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Isotope Shifts and Intersystem Crossing for Pentacene in *p*-Terphenyl. A Model System for Single-Molecule Dynamics

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We calculate isotope shifts and perform a normal-coordinate analysis to explain the observed systematic variation with isotopic composition of the intersystem crossing for deuterated pentacene in *p*-terphenyl. The tuning of a near resonance of the first excited singlet state S_1 and vibrational levels of T_3 by $S_1 \leftarrow T_3$ isotope shifts is analyzed. The physics of isotope shifts is discussed, and an explanation is given for the phenomenological sum rule dictating additivity of isotope shifts upon multiple substitution. We discuss mechanisms through which the host matrix interactions influence isotope shifts and increase inhomogeneous broadening.

1. Introduction

The mixed molecular crystal of pentacene in *p*-terphenyl has recently been the subject of renewed interest, as it has proved to be an ideal testing ground for single-molecule experiments.[1] The pentacene guest molecules substitutionally occupy one of four well-defined low-temperature crystal sites. For high-quality crystal flakes, small excitation volumes, and very low concentration, exceedingly narrow inhomogeneously-broadened lines have been observed.[2] For pentacene-d_{14}, the small degree of inhomogeneous broadening has enabled sidebands in the $S_1 \leftarrow S_0$ 0−0 excitation spectrum[3,4] to be resolved. These bands derive from molecules that contain ^{13}C in natural abundance, and/or ^1H due to imperfect deuteration. The so-called isotope shift of these bands with respect to the main band results from the change of the energy gap between the two electronic states, owing to the dependence of the zero-point energy on isotopic composition. In previous work, similar observations for the $T_1 \leftarrow S_0$ 0−0 transition of selectively enriched naphthalene and anthracene established an approximate sum rule for such isotope shifts, which holds that the shift for a multiply-substituted isotopic isomer equals the sum of the shifts of the corresponding singly-substituted isotopomers.[6,7] (This should not be confused with the exact sum rule valid for the sum of the *square* of normal-mode frequencies.[5]) For pentacene, this rule has been shown to hold to a remarkable degree of accuracy for both ^{13}C and ^1H isotope shifts.[3,8]

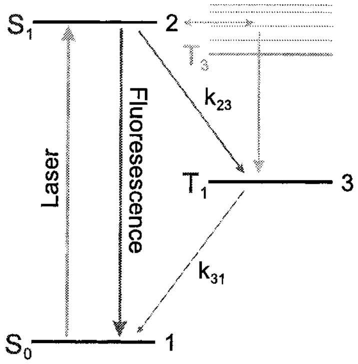

Figure 1. Level scheme of pentacene. As indicated in gray, vibrational levels of a higher triplet (T_3) can mediate intersystem crossing from S_1.

TABLE 1: Change in ISC upon γ and/or ϵ ^1H Substitution Relative to the Perdeuterated Case of O_1 and O_2, for Which Rates of Respectively 173.6 and 134.7 kHz Were Found[a]

	Δk_{23} (kHz)		
		γ	$\gamma\gamma$
O_1	0	−17.7	−31.0
ϵ	+13.7	−3.4	−25.3
$\epsilon\epsilon$	+32.1	+13.4	
$\epsilon\epsilon\epsilon$	+53.7		
O_2	0	−10.9	−27.8
ϵ	+8.8	−2.5	
$\epsilon\epsilon$	+17.9		

[a] The experimental error in these values is typically some 2−3 kHz.

The small degree of inhomogeneous broadening in single-molecule experiments also enabled the determination of the overall $S_1 \rightarrow T_1$ intersystem crossing (ISC) rates k_{23} (see Figure 1) of pentacene molecules for a wide range of isotopic compositions.[4] Analysis of these data showed that k_{23} exhibits an approximately additive trend for both the O_1 and O_2 sites of *p*-terphenyl. As seen in Table 1, the substitution of ^1H in the ϵ symmetry equivalent positions (see Figure 2) causes an increase of k_{23}, while substitution in the γ positions causes a decrease. It was reasoned that the observed k_{23} dependence most probably results from changes in vibrational frequencies, as these constitute the only molecular property of potential relevance significantly affected by changes in isotopic composition. However, vibrational frequencies increase when substituting a ^1H for a ^2H in roughly the same way for the various substitution positions. The opposite sign of Δk_{23} for ϵ and γ substitution instead suggests a dependence on the electronic structure of the molecule. As isotope shifts depend on both vibrational frequencies and electronic structure, and are additive for multiple

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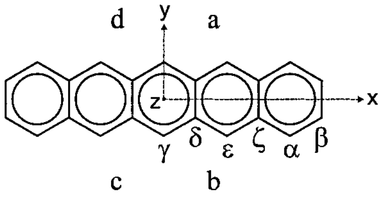

Figure 2. Molecular structure of pentacene, $C_{22}H_{14}$. The greek letters label the six symmetry-inequivalent carbon positions. The roman letters are used to discriminate between spatially inequivalent isotopic substitutions.

substitutions, it appeared likely that the observed trend was somehow caused by isotope shifts. In this work, we will give a full account of quantum-chemical and normal-coordinate calculations that corroborate this interpretation of the dependence of the intersystem crossing on isotope shifts.

The pentacene $S_1 \rightarrow T_1$ ISC rate is known to be exceptionally sensitive to the (site of the) host matrix. For *p*-terphenyl at liquid-helium temperatures, the rates for pentacenes in sites O_3 and O_4 exceed those for pentacenes in sites O_1 and O_2 by 2 orders of magnitude.[9,10] According to one hypothesis, this sensitivity results from site-dependent static deformations from planarity; these were examined through molecular packing calculations.[11,12] However, the splittings of symmetry-equivalent isotope-shifted satellite bands, which offer a qualitative measure of the distortion of pentacene, do not appear significantly different for the four sites.[13] Indeed, refined molecular packing calculations[14] show only moderate differences in the distortion of pentacene between the various *p*-terphenyl sites, which makes it unlikely that static distortion can account for the 2 orders of magnitude difference in ISC.

An alternative model proposes mediation of ISC through out-of-plane vibrational levels. This mechanism was proposed by Amirav et al.[15] to explain experiments on anthracene in supersonic jets. In this scheme, ISC from S_1 is mediated, through spin−orbit coupling (SOC) and subsequent internal conversion, by vibrational levels of an *n* th triplet state $\{T_n^k\}$ (see Figure 1). According to these authors, the ISC rate is proportional to

$$\sum_k \frac{V_{\mathrm{SO}}^2(k)\Delta_k}{[E(\mathrm{S}_1) - E(\mathrm{T}_n^k)]^2 + (\Delta_k/2)^2} \qquad (1)$$

where k runs over the vibrational levels, $V_{\mathrm{SO}}(k)$ is the $S_1-T_n^k$ SOC matrix element, and Δ_k is the decay width of T_n^k. Direct evidence for a similar mechanism being operational in pentacene was found by Corval et al.[16] By shifting triplet sublevels using a strong magnetic field, they observed a strong increase of the ISC caused by a T_n^k sublevel crossing with S_1 for pentacene in benzoic acid. Semiempirical CNDOM calculations implicated T_3 as the only plausible candidate.[16]

In terms of the mediation model, our interpretation of the observed isotope effects on ISC may be rephrased as follows. The rate quantified by eq 1 is sensitive to S_1-T_3 isotope shifts, as these modulate the energy difference in the denominator. It also depends on the vibrational frequencies of the individual T_3^k levels. The squared dependence on the energy difference means that a few T_3^k levels close to S_1 may dominate the ISC. In cases where the vibrational energy of these dominant T_3^k states varies little as a function of isotopic substitution, the corresponding S_1-T_3 isotope shifts will be primarily responsible for changes in k_{23}. This will be the case for the species under examination when the γ and ϵ hydrogens participate little in the near-resonant modes. The SOC matrix element $V_{\mathrm{SO}}(k)$ includes a Franck−Condon factor and, therefore, also depends on the isotopic composition. However, this effect is considered negligible, because of the minor changes in the geometry and force field of pentacene for the lowest excited states, and the lack of participation of the atoms being substituted.

TABLE 2: Properties of the Lowest Five Electronic States of Pentacene (146 Electrons), Calculated at their Optimized Geometry Using the 6-31G(d) Basis[a]

state	energy (cm^{-1})	E_{zp} (cm^{-1})	IR	CI coeff squared > 0.05
S_0	0	60 355	A_g	HF ground state
T_1	5 801	59 532	B_{2u}	$0.85\cdot(74 \leftarrow 73)$
T_2	15 731	59 541	B_{1g}	$0.43\cdot(74 \leftarrow 72) + 0.37\cdot(75 \leftarrow 73)$
T_3	23 518	59 341	B_{2u}	$0.31\cdot(74 \leftarrow 70) + 0.22\cdot(75 \leftarrow 72)$ $+0.25\cdot(77 \leftarrow 73)$
S_1	24 996	59 701	B_{2u}	$0.93\cdot(74 \leftarrow 73)$

[a] The given zero-point energies were calculated for the $^{12}C_{22}{}^{1}H_{14}$ isotopomer. The parentheses (...←...) denote the most important single excitations (between the molecular orbitals depicted in Figure 3) for the various excited states.

A quantitative analysis of the outlined scheme requires the calculation of S_1-T_3 isotope shifts (which are not experimentally accessible), as well as a normal-coordinate analysis. Results of the calculations are reported in the next section. Subsequently, in the Discussion section, we show that the calculations support the role of isotope shifts as regards the variation in the ISC rate with isotopic composition. In addition, we discuss the additivity of isotope shifts and their sensitivity to the host matrix. Finally, we examine evidence for a contribution to the inhomogeneous line width of isotope shifts induced by the host matrix.

2. Results

A. Isotope Shifts. A change in the isotopic composition of a molecule modifies its zero-point vibrational energy. Since the zero-point energy also depends on the electronic state of the molecule, the energy difference between the ground vibrational levels of two electronic states (say s_a, and higher lying state s_b) can exhibit a so-called isotope shift, when comparing two isotopic compositions i_0 and i_1. Let $E_{\mathrm{zp}}(s,i)$ denote the zero-point energy for a particular state and isotopic composition. The isotope shift then equals

$$[E_{\mathrm{zp}}(s_b, i_1) - E_{\mathrm{zp}}(s_b, i_0)] - [E_{\mathrm{zp}}(s_a, i_1) - E_{\mathrm{zp}}(s_a, i_0)] \qquad (2)$$

Calculating isotope shifts, as per eq 2, requires the vibrational frequencies for both electronic states involved. To this end we performed RHF and CI singles ab initio calculations for the ground state and the lowest few excited states of pentacene, using Gaussian 94.[17] Some properties of these states, obtained using the largest practicable basis set (6-31G(d)), are summarized in Table 2. As would be expected for ab initio calculations using such a limited basis and configuration interaction (CI), the relative energies of the electronic states are fairly inaccurate (the vacuum $S_1 \leftarrow S_0$ excitation energy is 18 628 cm^{-1} [18]). However, the order of the levels, and their symmetry, are consistent with those determined using semiempirical packages parametrized for spectroscopy, e.g. CNDOM calculations[16] ($T_1 = 3844\ \mathrm{cm}^{-1}$, $T_2 = 11\,584\ \mathrm{cm}^{-1}$, $T_3 = 18\,588\ \mathrm{cm}^{-1}$, and $S_1 = 18\,932\ \mathrm{cm}^{-1}$) or INDO ($T_1 = 4666\ \mathrm{cm}^{-1}$, $T_2 = 11\,691\ \mathrm{cm}^{-1}$, $T_3 = 17\,698\ \mathrm{cm}^{-1}$, and $S_1 = 19\,146\ \mathrm{cm}^{-1}$). The calculated order and symmetry of the π molecular orbitals (MOs) close to the HOMO−LUMO gap is consistent among the various packages and choices of basis, as is the approximate weighting of single excitations in the CI (see Table 2).

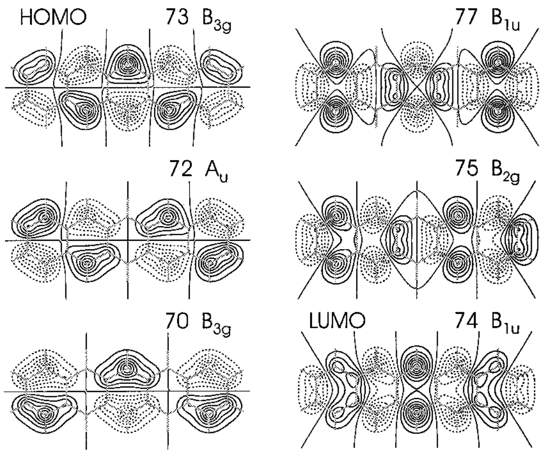

Figure 3. Molecular orbitals of relevance to the lowest excited states of pentacene. The continuous and broken contours differ in sign, and represent electron density sampled out of the molecular plane, which is a nodal plane for π MOs.

TABLE 3: Calculated $S_1 \leftarrow S_0$ Isotope Shifts Relative to the Perdeuterated Case, for a Series of Basis Sets[a]

	isotope shift (cm^{-1})				
isotopomer	STO-3G	3-21G	D95	6-31G(d)	exp
γ-^{1}H	−11.21	−7.94	−7.30	−6.75	−4.16
ϵ-^{1}H	−6.38	−4.33	−4.73	−5.04	−3.35
β-^{1}H	0.59	0.78	0.41	0.68	−0.89
α-^{1}H	1.17	1.56	1.82	1.02	−0.32
γ-^{13}C	2.42	1.87	1.80	1.82	0.61
ϵ-^{13}C	1.57	1.06	1.02	1.12	0.48
α-^{13}C	1.08	0.47	0.54	0.69	0.30
β-^{13}C	1.09	0.48	0.52	0.72	
δ-^{13}C	1.08	1.02	1.19	1.29	0.30
ζ-^{13}C	1.12	0.48	0.68	0.77	0.09

[a] The experimental values are listed also.[4]

The changes in the electronic structure accompanying the various excitations are largely determined by symmetry. The calculated MO electron densities vary somewhat depending on the choice of method but their overall nodal structure, as depicted in Figure 3, remains unchanged. It should therefore be possible to determine marked changes in bonding between electronic states, which result in isotope shifts, from quantum-chemical calculations, even if these must be somewhat coarse given the size of pentacene.

For each state, the pentacene geometry was optimized, and a vibrational analysis was performed by diagonalizing the mass-scaled Hessian for a series of isotopomers. To gauge the quality of the method, we calculated $S_1 \leftarrow S_0$ isotope shifts for the various singly substituted isotopomers, relative to pentacene $^{12}C_{22}\,^{2}H_{14}$, for a series of basis sets increasing in size. The results are summarized in Table 3 together with the experimental values determined from high-resolution $S_1 \leftarrow S_0$ excitation spectra.[4] Comparison with experiment shows sizable discrepancies, particularly for the ^{13}C shifts (semiempirical calculations of pentacene ^{13}C shifts were performed using the QCFF/PI+CISD method by Myers et al.[19]). The calculated ^{1}H shifts approach the experimental values, and their consistency improves as the basis set becomes larger. Part of the discrepancy between the calculations and experiment is due to the limited basis set and the limited treatment of electron correlation by CI singles. However, much of the discrepancy results from the *p*-terphenyl host matrix (see section 3C), which was not taken into account in the calculations. On balance, the calculations provide a reasonable qualitative prediction of the ^{1}H shifts.

TABLE 4: Calculated $S_1 \leftarrow T_3$ Isotope Shifts Relative to the Perdeuterated Case

	isotope shift (cm^{-1})			
isotopomer	STO-3G	3-21G	D95	6-31G(d)
γ-^{1}H	5.99	7.42	6.96	7.13
ϵ-^{1}H	−6.79	−5.84	−4.99	−4.77
α-^{1}H	18.84	16.11	15.52	14.29
β-^{1}H	7.96	5.84	5.32	5.36
γ-^{13}C	−0.38	−0.83	−0.77	−0.78

TABLE 5: Additivity of $S_1 \leftarrow T_3$ Isotope Shifts for a Selection of Doubly Substituted Isotopomers Using the 6-31G(d) Basis[a]

	isotope shift (cm^{-1})		
isotopomer	direct	sum rule	difference
$\gamma\gamma$-^{1}H	14.263 26	14.262 94	0.000 32
$\gamma_a\epsilon_a$-^{1}H	2.360 04	2.361 91	−0.001 87
$\gamma_a\epsilon_b$-^{1}H	2.361 12	2.361 91	−0.000 79
$\epsilon_a\epsilon_b$-^{1}H	−9.535 58	−9.539 12	0.003 54
$\epsilon_a\epsilon_c$-^{1}H	−9.539 91	−9.539 12	−0.000 79
γ_a-^{1}H γ_a-^{13}C	6.398 12	6.344 73	0.053 39
γ_a-^{1}H γ_b-^{13}C	6.345 49	6.344 73	0.000 76
$\gamma\gamma$-^{13}C	−1.572 77	−1.573 48	0.000 71

[a] The second column contains the directly calculated isotope shifts. The third column contains the shifts as obtained using the sum rule and the shifts γ-^{1}H = 7.131 47, ϵ-^{1}H = −4.769 56, and γ-^{13}C= −0.786 74 as calculated for the constituent singly substituted isotopomers. The subscripts a−d denote the spatial arrangement of those isomers not uniquely defined by the Greek labels (see Figure 2).

The $S_1 \leftarrow T_3$ isotope shifts, of relevance to the interpretation of the observed ISC trend, were calculated similarly and are summarized in Table 4. Opposite shifts for the γ and ϵ substitution positions are found. For the α-^{1}H isotopomer, a relatively large shift is calculated. Values for the shifts of multiply-substituted isotopomers can be obtained from this table by applying the sum rule. To gauge the validity of the sum rule, a selection of shifts for doubly-substituted isotopomers was calculated using a 6-31G(d) basis (see Table 5). The representation using five decimal digits provides sufficient dynamic range for assessing the small differences between the results and the predictions made using the sum rule.

B. Normal-Coordinate Analysis. As noted in the Introduction, out-of-plane (OOP) modes are expected to mediate intersystem crossing. This model predicts that the trend in k_{23} indicated in Table 1 can result from $S_1 \leftarrow T_3$ isotope shifts, if the frequencies of OOP modes of T_3 close to S_1 vary less than the isotope shifts upon γ and/or ϵ ^{1}H substitution. Furthermore, the dominant modes should be positioned below S_1, since the increased $E(S_1)-E(T_3)$ calculated for γ corresponds to a decrease in k_{23} (and vice versa for ϵ). To see if OOP modes consistent with these requirements exist, we performed a normal-coordinate analysis using the software and pentacene force field described in ref 12. We used this force field, in preference to the vibrational analysis specific to T_3 obtained via the quantum-chemical calculations (section 2A), because the latter do not result in accurate normal modes suitable for detailed analysis.

The calculation does indeed reveal OOP modes that barely shift with ϵ or γ ^{1}H substitution. These are the low-frequency OOP modes, corresponding to collective torsions or butterfly motions of the molecule, and the highest frequency OOP modes, which correspond to out-of-phase motions of adjacent α and β hydrogens. The frequencies of these modes, as a function of isotopic composition, are summarized in Figure 4. All isotopomers that can be attained by substituting up to three ^{1}H's in the γ and/or ϵ position are included.

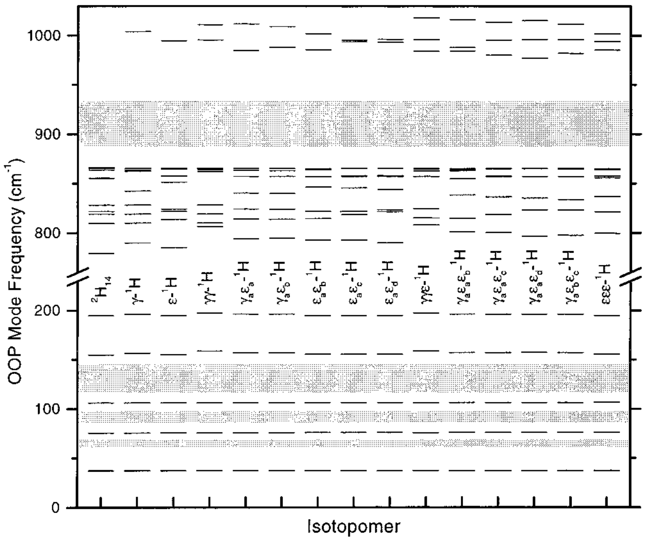

Figure 4. Subset of OOP normal-mode frequencies for pentacene isotopomers involving up to three ϵ or γ ^{1}H substitutions. The subscripts a−d denote the spatial arrangement of those isomers not uniquely determined by the greek labels (see Figure 2). The gray areas indicate positions for S_1 consistent with the observed ISC trend.

It should be noted that the force field used is valid for the ground state and does not incorporate the *p*-terphenyl crystal field. Also, the linear combinations of the local modes making up the calculated hydrogen OOP normal modes were found to be fairly sensitive to perturbations in the force field. Nevertheless, the insensitivity to γ and ϵ ^{1}H substitution of the lowest frequency OOP modes, whose character is determined by the overall shape of the molecule, is likely to be retained for the T_3 state. The same holds for the highest frequency OOP modes, given the relatively strong coupling between the neighboring α and β hydrogen out-of-plane motions. Other modes might well exhibit considerable Duschinsky effects.

It will prove instructive to consider the contribution of individual atoms to the zero-point energy of the molecule as a function of isotopic composition. Such a contribution can be obtained from the normal-coordinate analysis described above by summing the kinetic energies of a particular atom associated with the various normal modes. The kinetic energy of an atom for a particular normal mode at the equilibrium geometry of the molecule follows trivially from its mass, excursion amplitude, and the mode frequency. The results are summarized in Table 6. As a consistency check, it was verified that the sum of the contributions of all atoms was equal to the zero-point energy obtained by summing the normal-mode frequencies.

TABLE 6: Contributions of Various Atoms to the Zero-Point Energy for a Selection of Isotopomers

	contribution to zero-point energy (cm^{-1})				
	hydrogens			carbons	
isotopomer	γ_a	ϵ_a	α_a	γ_a	ζ_a
all-^{2}H	1678.17	1678.55	1673.52	1303.80	1330.05
γ_a-^{1}H	2420.12	1678.45	1673.50	1270.26	1329.96
ϵ_a-^{1}H	1678.07	2419.81	1673.40	1303.46	1328.39
$\gamma_a\gamma_b$-^{1}H	2420.03	1678.41	1673.48	1270.16	1329.92
$\gamma_a\epsilon_a$-^{1}H	2420.06	2419.75	1673.38	1269.89	1328.29
$\gamma_a\epsilon_b$-^{1}H	2420.10	1678.38	1673.44	1270.09	1329.45
$\epsilon_a\epsilon_b$-^{1}H	1678.03	2419.74	1673.35	1303.31	1327.88
$\epsilon_a\epsilon_c$-^{1}H	1678.03	2419.80	1673.40	1303.31	1328.38
$\epsilon_a\epsilon_d$-^{1}H	1677.97	2419.80	1673.40	1303.13	1328.37
$\gamma_a\gamma_b\epsilon_a$-^{1}H	2419.97	2419.72	1673.37	1269.79	1328.26
$\gamma_a\epsilon_a\epsilon_b$-^{1}H	2420.03	2419.68	1673.33	1269.72	1327.78
$\gamma_a\epsilon_a\epsilon_c$-^{1}H	2420.03	2419.74	1673.37	1269.72	1328.28
$\gamma_a\epsilon_a\epsilon_d$-^{1}H	2420.00	2419.74	1673.37	1269.52	1328.27
$\gamma_a\epsilon_b\epsilon_c$-^{1}H	2420.07	1678.37	1673.43	1269.92	1329.43
$\epsilon_a\epsilon_b\epsilon_c$-^{1}H	1677.98	2419.74	1673.34	1303.15	1327.86

3. Discussion

A. Intersystem Crossing. The opposite signs and the magnitudes calculated for the γ-^{1}H and ϵ-^{1}H $S_1 \leftarrow T_3$ isotope shifts (see Table 4), corroborate the hypothesis that the observed changes in k_{23} are induced by $S_1 \leftarrow T_3$ isotope shifts. As seen in Table 1, the decrease of k_{23} per γ-^{1}H substitution is somewhat larger than its increase per ϵ-^{1}H substitution. This is consistent with the ratio of magnitudes of the corresponding isotope shifts as calculated for all but the smallest basis set.

To establish whether the isotope shifts can give rise to the observed ISC trend via the proposed mechanism, the change in k_{23}, as quantified by eq 1, was examined as a function of isotopic composition. The quantum chemical calculations indicate that S_1 lies slightly above T_3, but do not accurately fix their energies relative to one another. For a range of positions of S_1 (indicated by the gray areas in Figure 4), the calculated changes in k_{23} can indeed be made to resemble the observed trend, given appropriate assumptions and choices for the unknowns in eq 1. Such a calculation carries little quantitative weight given the large number of unknowns; each mode *k* has a unique decay width Δ_k, and SOC matrix element $V_{SO}(k)$. Still, it seems safe to conclude that it is possible for the observed ISC trend to be the result of one or a few of the lowest or highest frequency OOP modes of T_3 dominating. Part of the overall ISC rate k_{23} might result from ISC mediated by multiple quanta of T_1 and T_2 vibrations, but these contributions are expected to be small relative to when only one quantum of an out-of-plane vibration is involved.[16]

If mediation by modes of T_3 that are largely frequency invariant does determine ISC, S_1 is predicted to lie a few tens of wavenumbers above these dominant modes. That is, S_1 must be somewhat out of resonance. This prediction is consistent with the comparatively low ISC yield of deuterated pentacene in the O_1 and O_2 sites.[9,10] The spectral origins of O_1−O_4 for perdeuterated pentacene are at 16 908.5, 16 912.2, 17 031.7, and 17 091.0 cm^{-1} respectively. A correlation between $E(S_1)-E(S_0)$ and $E(S_1)-E(T_3)$ can be expected. Thus, it is reasonable to assume that $E(S_1)-E(T_3)$ will be similar for O_1 and O_2, which is consistent with the observed slightly differrent k_{23} rates and retained isotopomer trend between these sites. Similarly, the $E(S_1)-E(T_3)$ gap will probably differ by several tens of wavenumbers for the O_3 and O_4 sites, as compared to that of O_1 and O_2. Therefore, it is conceivable that S_1 is in close resonance with one or more OOP modes for the O_3 and O_4 sites, and thereby causes a far larger ISC yield for deuterated pentacene in those sites. This does not preclude differences in the distortion of pentacene in the various sites from playing a role since these may cause variations of $E(S_1)-E(T_3)$ between the sites. Out-of-plane distortions can also directly account for some of the ISC, by mixing σ character into the $\pi\pi^*$ states.

B. Additivity of Isotope Shifts. As shown by Table 5, the calculated isotope shifts are indeed almost perfectly additive, apart from the case involving adjacent ^{13}C and ^{1}H substitutions, for which the deviation from additivity is somewhat larger. Here, we address the question of why this additivity of isotope shifts holds. It turns out that changes in zero-point energy between isotopomers (the left and right terms in eq 2) behave additively, thereby making the isotope shifts additive. This can be quantified by the normalized measure of the deviation from additivity

$$\left|\frac{\Delta_{zp}(s,i_1) + \Delta_{zp}(s,i_2) - \Delta_{zp}(s,i_{1,2})}{\Delta_{zp}(s,i_{1,2})}\right| \tag{3}$$

where $\Delta_{zp}(s,i) \equiv E_{zp}(s,i) - E_{zp}(s,i_0)$, and i_1, i_2, and $i_{1,2}$ denote isotopic compositions resulting from single-nucleus substitutions and the corresponding double substitution relative to the reference composition i_0. It should be noted that the relative deviation from additivity of isotope shifts probably differs somewhat from this measure because eq 2 involves the subtraction of two Δ_{zp}'s of similar magnitude.

From the normal-coordinate analysis it is found that for pentacene the normalized deviation for a pair of $^1H \rightarrow {}^2H$ substitutions ranges from 2×10^{-4} for adjacent hydrogens, to 1×10^{-6} for hydrogens on opposite ends of the molecule. For a pair of $^{12}C \rightarrow {}^{13}C$ substitutions, the deviations range from 1×10^{-3} for carbons separated by a single bond, to 4×10^{-6} for distant carbons. Even for small molecules the additivity holds remarkably well, e.g. better than 10^{-2} for any pair of "one-neutron" substitutions in methanol. As also evident from Table 5, the additivity improves the further apart the two substitutions are. But the sum rule even gives a good prediction for adjacent substitutions.

To qualitatively explain the additivity of zero-point energy, we note that a rough estimate of the zero-point energy of a molecule can be obtained by treating each atom as an independent oscillator with three orthogonal modes, and then summing the contributions of those modes

$$\frac{1}{2}\sum_{n}\sum_{j=1}^{3}\hbar\sqrt{\frac{k_{jn}}{m_n}}$$

where n indexes the atoms. Clearly, this estimate of the zero-point energy is perfectly additive for isotopic substitution, which, in part, explains the approximate additivity of the real zero-point energy. The contribution of hydrogen atoms to the zero-point energy in pentacene, and organic molecules in general, is indeed close to what one would estimate from the frequencies of the three local modes, as these couple only weakly to the carbon skeleton because of the large disparity in mass. A pair of hydrogens are always at least two bonds apart (three in the case of pentacene), so their mutual coupling is weak. For the tightly coupled backbone atoms, it is the weak dependence of vibrational frequency on mass (proportional to $1/\sqrt{m}$ for a single oscillator), together with the small differences in relative mass between isotopes that lead to approximate additivity; any smooth, differentiable, multivariate function behaves additively if variable perturbations are sufficiently small for a linear approximation to hold.

This argument can be made quantitative by consideration of the contribution of individual atoms to the zero-point energy (Table 6). Evidently, the contribution of an atom is nearly invariant between isotopic compositions that leave its mass unchanged, with only a slight change if a nearby substitution occurs. This independence of atom contributions implies additivity of the overall zero-point energy. It also implies that an isotope shift due to a single substitution is largely determined by the difference, between two electronic states, in the change of the zero-point contribution of the atom being substituted. The contributions of the other atoms hardly change, and, hence, cancel in the left and right terms of eq 2. Phrased differently, the isotope shift for a single substitution is a property, local to the atom being substituted, that reflects its change in bonding between the two electronic states involved. This explains the rough correlation noted by Doberer et al.[7] between $T_1 \leftarrow S_0$ ^{13}C isotope shifts and T_1 spin densities.

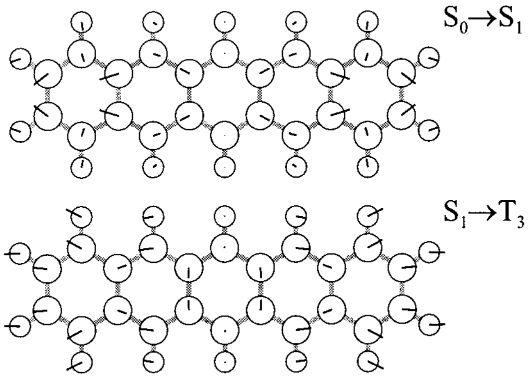

Figure 5. Changes in geometry of pentacene between electronic states, as calculated using the 6-31G(d) basis. The line segments depict the direction and magnitude (exaggerated by a factor of 20) of the displacements.

C. Host Matrix Effects. As shown in the previous section, an isotope shift is in good approximation determined by the change in frequency, between two electronic states, of the local modes associated with the substituted atom. Intramolecular properties are, therefore, of prime importance to isotope shifts. For example, as the lowest excited states of pentacene concern excitations between π MO's, a C−H stretch local mode will change little between states in comparison to the C−H in-plane rock and out-of-plane wag modes. Thus, the C−H stretch will be of minor importance for the intramolecular contribution to the isotope shift upon ^1H substitution, even though it makes the largest contribution to the zero-point energy.

Intermolecular interactions between pentacene and the *p*-terphenyl molecules that make up the host matrix were not included in the calculations of the isotope shift. Such interactions are evident in the excitation spectra, which show crystal-field-induced splittings of isotopomer bands.[3,4,8] These splittings, which are on the order of 0.25 cm^{-1} for the ^1H satellites,[4] reflect the degree to which shifts that should be equivalent, given the molecular D_{2h} symmetry, become inequivalent due to the inversion symmetry of the crystal site. The splittings are superimposed on a potentially larger host-matrix-induced isotope shift, common to a set of D_{2h} symmetry equivalent substitution positions.

One mechanism for an intermolecular contribution to isotope shifts involves changes in local mode frequencies stemming from the crystal-potential contribution to the Hessian that is invariant between electronic states. Such a contribution will scale with both the change in the affected local modes between the electronic states and the degree to which the isotope substitution modifies those modes. A second mechanism involves differences of the crystal potential contribution to the Hessian between electronic states, resulting from the slight changes in the geometry of the guest molecule (see Figure 5). Such a contribution will scale only with the degree to which the isotope substitution modifies the affected modes, and not with the changes in bonding between electronic states. For example, a pentacene C−H stretch local mode might participate in pentacene isotope shifts through this mechanism, particularly since the geometry changes between the lowest electronic states are in plane.

D. A Lower Limit to Inhomogeneous Broadening? In our experiments, we examined a considerable number of pentacene-doped *p*-terphenyl crystals, and the experimental setup allowed the probing of a range of locations across each crystal.[21] By making an effort to carefully grow the crystals and mount them in a way that induces little stress, it proved possible to observe very narrow inhomogeneous widths of the $S_1 \leftarrow S_0$ zero-phonon band of the O_1 and O_2 sites in selected regions of many of those crystals. Frequently, inhomogeneous line widths of roughly 750 MHz fwhm and slightly larger were observed[8] but never smaller values. It appeared as if there were a lower limit to the inhomogeneous broadening.

In addition to host crystals grown from natural abundance *p*-terphenyl, we also used deuterated *p*-terphenyl as a host. For those crystals, it proved impossible to reproduce such small inhomogeneous widths. The best value attained was roughly 2.5 GHz.[22] This would suggest some impurity in the host, but the *p*-terphenyl-d_{14} was chemically purified via zone refinement before sublimation, as was the case for the natural abundance *p*-terphenyl.

A clue to a possible explanation of these observations lies in the different positions of the zero-phonon lines for each host matrix. For pentacene-d_{14} in natural abundance *p*-terphenyl, the zero-phonon band of the O_1 site is located at 16 908.5 cm^{-1}, and that of the O_2 site at 16 912.1 cm^{-1}.[4] In the deuterated host, O_1 is found at 16 915.6 cm^{-1} and O_2 at 16 921.0 cm^{-1}. Clearly, the isotopic composition of the host matrix causes a marked site-dependent change in the absorption frequency of pentacene; in going from the natural abundance to the deuterated host, O_1 shifts by 7.1 cm^{-1} and O_2 by 8.9 cm^{-1}.

Given these observations, it must be that a variation in the isotopic composition of the host molecules contributes to inhomogeneous broadening, a contribution present even in perfectly grown crystals without chemical impurities. The *p*-terphenyl-d_{14} used was specified to have 98% ^2H isotopic purity. The contribution to the inhomogeneous broadening, due to the random spatial distribution of the 2% ^1H's in the host matrix around each pentacene molecule, must be roughly 0.02 times the overall shift, which does indeed come to a few GHz. In the natural abundance host matrix, the 0.015% ^2H can be neglected, but the 1.1% ^{13}C will contribute some inhomogeneous broadening and is likely to be responsible for the observed 750 MHz lower bound.

The line shape induced by such inhomogeneous broadening is a function of the spatial arrangement of the sites of the host matrix. When examining the low-temperature *p*-terphenyl crystal structure,[23] it is apparent that there is a "shell" of some 26 H atoms adjacent to each substitutional site. One would expect a broad distribution of the transition frequencies of pentacene molecules in *p*-terphenyl-d_{14} for which at least one of these adjacent hydrogens is a ^1H, and a relatively narrow distribution for the remaining pentacene molecules. (An example of a more quantitative analysis of inhomogeneous broadening can be found in ref 24.) Indeed, the observed inhomogeneous line shape for the deuterated host appears to have broad wings of low relative intensity.[22]

A likely mechanism through which the isotopic composition of the host matrix influences the transition frequency of the guest involves the zero-point vibrations of the host molecules. A change of isotopic composition will modify the ground vibrational wave function. In addition, the anharmonicity of the potential energy will cause a slight modification to the mean molecular geometry. For example, the higher zero-point energy contribution of the $C{-}^1H$ stretch local mode will cause a slight increase of the mean C−H distance relative to $C{-}^2H$, due to anharmonicity of the C−H potential energy curve. Using the Morse potential, with parameters typical for the C−H bond in organic compounds, it is found that the mean bond length increases by 0.6% in going from $C{-}^2H$ to $C{-}^1H$. Such subtle changes in the geometry of a host molecule will slightly modify the substitutional sites of nearby guest molecules and thus cause inhomogeneous broadening.

4. Conclusion

Isotope shifts resulting from a single substitution were found to be dominated by the change in the zero-point energy contribution of the atom being substituted. The contributions of other atoms remain approximately invariant and do not contribute to the isotope shift. This explains why the sum rule for isotope shifts is a good approximation. It also explains why fairly coarse quantum chemical calculations, followed by a vibrational analysis, can provide reasonable predictions for the isotope shifts; variations in the linear combinations of atom motions making up individual normal modes are not of relevance. The calculated $S_1 \leftarrow T_3$ isotope shifts, combined with a normal-coordinate analysis, corroborate the hypothesized dependence of the intersystem crossing of deuterated pentacene, in the *p*-terphenyl O_1 and O_2 sites, on isotope shifts. The proposed mechanism involves a near resonance between the first excited singlet state S_1, and vibrational levels of T_3.

A more accurate calculation of the observed isotope shifts would require the inclusion of the guest−host interaction in the vibrational analysis in addition to a more refined quantum-chemical treatment. The isotopic purity of the *p*-terphenyl host matrix was found to be the plausible cause of a lower limit to inhomogeneous broadening. Improved isotopic purity of the host should enable even narrower inhomogeneous widths.

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References and Notes

(1) Basché, T., Moerner, W. E., Orrit, M., Wild, U. P., Eds. *Single-Molecule Optical Detection, Imaging and Spectroscopy*; VCH: Weinheim, Germany, 1997.

(2) Basché, T.; Kummer, S.; Bräuchle, C. *Chem. Phys. Lett.* **1994**, *225*, 116.

(3) Köhler, J.; Brouwer, A. C. J.; Groenen, E. J. J.; Schmidt, J. *J. Am. Chem. Soc.* **1998**, *120*, 1900.

(4) Brouwer, A. C. J.; Köhler, J.; van Oijen, A. M.; Groenen, E. J. J.; Schmidt, J. *J. Chem. Phys.* **1999**, *110*, 9151.

(5) Wilson, E. B.; Decius, J.; Cross, P. *Molecular Vibrations*; Dover: New York, 1980.

(6) Port, H.; Rund, D.; Wolf, H. C. *Chem. Phys.* **1981**, *60*, 81.

(7) Doberer, U.; Port, H.; Rund, D.; Tuffensammer, W. *Mol. Phys.* **1983**, *49*, 1167.

(8) Brouwer, A. C. J.; Köhler, J.; Groenen, E. J. J.; Schmidt, J. *J. Chem. Phys.* **1996**, *105*, 2212.

(9) de Vries, H.; Wiersma, D. A. *J. Chem. Phys.* **1979**, *70*, 5807.

(10) Patterson, F. G.; Lee, H. W. H.; Wilson, W. L.; Fayer, M. D. *Chem. Phys.* **1984**, *84*, 51.

(11) Kryschi, C.; Fleischhauer, H. C.; Wagner, B. *Chem. Phys.* **1992**, *161*, 485.

(12) Fleischhauer, H. C.; Kryschi, C.; Wagner, B.; Kupka, H. *J. Chem. Phys.* **1992**, *97*, 1742.

(13) Köhler, J.; Brouwer, A. C. J.; Groenen, E. J. J.; Schmidt, J. *Chem. Phys. Lett.* **1996**, *250*, 137.

(14) Bordat, P.; Brown, R. *Chem. Phys. Lett.* **1998**, *291*, 153.

(15) Amirav, A.; Sonnenschein, M.; Jortner, J. *Chem. Phys. Lett.* **1983**, *100*, 488.

(16) Corval, A.; Kryschi, C.; Astilean, S.; Trommsdorff, H. P. *J. Phys. Chem.* **1994**, *98*, 7376.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision D.4*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(18) Amirav, A.; Even, U.; Jortner, J. *Opt. Commun.* **1980**, *32*, 266.

(19) Myers, A. B.; Tchénio, P.; Zgierski, M. Z.; Moerner, W. E. *J. Phys. Chem.* **1994**, *98*, 10377.

(20) Fleischhauer, H. C. Theoretische und spektroskopische Untersuchung der Normalschwingungen von Pentazen in p-Terphenyl und Naphthalin-Einkristallen; Ph.D. Thesis, Heinrich-Heine-Universität Düsseldorf, 1992.

(21) van der Meer, H.; Disselhorst, J. A. J. M.; Köhler, J.; Brouwer, A. C. J.; Groenen, E. J. J.; Schmidt, J. *Rev. Sci. Instrum.* **1995**, *66*, 4853.

(22) Köhler, J.; Brouwer, A. C. J.; Groenen, E. J. J.; Schmidt, J. *Science* **1995**, *268*, 1457.

(23) Baudour, J. L.; Delugeard, Y.; Cailleau, H. *Acta Crystallogr.* **1976**, B32, 150.

(24) Geissinger, P.; Kohler, B. E.; Kulikov, S. G.; Terpougov, V. *J. Chem. Phys.* **1998**, *108*, 1821.