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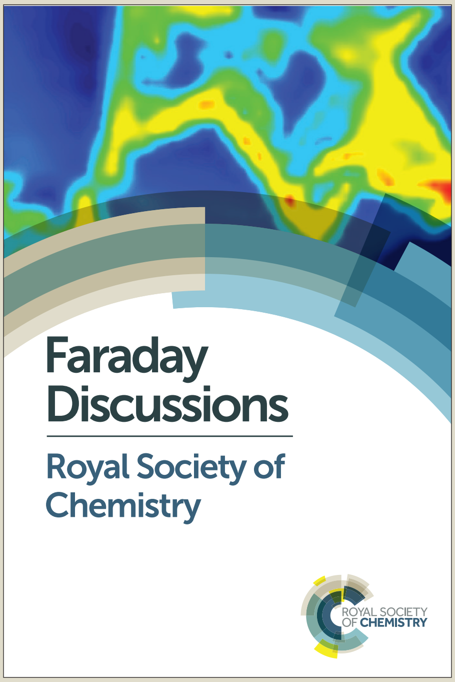

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Fluorescent microscopy and spectroscopy of subsurface layers dynamics of polymers with nanometer resolution in axial direction[†]

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We studied dynamics in ultrathin subsurface layers of amorphous polymer by spectra of single fluorescent molecules embedded into the layer by vapor deposition and subsequent controlled diffusion to desired depth in ≈0.5 nm steps. Spectral trails of single molecules were recorded at 4.5 K as a function of diffusion depth. In depths shallower than 20 nm the spectral dynamics deviates from that deep in the bulk. Less than 5 nm deep the linewidths increase rapidly, whereas the number of detected molecules decreases. No zero-phonon lines were observed closer than 0.5 nm to the polymer surface. Possible physical reasons of the observed phenomena are discussed.

1 Introduction

For most macroscopic objects, surface is composed of a tiny fraction of total count of object's atoms or molecules. Still, properties of surface play important role in many physical effects. As we turn to ever smaller – nanoscale – objects, surface-to-volume ratio increases many orders of magnitude and contribution of surface grows accordingly. In spite of extensive research, our knowledge of microscopic nature of surface processes is limited and many fundamental questions are still open. One the difficulties is that most experimental methods have access to surface only, while surface properties are determined by what happens below the surface as well. Furthermore, it is often unclear how deep is the subsurface layer affected by surface and what parameters define this depth.

In the present work we developed a method that yields information about local dynamics in transparent disordered solids on nanolevel. It is based on introducing fluorescent molecules into subsurface layer of desired depth. We studied single-molecule spectra slightly below the surface of thicker polymer films and report the results. One of the purposes was to determine in experiment the thickness of a subsurface layer where local parameters differ from those in bulk volume.

At cryogenic temperatures, individual fluorescent chromophore molecules in solids often feature strong and narrow zero-phonon lines with widths on the order of 10^{-5} – 10^{-6} nm due to weak coupling with the phonon bath. Hence, they can serve as sensitive probes for small spectral shifts caused, e.g., by the coupling to flipping tunneling systems in disordered materials. The investigation of these lines and their variation with time has been the subject of single-molecule spectroscopy for many years. In almost all cases, however, only molecules in the bulk of solids were recorded. Fleury et al.[1] investigated single terrylene molecules in crystalline n-hexadecane and found that the linewidth strongly increased close to the interface between the organic crystal and the silica substrate. On, or close to, the free surface of a polymer, zero-phonon lines of single molecules were never detected to our knowledge.

Unexpected fast and rich spectral dynamics of single chro-

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[†] Electronic Supplementary Information (ESI) available: More details on the experimental procedure and accuracy of determining the depth of performed diffusion; possible experimental artifacts that may be the real source of observed effect; dependence number of detected molecules on distance from surface. See DOI: 10.1039/b000000x/

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mophore lines at low temperatures was previously found in low-molecular-weight glass formers such as toluene [2], cumene, propylene carbonate and in oligomers of amorphous polyisobutylene (PIB).[3] The spectral diffusion was sometimes so fast that it was impossible to record single-molecule lines; only short fluorescence flashes were detected instead. The most probable explanation is that in these materials the lack of polymer entanglements leads to a large number of tunneling systems with low barriers, which are still active at temperatures of a few K.

Recently our group reported single-molecule studies in films of PIB with thicknesses between 5 – 300 nm [4]. These films were weakly and homogeneously doped with tetra-*tert*-butylterrylene (TBT). The detectable zero-phonon lines and their dynamics were investigated as a function of film thickness at $T = 4.5$ K. The basic finding was that in films thicker than about 100 nm, the majority of the spectra showed the usual behavior which is known from bulk PIB and consistent with the standard TLS model, i.e., well-defined and reversible jumps between a small number (2^n; n integer) of spectral positions. In thinner films an increasing fraction of chromophores feature non-standard spectral trails with richer dynamics. The largest number of them was found in the thinnest films (5 nm). Moreover, the fraction of non-standard lines increased with laser intensity, and also this influence was strongest in the thinnest films.[4] In ultrathin films both the substrate and the free surface of the polymer are close to the chromophores, and it is not clear, which of the interfaces is mainly responsible for the altered spectral dynamics. This ambiguity is also resolved in the present work, as we now address only the free surface interface.

We chose again the fluorescent dye TBT and deposited it on top of the surface of PIB films by evaporation at low temperature. Then the chromophores were allowed to diffuse into well-defined depths up to about 100 nm by heating to suitable temperatures. All spectroscopic measurements were performed at $T = 4.5$ K.

Our study adds new experimental data characterizing the low-temperature dynamics in the first few nanometers below a polymer surface. This can be viewed as a subdomain of molecular spectroscopy that lies between the well known spectroscopy of impurity molecules fixed inside a solid and the spectroscopy of nearly free molecules in gas or vacuum.

Low-temperature studies of surface dynamics are scarce; in the temperature range 250 – 400 K, the dynamics of polymer surfaces has been studied much better (for review see [5] and references therein; for single-molecule studies see e.g.[6]). It is established that, in most cases, free surface layers are more mobile than the bulk, more “liquid-like”, with faster relaxation processes.[7,8] But even at this temperature region, experimental results are often controversial: For example, it is still unclear, whether the glass transition temperature in ultrathin polystyrene films is higher or lower than in the bulk material.[9] So, there is a demand for new experimental data of polymer surfaces. The low temperatures used in our approach reduce the complexity of the dynamics to a large degree.

2 Experimental

PIB of high molecular weight ($M_w = 4,200,000$ g/mol) was purchased from Sigma Aldrich and used without further purification. The material was dissolved in toluene and thin films were prepared by spin-coating on microscope glass slides. The thickness of the polymer films was adjusted via the concentration of the solution and the rotation rate and was measured with a profilometer (Veeco DEKTAK 150) with vertical resolution about 3 nm.

The slide with the undoped polymer film was inserted in an optical He-4 cryostat (Cryovac) and cooled down to temperatures between 30 and 50 K, at which the translation diffusion of molecules can be neglected. A thin layer of TBT was placed on the surface of a ceramic cylinder carrying a coil of resistance wire for electrical heating. The ceramic cylinder with the dye was also placed in the cryostat, first at some distance from the polymer film, and the sample chamber of the cryostat was evacuated to about 10^{-5} mbar. The cylinder was heated to a temperature slightly below the sublimation temperature of TBT to remove impurities. Subsequently it was placed about 5 mm from the polymer film and heated to 100 – 200 °C for some seconds. The exact temperature of the cylinder could not be measured; the heating power and sublimation time were adjusted such that the desired amount of dye molecules were deposited on the polymer surface (below one molecule per 100 nm^2 surface area within a spectral interval of 1 cm^{-1} inside the inhomogeneous absorption spectrum).

After evaporation at low temperature (30-50 K), the dye molecules are immobile on the polymer surface. Thus, heating to elevated temperatures is required to induce their diffusive penetration into the material. At room temperature, the diffusion coefficient of large organic dye molecules in PIB is about 1000 nm^2/s, and it decreases at lower temperatures. By keeping the temperature of the sample low enough that dye molecules travel less than 1 nanometer per minute of conditioning, we were able to dye the ultrathing surface layer only (See Fig. 1 and Supplementary Fig. 1). To quantitatively estimate the diffusion depths from the well-known equation

$$d = 2\left[\int D\left[T(\tau)\right] \mathrm{d}\tau\right]^{1/2}, \tag{1}$$

we used the temperature dependence of the translational diffusion coefficient $D(T)$ of rubrene in PIB[10] and inserted the measured time-dependent temperature excursion $T(\tau)$ during our heating cycles. The actual diffusion depths may be 1 – 2 nm larger, since the diffusion coefficient in the first 1 – 2 nm below a polymer surface is known to be higher than in the bulk, at least at the glass transition temperature (see, e.g.,[7]).

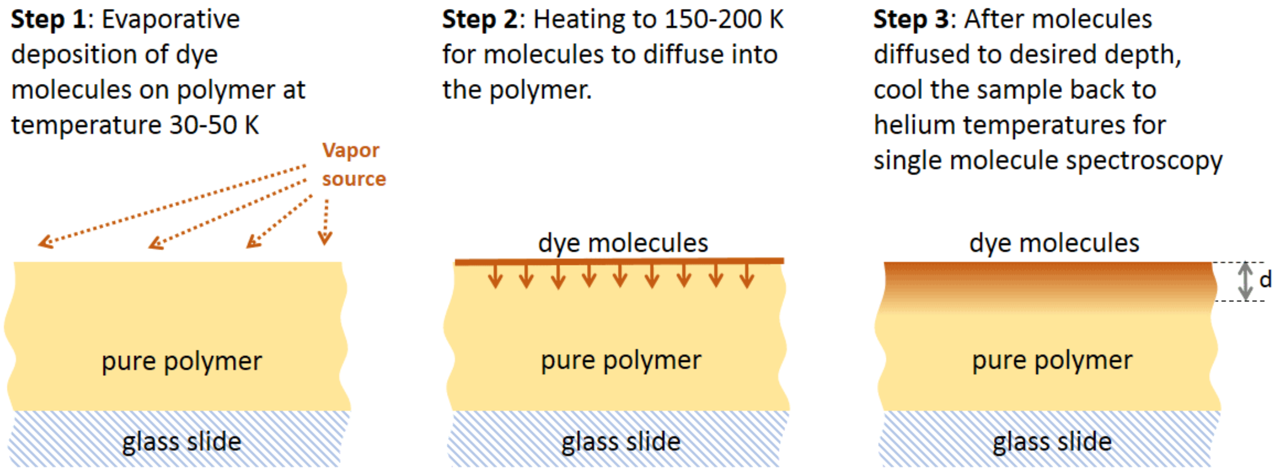

Fig. 1 (color online). Procedure for preparing samples of polymer having fluorescent dye molecules in ultrathin subsurface layers of desired depth. Thicknesses of polymer and glass slide are not to scale. Temperature was tracked and recorded every second during the entire procedure (See Supplementary Fig. 1) in order to integrate diffusion and calculate the total distance d travelled by dye molecules, thus obtaining the effective thickness of dyed subsurface layer.

The zero-phonon lines of single fluorescing TBT molecules were recorded with a low-temperature wide-field microscope, as described in detail previously.[11] The excitation light source was a tunable single-mode dye laser COHERENT CR 599-21 operating with Rhodamine 6G in the spectral range 565 – 625 nm. Its linewidth was roughly 2 – 3 MHz and the continuous tuning range 1 cm^{-1} (0.03 nm). The laser frequency was repeatedly scanned over the same spectral interval of 1 cm^{-1} width, and single fluorescing chromophores in the illuminated area of the sample of about 100 μm diameter were imaged onto the chip of a sensitive Peltier-cooled CCD camera (either PCO Sensicam or PCO Luca-S) with a microscope objective (Microthek, Hamburg, Germany, $NA = 0.85$) inside the cryostat. The duration of each laser scan was 75 s, the time between two scans about 1 s. During the scans, Doppler-broadened absorption lines of an iodine cell were recorded to control the tuning range of the laser. The signals of individual molecules were extracted from the data base of the CCD camera images and plotted in two-dimensional representation as a function of excitation frequency and time with the fluorescence intensity encoded on a gray scale – so called "spectral trails".

3 Results

The first surprising result was that immediately after evaporating the dye molecules onto the surface of the cold PIB films, no fluorescence images of individual TBT molecules were visible in any of the experiments. Instead, the films showed only spatially featureless fluorescence emission from the entire area illuminated by the laser light. Varying the temperature of the PIB substrate between about 10 and 30 K had no influence on this behavior. Spectral analysis with polychromator revealed that the fluorescence emission was close to typical spectrum of TBT. Hence, we can conclude that the homogeneous emission of the samples must be mainly due to TBT and not to an unknown fluorescing impurity.

The situation changed completely after a brief temperature cycle to an excursion temperature slightly above the glass point of PIB (180 K). After cooling the sample back down to 4.5 K, fluorescence images of single TBT molecules appeared immediately and the background fluorescence level decreased significantly. From the temperature-dependent diffusion coefficient we can estimate that the average diffusion depth reached in this temperature cycle is no larger than about 0.12 nm. Also the fluorescence emission spectrum changed distinctly during the cycle: After the diffusion process it developed the band around 620 nm which is also characteristic for the room temperature spectrum of TBT in liquid toluene solution. Photobleaching by prolonged laser irradiation did not cause any additional spectral changes but only a decrease in amplitude (see Fig. 2).

The observed change of the emission spectrum can be explained in the following manner. After molecules collide with the cold surface, their spatial structure is far from equilibrium; heating the sample above the glass transition allows them to relax to equilibrium.

The spectral dynamics of single TBT molecules close to the surface of PIB films is significantly different from that in the bulk and does, for many molecules, not agree with the standard tunneling

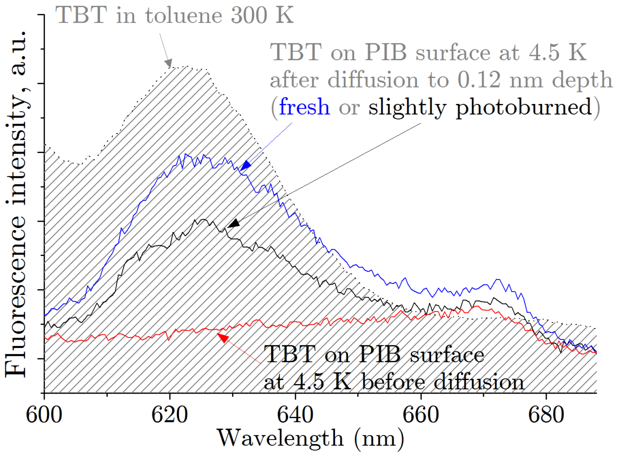

Fig. 2 (color online). Ensemble fluorescence emission spectra of TBT evaporated onto the surface of a cold PIB film before (red) and after (blue) a heating cycle causing diffusion into a depth of 0.12 nm. For comparison we show ensemble fluorescence emission spectra of TBT in toluene solution at room temperature (hatched). The black line shows the spectrum after some degree of photobleaching by the laser. The excitation wavelength for the low-temperature spectra is 575 nm. All spectra are ensemble spectra.

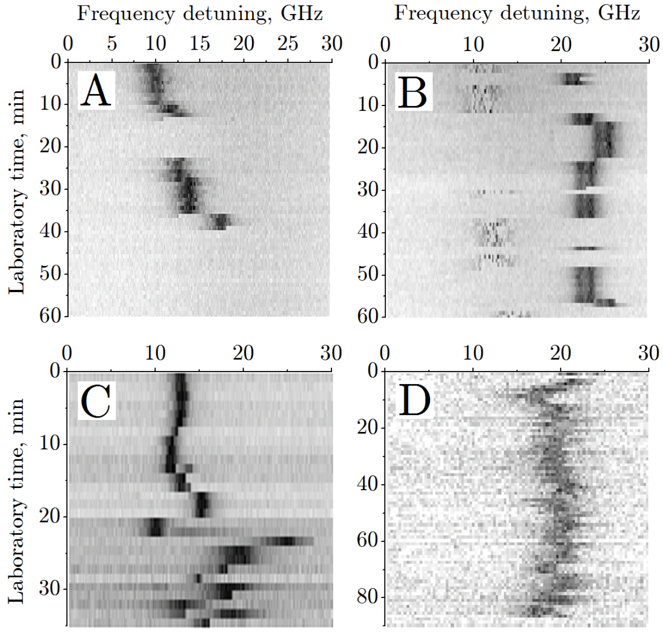

Fig. 3 Examples of spectral trails of single TBT molecules located up to 3 nm below the free surface of a PIB film. (a) Spectral drift in one direction. (b) The TLS which is responsible for the farthest spectral jump also changes the optical linewidth of the molecule, the coupling strength to a second TLS, and even the jump rate of the latter. (c) The amplitude and the frequency of spectral jumps gradually increase with time. (d) Continuous spectral drift of a single-molecule line in both directions resembling a random-walk process. The temperature was 4.5 K, the excitation intensity 8 W/cm^2, and the excitation wavelength around 566 nm.

model. Specifically, spectral jumps are more frequent and do not occur reversibly between a small number (2^n, n integer) of well-defined positions. More importantly, we see continuous spectral drifts and abrupt changes in linewidth and in the rate of spectral jumps. Fig. 3 shows some examples. Continuous spectral drifts as in panels (a) and (d) are possible, although uncommon, in the standard tunneling mode[12]. They require the weak coupling of the fluorescing molecule to numerous TLSs. Interactions between TLSs [panel (c)] and temporal variations of the TLS or coupling parameters [panel (d)] do not agree with the tunneling model. Spectral trails similar to those presented in Fig. 3 are also typical for low-molecular-weight glass formers[3] and ultrathin PIB films[4].

The fraction of single chromophore molecules featuring non-standard spectral dynamics decreases strongly with increasing diffusion depth. Figure 4 compares this variation (filled circles) with the relative number of non-standard spectral trails recorded in ultrathin PIB films (open circles)[4]. The behavior in both kinds of samples is similar. The offset in the depth dependence is most likely due to the proximity of the second interface (i.e. polymer-substrate one) in the ultrathin films.

Also the spectral width of the single-molecule lines varies with diffusion depth. The increase in linewidth begins at a depth of about 10 nm and proceeds rapidly towards the surface, as Fig. 5 illustrates. Some of the spectral trails of single molecules at those depths are presented on Fig. 7. In 0.6 nm depth, the average linewidth is about 20 times broader than in the bulk. For diffusion depths smaller than 0.6 nm, no zero-phonon lines could be observed. The number of detected zero-phonon lines increases with depth and reaches a constant value at roughly 7 nm.

4 Discussion

The fast and complex spectral dynamics of single-molecule lines close to the surface indicates the presence of a high density of tunneling systems, in particular with low barriers. Since the TLSs have a certain spatial extension, the high density is expected to give rise to a correspondingly large number of interactions between them[13]. Their jump rates may be additionally enhanced by the interaction with extra (i.e., non-Debye) low-frequency surface vibrational modes. We can assume that the penetration depth of the surface modes is roughly given by their wavelength. If we set the average excitation energy of the modes equal to the thermal energy at 4.5 K and insert the sound velocity of PIB of 1.5 km/s, we obtain a wavelength of about 16 nm, which is in good agreement with the depth in which the number of anomalous line shapes begins to increase (Fig. 4).

Two-level system in PIB causes significant shift of electronic transition frequency in nearby fluorescent molecule when this TLS is closer than about 10 nm to the molecule in question. Then

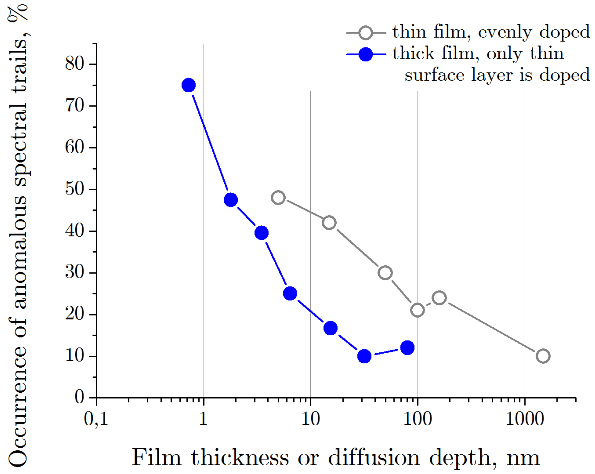

Fig. 4 (color online). Relative number of single TBT molecules in PIB exhibiting anomalous spectral dynamics as a function of film thickness or diffusion depth. The figure compares data measured in ultrathin films (Ref.[4]; empty circles) and in thicker films of which only the surface layer has been doped by diffusion (this work; filled circles). Spectral trails were considered non-standard if they featured any of the following effects: continuous spectral drifts in one direction; abrupt changes of linewidth or jump rate; spectral jumps which were irreversible during the measuring time. Temperature, 4.5 K; excitation intensity, 4 W/cm^2 (ultrathin films) or 8 W/cm^2 (surface doping).

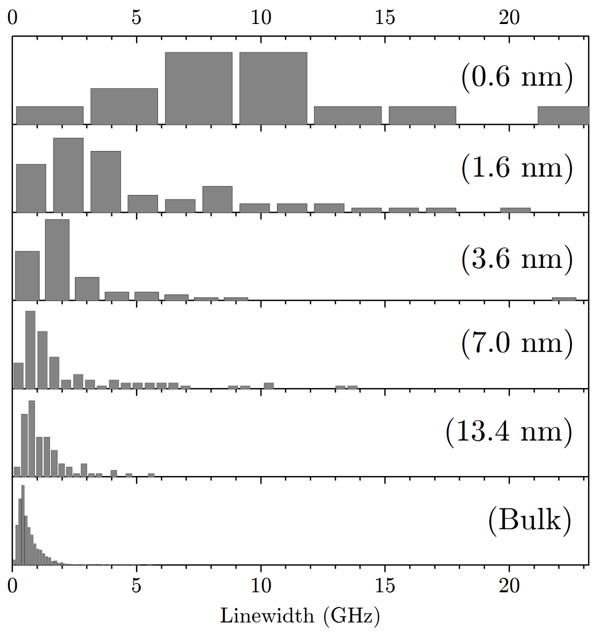

Fig. 5 Distribution of spectral linewidths of single TBT molecules in PIB in different diffusion depths between 0.6 nm and 13.4 nm and comparison with bulk data. Temperature, 4.5 K; excitation intensity, 8 W/cm^2; excitation wavelength between 565 and 568 nm.

if we suppose that spatial density of two-level systems is constant everywhere in the sample, one can expect that when fluorescent molecule is less than 10 nm below the surface it is influenced by fewer two-level systems. And when molecule is at the surface, the entire half-space is missing and this fact should halve the number of two-level systems influencing the molecule. This is not what happens in reality. If anything, spatial density of two-level systems near surface is larger than in the rest of the sample. To illustrate this, we performed computer simulations of single-molecule spectra by implementing the approach of Geva and Skinner.[14] Fig. 6 shows how spatial density of TLSs influences the simulated spectral trails of single fluorescent molecule. Halving the number of TLSs interacting with molecule means going from trails in the second row to trails in the first row. This is not what is observed exlerimentally. Comparing these simulations with experimentally recorded spectral trails on Fig. 7, it seems that going from 3.5 nm to 0.7 nm below surface modifies spectral trails as if density of TLSs has increased by about an order of magnitude.

Another possible cause of strongly increasing linewidths of molecules located 1 – 2 nm below the surface (Fig. 5) may, in part, be due to direct dephasing by the surface quasi-localized modes. In bulk PIB, quasi-localized low-frequency modes affect the linewidths of single chromophore molecules only at temperatures above 5 – 7 K,[16,17] since they have frequencies between about 300 and 600 GHz (15 – 30 K).[18] Close to the surface, their energies may be distinctly lower. If so, the absence of detectable single-molecule lines directly on the surface is probably either caused by their extremely broad linewidths or by strong linear electron-phonon coupling, so the lines consist only of phonon sidebands.

Absence of detectable single-molecule ZPLs directly on the surface is unclear. This may happen because the spectral position of zero-phonon line constantly changes in wide range of wavelengths. These changes may have several possible sources: coupling to low-energy degrees of freedom (e. g., surface vibrational modes); continuous transitions between larger number of accessible conformation states an impurity molecule obtains on surface; continuous translational motions of impurity molecule along the surface that can be induced by excitation laser light. High enough magnitude and frequency of such changes in wavelength can make the detection of ZPL impossible at a given temporal resolution and signal-to-noise ratio. In experiments, there is usual tradeoff between signal-to-noise and temporal resolution - both are defined by exposure time at a given laser excitation power density, and increasing the excitation power density may itself induce additional spectral dynamics. Since in cases where we still can observe ZPLs, their spectral dynamics intensifies as the impurity gets closer to the surface, the dynamical explanation of disappearance of ZPLs for impurity molecules on surface seem more likely than ascribing this disappearance to quenching of fluores-

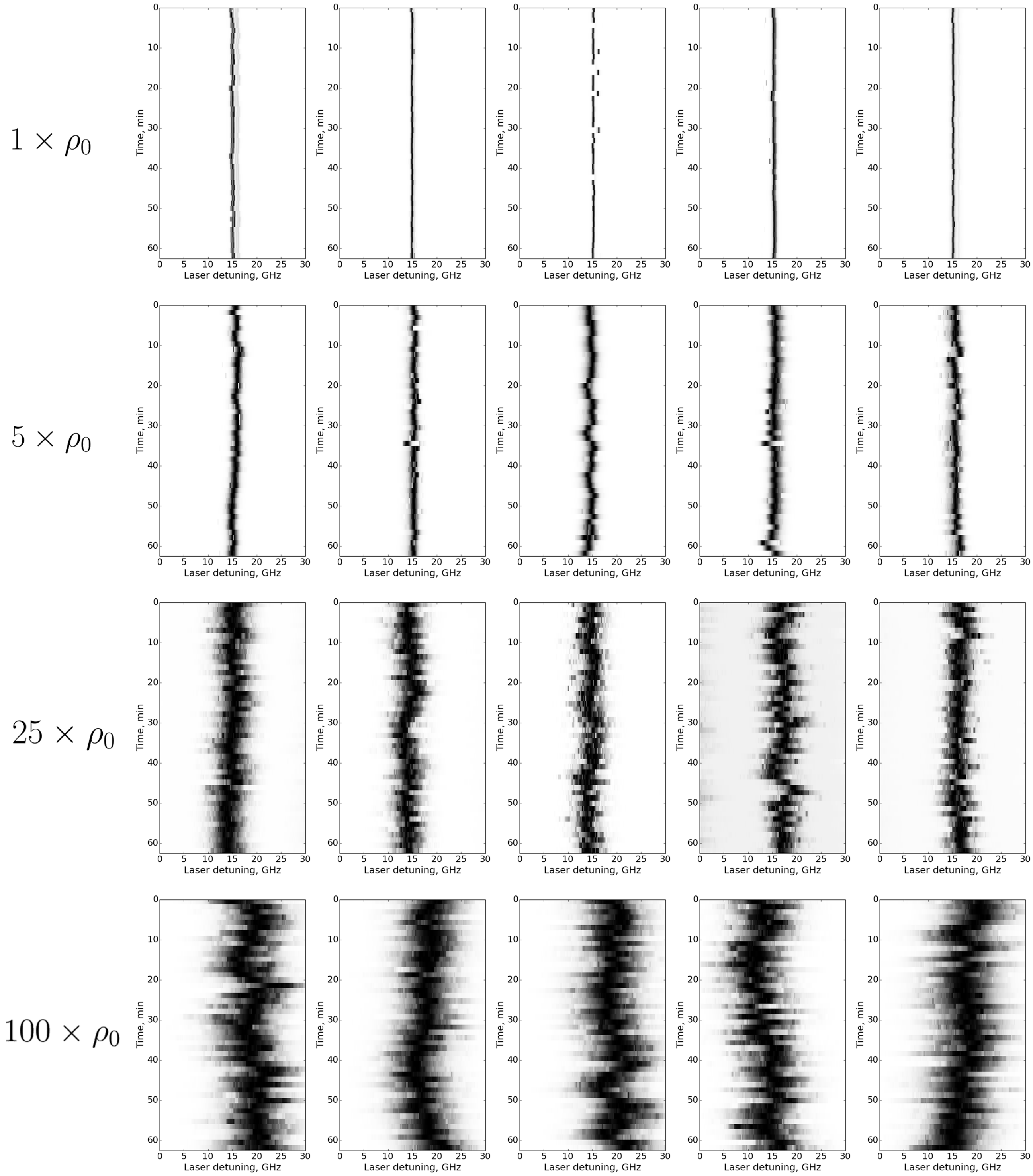

Fig. 6 Simulated spectral trails of single TBT molecules in PIB, for different spatial densities of TLSs indicated for each row of images. Here, ρ_0 means density of TLS used by Geva and Skinner who have shown that it gives good agreement with photon echo experiments and distributions of single molecule spectral line widths[14]. For each density we sampled 5 instantiations. For all trails, distributions of TLS parameters are kept the same (but parameters are generated anew for each trail) and these distributions are valid for bulky PIB sample as shown in Ref.[15]. Interactions between TLSs, however, were not taken into account in the simulations. For all trails, spectral range scanned by the excitation laser is 30 GHz, the time span of experiment (vertical axis) is 62.5 minutes.

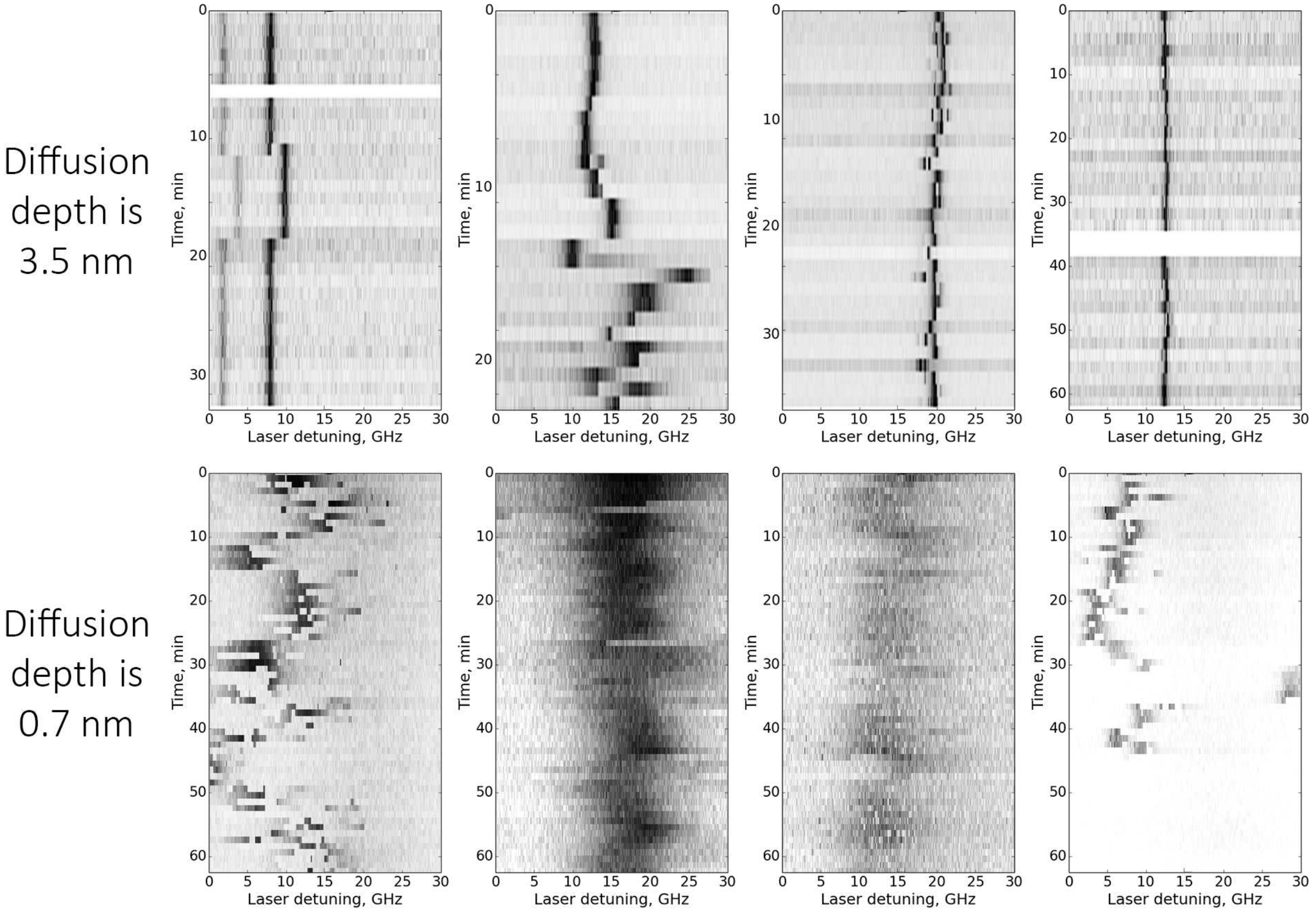

Fig. 7 Experimentally recorded spectral trails of single TBT molecules at diffusion depths of 3.5 nm (top row) and 0.7 nm (bottom row) below the free surface of a PIB film. For all trails, spectral range scanned by the excitation laser is 30 GHz.

cence itself.

Spectral broadening alone does not seem to be sufficient for explaining the total disappearance of detectable single molecule zero-phonon lines on the polymer surface. Let's turn to a more detailed analysis of impurity molecule interacting with light. Upon electronic excitation of molecule, vibrational part of full hamiltonian changes and in harmonic approximation hamiltonians of ground and excited states are

$$H^g = T(R) + R\frac{U}{2}R\,, \qquad H^e = T(R) + (R+a)\frac{U+W}{2}(R+a) \tag{2}$$

Here $T(R)$ is molecule kinetic energy operator, R is multidimentional vector of molecule's deviation from ground state equilibrium position, U and $U+W$ are force matrices for molecule's ground and electronically excited state. Electronic excitation causes changes not only in the force matrix, but induces shift a of equilibrium position as well. Electron-phonon coupling operator is the difference of vibrational hamiltonians:

$$H^e - H^g = a\frac{U}{2}a + aUR + R\frac{W}{2}R \tag{3}$$

Second and third terms describe linear and quadratic coupling respectively. Fig. 5 shows that zero-phonon line (ZPL) width of a single molecule is larger for molecules that are closer to the surface. Since ZPL width is defined solely by the magnitue of electron-phonon coupling W that is quadratic with respect to creation and annihilation operators (quadratic coupling), increasing of zero-phonon line widths means that quadratic coupling gets stronger as the distance to surface decreases. The same conclusion was drawn by Fleury et al.[1].

Chapter 4 of book[19] features a detailed calculation of shape of entire optical band under influence of interaction (3). According to these calculations, half-width at half-maximum is given by:

$$\gamma_{ph} = \int_0^\infty \frac{d\omega}{2\pi}\ln[1 + W^2\Gamma^e(\omega)\Gamma^g(\omega)/\sinh^2(\beta\omega/2)] \tag{4}$$

where $\Gamma^e(\omega)$ is the density of phonon states in ground (g) and extited (e) electronic states of impurity molecule:

$$\Gamma^e(\omega) = \frac{\Gamma^g(\omega)}{(1 - W\Delta^g(\omega))^2 + (W\Gamma^g(\omega))^2} \tag{5}$$

where

$$\Delta^g(\omega) = \int_0^\infty \frac{d\nu}{\pi}\Gamma^g(\nu)\frac{2\nu}{\omega^2 - \nu^2} \tag{6}$$

According to (4), when W becomes very large, half-width of ZPL stops growing with W. (One example where this 'saturation' of ZPL width manifests itself is optical line shape of paramagnetic crystals upon increasing temperature.[20])

But when a molecules gets spatially close to sample surface, there can be an increase in coupling $V = aUR$ as well. This coupling is not quadratic, but linear in phonon operators and thus does not affect width of zero-phonon line. Nonetheless, linear coupling V is capable of broadening the overall optical band much more strongly than quadratic coupling. This broadening effect of strong linear coupling is worked out in detail in [19] and the result is optical shape

$$I^{g,e}(\Delta) = e^{-\phi(0,T)}\frac{1/T_2\pi}{(\omega-\omega_0)^2 + (1/T_2)^2} + \frac{1}{\sqrt{2\pi B}}e^{-\frac{(\omega-\omega_0\mp A)^2}{2B}} \tag{7}$$

where function

$$\phi(t,T) = \sum_q \frac{a_q^2}{2}[n_q\exp(i\nu_q t) + (n_q+1)\exp(-i\nu_q t)] \tag{8}$$

depends on phonon frequencies ν_q and shifts a_q of equilibrium position under electronic excitation and describes influence of linear electron-phonon coupling on optical line shape. Here n_q denotes

$$n_q = \frac{1}{exp(\hbar\nu_q/kT) - 1} \tag{9}$$

At large shifts a_q the Lorentz shape of ZPL disappears entirely as Deby-Waller factor $e^{-\phi(0,T)}$ gets infinitely small, while Stokes shift

$$2A = \sum_{q=1}^{N} a_q^2\nu_q \tag{10}$$

of phonon side-band (in absorbtion and fluorescence) and half-width $\delta\omega_{1/2} = \sqrt{B2\ln 2}$ of gauss-shaped phonon side-band where

$$B = \sum_{q=1}^{N}\frac{a_q^2}{2}\nu_q\coth(\beta\nu_q/2) \tag{11}$$

can be orders of magnitude greater than broadening induced by quadratic coupling. For example, in spectral hole burning experiments it can be at least tens of thousands of GHz. In experimental schemes normally used to detect molecules with narrow zero-phonon lines, fluorescence of single molecule with such a wide optical line is practically impossible to detect on background light. We can only speculate what real microscopic motions possibly underlie this increased linear coupling, but from Fig. 5 and from seeing no molecules directly on the surface, we conclude that while this linear coupling may increase gradually starting at distance of several nanometers from surface but sharply increases when surface is reached.

5 Conclusion

To conclude, our single-molecule studies of a model disordered solid (amorphous polymer) have shown that dynamical properties of ultrathin subsurface layers differ from the properties of the polymer bulk. We found that this deviation becomes noticeable at distances less than about 20 nm from the surface. The spectral dynamics of single chromophores becomes faster and presents irreversible features. At depths less than 5 nm, along with drastic increase in complexity of spectral dynamics, we also observed an additional strong increase of the individual spectral linewidths. Finally, less than 0.6 nm below the surface, no zero-phonon lines were detected at all.

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