Structural Information for Conjugated Polymers from Optical Modeling

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Abstract

We use a Frenkel-Holstein model of uncoupled chains in the adiabatic limit to simulate the optical spectra of the conjugated polymer ladder-type poly(*para*-phenylene) derivative (MeLPPP), which is a planar conjugated polymer with especially low interchain interactions. The theoretical calculations correctly reproduce the vibronic spectra and yield reasonable torsion angles between adjacent phenyl rings. The success of this approach indicates that, in contrast to inter-chain coupling, the strong electronic coupling *along* a polymer chain is more appropriately described in the adiabatic limit.

Introduction

Organic semiconductors are increasingly replacing conventional semiconductors in technological applications, such as electronic displays and solar cells. With the release of devices, such as mobile phones and displays, that rely entirely on organic light-emitting diodes (OLEDs) instead of conventional LEDs, these organic semiconductors have reached a stage at which the commercial potential is being realised. Despite their widespread use, the electronic structure, in particular of conjugated polymers, and its dependence on the chain conformation and the morphology of the solid are poorly understood. Consequently, a limit is put on the intelligent design and processing of these materials, regarding technological advances and further innovations.

Central to this problem is the definition of a chromophore.[1–9] For oligomers or low molecular weight compounds the size of a chromophore typically corresponds to the size of the compound. Current theoretical approaches are well developed and can describe electronic interactions between such distinct and well-defined chromophores with high accuracy.[10,11] However, in the case of disordered conjugated polymers, the theoretical description of the excited states becomes more complicated, since a chromophore no longer extends over the entire length of the system. Rather, structural and environmental disorder leads to localisation of excitons, as has been shown previously,[12] thus redefining the chromophore. In addition, in amorphous thin films or solutions optical spectra, which are common probes for electronically excited states, become superpositions of many chromophores with slightly different transition energies and as a result these relatively easily obtainable signatures become less useful. This behavior has also been directly observed in single-molecule spectroscopy for excitons and trapped charges.[13–17]

The question of how to describe the electronic structure in an amorphous ensemble of conjugated polymers has been addressed previously by a method commonly referred to as the 'oligomer approach': the transition energies of polymers are compared to those of oligomers with increasing length and if a match has been found the length of the oligomer is taken to correspond to the length of the chromophore and the length is taken as 'effective conjugation length'.[18] A polymer is then seen as a sequence of chromophores of different lengths (due to conformational variations) which can be used to account for the observed spectra. Whilst being useful, this approach does not provide any insight into the formation of these chromophores and the parameters that govern their size.

Some of us have recently presented a theoretical description based on electronic coupling along an extended polymer chain that reproduces many of the characteristic features observed in amorphous films of conjugated polymers.[1,12,19] We use the same model presented there in the present work: starting from the picture of a 'classical' exciton band with excitons delocalised across the entire chain, even small amounts of disorder lead to localisation of the lowest energy excitons onto segments of about 10-20 repeat units which in turn fill the entire polymer chain. These excitons are referred to as LEGSs (Local Exciton Ground States). Higher energy excitons localised on the same segments of the chain are referred to to as LEESs (Local Excited Exciton States) while those delocalised over the entire chain are called QEESs (Quasi-Extended Exciton States).[20–23] The spatial extend of LEGSs can then be used as a theoretical definition of a chromophore and corresponds to the phenomenological definition obtained via the 'oligomer approach'.

Our model is based on the adiabatic limit, i.e., we consider the coupling between repeat units, J, to be strong compared to the phonon energy, $\hbar\omega$: $|J| \gg \hbar\omega$. Another choice, the anti-adiabatic limit ($|J| \ll \hbar\omega$), has been widely used in the models presented by Spano and co-workers.[10,11,24–26] They have been highly successful in describing the optical spectra of molecular ensembles, such as perylene and pentacene crystals, as well as explaining the effects of inter-chain interactions of the vibronic spectra of conjugated polymers (aggregation effects), e.g. P3HT.[27] The spectra of conjugated polymers, such as MEH-PPV and polydiacetylene, have also been accounted for using these models,[28,29] where the coupling between repeat units is thought of as J-coupling, while inter-chain coupling is described as H-coupling. However, the associated values for the intra-chain values are about an order of magnitude lower compared to values obtained when fitting an exciton model to the transition energies of a series of oligomers.[18]

In this letter we present spectral fitting for the conjugated polymer MeLPPP (Fig. 1) to probe whether the adiabatic limit can be used to describe such systems. The persistance length of MeLPPP is high, simplifying the theoretical treatment. More importantly, however, the inter-chain interactions are distinctively low by design, as the bulky side chains prevent electronic interactions between chains. Aggregation effects are basically not observed as a consequence and hence the spectra are dominated by intra-chain coupling.[30] We demonstrate that the Frenkel-Holstein Hamiltonian in the adiabatic limit can reproduce the absorption and emission spectra while using only parameters which can be obtained ab-initio, as well as a single vibrational energy, $\hbar\omega$, taken directly from observed spectra, and by adjusting the torsional angle between adjacent phenyl rings and its associated disorder. To our knowledge, this is the first verification of the applicability of the Frenkel-Holstein model within the adiabatic limit to model experimental data.

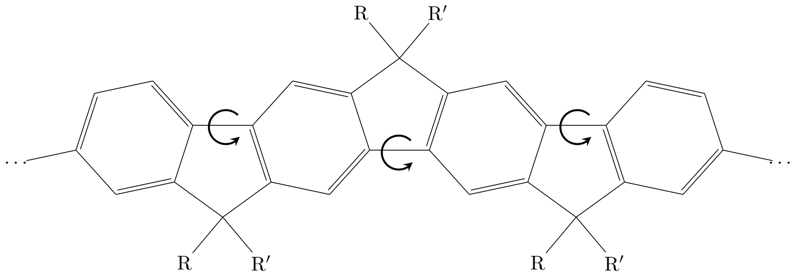

Figure 1: Structure of MeLPPP with torsional angles along the polymer backbone indicated.

Methodology

In the following discussion each parameter within the model has been fixed to a given value apart from the exciton transfer-integral, J_n, which is modeled as

$$J_n = J_{\mathrm{DD}} + J_{\mathrm{SE}} \cos^2 \phi_n, \tag{1}$$

where J_{DD} and J_{SE} are the dipole-dipole and super-exchange contributions to the transfer-integral and ϕ_n is the torsional angle between neighboring moieties, here modeled as a Gaussian random variable with mean ϕ_0 and standard deviation σ_ϕ. For further discussion of the model used we refer to previous publications.[1,12,19] Note that Eq. (1) directly implies that angles of $\phi_n = \pi/2$, albeit significantly reducing the transfer-integral, do not cause J_n to vanish and as such do not necessarily confine the exciton to either side of what is usually referred to as a conjugation break.

Invoking the Born-Oppenheimer approximation in the model (either sufficiently small number of moieties, N, or $\hbar\omega \ll |J|$, which is the adiabatic limit; if $\hbar\omega/|J| \sim 0.1$ then $N \lesssim 20$) allows for a direct evaluation of transition intensities. Within this limit, the vibronic progression for a linear polymer is given as (ignoring energy factors),

$$\frac{A^{00}}{A^{10}} = \frac{I^{00}}{I^{01}} = \frac{\mathrm{PN}}{g_1^2} = \frac{\left(\sum_{n=1}^{N} |\Psi(n)|^4\right)^{-1}}{g_1^2}, \tag{2}$$

where PN is the participation number, which is a measure of the delocalization length of the exciton and hence a direct probe of the chromophore length, g_1^2 is the monomeric Huang-Rhys parameter, and $\Psi(n)$ is the wave function of the corresponding LEGS. As the polymer under consideration has a fairly rigid chemical structure that does not allow for bending of the chain, we ignore higher-order post-Condon effects in our discussion, however explicit expressions have been derived by some of the authors[31] and Spano and co-workers[32] elsewhere. The localization of the exciton to segments of the chain corresponding to the LEGSs of the Hamiltonian means that the chromophore length is significantly smaller than the polymer length (usually 10-20 monomers). A consequence of this is that a much simpler Hamiltonian can be used to calculate the excitonic eigenstates and the expressions for the vibronic progression can be used to calculate the corresponding peaks. This has the effect that, computational cost is significantly reduced and allows the calculation of long polymer chains ($N > 500$) in large ensembles (number of chains, $M > 500$) leading to better averages in the properties. For the system under investigation here, due to the stiffness of the polymer chain and the localizing effect of even small amounts of disorder, both numbers, N and M, can be fixed to 100 while still giving good statistics. The eigenstates of this simplified (tight-binding) Hamiltonian then correspond to the vibrationally relaxed excited states of the polymer and as absorption can occur into any of these states each will contribute to the vibronic progression. For emission, Kasha's rule is assumed, i.e., higher excited states (LEESs and QEESs) relax non-radiatively into the lowest available, dipole allowed state before de-excitation occurs under photoluminescence. These states correspond to the LEGSs on the chain and therefore only these contribute to the photoluminescence.

Most parameters appearing in the Hamiltonian (moiety energy ε_0, dipole-dipole transfer integral J_{DD}, superexchange transfer integral J_{SE}, exciton-phonon coupling constant g_1) are available from ab-initio calculations (for further details see[12,19,33]) or, e.g. $\hbar\omega$, from experiment. We have used the values given in Tab. 1 which we have used previously to model poly(*para*-phenylene) (PPP). The use of these parameters is justified as the polymer backbone of MeLPPP is a PPP structure and the added side-chains do not contribute directly to the π-conjugated system, hence influencing the optical properties only indirectly, for instance by limiting the torsional flexibility of the polymer. The value for $\hbar\omega$ was directly extracted from the experimental spectra and ranges from 0.17 to 0.185 eV as a weak function of Temperature, T.

Table 1: Hamiltonian parameters used for the simulation of MeLPPP.

Parameter	Value
ε_0	6.05 eV
g_1	1.91
J_{DD}	-0.40 eV
J_{SE}	-1.30 eV
$\hbar\omega$	$\sim$ 0.175 eV

The structural data, ϕ_0 and σ_ϕ, is not as readily available and can therefore be treated as an optimization variable in the simulation allowing the extraction of this data from spectral fitting. The optimization of these parameters was achieved using the Nelder-Mead optimization procedure[34,35] to minimize the deviation of the calculated from experimental spectra using the energy of the 0-0 and 1-0/0-1 vibrational peaks and the intensity ratio, A^{10}/A^{00} and I^{01}/I^{00}, as optimization targets.

Results and discussion

We have used spectral data for the ladder-type polymer MeLPPP[30] to optimize our calculations (see Fig. 2). The parameters used are given in Tab. 1 and calculations were performed for all temperatures presented in Fig. 2 (between 80 K and 300 K); the equilibrium dihedral between neighboring moieties and the associated disorder were taken as optimisation variables, $\hbar\omega$ was taken directly from the experimental spectra for a given T. We proceeded to fit both the absorption and emission spectra for different sets of (ϕ_0, σ_ϕ), providing structural information on the ground and excited state, respectively. Due to the strong coupling of the exciton to the benzoid-quinoid distortion normal mode a stiffening of inter-moiety bonds is expected leading to (i) planarization, i.e., a smaller ϕ_0 and (ii) a reduction in the disorder, i.e., smaller σ_ϕ in comparison to the corresponding absorption spectrum for a given T. It can also be expected that these parameters show a reduced dependence on the temperature for the emission spectrum.

Fitted spectra for two different temperatures are shown in Fig. 3. As can be seen, the fitting to the 0-0 and 1-0/0-1 vibronic peaks is good; we largely ascribe the deviation at high energies and the not-accurately reproduced line-width to our model only including the coupling to a single normal mode.

The fitted structural parameters and their dependence on the temperature are shown in Fig. 4. The torsion angles found, about 14.5° for the ground and 13° for the excited state, are consistent with expectation. The results lead to the following conclusions: the adiabatic model used in this simulation reproduces the absorption and emission spectra at all observed temperatures. The values employed in our model to fit the absorption and emission spectra of MeLPPP polymer, i.e. $\varepsilon_0 = 6.05$ eV and $J = -1.7$ eV agree remarkable well with the parameters that result from fitting the transition energies in a series of LPPP oligomers with an exciton model,[18,30,33] $E(N) = \varepsilon_0 + 2J\cos[\pi/(N+1)]$, where N is the number of phenyl rings, which are $\varepsilon_0 = 6.05$ eV and $J = -1.6$ eV. From this agreement we conclude that our adiabatic approach is suitable to describe the electronic structure of conjugated polymers with predominantly intra-chain and negligible inter-chain interactions. Additionally, as described elsewhere,[1] the simulations may be used as a structural probe, providing information on the torsional angles and conjugations lengths within a polymer sample. The lack of long-range order in amorphous polymer films prevents the use of conventional techniques, such as X-ray diffraction, to probe the structure. Conformational information obtained by our approach, combined with device performance, is therefore suitable to provide guidelines on materials development.

For the case of MeLPPP we find that for the ground state the torsional angle increases from 13.8° at 80 K to 15.5° at 300 K with an almost linear dependence, while for the excited state the angle shows almost no temperature dependence and is at about 13.1°

more planar than the ground state. The findings can be explained by considering exciton migration to low-energy chromophores before de-excitation. As shown in previous work[36] shorter chromophores for a given mean torsional angle, or longer chromophores for a smaller mean torsional angle are lower in energy. As a result, the simulation of the emission spectra using an ensemble of chains with Gaussian disorder will give on average a lower torsional angle with apparently higher disorder. A more quantitative modeling of the emission spectra requires the simulation of exciton migration from the higher energy to the lower energy chromophores.

Conclusions

The accurate reproduction of experimental spectra using the Frenkel-Holstein model in the adiabatic regime leads to four conclusions: (i) the exciton in the polymer is localized by disorder and the resulting states are accurately described by LEGSs, LEESs, and high-energy QEESs; (ii) due to localization, the chromophore length renders the adiabatic regime more applicable to model the systems than the anti-adiabatic regime which becomes increasingly important for longer chromophores; (iii) conformational data for the polymers can be extracted from spectroscopic signatures; (iv) excitons diffuse to shorter, low-energy chromophores before decaying radiatively. This proof-of-principle calculation using a relatively simple model in the appropriate limit shows the power of spectroscopic methods to elucidate the structure of the polymers. In the case of MeLPPP, which shows very little to no aggregation effects, the model performs well, and in fact can be applied to many polymers that are poly(*para*-phenylene) and poly(*para*-phenylene vinylene) derivatives.

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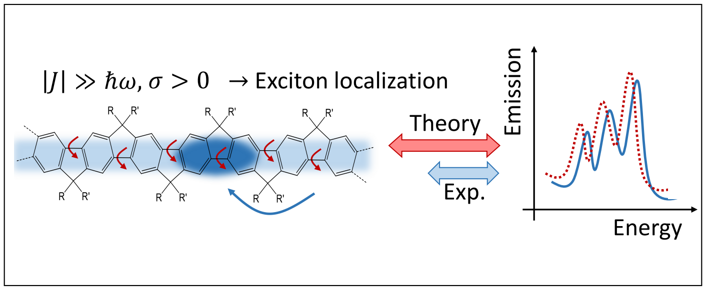
Graphical TOC Entry



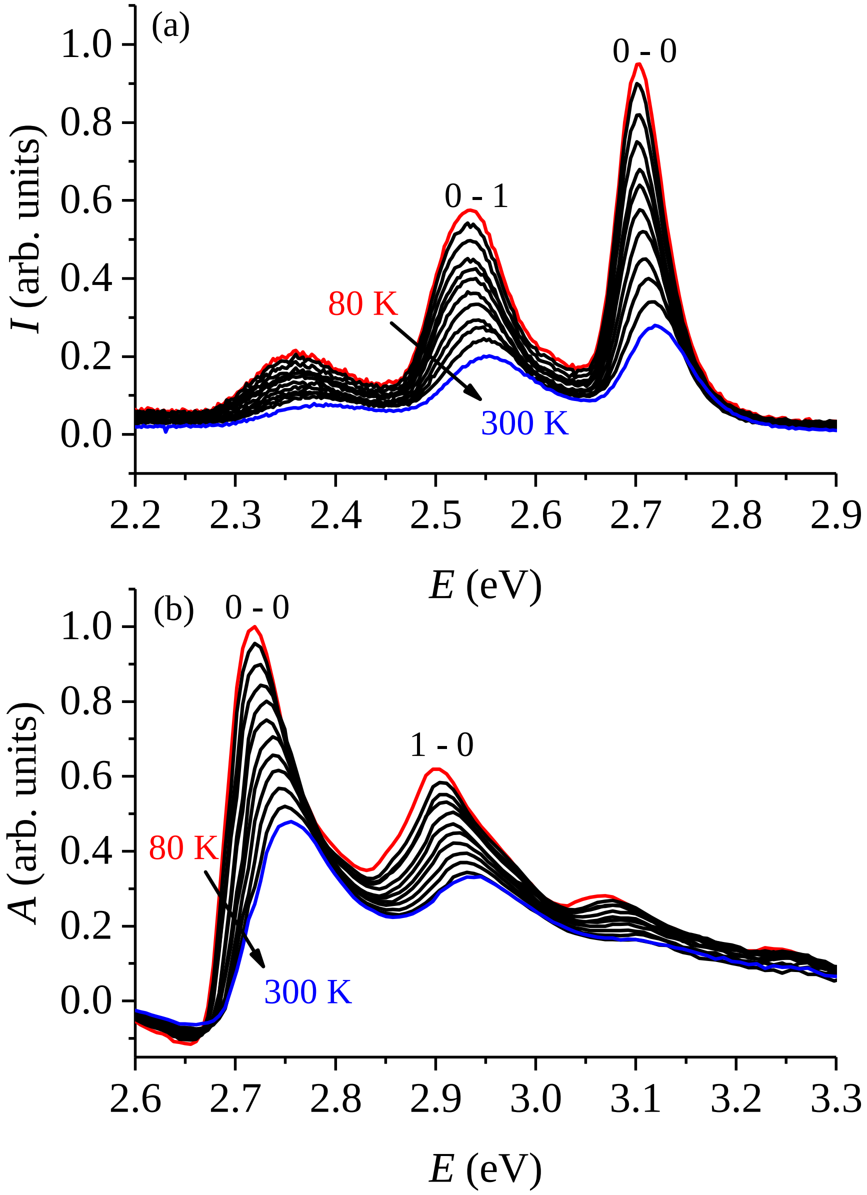


Figure 2: Experimental MeLPPP thin-film (a) photoluminescence and (b) absorption spectra at different temperatures. Reproduced from[30]

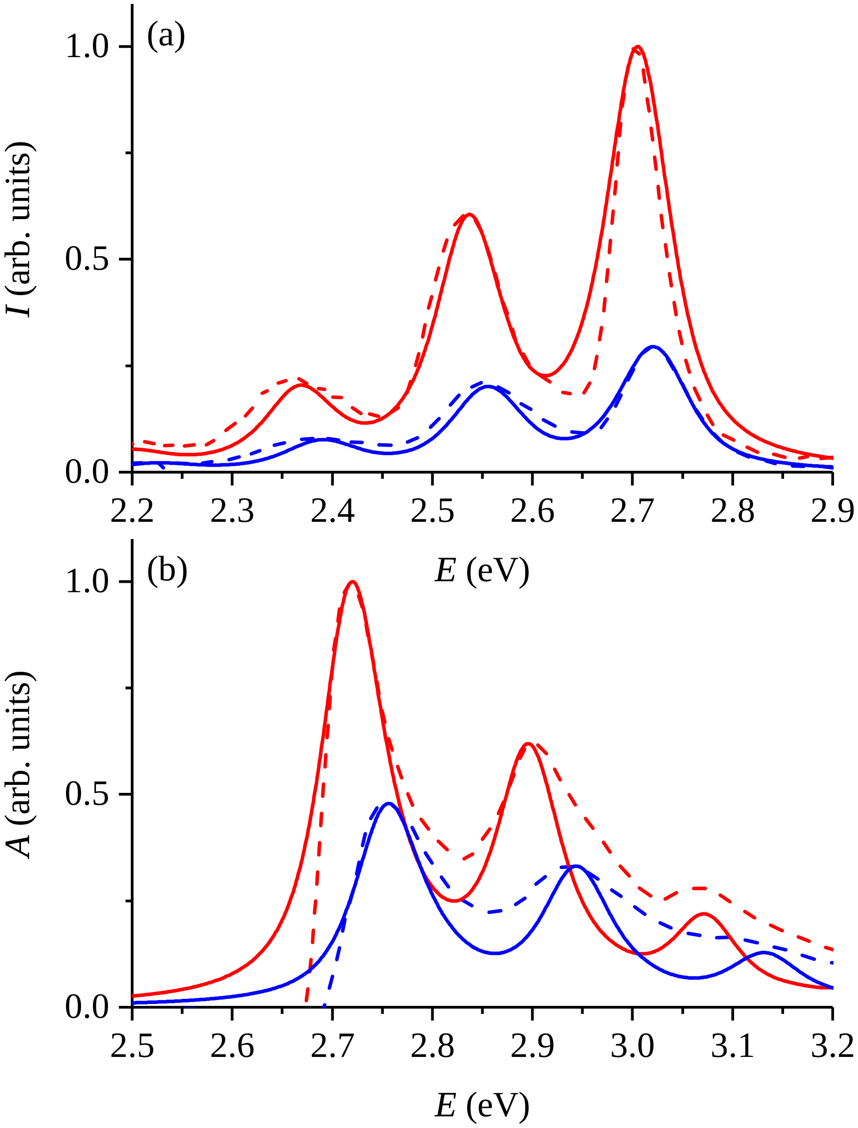


Figure 3: Experimental (dashed) and theoretical (bold) spectra for (a) photoluminescence and (b) absorption of MeLPPP thin-films at 80 K (red) and 300 K (blue).

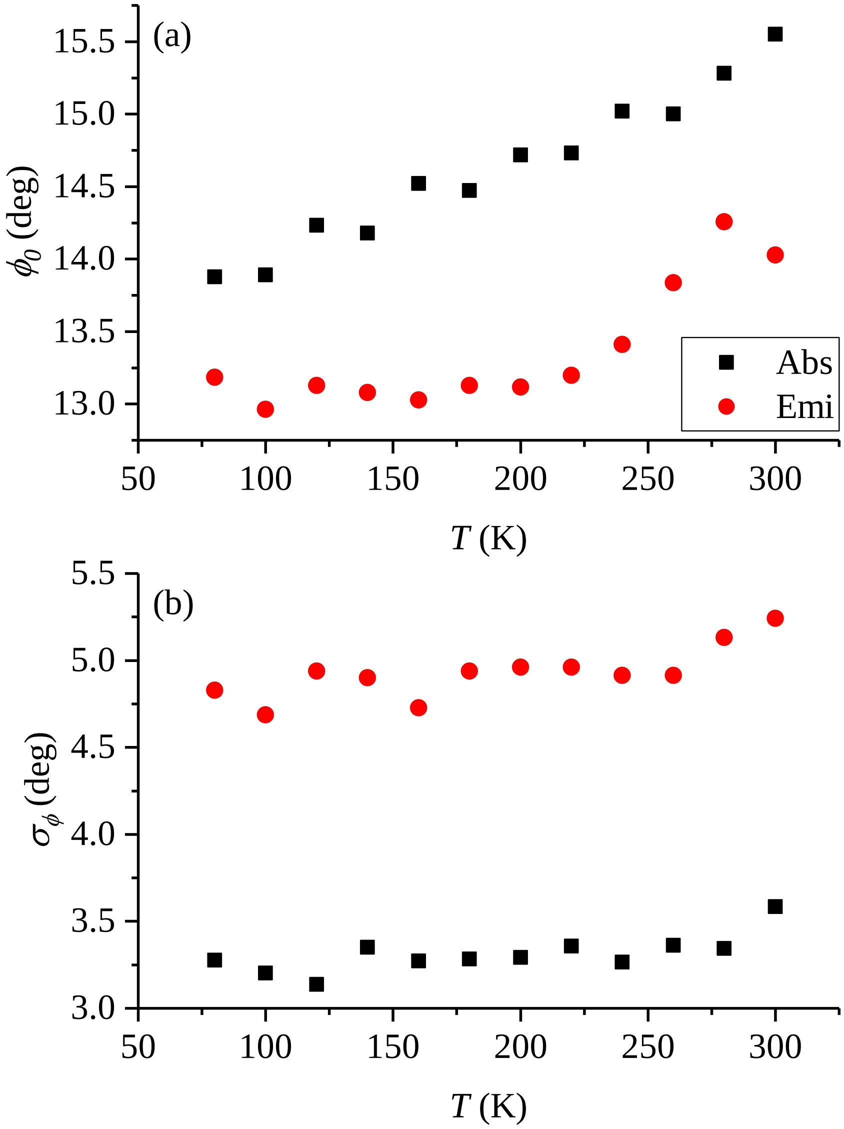


Figure 4: Variation in the mean, ϕ_0, and standard deviation, σ_ϕ, of the dihedral angle for the ground states and excited state as extracted from the absorption and emission spectra.