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Inhomogeneous and Homogeneous Line Broadening of Optical Spectra of PTCDA Molecules Adsorbed at Step Edges of Alkali Halide Surfaces

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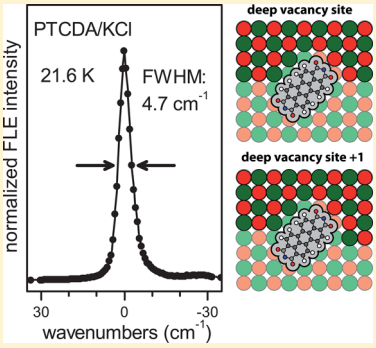
ABSTRACT: We report a detailed analysis of the line shapes of the 0−0 transitions in the fluorescence (FL) and fluorescence excitation (FLE) spectra of perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA) molecules adsorbed at terrace and step edge sites of (100)-oriented alkali halide films (KCl and NaCl). At low temperatures (6−20 K), we find very narrow FLE lines with a fwhm of 4.5 cm^{-1} (3.0 cm^{-1}) on KCl (NaCl). These line shapes are dominated by inhomogeneous broadening related to the structural variation of the environment of the PTCDA molecules. We explain this site broadening on the basis of structural models for the adsorption sites at the step edges from earlier scanning microscopy data and density functional theory calculations. With increasing temperatures, the 0−0 lines in the FL and FLE spectra broaden; e.g., in the FL, the fwhm increases to 26 cm^{-1} (18 cm^{-1}) at 100 K on the KCl (NaCl) surface. This temperature induced broadening is of Lorentzian shape and can be described by the theory of Hsu and Skinner, based on dephasing by coupling to acoustic phonons of the substrate. Discrepancies remain for experimentally observed small line shifts. We discuss how surfaces can be used and optimized as sample systems for a highly resolved optical spectroscopy of molecules.



1. INTRODUCTION

There exists a high interest in obtaining highly resolved fluorescence (FL) and absorption spectra of large organic molecules, for instance, because a detailed analysis of the vibronic modes yields information about the configuration and structures of the molecules.[1−5] A traditional way for obtaining such spectra is the use of Shpol'skiĭ matrices.[6,7] Another more recent approach is to attach the molecules to or into He nanodroplets.[4,5,8] Typical line widths of about 10 cm^{-1} can be achieved for molecules in Shpol'skiĭ matrices at low temperatures.[9−11] For He nanodroplets much narrower lines have been reported, e.g., of the order of 0.7 cm^{-1}.[5]

The line width of optical transitions of molecules in Shpol'skiĭ matrices is typically attributed to *inhomogeneous* line broadening in combination with *homogeneous* line broadening related to thermal induced dephasing.[12,13] However, it is difficult to obtain structural information about the local environment of the respective molecules in bulk matrices. This limits further interpretations of the detailed mechanisms responsible for the line width. In this work we demonstrate that highly resolved optical spectra with very narrow lines, comparable with those obtained for Shpol'skiĭ matrices,[9−11] can also be obtained, if molecules are deposited on a well-defined, i.e., chemically clean and structurally ordered, dielectric surface. Besides giving access to optical spectra of high quality, such experiments also allow one to investigate the structural details of the molecular sites by other experimental methods in parallel, e.g., scanning tunneling microscopy (STM). This can support the interpretation of line broadening mechanisms.

FL spectroscopy of molecules adsorbed on surfaces requires the use of wide-band-gap materials (insulators), since on metal or semiconductor surfaces, the fluorescence is rapidly quenched and no signal can be detected.[14] Notably, the adsorption and structure formation of organic molecules on insulator surfaces has gained increasing interest over the past years.[15−19] In this work we will consider the prototype π-conjugated organic molecule PTCDA. Important in the context of the present work is the following. On ionic surfaces, e.g., the KCl(100),[20] NaCl(100),[21] and KBr(100) surfaces,[22] it was found that Coulomb interactions between the negative partial charges on the anhydride groups of PTCDA and surface cations lead to adsorption at specific and well-defined sites, similar to the situation that is found for PTCDA on suitable metal surfaces.[23] This situation is advantageous, since the population of defined adsorption sites facilitates the discussion of the corresponding optical spectra, in particular the variations in the adsorption sites. However, so far no detailed experiments on the line shape and possible line broadening mechanisms of the optical transitions of fluorescent molecules adsorbed on such surfaces have been reported. This will be the topic of the present work. Importantly, we will consider the limit of very low molecular surface concentrations, where intermolecular interactions are negligible. This situation has to be discerned from that of a completed monolayer of molecules on a surface where intermolecular

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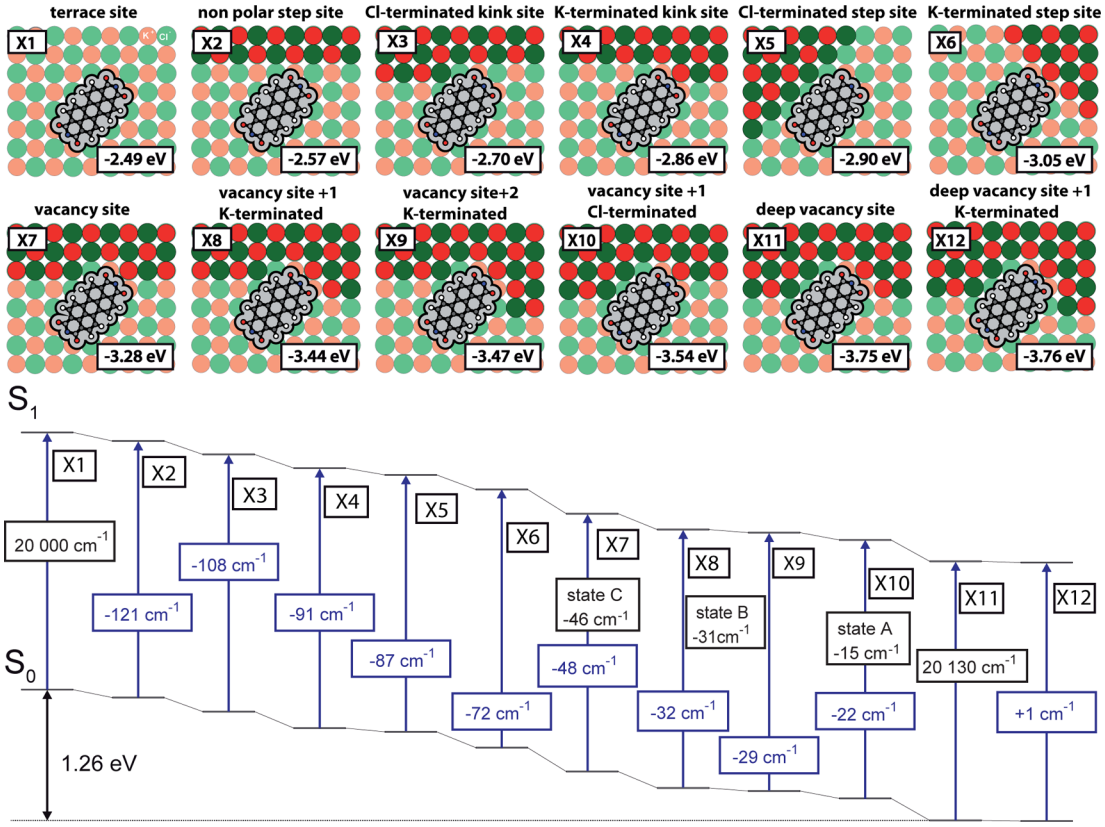

Figure 1. Top: schematic hard sphere models of the different adsorption sites of PTCDA on KCl(100). The sites are labeled by X1 to X12. We note that structural relaxations of the molecules or the substrate atoms are not included. The corresponding adsorption energies for the molecule at the specific sites (not including the energy for creation of the sites itself) are given. These energies were calculated earlier by DFT.[40,42,43] Bottom: graphical representation of adsorption energies of the molecule at the specific sites for the ground state (S_0) taken from the DFT[40,42,43] and the adsorption energies of the molecule in the excited S_1 state calculated by eq 2. The differences of the two adsorption energies correspond to the optical transition energies, i.e., the energetic position of the 0−0 transition in the optical spectra. Equation 2 was calibrated at the experimentally determined values for the transition energies of the X1 (*t site*) and the X11 (deep vacancy site) sites. These are given by black numbers. All other transition energies were calculated from eq 2 and are given relative to the transition energy of the site X11 (blue numbers). The experimentally observed transition energies of the earlier reported metastable states, A, B, and C,[39] are also included for comparison (black numbers). These values are also given relative to the transition energy of the site X11.

interactions are dominantly important for the optical spectra. For the PTCDA monolayer on KCl this latter situation was reported in an earlier work.[20]

Besides *inhomogeneous* line broadening effects, *homogeneous* line broadening mechanisms due to dephasing may play a role. For molecules in matrices, different dephasing mechanisms are discussed, e.g., tunneling in a two-level system (TLS),[24−26] coupling to low-frequency pseudolocal modes (phonons) (LFM),[27−30] or coupling to acoustic and optical phonons.[31] Whereas the broadening at low temperatures is dominated by TLS and LFM,[12,13] the increasing broadening at higher temperatures is due to acoustic phonons.[32] For an understanding of the electron−phonon coupling one usually studies the evolution of the optical spectra and the line widths of the transitions as a function of the temperature.[33−36] Here, we will report on such an analysis for PTCDA molecules adsorbed on the (100) surfaces of KCl and NaCl.

Before we turn to the details of the present experiment, we resume some information concerning the adsorption of PTCDA on the KCl and NaCl(100) surfaces which is relevant in the context of the present work. Optical spectra of isolated PTCDA molecules on KCl and NaCl surfaces have been reported before in refs 14 and 37−39. The fluorescence (FL) and fluorescence excitation spectra (FLE) spectra, which are observed directly after deposition of PTCDA onto the cold samples (<20 K), show dominant pure electronic transitions (0−0 transitions) and well-resolved molecular vibronic modes.[37−39] These initial state spectra correspond to molecules that are statistically distributed on the surface, since below 20 K the small mobility does not allow migration. From a statistical viewpoint it is evident that after the deposition most molecules are on terrace sites. Under thermal annealing or intensive optical illumination a change of the spectra to a final state spectrum is observed. The spectrum is blue-shifted with respect to the initial state spectrum by 130 ± 15 cm^{-1} on KCl and 144 ± 15 cm^{-1} on NaCl. This shift, that is best to be seen by the shift of the dominant 0−0 transition, is explained by a thermally or optically induced diffusion of PTCDA molecules from the initially populated terrace sites (*t sites*) to energetically favored sites located at step edges (*s sites*). We note that a small density of steps of monatomic height is always present on the considered surfaces due to growth defects, even when large flat terraces of several hundred angstroms exist.[21,40,41] The adsorption of PTCDA on the *t site* and different possible types of *s sites* on KCl are illustrated by hard-sphere models at the top of Figure 1. The observation of a spectral blue-shift means that the excited state (S_1) is less stabilized upon the transition from the *t* to *s sites* than the ground state (S_0). The azimuthal orientation of the adsorbed molecules is along the [011] directions and is

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identical on both *s* and *t sites*.[39] This site transition was also observed in STM investigations.[21,40] It was already briefly reported that the 0−0 transitions of the molecules on *s sites* exhibit much smaller fwhm compared to the molecules on the *t sites* due to a reduced inhomogeneous line broadening.[39] The details of this broadening will be the subject of this paper.

From STM data it was found that the PTCDA molecules prefer those *s sites* on KCl where the molecules are partially embedded into the step edges.[40] These sites together with other possible step edge sites are illustrated by hard-sphere models in Figure 1 (denoted as X7−X12). Because the theses sites involve the formation of a local vacancy at the step edge, they are addressed as "vacancy sites" (X7−X10) or "deep vacancy sites" (X11, X12). There are different types of both types of these sites, which differ by different numbers of additional rows of K^+/Cl^- ions attached to the sides of the embedded PTCDA molecules.[40] Please note that not all, but only the most relevant, possible sites have been illustrated in Figure 1. From concomitant density functional theory (DFT) calculations we know that the adsorption energies (E_{ad}) of the PTCDA molecules on the different *s sites* differ. For example, for the simple vacancy site (Figure 1, X7), the calculations yield $E_{ad} = -3.28$ eV, while for the "deep vacancy site+1" (Figure 1, X11) a by about −0.5 eV lower adsorption energy of $E_{ad} = -3.76$ eV is obtained.[40,42,43] For comparison, the adsorption energy of the PTCDA on the terrace site (Figure 1, X1) is considerably higher, namely, −2.49 eV.[42,43] The adsorption energies computed by DFT explain why the vacancy and the deep vacancy sites (X7−X12) are preferred with respect to the other step edge sites (X2−X6) and the terrace site (X1). Furthermore, the considerably lower adsorption energy of these sites (X7−X12) with respect to the terrace site (X1) causes that the PTCDA molecules, after they have once adsorbed at the step edges, are stabilized with respect to detachment and diffusion onto the terraces and remain adsorbed at the step edges even at elevated temperatures. Thus, after the sample has been annealed once, a situation that is stable within a certain temperature range is achieved. A similar situation exists on the NaCl(100) surface and was derived from analogous STM[21] and DFT data.[42−44]

In this work, we report that at low temperatures inhomogeneous line broadening is the dominant broadening mechanism for PTCDA molecules on *s sites*. The broadening is remarkably small, corresponding to a narrow spectral distribution of the optical transitions related to molecules at structurally slightly different *s sites*. At elevated temperatures, we find the line widths to increase and, on KCl, the position of the 0−0 transition to shift reversibly to smaller energies. As said above, for the relevant temperature range, migration of the molecules to other sites or structural modifications can be excluded. We have tested a description of our line width and line shift data by a model based on coupling to acoustic phonons. The temperature dependence of the line widths can be successfully described. However, the model fails to reproduce the line shift to smaller energies. Our results yield strategies how narrow line spectra of molecules can be optimized and how information on the statistical distribution of molecules on surface sites can be derived from optical spectra.

2. EXPERIMENTAL SECTION

The experiments were carried out under ultrahigh vacuum (UHV) conditions. The sample could be heated up to 1000 K by a tungsten filament and cooled by liquid helium. The lowest achievable sample temperature was 6 K. The experiment was recently optimized to achieve lowest temperatures; the details will be described in ref 45.

Sample temperatures below 150 K were generally measured by a calibrated silicon diode (DT-670B-SB from Lake Shore Industries). We estimate the total error in the given temperatures to be 1 K. For the NaCl sample, only temperatures below 20 K were measured with the silicon diode, while higher temperatures were measured with a chromel/alumel thermocouple for experimental reasons. For a temperature-dependent recording of optical spectra, we used two different procedures: heating of the sample by a tungsten filament, while keeping the helium flow constant, or reducing the helium flow through the cryostat without filament heating. In the former case, some unwanted stray light from the filament was found in the FL spectra. For the analysis, this was subtracted as a linear background.

For experimental reasons we work with epitaxially grown films of KCl and NaCl instead of bulk cleavage planes. Films of high structural quality were grown on a single crystal Ag(100) sample as described in refs 41 and 46, respectively. The films typically had a thickness of about 10 atomic layers. The PTCDA was sublimed onto the sample from a Knudsen cell. A quadrupole mass spectrometer, operated at $m/z = 392$ amu, was used for measuring the flux of PTCDA. We specify the surface coverage of PTCDA in monolayers (ML). Hereby, 1 ML refers to a coverage of 7.5×10^{-3} molecules per Å^2.[47] We used deposition rates of about 0.003 ML min^{-1} which were achieved at a Knudsen cell temperature of 730 K. During the PTCDA deposition, the sample was kept at 20 K in all experiments. At this low temperature, the molecules stick to the surface in a planar and azimuthally oriented orientation.[38] The PTCDA coverages in the experiments described here were about 0.1% of a ML (on NaCl) and 1% of a ML (on KCl). These coverages are sufficiently small enough that intermolecular interactions between the PTCDA molecules can be neglected.[38] Directly after deposition the molecules are statistically adsorbed on the terraces. For inducing a complete transition of all molecules from terrace to step edge sites (final state spectrum) the sample was annealed for 10 min at 150 K.

For the optical experiments the sample was transferred into a glass tube standing out at the end of the UHV chamber. For FL spectroscopy we used a solid state diode pumped laser (Sapphire LP USB CDRH) operated at 458.0 nm (21 834 cm^{-1}) for excitation. FL excitation (FLE) spectroscopy (often also termed as laser-induced fluorescence spectroscopy, LIF[4,5]) was performed by scanning a dye laser (Coherent 599 standing wave with a 3 plate Lyot filter) operated with coumarin 102 or coumarin 498 as dyes. We used different power densities on the sample of about 0.3−200 W/cm^2, depending on the excitation power of the laser (20−100 mW) and the focusing conditions of the laser beam onto the surface of the sample. The FL light was measured with a spectrometer (Acton 2300i, $f/\# = 4$, $f = 0.3$ m) equipped with a liquid nitrogen cooled CCD camera (Spec-10:100BR(LN)). The experimental resolution of the FL spectra is determined by the spectrometer and amounts to 5−9 cm^{-1} (depending on the width of the entrance slit) for a grating of 1200 grooves/mm. The instrumental broadening of the FLE spectra is limited by the spectral width of the dye laser only and amounts to 1 cm^{-1}. For the FL measurements, the detection times varied between 10 and 220 s. For recording FLE spectra the width of the entrance slit was increased to obtain good statistics. Recording an FLE spectrum, which required tuning of the laser excitation wavelength, took about 30−45 min.

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The FLE spectra were computed from FL spectra recorded for varying excitation wavelengths of the laser by integration of the fluorescence intensity over appropriate wavelength (λ_{det}) regimes, typically from 513 to 689 nm. For PTCDA on *s sites*, smaller regions of the detection wavelengths yielded identical FLE spectra (with only small variation of 0.5 cm^{-1} in the line positions and 0.1 cm^{-1} in the fwhm). Therefore, we generally used the entire fluorescence intensity, integrated over the complete above wavelength regime, for best statistics. However, in some cases, unwanted light from the sample heating was seen in the FL spectra. Then, only reduced wavelength regimes were used. Generally, molecules which are exposed to light can be damaged by photoinduced processes and lose their ability to fluoresce.[48] In our experiments, the FLE intensity, normalized to the excitation intensity, showed only a small decrease ~7% after a radiation time of 1 h. Therefore, photobleaching effects appear to be negligible here.

The DFT calculations were described in detail in refs 40, 42, and 43. For the present work, we additionally investigated the site X10 that has not been considered so far.

3. RESULTS AND DISCUSSION

3.1. Comparison of the Line Shapes in Spectra of PTCDA Adsorbed on *s* and *t Sites*. Figure 2 displays FLE spectra of the 0−0 transition, i.e., the transition between the vibronic ground states, of PTCDA molecules adsorbed at KCl and NaCl *s sites* at low temperatures. The fwhm of these spectra are 4.7 cm^{-1} (21.6 K) for KCl and 3.0 cm^{-1} (6 K) for NaCl. The corresponding FL spectra are given in Figure 3 (overview) and Figure 4 (0−0 transition on expanded scale). In the FL spectra and FLE spectra, the 0−0 transitions are at the same energies within the systematic errors of the experiment (±10 cm^{-1}), which indicates that both types of spectra sample the same ensemble of molecules.

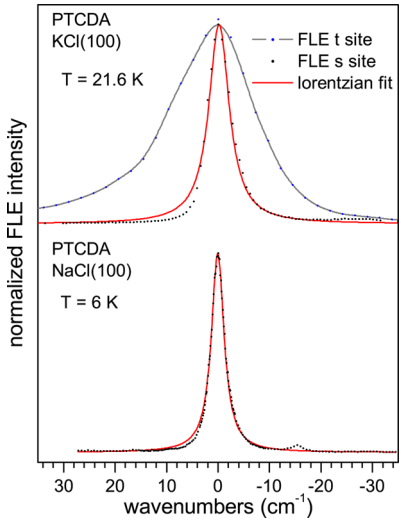

Figure 2. Fluorescence excitation (FLE) spectra of the 0−0 transition of PTCDA adsorbed at step edge sites (*s sites*) on the KCl and NaCl(100) surfaces. In addition, the spectrum of PTCDA molecules on terrace sites (*t sites*) is shown for the KCl surface (gray spectrum at the top). Both spectra of the molecules at the *s sites* correspond in good order to Lorentzian profiles which is demonstrated by the fitted red curves. The fwhm of the spectra of the *s sites* are 4.7 cm^{-1} on KCl and 3.0 cm^{-1} on NaCl. The fwhm of the spectrum of the *t sites* (gray spectrum) is 18 cm^{-1}. All spectra were aligned at the positions of their respective maxima. The detection wavelength regions were 545−690 nm on KCl and 513−690 nm for on NaCl. The small peak at −15 cm^{-1} (on NaCl) is related to a small minority species which has not been identified yet.

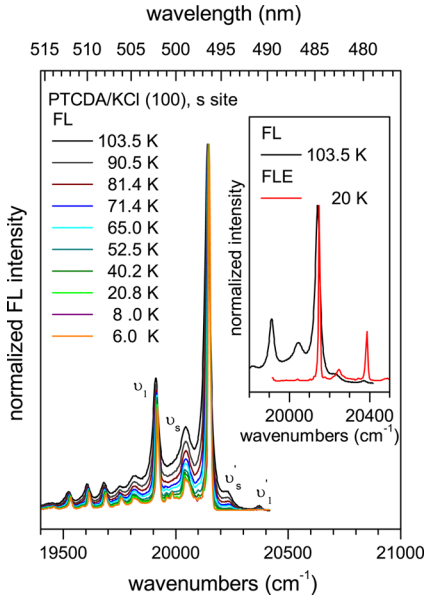

Figure 3. Overview FL spectra of PTCDA adsorbed at KCl *s sites* as a function of the temperature. The excitation wavelength was 458 nm. All spectra were normalized at the strongest line, i.e., the 0−0 transition at 20 149 cm^{-1}. The peaks on the low-energy side of the 0−0 line are due to intramolecular vibronic excitations. The mode ν_1 at 230 cm^{-1} below the 0−0 transition is the intramolecular vibronic mode of lowest energy. The modes at energies up to 230 cm^{-1} below the position of the 0−0 line are vibronic modes of the molecule versus the surface, i.e., surface modes. The strongest mode is marked as ν_S. For details of these modes see refs 38 and 49. The two small peaks at 70−84 and 230 cm^{-1} to higher energies with respect to the position of the 0−0 line, which are successively populated with increasing temperature, are due to FL from excited vibronic states, namely by the modes ν'_S and ν'_1 of the electronically excited S_1 state, to the vibronic ground state of S_0. In order to prove this, the inset shows the FL spectrum at 103.5 K in comparison with the FLE spectrum at 20 K (red curve) which also shows these two modes at identical positions. For further details see text.

However, the line profiles in the FL spectra are broader than in the FLE spectra. For example, on KCl, the fwhm in the FLE spectrum is 4.7 cm^{-1} (21.6 K); the fwhm of the FL spectrum is 10.5 cm^{-1} (20.8 K). A similar trend in the line width is also found for the spectra on NaCl. There we find a fwhm of 3.0 cm^{-1} (6 K) in the FLE spectrum and of 5.7 cm^{-1} in the FL spectrum (20 K). The larger line width of the FL spectra compared to the FLE spectra is explained by the smaller resolution of the spectrometer (varying between 5 and 9 cm^{-1}) compared to the line width of the dye laser (1 cm^{-1}) which determines the experimental resolution of FLE spectra. A possible overlap of the 0−0 line with tails from vibronic modes of small energy and the phonon sideband (see section 3.3) is eliminated by the above noted subtraction of stray light from the filament as a linear background.

For comparison, Figure 2 also displays the FLE spectrum that was measured for PTCDA molecules adsorbed at *t sites* on KCl directly after adsorption. The 0−0 transition of this spectrum has a fwhm of 18 cm^{-1}, which is considerable larger (by a factor of ~4) than the fwhm of the spectrum of molecules on the *s sites* that was obtained after thermal induced migration of the molecules to the step edges. Remarkably, the above given values

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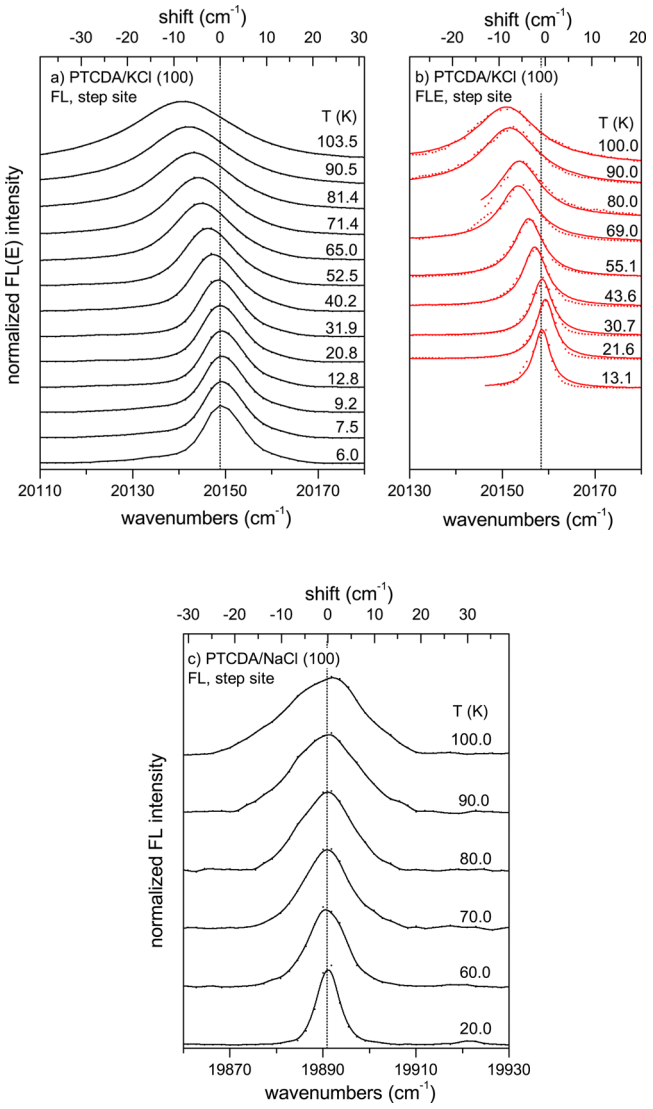

Figure 4. Normalized fluorescence (FL) and fluorescence excitation (FLE) spectra of the 0−0 transition of PTCDA molecules adsorbed at KCl *s sites* (a, b) and on NaCl *s sites* (c, only FL) as a function of the temperature. The solid lines in the FL spectra (a, c) are guide lines to the eye; the solid lines in the FLE (b) spectra are fits of a Lorentzian line shape to the data. The vertical lines are guide lines to the eye to illustrate the shift of the spectra with temperature. The excitation wavelength for the FL spectra (a, c) was 458 nm. The regions in the FL that were used to compute the FL intensity as a function of the excitation wavelength to obtain the FLE spectra (b) were chosen such that spectral regions containing stray light of the heating filament were systematically excluded. In detail, the evaluated regions were 534−597 nm for 13.1 K, 545−690 nm for 21.6 and 30.7 K, 535−618 nm for 43.6 K, 535−690 nm for 55.1 K, 534−555 nm for 69.0 K, 617−618 nm for 80.0 K, 534−618 nm for 90.0 K, and 618−619 nm for 100.0 K.

for the fwhm are subject to variations of the order of about ±30% from preparation to preparation. For instance in ref 39, a slightly larger fwhm of 27 cm^{-1}, compared to 18 cm^{-1} (here), was reported for molecules on *t sites*. As we will explain below, for the *t sites*, this is a consequence from small variations in the surface quality, leading to statistically different situations of inhomogeneous line broadening for repeated preparations.

What is the reason for the difference in the fwhm of the line profiles for the two situations, where molecules are preferentially adsorbed on *t* or *s sites*? We explain this by the fact that the profiles are determined strongly by inhomogeneous line broadening and the mechanisms behind this differ for the two situations. Principally, one may envisage two mechanisms that could be responsible for the inhomogeneous line broadening: intermolecular interactions and/or interactions of the molecules with surface defects, in particular step edges. As reported above, after deposition at low temperatures, the molecules are statistically distributed on the terraces.[40] This leads to a statistical distribution in both the intermolecular and the molecule-to-step edge distances on the surface. Both distributions could impose a corresponding spread in the interactions between molecules or molecules and steps, respectively. They would both be reflected in the variations of the optical transition energies of the individual molecules. As a result, the superposition of the energetically different transitions in the ensemble causes an inhomogeneous line broadening of the spectra. For clarity, we also call this mechanism *site broadening*.

Comparing the spectra of PTCDA on KCl in Figure 2 demonstrates that the broadening of the line is significantly reduced, when the transition of the molecules from the *t sites* to the *s sites* has been completed. For explaining the stronger site broadening of the *t site* spectra, we propose that the interactions of the molecules on the terraces with the nearby steps of the substrate surface constitute the relevant mechanism but that intermolecular interactions are less relevant. Our argument is a geometric one. Attachment of the molecules at about linear steps will obviously reduce the average intermolecular distances and can thus be expected to lead to a more pronounced broadening. However, since we observe the opposite effect, namely a reduction of the broadening upon step attachment, we deduce that intermolecular interactions cannot be the dominating mechanism here. Instead, we propose that the electrostatic and van der Waals interactions of the molecules with the local environment on the surface cause the variations in transition energies. For this effect, steps play an important role. The impact of the steps on the transition energy is indicated by the fact that the step attachment causes a line shift by about 130 cm^{-1} (on average) to higher energies on the KCl[39] and 144 ± 15 cm^{-1} on the NaCl surface.[49] Hence, it is plausible that the steps also modify the transition energies of molecules on the terraces in relation to their distance to the steps. In addition, experiments performed for systematically reduced coverages (1% ML down to 0.01% ML) did not show significant changes in the line widths. This reveals that intermolecular interactions, which would vary with the change in the intermolecular distances and hence the coverage, do not play a role in this regime of small coverages. When the molecules are adsorbed at the step edges, the interactions of the molecules with the step edges are much more similar than for the molecules distributed on the terraces, which results in the experimentally observed smaller site broadening.

3.2. Discussion of the Line Shapes as a Result of Site Broadening at Low Temperatures. In Figure 2, the experimental 0−0 line profiles measured by FLE spectroscopy have been fitted by Lorentzian profiles. The fits describe the experimental spectra very well, except a small and not meaningful discrepancy on the left side. This good fit is astonishing because Lorentzian profiles are usually expected for *homogeneous* line broadening due to lifetime effects and/or temperatures induced dephasing.[50] On the contrary, for *inhomogeneous* line broadening, *Gaussian* profiles are expected, which is clearly not the case here. We also note that instrumental effects cannot be responsible for the line shape because the experimental resolution of the considered FLE spectra is given by the line width of the laser

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which is 1 cm^{-1} and thus considerably smaller. We have also tested that the lines are not subject to broadening from bleaching of the transition by a too high laser intensity as it has been observed in the spectroscopy of single molecules.[9,11,29] We found no effect when the laser intensity was reduced from the standard value of 2×10^5 mW cm^{-2} by 6 orders of magnitude.

Hence, we propose that the line shape, although being Lorentzian, is due to inhomogeneous (site) broadening here, and not due to the noted lifetime effects and/or temperatures induced dephasing. Our main argument is that the broadening calculated on the basis of the lifetime of the excited stated is by 2−3 orders of magnitude too small to explain the experimentally observed line width. If we conservatively estimate the lifetime τ of the excited S_1 state by 0.150 ns,[51] we calculate a line width $\Delta\tilde{\nu} = (c2\pi\tau)^{-1}$ of 3.5×10^{-2} cm^{-1} (c denoting the speed of light). The minimal fwhm values we find are 2.4 (4.5) cm^{-1} for PTCDA on NaCl (KCl), corresponding to a much smaller lifetime of 2.2 (1.2) 10^{-3} ns. One may argue that the lifetime is considerably shortened by a nonradiative decay due to coupling of the excited state to the metallic Ag(100) interface below the alkali halide films. However, for the alkali halide film thicknesses of about 30 Å, which we used, the distance of the PTCDA molecules to the Ag interface is too large to cause sufficient shortening of the lifetime that would explain the line width.[52] A thermal dephasing effect can be also excluded because, as we will report below, temperature induced broadening is of relevant size only for temperatures above 30 K and can thus not be responsible for the line profiles below 20 K considered here.

Our final argument is that we observed a statistical variation of the FLE line width for different preparations. For KCl s sites the FLE values vary from 4.5 to 8.0 cm^{-1} and for NaCl s sites from 2.4 to 3.5 cm^{-1}. Lifetime effects should not vary for different independent sample preparations. Rather this observation demonstrates a dependence of the line width on the exact sample state (the morphology of the surface including the steps and the details of the distribution of the molecules at different step sites), in agreement with an inhomogeneous line broadening scenario. In conclusion, the observed line widths and also their shapes must be caused by an ensemble of molecules on different adsorption sites with different molecule environments leading to *inhomogeneous* (site) broadening of the transition.

For a further understanding of the inhomogeneous line broadening as an effect of site broadening, we discuss the different sites which can be populated by the PTCDA molecules at the steps and their impact on the transition energies. We concentrate on the KCl surface here. We come back to Figure 1, where the possible adsorption sites of PTCDA at the KCl step edge (X2−X12) are illustrated. As said already, these sites differ by the local arrangements of K^+ and Cl^- ions around the PTCDA molecules. Figure 1 also illustrates the trend of the corresponding adsorption energies for the molecule in the ground state (S_0) at the specific sites $E_{ad}^{S_0}(Xn)$ (n = 1−12) calculated by DFT.[40,42,43] Furthermore, Figure 1 shows the adsorption energies ($E_{ad}^{S_1}(Xn)$) of the optically excited states (S_1) which we calculated by an empirical formula that will be described further below. For our interpretation, the sites (X7−X12) which are structurally related to the vacancy site (X7) and the deep vacancy site (X11) are the relevant ones. As noted before, the adsorption energy $E_{ad}^{S_0}(Xn)$ decreases systematically when going from the vacancy site (−3.28 eV) (X7) to the "deep vacancy site+1" (−3.76 eV) (X12). The difference in $E_{ad}^{S_0}$ for the sites X11 and X12 is indeed very small, only 0.01 eV. From their adsorption energies the two sites X11 and X12 are thus equally well identified as the thermodynamically most stable ones. The sites X1, X7, X8, X9, and X11 have already been observed by STM.[40] Of course, other sites with further K^+ and Cl^- ions located around the PTCDA can be envisaged, but have not been observed experimentally, yet. Possibly they are kinetically less accessible.

We propose that the sites X11 and X12, with respective adsorption energies of −3.75 and −3.76 eV are responsible for the 0−0 line observed in the final state spectra at 20.130 cm^{-1}. This assignment is based on the following arguments: (a) These sites are the thermodynamically most stable ones, and a dominant population is thus expected. (b) This assignment also gives a plausible and consistent interpretation of the three (A, B, and C) metastable states which we observed during the preparation of the final spectra by intense illumination.[39] The transition energies of the metastable states are located 15 cm^{-1} (A), 31 cm^{-1} (B), and 46 cm^{-1} (C) below the line position of the final state (20.130 cm^{-1}).[39] We assign these states to the sites X10 (A), the two sites X8 and X9 (B), and X7 (C). The assignment is based on an observation we made. To explain this, we introduce the adsorption energy $E_{ad}^{S_1}(Xn)$ of the excited states. In order to facilitate the formulas, we define that $E_{ad}^{S_1}(Xn)$ is understood as the energy that is related to the optical excitation of the molecule in the vacuum (S_0/S_1 transition) followed by the adsorption process on the surface. This referencing has the consequence that the difference $E_{ad}^{S_1}(Xn) - E_{ad}^{S_0}(Xn)$ corresponds to the optical transition energy of the molecule at that site.

Tentatively, we assumed that the adsorption energy $E_{ad}^{S_1}(Xn)$ of the excited state at the site Xn scales in the same way as the adsorption energy of the ground state $E_{ad}^{S_0}(Xn)$, given by DFT, when one passes from the terrace site (X1) to the deep vacancy site (X11):

$$E_{ad}^{S_1}(Xn) = E_{ad}^{S_0}(Xn) + \tilde{\nu}_0 + \alpha(E_{ad}^{S_0}(X1) - E_{ad}^{S_0}(Xn)) \quad (1)$$

Hereby $\tilde{\nu}_0$ = 20 000 cm^{-1} = $E_{ad}^{S_1}(X1) - E_{ad}^{S_0}(X1)$ is the transition energy between the ground and excited states for the molecule on terrace site (X1) as measured from the energetic position of the 0−0 transition in the experiment. The above parameter α = 130 cm^{-1}/1.26 eV = 1.3% describes the destabilization of the excited states relative to the ground state when passing from the terrace site X1 to the deep vacancy site X11. For α = 0, the transition energy would be site independent, i.e., $\tilde{\nu}_0$. The parameter α is chosen in such a way that the calculated energy of the excited state at the site X11, i.e. $E_{ad}^{S_1}(X11)$, agrees with the experimental value. Equation 1 then yields the transition energies of all sites as

$$E_{ad}^{S_1}(Xn) - E_{ad}^{S_0}(Xn) = \tilde{\nu}_0 + 0.013(E_{ad}^{S_0}(X1) - E_{ad}^{S_0}(Xn)) \quad (2)$$

For the sites X10, X8/X9, and X7, which we proposed for being responsible for the metastable states A, B, and C, this formula predicts the transition energies to be at 22, 29/32, and 48 cm^{-1} below that of the transition of the deep vacancy site (X11) at 20 130 cm^{-1}. The experimental values are 15, 31, and 46 cm^{-1},[39] which are thus in good agreement with the predicted values. This agreement indicates that our assignment of the different sites to the observed transition energies is plausible.

Evidently, the above formula has been derived purely empirically without a physical mechanism behind. At present, without further quantum mechanical calculations, we can give only an argument based on plausibility: As noted, the formula states that the adsorption energy of the excited state is less

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stabilized at the step edge sites than the adsorption energy of the ground state. Hochheim and Bredow have recently found by DFT calculations that the electrostatic interaction of the molecule with the surface and the out-of-plane distortion of the molecule upon adsorption both play a role for the total red-shift of the transition when molecule is adsorbed from the gas phase onto the surface.[44] The respective experimentally measured shifts are −980 cm^{-1} (KCl) and −1307 cm^{-1} (NaCl).[37,38] For the adsorption at the step edges we find an additional blue-shift by 130 and 144 cm^{-1} for KCl and NaCl, respectively. We suggest that this effect is caused by a partial lifting of the molecular distortion due to lateral electrostatic interactions of the PTCDA with the additional ion pairs at a step edge site. In particular, the C_{2v} symmetry of the molecule at the *t site* is broken at the *s site*. Since the electrostatic interactions are dominantly responsible for bonding of the molecule to the surface, it is conceivable that the lifting of the distortion and, hence, the shift of the transition energy scales with the adsorption energy, as it is described by eq 1.

We now turn to the interpretation of the 0−0 line profile of the final state spectrum on KCl itself. As said, we assign contributions of two sites (X11 and X12) to this spectrum. These two sites differ by only 10 meV in $E_{ad}^{S_0}$. According to eq 2, we hence expect a small difference of 1 cm^{-1} in the transition energies, i.e., a difference which is about of the order of the fwhm of the line profile of the 0−0 transition (4.5 cm^{-1}). As can be seen from the respective models in Figure 1, this difference between X11 and X12 is given by an additional ion pair on the right side of the PTCDA molecule. We thus expect that any modifications of these sites by adding additional ion pairs on either sides of the PTCDA at the step edge will cause changes in the transition energies on the above order, i.e., 1 cm^{-1}. We hence suppose that any further variations in the step morphology on both sides of the molecules, e.g. due to kinks, leading to nonstraight step edges, which are so far included in neither the models given in Figure 1 nor the DFT calculations, should cause variations in the transition energies on this order. We thus explain the inhomogeneous line broadening to be due to the statistical variation of the step morphology, i.e., the existence of kinks and vacancies in the vicinity of the PTCDA molecule. Of course, we cannot explain so far why a Lorentzian profile is obtained. We speculate that this is related to the specific kinetics of the formation of the PTCDA adsorption sites and the resulting variation of the local step edge morphology at the sites.

On NaCl the situation is supposedly very similar to that on KCl. The line profile of the final state is also very well fitted by a Lorentzian profile (Figure 2). However, so far DFT calculations of the adsorption energy have been performed for a smaller set of sites only, i.e., the Na^+/Cl^- terminated kink sites (−3.64/−3.60 eV), the *t site* (−2.91 eV), and the vacancy site (−4.13 eV).[42,43] The trend of the adsorption energy for the different types of sites is, however, very similar to that on KCl. As for PTCDA on KCl, we propose that the deep vacancy site contributes dominantly to the final state spectrum. One may argue that this site has not been observed by STM so far;[21] however, we suppose that this is related to a higher coverage used in the STM experiments on NaCl compared to those performed on KCl.[40] The systematically by about 25−30% smaller fwhm of the NaCl spectra (3.0 cm^{-1}) compared to those of the KCl spectra (4.5 cm^{-1}) is remarkable. We speculate that this is due to a smaller variation in the local step morphology, possibly due to the by 10% higher lattice energies of NaCl with respect to KCl.[53]

3.3. Line Broadening at Elevated Temperatures. We start with a remark on the existence of the so-called *phonon sideband* (PSB).[12,54−56]

For this purpose we show a set of FL overview spectra taken for the *s site* on KCl for a series of increasing temperatures in Figure 3. All spectra are normalized at the position of the line of highest intensity, which is the 0−0 transition. The 0−0 transition resembles the zero phonon line (ZPL). The FL spectra show lines at lower energies with respect to the 0−0 transition which can be identified by in-plane intramolecular vibronic modes[38,49] and vibronic modes of the molecule with respect to the surface (surface induced modes).[38] The details of the latter modes will be reported elsewhere.[49] The broadening and the red-shift of the peaks related to the vibronic modes upon heating are identical with those of the 0−0 line. Looking at Figure 3, we see a broad unstructured background in the spectra on the low energy side of the 0−0 transition that increases with temperature and lifts the peaks of the vibronic modes sitting on this background to higher intensity values. This background could be the so-called PSB.[12,54−56] However, we cannot further separate the PSB from our spectra.

The small lines above the 0−0 transition, which increase with temperature (see Figure 3), can be identified as emission lines of vibronic states, which are populated with increasing temperature. Here we see emission from the dominant surface induced vibronic mode ν'_S and the intramolecular vibronic mode ν'_1 of the smallest energy to the vibronic ground state of S_0.[38]

The profile of the 0−0 transitions broaden with increasing temperature. Figure 4 illustrates this for the FL and FLE spectra of PTCDA at KCl *s sites* (Figure 4a,b) and at NaCl *s sites* (Figure 4c). In addition, a reversible red-shift of the position of the transition by −10 cm^{-1} is observed on KCl for a temperature increase to 100 K. However, within the resolution of the experiment, no shift is seen on NaCl. The temperature-dependent values of the fwhm of the 0−0 transitions and the respective shifts are given in Figure 6.

For PTCDA on KCl, the FLE line width varies between 4.5 ± 1.0 cm^{-1} at 13.1 K and 18 ± 1 cm^{-1} at 100 K, while the FL line width varies between 10.0 ± 1.0 cm^{-1} at 6.0 K and 26 ± 1 cm^{-1} at 100 K. The FL line width for PTCDA on NaCl exhibits an analogous behavior. It varies between 5.7 ± 1.0 cm^{-1} at 20 K and 17.7 ± 1.0 cm^{-1} at 100 K. As noted above, the fwhm of the FL spectra on NaCl are generally smaller than on KCl due to a smaller inhomogeneous line broadening.

All these mentioned changes of the spectra are reversible in temperature, which means that the original line profile is reobtained after the sample has been cooled to the starting temperature again. This is shown in Figure 5 for the KCl surface. The sample was cooled down again to 6 K after a heating cycle of about 1 h to 100 K. The same line position was found before and after heating. The very small increase of the fwhm from 10.7 to 10.9 cm^{-1} after the heating cycle is within the statistical uncertainty. The only difference in the line profiles before and after heating is the disappearance of the small shoulder in the region of 20 130− 20 140 cm^{-1}. These observations indicate that the molecules do *not* detach from the step sites at elevated temperatures up to 100 K. In that situation we would expect a stronger red-shift of the order of 130 cm^{-1}, i.e., the reverse line shift that was seen for the migration of the molecules to the steps. However, detachment from steps is also not plausible due to an energetic difference of the adsorption energy at the step sites

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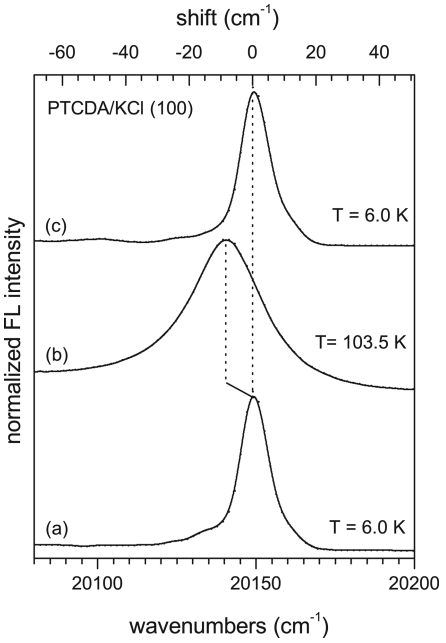

Figure 5. Comparison of the 0−0 line profiles of FL spectra of PTCDA on KCl *s sites* at 6.0 K (a), 103.5 K (b), and 6.0 K (after heating to 103.5 K and cooling again to 6.0 K (c)). The spectra demonstrate that the temperature induced shift (indicated by the dashed vertical lines) and broadening of the line profile are reversible. The change in the fwhm of the line after recooling is very small, namely 2% at the most.

versus that on the terrace sites of about 1.26 eV.[40,42,43] The small change in the line profile (disappearance of the shoulder) may nevertheless indicate small changes in the morphology of the KCl steps in the vicinity of the molecules due to a thermally activated diffusion of KCl ion pairs. Such small variations in the line shape upon repeated heating were often found and support our above interpretation of the line profile by site broadening. In essence, the adsorption sites of PTCDA at the steps are well-defined and stable within the considered temperature range. The broadening, which is observed at elevated temperatures, can thus not be due to temperature-induced disorder or detachment of the molecules from the steps. In addition, coupling to low energy vibronic modes can also not be responsible for the broadening because the first vibronic modes appear at energies of 97 cm^{-1} on KCl and 63 cm^{-1} on NaCl.[49] These modes are thus far away from the 0−0 lines. As a result, we propose that the temperature induced broadening is due to dephasing caused by phonons of the substrates which we will analyze below. Finally, we note that the integrated intensity of the 0−0 transition in the FL spectrum was constant within 20% during the heating cycle to 100 K. This indicates that a dominant thermally activation of nonradiative decay channels does not play a dominant role here and cannot explain the broadening by dephasing.

3.4. Modeling of the Temperature Induced Broadening. For a further quantitative evaluation of the line broadening with temperature, we analyzed the experimentally determined fwhm of the 0−0 transitions as a function of temperature. Because of the higher experimental resolution the analysis of the FLE spectra is more straightforward than that of the FL spectra where the experimental broadening due to the spectrometer plays a role. We thus start with the analysis of the FLE spectra.

The broadening of the line in the FLE spectra with temperature can be described in good approximation by a Lorentzian broadening. This is demonstrated in Figure 4b. All line profiles can be described satisfactorily by Lorentzian profiles with increasing fwhm for higher temperatures. These profiles at elevated temperatures can be obtained by a convolution of the low temperature profile and a Lorentzian profile which exhibits a fwhm increasing with temperature. In our case, the line low temperature profile, which is given by site broadening, is also in good approximation of Lorentzian shape. Since the fwhm of the convolution of two Lorentzians equals the sum of the fwhm of the contributing Lorentzians, the fwhm of the experimentally observed temperature-dependent profiles is given by the sum of fwhm of the low temperature profile and the fwhm of the temperature dependent Lorentzian. We will take advantage of this aspect in our analysis below.

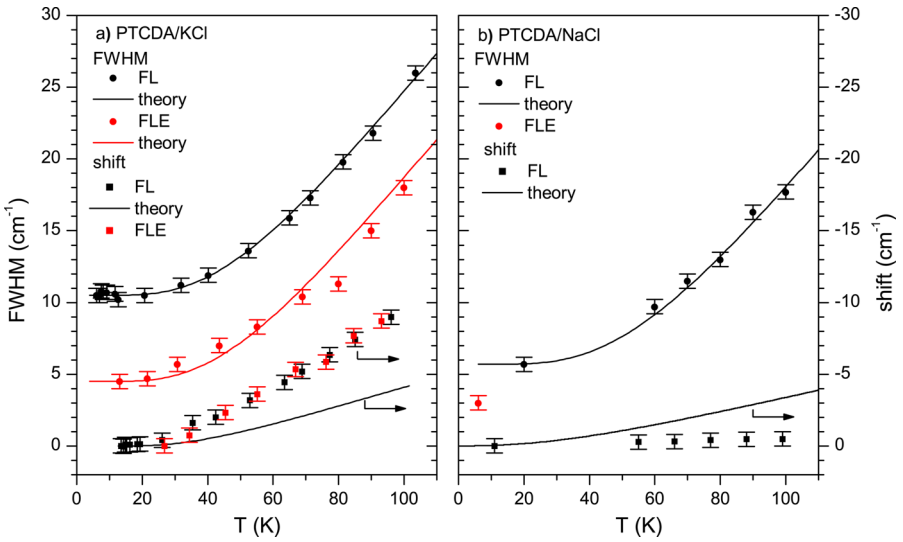

Figure 6. The fwhm and line shift of the 0−0 transition of PTCDA on KCl (a) and NaCl (b) as a function of the temperature obtained from FL and FLE spectra. In addition, the lines are given by the respective model calculations based on electron-acoustic-phonon interactions (T_D^{KCl} = 310 K, T_D^{NaCl} = 360 K, and W = −0.645 for both KCl and NaCl). For further details see text.

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We turn to the question, which model could describe our data? In the regime of 6−100 K the temperature broadening should be dominated by the interaction with acoustics phonons because, as noted above, TLS and LFM are only relevant at very low temperatures (<10 K).[13] Therefore, we have tested a description by a theory developed by Hsu and Skinner which explains the broadening due to interaction with acoustic phonons.[31] We note that this model has been used to describe the temperature induced line broadening for molecules embedded in crystals or matrices.[33−35] It predicts the following temperature dependence of the line width $\Delta\nu$ (fwhm in s^{-1}) of the ZPL:

$$\Delta\nu = \frac{\omega_D}{4\pi^2}\int_0^1 dx \ln\left[1 + 9\pi^2 W^2 x^6 \frac{\exp(xT_D/T)}{(\exp(xT_D/T)-1)^2} \times \left(\left\{1 + W\left(1 + 3x^2 + \frac{3}{2}x^3 \ln\left[\frac{1-x}{1+x}\right]\right)\right\}^2 + W^2\frac{9\pi^2}{4}x^6\right)^{-1}\right] \quad (3)$$

while the line shift $\delta\nu$ is given by

$$\delta\nu = \frac{\omega_D}{4\pi^2}\int_0^1 dx \times \arctan\left\{\frac{3\pi W x^3(1 + W(1 + 3x^2 + 1.5x^3 \ln[(1-x/1+x)]))}{(\exp(xT_D/T)-1)} \times [(1 + W\left(1 + 3x^2 + \frac{3}{2}x^3 \ln[(1-x/1+x)]\right)^2 + \coth\left(\frac{xT_D}{2T}\frac{W^2 9\pi^2}{4}x^6\right)^{-1}\right\} \quad (4)$$

Hereby, W denotes the quadratic electron−phonon coupling constant and T_D the Debye temperature of the matrix material ($\omega_D = k_B T_D/\hbar$). Evidently, the spectral broadening depends on the matrix material through the Debye temperature.

The theory by Hsu and Skinner predicts a Lorentzian line broadening,[31,35] as it is observed here. We used this theory to model the observed fwhm as a function of temperature. For this purpose we calculated the fwhm of the temperature dependent Lorentzian according to eq 3, and we added the fwhm of the Lorentzian of the low temperature profile to this fwhm in order to describe the inhomogeneous line broadening. As noted above, this procedure describes the convolution of the two Lorentzians correctly. The so-obtained fwhm values are shown as a function of the temperature as the solid red line in Figure 6a together with the experimental data. We also calculated the line shift predicted according to this theory, which is shown as the black solid line. The theory by Hsu and Skinner contains the quadratic electron−phonon coupling constant W and the Debye temperature T_D as free parameters. We varied these parameters until a good fit of the experimental fwhm data by the calculated fwhm values was obtained (see Figure 6a). Notably, the electron−phonon coupling constant W has large influence on the fwhm values and only W values in the regime between $W = -0.7$ and -0.5 yield fwhm values which are in the range of the experimental data. We find the best agreement with the experimental fwhm for $W = -0.645 \pm 0.03$ and $T_D^{KCl} = 310 \pm 30$ K. We note that while a variation of W changes the slope of the fwhm versus T curve (increase of W leading to a smaller slope), a variation of T_D causes mainly a vertical shift of the curve.

For the FL spectra the analysis is less straightforward since the low temperature profile is not purely of Lorentzian shape. Because of the experimental resolution of the spectrometer, an additional Gaussian contribution is contained in the line profiles. However, we ignored this and computed the fwhm values as a function of temperature, likewise, as the fwhm from FLE profiles above, as a sum of a fwhm describing the low temperature profile and the fwhm value calculated according to eq 3. We obtained an equally good fit to the experimental FL data with the same parameters used for the FLE data before (see Figure 6a). This justifies our above neglection of the Gaussian contribution to the low temperature line shape. The shift of the 0−0 line with temperature is described qualitatively correct by eq 4, using the above fitted parameters W and T_D. However, the calculated absolute values of the shift are by a factor of 0.5 smaller than the experimental ones (see Figure 6a).

For NaCl, we unfortunately could only measure the FL spectra as a function of temperature. The fwhm data are fitted well by the same value of $W = -0.645 \pm 0.03$ used for KCl, but in combination with a different Debye temperature $T_D^{NaCl} = 360 \pm 30$ K (see Figure 6b). However, concerning the line shift, the agreement is again poor, since experimentally no shift was seen at all, while the model calculation predicts a shift. The reasons for this discrepancy are not clear up to now.

In this context it is interesting to note that the here fitted electron−phonon coupling constant $W = -0.645$ compares well with the values found for other material systems. The following values were reported: $W = -0.79$ for 1,3-diazaazulene in a naphthalene,[35] $W = -0.65$ for perylene in *n*-octane matrices,[54] and $W = -0.65$ for Al_2O_3:Mn^{4+}.[34] All these examples correspond to the case of strong electron−phonon coupling.[31,35]

The finding that both of our data sets (KCl and NaCl) can be fitted by the same value of W is understandable because the bonding of the molecule on the two surfaces is of the same nature and hence the influence of lattice phonons of the two surfaces are comparable. We note that the phonon dispersions of the bulk are similar for KCl[57] and NaCl.[58] The respective literature values of the Debye temperatures are $T_D^{KCl} = 230$ K and $T_D^{NaCl} = 320$ K.[59] For the fitted values we likewise find a smaller value of $T_D^{KCl} = 310 \pm 30$ K compared to $T_D^{NaCl} = 360 \pm 30$ K. However, for both KCl and NaCl, our fitted T_D values are considerably larger than the respective literature bulk T_D values. This is in opposition to the expectation that our surface related T_D values are smaller than the bulk T_D values. For instance, values determined from surface sensitive low energy electron diffraction were reported as $T_D^{KCl} = 146$ K and $T_D^{NaCl} = 174$ K.[60]

3.5. Final Discussion. It is interesting to compare the here observed fwhm values with those reported for other samples where inhomogeneous line broadening was identified. Quite generally, the minimal fwhm values of the 0−0 transitions of 4.5 and 3.0 cm^{-1} are very small in comparison with other inhomogeneous line widths reported in the literature. For example, for different Shpol'skiĭ matrices the following values were given: dibenzanthanthrene in *n*-hexadecane 15 cm^{-1},[9] terrylene in *n*-hexadecane 13.5 or 16.5 cm^{-1},[10,11] and terrylene in dodecane 8 cm^{-1}.[11] These values demonstrate that the inhomogeneous line broadening of PTCDA molecules on *s sites* is rather small which indicates a well-defined and narrow distribution of adsorption sites. For comparison, the smallest line width for PTCDA reported so far at all was 0.7 cm^{-1}. It was obtained for PTCDA dissolved in He nanodroplets[4] and explained by inhomogeneous line broadening from the size distribution of the He droplets.[61]

What did we learn from our experiment? First, the line width at low temperatures is not limited by temperature, but the distribution of the molecules on the different adsorption sites.

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Second, for the small coverages discussed here, the interactions between molecules play only a minor role. Similar to the situation that has been observed for molecules in bulk matrices, inhomogeneous line broadening due to structural variations of the adsorption sites plays a role. In order to achieve even smaller line width, one would have to seek for surfaces, where the molecules adsorb very preferentially at specific and well-defined sites, possibly given by specific surface defects. We note that lifetime broadening of the lines due to quenching of the excitation by dipole interaction with the metallic Ag substrate does not play a role for our KCl films with a thickness of about 10 layers.[52]

The temperature induced broadening can be successfully described by a model otherwise used for molecules embedded in solids. This indicates that the mechanisms for our molecules on a surface are the same as for molecules fully embedded in a bulk matrix. The determined values of the Debye temperatures are larger than the literature bulk values. This is somehow unexpected, since Debye temperatures of surfaces are usually smaller that the respective bulk values. This aspect is not understood up to now, similarly to the failure in the description of the observed peak shifts. The broadening due to dephasing due to coupling to acoustic phonons does not play a significant role for temperatures below 30 K, where the dephasing causes an increase of the line width by about only 10% of the value of the inhomogeneous line width. Extrapolated the broadening caused by the electron−acoustic phonons interactions to 6 K yields a contribution of 1×10^{-5} cm^{-1} to the line width. This is in agreement with estimations given in the literature, where a negligible broadening due to coupling to acoustic phonons and the dominance of other effects is proposed for temperatures below 10 K.[13]

4. SUMMARY

We studied the inhomogeneous and homogeneous line broadening of the 0−0 transitions in FL and FLE spectra of PTCDA molecules adsorbed at step edges on KCl and NaCl (100) oriented surfaces. The inhomogeneous line broadening, which is dominant at low temperatures, is slightly larger for PTCDA on KCl than on NaCl. However, we obtain very small line widths of 4.5 cm^{-1} (KCl) and 3.0 cm^{-1} (NaCl), yielding optical spectra with highly resolved vibronic fine structures. This demonstrates that surfaces of dielectric materials can be used alternatively to Shpol'skiĭ matrices as sample systems for optical spectroscopy of molecules. The residual inhomogeneous broadening is related to variations in the structural details of the adsorption sites of the molecules, which are given in our example by step edges. Since the differences in the adsorption energies for the different sites are small and since kinetic processes play a role, different sites (leading to different transition energies) are populated and contribute to the optical spectra. The resulting inhomogeneous line broadening is thus a consequence of the specific surface related energetic spread in the different adsorption sites. The temperature induced homogeneous line broadening is due to dephasing and can be described by a model based on coupling to acoustic phonons which has formerly been used for molecules embedded in matrixes or crystals.

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Notes

The authors declare no competing financial interest.

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