

# Vibronic Excitation of Single Molecules: A New Technique for Studying Low-Temperature Dynamics

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*Herein, we present vibronic excitation and detection of purely electronic zero-phonon lines (ZPL) of single molecules as a new tool for investigating dynamics at cryogenic temperatures. Applications of this technique to study crystalline and amorphous matrix materials are presented. In the crystalline environment, spectrally stable ZPLs are observed at moderate excitation powers. By contrast, investigations at higher excitation intensities reveal the opening of local degrees of freedom and spectral*

*jumps, which we interpret as the observation of elementary steps in the melting of a crystal. We compare these results to spectral single-molecule trajectories recorded in a polymer. The way in which much more complicated spectral features can be analysed is shown. Surprisingly, pronounced spectral shifts on a previously not accessible large energy scale are observed, which are hard to reconcile with the standard two-level model system used to describe low-temperature dynamics in disordered systems.*

## 1. Introduction

Single-molecule spectroscopy gives exciting insights into the energetics and the dynamics of the interaction between a chromophore and its local environment.<sup>[1]</sup> By avoiding ensemble averaging, many hitherto only postulated processes can now be observed directly. With hindsight, it is astonishing that the first single-molecule experiments were not performed at room temperature with the high-quality excitation and collection optics readily available from standard room-temperature microscopy. Instead, optical single-molecule detection first succeeded under much more difficult optical conditions at cryogenic temperatures.<sup>[2,3]</sup> This is due to the fact that the apparent disadvantages compared to the nowadays dominating room-temperature experiments are for some specific chromophore–host systems compensated by narrow absorption linewidths and concomitant high absorption cross-sections. Under favourable conditions, the purely electronic zero-phonon lines (ZPL) of chromophores in such systems can have linewidths which are only limited by the lifetime of the excited electronic state. Yet, the electronic transitions of the chromophore still couple to its environment via, for example, electrostatic interactions. Disorder in the matrix therefore results in the spreading of the chromophore's absorption frequencies while dynamical matrix changes lead to spectral jumps. Thus, on the one hand, the narrow ZPL facilitates the spectral selection of individual molecules with a narrow bandwidth laser. On the other hand, single-molecule ZPLs are most sensitive reporters for changes in their environment. Repeated scans of the excitation frequency can thus reveal temporal changes of the absorption frequency of one chromophore caused by structural changes in its surrounding.

While this method has been an extremely successful tool for investigations of low-temperature dynamics, its application remains restricted to a few systems with spectrally narrow ZPLs.

In addition, the ZPL has to be reasonably stable. For ZPLs which jump on a small energy scale of a few wavenumbers, it has been demonstrated that even fast jumps can be resolved with high temporal resolution using intensity–time–frequency correlations.<sup>[4]</sup> To date, it was however not possible to use excitation spectroscopy for the investigation of systems in which frequent and far-spectral ZPL jumps occur. Unfortunately, many interesting systems such as dye-doped polymers or chromophore containing proteins fall into this category. Exactly for these, however, high-resolution single-molecule spectroscopy of ZPLs would offer a unique and most elegant way to test theoretical models, describing their complicated energy landscapes.

Herein, we report applications of vibronic excitation as a new experimental scheme for studying low-temperature dynamics in solids. Vibronic excitation at cryogenic temperatures has previously been employed for single-molecule detection in two manners. In the first scheme, a second laser, slightly detuned from the purely electronic ZPL was used to saturate the electronic transition.<sup>[5]</sup> While this method also works for low-frequency transitions, its application remains limited to excep-

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tionally photostable single molecules. Vibronic absorption bands can on the other hand be additionally broadened by electronic coupling in multichromophoric systems and the broad absorption bands can then be exploited for excitation.<sup>[6]</sup> This method is similar to the approach presented here, but leads to the detection of relatively broad emission bands. Narrow ZPL emission can however be obtained by exciting a vibronic transition of a single chromophore. In the following, we will outline the spectroscopic method and show how this approach complements high-resolution excitation spectroscopy of single molecules at cryogenic temperatures. We will then first discuss results of measurements on a dye-doped crystalline matrix. Excitation with moderate excitation powers leads to the observation of stable, ultranarrow ZPL emission, which has potential use as a single photon source in quantum optical applications. In contrast, raising the excitation power allows the direct observation of the opening of local degrees of freedom. These could represent elementary steps in the melting of the crystalline host structure. The last part of this work is finally dedicated to studies of amorphous systems. Our aim here is not to present systematic studies of low-temperature dynamics. Rather much, we will discuss typical examples of how vibronic excitation can be employed in such investigations and propose approaches which are suited for the analysis of the acquired data.

## 2. Results and Discussion

### Vibronic Excitation

Commonly, the fluorescence detection of single molecules at cryogenic temperatures is achieved by a combination of three criteria. These are the high dilution of chromophores in a host material, spectral selection by the excitation of the narrow ZPL absorption of the chromophores, and spatial selection by the restriction of excitation and collection to a small sample volume. If a low-temperature microscope is used in order to increase the spatial selection, the requirements on spectral selection become less stringent. Use of a microscope therefore allows us to excite a vibronic molecular state and observe the purely electronic ZPL in emission instead of exciting the ZPL and observing the Stokes-shifted fluorescence. This has two major advantages: Firstly, the lifetime of molecular vibrations in condensed phase is orders of magnitudes shorter than that of the purely electronic states. Vibronic absorption bands are thus significantly broader than purely electronic ZPLs. This in turn means that a single molecule under observation is still being excited even if its absorption frequency changes due to structural rearrangements in the matrix. In contrast to using absorption bands which are broadened by electronic coupling between several chromophores,<sup>[7]</sup> the ZPL emission of a single chromophore still possesses a narrow spectrum. Spectral jumps of the chromophore can therefore still be monitored with high accuracy. The second advantage is that the detection efficiency increases. While the absorption cross-section of the vibronic state is much lower than that of the corresponding ZPL, much more of the fluorescence emission is now collected,

since a major part of the fluorescence is emitted in the ZPL. Especially with multi-channel detection, it is helpful that the ZPL emission is concentrated on a narrow spectrum.

The excitation and relaxation scheme is depicted in Figure 1a. Excitation takes place from the vibrational and electronic ground state  $|S_0\rangle$  into an excited vibrational state of the

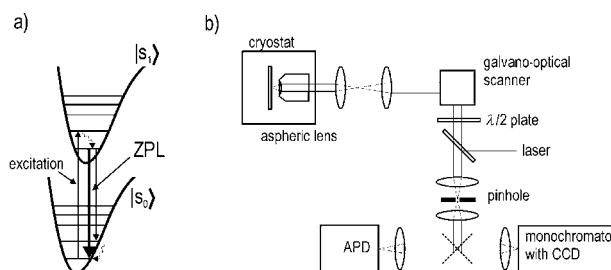
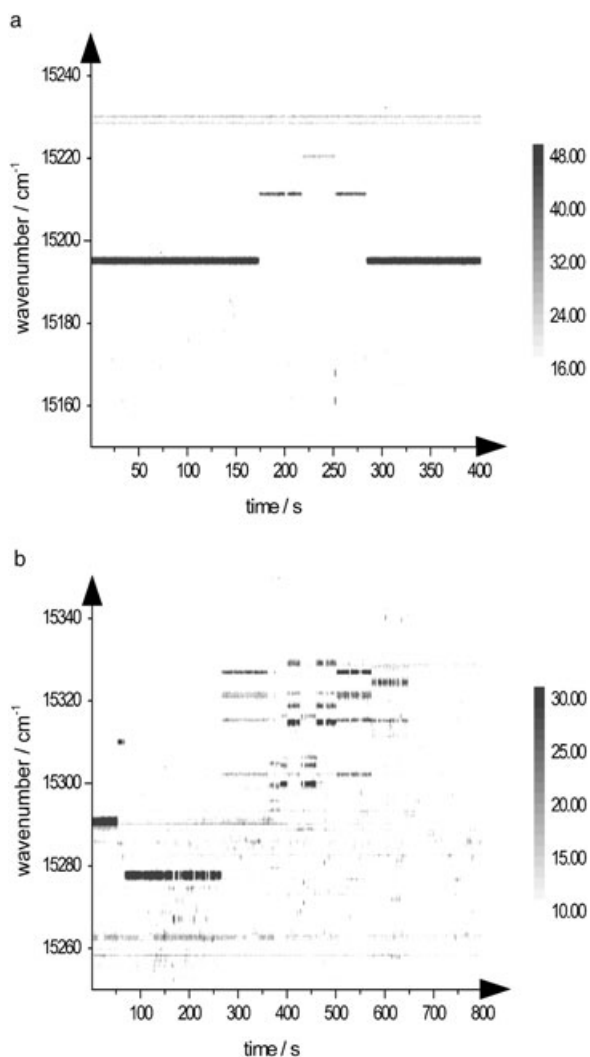


Figure 1. a) Vibronic excitation scheme and b) experimental setup.

excited electronic  $|S_1\rangle$  state of a dye. For terrylene diimide (TDI), which we use here, an energy of approximately  $1300\text{ cm}^{-1}$ – $1400\text{ cm}^{-1}$  above the purely electronic transition energy is chosen. This leads to the excitation of breathing modes of the aromatic system which couple efficiently to the electronic transition. The transitions thus have a sufficiently large Franck–Condon factor and high absorption cross-sections. Note that the purely vibronic modes are accompanied by phonon side bands which additionally broaden the absorptions. It will be seen later that a spectral region of up to  $80\text{ cm}^{-1}$  is covered. Finally, the vibrational excitation in the  $|S_1\rangle$  state decays within a few picoseconds and fluorescence emission occurs as a spectrally narrow ZPL into the vibrational ground state of  $|S_0\rangle$  or into a vibrationally excited state of  $|S_0\rangle$ .

### Investigations of Crystalline Samples

As a first example, we have investigated samples of TDI diluted in hexadecane (HD), which forms a crystalline Shpol'skii matrix at low temperatures. Vibronic excitation and spectrally dispersed detection leads to the emergence of intense ZPLs, as depicted in Figure 2. Under moderate excitation conditions, no or very few spectral jumps of the ZPL are observed in the course of many minutes of up to several hours. In one case, an individual TDI molecule was observed over five days, including several freeze and thaw cycles between 1.4 and 100 K. This specific molecule exhibited rare spectral jumps of the ZPL from  $14988\text{ cm}^{-1}$  to  $15042\text{ cm}^{-1}$ , but could always be switched back by a few seconds of illumination in the new spectral position. A similar switching behaviour has been described for terrylene in *p*-terphenyl and was explained by the reorientation of phenyl groups in the solvent shell of the matrix molecules.<sup>[8,9,10]</sup> Note that the ZPL linewidth which we determine is given by the 30-GHz resolution of our monochromator. Summing of all spectra acquired over 1000 s does not lead to an increase of the linewidth. This proves that in this molecular system, no spectral diffusion exceeding 30 GHz per 1000 s



**Figure 2.** Spectral trajectories of TDI in HD. a) Trajectory of a single TDI molecule in HD. Before the beginning of this trajectory, the molecule was already excited with 11 mW for 1600 s and jumped only once in a fashion similar to the three-level jump around 225 s. b) The molecule was excited for more than 1400 s with less than 2 mW before the beginning of this trajectory. No spectral jump was observed during this time. After several well-defined jumps, the ZPL is split among four positions. These shift between four states with different splittings before the molecule disappears.

takes place under excitation powers of 1 mW. In addition, it gives an indication of the long-term stability of the setup. We have previously shown in a separate experiment using vibronic excitation and a high-finesse Fabry–Perot interferometer that the ZPL emission linewidth of TDI in HD indeed reaches nearly lifetime-limited values of 65 MHz.<sup>[11,12]</sup>

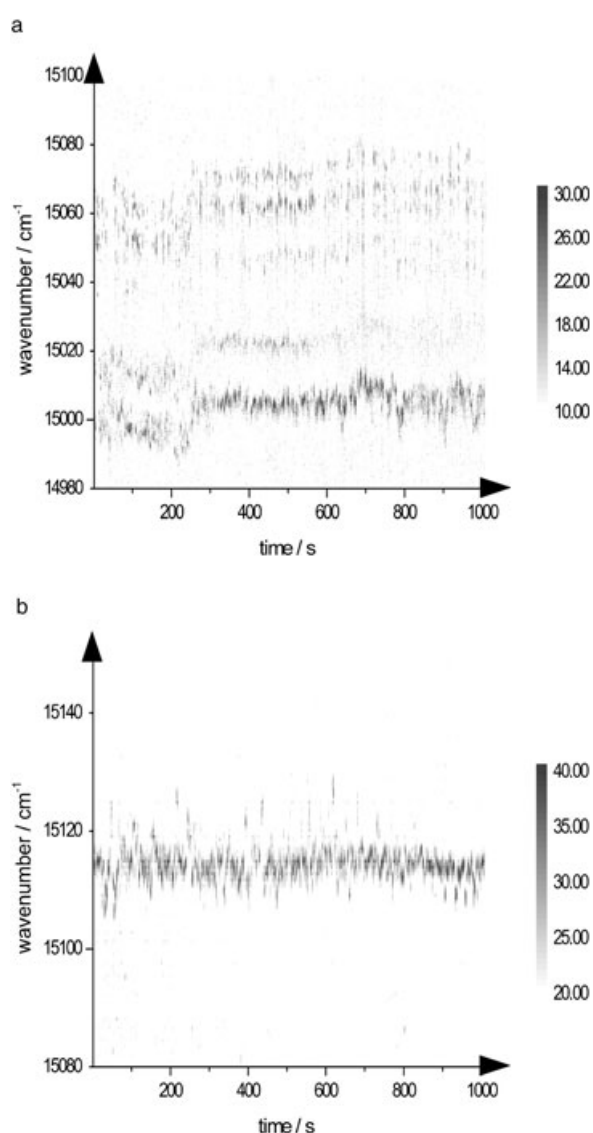
The common scanning of the excitation laser line is superior for the resolution of small spectral jumps in crystalline systems. However, only vibronic excitation can reveal wide spectral jumps of the ZPL in a crystalline sample as depicted in Figure 2a. In room-temperature experiments on single molecules of perylene derivatives, different spectral populations were found to be due to the presence of different conformers of the chromophore.<sup>[13,14]</sup> Here, this explanation seems unlikely, since in the cases investigated so far, we observed a variety of ZPL

jump amplitudes ranging from 3 to 54 cm<sup>-1</sup>. Therefore, even if extended statistics are still needed, we assume that the spectral jumps are caused by two-level systems (TLS) in the crystalline environment. Two further points are worth mentioning here. Firstly, it should be noted that the spectral jump amplitudes described here are two to three orders of magnitude larger than those previously observed in fluorescence excitation spectroscopy of single molecules at cryogenic temperatures.<sup>[11]</sup> The only exception known to us is the previously cited work on terrylene in *p*-terphenyl,<sup>[8,9,10]</sup> in which the chromophores can reside in different well-defined crystallographic sites. Secondly, in addition to observing far jumps, we also detect jumps which are violating the standard TLS model. In this model, the coupling of one or several TLSs to a chromophore will give rise to 2<sup>n</sup> different spectral positions. Deviations are only expected for degenerate TLSs. Figure 2a depicts the observation of a three-level system in HD. The energetic positions of 15195, 15211, and 15220 cm<sup>-1</sup>, respectively, exclude the haphazard degeneracy of two coupled TLSs. A similar observation on a smaller energy scale has been described by Boiron et al.<sup>[15]</sup> In contrast to us, these authors observed a distinct order in the successive population of the energy levels. In our case, it is therefore likely that the barrier crossing is thermally activated.

While the high-resolution measurements of ZPL emission linewidths demonstrate that laser-induced heating is negligible at low excitation intensities,<sup>[12]</sup> its effect becomes observable as induced spectral jumps at higher excitation intensities. Figure 2b shows the spectral ZPL trajectory of a molecule which has been excited with an illumination power of 200 μW for more than 20 min. During this time, no spectral jump occurred. Also 200 s of excitation with 2 mW did not lead to any spectral jumps. Only 50 s after raising the excitation powers to 5 mW, the ZPL starts to jump, first by 19 cm<sup>-1</sup> to higher energies, before going back 33 cm<sup>-1</sup> to lower energies. Apart from short occasional excursions of 9 cm<sup>-1</sup> to the red, the molecule then stays at this position for more than 3 min. At this point in time the still well-defined ZPL splits up into at least four spectral positions. In the standard TLS picture this corresponds to the coupling of the chromophore to two or more TLSs. In view of the spectral stability of the same ZPL under moderate excitation conditions, we conclude that laser heating leads to the activation of the two TLSs. Photoinduced spectral jumping is ruled out, since this should not have a cumulative effect as seen here, but instead leads to an instantaneous increase in the jumping rate after an increase of the excitation power. After 400 s of this spectral trajectory, the four intense parts of the ZPL sequentially shift between four states before the ZPL finally disappears. Each of these states is characterised by a specific spectral splitting between the positions of each line. In the frame of the standard TLS model one has to conclude that the two observed coupled TLSs further interact strongly with at least two other TLSs. Thus, our data reflect the opening of local degrees of freedom. While at this stage no further analysis is possible, one might argue that this corresponds to the first elementary steps in the melting of the crystalline matrix at a molecular level.

## Investigations of Polymeric Systems

The appearance of the ZPL emission spectra changes drastically if the crystalline HD matrix is exchanged by the amorphous host poly(methylmethacrylate) (PMMA). Instead of the stable, resolution-limited ZPLs of TDI in HD, the ZPLs are now broadened, exhibit a lot of dynamical changes, and are in nearly all cases distributed over several spectral positions. Typical spectra are depicted in Figure 3. Low-temperature dynamics of single molecules in polymeric host matrices have been investigated by a number of groups.<sup>[1]</sup> Yet, to date only spectral dynamics up to 30 GHz could be covered in such studies. As has been explained above, due to the use of a monochromator in our experimental scheme, the spectral resolution of our data is worse than that obtainable with excitation spectroscopy. The



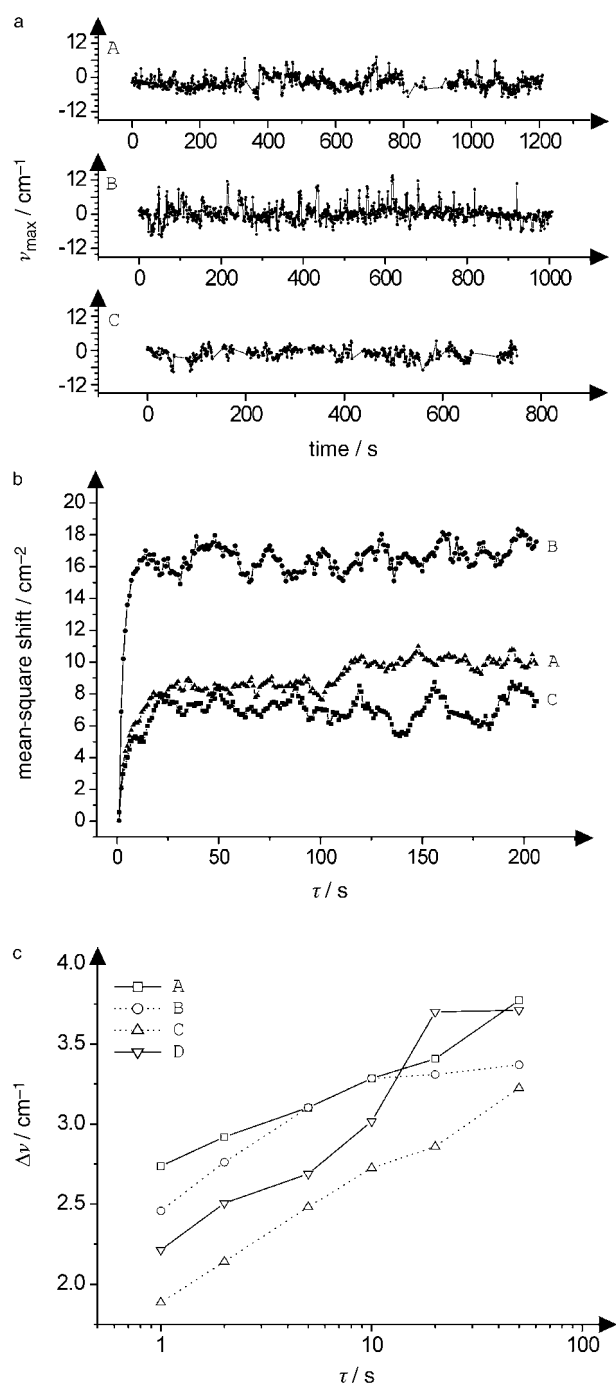
**Figure 3.** a) Spectral trajectory of a single TDI molecule in PMMA. The electronic states of the molecule couple to (at least) two TLSs. The different splittings of the spectral positions show that the TLS in turn couple strongly among each other. Spectral drift around 200 s and 700 s is clearly visible. b) Spectral trajectory of another single TDI molecule in PMMA.

energy range which is covered here, however, is three orders of magnitude larger. Not all parameters of a TLS can be recovered from fluorescence spectroscopy of single molecules. In particular jump rates between the two states of the TLS are difficult to interpret, since photoinduced and thermally induced barrier crossings cannot be excluded. Systematic intensity-dependent measurements are necessary in order to shed light on this aspect. It has however been pointed out previously that assumptions of the TLS model, such as the temporal stability of TLSs, the weak coupling between TLSs, and the splitting into only two states, can nevertheless be tested.<sup>[15]</sup> Vibronic excitation is not different from excitation spectroscopy in this respect. At this point it is helpful to compare the heat transfer to the system with the two excitation mechanisms. With vibronic excitation the energy that is necessary for the excitation of the vibrational level is additionally transferred to the system. Independent of the excitation mechanism, a certain part of the emission will however always relax into a vibrationally excited level of the electronic ground state. This limitation of vibronic excitation is however compensated by the efficient collection of the ZPL emission.

Inspection of all spectral trajectories immediately shows that the spectral positions of the lines are not stable and that instead, spectral drifts are a common phenomenon. Spectral diffusion in the range of 100 GHz is clearly seen if the spectral widths are plotted as a function of the integration time (Figure 4). This behaviour has previously been simulated in the framework of the standard TLS model<sup>[16]</sup> and has been detected earlier on an energy scale of 1 GHz.<sup>[15]</sup> In order to analyse the experimental data, two approaches are taken. The results of both are depicted for three and four molecules in Figure 4. Similar to the analysis of diffusion phenomena, for example, in liquids, we plot the spectral mean square displacements of the centre frequency in the successive spectra.<sup>[17]</sup> While we have to assume an average spectral shape and to introduce a fast frequency cutoff, this approach reveals details about spectral diffusion processes. For example, it is possible to distinguish spectral diffusion within a limited spectral range, a directed spectral drift, or random spectral diffusion.

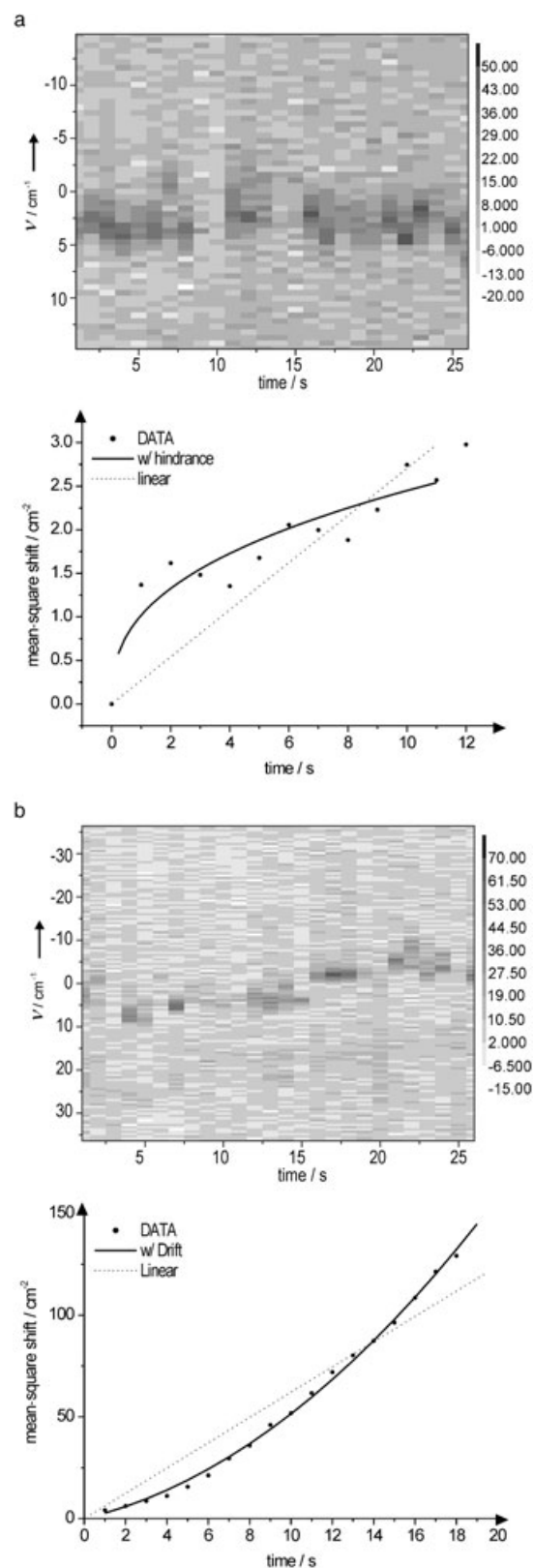
Figure 4 shows spectral trajectories recorded from different molecules. In all cases, we detect an unbiased diffusion behaviour within a limited spectral range of a few wavenumbers. Plotting of the spectral mean square shifts furthermore reveals that most often the spectral range accessible to each molecule is explored within less than 25 s. The following plateau, however, is certainly not the limiting value since larger spectral jumps may occur on a longer time scale. The comparatively small number of such large jumps, however, does not allow us to make statements about plateaus on longer time scales, which could reflect a hierarchy of TLSs. In principle, spectral diffusion in a region of the potential energy landscape characterised by small energy barriers and limited by larger barriers would lead to a fast exploration of the spectral region framed by the larger barriers. Crossing of the larger barriers and subsequent exploration of a new spectral region would occur less frequently and would appear as, for example, the step around 100 s in the curve for molecule A (Figure 4). The potential of





**Figure 4.** Analysis of the spectral diffusion detected in the spectral trajectories of three different TDI molecules in PMMA. The three uppermost traces (a) depict the spectral displacement of the centre frequency as a function of time determined for three molecules A–C. In the middle graph (b), mean-square spectral displacements of this centre frequency are plotted, whereas the lower graph (c) depicts the increase in spectral width as a function of integration time.

this type of analysis is exemplified in Figure 5. Here we plot results of the same analysis for short parts of the spectral trajectory of the molecule depicted in the bottom part of Figure 3 (from  $t=410$ – $435$  s and  $t=765$ – $790$  s). The latter is a region in which spectral drift was observed, while the molecule



**Figure 5.** Analysis of spectral trajectories: Parts of the spectral trajectories of the molecule depicted in the bottom of Figure 3 (a:  $t=410$ – $435$  s, b:  $t=765$ – $790$  s) are shown in the upper part. In the lower part, the spectral mean-square displacements are plotted for each case. The behaviour in the earlier part of the trajectory corresponds to spectral diffusion within a potential well, whereas the later part clearly shows spectral diffusion with drift ( $1.5 \text{ cm}^{-1} \text{ s}^{-1}$ ).

seemed to diffuse randomly in the first region. It is clearly seen in the plot that, apart from a diffusive part, the short second trajectory also contains a drift with a velocity of  $1.5 \text{ cm}^{-1} \text{ s}^{-1}$ . In contrast, no such effect is seen in the first trajectory. As a second possibility, the data can be analysed by plotting the mean spectral width  $\Delta\nu$  as a function of time. In this case, no assumption on the spectral shape is necessary, but the analysis does not give any information about the diffusion mechanism. For the four molecules presented here, a logarithmic dependence of the observed spectral width on the integration time  $\tau$  is observed. This confirms earlier investigations on a sub-1-GHz energy scale<sup>[15]</sup> and the modelling results based on the standard TLS model.<sup>[16]</sup> In our case, however, the prefactor is two orders of magnitude larger than those previously determined. This larger value might be caused by a higher temperature at the location of the molecule, even if we do not see such an effect in high-resolution measurements in the crystalline matrix. Further intensity-dependent measurements are necessary to clarify this point.

The spectral drift described above concerns each of the spectral positions of the ZPL in the same manner, since no differences in the slope are apparent. Spectral drift was observed earlier in a crystalline host<sup>[18]</sup> and in a polymer,<sup>[15]</sup> but again only on a much smaller energy scale. In the TLS model, the observed pronounced effects on the absorption of the chromophore would necessitate a strong coupling of the respective TLSs to the chromophore. However, the density of such TLSs around the chromophore should be small,<sup>[19]</sup> which makes a collective interaction between several TLS rather improbable. Instead the trajectories are reminiscent of models describing structural relaxation in disordered systems, such as the folding funnel of proteins.<sup>[20]</sup> One has to keep in mind that the spectral position of the ZPL, which is determined in excitation or emission spectroscopy, is only a measure of the absolute energy difference between  $|S_0\rangle$  and  $|S_1\rangle$ . The coupling of these two electronic states to the energy hypersurface of the surrounding which is modeled with the TLSs can be different. This however means that structural relaxation of the amorphous matrix towards its global energetic minimum is not necessarily coupled to spectral drift of the ZPL in only one direction. Thus, recurrent changes in the spectral drift direction as observed here and by Orrit and co-workers can be reconciled with this model.<sup>[1]</sup>

### 3. Conclusions

In conclusion, we have presented applications of a newly developed excitation scheme for single molecules at cryogenic temperatures. On the one hand, our approach gives access to spectrally narrow ZPL emission of single molecules. This presents an attractive source of indistinguishable single photons for quantum optical applications. On the other hand, we have shown that our technique allows experiments with new systems, which to date could not be investigated with fluorescence excitation spectroscopy of the ZPL. It was demonstrated that this can give detailed insight into the dynamics of ordered and disordered solids at low temperatures. It is conceivable

that our technique can also be applied for investigations of single chromophore-containing proteins.

### Experimental Section

The experiments reported here were performed with a home-built low-temperature microscope operating in a liquid He bath cryostat at 2 K. An aspherical lens (NA 0.55) was used to focus 50  $\mu\text{W}$ –5 mW of light from a ring dye laser (Coherent 899) onto the sample and to collect the Stokes-shifted fluorescence. In order to first obtain fluorescence images of the sample, the excitation beam was raster-scanned using galvo-optical mirrors. After passing a dichroic mirror, the fluorescence signal was further filtered with appropriate bandpass filters before being directed through a confocal pinhole (300  $\mu\text{m}$  diameter) onto an avalanche photodiode (APD, Perkin-Elmer SPCM-AQR-16). After an appropriate sample location was found, the beam was parked on the molecule and its signal was directed into a monochromator (Jobin-Yvon HR 460) equipped with slow-scan CCD camera (Acton Research HB128). In all cases an integration time of 1 s/spectrum was used and a spectral resolution of 30 GHz was obtained.

TDI/HD samples were prepared by adding HD to a solution of TDI in  $\text{CHCl}_3$ . The solvent and atmospheric  $\text{O}_2$  were carefully removed by several thaw and freeze cycles with liquid  $\text{N}_2$  and intermediate evacuation. The TDI/HD solution was then saturated with Ar before being quickly inserted into the liquid He bath. By contrast, TDI/PMMA samples were produced by preparing a solution of TDI and PMMA in  $\text{CHCl}_3$  which was spin-coated onto a glass cover slip. The thickness of the resulting film was approximately 200 nm.

The spectra were analysed using computerised support. They are obtained as a sequence of about 1000 individual spectra with 1 s integration time for each spectrum. The entire sequence is background-corrected and the positions of all peaks occurring in all data sets are estimated using a threshold and a width criterion. These positions are used to excise the individual peaks from the entire spectrum, and to generate initial guess parameters for the subsequent fitting procedure. The individual excised peaks are fitted to a Gaussian function, given in Equation (1)

$$I(x) = c + A \exp[-(x-x_c)^2/w^2] \quad (1)$$

in which  $c$  is a generic offset,  $A$  the amplitude,  $x_c$  the central position of the bell-shaped curve, and  $w$  is related to the full-width-at-half-maximum by  $\text{FWHM} = w[8(\ln 4)]^{1/2}$  or  $1.665w$ . A table consisting of the spectrum number (equivalent to time), the peak number (which may vary, as a different number of peaks may occur from spectrum to spectrum), and the fit parameters ( $A, w, c, x_c$ ) for this peak is generated. The same procedure can be repeated for a sequence in which the individual spectra are binned together. Thus, longer integration times can be simulated. We used two different ways to analyse the spectral dynamics: 1) Analogous to the analysis of thermal or particle diffusion, we calculate spectral mean square displacements as a function of time. We thereby assume that the determined average linewidth of the spectra remains constant. Note that this corresponds to the introduction of an artificial cutoff at short times. The mean spectral shift is then calculated by averaging the squares of the differences in  $x_c$  after skipping one, two, three, etc. spectra (middle part of Figure 4). 2) The mean spectral widths  $\Delta\nu$  are calculated from the fits to the binned data in dependence of the binning size, which corresponds to a fictitious integration time  $\tau$ .

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