

Limitations of Generic Chromophore Concept for Femtosecond Vibrational Coherences

Marcin Andrzejak, Tomasz Skóra, and Piotr Petelenz*

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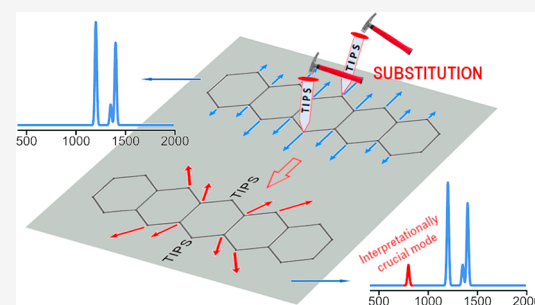
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ABSTRACT: The spectrum of vibrational coherences modulating transient triplet–triplet absorption of bis-triisopropylsilylethynylpentacene that propagate in the course of the fission process from the singlet state of this molecule to the triplet manifold has been lately reproduced by ab initio calculations. This has led to the conclusion that, contrary to a recent hypothesis, spontaneous generation of coherent vibrational wave packets is not a constitutive feature of singlet exciton fission. Here we demonstrate by calculations that the corresponding spectrum of unsubstituted pentacene is significantly different, so that the two systems cannot be viewed as different models of the same generic chromophore. This shows that femtosecond pump–probe spectra of vibrational coherences are sensitive to subtle features of molecular structure, which we identify here, thereby rationalizing the registered spectral differences. The crucial factor is the substituent-induced coupling between some pentacene normal modes that in other contexts may be safely ignored. Overall, our study indicates that this kind of spectroscopy requires great caution in using the generic chromophore concept for interpretative purposes and experimental design.



1. INTRODUCTION

Singlet exciton fission is presently extensively investigated because of its prospective application in increasing the efficiency of photovoltaic devices by charge carrier multiplication. In order to attain ultimate understanding of the process and optimize its conditions, considerable effort is invested in synthesizing and examining new compounds endowed with fissionable singlet state.^{1–9} Their majority derive from tetracene and pentacene, which at interpretational level are treated as generic chromophores in the sense that the relevant photophysical mechanisms operative in the acenes are tacitly assumed to be unaffected by chemical modifications. The most common substituents, designed to make the samples solution-processable, are the triisopropyl-silylethynyl (TIPS) groups. On their example, we will now demonstrate that even this seemingly innocuous change may critically influence interpretation of crucial experimental data. Vibrational coherence spectroscopy, widely used in recent singlet fission studies,^{4,8,9} seems to be particularly sensitive to this effect.

The fission process, consisting in the decay of an intramolecular singlet state into an entangled pair of triplets located at different molecules, is a very fast one. For this reason, major progress in this field that has been registered in recent years is largely due to application of femtosecond spectroscopy, enabling one to probe in real time the progress of the radiationless transition in hand, which can be accomplished, for instance, by measuring transient absorption of the emergent triplet states in the pump–probe regime.

These transients are modulated by coherent vibrational wave packets (CVWP) generated by the pumping pulse in the initially excited singlet state; those, according to recent literature, freely penetrate into the intramolecular triplet manifold, being practically unaffected by the boundary between the S_1 and TT potential energy surfaces (PES).

In a study performed by Stern et al. on TIPS-tetracene⁴ (bis-triisopropylsilyl-ethynyl-tetracene), a similar technique enabled the authors to detect wave packets (in 760 cm^{-1} normal mode) created directly in the triplet manifold as a kind of byproduct of the singlet fission process (without any precursor CVWP in the singlet manifold). On the other hand, the results of the pump–probe experiment performed by Musser et al. for the related TIPS-pentacene,⁸ when assisted by theoretical study,¹⁰ demonstrated that in this system no such phenomenon occurs, i.e., that all coherent wave packets that reach the triplet manifold are those induced by the initial pump pulse. This refuted the hypothesis that generation of a coherent vibrational wave packet is a general constitutive feature of singlet fission.

The above conclusion was based on comparison of the coherence power spectrum obtained from accurate ab initio calculations¹⁰ with the experimental results of Musser et al.⁸

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The resultant meticulous inventory revealed quantitative agreement between the vibrational coherences generated by the pumping pulse and those detected by probing the transient triplet–triplet absorption. Here we will show that to reach this conclusion it was absolutely necessary to do the calculations with the TIPS substituents explicitly taken into account (as was actually done)¹⁰ and that the generic pentacene chromophore alone would indeed fail to render a pivotal feature of the underlying physical mechanism. We will also analyze the physical causes of this sensitivity to the presence of substituents, with potential consequences for future studies of other singlet-fissionable materials in mind.

So far, in such studies the conjectures highlighting crucial involvement of vibrational coherences in singlet fission have been continually reappearing,^{4,11–14,15–19} and it is to be expected that this trend will be further pursued. The femtosecond coherent vibrational wave packet spectroscopy is the technique of choice for this kind of experimental investigations. In this context, the interpretational paradigm of this spectroscopy seems to be a fundamental problem, which we are addressing in this paper.

Our strategy is to compare (in Section 3) the vibrational coherence spectra which we theoretically predict for pentacene with those of TIPS-pentacene¹⁰ (the latter, as mentioned above, exhibited very good agreement with experiment).⁸ To make the comparison valid, in the present treatment we will exactly repeat our previous procedure (briefly summarized in Section 2). The differences between the calculated spectra of the two compounds will be exposed and rationalized to pinpoint the underlying physical mechanisms

2. THEORY

2.1. Theoretical Simulation of Coherence Power Spectra. The gist of the experiment of Musser et al., the results of which are our main reference, consisted in using a femtosecond laser pulse of 10 fs duration to generate vibrational wave packets on the S_1 potential energy surface.⁸ Those, according to the presently accepted paradigm, subsequently penetrated onto the PES of the triplet-pair state, to be interrogated after a variable time delay by a (probe) white-light continuous pulse. Transient absorption of the probe pulse was recorded in the energy ranges corresponding to the $T_2 \leftarrow T_1$ and $T_3 \leftarrow T_1$ electronic transitions. The absorption intensity was found to oscillate in time, being periodically modulated by the CVWPs propagating on the T_1 PES. Each of the spectrally resolved $T_2 \leftarrow T_1$ and $T_3 \leftarrow T_1$ absorption signals was subsequently Fourier-analyzed, and the resultant Fourier amplitudes for individual vibrational modes were integrated over the corresponding ($T_2 \leftarrow T_1$, $T_3 \leftarrow T_1$) energy range, yielding the power spectrum to be interpreted.

It should be mentioned for completeness that the scheme presented above is oversimplified, as it disregards a third (dump) laser pulse, interposed between those already described. It served to eliminate the contributions from the CVWPs generated by the pump on the S_0 PES. By ignoring them in our simulations, we implicitly take the dumping pulse into account.

In this work the general premises and basic formulas for predicting the CVWP power spectrum are the same as in our recent paper¹⁰ and its Supporting Information, to which the reader is referred for details. Here is their brief summary.

The calculations are rooted in a wave function-based model describing temporal evolution of a wave packet generated in

the S_1 state of a chromophore molecule.¹⁰ The molecule (with the vibrational wave packet on its S_1 PES) is viewed as a moiety of a hypothetical dimer, prepared by the pumping pulse in its excited singlet state *eg*. This state is assumed to radiationlessly relax to the triplet-pair state *tt* by triplet exciton transfer to the other moiety, while a second triplet exciton (accompanied by the originally generated vibrational wave packet) is left behind. The mechanism of this transition is not explicitly decreed, presumably being mediated by a black box that consists of the originally unexcited moiety (which takes care of energy balance) and the surroundings.

In other words, for further considerations the above dimer model is projected onto the single-molecule subspace of the originally excited moiety, to which the coherent vibrational wave packet is presumably confined. Within the coherence lifetime, the molecule's PES (that supports the packet) changes from singlet to triplet, the latter serving as the initial state for the probing $T_n \leftarrow T_1$ transition.

The above picture, although obviously simplified, is conceptually convenient. In reality the pertinent electronic states are delocalized over both moieties, but the requisite matrix elements of the Hamiltonian and dipole moment are readily obtained from those derived in the localized representation. The resultant coherence spectra, defined correct to a constant factor, are not affected by this transformation.

The fundamental equation that describes the temporal modulation of net absorption intensities in transient triplet spectra (eq 3 of ref 10) was derived by time-dependent perturbation theory, deviating from the textbook standard only in assuming the optical transition to have a nonstationary vibrational wave packet as the initial (or final) state. The latter and the former apply, respectively, to the pumping ($S_1 \leftarrow S_0$) and the probing ($T_n \leftarrow T_1$) stages, and the equation we are referring to above combines both stages. Each band $I_{T_n}^{\text{int}}(\omega_\lambda)$ in the calculated coherence power spectrum (vide infra) corresponds (in the experiment of Musser et al.⁸) to the squared module of the Fast Fourier Transform coefficient (IFFT²) for an individual normal mode ω_λ , integrated over the T_n energy range.

According to experimental conditions in the measurements we are theoretically reproducing,⁸ the pump pulse is assumed to be instantaneous (as justified by its actual duration of 10 fs), and its spectral shape (centered at 2.18 eV and covering the 500–650 nm range) strictly mimics that used in the pertinent experiment (cf. the Supporting Information of ref 10). The calculated $I_{T_n}^{\text{int}}(\omega_\lambda)$ signals are averaged over the estimated experimental error in time domain, for which we adopt the same value of 20.7 fs as in our preceding paper.¹⁰ The set of technical details of the experiment in hand is completed by adding that the texture-related inhomogeneous broadening of spectral lines is approximated by Gaussian distribution with dispersion $\sigma \approx 450 \text{ cm}^{-1}$, derived from the experimentally observed differences between the spectra of the TIPS-pentacene thin film and its constituent individual crystalline domains,^{20,21} and also consistent with the pentacene single crystal spectral characteristics.

The needed molecule-specific input data are the following: (i) The S_1 state energy of 1.75 eV for TIPS-pentacene, and 1.83 eV for pentacene (0–0 lines²²). We adopt these experimental values in our present calculations. (ii) The Franck–Condon parameters (FCP) for the pumping

Table 1. Frequencies and Franck-Condon Parameters of Interpretationally Relevant Normal Modes for Low Energy Singlet–Singlet and Triplet–Triplet Transitions in the Pentacene Molecule

normal mode	wavenumber (cm ⁻¹)					dimensionless displacement				
	S ₀	S ₁	T ₁	T ₂	T ₃	S ₀ -S ₁	S ₁ -T ₁	S ₀ -T ₁	T ₁ -T ₂	T ₁ -T ₃
ω_2	264	262	261	261	262	-0.678	-0.105	-0.785	-0.257	-0.152
ω_3	617	613	613	614	609	0.197	-0.029	0.212	-0.014	-0.037
ω_4	648	628	631	637	627	-0.103	0.016	0.109	0.080	0.036
ω_5	764	757	755	768	762	0.327	-0.090	0.213	-0.042	-0.047
ω_6	797	804	807	804	802	-0.111	-0.121	-0.258	0.233	0.218
ω_9	1019	1048	1051	1049	1045	-0.071	-0.043	-0.120	-0.030	-0.079
ω_{11}	1186	1183	1183	1180	1182	-0.402	-0.018	-0.434	0.043	-0.014
ω_{12}	1209	1221	1216	1216	1220	-0.527	-0.200	-0.701	-0.567	-0.330
ω_{13}	1333	1312	1271	1264	1285	-0.172	-0.019	-0.311	-0.200	-0.085
ω_{14}	1410	1382	1435	1433	1429	-0.755	0.179	0.214	0.994	0.562
ω_{15}^a	1433	1426	1358	1351	1382	0.448	-0.229	0.958	-0.537	-0.315
ω_{16}	1497	1511	1496	1508	1496	-0.136	0.182	0.578	0.577	0.301
ω_{17}	1558	1536	1535	1556	1539	0.495	0.105	0.494	-0.040	-0.065
ω_{18}	1576	1578	1592	1578	1569	-0.181	0.007	-0.212	0.384	0.183

^aNote that this frequency considerably decreases upon excitation. As mode numbering is based on the ground state, this may be confusing when confronted with the presented spectra.

(S₁ ← S₀), probing (T₂ ← T₁, T₃ ← T₁), and radiationless (T₁ ← S₁) electronic transitions in all relevant normal modes, which have been calculated as described below.

2.2. Evaluation of Franck–Condon Parameters. The Franck–Condon parameters for the S₁ ← S₀, T₂ ← T₁, T₃ ← T₁, and T₁ ← S₁ electronic transitions are the prime input data to generate the coherence power spectrum of interest. To calculate them for the pentacene molecule, we have applied the TDDFT approach with the B3LYP energy functional and def2-TZVPP basis, in the TURBOMOLE V6.4 2011 implementation.²³ This guarantees perfect consistency with our previous paper,¹⁰ which we have now followed also in treating the T₁ state as the ground state in the triplet manifold; then, the higher triplet states have been generated in subsequent TDDFT procedure. Next, we have projected the geometry changes on the normal modes of the initial and final state of each transition of interest.

On the basis of the arguments presented earlier,¹⁰ in the conditions of the Musser et al. experiment⁸ the FC parameters relevant for the S₁ ← S₀ pumping step are those obtained by projecting the S₀-S₁ geometry change on the normal modes of the (final) S₁ state, as usually practiced in absorption spectroscopy; the same applies to the radiationless T₁-S₁ step. In contrast, for the transitions in the triplet manifold, the geometry change is projected on the normal modes of the (initial) T₁ state on which the CVWPs that drive the probed absorption are moving. These values are listed in Table 1 for all FC-active normal modes (the modes exhibiting negligible parameter values for all the transitions under consideration are omitted).

To reduce the computational effort, in our recent calculations¹⁰ the target 6,17-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) was mimicked by 6,17-bis-silylethynylpentacene (SE-pentacene), which was justified by the fact that the influence of the remote propyl groups on the chromophore electronic states is negligible, and the alkyl vibrations are also well separated. Nonetheless, owing to the presence of SE groups, even for the latter molecule the number of normal modes inevitably exceeds that of pentacene. On the basis of frequency and displacement analysis, we have pinpointed the SE-pentacene modes that have no counterparts

in pentacene to be those previously labeled as ω_1 , ω_7 , ω_8 , and ω_{10} . To facilitate the comparison, we skip these numbers in our present labeling of pentacene modes, which then becomes entirely consistent with that of ref 10. The coherence amplitudes of those modes for TIPS-pentacene were below the detectability level anyway, except for $\omega_1 \cong 250$ cm⁻¹ (which we ignored then because its frequency was beyond the range covered by the referential experiment⁸ and consistently ignore here).

Direct confrontation indicates that in most modes the qualitative picture for pentacene is very similar to that earlier obtained for TIPS-pentacene.¹⁰ Specifically, it turns out that for the radiationless T₁ ← S₁ electronic transition, the FC parameters are negligibly small in all relevant normal modes, so that in actual calculations we follow ref 10 in assuming that the vibrational quantum numbers ν do not change when the wave packet crosses the boundary between the two PES.

This prevailing picture notwithstanding, for a few modes the situation in pentacene substantially differs from that in its TIPS derivative. It so happens that these differences are interpretationally crucial.

3. RESULTS AND DISCUSSION

3.1. Differences between TIPS-Pentacene and Pentacene Spectra. The mission of a generic chromophore is to serve as an idealized proxy of the actual chromophore, providing a more general view of a problem by ignoring those details of the molecular structure that are deemed insignificant in the pertinent context. It usually also offers a chance to reduce the needed computational effort.

In the present case, neither of those is our aim. Pentacene is introduced here as a generic chromophore for a slightly different purpose: its comparison with TIPS-pentacene is intended to highlight the details that are relevant specifically for fission studies performed by means of femtosecond pump–probe spectroscopy of vibrational coherences. The clues in this regard will be provided by revealing the features of the TIPS-pentacene coherence spectrum that cannot be reproduced by the generic pentacene model.

Figure 1a,b shows the calculated power spectra of vibrational coherences modulating the T₂ ← T₁ and T₃ ← T₁ transient

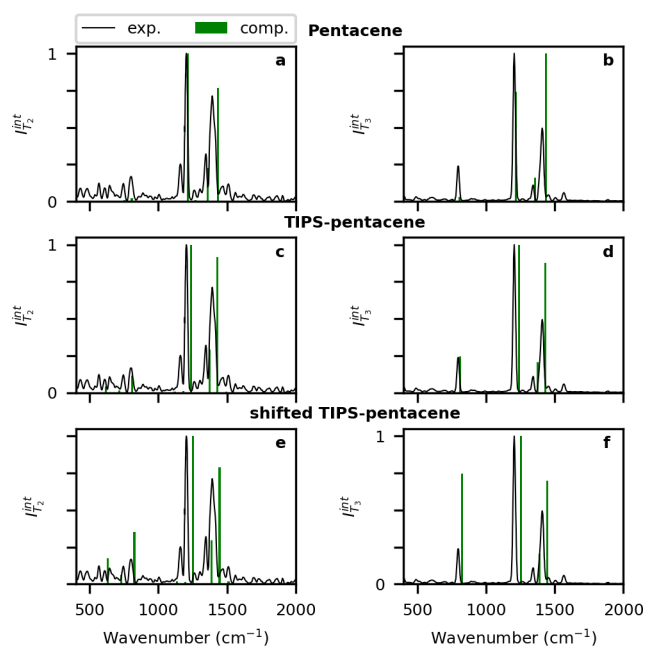


Figure 1. Vibrational coherences (green sticks) modulating the (a) $T_2 \leftarrow T_1$ and (b) $T_3 \leftarrow T_1$ transient absorption, calculated for pentacene (viewed as generic chromophore), compared with the corresponding experimental spectrum measured for TIPS-pentacene (from ref 8, solid black line). Panels (c) ($T_2 \leftarrow T_1$) and (d) ($T_3 \leftarrow T_1$): the same TIPS-pentacene experimental spectrum compared with the spectrum calculated specifically for TIPS-pentacene (using the same methodology). Panels (e) ($T_2 \leftarrow T_1$) and (f) ($T_3 \leftarrow T_1$): analogous comparison for TIPS-pentacene but with the $S_1 \leftarrow S_0$ 0–0 line energy replaced by that of pentacene (0.08 eV blue shift).

absorption of pentacene in a hypothetical pump–probe experiment strictly analogous to that of Musser et al. They are based on the set of input parameters described above, to be compared with the corresponding TIPS-pentacene spectra (Figure 1c,d) generated in ref 10 within exactly the same computational scheme (but with the input parameters calculated specifically for that molecule). In all figures the continuous lines represent the reference experimental spectra of TIPS-pentacene,⁸ and the calculated amplitudes are normalized against the most intense signal of the spectrum in hand.

The TIPS-pentacene amplitudes, calculated in ref 10 and reported here for comparative purposes, need some comments concerning their quality with respect to the experimental references. In the first place, the experimental $T_2 \leftarrow T_1$ spectrum exhibits a high level of background noise, which results from the low intensity of the pertinent electronic transition, combined with inherent errors of the complex data collection and numerical processing procedures. It complicates the analysis of the experimental spectrum, as the real, less intense bands are difficult to distinguish from random wiggles. Specifically, the apparent coherence signal at around 1150 cm^{-1} is an artifact generated at the stage of eliminating (with application of the dump pulse) the contributions from the CVWPs generated by the pump on the S_0 PES.⁸ The situation is much clearer for the $T_3 \leftarrow T_1$ spectrum, which (owing to higher intensity of this electronic transition) displays a much lower level of background noise. For both spectra, however, the prominent bands at around 800 cm^{-1} , as well as 1200 and

1400 cm^{-1} , are well reproduced in both the frequency and intensity domains.

The consistent overestimation of vibrational frequencies by several percent is only to be expected, as it is an inherent feature of most ab initio methods and of the B3LYP functional applied here, as well as of the harmonic approximation. It could have been corrected with one of the scaling procedures often used in such situations, but we preferred to leave the results of our calculations unaltered, having the (quite small) errors under control. Besides, in order to show precisely the location of the calculated bands we used the stick representation. The stick spectrum seemingly overrates the signals around 1400 cm^{-1} . The discrepancies, however, are mostly due to the larger experimental widths of these bands with respect to the rest of the spectrum, thus the relative integral intensities of the experimental bands would be much closer to the theoretical predictions. In view of the fact that photoinduced absorption is actually a nonlinear optical phenomenon (which makes the intensities especially sensitive to the quality of applied methodology) and that calculations for excited states (especially the triplet ones) are more prone to errors than those for the ground state,¹⁰ the agreement with the experiment that has been attained¹⁰ may be considered nearly perfect.

The imperfect match between the TIPS-pentacene spectra (calculated and experimental alike) and the ones calculated for the native pentacene is readily justified by the fact that these are different molecules, after all. However, in the respect in which pentacene (serving as generic chromophore) should precisely mimic its TIPS derivative, the two differ so blatantly that it disqualifies pentacene in this capacity. The discrepancies in the high frequency region, although for $T_3 \leftarrow T_1$ large in scale, are of lesser interpretational importance because none of those coherences was ever claimed to be generated in the course of singlet fission, so they are unlikely to shed light on that phenomenon. In contrast, the role of the $\omega_6 = 802 \text{ cm}^{-1}$ mode is pivotal in assessing the recently postulated⁴ proclivity of the fission process to spontaneously generate coherent vibrational wave packets. The agreement of our earlier results¹⁰ with the experiment⁸ demonstrated that in TIPS-pentacene the pumping step entirely accounts for coherent activity of all modes detected in the probing step, which eliminated the need to invoke coherence generation in the fission step itself. The fact that no coherence deficit was detected in the ω_6 mode is especially important because it contrasts with the situation in TIPS-tetracene⁴ where the coherences experimentally observed just in a related 760 cm^{-1} mode were reported to emerge in the course of the fission process.

The essential point is that, had our calculations at that time used pentacene as a model for TIPS-pentacene, the minuscule intensity predicted for ω_6 would have led us to a contrary (and erroneous) inference, so that our ultimate (negative) conclusion concerning fission-induced spontaneous CVWP generation would be reverted. This demonstrates that in this specific context neither could pentacene serve as a model for TIPS-pentacene, nor vice versa, since their spectra drastically differ just in the region that is interpretationally crucial for fission considerations;^{4,10} manifestly, the generic chromophore approach is blatantly inapplicable here. On the other hand, to most intents and purposes of standard UV–vis vibronic spectroscopy (except high-resolution low-temperature measurements), both molecules can be used practically on equal footing as the same generic chromophore. Our present

objective is to determine what makes the femtosecond pump–probe spectroscopy different in this regard.

3.2. Causes of the Differences: Numerical Test. In our input, the molecules of pentacene and TIPS-pentacene differ in two respects: singlet excitation energy (point *i* in the itemized list above) and Franck–Condon parameters (point *ii*). We have tested the influence of the former by repeating the calculations using the FC parameters of TIPS-pentacene and the 0–0 line energy of the native pentacene. The resultant coherence spectra are displayed in Figure 1e,f.

Evidently, the blue shift of 0.08 eV has substantially increased the amplitude of the ω_6 coherences. Hence, it has to be noted that even a minor spectral shift of the $S_1 \leftarrow S_0$ absorption underlying the pumping process may significantly affect the relative contributions of different vibrational modes to the measured coherence power spectrum.

It is clear, however, that the low amplitude of the ω_6 wave packets in the spectra of unsubstituted pentacene is definitely not caused by the higher energy of its 0–0 line; on the contrary, this location promotes the contribution from ω_6 coherences. Despite this favoring factor, the ω_6 mode in the pentacene spectrum is less prominent than in its TIPS derivative, so the difference must have its roots in the FC parameters (vide infra).

3.3. Role of TIPS Substituents. As inferred in Section 3.2, the main dissimilarity between the pentacene and TIPS-pentacene vibrational coherence spectra must be due to some difference(s) in their Franck–Condon parameters. In this context one should bear in mind that, in order to considerably modulate triplet–triplet absorption, a normal mode must combine (i) substantial supply of coherent wave packets in the singlet state, with (ii) substantial wave packet detectability in the triplet manifold.

As mentioned above, the former requirement implies that the pumping pulse, when creating the S_1 state, must simultaneously excite in this mode nonnegligible contributions from at least two vibrational eigenstates (differing in the quantum number ν), which necessitates an appreciable FC parameter for the $S_1 \leftarrow S_0$ transition. Likewise, it ensues from the latter of the two stipulations formulated above that, by virtue of the selection rule derived in the past,¹⁰ a similar inference applies to FCP modulation of the $T_n \leftarrow T_1$ transitions.

When applied to pentacene, the above criteria clearly explain why neither of the two modes (cf. Table 1) with frequencies in the 700–800 cm^{-1} range effectively modulates triplet–triplet absorption. Coherent wave packets in the ω_5 mode (at about 760 cm^{-1}), with displacements occurring primarily along the short axis of the molecule and concentrated mostly in its central part (Cf Figure 2a), although abundantly generated by pumping due to a large $S_1 \leftarrow S_0$ FC parameter (0.327), are practically unable to modulate $T_n \leftarrow T_1$ absorption because for both T_2 and T_3 the corresponding parameters (−0.042 and −0.047, respectively, according to Table 1) are negligible. The situation is reversed for ω_6 (around 800 cm^{-1}), for which detectability is promising (with FCPs of about 0.2), but coherence generation by the pump is rather inefficient (FCP = 0.111). The largest displacements in this mode contain a large component parallel to the L molecular axis (cf. Figure 2b) and are distributed more or less evenly over all benzene rings, with slight prevalence of the peripheral ones.

In TIPS-pentacene, however (for complete FCP sets see ref 1), the heavy TIPS side groups constrain the motion of the

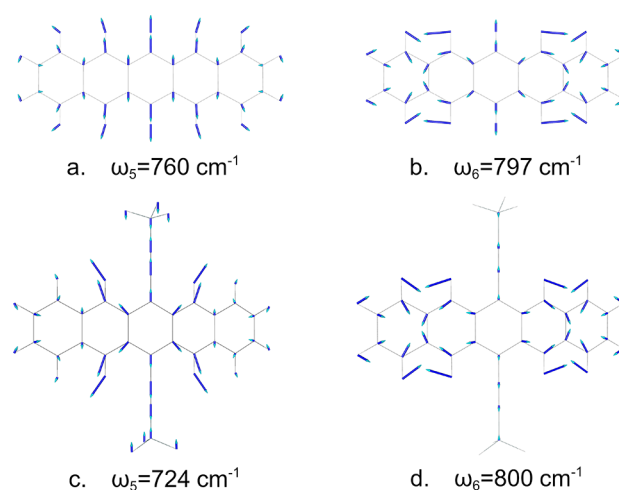


Figure 2. Displacement patterns for the ω_5 and ω_6 normal modes of the pentacene and TIPS-pentacene molecules.

ring carbon atoms to which they are attached, dramatically distorting the ω_5 displacement pattern. When the ring bonds parallel to the short molecular axis (cf. Figure 2a) stretch with the positions of the 6 and 13 carbons fixed, the angles between the bonds in the central ring are inevitably deformed and this ring expands/contracts sideways, i.e., along the L axis of the molecule (as depicted in Figure 2c). This motion is bound to interfere with ω_6 vibrations (Figure 2b), and the emergent coupling affects both modes, as displayed in Figure 2c,d.

As a consequence, in TIPS-pentacene the module of the ω_5 FCP for pumping ($S_1 \leftarrow S_0$) diminishes to 0.195 but that for the $T_2 \leftarrow T_1$ probing transition grows to 0.119 (which makes this coherence spectrally discernible) with its $T_3 \leftarrow T_1$ counterpart barely affected (−0.030).

The impact of the coupling is much more pronounced for ω_6 . Apart from the probing $T_2 \leftarrow T_1$ transition, for which the Franck–Condon parameter is practically unchanged (0.216), the FCPs for ω_6 increase substantially, namely to 0.309 for $T_3 \leftarrow T_1$ probing and to 0.304 for pumping. Especially the latter is crucial, ascertaining a sufficient wave packet supply to make this mode appear pretty prominently in both probing transitions. It is due to this effect that in the experimental modulation spectra the ω_6 mode is the most noticeable low-frequency coherence.

The above effect is reminiscent of intensity borrowing, which is a rather common phenomenon in UV–vis spectroscopy. By mixing the electronic states of a molecule, a perturbation (be it a vibration or a substituent) transfers a part of the transition moment from an allowed (lending) electronic transition to a spectroscopically mute (borrowing) state, thereby making the latter spectroscopically observable. Analogously, the coupling mediated by a heavy substituent endows the original pentacene ω_6 mode with the substantial $S_1 \leftarrow S_0$ FC parameter of 0.304, thereby enabling this vibration to efficiently form coherent wave packets in the pumping $S_1 \leftarrow S_0$ transition, which then conspicuously appear in probing, owing to this mode's substantial FC parameters in the triplet manifold (of which one is also enhanced by the coupling). The ω_5 mode, on the other hand, gains a sufficient increment in the $T_2 \leftarrow T_1$ FCP to become discernible in probing, since its supply in pumping, although reduced by the coupling, is still considerable.

4. CONCLUSIONS

In contrast to traditional (for instance, absorption) spectroscopies, vibrational coherences observed by femtosecond pump–probe technique are sensitive to even minor energy shifts of the absorbing electronic state. Thus, small dissimilarities in this regard between two compounds may lead to their qualitatively different coherence spectra.

Besides, the two-step nature of the pump–probe technique makes it very selective, as it imposes on any normal mode two independent selection rules concerning the Franck–Condon factors: one in the singlet (pumping) and the other in the triplet (probing) manifold. In consequence, the mere mass of an inert substituent may suffice to modify these selection rules by mode coupling, substantially changing the coherence spectra. As we have shown on the pentacene/TIPS-pentacene example, even if the coupling affects just a couple of modes, but at least one of those happens to be interpretationally crucial for the phenomenon under study, this may dramatically alter not only the quantitative but also the qualitative conclusions concerning the photophysical mechanisms under study. In practical terms, such a situation defies the usefulness of the chromophore in hand in the capacity of a generic chromophore. Yet, its unsuitability may be nontrivial to detect, since the mode couplings introduced by substitution (while influencing the coherence signals) may barely affect the mode frequencies, so that the latter may seemingly corroborate resemblance to the unsubstituted chromophore.

As a consequence, ill-considered application of the generic chromophore concept may lead to qualitatively erroneous interpretations. As far as we can see, pitfalls of this kind may be detected only by accurate quantum chemistry calculations for all the states involved in pumping and probing. Overall, our results suggest that special caution must be exercised when applying intuitive notions of chemical similitude that underlie the generic chromophore concept (firmly established in absorption and emission spectroscopy) for planning and interpreting pump–probe vibrational coherence experiments.

AUTHOR INFORMATION

Corresponding Author

Piotr Petelenz – *The K. Gumiński Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, 30-387 Kraków, Poland*; orcid.org/0000-0001-5481-1958; Phone: +48 12 6325456; Email: petelenz@chemia.uj.edu.pl

Authors

Marcin Andrzejak – *The K. Gumiński Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, 30-387 Kraków, Poland*

Tomasz Skóra – *Department of Complex Systems, Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland*; orcid.org/0000-0003-4394-4928

Complete contact information is available at:
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Notes

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