State-specific studies of internal mixing in a prototypical flexible bichromophore: Diphenylmethane

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Laser-induced fluorescence, resonant two-photon ionization, UV-UV hole burning, UV depletion, and single vibronic level fluorescence (SVLF) spectra of jet-cooled diphenylmethane (DPM) have been recorded over the 37 300–38 400 cm⁻¹ region that encompasses the S₁ ← S₀ and S₂ ← S₀ transitions. All transitions in the laser-induced fluorescence excitation spectrum are due to a single conformational isomer of DPM with C₂ symmetry. The S₁ ← S₀ origin transition occurs at 37 322 cm⁻¹, supporting a short progression in the symmetric torsion T with spacing of 28 cm⁻¹. The S₂ ← S₀ origin transition occurs 123 cm⁻¹ above the S₁ origin and possesses very weak torsional structure, observable only under saturating laser power conditions. A combination of SVLF spectroscopy and hot band studies is used to assign the frequencies of the symmetric torsion (T), antisymmetric torsion (T̄), and butterfly (β) vibrations in the S₀, S₁, and S₂ states. The emission from the S₂ origin is composed of two components, a set of sharp transitions ascribable to the S₂ state and a dense “clump” of transitions ending in ground-state levels 81, 88, and 93 cm⁻¹ above the S₀ zero-point level ascribable to S₁(υ) emission. Assignment of the transitions in the clump leads to the conclusion that the single vibronic level responsible for the emission has mixed S₂/S₁ character. The mixing involves several torsional vibronic levels in the S₁ manifold close in energy to the S₂ origin, with the correct symmetry to couple the two states. These levels involve significant torsional excitation. The close energetic proximity of these levels leads to a breakdown of typical vibronic coupling selection rules. © 2008 American Institute of Physics. [DOI: 10.1063/1.2977730]

I. INTRODUCTION

From a spectroscopic viewpoint, diphenylmethane (DPM) is an interesting molecule because it contains two identical ultraviolet chromophores in very close proximity, linked only by a methylene group. Furthermore, the torsional coordinates connecting the two rings to the methylene group are extremely flexible. Excitonic coupling between the two aromatic rings will depend on their orientation. In a face-to-face configuration, electronic coupling will be significant, but if the rings are perpendicular, as in benzene dimer or spirobifluorene, the two π electron systems will be orthogonal and interaction will be minimal. Furthermore, the direction of the S₀–S₁ transition moment of phenyl derivatives is known to depend sensitively on the nature and conformation of the substituent. The combination of excitonic coupling and flexible degrees of freedom is present in many other molecules, but rarely are both aspects investigated in the same molecule. Thus, our anticipation is that the first two excited states of DPM will be closely intertwined with one another in a way that could have fascinating consequences for the ultraviolet spectrum of the molecule.

Beyond locating the two excited states and determining their minimum-energy structures, one can also probe the spectroscopic consequences of their interaction with one another. In the time domain, this is the process of internal conversion or electronic energy transfer, but in the frequency domain, these interactions are more aptly referred to as “internal mixing” since the interactions produce vibronic levels with mixed electronic character. Internal mixing has been a subject of several previous experimental and theoretical studies, but so far no state-to-state view of internal mixing has developed.

We have used both vibrationally and rotationally resolved ultraviolet spectroscopy to study DPM in the unperturbed environment of the supersonic jet. In the present paper, resonant two-photon ionization (R2PI) and single vibronic level fluorescence (SVLF) spectroscopy are used to examine the role of torsional motions in the electronic structure of DPM. The origins of S₁ and S₂ states of DPM are assigned and the vibronic structure of each state is examined. In contrast to molecules such as naphthalene or ovalene, where the energy separation between S₁ and S₂ states is several thousand cm⁻¹, the S₁ and S₂ origins of DPM are separated by only 123 cm⁻¹, making it an example of a molecule in the “sparse coupled level structure” limit. As we shall see, SVLF spectra of the S₂ origin and S₂ vibronic bands exhibit distinct components that reflect the mixed S₂/S₁ char-

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acter of these levels. We analyze the emission in order to
determine which $S_1$ vibronic levels are mixed, providing a
state-to-state perspective on the internal mixing at a level of
detail not possible in previous studies. The fully deuterated
(DPM-$d_{12}$) isotopomer of DPM has also been studied to help
clarify aspects of the vibronic spectroscopy. The results of
high resolution laser-induced fluorescence (LIF) spectroscopy
and extensive calculations of the excited state torsional
surfaces will be discussed elsewhere.8

II. EXPERIMENTAL METHODS

R2PI, LIF, UV-UV hole burning (UVHB), UV-UV
depletion (UVD), and SVLF spectroscopies were used to fo-
cus on various aspects of the ultraviolet spectrum of DPM.
UVHB and UVD are both pump-probe spectroscopies using
two ultraviolet lasers, spatially overlapped and separated in
time by 200 ns, with the pump laser operating at 10 Hz and
the probe laser at 20 Hz. When the wavelengths of the two
lasers are on transitions which share a common ground state,
the probe laser signal will be depleted, providing conformer-
specific spectra. In UVHB, the pump laser is fixed while the
probe is tuned. Conversely, in UVD, the constant signal from
the probe laser is monitored while the pump laser is scanned.
The former method provides spectra with better signal to
noise while the latter allows detection of transitions that do
not appear in the R2PI spectrum due to lack of ionization
efficiency.9

R2PI, UVHB, and UVD spectroscopies were all carried
out in a supersonic jet time-of-flight mass spectrometer
which has been described previously.16 LIF and SVLF spec-
tra were recorded in a free jet fluorescence detection vacuum
chamber which has also been described previously.11 For the
present work, the fluorescence apparatus described in Ref. 11
was modified to accommodate detection with a 2048×512
pixel charge coupled device (CCD) camera (Andor series
DU440BT). The camera was typically kept at −80 °C via
thermoelectric and water cooling. Background subtraction
and cosmic ray removal were carried out by the ANDOR soft-
ware. Total acquisition times ranged from 20 min to over an
hour. The amount of scattered light at the excitation wave-
length was determined by adjusting the time the laser fired,
so the laser entered the vacuum chamber prior to the gas
pulse from the pulsed valve. The signal from scattered light
was recorded and subtracted from the single vibronic fluo-
rescence spectrum, giving quantitative fluorescence intensi-
ties at the excitation wavelength. Typical resolution with a
50–100 μm entrance slit to the monochromator was
6–8 cm$^{-1}$. The frequency-doubled output of a neodymium
doped yttrium aluminum garnet (Nd:YAG) pumped dye laser
was used for all ionization and fluorescence experiments.
DPM was commercially available (Sigma-Aldrich) and was
used directly with gentle heating (50–70 °C) to achieve a
vapor pressure of 1 Torr in 2 bars of helium for supersonic
expansion.

DPM-$d_{12}$ was synthesized in our laboratory based on a
Friedel–Crafts alkylation as outlined in a textbook by
Wade.12 The details of the synthesis are given in Sec. I of the
supplementary information.13 The liquid sample of DPM-$d_{12}$
was treated in the same manner as DPM-$d_0$ for supersonic
expansion.

III. COMPUTATIONAL METHODS

Electronic structure calculations on DPM were carried
out using GAUSSIAN03.14 Various stationary points in the
ground state were optimized using density functional theory
with the Becke3LYP functional15 and a 6–31+G* basis set.16
These were followed up with ground-state optimizations us-
ing second-order Møller–Plesset perturbation theory17 (MP2)
with a 6–311++G** basis set. Vertical excitation energies,
not including zero-point energy corrections, were calculated
using configuration interaction singles18 (CIS)/6–31G, time-
dependent density functional theory19 (TDDFT)/6–31+G*,
and complete active space self-consistent field20
(CASSCF)/6–31G*, restricting the system to $C_2$ symmetry.
The GAMESS computational package21 was used to carry out
the CASSCF calculations. Eight electrons were distributed
among eight orbitals, those $\pi$ and $\pi^*$ orbitals corresponding
to linear combinations of the toluenelike highest occupied
molecular orbitals and lowest unoccupied molecular orbitals
on each ring. The potential energy surfaces of the excited
states were further investigated using TDDFT. The relaxed
ground-state potential energy surface was first calculated for
a number of ring torsion angles and then single point excited
state energies were calculated at those geometries.

IV. RESULTS AND ANALYSIS

A. R2PI and LIF excitation spectra

The R2PI spectrum of DPM is shown in Fig. 1(a). The
$S_1 \leftrightarrow S_0$ origin transition is located at 37 322 cm$^{-1}$, just
155 cm$^{-1}$ red of the literature value22 for the $S_1 \leftrightarrow S_0$ origin
of toluene. The low-frequency portion of the spectrum shows
a progression with a 28 cm$^{-1}$ spacing, and additional peaks
at 43 and 123 cm$^{-1}$. Two other prominent peaks appear in
the spectrum, at 562 and 960 cm$^{-1}$, each with a 28 cm$^{-1}$
progression built off of them. These higher-frequency vi-
bronic transitions have close analogs in the spectrum of
toluene.22
Figure 2(a) presents an expanded view of the first 160 cm\(^{-1}\) of the LIF excitation spectrum of DPM, recorded under unsaturated conditions. This spectrum shows low-frequency vibronic transitions involving the inter-ring torsional vibrations (symmetric torsion \(T\) and antisymmetric torsion \(\bar{T}\) in \(C_2\) symmetry) and inter-ring bending mode \(\beta\). The assignments for these transitions follow from analysis of their SVLF spectra in Sec. IV C, aided by the calculations which are described in Sec. II of the supplementary material.\(^{13}\)

The 123 cm\(^{-1}\) transition is unusual in the spectra of Figs. 1(a) and 2(a), as it is the only transition that does not have appreciable torsional vibronic structure built off of it. Calculations predict no fundamental vibrations between 64 and 180 cm\(^{-1}\). It is unlikely that the 123 cm\(^{-1}\) band is an overtone of the 64 cm\(^{-1}\) vibration (\(\beta_0\)) because this is a totally symmetric vibration and should appear in the fundamental. Given that this band is not easily assignable as a vibration of the \(S_1\) state, it seems plausible to explore the possibility that it is another origin transition, either of a second conformation or of the \(S_2\) state. The assignment of the \(S_2\) origin to a band 145 cm\(^{-1}\) above the origin in the crystal spectrum of DPM is consistent with this assignment.\(^{23,24}\) The excited state calculations support a low-lying \(S_2\) state, with an exciton splitting on the order of hundreds of wavenumbers (Sec. II, supplementary material).\(^{13}\)

**B. UVHB and UVD spectra**

UVHB spectroscopy was used to establish whether the +123 cm\(^{-1}\) band was due to a second conformation of DPM. Figure 1(b) shows the UVHB spectrum recorded with the hole-burn laser set to the DPM 0\(_0^0\) band at 37 322 cm\(^{-1}\). Every peak in the R2PI spectrum, including the transition at 123 cm\(^{-1}\), burned out, and must therefore be due to the same ground-state species. On this basis we surmise that only one conformation of DPM exists in the supersonic expansion. It is likely, then, that the peak at +123 cm\(^{-1}\) is the origin of the second excited state.

A striking feature of the +123 cm\(^{-1}\) band is that there are no sizable vibronic bands built off of it, either in the low-frequency torsional region or in the higher-frequency region of the ring vibrations. One possible explanation for this is that these bands undergo rapid nonradiative processes that make them difficult to detect via R2PI. The technique of UVD spectroscopy should allow us to see any additional absorption transitions in the spectrum. As Fig. 1(c) shows, however, the depletion spectrum contains only those transitions present in R2PI within the signal to noise of the experiment.

**C. High resolution UV spectra**

Based on exciton theory,\(^{2,23-26}\) our expectation is that the transition dipole moments of the \(S_0-S_1\) and \(S_0^*-S_2\) origin transitions will be orthogonal to one another. Therefore, one important confirmation of the assignment of the +123 cm\(^{-1}\) transition to the \(S_2\) origin would be the changes so produced in the rotational structure of the band. To that end, high resolution spectra (32 MHz resolution) of the \(S_0^*-S_1\) band and +123 cm\(^{-1}\) transitions have been recorded at NIST and are shown in Figs. 3(a) and 3(b), respectively. The \(S_0^*-S_1\) origin has a strong \(Q\)-branch indicative of significant \(a\)-character to the band structure (67% \(a\); 33% \(c\)), while the +123 cm\(^{-1}\) transition shows no central \(Q\)-branch, characteristic of a pure \(b\)-type band. Detailed analysis of these spectra will be presented elsewhere.\(^8\) For the present purposes, we surmise that the +123 cm\(^{-1}\) band has a transition dipole moment direction perpendicular to the \(S_0^*-S_1\) origin, marking its different electronic character.

**D. SVLF spectra**

1. \(S_1\) origin and torsional vibronic levels

The SVLF spectrum of the \(S_1\) origin is shown in Fig. 4(a), with the relative position (in cm\(^{-1}\)) of many of the
higher-frequency peaks labeled. As shown in Table I, most of this structure can be interpreted directly in terms of toluene-like vibrations involving in-plane ring distortions. Not surprisingly, the spectrum is very similar to that of toluene, with major transitions at 554, 622, 822, and 1006 cm\(^{-1}\) ascribable to \(6\bar{a}_1^0, 6\bar{b}_1^0, 1\bar{t}_1^0,\) and \(12\bar{t}_2^0,\) respectively. The intensity pattern of these transitions follows that from toluene’s \(S_1\) origin,\(^{27}\) as might be anticipated.

The first 150 cm\(^{-1}\) of the SVLF spectrum from the DPM origin are shown in an expanded view in Fig. 5(a). As with the R2PI spectrum, there is a significant progression in the symmetric phenyl ring torsion mode \(T,\) with ground-state frequency of 19 cm\(^{-1}\). Figures 5(b)–5(d) show the SVLF spectra from the \(T^1, T^2,\) and \(T^3\) levels. Transitions appear at 19 cm\(^{-1}\) intervals up to about 120 cm\(^{-1}\) and are fitted reasonably well by a harmonic Franck–Condon (FC) analysis with displacement parameter \(D = 1.0\) (taking into account the frequency change between the \(S_0\) and \(S_1\) states).\(^{28}\) The stick spectra in Figs. 5(a)–5(d) show the results of this analysis. The same structure is built off transitions associated with all the other ring vibrations present in the origin spectrum.

Two other peaks appear in the SVLF spectrum shown in Fig. 5(a), a shoulder at ~31 cm\(^{-1}\), and a peak with torsional structure built off of it at 64 cm\(^{-1}\). There are two other calculated low-frequency vibrations besides the symmetric phenyl ring torsion, which has already been assigned. The peak at 64 cm\(^{-1}\) is assigned to the symmetric butterfly vibration by virtue of its close match with calculation (Table I) and is designated \(\beta_1^T.\) Its corresponding transition in the excitation spectrum appears as a shoulder on the high-frequency edge of the 54 cm\(^{-1}\) transition [Fig. 2(b)]. This assignment is clarified and strengthened by results from DPM-d\(_{12}\) (included in the supplementary material),\(^{13}\) where \(\beta_1^T\) transition is well resolved. The peak at ~31 cm\(^{-1}\) must therefore involve the nontotally symmetric (nts) phenyl ring torsion \(\bar{T}.\)

The SVLF spectrum of the transition 43 cm\(^{-1}\) above the \(S_1\) origin is connected with this 31 cm\(^{-1}\) level in \(S_0,\) which acts as a false origin for a progression with a 31 cm\(^{-1}\) spacing.

The assignment of the 31 cm\(^{-1}\) level in \(S_0\) and 43 cm\(^{-1}\)
level in $S_1$ is crucial to our understanding of the geometry of the $S_1$ state. Frequencies for $\bar{T}$ of 31 cm$^{-1}$ in $S_0$ and 43 cm$^{-1}$ in $S_1$ are roughly twice the predicted values from DFT B3LYP/6–31+G* calculations (19 and 25 cm$^{-1}$, respectively), suggesting assignments as $\bar{T}^0_1$ and $\bar{T}^0_0$. However, the accuracy with which B3LYP calculations predict these low-frequency torsions is uncertain. If these levels were assigned to the $S_1$ state, we can predict the FC intensities based on a harmonic analysis with a displacement along $\bar{T}^0_0$; the $S_0$ and $S_1$ frequencies of $\bar{T}$ at 15.5 and 21.5 cm$^{-1}$, respectively, leads to the assignments shown in Fig. 7(a) for the observed transitions in the emission spectrum of $\bar{T}^2$. In the absence of $\bar{T}^2$, which we shall assign to $\bar{T}^0_0$ and $\bar{T}^0_1$, the lack of transitions at half the separation from the origin ascribable to $\bar{T}^0_0$ and $\bar{T}^0_1$ would provide strong evidence that the $S_1$ state retains the $C_2$ symmetry of the ground state.

To distinguish between these possibilities, LIF excitation and SVLF spectra were taken when exciting closer to the nozzle exit, where the expansion was warmer, thereby creating hot bands and sequence bands which were detected by LIF. If the +43 cm$^{-1}$ band is actually a hot band from the +43 cm$^{-1}$ sequence band should be observed +6 cm$^{-1}$ (21.5–15.5 = 6) from the origin transition.

Figure 6 shows the cold [Fig. 6(a)] and warm [Fig. 6(b)] LIF spectra of the DPM origin region. A sequence band clearly appears 5–6 cm$^{-1}$ above the $S_1$ origin ($\bar{T}^0_1$), while no band is observed at +12 cm$^{-1}$. This indicates that the +43 cm$^{-1}$ band in the R2PI spectrum is actually $\bar{T}^0_0$, making the fundamental $\bar{T}$ frequencies 21.5 cm$^{-1}$ in $S_1$ and 16.5 cm$^{-1}$ in $S_0$. The hot band at +47 cm$^{-1}$ is then assigned to $\bar{T}^0_0$. A hot band also appears 6 cm$^{-1}$ above the $S_2$ origin (129 cm$^{-1}$ above the $S_1$ origin), which we shall assign (Sec. IV D 2) to $S_2$ $\bar{T}^1_0$ based on its SVLF spectrum.

The SVLF spectra of the +5 and +47 cm$^{-1}$ hot bands shown in Figs. 7(b) and 7(c), respectively, confirm these assignments, with transitions labeled accordingly. On the basis of these assignments, combined with the absence of a $S_1$ $\bar{T}^0_0$ transition, a $C_2$ symmetric structure for the $S_1$ excited state is deduced. The retention of $C_2$ symmetry in the $S_1$ state is also consistent with the transition dipole orientation observed in the rotationally resolved study [Fig. 3(a)].

Before leaving this discussion of the SVLF spectra of the $S_1$ torsional levels, we take a final look at the intensity patterns these levels produce. The assignment of the $S_0$ and $S_1$ frequencies of $\bar{T}$ at 15.5 and 21.5 cm$^{-1}$, respectively, leads to the assignments shown in Fig. 7(a) for the observed transitions in the emission spectrum of $\bar{T}^2$. In the absence of $\bar{T}^2$, which we shall assign to $\bar{T}^0_0$ and $\bar{T}^0_1$, the SVLF spectrum of $\bar{T}^2$ is a nearly pure progression in even quanta of $\bar{T}$, with almost no intensity in the symmetric torsion $T$ progression. Since we know the vibrational frequencies of $\bar{T}$ in $S_0$ and $S_1$ and have deduced that the molecule retains $C_2$ symmetry in $S_1$, we can predict the FC intensities based on a harmonic analysis with a displacement along $\bar{T}$ of zero. This prediction, shown in the stick diagram of Fig. 7(a), substantially underestimates the intensity of the $\Delta T = 0$ transitions involving $\bar{T}$. Thus, $\bar{T}^2$ emission has more intensity in the $\bar{T}$ progression than expected, at the expense of a near-complete loss of the progression in $T$. Finally, the intensity of $\bar{T}^0_0$ is much smaller than $\bar{T}^0_4$, a substantial skewing of the intensity toward ground-state levels involving large quantum numbers in $\bar{T}$. These unique intensity patterns carry over to the $\bar{T}^3$ emission as well.

In what follows, we use these unique intensity patterns as diagnostics of the presence of $\bar{T}^0$ excited state character. It seems likely that these unusual intensity patterns arise from the unusual shape of the torsional potential energy surfaces in $S_0$ and $S_1$.

### 2. $S_2$ origin and torsional vibronic levels

Figure 4(b) shows the SVLF spectrum from the band 123 cm$^{-1}$ above the $S_1$ origin. The same toluene-like vibronic bands appear in this spectrum with a similar relative intensity pattern to those of the DPM $S_1$ origin, shown directly above it in Fig. 4(a). However, these vibronic transitions are substantially more intense relative to the resonance fluorescence.
peak than they are in the $S_1 0^0$ emission spectrum. Thus, the 123 cm$^{-1}$ band has different FC factors (FCFs) in the ring modes than the $S_1$ origin, consistent with its assignment to the $S_2$ origin.

The low-frequency portion of the spectrum in Fig. 4(b) is quite intriguing. The lack of torsional structure built directly off the excitation wavelength is consistent with the lack of such torsional structure built off the 123 cm$^{-1}$ band in the R2PI spectrum, indicating little change in geometry along the torsional or butterfly modes upon electronic excitation. More interesting is the closely spaced clump of transitions starting about 80 cm$^{-1}$ to the red of the excitation wavelength. Careful checks were carried out to ensure that these peaks were not the result of collisional cooling occurring on the timescale of the fluorescence.

Despite the lack of sizable transitions built off of the +123 cm$^{-1}$ band, there were a couple of minor transitions in the LIF excitation spectrum just above the 123 cm$^{-1}$ band that deserved further investigation. In order to enhance the intensities of these transitions, a LIF spectrum was recorded with sufficient UV laser power to saturate the strong transitions in the spectrum. Figure 2 compares the unsaturated [Fig. 2(a)] and saturated [Fig. 2(b)] LIF spectra. In particular, the saturated spectrum clearly shows a couple of small transitions just to the blue of the +123 cm$^{-1}$ band at +136 and +145 cm$^{-1}$.

The SVLF spectra of the +136 and +145 cm$^{-1}$ cold vibronic bands and the +129 cm$^{-1}$ hot band are compared to the emission from the $S_2$ origin in Figs. 8(a)–8(d). The emission from the +136, +145, and +129 cm$^{-1}$ bands shows a combination of “sharp” transitions with no torsional side bands and a “clump” of transitions shifted from the resonance fluorescence by an amount comparable to that observed in the $S_2$ origin emission [Fig. 8(a)].

The SVLF spectrum of the +136 cm$^{-1}$ band [Fig. 8(b)] shows a false origin shifted from the excitation wavelength by 20 cm$^{-1}$, consistent with emission to the $v''=1$ level of the symmetric torsion $T$. The sharp vibronic transitions built off this false origin look nearly identical to the sharp transitions in the $S_2$ origin spectrum, apart from being shifted by 20 cm$^{-1}$. On this basis, the +136 cm$^{-1}$ band is assigned to the $S_0^0$-$S_2^0$ transition. This makes its frequency 13 cm$^{-1}$ in $S_2$ and demonstrates that an $A$ symmetry $S_2$ vibronic level emits to a ground-state vibrational level.

The +145 cm$^{-1}$ band [Fig. 8(c)] also shows a series of sharp transitions nearly identical to those in Figs. 8(a) and 8(b), but in this case the sharp transitions are built off a false origin which is shifted 15 cm$^{-1}$ from the excitation frequency, an amount equivalent to one quantum of $\tilde{T}$ in $S_0$. The +145 cm$^{-1}$ band is therefore assigned to $S_2$ $\tilde{T}_1^0$ and the false origin emission to $\tilde{T}_1^1$, appearing by virtue of strong $\Delta\nu=0$ FCFs involving $\tilde{T}$ in the $S_2 \rightarrow S_0$ emission. This assignment makes the frequency of $\tilde{T}$ in $S_2$ 22 cm$^{-1}$. This transition accesses an upper state with $A \times b=B$ vibronic symmetry, which is the same symmetry established for the $S_1$ origin from the observed rotational structure. Therefore, the $S_2$ $\tilde{T}_1^0$ transition must be gaining intensity from the $S_1$ state via vibronic coupling.

If the assignment of the +145 cm$^{-1}$ band to $S_0^0$-$S_2^0$ $\tilde{T}_1^0$ is correct, it predicts the presence of the $S_0^0$-$S_2^0$ $\tilde{T}_1^1$ sequence band 6 cm$^{-1}$ above the $S_0^0$-$S_2^0$ origin, at 145−16.5 = +129 cm$^{-1}$. A hot band at that position is indeed observed [Fig. 6(b)], with a SVLF spectrum [Fig. 8(d)] identical to the +145 cm$^{-1}$ transition [Fig. 8(c)] in absolute wavelength, indicating that the two transitions share the same excited state level $S_2$ $\tilde{T}_1^1$.

Based on the R2PI and SVLF spectra, we have assigned the symmetric and antisymmetric torsional levels in the $S_0$, $S_1$, and $S_2$ electronic states. Table II summarizes the frequencies of $T$, $\tilde{T}$, and $\beta$ in $S_0$, $S_1$, and $S_2$ for both DPM-$d_0$ and $d_{12}$. The most dramatic difference between these vibrations in the three electronic states is in the symmetric torsion $T$, which drops in frequency by more than a factor of 2 in $S_2$ (13 cm$^{-1}$) relative to $S_1$ (28 cm$^{-1}$).

The spectra in Fig. 8 provide evidence that the combination of sharp toluenelike vibronic transitions and the clump of closely spaced transitions shifted to the lower wavenumber side of them are characteristic signatures of the $S_2$ vibronic bands. The shape of the clump of bands is similar in the three examples available ($S_0^0$, $T_1^1$, and $\tilde{T}_1^0$), but not identical, with peak positions shifted from their respective false origins that are similar. What does change from one band to the next is the intensity of the clump transitions relative to the sharp bands. In particular, the +136 cm$^{-1}$ tran-

\begin{table}[h]
\centering
\caption{Experimental frequencies of the lowest vibrational frequencies in $S_0, S_1$, and $S_2$ for both isotopomers of DPM.}
\begin{tabular}{llll}
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<table>
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<th>Isotopomer</th>
<th>State</th>
<th>$T$ (cm$^{-1}$)</th>
<th>$\tilde{T}$ (cm$^{-1}$)</th>
<th>$\beta$ (cm$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>DPM-$d_0$</td>
<td>$S_0$</td>
<td>19</td>
<td>16.5</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>29</td>
<td>21.5</td>
<td>$\sim$56</td>
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<tr>
<td></td>
<td>$S_2$</td>
<td>13</td>
<td>22</td>
<td>\ldots</td>
</tr>
<tr>
<td>DPM-$d_{12}$</td>
<td>$S_0$</td>
<td>18</td>
<td>15</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>25</td>
<td>20</td>
<td>54</td>
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<td></td>
<td>$S_2$</td>
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\end{tabular}
\end{table}

\textsuperscript{a}This value is approximate since the transition was not completely resolved.
sition (now assigned as $S_2 T^1_{00}$) has a relative integrated intensity of the clump transitions which is significantly greater than from the $S_2 T^0_{00}$ or $S_2 T^1_{00}$ level.

Most importantly, as the tie lines and brackets in Fig. 8(a) show, the intensity of the first clump of transitions built off the resonance fluorescence or false origin is significantly greater than the corresponding intensity of the clump emission built off of higher vibronic bands. Therefore, the clump emission has more nearly $\Delta v=0$ FCFs in the toluenelike vibronic bands, with relative intensities similar to those found in the $S_1$ SVLF spectra [Fig. 4(a)]. This is a confirming piece of evidence that the closely spaced clump emission reflects the $S_1$ character of the upper state(s).

In order to test this hypothesis further, analogous scans were recorded for the fully deuterated isotopomer, DPM-$d_{12}$. Indeed, similar characteristic features of the $S_1$ and $S_2$ vibronic levels are found in DPM-$d_{12}$. The resulting assignments for $T$ and $\bar{T}$ in $d_{12}$ are included in Table II. The presentation and analysis of these spectra are included in the supplementary material.$^{13}$

E. Analysis of the mixed character of the $S_2$ levels

Up to this point, the analysis of the emission from the $S_2$ vibronic bands has shown that the $S_2$ origin and $S_2$ vibronic bands in DPM-$d_0$ and -$d_{12}$ are of mixed character, with part of the emission ascribable to the $S_2$ character (the sharp bands lacking torsional activity) and part due to the $S_1$ vibronic levels which are coupled to the $S_2$ level (the clump emission). In this section, an attempt is made to assign the transitions in the $S_1$ vibronic emission in order to extract further information about the nature of the vibronic coupling involved under the present circumstance of near-degenerate electronic states.

1. The $S_2$ origin of DPM-$d_0$ ($S_2 0^0_0$, $S_1+123$ cm$^{-1}$)

Figure 9 presents another view of the low-frequency region of the SVLF spectra of the $S_2$ origin transition of DPM-$d_0$. In order to better resolve the clump emission, this spectrum was taken with higher laser power and slightly improved resolution over the spectrum in Figs. 4 and 8. In this expanded view, the clump of transitions ascribable to the $S_1$ vibronic character of the band is displayed in significant detail. One striking aspect of the emission in DPM-$d_0$ is the sharp onset in intensity at 81 cm$^{-1}$.

The clump emission in Fig. 9 is dominated by two sets of three transitions, with the first triad at 81, 88, and 93 cm$^{-1}$, followed by a second set at 112, 118, and 125 cm$^{-1}$. The separation between these sets of transitions is thus 31 cm$^{-1}$, an amount equal to two quanta of $\bar{T}$. This nearly pure progression in even quanta of $\bar{T}$ built off each of these false origins is reminiscent of the nearly pure $\bar{T}$ progression that appears in the emission from $S_1 \bar{T}^1_{00}$ [Fig. 7(a)] and $\bar{T}^2$ [Fig. 7(c)]. Recall that in these spectra, a clear progression in $\bar{T}$ is accompanied by a near-complete lack of intensity in transitions involving $T$ (which would have a spacing of 19 cm$^{-1}$) and a skewing of the $\Delta v=0$ intensity toward $T_{n+2}$ rather than $T_{n-2}$. This suggests that the upper states responsible for these transitions have considerable $\bar{T}$ excitation, with the set of transitions at 81, 88, and 93 cm$^{-1}$ possessing $\Delta v=0$ FCFs from the upper states responsible for them. The tie lines and quantum number designations in Fig. 9 provide proposed assignments for the six transitions that dominate the clump emission. These have odd quanta of $\bar{T}$, as required for vibronic coupling with the $S_2$ origin.

The energy level diagrams in Fig. 10 show the experimentally determined or extrapolated values for a subset of the low-lying torsional energy levels in the $S_0$ and $S_1$ states of DPM-$d_0$. While Fig. 10 shows only a subset of the levels, Tables S4 and S5 of the supplementary material$^{13}$ give all of the energy levels up to 150 cm$^{-1}$. The vibrational levels in Fig. 10 are separated by symmetry, with $a/b$ symmetry levels on the left/right. The (mn) labels on the energy levels indicate the level's vibrational quantum numbers [$v(T)$, $v(\bar{T})$, and $v(\beta)$].

Based on Fig. 10, we assign the emission to levels 81, 88, and 93 cm$^{-1}$ to transitions ending in the ground-state (050), (230), and (410) levels [in red in Fig. 10(a)], which are predicted to be 83, 89, and 97 cm$^{-1}$ above the $S_0$ zero-point level based on harmonic extrapolation of the $T$ and $\bar{T}$ $S_0$ frequencies. The corresponding levels in $S_1$ have estimated energies of 109, 120, and 129 cm$^{-1}$ above the $S_1$ origin based on the known experimental frequencies for $T$ and $\bar{T}$ in $S_1$, placing them in close proximity to the $S_2$ origin (123 cm$^{-1}$). These three $S_1$ vibronic levels are three of the four closest-energy levels of the right symmetry to couple to the $S_2$ origin. Furthermore, the fourth close-lying $b$ symmetry level in $S_1$, (031), has predicted energies of 121 cm$^{-1}$ in $S_1$ and 114 cm$^{-1}$ in $S_0$. Thus, the $S_1$ (031) level may also be involved in the mixing, contributing to the intensity of the transition at 112 cm$^{-1}$ in the clump emission (Fig. 9). Based on what we know about the emission spectrum from $\beta^1$, we can rule out the possibility that the (011) band at 78 cm$^{-1}$ in $S_1$ (81 cm$^{-1}$ in $S_0$) may also contribute to the 81 cm$^{-1}$ band in the SVLF spectrum because if it did, the $\beta^1 T^1_{00}$ combination band should also be visible at 100 cm$^{-1}$ (directly between the two maxima of the clump), which it is not.
In summary, these postulated assignments indicate that the clump of bands observed in emission from the (nominally) $S_0$ origin have imprinted in their unusual closely spaced pattern the vibronic character of the $S_1$ levels that are mixed with the $S_2$ zero-point level to produce an upper state of mixed character,

\[
\psi(+123 \text{ cm}^{-1}) = c_{2000}(S_2,000) + c_{050}(S_1,050) + c_{1230}(S_1,230) + c_{1410}(S_1,410) + c_{1031}(S_1,031).
\]  

(1)

2. The $S_2 T_0^1$ transition ($S_2+13 \text{ cm}^{-1}$, $S_1+136 \text{ cm}^{-1}$)

As Fig. 8(b) shows, the clump emission in the SVLF spectrum of the $S_2 T_0^1$ transition at +136 cm$^{-1}$ is less resolved, but has two transitions at 117 and 145 cm$^{-1}$ that dominate the spectrum. Applying the same arguments used to assign the clump emission from the $S_2$ origin, we look for $b$ symmetry $S_1$ vibrational levels in close energetic proximity to the $S_2 T^1$ level at 136 cm$^{-1}$ and use $\Delta \nu=0$ FCFs to predict the position of the dominant band(s) in emission. In this case, the $b$-symmetry [012] and [211] levels are closest in energy (Fig. 10), with corresponding levels in $S_0$ at 145 and 120 cm$^{-1}$, precisely as observed. Other levels may also be involved in the mixing, but are unresolved in the weak emission from this band. The close proximity of these coupled states may be responsible for the larger intensity of the clump emission relative to the sharp transitions due to $S_2 T^1$, reflecting a greater $S_1$ character to the emitting mixed excited state level.

3. The $S_2 T_0^1$ transition ($S_2+22 \text{ cm}^{-1}$, $S_1+145 \text{ cm}^{-1}$)

If the $S_2$ state retains the $C_2$ symmetry of $S_0$, then the $S_2\rightarrow S_0 T_0^1$ transition would gain oscillator strength from $a$ symmetry vibrational levels in $S_1$. In this case [Fig. 8(c)], transitions in the clump region are unresolved, giving rise only to the same general shape as the $S_2 0^0$ clump emission, but shifted from the corresponding maxima in the $S_2 0^0$ emission by one quantum of $T^1$ (17 cm$^{-1}$). Since the frequencies of the antisymmetric torsion $T^1$ are 22 cm$^{-1}$ in $S_2$ and 21 cm$^{-1}$ in $S_1$, the likely $S_1$ vibronic levels involved in the mixing are the same ones involved in the $S_2$ origin emission, but with one additional quantum of $T^1$; that is, $|S_1,060)$, $|S_1,240)$, $|S_1,420)$, and $|S_1,041)$.

V. DISCUSSION AND CONCLUSIONS
A. Excitonic splitting in DPM

A primary goal of the present investigation is to understand the excitonic coupling in DPM and its dependence on the two low-frequency torsional coordinates ($T$ and $T^1$) along which the molecule can so easily distort. A first level of analysis is simply to identify the $S_1$ and $S_0$ origins, and hence determine the excitonic splitting in DPM in the region near the ground-state geometry. We have presented several pieces of experimental evidence that the $S_2$ origin is located 123 cm$^{-1}$ above the $S_1$ origin. By comparison, CASSCF calculations predict a splitting of 136 cm$^{-1}$, in fortuitous agreement. McClure observed a similar $S_1$-$S_2$ splitting in the absorption spectrum of crystalline DPM, although the as-

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### Table: Energy Levels

<table>
<thead>
<tr>
<th>$S_2(A)$</th>
<th>$S_1(B)$</th>
<th>$S_2(A)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>012</td>
<td>015</td>
</tr>
<tr>
<td>401</td>
<td>014</td>
<td>145</td>
</tr>
<tr>
<td>440</td>
<td>011</td>
<td>125</td>
</tr>
<tr>
<td>700 260</td>
<td>137</td>
<td>133</td>
</tr>
<tr>
<td>080</td>
<td>131</td>
<td>133</td>
</tr>
<tr>
<td>340</td>
<td>121</td>
<td>117</td>
</tr>
<tr>
<td>301</td>
<td>250</td>
<td>122</td>
</tr>
<tr>
<td>600</td>
<td>700</td>
<td>117</td>
</tr>
<tr>
<td>160</td>
<td>114</td>
<td>117</td>
</tr>
<tr>
<td>121</td>
<td>230</td>
<td>109</td>
</tr>
<tr>
<td>320</td>
<td>230</td>
<td>109</td>
</tr>
<tr>
<td>101</td>
<td>050</td>
<td>083</td>
</tr>
<tr>
<td>a-symmetry</td>
<td>b-symmetry</td>
<td></td>
</tr>
<tr>
<td>201</td>
<td>100</td>
<td>102</td>
</tr>
<tr>
<td>240</td>
<td>190</td>
<td>102</td>
</tr>
<tr>
<td>203</td>
<td>99</td>
<td>98</td>
</tr>
<tr>
<td>021</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>101</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>a-symmetry</td>
<td>b-symmetry</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>011</td>
<td>011</td>
</tr>
<tr>
<td>300</td>
<td>011</td>
<td>011</td>
</tr>
</tbody>
</table>

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FIG. 10. (Color online) Experimentally determined or extrapolated values for the energy levels of the $S_0$ and $S_1$ states of DPM-$d_8$. The $a$ and $b$ symmetry levels have been separated for convenience. Each energy level is designated with a set of quantum numbers and a position (in wavenumbers) as shown in bottom right corner. The dotted lines indicate levels that are coupled.
B. Internal mixing between the excitonic states

The present data set, particularly the SVLF spectra, has provided a detailed look at the mixed electronic state character of the low-lying $S_2$ vibronic levels due to internal mixing with near-degenerate $S_1$ vibronic levels. The close proximity of the two electronic states gives rise to a situation in which the density of $S_1$ vibrational levels is still quite sparse in the region of the $S_2$ origin, as shown in Fig. 10. As a result, we are afforded state-specific insight to the process of internal mixing in the isolated molecule. Under nanosecond laser excitation, the upper states responsible for the emission are single vibronic levels of mixed $S_1$/$S_2$ character, with no time dependence in the nanosecond experiment we have carried out.

In DPM, the $S_2$ (|000⟩, |100⟩, and |010⟩) levels all show dual emission, with sharp vibronic bands ascribable to the $S_2$ character of the excited state level and clump emission from the $S_1$ character. In Sec. IV.F we analyzed the $S_1$ clump emission and deduced that the $S_2$ origin is, in fact, of mixed $S_2$/$S_1$ character, with the $S_1$ character arising from several levels of the right symmetry within about 10 cm$^{-1}$ of the $S_2$ upper level of interest. In fact, as Fig. 10 shows in pictorial fashion, the four identified $S_1$ vibronic levels mixed with |$S_2$,000⟩ are the four closest-energy $b$ symmetry vibrational states in the $S_1$ manifold.

When two electronic states well separated from one another are vibronically coupled, the perturbative treatment laid out in standard Herzberg–Teller theory leads to $\Delta v(Q_0) = \pm 1$ selection rules in the coupled vibration $Q_1$. However, in DPM and DPM-d$12$, the two excitonic states of different symmetries (A and B) are in close proximity to one another, where the closely related theories of internal conversion (time-dependent picture) or internal mixing (stationary-state picture)$^{33}$ are more appropriate. In this case the standard perturbative treatment begins with adiabatic Born–Oppenheimer states, in which the perturbative operator inducing internal conversion is the nuclear kinetic-energy operator.$^{32,33}$

Using the treatment of internal mixing from Sharf et al.$^{34}$ we have developed an expression$^{33}$ for the vibronic coupling matrix element $V$ applied to the case at hand in which the two vibronic states differ only in their vibrational quantum numbers in a single non-totally symmetric promoting mode ($T$) and a single totally symmetric accepting mode ($S$).

$$V = \gamma \left[ 1 - \frac{\epsilon_{S}^{S} - \epsilon_{S}^{S}}{E_{S}^{S}(Q_0) - E_{S}^{S}(Q_0)} \right] \langle X_{2}^{2} | Q_{0}^{2} | X_{1}^{1} \rangle_{T} \langle X_{2}^{2} | X_{1}^{1} \rangle_{Q_{0}}$$

$$\times \prod_{j=M}^{N} \langle X_{2}^{j} | X_{1}^{j} \rangle_{Q_{j}}$$

(2)

Here $\gamma$ is the electronic coupling matrix element,

$$\gamma = \langle \psi_{S}(q;Q_{0}) \left| \frac{\partial U(q,Q)}{\partial Q_{T}} \right| \psi_{S}(q;Q_{0}) \rangle_{Q_{0}}$$

(3)

$\epsilon_{S}^{S}(Q)$ is the one-dimensional harmonic oscillator wave function with energy $\epsilon_{S}^{S}$ for mode $Q$ in vibrational level $v$ and electronic state $S_a$. Thus, the coupling matrix element $V$ between two vibronic adiabatic Born–Oppenheimer states with unperturbed energies $\epsilon_{S}^{S}$ and $\epsilon_{S}^{S}$ is a product of several terms: (i) the electronic coupling matrix element $\gamma$, (ii) an energy-dependent term that is maximized when the difference in vibronic energies is much smaller than the difference between the electronic state energies $(E_{S}^{S}(Q_0) - E_{S}^{S}(Q_0) = 123$ cm$^{-1}$), (iii) an integral in $T$ that yields the usual $\Delta v = \pm 1$ propensity rule for the coupling coordinate $Q_{T}$ inducing the radiationless transition,$^{33}$ (iv) a vibrotional overlap integral in $T$, and (v) the product of all other vibrational overlap integrals.

The levels in DPM which are measurably mixed with |$S_2$,000⟩ are |$S_1$,050⟩, |$S_1$,230⟩, |$S_1$,410⟩, and |$S_1$,031⟩. These levels involve total quantum number changes of $\Delta v(Q_0)=5$, 5, 5, and 4, respectively. The relevant quantum number change for vibronic coupling between $S_1(B)$ and $S_2(A)$ is that involving $T$, the lowest-frequency vibration of $b$ symmetry, with $\Delta v(T)=3$, 1, and 3 for the four $S_1$ vibronic levels involved in the mixing, in apparent violation of the $\Delta v(T)=\pm 1$ selection rule. Thus, in order for the |050⟩, |230⟩, and |031⟩ levels of $S_1$ to couple to the $S_2$ origin, third-order and fifth-order terms in the electronic Hamiltonian Taylor series expansion would be required, terms discarded in the perturbative treatment just described.$^{34,35}$ These higher-order terms are anticipated to drop off steeply with increasing $\Delta v(T)$, likely by about an order of magnitude with each integer increase in $\Delta v$. At the same time, the quantum number changes in the symmetric torsion $T$ for these same levels are $\Delta v(T)=0,2,4$, and 0, respectively. Since the geometry change between $S_1$ and $S_2$ in $T$ is small, the overlap integrals strongly favor $\Delta v(T)=0$ and will also fall off rapidly as $\Delta v(T)$ increases.

As Table III summarizes, the $\Delta v(T)$, $\Delta v(T)$, and $\Delta E$ contributions to the fractional mixing given in Eq. (5) counterbalance one another in the levels in close proximity to |$S_2$,000⟩. Given the similar relative intensities of the clump emission transitions ascribable to four $S_1$ vibronic levels (Fig. 9), it appears that all four close-lying levels have comparable fractional mixing with the $S_2$ origin. The energy levels involved are within about 10 cm$^{-1}$ of |$S_2$,000⟩, so that vibronic coupling reaches across a very small energy gap, with coupling matrix element $V \sim 5$ cm$^{-1}$. 


TABLE III. Quantum number changes and contributions to the magnitude of the mixing coefficient between the $S_1$ origin and the indicated $S_2$ vibronic levels of DPM-$d_0$.

<table>
<thead>
<tr>
<th>$S_1$ level</th>
<th>$\Delta v(T)$</th>
<th>$\Delta v(\tilde{T})$</th>
<th>$\Delta v(\beta)$</th>
<th>$\Delta E$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[050]</td>
<td>0, large</td>
<td>5, small</td>
<td>0, large</td>
<td>$-14$, medium</td>
</tr>
<tr>
<td>[230]</td>
<td>2, med</td>
<td>3, med</td>
<td>0, large</td>
<td>$-3$, small</td>
</tr>
<tr>
<td>[410]</td>
<td>4, small</td>
<td>1, large</td>
<td>0, large</td>
<td>$+6$, medium</td>
</tr>
<tr>
<td>[031]</td>
<td>0, large</td>
<td>3, med</td>
<td>1, small</td>
<td>$-2$, small</td>
</tr>
<tr>
<td>[010]</td>
<td>0, large</td>
<td>1, large</td>
<td>0, large</td>
<td>$-100$, very large</td>
</tr>
</tbody>
</table>

$\Delta E = $ experimentally observed energy difference between the $S_1$ levels and the $S_2$ origin.

$^b$[010] does not contribute significantly to the mixing with the $S_2$ origin. See text for further discussion.

In principle, the integrated intensity of each component of the dual emission can be used to determine the extent of mixing present in the upper state giving rise to the emission. As described in greater detail in the supplementary material, we estimate based on our spectra that the fractional $S_1(050)$ character in the $S_2$ (000) level is

$$\left| \frac{C_{S_1,050}}{C_{S_2,000}} \right|^2 \approx 0.08.$$  

(4)

This estimate indicates that the mixing of any one of the $S_1$ vibronic levels into the $S_2$ zero-point level is less than 10%, but its effect on the SVLF spectrum of $S_2$ (000) in the first 200 cm$^{-1}$ of the spectrum is amplified by the greater oscillator strength of the $S_1 \rightarrow S_0$ emission and nearly $\Delta v = 0$ FCFs in the ring modes. Combining this result with the two-level energy formula (see supplementary material) leads to estimates for the internal mixing coupling matrix elements $V$ in the 0.8–3.7 cm$^{-1}$ range.

These estimates explain our inability to clearly pick out the coupled levels directly in the R2PI (Fig. 1) or LIF excitation spectrum (Fig. 2). The $S_1(050)$, (231), (410), and (031) levels are dark from the $S_0$ zero-point level, but gain oscillator strength from the $S_2$ origin. However, since each $S_1$ vibronic level is anticipated to have less than 10% $S_2$ origin character, their intensities are anticipated to be at least ten times smaller than the $S_2$ origin.

Before leaving this section, it is worth returning to one aspect of the LIF spectra of DPM (Fig. 2) that we are only now prepared to discuss. Given the close proximity of the $S_1$ and $S_2$ states, one might have thought that the $S_1 \tilde{T}_0^0$ transition should be visible in the spectrum (21.5 cm$^{-1}$ above the $S_1$ origin) due to vibronic coupling with the $S_2$ origin, which is only 101.5 cm$^{-1}$ above it in energy. The $S_1(010)$ and $S_2(000)$ states have $\Delta v(\tilde{T}) = -1$, $\Delta v(T) = 0$, and $\Delta v(\beta) = 0$, fulfilling the propensity rules for vibronic coupling, which often reaches over energy separations of thousands of inverse centimeters to produce measurable intensity in ultraviolet spectra. From our experimental spectrum, we can place an upper bound on the intensity of the $S_1 \tilde{T}_0^0$ transition of 0.3% of the $S_2$ origin, from which it would gain intensity. Thus, the fractional internal mixing of $S_2$ (000) into $S_1$ (010) must be less than 0.3%. Solving as before leads to an upper bound for the coupling matrix element $V$ between these two levels of 5 cm$^{-1}$. Note that $V/\delta = 0.05$ so that these two levels are in the weak coupling limit in which $V/\delta$ can be equated with the mixing coefficient. This value for $V/\delta$ is six times less than for the near-resonant levels, consistent with its weak intensity. When compared to the 0.8–3.7 cm$^{-1}$ estimate for $V$ in the cases where $\Delta v(\tilde{T}) > 1$ and/or $\Delta v(T) > 1$, we see that our upper bound for the fully vibronically allowed $S_1(010)$ level is in the same range, while we would have expected it to be much greater based on Table III. Whether this arises from the large-amplitude character of the torsion or a breakdown of the perturbative treatment leading to Eq. (2) is an open question worthy of further investigation.

It will be important to study other bichromophores in which the energy separation between $S_1$ and $S_2$ is varied systematically in order to see how the state-specific internal mixing evolves with changes in the energy separation and densities of states. This we are currently pursuing.

C. The lack of vibronic bands built off the $S_2$ origin

A final, particularly intriguing aspect of the vibronic spectroscopy of the $S_2$ state of DPM-$d_0$ and -$d_{12}$ is the near-complete lack of vibronic structure built off the $S_2$ origin. The lack of torsional structure built off the $S_2$ origin is a simple consequence of a small change in geometry along the torsional coordinate(s), leading to $\Delta v(T, \tilde{T}) = 0$ FCFs. This is borne out by the lack of torsional structure in the sharp $S_2$ vibronic emission [Fig. 4(b)]. However, the strong tunolene-like vibronic bands observed in emission argue for strong vibronic coupling and/or significant geometry changes along a few of the ring modes, analogous to those in tunolene. On this basis, we should anticipate strong vibronic bands in the R2PI spectrum, appearing about 123 cm$^{-1}$ above the analogous levels in the $S_1$ state. As shown in greater detail in the supplementary material, these transitions are not identifiable in the spectrum.

One possible solution is simply that the $S_2$ vibronic bands are so strongly coupled to the dense manifold of $S_1$ vibrational levels at these energies, that the oscillator strength is spread over a wide energy range that makes the broadened bands difficult to observe. In this scenario, the $S_1/S_2$ coupling favors internal conversion from $S_2$ to $S_1$ vibronic levels by virtue of the higher density of $S_1$ states at a given excitation energy due to the fact that the $S_2$ state zero-point level is 123 cm$^{-1}$ above that for $S_1$.

An alternative is that the $S_2$ “origin” could be one of only a few bound levels supported by a shallow “dimple” in the $S_2$ surface near the $S_0$ minimum geometry. Figure 11 supports the notion that the $S_2$ state surface is quite different in shape than that due to $S_1$. The figure portrays a cut along the $C_2$ diagonal on the two-dimensional (2D) torsional surface of $S_1$ and $S_2$, calculated at the TDDFT B3LYP/6–31 +G* level of theory. Along this diagonal, the two excited states necessarily retain their delocalized character. Note that the state designated as $S_2$ at the $S_0$ geometry crosses the $S_1$ state to form a minimum below that state near $r_1 = r_2 = 90^\circ$. The unusual shape of the torsional surface of the $S_2$ state may be reflected in the sharp drop in frequency of the symmetric torsion $T$, which is 29 cm$^{-1}$ in $S_1$, but only 13 cm$^{-1}$.
minimum-energy geometry of the ground state, is the upper solid curve in $S_2$. This indicates a substantial softening of the potential along the $C_2$ diagonal. On this basis, even in a harmonic description of the two states along coordinate $T$, the $S_1$ and $S_2$ states would cross not too far above the $S_2$ minimum.

In order to resolve these issues, it would be helpful to study other deuterated isotopomers of DPM that vary the degree of asymmetry between the two rings. Such a study is currently being pursued. On the theoretical side, the close-lying entangled nature of the $S_1$ and $S_2$ states will present a particular challenge that requires methods that extend beyond CIS or TDDFT to correctly describe the excited states of DPM. Ultimately, accurate calculations of the full 2D torsional surface for the $S_1$ and $S_2$ states would be of great use, in which the energy separation, degree of electronic localization, and torsional energy levels/wave functions are mapped out over the entire surface.

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13. See EPAPS Document No. E-JCPSA6-129-612836 for all supplementary information, including synthesis, SVLF spectra, and more in-depth discussions. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

