures because acoustic phonons are nearly harmonic.

The shift of the single molecule line by lattice phonons is usually comparable to the broadening of the line. Here the shift dominates the broadening by at least one or two orders of magnitude.

All the results presented here were obtained in superfluid helium. We also measured the voltage-induced broadening and shift of the lines in a He gas atmosphere, which is a poor heat conductor. Under these conditions, we observed thermal broadening for voltages larger than 0.5 V, which, after independent calibration of the thermal molecular broadening, was found to correspond to a temperature of 4 K. The ratio of thermal conductivities for gas and superfluid helium is about six orders of magnitude.[37] Therefore, we could calculate that the temperature raise of the helium bath at the sample could not exceed some mK, which is negligible. This analysis was confirmed by changing the geometry or conductivity of the sample, which did not change the shifts dramatically, although it should change the boundary conditions for heat conduction, and therefore the lattice temperature of the sample. The estimate of the temperature rise in helium also allows us to eliminate second sound or boiling effects in superfluid helium. The appearance of bubbles or similar nonlinear phenomena in superfluid helium, even if they could occur on such extremely local scales, does not appear to be compatible with the low resonance frequencies we observed.

The above discussion has ruled out thermal effects in the lattice. Yet, thermal effects in the electron gas itself are another matter. It is known that the resistance varies as a function of the joule power dissipated in a sample, because the transfer of heat between hot electrons and acoustic phonons becomes very unefficient at low temperatures.[26] By measuring the sample resistance for various voltages, we indeed found sizeable variations, following the T^5 electron-phonon coupling law reported earlier.[26,27] We therefore propose as a model that the permittivity of the electron gas in the semiconductor is changed by joule heating, as a consequence of the temperature change of the electron gas. For the largest voltages applied, we estimated the variation of the charge carriers' temperature to be about 10 K. This must be compared to the Fermi temperature of the carrier gas, which may be estimated from the carrier density ($5\times10^{20}\,\mathrm{cm}^{-3}$) to about 10^4 K. Assuming that the permittivity of the semiconductor varies linearly with temperature in a small interval, this change is small (of the order of 10^{-3}), but it can nevertheless cause large shifts of the molecular transition if the molecule is close enough to the interface. In our model, the heating is related to the local current density and therefore to the electric field for a given conductivity. Therefore, it must be insensitive to heat transport at the scale of the whole sample and to sample geometry at constant current density.

The mechanism we propose for the shift involves the interaction of the molecule's optical electron with the electrons of the semiconductor. Assuming the semiconductor-matrix interface to be flat, these interactions can be easily calculated. Since the distances are much less than the wavelength of light, we may use the electrostatic approximation and the theory of electrostatic images. We see three distinct mechanisms for the interaction of a molecule with images in an absorbing dielectric half-space (two of them are discussed theoretically in Ref. 38).

(i) The interaction of the transition dipole of the molecule with its image. In this mechanism, an increase in polarizability of the semiconductor will always lead to a red shift of the transition frequency. Since the transition dipole oscillates at the optical frequency, the dielectric permittivity of the semiconductor should be taken in the high frequency limit.

(ii) The interaction of the static dipole of the molecule with its image. Because the static moments differ in the ground and in the excited molecular states, this interaction leads to a shift of the transition energy when the image strength changes. Moreover, the transition shift can be positive or negative, depending on the respective strengths of the static dipole moments in the ground and the excited states. This mechanism involves quasistatic images, and therefore the dielectric permittivity of the semiconductor at low frequencies. Note, however, that these frequencies cannot be much lower than the inverse dwell time in each molecular state, of the order of the excited state lifetime, a few nanoseconds.

(iii) The interaction of the molecule with the additional electric fields created by the images of the static charges surrounding the molecule. Depending on the orientation of the electric field created by the images with respect to the static dipole moment change of the molecule, this interaction energy can also be positive or negative. Since the charges around the molecule are fixed in time, we must use the truly static dielectric permittivity of the semiconductor to calculate this interaction.

The order of magnitude of the expected shifts can be easily calculated in this model. For example, for the first mechanism, the frequency shift δv is given by

$$h\,\delta\nu=\frac{-1}{2\pi\varepsilon_0}\,\frac{1}{(2d)^3}\,\frac{\varepsilon_1\delta\varepsilon_2}{(\varepsilon_1+\varepsilon_2)^2}\,\mu_{eg}^2$$

if the transition dipole μ_{eg} is parallel to the interface, ε_1 and ε_2 being the relative permittivities of the matrix and of the semiconductor, respectively, $\delta\varepsilon_2$ the change in ε_2 due to the applied voltage, d the distance of the molecule to the interface, and ε_0 the permittivity of vacuum. Note the inverse-cube dependency of the shift on the distance to the interface. By taking a dielectric constant change of 10^{-3}, a distance d of 1 nm, the frequency shift is of the order of a few GHz, in good agreement with the order of magnitude of the observed effect. The model requires, however, that most of the probe molecules should be very close to the interface (within a few nm).

Although this simple model is able to yield the right order of magnitude for the shift, we should stress that it can only explain the quadratic dependence of the shift for low voltages (because the temperature change is quadratic in current), but neither the threshold, nor the more complex behaviors observed above threshold. Moreover, although this model is the simplest one compatible with the observations and derived from what is known about the effects perturbing single molecules, it remains highly speculative and should be tested in future experiments.

The model of the dielectric images does not account for the frequency dependence of the ac shift, nor for the self-oscillations at high voltages. The most surprising observation in this context is the very low value of the resonance frequencies, although our model for the dc shift only involves the motion of light charges, electrons or holes. The wavelengths related to acoustical waves, not to mention electromagnetic waves, are much too large to be compatible with the strongly local character of the effect. Relaxation oscillations can be obtained when a capacitor, for example a conducting grain or island in our film, is charged through a large resistor. We have observed such grains in AFM images of the layer, with typical diameters of 10–30 nm. However, the resistance necessary to obtain relaxation times in the millisecond to microsecond range would have to be about $10^{14}\,\Omega$, which is obviously not realistic in our highly conducting layer. Slow effects have been observed upon laser irradiation of the DX centers in doped semiconductors,[39] but we checked that all the reported phenomena are independent of laser power. A very interesting possibility to explain slow movements are the recharging waves predicted by Suris *et al.* more than 25 years ago.[40,41] In a compensated semiconductor, charges may be exchanged between the free carrier gas and acceptor or donor impurities. The long characteristic times (milliseconds or longer[42]) of such exchanges can give rise to waves with extremely low velocities, and would also affect the local permittivity of the semiconductor. The localization of slow waves in the disordered structure of our sample could give rise to low-frequency resonances observed locally by single molecules. This interpretation, however, is purely speculative at this point. Much theoretical effort and experiments on better defined samples are required to confirm or reject recharging waves as the phenomenon responsible for resonances in the ac shift of single molecules on semiconductors.

VI. CONCLUSION

By placing single organic molecules in the vicinity of the surface of a thin semiconductor film, we have demonstrated that charge transport can be probed at nanometer scales. The method was applied here with organic molecules, but it could obviously be carried out with other single quantum systems, like single nanocrystals or quantum dots. In the course of this study, we have found that a molecule is not only sensitive to an electric field, but that it can feel various effects of a current. For example, the molecule in a suitable matrix can act as a local thermometer. We have seen that such a thermometer can detect hot spots in a macroscopically homogeneous conducting sample. We deduced that these hot spots are not larger than 100 nm in diameter, but they could be much smaller still. Furthermore, a molecule can also feel local currents by their heating effect on the electron gas, although the lattice temperature remains undisturbed (in that case, the molecule acts as a local nanowattmeter). We checked that this unexpected effect can also be observed on thin metal layers, using 10 nm thick Cr films. We found evidence for a unexpected effect, to our knowledge unobserved so far, namely the low frequency resonances and auto-oscillations in very small structures, again with sizes not larger than 100 nm. This effect could perhaps be used to generate low frequencies in future nanodevices. However, much further work is required to control and understand these phenomena. A very important step could be the correlation of optical and electrical properties measured on comparable scales. For example, single molecules could be deposited on microresistors in microfabricated structures, and the oscillatory behavior observed in the fluorescence could be correlated to the local current-voltage characteristic. In addition to the clarification of the phenomena reported in the present paper, we expect that fascinating new effects would arise from investigations of electric conduction processes at molecular scales.

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