Methyl-torsion-facilitated internal energy delocalization following electronic excitation in \textit{m}-fluorotoluene: Can \textit{meta} and \textit{para} substitution be directly compared?

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Methyl-torsion-facilitated internal energy delocalization following electronic excitation in \( m \)-fluorotoluene: Can \textit{meta} and \textit{para} substitution be directly compared?

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Abstract
Coupling between vibrations, and between vibrations and torsions—a generalization of intramolecular vibrational redistribution (IVR)—provides routes to internal energy delocalization, which can stabilize molecules following photoexcitation. Following earlier work on \( p \)-fluorotoluene (\( p \)FT), this study focuses on \( m \)-fluorotoluene (\( m \)FT) as probed via the \( S_1 \leftrightarrow S_0 \) electronic transitions and the \( D_0^+ \leftrightarrow S_1 \) ionization, using two-dimensional laser-induced fluorescence and zero-electron-kinetic energy spectroscopy, respectively. Wavenumbers are reported for a number of vibrations in the \( S_0 \), \( S_1 \), and \( D_0^+ \) states and found to compare well to those calculated. In addition, features are seen in the \( m \)FT spectra, not commented on in previous studies, which can be assigned to transitions involving vibration–torsion (“vibtor”) levels. Comparisons to the previous work on both \( m \)-difluorobenzene and \( m \)FT are also made, and some earlier assignments are revised. At lower wavenumbers, well-defined interactions between vibrational and vibtor levels are deduced—termed “restricted IVR,” while at higher wavenumbers, such interactions evolve into more-complicated interactions, moving toward the “statistical IVR” regime. It is then concluded that a comparison between \( m \)FT and \( p \)FT is less straightforward than implied in earlier studies.

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I. INTRODUCTION

Anharmonic coupling in molecules leads to delocalization, and so dispersal, of internal energy within a molecule—an important aspect to enhanced photostability.\(^1\)–\(^4\) Which of the vibrations in a molecule can couple, and to what extent, depends on a number of factors, but having the same symmetry and being close in energy are two key considerations,\(^1\) along with the relative motions of the atoms in those vibrations. Such coupling leads to actual vibrational motions having mixed character, and this can be discerned through an analysis of the vibrational activity in electronic and photoelectron spectra, where vibrational eigenfunctions of one electronic state are projected onto those of another. To first order, vibrational fundamentals do not couple anharmonically, but sometimes activity in fundamentals other than that excited can be seen in experimental spectra. This can be caused by changes in geometry that lead to significant Franck–Condon factors (FCFs), or as a result of Duschinsky rotations.\(^5\)

Methylation in biomolecules has been invoked as a key factor in photoinduced carcinogenicity,\(^6\) and consequently, an understanding of the role of methyl groups in the modification of a molecule’s photobehavior is of key importance. Parmenter and co-workers have published numerous studies on the effect of methylation on intramolecular vibrational redistribution (IVR), with the most pertinent study here being that of Timbers \textit{et al.} In that work, it was concluded that \( m \)-fluorotoluene (\( m \)FT) undergoes intramolecular vibrational redistribution (IVR) more than an order of magnitude faster than \( p \)-fluorotoluene (\( p \)FT) and, hence, that the location of substituents is important in internal energy delocalization.

Recently, we published resonance-enhanced multiphoton ionization (REMPI) and zero-electron-kinetic-energy
scheme is used—as will be seen, this expectation is largely borne out. Of course, the spectrum of $m$FT will be complicated by the contributions from torsion and vibtor levels, as noted above.

II. EXPERIMENTAL

The REMPI/ZEKE\textsuperscript{28} and 2D-LIF\textsuperscript{29} apparatuses are the same as those employed recently. In both experiments for $m$FT, a free-jet expansion of $m$FT (Sigma-Aldrich, 99% purity) in 2 bar Ar was employed.

For the 2D-LIF spectra, the free-jet expansion was intersected at $X/D \sim 20$ by the frequency-doubled output of a single dye laser (Sirah Cobra-Stretch), operating with Coumarin 503 and pumped with the third harmonic of a Surelite III Nd:YAG laser. The fluorescence was collected, collimated, and focused onto the entrance slits of a 1.5 m Czerny–Turner spectrometer (Sciencetech 9150) operating in single-pass mode, dispersed by a 3600 groove/mm grating, allowing $\sim 300$ cm$^{-1}$ windows of the dispersed fluorescence to be collected by a CCD camera (Andor iStar DH334T). At a fixed grating angle of the spectrometer, the excitation laser was scanned, and at each excitation wavenumber, the camera image was accumulated for 2000 laser shots. This allowed a plot to be produced of fluorescence intensity $vs$ both the excitation laser wavenumber and the wavenumber of the emitted and dispersed fluorescence, termed a 2D-LIF spectrum.\textsuperscript{35,36} Band positions for the 2D-LIF spectra are given for the estimated band center.

For the REMPI and ZEKE spectra of $m$FT, the focused, frequency-doubled outputs of two dye lasers (Sirah Cobra-Stretch) were overlapped spatially and temporally and passed through a vacuum chamber coaxially and counterpropagating, where they intersected the free-jet expansion. The excitation laser was operated with Coumarin 503 and pumped with the third harmonic (355 nm) of a Surelite III Nd:YAG laser, while the ionization laser was operated with Pyrromethene 597 and pumped with the second harmonic (532 nm) of a Surelite I Nd:YAG laser. The jet expansion passed between two biased electrical grids located in the extraction region of a time-of-flight mass spectrometer, which was employed in the REMPI experiments. These grids were also used in the ZEKE experiments by application of pulsed voltages, giving typical fields of $\sim 10$ V cm$^{-1}$, after a delay of up to 2 $\mu$s; this delay was minimized while avoiding the introduction of excess noise from the prompt electron signal. The resulting ZEKE bands had widths of $\sim 5$ cm$^{-1}$–7 cm$^{-1}$. Electron and ion signals were recorded on separate sets of microchannel plates. Band positions for REMPI and ZEKE bands are given for the maximum, and ZEKE spectra were generally obtained when exciting through the intermediate band maximum.

For the REMPI spectrum of $m$DFB, a free-jet expansion of $m$DFB (Sigma-Aldrich, 99% purity) in 5 bar Ar was employed.

III. RESULTS AND ASSIGNMENTS

A. Nomenclature and labeling

1. Vibrational and torsional labeling

We shall employ the $D_i$ labels\textsuperscript{27} for the $m$FT vibrations, as used in Refs. 8–10; this $C_i$ point group labeling scheme is based on the vibrations of the $m$DFB molecule. As such, we shall transcribe the Wilson/Varsányi labels in Ref. 11 and the $C_{2v}$ Mulliken labels used...
in Ref. 33 for mDFB to the $D_i$ labels for the purposes of comparison with the present work. These, and the available experimental vibrational wavenumbers for mDFB, are presented in Table I, alongside the calculated wavenumbers—the calculated and experimental $S_0$ values are generally taken from Ref. 27 (some of which were deduced from Refs. 33 and 37), while the experimental values for the $S_1$ state were obtained from Ref. 33, with the calculated values for this electronic state being obtained in the present work.

Since we shall also be referring to the methyl torsional motion for mFT, for which use of the $G_6$ molecular symmetry group (MSG) is appropriate, we shall employ those symmetry labels throughout. The torsional levels will be labeled via their $m$ quantum number, $^{4,10}$ and the correspondence between the $C_i$ point group labels and the $G_6$ MSG labels is given in Table II. To calculate the overall symmetry of a vibtor level, it is necessary to use the corresponding $G_6$ label for the vibration and then find the direct product with the symmetry of the torsion (Table II), noting that a $C_{3v}$ point group direct product table can be used, since the $G_6$ MSG and the $C_{3v}$ point group are isomorphic. The torsional levels in mFT are labeled with the signed quantum number $m$ ($m = 0, 1, 2, \ldots$). The $m = 0$ level is singly degenerate, while levels with $|m| \geq 3n$ ($n = 1, 2, \ldots$) are doubly degenerate, consisting of $+/−$ pairs, and levels with $m = 3n$ form linear combinations of the $+/−$ pairs that split in energy under the influence of the torsional potential; these are labeled $m = 3(+) \text{ and } m = 3(−).^{3}$

Under the free-jet expansion conditions employed here, almost all molecules are expected to be cooled to their zero-point vibrational level, and thus essentially, all $S_0 \leftrightarrow S_1$ excitations are expected to originate from this level. In contrast, owing to nuclear-spin and rotational symmetry, the mFT molecules can be in one of the $m = 0 \text{ or } m = 1$ torsional levels, with approximately equal population in each; the residual population in the $m = 2$ level is also seen.\

The available experimental vibrational wavenumbers for mFT are presented in Table III, alongside the calculated wavenumbers—the experimental $S_0$ values are generally taken from Ref. 27, while the experimental values for the $S_1$ state were obtained from Refs. 8 and 10 and the present work; the calculated $S_0$ and $S_1$ values are obtained in the present work and generally agree well with those presented in Ref. 10. The experimental values for the $S_0^+$ state are from Ref. 8 and the present work, while the calculated values are from the present work.

The level of theory employed is given in the footnotes of Tables I and III, and Gaussian 16$^{39}$ was used for all of these calculations.

### 2. Coupling and transitions

In the usual way, vibrational transitions will be indicated by the number, $i$, of the $D_i$ vibration, followed by a superscript/subscript specifying the number of quanta in the upper/lower states, respectively. When required, torsional transitions will be indicated by $m$.

#### Table II. Correspondence of the $C_6$ point group symmetry classes with those of the $G_6$ molecular symmetry group. Also indicated are the symmetries of the $D_i$ vibrations and the different pure torsional levels.

| $C_i$ | $G_6$ | $D_i$ | $m$ |
|-------|-------|-------|------|
| $a'$  | $a_1$ | $D_{1h}$ | 0, 3(+), 6(+), 9(+) |
| $a''$ | $a_2$ | $D_{2h}$ | 3(−), 6(−), 9(−) |
| $c$   |      |       | 1, 2, 4, 5, 7, 8 |

$^{4}$Symmetries of vibtor levels can be obtained by combining the vibrational symmetry (in $G_6$) with those of the pure torsional level, using the $C_{3v}$ point group direct product table.

$^{b}$The $D_i$ labels are described in Ref. 27, where the vibration mode diagrams can also be found.

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**Table I.** Calculated and experimental wavenumbers (cm$^{-1}$) for the vibrations of m-difluorobenzene.

| $D_i$ ($C_6$) | $S_0$ Calculated$^a$ | $S_0$ Expt.$^a$ | $S_1$ Calculated$^d$ | $S_1$ Expt.$^d$ |
|---------------|-----------------------|-----------------|-----------------------|-----------------|
| $D_1$ (1)     | 3122                  | 3095            |                       |                 |
| $D_2$ (2)     | 3116                  | 3086            |                       |                 |
| $D_3$ (21)    | 3112                  | 3086            |                       |                 |
| $D_4$ (3)     | 3090                  |                 |                       |                 |
| $D_5$ (4)     | 1597                  | 1611            | 1529 (1519)           |                 |
| $D_6$ (22)    | 1592                  | 1613            | 1480                  |                 |
| $D_7$ (23)    | 1475                  | 1490            | 1375                  |                 |
| $D_8$ (5)     | 1439                  | 1435            | 1378 (1346)           |                 |
| $D_9$ (24)    | 1304                  | 1337            | 1435                  |                 |
| $D_{10}$ (6)  | 1255                  | 1277            | 1250                  |                 |
| $D_{11}$ (25) | 1252                  | 1292$^b$        | 1228 (1267)           |                 |
| $D_{12}$ (26) | 1145                  | 1157            | 1118 (1145)           |                 |
| $D_{13}$ (27) | 1102                  | 1120            | 1094 (1206)           |                 |
| $D_{14}$ (7)  | 1058                  | 1068            | 995 (998)             |                 |
| $D_{15}$ (8)  | 994                   | 1012            | 958 (966)             |                 |
| $D_{16}$ (28) | 941                   | 956             | 883 (936)             |                 |
| $D_{17}$ (9)  | 726                   | 739             | 698 (701)             |                 |
| $D_{18}$ (10) | 514                   | 522             | 438 (442)             |                 |
| $D_{19}$ (29) | 502                   | 513             | 440 (444)             |                 |
| $D_{20}$ (30) | 467                   | 477             | 462 (468)             |                 |
| $D_{21}$ (11) | 320                   | 329             | 315 (317)             |                 |

**Table II.** Correspondence of the $C_6$ point group symmetry classes with those of the $G_6$ molecular symmetry group. Also indicated are the symmetries of the $D_i$ vibrations and the different pure torsional levels.

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$^a$The $D_i$ labels are described in Ref. 27, where the vibration mode diagrams can also be found.

$^b$Taken from Ref. 33; values in parentheses are those about which the authors of that work were less certain.

$^c$Calculated and experimental wavenumbers—the calculated and experimental $S_0$ values originate from Ref. 33. For $D_{10},$ we have reverted to the original liquid-phase value, since we deduce that the reassignment of $D_{10}$ in Ref. 33 is likely incorrect.

$^d$TD-B3LYP/aug-cc-pVTZ, scaled by 0.97. Present work.

$^e$Reassigned in the present work.
TABLE III. Calculated and experimental wavenumbers (cm\(^{-1}\)) for the vibrations of m-fluorotoluene.

| \(D \) | \( S_0 \) | \( S_1 \) | \( D_0^* \) |
|---|---|---|---|
| \( a_1 \) | Calculated | Expt. | Calculated | Expt. | Calculated | Expt. |
| \( D_1 \) | 3107 | [3081] | 3128 | 3119 |
| \( D_2 \) | 3088 | [3060] | 3114 | 3107 |
| \( D_3 \) | 3086 | 3123 | 3111 |
| \( D_4 \) | 3072 | 3084 | 3092 |
| \( D_5 \) | 1578 | [1595] | 1512 | 1541 | 1569 |
| \( D_6 \) | 1603 | [1623] | 1494 | 1490 |
| \( D_7 \) | 1479 | [1492] | 1392 | 1444 |
| \( D_8 \) | 1420 | [1460] | 1363 | 1385 |
| \( D_9 \) | 1302 | [1295] | 1294 | 1299 | 1290 |
| \( D_{10} \) | 1239 | [1251] | 1243 | 1229 |
| \( D_{11} \) | 1271 | [1266] | 1252 | 1260 | 1258 | 1275 |
| \( D_{12} \) | 1148 | [1160] | 1132 | 1122 | 1143 |
| \( D_{13} \) | 1126 | [1143] | 1115 | 1113 | 1101 |
| \( D_{14} \) | 1071 | [1079] | 1081 | 1023 | 1074 |
| \( D_{15} \) | 988 | [1003] | 1004 | 958 | 965 | 997 | 984 |
| \( D_{16} \) | 912 | [924] | 930 | 866 | 840 | 873 | 874 |
| \( D_{17} \) | 720 | [728] | 731 | 685 | 684 | 700 | 710 |
| \( D_{18} \) | 519 | [527] | 525 | 459 | 460 | 509 | 510 |
| \( D_{19(X)} \) | 505 | [513] | 512 | 448 | 457 | 410 | 415 |
| \( D_{20(Y)} \) | 435 | [450] | 445 | 410 | 420 | 442 | 456 |
| \( D_{21} \) | 285 | [296] | 294 | 281 | 285 | 290 | 298 |
| \( D_{22} \) | 967 | [970] | 760 | 988 |
| \( D_{23} \) | 886 | [886] | 705 | 916 |
| \( D_{24} \) | 859 | [858] | 501 | 855 |
| \( D_{25} \) | 773 | [778] | 775 | 575 | 787 | 780 |
| \( D_{26} \) | 683 | [683] | 468 | 592 | 592 |
| \( D_{27} \) | 557 | [556] | 554 | 377 | 367 | 514 | 517 |
| \( D_{28} \) | 443 | [442] | 441 | 241 | 253 | 373 | 380 |
| \( D_{29} \) | 236 | [243] | 237 | 184 | 174 | 190 | 190 |
| \( D_{30} \) | 199 | [212] | 201 | 122 | 128 | 167 | 169 |

\( a \) Labels are discussed in Ref. 27, where mode diagrams are presented. For \( D_{14} \) and \( D_{20} \), the motions are very mixed in the \( S_1 \) state, as discussed in Ref. 15, and are denoted \( D_X \) and \( D_Y \), respectively.

\( b \) B3LYP/aug-cc-pVTZ, scaled by 0.97. Present work—essentially the same as the values published in Ref. 10, which employed the same quantum chemical method.

\( c \) The values in square brackets are IR/Raman values that have been discussed in Ref. 27. Updates to some of these values have been made in gas-phase studies: Ref. 15 and the present work, in some cases confirming a value reported in Ref. 10.

\( d \) TD-B3LYP/aug-cc-pVTZ, scaled by 0.97. Present work—these values are close to the TD-B3LYP/cc-pVTZ values presented in Ref. 10, but several of the values do seem to be sensitive to the addition of diffuse functions to the basis set.

\( e \) Gas-phase values taken from Refs. 8 and 15 and the present work, in some cases confirming a value reported in Ref. 10.

\( f \) UB3LYP/aug-cc-pVTZ, scaled by 0.97; \( \langle S_2 \rangle = 0.76 \). Present work.

\( g \) Values taken from Refs. 8 and 15 and the present work.

\( h \) Experimental values for these two vibrations were reported in Ref. 11 but have been concluded to have been misassigned, and we concur with this conclusion.

followed by its superscripted value, and vibtor transitions will be indicated by a combination of the vibrational and torsional transition labels. When designating transitions, we shall generally omit the initial level, since it will be evident from either the jet-cooled conditions or the specified intermediate level.

As has become common usage, we will generally refer to a level using the notation of a transition, with the level indicated by the specified quantum numbers, with superscripts indicating levels in the \( S_1 \) state and subscripts indicating levels in the \( S_0 \) state. Since we will also be referring to transitions and levels involving the
ground state cation, $D_0^+$, we shall indicate those as superscripts, but with a single, additional, preceding superscripted "$+$" sign. Relative wavenumbers of the levels will be given with respect to the relevant zero-point vibrational level with $m = 0$, in each electronic state.

For cases where the geometry and the torsional potential are both similar in the $S_1$ and $D_0^+$ states, the most intense transition is usually expected to be that for which no changes in the torsional and/or vibrational quantum numbers occur, designated as $\Delta m = 0$, $\Delta \nu = 0$, or $\Delta (\nu, m) = 0$ transitions, as appropriate. However, as will be seen (and as reported in Refs. 8, 9, 14, and 15), the $\Delta m = 0$ and $\Delta (\nu, m) = 0$ transitions are almost always not the most intense bands in the ZEKE spectra for $m$FT, indicative of a significant change in the torsional potential upon ionization. The intensities of low-wavenumber features in the $S_1 \leftrightarrow S_0$ transitions have been discussed in Ref. 10, and reference will be made to that work when appropriate.

If two levels are close in wavenumber and have the same overall symmetry, then (except between vibrational fundamentals, to first order) interactions can occur, with the simplest example being the anharmonic interaction between two vibrational levels—the classic Fermi resonance. Such couplings are only expected to be significant for small changes in the vibrational quantum number, $\Delta \nu \approx 3$, and for levels that lie close in energy. For molecules that contain a hindered internal rotor, such as $m$FT and $p$FT, and if vibration–torsion coupling occurs, then interactions can also involve torsional or “vibtor” levels. This is expected to be significant only for changes in the torsional quantum number, $\Delta m$, of $\pm 3$ or $\pm 6$ in descending order of likely strength. The result of such interactions is the formation of eigenstates with mixed character. Often, the resulting eigenstates will be referred to by the dominant contribution, with the context implying if an admixture is present.

B. An overview of the REMPI spectrum

In Fig. 1, we show the $S_1 \leftrightarrow S_0$ REMPI spectrum of $m$FT over the range $0 \text{ cm}^{-1} \text{–} 1350 \text{ cm}^{-1}$. It may be seen to be rich in structure, some of which has been assigned previously. We note the good agreement with the appearance of the LIF spectrum in Ref. 11, which covers a similar range. Wavenumbers of some of the $S_1$ vibrations are in dispute. We highlight that the $0 \text{ cm}^{-1} \text{–} 350 \text{ cm}^{-1}$ region has been discussed in depth in Refs. 8 and 10, and the $400 \text{ cm}^{-1} \text{–} 480 \text{ cm}^{-1}$ region was the focus in Ref. 15. Also in Fig. 1, we present the corresponding REMPI spectrum of $m$DFB, which compares very well with the LIF spectrum presented in Ref. 33.

![FIG. 1. Overview of the REMPI spectrum of the $S_1 \leftrightarrow S_0$ transition in the range $0 \text{ cm}^{-1} \text{–} 1350 \text{ cm}^{-1}$ for (a) $m$DFB and (b) $m$FT. Only selected assignments are shown—see the text. For $m$FT, the origin bands, $m^2$ and $m^1$, have been truncated—see Ref. 8 for the $0 \text{ cm}^{-1} \text{–} 350 \text{ cm}^{-1}$ region of the spectrum. The most intense bands in the expanded view were discussed and assigned in Ref. 15. See the text for further discussion on the assignments.](https://example.com/fig1.jpg)
Overall, ignoring the torsional transitions for \( m \) FT, the correspondence between the main activity in both REMPI spectra in Fig. 1 is striking and adds confidence to the assignments for \( m \) FT discussed later.

A number of values and assignments in Table III are from the present work and will be discussed in Subsections III C–III G, where we break the discussion up into five main regions. Through these five regions, it will be seen that the coupling evolves from being absent, through well-defined coupling between a small number of levels at low wavenumber, into widespread coupling, approaching statistical IVR at higher wavenumbers.

In some of the figures, vertically integrated traces of the 2D-LIF spectra are presented. Each of these looks very similar to the corresponding section of the REMPI spectrum, confirming that the fluorescence collected is representative of the absorption spectrum in that region.

C. 2D-LIF and ZEKE spectra via the origin \( m = 0 \) and \( m = 1 \) levels

In Fig. 2, we show the 2D-LIF spectrum recorded when exciting through the pure torsional \( m^1 \) and \( m^2 \) excitations, and many assignments are also shown. The 0 cm\(^{-1}\)–550 cm\(^{-1}\) region of the emission spectrum has been assigned and discussed in depth by Stewart et al.,\(^{10,27}\) and we concurred with those assignments in our ZEKE study.\(^1\) In Ref. 10, only the 0 cm\(^{-1}\)–65 cm\(^{-1}\) region of the 2D-LIF spectrum via the \( m^1 \) and \( m^2 \) bands was presented, although DF spectra were presented up to 550 cm\(^{-1}\), with full assignments. These will prove useful in assigning the 2D-LIF spectra in the present work, when we excite at higher wavenumbers.

The assignment of these vibrational bands allows \( S_0 \) vibrational wavenumbers to be established, which are included in Table III, some of which were reported by Stewart et al.\(^{10,27}\) These values are close to those established by IR and Raman spectroscopy\(^{27,37}\) and those discussed in Ref. 27, providing further confirmation of the assignments. Other features can be identified as vibtor levels associated with these vibrational transitions, and indeed, subject to sensitivity, we expect to see the main pattern of vibtor and related transitions that are observed for the origin, for each vibrational transition.

In Fig. 3, we show the ZEKE spectra recorded via both \( m^1 \) and \( m^2 \). The regions up to \( \sim 850 \) cm\(^{-1}\) were assigned in Ref. 8; in the present work, the spectra are extended up to \( \sim 1850 \) cm\(^{-1}\) and show more vibrational bands with their associated vibtor structure. As will be seen, these help in the assignment of other ZEKE spectra presented later. The vibrational wavenumbers arising from these spectra are also included in Table III.

D. The 410 cm\(^{-1}\)–555 cm\(^{-1}\) region

The integrated 2D-LIF trace covering this region of the \( S_1 \leftarrow S_0 \) excitation is shown at the top of Fig. 4. The three most intense features in this region are \( Y_1 \) and the overlapped \( X_1 \) and \( 18^1 \) bands. The \( S_1 \) \( D_X \) and \( D_Y \) vibrations are highly mixed forms of the \( S_0 \) \( D_{19} \) and \( D_{20} \) vibrations, and these assignments, alongside the Duschinsky mixing that gives rise to the mixed character, have been discussed in Ref. 15. In Fig. 4, we also show an extended 2D-LIF spectrum recorded across this region. It can be seen that numerous features can be identified in the 2D-LIF image that are not obviously associated with discrete features in the integrated 2D-LIF (nor REMPI) spectrum; this highlights one aspect of the extra information that 2D-LIF spectra provide. The assignments of many of the bands are straightforward, combining the knowledge of the torsional levels from Refs. 8 and 10 and the vibrational levels from Ref. 15, and these are indicated in the figure, with numerous features arising from \( \Delta(v, m) = 0 \) transitions. However, there were also numerous cases where the assignment was less obvious, and some of these will be discussed in the following.

We see a 2D-LIF feature at (428, 675) cm\(^{-1}\), whose assignment is to the \( \Delta(v, m) = 0 \) band (28\(^{10}\), 29\(^{10}\) \( m^0 \), 28, 29 \( m_0 \)). This assignment is reached on the basis of a weak associated band in the expected
FIG. 3. ZEKE spectra via the (a) $m^1$ and (b) $m^0$ excitation bands. The preceding "+" sign used in the text is omitted from the assignments for clarity. These cover a wider range than those presented in Ref. 8, where further ZEKE spectra are shown when exciting through other torsional levels.

FIG. 4. 2D-LIF over the excitation range 410 cm$^{-1}$–555 cm$^{-1}$. At the top of the 2D-LIF spectrum, the trace shows the result of integrating vertically over the presented section of the 2D-LIF spectrum and closely resembles the corresponding region of the REMPI spectrum. The 415 cm$^{-1}$–465 cm$^{-1}$ excitation range of the spectrum has been shown, and the main features are discussed and assigned, in Ref. 15. The majority of the vibitor structure and other 2D-LIF features whose assignments are indicated in white on the spectrum are presented here for the first time. The region between ~480 cm$^{-1}$ and 550 cm$^{-1}$, as indicated, has been enhanced by 4× to highlight the weaker bands present in this region. Colored text is used for clarity. See the text for further discussion on the assignments.
position for $28,29, m_{3(\pm)}$ and also the ZEKE spectrum [Fig. 5(a)], which only shows the structure that is consistent with an $m = 0$ component. Furthermore, this is consistent with the observation of $28^1 29^1 m_3(\pm)$ by Graham and Kable in the case of mDFB, see Fig. 1(a).

Interestingly, there is no evidence for the corresponding $(28^1 29^1 m_1, 28^1 29^1 m_3(\pm))$ band at this excitation position, and as just noted, the lack of the expected $e$ symmetry bands in the ZEKE spectrum excludes the possibility of its being overlapped with the $m = 0$ component. It is interesting to note, however, that dual $m = 0$ and 1 component activity is observed for the corresponding emission when exciting at $\sim 449$ cm$^{-1}$–459 cm$^{-1}$. [This observation precludes an alternative assignment of the $(428, 675)$ cm$^{-1}$ band to a vibtor transition.]

Overall, this behavior is reminiscent of the fact that the $(29^1 30^1 m_1, 29^1 30^1 m_3(\pm))$ band was also observed to be very much weaker than $(29^1 30^1 m_0, 29^1 30^1 m_0)$. The reason for the weakness of the transition involving $m = 1$ was not entirely clear, but the assigned $(29^1 30^1 m_1, 29^1 30^1 m_3(\pm))$ band was suggested as being significantly shifted from its expected excitation position, and it was hypothesized that there could be a $29^1 30^1 m_1 \ldots m_7$ interaction, although this would be a $(\Delta \nu = 2, \Delta m = 6)$ interaction, and so perhaps this is not expected to be strong. In general terms, although we do expect more widespread vibtor coupling involving $e$ symmetry torsions, there is no evidence of such coupling for the $28^1 29^1 m_1$ level in the 2D-LIF spectrum, and so the absence of the $m = 1$ component is somewhat puzzling.

In Fig. 5(a), we show the ZEKE spectrum recorded when exciting at 427 cm$^{-1}$, which shows a strong $\Delta m = 3$ band, $^*28^1 29^1 m_3(\pm)$, in line with expectations when exciting through totally symmetric vibrations. There are also the expected weaker $^*28^1 29^1 m_0$ and $^*28^1 29^1 m_6(\pm)$ bands. There is no clear evidence for the ZEKE bands expected to arise from ionization from $28^1 29^1 m_0$, confirming that the major contribution to the REMPI spectrum at this wavenumber is indeed $28^1 29^1 m_0$.

We also see evidence in the 2D-LIF spectrum (Fig. 4) for bands associated with excitation of $27^1 m_2$ and $27^1 m_3(\pm)$. Evidence for the former arises from observation of $27^1 m_2$ and $27^1 m_3$ emission bands at excitation positions close to 415 cm$^{-1}$. We speculate that the $27^1 m_2$ level is interacting weakly with $Y_1 m_1$, which both have $e$ symmetry; this is supported by their proximity in wavenumber, but also the extension of the emission bands underneath the $27^1 m_2$ excitation region. The $27^1 m_3(\pm)$ band is symmetry allowed and is in line with $28^1 m_3(\pm)$ and $30^1 m_3(\pm)$ activity reported previously, but this level could also be interacting with $Y_1 m$. The latter is supported by

![FIG. 5. ZEKE spectra recorded when exciting via the S1 levels at (a) 0$^0$ + 427 cm$^{-1}$ and (b) 0$^0$ + 435 cm$^{-1}$. The preceding “+” sign used in the text is omitted from the assignments for clarity. See the text.](image-url)
there being 27,1m(-) activity also at the Y^1 m^0 excitation position, and the "reverse" activity with the 20,1m(0) band extending to higher excitation wavenumbers. The width of the bands, and their limited activity, makes it difficult to ascertain whether shifts from expected band positions have occurred, which would be another signature of such an interaction.

Owing to the energetic closeness of the 27^1 m^3(-) and 29^1 m^0 bands in the S_1 state (Fig. 4), it may be expected that when recording ZEKE spectra when exciting at 0^0 + 427 cm^{-1}, we might also observe bands arising from excitation of 27^1 m^3(-). The weak feature at 816 cm^{-1} in the ZEKE spectrum when exciting here, shown in Fig. 5(a), is at about the expected wavenumber for the Δm = 3 band, "27^1 m^6(-)", to which it is tentatively assigned. This is in line with the increased propensity of Δm = 3 transitions seen in the ZEKE spectra. Overall, therefore, the ZEKE spectrum recorded when exciting at 427 cm^{-1} is consistent with the assignments shown in the 2D-LIF spectrum in Fig. 4 but is not definitive. In addition, even though the 27^1 m^3(-) and 28^1 m^0 transitions overlap to some extent, no evidence of an interaction is seen.

A reasonable assignment for the weak 2D-LIF features in Fig. 4 that appear at an excitation wavenumber of 435 cm^{-1} can be proposed. This is close to the expected excitation wavenumber for 29^2 m^3(-), and a ZEKE spectrum recorded at this position, see Fig. 5(b), shows bands that are assignable to "29^2 m^0" and "29^2 m^2(-)". In line with observations in our previous paper, the "29^2 m^3(-)" band is expected to be weak and is not discernible in the spectrum. The prominent feature at (514, 880) cm^{-1} in Fig. 4 is straightforwardly assignable as (28^2 m^1, 28,m_1), based on the appearance of the corresponding m = 2 component at (515, 899) cm^{-1}. This is consistent with the observation of 28^2 in the case of mDFB. Accompanying the prominent band is a weaker feature at (522, 879) cm^{-1}, which can be assigned as (28^2 m^0, 28_2 m_0). It is initially surprising that this feature is so weak, as usually the m = 0 and m = 1 components for a vibrational band have comparable intensities, with the m = 1 band being slightly more intense (see Fig. 2). A clue as to the interpretation of these anomalous relative intensities comes from the ZEKE spectra, presented in Fig. 6, recorded at positions corresponding to the maxima of each of these features. The spectrum when exciting at 515 cm^{-1} is seen to be more complicated than the spectrum recorded at 520 cm^{-1}. With insight from the appearance of the ZEKE spectrum via m_1 [see Fig. 3(a)], which demonstrates prominent "m^1", "m^0", and "m^2" vibtor bands, and those via m_0 levels, which show prominent "m^0" and "m^2" vibtor bands [Fig. 3(b)], the bands arising from both the 28^2 m_1 and 28^2 m_0 levels can be straightforwardly identified. Two aspects of the spectra then become clear: first, there are bands arising from 28^2 m_1 in both spectra, and second, there are other bands in the spectra. The "19^2 m_1" and "20^2 m_1" bands in the 515 cm^{-1} ZEKE spectrum, and the "21^29^1 m^3(-)" band in the 520 cm^{-1} spectrum, arise from Franck-Condon (FC)-like activity; however, there are some other relatively intense bands that appear in both sets of spectra. Our favored assignment of these is to "28^2 m^3" vibtor transitions, and their assignment suggests their source is 28^2 m^3(+), with the "28^2 m^3(+)"/28^2 m_0 band being clearly seen in Fig. 6(a), but not immediately in Fig. 6(b), where its position is indicated.

The expected position of 28^2 m^3(+) in S_1 is around 522 cm^{-1}, and this has the same symmetry, a_1, as the 28^2 m_0 level, which is also expected to be close to this position; consequently, these two levels can interact. Furthermore, they differ by Δv = 2 and Δm = 3, making the suggested interaction sensible. We thus suggest a

![FIG. 6. ZEKE spectra of the 28^2 m^3 bands: (a) 0^0 + 515 cm^{-1} and (b) 0^0 + 520 cm^{-1}. The preceding "+" sign used in the text is omitted from the assignments for clarity.](image-url)
28°m...28°29°m(+) interaction that gives rise to two eigenstates of mixed composition. The relative intensities of the ZEKE bands suggest that the 28°m0...28°29°m(+) state (note that the leading term implies the dominant contribution to the eigenstate) gives rise to the higher, ~520 cm−1, feature, while the 28°29°m(+)...28°m0 eigenstate gives the lower feature; its transition is overlapped with that of 28°m1 at ~515 cm−1, explaining the more-complicated structure in the ZEKE spectrum recorded at that position, Fig. 6(a).

This assignment is also consistent with the appearance of the 2D-LIF spectrum (Fig. 4), where the 28°29°m(+) emission band has intensity across the 513 cm−1...523 cm−1 region, consistent with the proposed interaction. We note the coincidence in the wavenumber of 17°1 and 28°129°1m3(+) assignment, which makes the interpretation of the 2D-LIF spectrum less straightforward initially, but we accept the 28°129°1m3(+) assignment based upon the ZEKE spectra and the 28°m0,1 band profiles.

E. The 670 cm−1–750 cm−1 region

The region of the REMPI spectrum of mFT between 670 cm−1 and 750 cm−1 can be seen to consist of three main features (Fig. 1), with the lowest wavenumber of these excitation bands being assigned to 17°1 (designated 1°1 by Okuyama et al.11). The other two features were assigned to 12°1 and 13°1 (designated 9b1 and 18b1 by Okuyama et al.11), but these two assignments have been questioned by Stewart et al.10 When comparing to the mDFB spectrum (see Fig. 1), it can be seen that similar activity is seen, with Graham and Kable33 having assigned these four main features to 26°28°, 17°1, 27°1 and an overlapped feature consisting of 24°28° and 25°28°. In a future paper,22 we shall examine the two higher-wavenumber features in this region of the mFT spectrum in more detail, but for the purposes of the present work, we concentrate on the lowest wavenumber feature.

The integrated 2D-LIF trace is shown at the top of Fig. 7(c), which closely resembles the corresponding section of the REMPI spectrum. This excitation feature is assigned to the two m components of the 17°1 transition, in agreement with the assignment of Okuyama et al.11 and consistent with the mDFB spectrum33 (Fig. 1). Both the 2D-LIF spectrum [Fig. 7(c)] and the ZEKE spectra [Fig. 7(b)] support the 17°1m1 and 17°1m0 assignments; however, there are significant additional features in both spectra. Furthermore, although, when the 2D-LIF spectrum is examined, the strongest emission does indeed correspond to the two m components of 17°1, it is clear that the 17°1m0 emission band is more intense.

FIG. 7. (a) Duschinsky matrices showing the character of selected vibrations between excitation and ionization. The depth of shading represents the coefficients of mixing between vibrations in the two electronic states, between 0 (white) and 1 (black). (b) ZEKE spectra recorded at 0° + 681 and 0° + 684 cm−1, which correspond to the m1 and m0 components of 17°1, respectively. The preceding “+” sign used in the text is omitted from the assignments for clarity. (c) 2D-LIF over the excitation range 673 cm−1–690 cm−1. At the top of the 2D-LIF spectrum, the trace shows the result of integrating vertically over the presented section of the 2D-LIF spectrum and closely resembles the corresponding region of the REMPI spectrum. Colored text is used for clarity. Selected assignments are shown, and the spectra are discussed further in the text.
than $17\text{m}_1$—also reflected in the associated vibtor levels. The $15\text{m}$ bands are notably intense—cf. the 960 cm$^{-1}$ feature (Sec. III F.). Despite these observations, the Duschinsky matrices [Fig. 7(a)] indicate that there is almost no mixing between these modes during excitation or ionization. (In the matrices, the depth of shading of $D_{15}$ implies that there is some predicted mode mixing of $D_{15}$ between electronic states, but this is composed of several minor contributions from vibrational modes other than $D_{17}$ and so is not discussed further here.) In contrast, via the origin, the $m^*$ band is more intense than $m^1$ (see Fig. 2), and this is the case with each vibrational emission band. We interpret this as an indication that the $17^m$ (e symmetry) $S_1$ level emits to more $S_0$ levels than $17^m$ ($a_1$ symmetry); furthermore, the ZEKE spectrum recorded via $17^m$ shows more bands than that recorded via $17^m$. Taken together, it is concluded that the $17^m$ level is likely interacting with other $e$ symmetry levels.

In the 0 cm$^{-1}$–550 cm$^{-1}$ emission region (not shown) of the 2D-LIF spectrum recorded via $17^m$ (e symmetry) $S_1$ level emits to more $S_0$ levels than $17^m$ ($a_1$ symmetry); furthermore, the ZEKE spectrum recorded via $17^m$ shows more bands than that recorded via $17^m$. Taken together, it is concluded that the $17^m$ level is likely interacting with other $e$ symmetry levels.

The largely discrete nature of the emission spectrum suggests interactions will be between a small number of levels, and we initially considered an interaction with an $m = 2$ level for the most efficient coupling with $17^m$ ($\Delta m = 3$, recalling that the $m$ quantum number is signed) and with $\Delta \nu \lesssim 3$. This led to the assignment of the emission band at (682, 784) cm$^{-1}$ to 18, 29, $m_2$, which is supported by the observation of the weaker 19, 29, $m_2$ emission band at (682, 767) cm$^{-1}$. There are other emission bands that can be assigned when exciting at 682 cm$^{-1}$—these can be associated either with activity from 18$^m$ or with further interactions between $e$ symmetry levels in $S_1$. Although it is not possible to be definitive, the latter is supported by the fact that a number of levels are at a wavenumber position in $S_1$ that suggests that they could interact with 18$^m$, each related by $\pm 3$ changes in $\nu$ and/or $m$. As such, we conclude that a number of concurrent stepwise interactions are occurring, which link $17^m$ to a number of $e$ symmetry levels, explaining the significantly lower $17\text{m}_1$ intensity compared to that of $17\text{m}_0$. For example, 18$^m$ can interact with 21$^m$ via $\Delta \nu = 3$ interaction, and the latter can then undergo a further $\Delta \nu = 3$ interaction with 29$^m$. That multiple interactions are likely to be occurring is supported by the significant amount of underlying activity that can be seen in the 2D-LIF and ZEKE spectra in Fig. 7.

Another prominent band in the 2D-LIF spectrum is the band at (681, 665) cm$^{-1}$, which is assigned to (21$^m$, 21$^m$), and we suggest 21$^m$ is interacting with other $e$ symmetry bands, including $17^m$, which would be $\Delta \nu = 3$, $\Delta m = 3$. At this excitation position, we also see other active bands, including 18, 21, $m_4$, 19, 21, $m_4$, and the overlapped 20, 21, $m_4$; at higher emission wavenumbers, we also see the 19, 30, $m_3$ band. We suggest that these bands arise from the 21$^m$ activity.

In general, for solely anharmonic vibrational coupling, each $m$ level of a particular vibration would behave similarly. However, in the case under discussion, the coupling is with a vibtor level that can only interact with one of the $m$ levels of $17^m$, and generally, there is a greater likelihood of coupling between $e$ symmetry levels than for $a_1$ (or $a_2$)—see Sec. IV. Another possibility for an $m$-specific interaction with $17^m$ would be with the $m = 1$ level of an $a_2$ symmetry vibrational energy level, as the vibtor symmetry would then be $e$ in both cases. However, the coupling mechanism could not simply be anharmonicity but would have to result from a breakdown in the separability of vibrational and torsional motions. It is also possible for $m$-specific interactions to occur with other vibtor levels of $a_1$ symmetry, but we do not see evidence of such interactions here.

The ZEKE spectrum via $17^m$, presented in Fig. 7(b)(i), is consistent, but not definitive, with regard to the suggested couplings; for example, although we do see 18$^m$, we do not see a clear band for 18$^m$, which would be expected at 805 cm$^{-1}$ and, if present, would be overlapped by the 17$^m$ band. Furthermore, the expected 17$^m$ ZEKE band would be 18$^m$, anticipated at 952 cm$^{-1}$, which would overlap the 17$^m$ band, and could contribute to the higher-than-expected intensity for this feature. In addition, bands associated with ionization from 21$^m$ are all expected in positions that overlap with other bands. However, the greater complexity of the $m = 1$ ZEKE spectrum compared to that of $m = 0$ is consistent with $m$-specific coupling. Part of the difficulty in reaching definitive conclusions from the ZEKE spectra is that the significant change in the magnitude of the torsional barrier, coupled with the change in phase upon ionization, leads to activity arising from a number of $m$ levels in the ZEKE spectrum for a specific $m$ intermediate level. For a limited amount of vibrational activity, this is actually a good assignment tool, as distinct patterns of bands can be identified for each FC active vibration. However, when interactions in $S_1$ have occurred, particularly those involving vibtor levels, the resulting increase in the number of bands leads to difficulties in reaching a definitive assignment. In both ZEKE spectra in Fig. 7(b), we have given suggested assignments to most of the intense bands at lower wavenumbers, and a number of these also appear in combination with 18$^4$ at higher wavenumbers (not indicated). Also present in those spectra are bands that are assigned to combinations, and these appear to arise from FC-like activity.

F. The 952 cm$^{-1}$–976 cm$^{-1}$ region

The relevant region of 2D-LIF and three ZEKE spectra recorded across this region are shown in Fig. 8. Okuyama et al.$^{[1]}$ assigned the main feature to 15$^4$ (denoted 12$^4$ in their work), and we concur with this assignment of the main excitation bands to 15$^4$.$^{[0.1]}$

The integrated 2D-LIF spectrum is shown at the top of Fig. 8(b), which closely resembles this region of the REMPI spectrum. The 2D-LIF spectrum consists of a number of well-defined bands, falling into two main columns of activity, centered at excitation wavenumbers of 960 cm$^{-1}$ and 964 cm$^{-1}$; a weaker column of activity is seen at excitation wavenumbers close to 970 cm$^{-1}$. Above about 1000 cm$^{-1}$ in emission, there is a less well-defined structure extending across the spectrum, suggesting that this emission originates from coupled levels, which will be discussed below.

The band intensities in the 2D-LIF spectrum are not as expected, with the 17$\text{m}_1$ emission bands being significantly more intense than the 15$\text{m}_1$ emission bands; the assignment is clear, however, since the 17$\text{m}_1$ bands were straightforwardly assigned above in Sec. III E, where we also commented that the 15$\text{m}_1$ emission bands were unexpectedly intense when exciting 17$^4$. The assignment is also supported by the ZEKE spectra recorded at positions of the intermediate band maxima, 0$^0 + 961$ cm$^{-1}$ and 0$^0 + 965$ cm$^{-1}$ [Fig. 8(a)(i)]...
and Fig. 8(a)(ii)], which show the expected strong vibtor bands associated with \( ^{15}\text{m}$^1 \). We thus conclude that there are non-diagonal FCFs associated with emission from \( ^{15}\text{m}$^1 \), which must be related to geometry changes, since we do not see evidence of a Duschinsky rotation between these vibrations in the Duschinsky rotation matrix [see Fig. 7(a)], and indeed, the ZEKE spectra [Fig. 8(a)] do not exhibit \( ^{17}\text{m}$^2 \) bands; neither do we see \( ^{15}\text{m}$^2 \) bands when exciting via \( ^{17}\text{m}$^0 \) [see Fig. 7(b)]. The 2D-LIF spectrum [Fig. 8(b)] also shows significant torsional bands, together with vibtor bands associated with the main emissions. These are largely as expected, and their assignments are straightforwardly obtained both by the 2D-LIF spectrum obtained via \( m^s \) and \( m^t \) (Fig. 2) and by comparison with the work of Stewart et al., as well as the wavenumbers of other vibrations, obtained in the present work (see Table III).

When exciting at 970 cm\(^{-1} \), the strongest 2D-LIF band is at \( 970, 1402 \) cm\(^{-1} \). The assignment of this band to the \( \Delta(v, m) = 0 \) band (18\(^{18}\text{m}$^0 \), 18\(^{28}\text{m}$^0 \)) is relatively straightforward, fitting the expected wavenumbers in both the \( S_0 \) and \( S_1 \) states, and also being consistent with the 18\(^{28}\text{m}$^0 \) band seen for mDFB (Fig. 1). Furthermore, vibtor bands associated with \( ^{18}\text{m}$^0 \) are seen in the ZEKE spectrum recorded when exciting via the intermediate band maximum \( 0^0 + 971 \) cm\(^{-1} \), although it is noted that \( ^{18}\text{m}$^0 \) is not the most intense band in the spectrum, as would be expected. We note that the strongest emissions seen when exciting across 957 cm\(^{-1} \)–978 cm\(^{-1} \) all extend to higher excitation wavenumbers, consistent with either coincidental FC activity or an interaction between one or both \( ^{15}\text{m}$^0 \) levels and a level at 970 cm\(^{-1} \). Since the profile of the 18\(^{28}\text{m}$^0 \) emission band is strongest for the \( m_0 \) component, we suggest there is a 15\(^{15}\text{m}$^0 \) interaction for both \( m \) components, but for the \( m = 1 \) levels, further interactions cause a dissipation of the emission intensity across numerous transitions. In contrast, the interaction with 18\(^{28}\text{m}$^0 \) is weaker and less profligate, and so the emission band is more pronounced.

At this excitation wavenumber, we can also anticipate possible activity from other levels, including 17\(^{21}\text{m}$^0 \) and the vibtor levels 18\(^{19}\text{m}$^{3(+) \) and 18\(^{20}\text{m}$^{3(+) \). Relatively weak, but clearly observable bands at the correct wavenumbers for the 17\(^{21}\text{m}$^0 \), \( m_0 \), emissions can be seen in the 2D-LIF spectra; moreover, bands arising from \( ^{17}\text{m}$^1 \) vibtor levels can also be seen in the ZEKE spectrum in Fig. 8(a)(iii). In addition, \( ^{18}\text{m}$^0 \) ZEKE bands are seen, but these are thought to arise from FC activity, since these are also seen in other spectra when exciting fundamentals. In summary, it seems clear that interactions are occurring, and the evidence is that this predominantly involves the \( m = 1 \) components and involves widespread

\[ \text{FIG. 8. (a) ZEKE spectra via } 15^m, 15^m, \text{ and the feature at } 0^0 + 971 \text{ cm}^{-1}. \text{ In the ZEKE spectra, the preceding } ^+ \text{ sign used in the text is omitted from the assignments for clarity—see the text regarding the } Q^m \text{ bands. Colored text is used for clarity. (b) 2D-LIF over the excitation range } 950 \text{ cm}^{-1} \text{–978 cm}^{-1}. \text{ At the top of the 2D-LIF spectrum, the trace shows the result of integrating vertically over the presented section of the 2D-LIF spectrum and closely resembles the corresponding region of the REMPI spectrum. The region between } 0^0 + 967 \text{ and } 0^0 + 975 \text{ cm}^{-1} \text{ has been enhanced by a factor of six, as indicated, as this structure is weak compared to the main activity. Selected assignments are shown—see the text for further discussion.} \]
coupling; the coupling with the $m = 0$ component is less definitive and is at best restricted in nature. The main activity comes from $15^1m^{0,1}$, but there is clear activity from $18^228^0m^{0,1}$ and persuasive evidence for involvement of $17^121^1m^{0,1}$; however, whether these levels are interacting significantly or not is less clear, but if they are, then the stronger interaction might be expected to be between $15^1$ and $17^121^1$, which is $\Delta v = 3$, while the other interaction would be $\Delta v = 4$.

The ZEKE spectrum recorded via $0^0 + 971$ cm$^{-1}$ [Fig. 8(a)(iii)] is rich in structure, and its assignment is challenging. We highlight that there are ZEKE bands at the correct position for $17^121^1m^{0,1}$ activity, for example, the intense $+17^121^1m^{3(+)}$ band, but the corresponding activity expected for $17^121^1m^{1,1}$ is not seen, in line with comments in the previous paragraph. We note a strong series of bands at 1026 cm$^{-1}$, 1212 cm$^{-1}$, and 1338 cm$^{-1}$ that appear to be the $m = 0, 3(+)$, and $6(+)$ components associated with $^18^2$, which are indicated in the figure. Although possible assignments could be put forward for other bands in this spectrum, we generally refrain from doing so, since these are not definitive. For example, in cases where an interaction can be suggested, such as $19^121^1m^{29}(\pm)$ and $18^221^1m^{29}(\mp)$, each being $(\Delta v = 3, \Delta m = 3)$ from $17^121^1m^0$, it is not possible to identify all of the expected bands in this complicated spectrum.

Looking at the ZEKE spectra via $15^1m^x$ [Fig. 8(a)(i) and Fig. 8(a)(ii)], there are a series of bands labeled "Q$m^x$" and we show the $\Delta v = 0$ band as well as the corresponding vibtor structure. Despite these bands being well-resolved and prominent in both ZEKE spectra, there is no evidence for corresponding activity in the 2D-LIF spectrum. Although it is difficult to determine the identity of "Q", it may be associated with a level that is in Fermi resonance with $^15^1$ in the cation (and so each corresponding pair of vibtor levels is also interacting); one promising candidate is $Q = ^23^129^1$. This could also simply arise from FC-like activity, of course, and we noted the appearance of $^23^129^1m$ bands when exciting via $17^1m^3$ [Fig. 7(b)].

In summary, at the very least, the 2D-LIF and ZEKE spectra suggest that there are likely numerous interactions occurring with the $15^1$ level, supported by the appearance of many bands alongside those of $^15^1m^0$ in the ZEKE spectrum recorded at $0^0 + 971$ cm$^{-1}$. We also see clear evidence for $18^228^0m^{1,1}$ activity and persuasive evidence for $17^121^1m^{0,1}$.

**G. The 1251 cm$^{-1}$–1266 cm$^{-1}$ region**

The 2D-LIF spectrum [Fig. 9(c)] consists of several well-defined bands on top of a broad background emission, particularly above...
a) $m$-fluorotoluene

$D_{10} - a_1$

\[ \text{Diagram for } D_{10} - a_1 \]

$D_{11} - a_1$

\[ \text{Diagram for } D_{11} - a_1 \]

b) $m$-difluorobenzene

$D_{10} - a_1$

\[ \text{Diagram for } D_{10} - a_1 \]

$D_{11} - b_2$

\[ \text{Diagram for } D_{11} - b_2 \]

FIG. 10. Calculated mode diagrams for the $D_{10}$ and $D_{11}$ vibrations of (a) mFT ($G_6$) and (b) mDFB ($C_2v$) in the three electronic states under consideration, obtained using quantum chemistry calculations, as indicated in Tables I and II (for mDFB, the level of theory used for the cation was the same as that used for mFT). The motions are distinctive, and hence, assigning each vibration from the mode diagram is straightforward.
1200 cm\(^{-1}\), and the integrated spectrum at the top of the spectrum closely resembles this region of the REMPI spectrum.

The main emission band for m\(\text{FT}\), when exciting across 1254 cm\(^{-1}\)-1262 cm\(^{-1}\), is at 1271 cm\(^{-1}\). Comparing this value with the liquid-phase IR/Raman values suggests an assignment of the emission to 11\(^1\), and this would be in line with the calculated wavenumbers. Note that Okuyama et al.\(^{11}\) assigned a value of 1267 cm\(^{-1}\) to an \(S_0\) vibration, which they labeled \(v_{14}\) in Varsányi\(^{19}\) notation and would correspond to \(m\text{DFB}\) mode \(v_{25}\) in Mulliken notation\(^{1}\) and, hence, \(D_{11}\) here; however, it was shown in previous work that Varsányi modes \(v_{23}\) and \(v_{14}\) have got confused over the years and, further, that these labels do not describe the motions of the atoms in disubstituted benzene molecules.\(^{2,3}\) With these caveats, the present assignment and that of Ref. 11 are in agreement.

In Table I, this is then consistent with the calculated values for \(m\text{DFB}\) and \(m\text{FT}\) in each of the three electronic states, showing that their motions are distinctive and, hence, assignment of each from the calculations is unambiguous.

A comparison of the REMPI spectrum of \(m\text{FT}\) with that of \(m\text{DFB}\) also suggests that the excitation at 1267 cm\(^{-1}\) should be assigned as 11\(^1\); however, this was assigned as 10\(^1\) (denoted 6\(^1\)) in the fluorescence study.\(^{3,29}\) In \(m\text{DFB}\), under C\(_2\) point group symmetry, the \(D_{00}\) vibration is of \(a_1\) symmetry, while that of \(D_{11}\) is \(b_2\); thus, the 10\(^1\) transition would be symmetry allowed. However, other transitions involving \(b_2\) symmetry vibrations were assigned in Ref. 33, with 21\(^1\), 19\(^1\), and 20\(^1\) transitions being notable; these are likely to be vibronically induced. These are also all seen in \(m\text{FT}\)\(^{1}\) (where they all become symmetry allowed), but also the 18\(^1\) transition is moderately intense in \(m\text{FT}\) but is absent in the \(m\text{DFB}\) spectrum (see Fig. 1 and Ref. 33), even though \(D_{18}\) is totally symmetric in both molecules.

Hence, there is no prima facie reason not to assign the \(m\text{DFB}\) transition at 1267 cm\(^{-1}\) to 11\(^1\), which would bring consistency with the \(m\text{FT}\) assignment. We highlight that Table I shows that the calculated values for \(D_{00}\) and \(D_{11}\) in the \(S_0\) state of \(m\text{DFB}\) are too close to be discriminant (but their motions and so identities are clear—see Fig. 10), and with either assignment, there is a 40 cm\(^{-1}\) difference between the calculated value and the experimental value. Additionally, we are particularly cautious regarding the calculated \(S_1\) values, which we have found to be often less reliable than those for the \(S_0\) and \(D_0^+\) states.\(^{24,4}\)

Further evidence is gleaned from related symmetrically substituted molecules: in Ref. 27, vibronational wavenumbers are presented for five such molecules. Excluding \(m\text{DFB}\), the wavenumber for the \(D_{00}\) vibration lies below that of \(D_{11}\) for both the experimental and calculated values for all of the other molecules. For \(m\text{DFB}\), as noted, the calculated values are only a few cm\(^{-1}\) apart, but the experimental values, as assigned, are clearly reversed compared to those of the other molecules. Given the variation in these wavenumbers with mass—and given that the corresponding values for \(m\)-xylene and resorcinol are consistent with each other, but the reverse of the previously assigned values for \(m\text{DFB}\)—we suggest that the \(D_{00}\) and \(D_{11}\) assignments need to be reversed as well, and this has been done in Table I. This is then consistent with the \(m\text{FT}\) results obtained herein. Consequently, as with 18\(^1\), it appears that 10\(^1\) simply is not active in \(m\text{DFB}\), despite being totally symmetric, while we conclude that 11\(^1\) must be vibronically active. Furthermore, we note that Graham and Kable\(^{15}\) have commented that previous assignments of the \(b_2\) symmetry vibrations of \(m\text{DFB}\) are questionable, noting that the assignment of 11\(^1\) in \(S_1\) to a value of 1608 cm\(^{-1}\) does not seem to be correct, and indeed, this would not agree well with the calculated value in Table I.

In summary, the most intense 2D-LIF band for \(m\text{FT}\) in Fig. 9(c) at (1260, 1271) cm\(^{-1}\) is assigned as (11\(^2\)\(^m\), 11\(^m\)\(m\)) and is significantly more intense than the corresponding \(m = 1\) band. The ZEKE spectra [Fig. 9(b)] are consistent with this assignment, with the main bands being assigned as the expected vibtor levels via the two \(m\) components. Several other fundamentals are also seen, and, where the sensitivity allows, the expected associated vibtor structure is seen.

With the assignment of the excitation to 11\(^1\), the observed structure in the ZEKE spectrum allows a vibrational wavenumber of 1275 cm\(^{-1}\) to be obtained for 11\(^1\). (We note that, unhelpfully, the experimental value for this vibration falls between the calculated values for 11\(^1\) and 10\(^1\), and so this cannot be used as further evidence for this assignment, which is largely based on the 2D-LIF spectrum—see Table III.) The ZEKE spectra have a significant underlying unstructured signal, which is akin to the broad background in the 2D-LIF spectrum and again is consistent with significant IVR occurring. Another progression of vibtor levels is also seen in both ZEKE spectra, consistent with a vibration with the wavenumber 1330 cm\(^{-1}\), which can be plausibly assigned to 16\(^2\)\(^b\), which could be arising from a \(\Delta v = 3\) interaction; the activity in 10\(^1\)\(^b\) likely arises from FC activity, since the Duschinsky matrices, Fig. 9(a), show that \(D_{00}\) and \(D_{11}\) are not significantly mixed upon ionization. If the 16\(^2\)\(^b\) assignments are correct and an interaction is indeed occurring, then this suggests a value for \(D_{10}\) in \(S_1\) of \(-840\) cm\(^{-1}\), which is in fair agreement with the calculated value. The interaction would be expected for both \(m\) components, which is consistent with the ZEKE spectrum. The 16\(^2\)\(^b\) bands, expected at \(-1370\) cm\(^{-1}\), are in a region of the 2D-LIF spectrum that consists of unstructured emission, effectively ruling out the possibility of definitive identification. This emission, together with the unstructured background in the ZEKE spectra, suggests significant interactions are occurring, but we cannot provide unambiguous assignments for all of the bands nor identify the likely myriad of interacting levels in the spectrum.

IV. FURTHER DISCUSSION

In the above, we have looked at the assignment of a selection of bands across the lowest \(-1350\) cm\(^{-1}\) of the \(S_1\) state of \(m\text{FT}\). Clearly, IVR cannot occur for the origin and the very lowest levels, but as discussed in Ref. 10, even below 350 cm\(^{-1}\), there are interactions occurring between vibrations, torsions, and vibtor levels. Here, we have extended the examination of levels, where we see limited interactions are present for levels below 950 cm\(^{-1}\), but significant IVR occurs above this, moving toward the statistical (dissipative) IVR regime; the latter is demonstrated by the presence of a largely unstructured underlying background in both the 2D-LIF and ZEKE spectra recorded at \(-960\) cm\(^{-1}\) and \(-1260\) cm\(^{-1}\). On top of this underlying background, there are numerous well-resolved bands, showing that in the present experiments, some energy remains localized to particular vibrations, while some is dissipated through a range of motions.

We noted above that Timbers et al.\(^{25}\) have compared the behavior of \(m\text{FT}\) and \(p\text{FT}\), concluding that at about 1200 cm\(^{-1}\), the
rate of IVR was an order of magnitude faster for mFT than for pFT, based upon quenching experiments. We have studied pFT in a range of internal energies, and we have found that below 1000 cm$^{-1}$, limited IVR occurs involving both anharmonic and vibration–torsional coupling. At $\sim 1015$ cm$^{-1}$, we found that coupling occurred involving two largely separate overtone levels, providing two routes for energy delocalization in pFT, while in the region 1190 cm$^{-1}$–1240 cm$^{-1}$, there was more widespread IVR, but two levels less than 40 cm$^{-1}$ apart behaved significantly differently. In both of the latter, there were still structured bands on top of a broad background, suggesting at least some energy remains localized. In the case of pXyl, however, at these energies, most structure was lost in the ZEKE spectra recorded, suggesting almost complete delocalization of energy; these observations were discussed in terms of symmetry and the density of states (DOS). It was concluded that although the DOS buildup is critical in providing pathways to widespread IVR, this is determined largely by the presence of one or more methyl groups, rather than the symmetry per se. On top of this, the DOS buildup is not smooth, and so at lower internal energies, serendipity can play a large role in determining whether a particular vibration is located in a “clump” of levels; even then, there needs to be a means of efficient coupling to these. Such coupling will clearly depend on symmetry, but also on the motions involved; such considerations lead to the “Tier Model” of IVR, whereby coupling between particular levels is efficient and facilitates pathways to coupling with a wide range of “bath states.”

Here, we make further comparison between mFT and pFT. In Fig. 11, we show their DOS plots for totally symmetric vibrations, and also when including torsions and vibtor levels. It is clear that for mFT, there are more totally symmetric vibrations, as all in-plane vibrations are totally symmetric, while for pFT, these split into $a_1'$ ($a_1$ in C$_{2v}$) and $a_1''$ ($b_2$ in C$_{2v}$) subgroups—this is evident in Fig. 11.

**FIG. 11.** Density of states (DOS) plots for mFT and pFT, using calculated vibrational wavenumbers from Table III and Ref. 23. In plots (a) and (b), only vibrational levels are included, while in plots (c) and (d), vibrations and vibtor and torsional levels are included. In both plots, we indicate levels that are accessible from the $m=0$ and $m=1$ levels, which are those that are the most populated in the free-jet expansion ($a_1 + e$ for mFT and $a_1' + e''$ for pFT), together with all levels. Note that we do not consider rotational levels in this work.

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Notably, the buildup in the DOS is more erratic for pFT than for mFT. This difference is clearer once vibtor levels are included, where again an approximate doubling of the available energy levels is seen for mFT compared to pFT, for levels accessible from \( m = 0 \) and \( m = 1 \). Furthermore, it can be seen that the buildup of levels is generally more continuous once vibtor levels are included compared to only the vibrations, which is somewhat erratic, particularly for the totally symmetric levels in pFT.

With regard to previous IVR experiments on pFT, there has been some uncertainty regarding the vibrations excited, which has been discussed.\(^4^5\) For pFT, there are two main fundamentals at 1196 cm\(^{-1}\) and 1232 cm\(^{-1}\), but there are other levels nearby, as examined in depth in our recent work.\(^5^6\) In Ref. 7, it seems the latter level is excited, which is the 5\(^{1}\) vibration, mainly corresponding to an in-phase stretch of the C–F and C–CH\(_3\) bonds, with the former motion dominating.\(^5^7\) As we have discussed in the present work, for mFT, the 1260 cm\(^{-1}\) transition is assigned as the vibronically induced 1\(^{1}\), which is largely a ring-based distortion. As such, the vibrational motion is quite different for the two molecules, making the comparison less straightforward. Indeed, the motion of D\(_{1}\) (see Fig. 10) in mFT will involve the adjacent C–H bonds interacting with the methyl group more strongly than for the 5\(^{1}\) vibration in pFT, which would be one explanation for the increased IVR as a result of vibration–torsional coupling.

In the experiments by Parmenter’s group,\(^4^8\) reliance is placed upon collision quenching with O\(_2\). The idea is that the excited electronic state is vibrationally excited following laser excitation and that there is time dependence for the IVR to occur. In addition, the higher the partial pressure of O\(_2\), the more rapid the quenching, and the less the time molecule had to undergo IVR. However, this can only occur with levels that are excited coherently within the width of the laser pulse, which will be a few cm\(^{-1}\) for a nanosecond pulse (not stated in Ref. 7, but the laser system mentioned suggests this was the case). In Ref. 7, a fit is made to the data to determine \( k_{\text{IVR}}\), with electronic and vibrational collision quenching, \( k_{\text{V}}\), included. Various assumptions were made in determining \( k_{\text{IVR}}\), with the end conclusion being that this was roughly an order of magnitude larger than that for pFT. A discussion of the possible rationalization of this observation was then made, including the DOS of the coupled vibrational levels, the effect of the methyl rotor not being on a principal axis, and the magnitude of the torsional barrier.

With regard to the DOS, we note that there are two factors that increase this in mFT relative to pFT, both related to the reduction in molecular (point group) symmetry from G\(_{1}\) (C\(_{2v}\)) for pFT to G\(_{6}\) (C\(_{1}\)) for mFT. For the vibrations, using molecular symmetry group labels, mFT will have a greater number of totally symmetric vibrations as both the \( a_{1}\) and \( a_{1^\prime}\) symmetry vibrations in pFT have the same symmetry (\( a_{1}\) in mFT; Fig. 11) indicates that the number of \( a_{1}\) vibrations in mFT is comparable to the number of \( a_{1^\prime} + a_{1^\prime}\) symmetry vibrations in pFT but with a smoother buildup for mFT. Furthermore, considering molecular symmetry, the number of \( e\) torsional levels in mFT is about the same as the number of \( e^\prime + e^\prime\) torsional levels in pFT. Taken together, see Fig. 11, it can be seen that the total number of vibrational + vibtor levels is about the same in pFT and mFT. However, considering only the states that have the same symmetries as the \( m = 0\) and \( m = 1\) levels (the ones with the dominant populations in the free-jet expansion), then there are about twice as many levels for mFT as for pFT.

The aforementioned DOS does not include rotational levels, and it was argued in Ref. 7 that coupling with rotational levels would be more significant in mFT than in pFT; if so, then it may be that there is an effect from the use of room temperature and high pressure conditions in Ref. 7, where rotational effects would be expected to be more significant than they would be in jet-cooled, gas-phase studies.\(^4^9\) It was also commented in that work that at the internal energies employed, pFT will couple to 10–50 levels, while mFT will couple to essentially an infinite number. The DOS plots in Fig. 11 do not support this latter comment and, further, the 2D-LIF spectra do not either, where the structure is seen, albeit on a background, for both pFT (Ref. 19) and mFT (present work); this is in contrast to the fluorescence spectrum for mFT reported in Ref. 7, where no structure is evident when the quencher is absent.

We concur with the comments in Ref. 7 that the significantly higher barrier in mFT is expected to produce larger torsion–vibration coupling terms. One rationale for the higher barrier in mFT compared to pFT is in terms of hyperconjugation: in pFT, hyperconjugation is not expected to be a large effect and weaker van der Waals type interactions are thus expected to dominate, explaining the lower torsional barrier.

As noted above, there has been some ambiguity in the levels employed for IVR studies on pFT,\(^5^1\) which is pertinent as the vibrational motion is expected to be critical in the observed coupling. For pFT, at 1200 cm\(^{-1}\), a rather different time-dependent behavior has been observed for the two main levels,\(^4^5\) which was discussed in terms of a rotation-dependent vibration–torsion interaction that occurred specifically for one of the \( m\) levels. Rotational dephasing was concluded to be a time-dependent effect only and is not seen in frequency-resolved experiments.\(^4^5\)

In summary, direct comparison between different isomers of substituted benzene molecules is difficult because of the different forms of the vibrations, even if the observed activity seems quite similar. Furthermore, the conditions used in an experiment are expected to have a strong bearing on the results,\(^4^5\) and so caution is strongly advised when making general deductions from a single experiment. Having the ability to resolve vibrational, vibtor, and torsional structures in a spectrum does seem to give the ability to identify explicit coupling channels, but only when the coupling is reasonably limited. Once the coupling becomes widespread, however, this advantage is lost in frequency-resolved experiments if the resolution is not sufficient to resolve all features, or if the spectrum becomes too complicated to assign definitively. Time-resolved photoelectron spectroscopy experiments with picosecond pulses can, however, still be useful in picking out zero-order state contributions in such circumstances, as long as the frequency resolution can be maintained at tens of cm\(^{-1}\).\(^4^6\)

V. CONCLUSIONS

We have presented 2D-LIF and ZEKE spectra obtained when exciting through selected levels up to 1350 cm\(^{-1}\) in the lower wavenumber region of the S\(_1\) ← S\(_0\) excitation in mFT. We have assigned the majority of the main features observed, but there are many weak features and also broad unstructured backgrounds in some cases. The assigned features confirm that there is widespread vibtor coupling occurring in this molecule, as well as some anharmonic vibrational coupling; these become more prevalent to
higher internal energies and are more common for the $e$ symmetry torsional levels than for the $a_1$ symmetry levels. Explicit couplings can be identified in some cases, while, in others, only potential couplings have been suggested, based upon some of the observed 2D-LIF bands. When there are numerous couplings, the ZEKE spectra become very difficult to assign, owing to the number of bands arising, also causing each to have a lower intensity, and these are located on a rising unstructured background.

Comparing pFT and mFT, we agree with many, but not all, of the ideas expressed in Ref. 7, but we have highlighted that both the number of vibrations and also torsions, and so vibrot, levels are responsible for the stark increase in the DOS; of course, all of these levels will have an associated set of rotational levels, and hence in room temperature studies, this difference will be exacerbated compared to experiments employing a free-jet expansion. We have emphasized that it is difficult to compare these molecules directly, with the particular vibration excited at ~1250 cm$^{-1}$ being different for the two molecules. Moreover, relying on Wilson/Varsányi labels to identify a vibration can be misleading, since the motions of the atoms for a particular vibrational wavenumber can be very different for meta and para substituted molecules as discussed in Ref. 27. Last, the buildup in vibrational levels is somewhat erratic at these low wavenumbers, and this suggests that at low energies, notwithstanding the more-rapid buildup in the DOS for mFT, the rapidity with which IVR efficiency can increase is restricted since coupling elements will still depend on $\Delta\nu$ being small.

Our conclusion is that it seems clear that mFT undergoes more rapid IVR than pFT, but ascertaining the precise reasons for this, and quantifying them, is far from straightforward.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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