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Single-molecule fluorescence autocorrelation experiments on pentacene: The dependence of intersystem crossing on isotopic composition

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Single pentacene molecules containing $^{13}$C or $^3$H in a pentacene-$d_{14}$ doped $p$-terphenyl crystal have been studied by fluorescence autocorrelation. The triplet dynamics has been analyzed and a systematic dependence of the $S_1\rightarrow T_1$ intersystem crossing rate on isotopic composition was found. This variation is discussed in terms of a modulation of the near resonance of the first excited singlet state $S_1$ and vibrational levels of an intermediating triplet state $T_3$ which results from the distinct isotope dependence of the zero-point energy of both electronic states. © 1999 American Institute of Physics. [S0021-9606(99)01518-4]

I. INTRODUCTION

The development of spectroscopy on single molecules in solid matrices has enabled novel experiments and allowed the discrimination of subtle effects as reviewed in Refs. 1–4. For example, the fluorescence signal of a single molecule, as opposed to ensemble fluorescence, contains information on the evolution of the molecular wave function through the quantum states accessible under optical excitation. This information can be exploited to determine the intersystem crossing rates between the singlet and triplet manifold either by recording the intensity autocorrelation of a molecule’s fluorescence or by directly timing the singlet and triplet residence of a molecule through the presence or absence of fluorescence. In previous work we have explored the effects of isotopic composition of pentacene through optical excitation spectroscopy and magnetic resonance. Here we extend this work and refine the involved techniques so as to examine the dependence of the intersystem crossing (ISC) of pentacene on its isotopic composition.

Pentacene substitutionally occupies one of four low-temperature crystal sites in the $p$-terphenyl host crystal giving rise to four spectral origins in the $S_1\rightarrow S_0$ excitation spectrum labeled $O_1$–$O_4$ in order of increasing frequency. The low ISC for the $O_1$ and $O_2$ sites makes them suited to single-molecule spectroscopy. In fact, pentacene in $p$-terphenyl was the first system used in single-molecule spectroscopy. The isotope shifts of the $S_1\rightarrow S_0$ 0–0 transition as observed in the spectrum shown in Fig. 1 result from the dependence of the zero-point energy on isotopic composition and electronic state. Clearly, many isotopic isomers are present, at a low relative concentration, in the used batch of deuterated pentacene. These isomers result from a small residue of $^3$H left after deuteration so that no additional synthesis was required to obtain them. By combining frequency and spatial selectivity it proves possible to select single molecules for a wide range of these species so as to study their intersystem crossing on an equal footing irrespective of the apparent vast differences in concentration.

Our interest is motivated by the remarkable sensitivity of the pentacene $S_1\rightarrow T_1$ ISC to the (site of the) host matrix. When embedded in $p$-terphenyl at liquid-helium temperatures, the $O_3$ and $O_4$ sites have rates exceeding those of the $O_1$ and $O_2$ sites by two orders of magnitude. When increasing the temperature, the $O_1$ and $O_2$ ISC rates were observed to converge to those of $O_3$ and $O_4$. For pentacene in benzoic acid at 1.6 K, the ISC was shown to be dominated by a near-resonance of the first excited singlet state $S_1$ and a vibrational level of a higher triplet state. A level crossing was observed when shifting the triplet sublevels by applying a strong magnetic field.

At a microsecond time scale, the fluorescence of a pentacene molecule exhibits a phenomenon called photon bunching. This is due to the fact that the repeated excitation to the $S_1$ state followed by the emission of a fluorescence photon is interrupted when the molecule crosses over to the triplet state thus leading to bunches of photons separated by dark periods. It was shown by Bernard et al. that photon bunching can be used to determine intersystem crossing rates. In this study we deploy their method to determine the dependence of the ISC on isotopic composition. We will show how the measured changes in ISC can be interpreted in terms of electronic structure differences between $S_1$ and a mediating triplet state. Isotope shifts are found to be crucial because they tune the near resonance of $S_1$ and vibrational levels of the triplet.

II. EXPERIMENT

A. Instrumentation

A single-mode dye laser (Coherent, 599-21), intensity stabilized using an electro-optical modulator (EOM, ConOptics 370), served as excitation light source. The limited dynamic range of the EOM was extended using a variable grey filter. The light is delivered via a polarization preserving single-mode fiber to a confocal detection arrangement (see Fig. 2). Neutral density filters placed in the intensity stabilization feedback path allowed a calibrated change of the excitation intensity in doubling steps over a range of three decades. A fine lateral optimization of the detection volume...
could be achieved by tilting a telecentrically placed motorized scan mirror. Experiments were performed at a temperature of 2 K with the sample mounted inside a helium bath cryostat. A translation mechanism allows movement of the sample perpendicular to the excitation cone over a range of 2 mm. The depth of the excitation focus was tuned by moving the objective lens towards or away from the sample. The focal volume is roughly 2 μm³. After separation using a dichroic and long-pass filter, the fluorescence photons were detected using an avalanche photodiode (EG&G SPCM-200-PQ). Photon counts were read by a multichannel scaling card (EG&G 923 MCS-plus) configured for continuous circularly buffered counting. Autocorrelation measurements were performed by applying a highly optimized algorithm to this incoming stream of counting values at a time resolution of 2 μs.

The experiments were controlled and processed through a fully integrated computerized data acquisition system. The laser scan range was linearized and calibrated in relative units by reference to a Fabry–Perot etalon. Wide excitation spectra were obtained by recording overlapping (<30 GHz) single-mode sweeps and combining these using the frequency specific excitation pattern of an iodine cell recorded in parallel. The corresponding composite iodine spectrum allowed absolute calibration (±0.002 cm⁻¹) by reference to tabulated iodine lines.16,17 For random positioning of the laser to a particular frequency or relative to a previously recorded excitation spectrum, a current small iodine excitation sweep is matched to a preconstructed composite iodine spectrum covering the spectral range of interest, a method that works even when tabulated iodine lines are sparse. While averaging subsequent laser sweeps for excitation spectra, the laser drift was compensated for to within roughly 1 MHz using the iodine pattern recorded simultaneously. While performing measurements on a single molecule (fixed laser frequency), the laser drift was removed by periodically interrupting the measurement and making a small excitation sweep around the molecule after which the laser was returned to the center of its absorption. For improved accuracy, power broadening is circumvented by switching the laser to low intensity during such a compensation sweep.

While recording fluorescence-detected magnetic-resonance (FDMR) spectra the sample was exposed to microwaves by way of a small ground loop close to the sample. The microwaves were generated by a sweep oscillator (HP 8350 B) and amplified. Magnetic resonance was detected directly as a decrease in fluorescence. The microwave frequency range was calibrated using a frequency counter (EIP 371). During averaging, the drift was compensated to 10 kHz rms by periodically interrupting the microwave sweeps for a frequency reading.

Excitation and FDMR spectra were recorded at an excess spectral resolution. An optimal tradeoff between spectral resolution and intensity noise was made after the measurements by fitting cubic splines to the data. The “bandwidth” of the splines was chosen such that the narrowest spectral features could still be well represented.

B. Sample preparation

The spectrum shown in Fig. 1 was recorded for a deuterated p-terphenyl crystal containing a relatively high pentacene concentration so that even isotopomeric species with a very low abundance could be resolved. The same batch of mostly deuterated pentacene was used at a much lower concentration for the experiments described in this article but instead of deuterated p-terphenyl, natural abundance p-terphenyl served as a host matrix. This explains the slight difference in the frequencies of the S₁→S₀ 0→0 transition of the spectral sites in Fig. 1 compared to the other spectra.

Thin, doped crystal flakes were grown by cosublimation of pentacene and zone-refined p-terphenyl. The sublimation temperatures were independently stabilized to control the growth rate and pentacene concentration. Most experiments were performed on a flake sublimed at 170 °C for p-terphenyl and 60 °C for pentacene-d₁₄ resulting in a pentacene concentration of roughly 10⁻⁸ mol/mol. Molecules belonging to the two most abundant isotopomeric species (those fully deuterated or protonated in the γ position only) were selected from a crystal sublimed at 180 °C/50 °C resulting in a somewhat lower pentacene concentration which made it easier to select isolated molecules.

The chosen crystals had a very small degree of inhomogeneous broadening [roughly 1 GHz full width at half maxi-
mum (FWHM)]. This is a prerequisite since it has been shown that for crystals with a large degree of inhomogeneous broadening a wide spread of the intersystem crossing rates for individual molecules results so that any isotopomer specific effects would be hard to resolve. Furthermore, a smaller degree of inhomogeneous broadening diminishes overlap between the isotopomer bands causing the isotope shift to become a more accurate selection criterion.

As will be explained later, determining intersystem crossing rates requires autocorrelation measurements over a wide range of excitation intensities. At high excitation intensity, power broadening (up to a couple of hundred MHz) and an increase in the background relative to the fluorescence of the saturated molecule occurs so that the molecule is required to be spectrally very well isolated. For this reason the pentacene concentration was chosen sufficiently low to make sure that for a range of isotopomers at most a couple of molecules were present within a focal volume (see Fig. 3). To nevertheless find single molecules for rare species, different spots across the crystal were probed for as long as it took to stumble over a molecule. An added advantage of this method is that for most isotopomer species the spectral density of molecules was sufficiently low to allow selection of a molecule from the middle of the corresponding inhomogenous range thus decreasing the odds of selecting a molecule from another site or isotopic composition in an exceptional environment.

C. Experimental protocol

A sizable set of molecules belonging to various isotopomer species were examined in this study. Instead of detailing how each molecule was selected and identified, we limit ourselves to describing the general protocol used.

Previously we have shown that the isotope shifts of $^{13}$C-containing pentacene isomers present in natural abundance and $^1$H isomers resulting from incomplete deuteration obey a sum rule such that the shift for an isotopomer containing multiple $^{13}$C’s or $^1$H’s can be predicted, to a high degree of accuracy, by summing the shifts of the corresponding singly substituted isotopomers. Thus, after deciding upon the isotoperic species and site of the molecule to be studied, the expected isotope shift can either be looked up (see Table I) or calculated using this sum rule. Subsequently, the precise center frequency of the corresponding all-deutero site at the current sample position is determined by recording an excitation spectrum. Adding the shift to the site frequency gives the position of the center of the isotopomer band. Next, an excitation scan a few GHz wide around the band center is repeatedly performed while the sample is slowly translated until a molecule appears in the spectrum. If the sample had to be translated by a large amount before the molecule was found, the center frequency of the related all-deutero site is verified once more since it shifts slightly (less than 1.5 GHz) over the probed range of sample positions.

Having found a molecule, the focal volume is centered on it by translating the objective lens and fine tuning the scan mirror until the detected fluorescence at nonsaturating excitation power is maximized. Next, high-resolution excitation spectra of the molecule are averaged at low and high excitation power. If the low-power line shape is symmetric and has a width corresponding to the lifetime limited value plus a small fixed instrumental contribution, the molecule can be assumed to be spectrally stable and isolated. The high power spectrum serves to check whether the fluorescence background does not swamp the fluorescence of the saturated molecule and whether the molecule remains spectrally isolated at excitation intensities that cause significant power broadening (up to a couple of hundred MHz FWHM). If the results are satisfactory, the laser frequency is stabilized to the center of the molecule’s absorption resulting in a fluorescence signal stemming solely from that molecule.

To verify the identity of the molecule, FDMR spectra of the $T_1 - T_2$ transition are recorded at a couple of microwave powers (see Sec. III B). If the line shape is as expected for the desired isotopomer and the zero-field splitting matches that of the site the molecule is supposed to belong to, the identity of the molecule is confirmed and the correlation measurements (see Sec. IV) can commence. At each excitation power, the autocorrelation histogram is accumulated to an accuracy that allows a proper exponential fit. The series of correlation measurements is repeated as allowed by the avail-

![Figure 3](image-url)  
**FIG. 3.** In-focus excitation spectrum of the pentacene-$d_{14}$ doped $p$-terphenyl crystal from which nearly all examined molecules were selected. Individual molecules appear as spikes. Evidently, for most isotopomer species only a couple or less molecules are in focus.
ability of liquid helium so as to gauge reproducibility and improve the accuracy of the overall fit.

III. OPTICAL SHIFTS AND MAGNETIC RESONANCE OF ISOTOPIC ISOMERS

The main thrust of this article concerns the measurement of the intersystem crossing rates of pentacene isotopomers and their interpretation. In order to enable the selection of molecules belonging to particular isotopomer species, intermediate experiments have to be carried out as will be discussed in this section. Specifically, excitation spectra serve the determination of $S_0-S_1$ isotope shifts as well as the optical selection of single molecules. Fluorescence-detected magnetic resonance is used to assign isotope shifted sidebands and verify the composition and site of selected single molecules.

A. Excitation spectra and isotope shifts

Figure 4 shows an excitation spectrum of pentacene-$d_{14}$ in $p$-terphenyl covering the range that includes all singly substituted isotopomer satellites of the $O_1$ and $O_2$ spectral sites. The spectrum was recorded from the same sample from which nearly all molecules were selected. Statistical fine structure due to the low concentration was avoided by tuning the objective lens out of focus and reducing the spatial selectivity of the detection optics. The spectrum is somewhat complicated by the presence of smooth, slightly redshifted sidebands (see Fig. 5) caused by spectrally diffusing molecules. Since the various isotopomers share the same distribution of local environments and have virtually identical photophysical properties, the inhomogeneous broadening and sidebands are replicated for all isotopomer satellites of a site. For $O_2$, relatively many spectrally diffusing molecules appear at a redshift of roughly $1 \text{ cm}^{-1}$ which explains the broad intensity below satellites $\beta_1$ and $\beta_2$. With these provisos in mind it can be seen that $O_1$ and $O_2$ have nearly identical satellite patterns which partially overlap.

The assignment of the $13C$ satellites to the blue of either site was made in analogy with the assignment in Ref. 8 for pentacene-$h_{14}$. Because of the lowered vibrational frequencies for pentacene-$d_{14}$, the pattern is somewhat compressed relative to that of pentacene-$h_{14}$. The Greek letters label the symmetry-equivalent carbon positions where a $13C$ nucleus is located or to which a $^3H$ is bound (see Fig. 6). For the $\gamma-^1H$ and $\epsilon-^1H$ satellites, the assignment could readily be verified through FDMR (see Sec. III B). The appearance of two $\epsilon$ satellites, labeled with the subscripts 1 and 2, is due to the lowering of the molecular symmetry caused by the embedding in the crystal sites which have inversion symmetry $S_2$ (point group $S_2^2$). Instead of four $D_{2h}$ symmetry-equivalent $\epsilon$ positions, two pairs of equivalent, diametrically opposite $\epsilon$ positions remain. A similar splitting is expected for the other groups of symmetry-equivalent positions apart from the two $\gamma$ positions.

The identity of the other satellite bands (labeled $\beta_2$, $\beta_1$, and $\alpha_2$) is somewhat ambiguous. It is obvious that they must
be due to isotopomers with a $^1$H at one of the two remaining bonding positions, $\alpha$ and $\beta$. However based on FDMR spectra, no definitive assignment could be made. One would expect two pairs of split bands, one pair for $\alpha$ the other for $\beta$. Only three bands are observed. A possible interpretation is that for one pair the site distortion accidentally results in exactly the same isotope shift. However a more likely interpretation is that one of the bands is hidden under the flank or sideband of the main all-deutero band. This interpretation is supported by an observed excess occurrence of single molecules at a shift of roughly $-0.11 \text{ cm}^{-1}$ relative to the main all-deutero bands (see for example Fig. 5). Molecules 4 and 19 were selected at such a small shift.

Since a large splitting of a pair of bands of one isotopomeric species is unlikely, the two most redshifted bands can be assumed to correspond to one species, and the two least redshifted bands (one of which is hidden) to the other species. The assignment of $\beta$ to the former and $\alpha$ to the latter is based on quantum-chemical calculations (see Table IV). This assignment is somewhat tentative given the moderate discrepancy between theory and experiment. The isotope shifts and assignments of the bands are summarized in Table I.

The intensities of the bands reflect the prevalence of the corresponding isotopomeric species. However the ensemble spectra were measured at an excitation intensity close to saturation so that the intersystem crossing rates particular to a species might also influence the observed intensity. For the $^{13}$C isotopomer bands, the intensities were shown to be consistent with the prevalence of the isotopomers as calculated from the 1.1% $^{13}$C natural abundance. The $^1$H impurities result from incomplete deuteration. Since the probability of $^1$H–$^2$H exchange depends on the bonding position, the relatively large intensity of the $\gamma$–$^1$H bands need not be surprising. What does surprise is that the prevalences of isotopomers with multiple $^1$H’s, as judged from the intensities of the corresponding bands (see Fig. 1), are considerably higher than one expects given the probabilities of finding a $^1$H in particular positions as determined from the intensity of the singly substituted bands. This might indicate that not all pentacene molecules had the same chances for exchange during deuteration. Alternatively it might be that there are large changes in the intersystem crossing rates between isotopic isomers. These considerations in part motivated us to study the intersystem crossing of these isotopomers.

**B. Fluorescence-detected magnetic resonance**

In previous work we have shown that the fluorescence-detected magnetic-resonance (FDMR) spectrum of the triplet state of a single pentacene molecule can serve to probe its isotopic composition. Briefly, the nuclei present in the molecule may have a hyperfine and quadrupole interaction and influence the shape of the magnetic-resonance spectrum. The strength of the hyperfine interaction depends on the projection of the triplet-spin density over the molecule which is known for pentacene and thus allows a correlation between line shape and the presence and position of nuclei carrying a large magnetic moment ($^{13}$C and $^1$H).

The lowest triplet state $T_1$ is populated after ISC from $S_1$. As depicted in Fig. 7, hyperfine and quadrupole interactions cause a slight additional splitting of the three $T_1$ sublevels so that transitions between these sublevels established by means of applied microwaves will be broadened accordingly. As a specific example consider the FDMR spectrum shown in Fig. 8. The microwave frequency was scanned over the $T_{g} - T_z$ and $T_{z} - T_y$ sublevel transitions while saturating the $S_0 - S_1$ transition using laser light. When inducing the $T_{y} - T_z$ or $T_{z} - T_x$ transition, the molecule will spend more time in the triplet state. Its time-average fluorescence decreases which allows the detection of the transition. The hyperfine broadening apparent in Fig. 8 can be used to confirm that molecule 18 contains $^{13}$C nuclei at both $\gamma$ positions (see Fig. 6). We will forego a discussion of the quantitative analysis which was performed using the method detailed in previous work. Qualitatively, the sharp onset of each transition corresponds to an orientation of the two equivalent $^{13}$C nuclear spins such that their hyperfine interactions cancel. The broad sideband of each transition corresponds to the case where the hyperfine interactions enhance each other.

The $T_{x} - T_z$ transition rate depends on the projection of the microwave $\textbf{B}$ field on the molecular $y$ axis. Consequently, the intensities of spectra recorded for molecules be-
FIG. 9. Hyperfine-broadened FDMR lines of the $T_x-T_z$ transition for the molecules studied. Each molecule was examined at a couple of microwave powers. The vertical scale is proportional to the FDMR effect which typically approached $-30\%$ at high microwave power.

FIG. 10. Intensity dependence of the autocorrelation decay for $\gamma y^{13}C-O_2$ molecule 18. The insets show the autocorrelation traces and exponential fits for two excitation intensities.

transition frequency is, on average, 2 MHz higher for the $O_1$ site. The variation in zero-field splitting for molecules belonging to the same site is relatively small (on the order of a few hundred kHz).

**IV. RESULTS**

The intersystem crossing rates of single pentacene molecules have been obtained by recording the autocorrelation of their fluorescence intensity as a function of the excitation intensity. The intensity autocorrelation function is defined as

$$g^2(\tau) = \langle I(t)I(t+\tau)\rangle/\langle I(t)\rangle^2,$$

where the angular brackets denote an average over time $t$. It can be measured by building a histogram counting the number of detected photon pairs separated by various $\tau$ times. By assuming a three-level system with level 1 the ground state $S_0$, level 2 the first excited singlet state $S_1$, and level 3 the lowest triplet state $T_1$ (see Fig. 7) Bernard et al. showed that at intermediate time scales $(0.1 \mu s < \tau < 100 \mu s$ for pentacene/p-terphenyl) $g^2(\tau)$ is well approximated by a single exponential

$$g^2(\tau) = 1 + C \exp(-\lambda \tau)$$

where

$$\lambda = k_{31} + \frac{k_{31}I_s/I_x}{1 + 2(k_{31}/k_{23})I_s/I_x},$$

with $I$ the excitation intensity, $I_s$ the saturation intensity, $k_{23}$ the intersystem crossing rate to the triplet state, and $k_{31}$ the decay rate from the triplet to the ground state. Clearly, the correlation decay rate $\lambda$ can be determined by fitting a single exponential to a recorded autocorrelation trace. By recording autocorrelation traces at a series of excitation intensities and determining $\lambda$ for each intensity, a series of points is obtained to which Eq. (3) can be fit. Such a fit provides values for $I_s$, $k_{23}$, and $k_{31}$. Figure 10 shows an example fit together with a couple of the constituent autocorrelation traces.

By now one might wonder why a method based on treating the triplet as a single level is at all applicable. After all, the triplet $T_1$ state has three sublevels $T_x$, $T_y$, and $T_z$ with...
mutually differing populating and decay rates. For a complete description of the kinetic parameters a five instead of a three-level model is needed. Indeed, Brown et al. have performed such a complete analysis.\textsuperscript{22} It turns out that the three-level model works well for the present purposes because the populating rate of the $T_z$ sublevel is much smaller than that of the $T_x$ and $T_y$ levels which have nearly identical lifetimes as evident from the fact that the $T_x-T_y$ transition was not detectable in spite of markedly different $T_x$ and $T_y$ populating rates (see Fig. 8). With no microwaves applied, the relatively long-lived $T_y$ only slightly perturbs the monoexponential shape of the autocorrelation. Thus the described method determines the total intersystem crossing rate $k_{23}$ as well as a triplet decay rate $k_{31}$ that applies to both $T_x$ and $T_y$ but not $T_z$.

An overview of the autocorrelation data and corresponding fits for all examined molecules is given in Fig. 11. The kinetic parameters as determined through the fits are listed in Table II together with the site and isotopomer species. A subset of the isotopomers examined for the O$_1$ site were examined for the O$_2$ site so as to discriminate site dependent effects and gauge the reproducibility of any isotopomer dependence. To assist in the interpretation the change in intersystem crossing $\Delta k_{23}$ relative to the perdeuterated species of each site is also tabulated.

V. DISCUSSION

The kinetic parameters summarized in Table II reveal that the triplet lifetimes ($\tau_{31}=k_{31}^{-1}$) are mostly clustered near an average of 110 $\mu$s for both the O$_1$ and O$_2$ site. No clear isotopomer dependent trend can be discerned within the rather limited precision. In contrast, the $S_1 \rightarrow T_1$ intersystem crossing rate $k_{23}$ does differ significantly between the sites. O$_1$ molecules have, on average, a 29% higher $k_{23}$ rate as compared to O$_2$ molecules of the same isotopic composition. In addition, there is a marked dependence of $k_{23}$ on isotopic composition that reproduces for both sites. A single $^1$H in the $\epsilon$, $\alpha$, or $\beta$ position causes an increase in ISC of roughly 5%-8%. In contrast, a $^1$H in the $\gamma$ position decreases $k_{23}$ by about 10%. Only for the $\alpha$ position is a significant discrepancy between molecules from either distortion-split band ($\alpha_1$ and $\alpha_2$) observed. When examining the results for molecules containing multiple $^1$H, a trend in $\Delta k_{23}$ becomes evident as made explicit in Table III. Clearly $k_{23}$ decreases with the number of $^1$H’s and increases with the number of $^2$H in a way that is approximately additive.

Changes in the isotopic composition of a molecule have a marked influence on vibrational frequencies. Consequently the observed dependence of the $S_1 \rightarrow T_1$ ISC rate $k_{23}$ on the isotopic composition most probably relates to changes in vibrational frequencies between isotopic isomers. When substituting a $^1$H for a $^2$H the mass of the involved atom is halved which causes all associated normal-mode frequencies (particularly those of the C–H stretch, in-plane rock and out-of-plane wag modes) to increase in a way that is very similar for the various substitution positions. Yet $k_{23}$ is found to decrease for a $\gamma$ substitution and to increase for an $\epsilon$ substitu-

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<td>$\epsilon_{2}$-$^2$H</td>
<td>148.3±3.0</td>
<td>-25.3</td>
<td>82±9</td>
</tr>
<tr>
<td>17</td>
<td>O$_1$</td>
<td>all-$^2$H</td>
<td>134.7±4.3</td>
<td>0</td>
<td>101±20</td>
</tr>
<tr>
<td>18</td>
<td>O$_1$</td>
<td>$\gamma$-$^1$C</td>
<td>136.7±1.7</td>
<td>+2.0</td>
<td>124±9</td>
</tr>
<tr>
<td>19</td>
<td>O$_1$</td>
<td>$\epsilon_1$-$^1$H</td>
<td>145.4±1.5</td>
<td>+10.7</td>
<td>121±8</td>
</tr>
<tr>
<td>20</td>
<td>O$_1$</td>
<td>$\epsilon_1$-$^2$H</td>
<td>143.6±1.3</td>
<td>+8.9</td>
<td>112±5</td>
</tr>
<tr>
<td>21</td>
<td>O$_1$</td>
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<td>147.9±1.7</td>
<td>+13.2</td>
<td>128±10</td>
</tr>
<tr>
<td>22</td>
<td>O$_1$</td>
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<td>141.8±1.8</td>
<td>+7.1</td>
<td>124±10</td>
</tr>
<tr>
<td>23</td>
<td>O$_1$</td>
<td>$\epsilon_2$-$^1$H</td>
<td>143.5±1.5</td>
<td>+8.8</td>
<td>115±7</td>
</tr>
<tr>
<td>24</td>
<td>O$_1$</td>
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<td>123.8±1.9</td>
<td>-10.9</td>
<td>104±8</td>
</tr>
<tr>
<td>25</td>
<td>O$_1$</td>
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<td>152.6±1.6</td>
<td>+17.9</td>
<td>114±8</td>
</tr>
<tr>
<td>26</td>
<td>O$_1$</td>
<td>$\epsilon_{1}$-$^2$H</td>
<td>132.2±1.8</td>
<td>-2.5</td>
<td>107±8</td>
</tr>
<tr>
<td>27</td>
<td>O$_1$</td>
<td>$\gamma$-$^1$H</td>
<td>106.9±2.5</td>
<td>-27.8</td>
<td>89±8</td>
</tr>
</tbody>
</table>

FIG. 11. Autocorrelation decay data and corresponding fits for all examined molecules. The crosses, plusses, circles, and squares discriminate repeated measurements at the same excitation intensity. The curves are mutually offset along the intensity axis to avoid overlap.
TABLE III. The change in ISC upon γ and/or ε 1H substitution relative to the perdeuterated case. An additive trend is apparent.

<table>
<thead>
<tr>
<th>Isotopomer</th>
<th>Experimental ∆ε23 (kHz)</th>
<th>Calculated ∆ε23 (kHz)</th>
<th>Calculated T3–S1 (cm⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>O1</td>
<td>γ: 0.53 0.68 14.3 5.4</td>
<td>γ: 0.53 0.68 14.3 5.4</td>
<td>γ: 0.53 0.68 14.3 5.4</td>
</tr>
<tr>
<td>O2</td>
<td>ε: +1.2 0.1 5.0 1.5</td>
<td>ε: +1.2 0.1 5.0 1.5</td>
<td>ε: +1.2 0.1 5.0 1.5</td>
</tr>
<tr>
<td>O3</td>
<td>γ: –14.2 9.2 0.5 3.4</td>
<td>γ: –14.2 9.2 0.5 3.4</td>
<td>γ: –14.2 9.2 0.5 3.4</td>
</tr>
</tbody>
</table>
VI. CONCLUSION

We have demonstrated the feasibility of studying a large set of isotopic isomers not through synthesis and ensemble spectroscopy, but rather through the selection, by means of excitation spectroscopy and fluorescence-detected magnetic resonance, of single molecules belonging to specific isotopomer species present as an accidental impurity. The triplet kinetics of pentacene molecules was determined through fluorescence autocorrelation. A marked trend in the $S_1 \rightarrow T_1$ intersystem crossing of pentacene for various isotopomers was observed. We attribute this trend to the modulation of a near resonance between the first excited singlet state and vibrational levels of a higher lying triplet $T_3$ by isotope shifts of these electronic states, an interpretation corroborated by quantum-chemical calculations.

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