Vibration-modified torsional potentials and vibration-torsion ("vibtor") levels in the \( m \)-fluorotoluene cation

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Zero-kinetic-energy (ZEKE) spectra are presented for \textit{m}-fluorotoluene, employing different low-lying \((< 350 \text{ cm}^{-1})\) intermediate torsional and vibration-torsional ("vibtor") levels of the \(S_1\) state. The adiabatic ionization energy (AIE) is found to be \(71997 \pm 5 \text{ cm}^{-1} (8.9265 \pm 0.0006 \text{ eV})\). It is found that the activity in the ZEKE spectra varies greatly for different levels and is consistent with the assignments of the \(S_1\) levels deduced in the recent fluorescence study of Stewart \textit{et al.} \cite{Stewart2019}. For cation torsional levels, the most intense band corresponds to changes in the torsional quantum number, in line with the known change in the phase of the torsional potential upon ionization. This leads to the observation of an unprecedented number of torsions and vibtor levels, with the pronounced vibtor activity involving out-of-plane vibrations. Interactions between levels involving torsions are discussed, with evidence presented, for the first time it is believed, for modification of a torsional potential induced by a vibration. Also, we discuss the possibility of distortion of the methyl group leading to a change from \(G_6\) molecular symmetry to \(C_3\) point group symmetry.

I. INTRODUCTION

The coupling of methyl torsion and vibrational motions has been the subject of a series of studies on toluene, \cite{Timbers1976, Ito1985, Ito1986, Lu1990, Feldgus1991} \textit{para}-fluorotoluene (pFT), \cite{Ito1985, Ito1986, Lu1990} and \textit{para}-xylene (pXyl) \cite{Ito1985, Ito1986, Lu1990} using a combination of fluorescence and photoionization spectroscopies. These studies have shown that such coupling can be examined and understood in detail in the low-wavenumber region and is likely to be prevalent to higher wavenumbers, driving the transition to statistical ("dissipative") intramolecular vibrational redistribution (IVR). This underpins the ability to understand energy dispersal, photostability, and photochemical control. Timbers \textit{et al.} \cite{Timbers1976} have concluded that \textit{meta}-fluorotoluene (mFT) undergoes IVR more than an order of magnitude faster than pFT, showing that the location of substituents is likely to be important in the coupling.

Recently, Stewart \textit{et al.} \cite{Stewart2019} have examined the first 350 cm\(^{-1}\) of the \(S_1 \leftarrow S_0\) transition of mFT, assigning the spectra with the use of two-dimensional laser-induced fluorescence (2D-LIF). \cite{Stewart2019} The spectra were assigned in terms of torsional and vibration-torsional ("vibtor") levels in the \(S_0\) and \(S_1\) states. In the present work, we shall use the same \(S_1\) levels as intermediates in the recording of zero-kinetic-energy (ZEKE) spectra to obtain detailed information on the low-lying levels in the cation. The work of Stewart \textit{et al.} \cite{Stewart2019} and the present study build on that of Ito and co-workers \cite{Ito1985, Ito1986, Lu1990} who have recorded laser-induced fluorescence (LIF), dispersed fluorescence (DF), resonance-enhanced multiphoton ionization (REMPI), and ZEKE spectra of the low-wavenumber region of mFT. Additionally, Lu \textit{et al.} \cite{Lu1990} have put forward a rationalization of the torsional barrier heights in substituted toluenes. We also note that Feldgus \textit{et al.} \cite{Feldgus1991} have recorded REMPI and ZEKE spectra of \textit{m}-chlorotoluene (mCIT). We shall refer to these studies later.

Stewart \textit{et al.} \cite{Stewart2019} reported that there is interaction between the torsional motion and low frequency vibrations in both \(S_0\) and \(S_1\) and postulated that such interactions may be present in the cation. Here, we explore the torsional and vibtor states of the cation with the aim of exploring the extent of such interactions in the mFT cation. It will be seen that mFT is an excellent molecule for investigating torsions
and vibtor interactions since the torsional levels in the S\(_0\) state are close to freely rotating, while those in the S\(_1\) state are moderately hindered and those in the cation are severely hindered. In the latter case, the lowest few torsional levels might be regarded as torsional vibrations. In addition, we find that numerous vibtor levels are seen involving the lowest-wavenumber vibrations.

II. EXPERIMENTAL

The REMPI/ZEKE apparatus was the same as that used in earlier work. The focused, frequency-doubled outputs of two dye lasers (Sirah CobraStretch) were overlapped spatially and temporally and passed through a vacuum chamber coaxially and counterpropagating, where they intersected a free jet expansion of mFT (Sigma Aldrich, 98% purity) in 1.5 bars Ar. The excitation laser operated with Coumarin 503 and was pumped with the third harmonic (355 nm) of a Surelite III Nd:YAG laser, while the ionization laser operated with Pyromethene 597, 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 \(-10\) 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 \(-5\) to 7 cm\(^{-1}\). Electron and ion signals were recorded on separate sets of microchannel plates.

III. RESULTS AND ASSIGNMENTS

A. Nomenclature and labeling

1. Vibrational and torsional labeling

Since neither Wilson\(^7\)/Varsányi\(^1\) nor Mulliken\(^3\)/Herzberg\(^6\) notations are appropriate for the vibrations of mFT,\(^4\)\(^5\) we shall employ the \(D_i\) labels from Ref. 35, as used in the recent work by Stewart et al.\(^2\) This \(C_3\) point group labeling scheme is based on the vibrations of the meta-difluorobenzene (mDFB) molecule, for which the \(S_1 \leftrightarrow S_0\) transition has been investigated using LIF and DF spectroscopy.\(^6\)\(^7\) (While mDFB has \(C_{2v}\) point group symmetry, the labeling scheme in Ref. 35 was developed to be applicable to both symmetric and asymmetric substitutions.) Although not pursued in the present work, we find that the vibrational activity in the corresponding electronic transition of mDFB is similar to that in mFT, consistent with comparisons made for the corresponding \(p\)-substituted molecules.\(^3\)\(^7\)

Since the \(G_6\) molecular symmetry group (MSG) is appropriate for vibtor levels in mFT, we shall use these symmetry labels throughout. In addition, torsional levels will be labeled via their \(m\) quantum number. (The reader may find it useful to refer to Refs. 19 or 22 if they are not familiar with these labels.) The correspondence between the \(C_3\) point group labels and the \(G_6\) MSG ones is given in Table 1. 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 1), noting that a \(C_{3\nu}\) point group direct product table can be used, since the \(G_6\) MSG and the \(C_{3\nu}\) point group are isomorphic.

Under the free-jet expansion conditions employed here, almost all of the molecules are expected to be cooled to their zero-point vibrational level, and thus, essentially all \(S_1 \leftrightarrow S_0\) pure vibrational excitations are expected to be from this level. In contrast, owing to nuclear-spin and rotational symmetry, the molecules can be in one of the \(m = 0\) or \(m = 1\) torsional levels.

2. Coupling and transitions

When designating excitations, we shall generally omit the lower level since it will be obvious from the jet-cooled conditions. In the usual way, vibrational transitions will be indicated by the cardinal number, \(i\), of the \(D_i\) vibration, followed by a super-/subscript specifying the number of quanta in the upper/lower states, respectively; torsional transitions will be indicated by \(m\) followed by its value. Finally, vibtor transitions will be indicated by a combination of the vibrational and torsional transition labels.

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, superscripts indicating levels in the \(S_1\) state, and, when required, subscripts indicating levels in the \(S_0\) state. Since we will also be referring to transitions and levels for the ground state cation, \(D_0^+\), we shall indicate those as superscripts, but with an additional single 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 expected to be that for which no changes in the torsional and/or vibrational quantum numbers occur: these will be 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 Ref. 27), the \(\Delta m = 0\) and \(\Delta (\nu, m) = 0\) transitions are almost always not the most intense bands in the ZEKE spectra for mFT, indicative of a significant change in the torsional potential upon ionization.

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.\(^6\) For molecules that contain a hindered internal

| \(C_3\) | \(G_6\) | \(D_i\) | \(m\) |
|---|---|---|---|
| \(a'\) | \(a_1\) | \(D_1 \sim D_{21}\) | \(0, 3(\), 6(\), 9(\) |
| \(a''\) | \(a_2\) | \(D_{21} \sim D_{30}\) | \(3(\), 6(\), 9(\) |
| \(c\) | | | | 1, 2, 4, 5, 7, 8 |

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

\(^b\)The \(D_i\) labels are described in Ref. 35, where the vibration mode diagrams can also be found.
rotor, and if vibration-torsional coupling occurs, then interactions can also involve torsional or vibrot levels. The end result of such interactions is the formation of eigenstates with mixed character. Such couplings are only expected to be significant for small changes, \( \Delta n \approx 3 \), of the vibrational quantum number, and also for changes, \( \Delta m \), of 0, ±3, or ±6 in the torsional quantum number in descending order of likely strength.\(^{39,40}\) Often the eigenstates will be referred to by the dominant contribution, with the context implying if an admixture is present.

3. Torsional energies

The energy levels of a hindered methyl rotor have been the subject of numerous studies, with the paper by Spangler\(^{41}\) being a good starting point. For a hindered methyl rotor, the lowest couple terms of the torsional potential may be expressed as

\[
V(\alpha) = \frac{V_1}{2} (1 - \cos 3\alpha) + \frac{V_2}{2} (1 - \cos 6\alpha),
\]

where \( \alpha \) is the torsional angle. In the cases of toluene and \( p \text{FT} \), the \( V_3 \) term is zero by symmetry, but in \( m \text{FT} \), this is the largest term. If the \( V_6 \) term is small relative to \( V_3 \), which is usually the case, then its effect is simply to modify the shape of the potential. (For larger values of \( V_6 \), local minima appear in between the ones arising from the \( V_3 \) term.) Previous work\(^{22,27,28}\) has shown that for \( m \text{FT} \), \( V_3 \) has approximate values of 20 cm\(^{-1}\) for the \( S_0 \) state, 115 cm\(^{-1}\) for the \( S_1 \) state, and –300 cm\(^{-1}\) for the \( D_0^\pi \) state. Thus, these three states of the same molecule are, respectively, close to a free rotor, a moderately hindered rotor, and a highly hindered rotor.

The effect of the magnitude of the \( V_3 \) term on the energies of the \( m \) levels may be seen in Fig. 1(a), where the \( V_6 \) term has been set at zero and the \( V_3 \) term varied. (Note that the sign of the \( V_3 \) parameter, which is a way of indicating the phase of the torsional potential, does not affect the energy levels, but it can be deduced from the calculated geometry.\(^{22,27}\)) As described in Spangler,\(^{41}\) as \( V_3 \) increases, deep within the potential well, the free-rotor \( m \) levels evolve into triply degenerate torsional vibrations, with each torsional vibration arising from one degenerate pair of \( m \neq 3n \) levels, plus one \( m = 3n \) level. These latter levels lose their degeneracy in \( V_{3n} \) potentials, and the resulting levels can be denoted \( m = 3n(+) \) and \( m = 3n(-) \), with the former being of \( a_1 \) and the latter of \( a_2 \) symmetry in \( G_6 \). Thus, if the torsional barrier is high, we can expect low-lying \( c \) symmetry levels to be close-to-degenerate with an \( m = 3n(+) \) or \( m = 3n(-) \) level. As may be seen from Fig. 1(a), in \( G_6 \), the splitting between the \( m = 3n(+) \) and \( m = 3n(-) \) levels is largely an effect of \( V_3 \) but is also affected by (the smaller-valued) \( V_6 \)—see Fig. 1(c). If \( V_3 \) is very small, or is zero as in a \( G_12 \) molecule such as toluene or \( p \text{FT} \) [see Fig. 1(b)], then the sign of \( V_6 \) determines the energy ordering of the \( m = 3n(+) \) and \( m = 3n(-) \) levels, particularly for \( n = 1 \). It is also the case that the energies of the other \( m \) levels depend on both parameters, as well as the effective rotational constant for torsion of the –CH\(_3\) group, denoted \( F \), whose value is expected to be only slightly different in the three electronic states under consideration. As a consequence, it is not straightforward to deduce the values of the torsional parameters from the spectrum directly, and that difficulty is further exacerbated by possible interactions between torsional, vibrot, and vibrational levels.

B. Overall comments on the spectra

1. The \( S_1 \) ← \( S_0 \) spectrum

The REMPI spectrum covering the first 350 cm\(^{-1}\) of the \( m \text{FT} \) \( S_1 \) ← \( S_0 \) spectrum is shown in Fig. 2. It is very similar in
appearance to the LIF spectra of Stewart et al. and Okuyama et al. Some of the assignments in Ref. 24 have been superseded by those in Ref. 22, and it is the latter that will be referred to in the present work.

The $S_1$ $0^0 m^0 \rightarrow S_0$ origin transition is located at 37 385.9 cm$^{-1}$, with the $S_1$ $m^1 \rightarrow S_0$ $m_0$ transition located 4.0 cm$^{-1}$ below this (Ref. 22)—see Fig. 2. It may be seen that there are vibtor as well as “pure” torsional transitions observed in this region of the spectrum.

For each vibration of $a_1$ symmetry (fundamental, overtone, or combination), it is expected to see transitions corresponding to both $m^0$ and $m^1$ transitions. Vibrations of $a_2$ symmetry are only expected as vibtors in combination with $m = 3(\pm)$, and perhaps weakly with $m = 6(\pm)$, when exciting from $S_0 m = 0$, while weak $X^{m^1} \rightarrow 0^1 m^1$ transitions are also seen for $X$ being a vibration of $a_2$ symmetry, and their activity is likely induced by second order couplings.

2. ZEKE spectra via torsional levels of $S_1$

We shall now discuss the ZEKE spectra. In Table II, we have tabulated the wavenumbers of the vibtor levels relative to their respective ($m = 0$) vibrational fundamentals—these assignments will be deduced in Secs. III B 3–III B 7. In the figures, we have indicated the assignments of many of the bands, but for clarity, we have omitted the preceding superscript "s" on these. Note that in the figures, we have not indicated all of the observed weak transitions although many of these can be deduced from the values given in Table II.

We initially consider the first ~880 cm$^{-1}$ of each of the ZEKE spectra recorded via $S_1 m^0$ and $S_1 m^1$, which are shown in Figs. 3(a) and 3(d), respectively. As may be seen, very different activity is seen in both cases with transitions from $S_1 m^1$ maintaining $e$ symmetry in the final states, while transitions from $S_1 m^0$ lead to the most intense bands being of $a_1$ symmetry, but also some bands are associated with symmetry-forbidden levels whose activity is discussed further in Sec. IV. It is also clear in each spectrum that the $\Delta v, m = 0$ band is not the most intense feature. The spectra have been shifted so that the bands are on the same internal wavenumber scale.

TABLE II. Separations of vibtor levels built on different vibrations (cm$^{-1}$). a

| Torsion | $0^0 [0]$ | $30^1 [167]$ | $29^1 [194]$ | $21^1 [296]$ | $29^2 30^1 [365]$ | $30^2 [335]$ | $28^1 [372]$ | $29^2 [384]$ | $18^1 [510]$ |
|---------|------------|-------------|-------------|-------------|-------------|------------|-------------|-------------|-------------|
| $m^0$  | 0          | 0           | 0           | 0           | 0           | 0          | 0           | 0           | 0           |
| $m^1$  | 101        | 99          | 98          | 102         | 91          | 106        | 98          | 100         |            |
| $m^2$  | 103        | 97          | 100         | (107)       | 92          | 105        | (97)        | 102         |            |
| $m^3$  | 185        | 186         | 181         | 189         | 180         | 178        | 181         | 186         |            |
| $m^4$  | 192        | 179         | 191         | 195         | (187)       | (170)      | 193         | 190         | 192         |
| $m^5$  | 250        | 244         | 251         | 253         | (249)       | (236)      | 252         | 246         | 250         |
| $m^6$  | 292        | 282         | 294         | 294         | 284         | 293        | 286         | 293         |            |
| $m^7$  | 311        | 311         | 317         | 304         | 299         | 313        | 306         | 311         |            |
| $m^8$  | 368        | 366         | 369         | 369         | 369         | 366        |             |             |            |
| $m^9$  |            |             |             |             |             |             |             |             | 526         |

a) Torsional spacings are given with respect to the band position of the $m = 0$ level of the indicated vibration.

b) Values in square brackets in the column headers are the wavenumbers of the $m = 0$ level of the indicated vibration.

c) The "$m^0$ and "$m^1$ levels are degenerate at our resolution. Levels with $m = 3n$ have degenerate $+$ and $-$ levels. The "$m^{(+)}$ and "$m^{(-)}$ levels are expected to be close to degenerate as they lie above the $V_1$ barrier; it is the "$m^{(+)}$ level that is seen in this work, via $m^{(+)}$.

d) The fundamental value for "$29^0$ is tentative.

e) These values in parentheses are weak, and/or their assignment/band center is uncertain.
The adiabatic ionization energy (AIE). (Note that we have not adjusted
of 71 997 + Δ with a sizeable S separated, and the latter is quite close to
m are noticeably separated. Since the top of the barrier is now being
m = 0 band, *m1*; furthermore, the most intense band is the
Δm = 6 band, *m6*, while the *m2* band is clearly seen and is of a similar intensity as *m1*. (Note that the m levels are degenerate for m ≠ 3n and so, as an example, the *m2* band, Δm = 3, actually arises from a combination of *m2* ↔ *m1* and *m2* ↔ *m−1* transitions.) Although weak, a clear series of vibtor bands associated with each of *30* and *29* (not indicated—see Table II) can be seen, as well as several with *28* (not indicated—see Table II). To higher wavenumbers, a very similar pattern of bands can be observed, arising from combinations with *18*.

Moving onto the ZEKE spectrum via m [Fig. 3(c)], we note that this S torsional level can be reached via two transitions, *m2* and *m3*. The former is a hot band, caused by incomplete cooling of the S2, m = 2 population into m = 1. Both ZEKE spectra are essentially the same, but the spectrum via the cold band is the more intense, and it is this one that is presented. Again, we note that the Δm = 0 band is not the most intense, with this being the Δm = 3 band, accessing *m6*. Also, the *m2* band corresponding to Δm = 6 is more intense than the Δm = 0 band. The Δm = 3 band, *m2*, is also clearly seen, as is the Δm = 6 band, *m8*. As with the ZEKE spectra via m* and m*, we also see combination bands involving *18*. There are also vibtor bands evident in this spectrum: *30m*, *30m*, *30m, and *30m*. and (not indicated) *29m*, *29m*, and *29m* are seen (noting that *29m* is likely overlapped by the *m4* band)—see Table II.

The m* band is extremely weak (see Fig. 2), but a ZEKE spectrum was obtained via this level, giving rise to *m3* and *m3*, with the latter slightly more intense—Fig. 3(b). The *m3* band is a symmetry-allowed Δm = 3 band and has a similar intensity as the Δm = 0 band. A weak band assignable as *18* is also evident.

The ZEKE spectrum recorded via m*—Fig. 3(c)—is interesting in that the Δm = 0 band is very weak, with the width of the feature suggesting that there is likely partial overlap with *29m*. The torsional region of the spectrum is dominated by the two Δm = 3 bands, *m0* and *m6*, the Δm = 6 band, *m2* is also seen. There are also symmetry-forbidden torsional bands *m5* and *m6*, as well as weak, symmetry-forbidden vibrational bands, *30m*, and (not indicated—see Table II) *29m*, *29m, and *29m*. Additionally, a symmetry-allowed vibrational band is seen for *18m*, with *21m* likely overlapped by the *m6* band; also, a weak *30m* band (not indicated—see Table II) is seen. Above 500 cm−1, there are the now-expected combinations of the earlier bands with *18*. There are several other weak features, for which there are possible, but not definitive, assignments, and so we refrain from discussing those. We do note that the symmetry-allowed *30m* band is clearly observed, while *29m* would be obscured by the *m6* band.
The ZEKE spectrum recorded via $m^3$—Fig. 3(f)—exhibits a sizeable $\Delta m = 0$ band, but it is not the most intense, with this being the $^+m^1$ band, corresponding to $\Delta m = 3$, and the (also $\Delta m = 3$) $^+m^0$ band is also clearly seen. The $\Delta m = 6$ band, $^+m^2$, is also very intense, while the $\Delta m = 9$ band, $^+m^5$, is also clearly active. We also see generally weak bands corresponding to vibtor versions of these torsions in combination with $^+30^1$; the exception to this is the $^+30^3m^1$ band, which demonstrates a significant intensity—this is commented on in Subsection III B 3. A number of corresponding vibtor bands involving $^+29^1$ are also seen (not indicated—see Table II). Above 500 cm$^{-1}$ are seen the $^+18^1$ band and vibtor bands involving this vibration.

The ZEKE spectrum recorded via $m^5$ is quite weak, see Fig. 3(g), but clear torsional bands can be seen. The $\Delta m = 0$ band is fairly intense but is slightly weaker than the most intense $\Delta m = 9$ band, $^+m^4$; the two $\Delta m = 3$ bands, $^+m^2$ and $^+m^8$, are also sizeable. The $^+30^1m^1$ band is also seen clearly. Above 500 cm$^{-1}$, vibtor bands built upon $^+18^1$ are seen.

3. Vibtor levels involving $30^1$

In Fig. 4(a), we show the ZEKE spectrum recorded via the two overlapped vibtor transitions, $30^1m^2$ and $30^1m^3(-)$. Transitions to these levels are symmetry allowed from the $S_0 m = 1$ and $m = 0$ levels, respectively. It was shown in Ref. 22 that interactions in the $S_1$ state cause the $30^3m^2$ and $30^3m^3(-)$ bands to be almost coincident, but the separate contributions could be extracted from the 2D-LIF spectrum; the latter band is significantly the stronger one. As a consequence, we expect the ZEKE spectrum to demonstrate bands arising from both levels but be dominated by bands arising from $30^3m^3(-)$. The two strongest bands can be assigned to the $\Delta(v,m) = 0$ band, $30^3m^3(-)$ and the $\Delta m = 3$ band, $30^4m^3(-)$. Furthermore, the presence of these two strong bands is consistent with the observation of the $^+m^3(-)$ and $^+m^3(-)$ bands seen when ionizing from $m^3(-)$—Fig. 3(b). Note that in the cation, the $^+30^3m^0$ band is expected to be very close in energy to the $^+30^3m^3(-)$ band. The $^+30^3m^3(-)$ band is fairly close in energy (Table II). On symmetry grounds, the observed weak $^+m^0$ could arise from $30^3m^0$, but we note that $^+m^4$ and $^+m^5$ are not seen. An alternative source of activity would be a deviation of the symmetry away from $G_6$—see Sec. IV C. The $^+m^3(-)$ band can arise from $30^3m^3(-)$. Overall, there is support from this ZEKE spectrum for the REMPI feature to arise from an overlap of $30^3m^3(-)$ and $30^4m^2$, consistent with the deductions of Ref. 22. Other assignments are noted in Fig. 4(a), with combinations involving $^+18^1$ being seen to higher wavenumbers.

Overall, a fairly complete set of vibtor levels built on $^+30^1$ is seen, and these are tabulated in Table II. As well as a possible “closing up” of the levels compared to the pure torsional levels, a key observation here is that the $^+30^3m^3(-)$ level lies below the $^+30^1m^1$ level. These two points suggest that the values of one or more of the torsional parameters may have changed in these vibtor levels and also that there are specific vibtor interactions between levels—further comment is made in Sec. IV D.

In the ZEKE spectrum recorded via $30^1m^4$—Fig. 4(b)—we can see that the spectrum is dominated by the $\Delta m = 3$ band, $^+30^1m^1$, with the other symmetry-allowed vibtor levels also prominent. Interestingly, consistent with the strong $^+30^1m^4$ band seen when exciting via $m^4$—see Fig. 3(f)—we see a reasonably strong $^+30^3m^4$ band in the spectrum in Fig. 4(b); further discussion will be presented in Sec. IV D. To higher wavenumbers, we see combinations with $^+18^1$.

Via the $29^1m^2$ band at 216 cm$^{-1}$, a weak ZEKE spectrum is seen, showing the $\Delta(v,m) = 0$ band [Fig. 4(c)], as well as $^+m^3$ and a band that likely arises from overlapped $^+m^4$ and $^+29^1m^1$ transitions. The activity is consistent with the assignment$^{22}$ of this band to $29^3m^2$. Similarly, when exciting via the $^+29^3m^3(-)$ band at 234 cm$^{-1}$ [Fig. 4(d)], we saw weak bands assignable as an overlapped $^+m^3(-)/^+29^3m^0$ pair of transitions, together with the $\Delta(v,m) = 0$ band. Although we might have expected to see $^+29^3m^3(-)$ by analogy with the ZEKE spectra recorded via $m^3(-)$ and $30^3m^3(-)$ (see Secs. III B 1 and III B 2), and as will be seen $28^3m^3(-)$ (Sec. III B 6), the signal in the higher wavenumber region of the spectrum via $29^3m^0$ was too poor to be reliable.

4. Spectra via $30^2m^0$ and $30^2m^1$

The ZEKE spectra recorded via the $30^2m^0$ and $30^2m^1$ levels are shown in Fig. 5. The band intensity profile of the spectrum via $30^2m^1$ [Fig. 3(b)] somewhat resembles that of the spectrum via $0^0m^1$.

![FIG. 4. ZEKE spectra recorded via the following intermediate $S_1$ levels: (a) the overlapped $30^1m^2/30^1m^3(-)$, (b) $30^1m^4$, (c) $29^1m^2$, and (d) $29^1m^3(-)$. The preceding superscripted ‘$^+$’ used in the text is omitted in the labels for clarity. See text for further discussion.](image-url)
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5. Spectra via $29^1 0^0$ and $21^1 m^1$

The ZEKE spectra recorded via the two lowest torsional levels of $21^1$ are shown in Fig. 6. When exciting via $21^1 m^1$ [Fig. 6(b)], a fairly similar profile is seen to that observed when exciting via $0^0 m^1$ [Fig. 3(d)] with a strong activity in $21^1 m^1$, $21^1 m^1$, and $21^1 m^1$, and clear bands are also seen for $21^1 m^1$ and $21^1 m$. In addition, weak bands are seen for $^m 0^0$ and $^m 0^0$, $^m 0^0$, $^m 0^0$, and (overlapped) $^m 0^0$. A similar set of vibror bands is seen with $^m 0^0$.

The ZEKE spectrum via $21^1 m^0$ [Fig. 6(a)] is somewhat more straightforward, with the spectrum resembling that recorded via $0^0 m^0$ [Fig. 3(a)] with the most-intense band being the sizeable $^m 0^0$, $^m 0^0$, $^m 0^0$, and $^m 0^0$. Although the recording of ZEKE spectra was attempted via $21^1 m^0$, no discernible structure was evident owing to the very weak transition.

6. Spectra via $29^1 30^1 0^0$, $28^1 m^2$, and $28^1 m^3$

The recording of ZEKE spectra via $29^1 30^1 m^0$ was attempted, but no bands were evident. The ZEKE spectrum via the overlapped $29^1 30^1 m^0$, $28^1 m^2$, and $28^1 m^3$ transitions is shown in Fig. 7(a). From $29^1 30^1 m^0$, by comparison with the $0^0 m^0$ spectrum [Fig. 3(a)], the expected $29^1 30^1 m^0$ band is seen, together with $29^1 30^1 m^0$. From $28^1 m^2$, by comparison with the spectrum via $m^0$ [Fig. 3(e)], we only see the two more intense features: $28^1 m^2$ and $28^1 m^2$. A very weak feature can be seen that is in the expected position for $30^1 m^2$, which is consistent with $30^1 m^2$ being a very weak feature overlapped by $29^1 30^1 m^0$ and $28^1 m^2$.

The spectrum via $28^1 m^3$—Fig. 7(b)—is very similar to those via $m^3$ and $30^1 m^3$ in that both $28^1 m^3$ and $28^1 m^3$ bands are clearly seen. As noted above, we did see the $29^1 m^3$ band when exciting via $29^1 m^3$, but the signal was too poor to see the now-expected $29^1 m^3$ band.

7. Spectra via $29^2 0^0$ and $29^2 m^1$

The ZEKE spectra via these two levels are shown in Fig. 8. When exciting via $29^2 m^1$ [Fig. 8(b)], expected bands are seen for $29^1 m^1$, $29^1 m^1$, $29^1 m^1$, and $29^1 m^1$. There are also clear bands associated with $29^1 30^1 m^1$, $28^1 29^1 m^1$, and some $29^1$ vibror bands.

FIG. 5. ZEKE spectra recorded via the following intermediate $S^2$ levels: (a) $30^2 m^0$ and (b) $30^2 m^1$. See the text for further discussion.

FIG. 6. ZEKE spectra recorded via the following intermediate $S^2$ levels: (a) $21^1 m^0$ and (b) $21^1 m^1$. The preceding superscripted “+” used in the text is omitted in the labels for clarity. See text for further discussion.

[Fig. 3(d)] in which the $\Delta (v, m) = 0$ band is extremely weak, but there are clear bands for the $\Delta m = 3$ band, $30^2 m^0$, with the $\Delta m = 0$ band, $30^2 m^0$, the most intense. With these bands seen, it might also be expected to observe clear $30^2 m^0$ and $30^2 m^0$ bands; however, the former is weak, and the latter is not obviously seen. Also evident are the $m^0$ and $30^2 m^0$ bands. Other weak bands can be assigned as the set of vibrors: $21^1 m^0$, $21^1 m^0$, and $21^1 m^0$.

When exciting via $30^2 m^0$ [Fig. 5(a)], again there is a strong similarity with the activity seen via $0^0 m^0$ [Fig. 3(a)] with a dominant $30^2 m^0$, $30^2 m^0$, $30^2 m^0$, and $30^2 m^0$. There are also bands arising from $30^2 m^0$ and $30^2 m^0$ and (likely, unobserved) $30^2 m^0$ and $30^2 m^0$, as well as the torsional bands $30^2 m^0$ and $30^2 m^0$. Additionally, overlapped bands arising from $21^1 m^0$ and $21^1 m^0$ appear to be present, as well as a band assigned as $21^1 m^0$. Finally, bands that are assignable to the $29^1 30^1$, $28^1 m^0$ (overlapped), and $28^1 m^0$ combination bands are evident, with the corresponding $30^2 m^0$ vibror levels seen for the first two of these in the range scanned.

Overall, a fairly complete set of vibror levels built on $30^2$ is seen, and these are tabulated in Table II. As well as a distinct “closing up” of the levels compared to the pure torsional levels, it is interesting to note the change in ordering of the $30^2 m^0$ and $30^2 m^0$ levels. As with the $30^2$ vibror levels, this suggests that the values of one or more of the torsional parameters have changed, but also that there are specific vibror interactions between levels. This is discussed further in Sec. IV D.

5. Spectra via $21^1 m^0$ and $21^1 m^1$
The ZEKE spectrum via $29^3m^0$ [Fig. 8(a)] has the expected [by comparison with Fig. 3(a)] most-intense band as $29^3m^3(\pm)$, with the other expected bands $29^3m^0$, $29^3m^6(\pm)$, and $29^3m^6(\mp)$. We also observe the weak, symmetry-allowed vibtor band $29^1m^3(\pm)$, noting that the symmetry-allowed vibtor band $29^1m^6(\pm)$ could be overlapped with $29^1m^3(\mp)$. Weak, symmetry-forbidden $29^1m^3(\pm)$ (overlapped) and $29^1m^6(\pm)$ bands are also tentatively assigned.

FIG. 8. ZEKE spectra recorded via the following intermediate $S_1$ levels: (a) $29^3m^0$ and (b) $29^3m^1$. The preceding superscripted “+” used in the text is omitted in the labels for clarity. See text for further discussion.

IV. DISCUSSION

A. The strong propensity away from $\Delta m = 0$ bands

One of the most prominent aspects of the spectra is that the $\Delta m = 0$ bands are not the most intense. Similar observations have been made in the $m$FT work of Ito et al.\textsuperscript{27-29} and Weisshaar et al. on mCIT.\textsuperscript{7} This stems from the change in the global minimum from pseudo-trans in the $S_1$ state to pseudo-cis in the $D_0^*$ state;\textsuperscript{30,31} these geometries are shown in Fig. 9. This implies that the phase of the torsional potential is different in the two states, which can be expressed as the sign of the $V_3$ parameter being different. Using the same convention as Lu et al.,\textsuperscript{27} we use $\alpha = 0^\circ$ to represent the pseudo-trans structure and $V_3$ positive, and $\alpha = 180^\circ$ for the pseudo-cis structure, where $V_3$ is negative. As noted above, the sign of the $V_3$ parameter does not change the energies or ordering of any of the torsional levels, and so the sign can only be directly deduced from the geometry.\textsuperscript{32,33} However, the fact that there are different signs of $V_3$ between the $S_1$ and $D_0^*$ states is useful since it gives rise to a greater activity in the ZEKE spectra. Consequently, this gives more levels from which to deduce the torsional parameters.

Previous work has looked at both the form of the torsional potential in substituted benzenes with $G_6$ symmetry [Eq. (1)] and the values of the torsional parameters $F, V_3$, and $V_4$ in the three electronic states $S_0, S_1$, and $D_0^*$. Although an earlier microwave study\textsuperscript{34} deduced values for these parameters in the $S_0$ state, two possible sets of values were offered. The recent study by Stewart et al.\textsuperscript{22} has obtained revised values for these parameters, taking into account vibtor interactions, which are in reasonable agreement with one of the sets of values from Ref. 45 and with the low-level quantum chemical calculations by Lu et al.\textsuperscript{28} Similarly, in the same study,\textsuperscript{22} these parameters were deduced for the $S_1$ state and provide more robust values than those in the previous LIF study of Okuyama et al.,\textsuperscript{21} where there were a number of misassignments.

As mentioned, Takazawa et al.\textsuperscript{27} have deduced that the phases of the $S_0$ and $S_1$ torsional potentials are the same, but that they are out of phase with that for the $D_0^*$ state, in agreement with the geometries obtained in Ref. 28, and this is in agreement with the conclusions reached for mCIT.\textsuperscript{22} We have confirmed with B3LYP/aug-cc-pVTZ quantum chemistry calculations that, indeed, the $S_0$ and $S_1$ states have pseudo-trans global minima, while the $D_0^*$ state is pseudo-cis (see Fig. 9) so that $V_3$ in $D_0^*$ is negative. (Note that for the $S_1$ state, TD-B3LYP was employed, while for the $D_0^*$ state, UB3LYP was employed, $\langle \bar{S}_1^2 \rangle = 0.76$.) This change in the phase between the $S_1$ and $D_0^*$ states was discussed in Refs. 27 and 29 in relation to the nondiagonal intensities seen in the spectra of $m$FT and mCIT and seen in the present work.

As can be seen from Fig. 1(a), for $m$ levels that are contained within the well, triplets of these move toward degeneracy as $V_3$ increases (see Sec. III B 3). Since previous work\textsuperscript{5} has determined that $V_3$ in $m$FT is around $-300$ cm$^{-1}$, we would expect this picture to hold here, as indeed is confirmed by the ZEKE spectra. As part of this evolution, $V_1$ leads to a separation of the $m = 3(\pm)$ levels, with $m = 3(\pm)$ moving toward the $m = 4$ level, and $m = 3(\mp)$ converging with the $m = 2$ level; thus, $m = 3(\pm)$ will lie above $m = 3(\mp)$ on the basis of this parameter alone. Since $V_6$ is generally very much smaller than $V_3$ for $G_6$ symmetry molecules, this ordering is not expected to change, as may be seen in Fig. 1(c); indeed, the variation of the energies of the $m$ levels is rather small for $V_6$ values
of a few tens of cm\(^{-1}\). (The value of \(F\) we employ here, 5.4 cm\(^{-1}\), is significantly different to that employed by Ito and co-workers\(^{25-27}\). A similar value was used by the same group for the S\(_1\) state.\(^\text{24,27}\) and this was discussed by Stewart et al.\(^\text{46}\) and concluded to be physically unreasonable.) The principal differences between our assignments and those of Ref. 27 are the energies of the \(m^{(+)}\) and \(m^{(-)}\) levels. The former is a slight difference that could result from estimating band centers, the second is a band that is reassigned in the present work to \(30\) m\(^{-1}\) — i.e., a vibtor transition. In Refs. 24, 25, 26, and 27, vibtor transitions were not considered, and some similar reassignments were discussed in Ref. 22 for the S\(_1\) state. For this reason, the present results and assignments are expected to be the more reliable.

### B. Appearance of strong \(m^{3(-)}\) and \(m^{6(-)}\) bands, when exciting via \(m^0\)

Both the \(m = 3(-)\) and \(m = 6(-)\) levels have \(a\)\(_2\) symmetry and are therefore symmetry forbidden when exciting via \(m^0\). One explanation for the appearance of these symmetry-forbidden bands could be rotation-torsional coupling, which is the source of the weak activity for \(m^{(+)}\) in the S\(_1\) state\(^\text{21,22}\) [and this could also apply to the \(m = 6(\pm)\) levels]. That the \(m^{(+)}\) REMPI band is very weak (see Fig. 2) in the present work is likely the result of the very cold rotational temperatures herein. In the cation, each of the \(m^{(3)}\) and \(m^{(6)}\) pairs of levels is more-separated energetically, and so we rule out a strong torsion-rotation coupling here and reject this as the main explanation for the appearance of the \(m^{(3)}\) and \(m^{(6)}\) ZEKE bands.

Since the S\(_1\) \(m = 0\) level is of \(a\)\(_1\) symmetry, it is not expected to see the \(m^{(3)}\) and \(m^{(6)}\) bands in the ZEKE spectrum when exciting via this level; however, these bands are relatively strong. It is notable that vibrations with these corresponding symmetries are often seen in photoelectron spectra of relevant substituted benzenes. In our work on toluene and pFB,\(^\text{2}\) we also assigned the \(m^{(3)}\) band when exciting via S\(_1\) \(m^0\). Recently, we discussed this issue in the D\(_{2h}\) molecule, pFB,\(^\text{26}\) where nontotally symmetric bands of \(b\)\(_{3u}\), \(b\)\(_{2g}\), and \(a\)\(_2\) symmetry were observed (these all correlate with \(a\)\(_2\) symmetry in G\(_0\)). In that work, we argued that there were no excited cationic states of the correct symmetry to allow vibronic coupling to be the source of the intensity of these bands and we invoked a variant on the intrachannel coupling mechanism put forward by Poliakoff et al.,\(^\text{47}\) adapting it to the production of the high-lying Rydberg states that are formed in the pulsed-field ionization ZEKE method.

Assuming that the corresponding excited states for mFT\(^\text{+}\) are at relatively similar energies to those for pDFB\(^\text{+}\) (Ref. 48) and then adapting the symmetries to G\(_0\), it can be seen that it is now possible that vibronic coupling in mFT\(^\text{+}\) is a mechanism for the observed torsional and vibrational activity as there are low-lying cation states of both \(a\)\(_1\) and \(a\)\(_2\) symmetry; albeit that it is unclear how strong this coupling would be.

Considering now the intrachannel coupling mechanism,\(^\text{46,47}\) the basic idea is that the Rydberg electron interacts with the vibrations of the nuclear core and so does not require another electronic state to be involved, and we suggested in Ref. 46 that this was most likely for s and p Rydberg electrons, which are more penetrating. In the present G\(_0\) case, the symmetries of these electrons are \(a\)\(_1\) (s, p\(_x\), and p\(_y\)) and \(a\)\(_2\) (p\(_z\)), and so, when combining the electronic symmetry of the ground state cation (\(A\)\(_2\)) with that of the Rydberg electron, both \(a\)\(_1\) and \(a\)\(_2\) symmetry vibrations and torsions can be activated by this process. Hence, this also provides an explanation for the observation of symmetry-forbidden bands in the ZEKE spectra. It is plausible that both the vibronic and intrachannel coupling mechanisms are operating in mFT\(^\text{+}\), with the intensity of each band depending on the strengths of these interactions.

Although we see symmetry-forbidden torsional levels of \(a\)\(_2\) symmetry in the ZEKE spectra recorded when exciting via the S\(_1\) \(m^0\) band, we do not see nontotally symmetric vibrations, suggesting that the coupling to the torsional motion is stronger than that to the low-frequency vibrations in mFT\(^\text{+}\). That said, both \(30\) m\(^{-1}\) and \(29\) m\(^{-1}\) are seen weakly in the ZEKE spectrum recorded via \(m^{(+)}\) — see Fig. 3(c) and Table II, and \(30\) m\(^{-1}\) and \(29\) m\(^{-1}\) are seen weakly via S\(_1\) \(m^1\) [Fig. 3(d) and Table II]. The fact that only low-frequency

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**FIG. 9** Calculated geometries for the (a) S\(_0\) (B3LYP/aug-cc-pVTZ), (b) S\(_1\)(TD-B3LYP/aug-cc-pVTZ), and (c) D\(_{2h}\)\(^+\) (UB3LYP/aug-cc-pVTZ) electronic states of \(m\)-fluorotoluene. The bond lengths are in Å. Note the differing conformation of the cation relative to the two neutral states. The filled circles represent the F atom, and the unfilled circles represent the C and H atoms.
vibrations or torsions are seen is consistent with these nuclear motions being on a time scale that allows interaction with the Rydberg electrons.

One final explanation would be movement of the CH₃ group off-axis as a result of interactions with vibrational motion, which is discussed further in Subsection IV C. In this case, the a₁ and a₂ classes combine, and this would make \( \tilde{m}^5 \) and \( \tilde{m}^6 \) transitions allowed.

### C. The appearance of \( \tilde{m}^5 \) in the ZEKE spectrum via \( m^5 \)

Under the normally strong selection rule of no change in torsional state symmetry, we expect to see transitions to only a₁ symmetric levels when exciting via \( m^0 \) and to only e symmetry levels when exciting via \( m^1 \). It is thus difficult to explain the observed activity of \( \tilde{m}^5 \) via \( S_1 m^0 \), which involves an apparent change in nuclear symmetry. There are two possible explanations for this band.

Since we excite at wavenumbers where there is no significant overlap in the \( m^0 \) and \( m^1 \) band profiles, this excludes a dual excitation; furthermore, there are no obvious hot bands that would appear under \( m^n \). One possibility is in terms of a coincident band, and among others, Lawrance and co-workers have shown that \( 13 \)C isotopologues of substituted benzenes give rise to features in the excitation spectrum that generally appear \( \sim 4 \) cm\(^{-1} \) to higher wavenumbers than the \( 12 \)C bands.\(^{49} \) As such, by reference to Fig. 2, it may be seen that the \( 13 \)C-mFT \( m^1 \) band is expected to lie under the \( 12 \)C-mFT band, and as can be seen from Fig. 3(d), we expect a prominent \( \tilde{m}^5 \) band when exciting \( m^1 \). Since a \( 13 \)C/\( 12 \)C substitution will not affect the torsional levels to an extent that will be discernible within the present resolution, we might expect to see a weak version of the \( m^0 \) ZEKE spectrum, arising from \( 13 \)C-mFT, to appear when exciting via \( 12 \)C-mFT \( m^5 \). To test if this is a possible explanation, in Fig. 10(a), we have overlaid the \( m^5 \) ZEKE spectrum with the \( m^5 \) ZEKE spectrum, scaled to match the intensities of the \( \tilde{m}^5 \) bands in the two spectra. As may be seen, both the \( \tilde{m}^5 \) and \( \tilde{m}^6 \) bands are not diagnostic since they are almost perfectly coincident with the \( m^5 \) and \( m^{6\text{e}} \) bands, respectively, because of the large \( V_3 \) term (see Fig. 1). However, the \( m^6 \) band is displaced from the \( \tilde{m}^{6\text{e}} \) band—see Fig. 3 and Table II—and from Fig. 10(a), it can be seen that there is no definitive evidence for the \( \tilde{m}^5 \) band in the \( m^5 \) ZEKE spectrum, although it is not possible to rule this out entirely.

We now highlight that no coupling with molecular motion can induce the activity for the \( \tilde{m}^5 \) transition in \( G_6 \), with translations, rotations, and vibrations all having \( a_1 \), or \( a_2 \) symmetry. In addition, there is no other vibron that can lead to the (e symmetry) \( \tilde{m}^5 \) activity via interactions, when exciting via the (a₁) symmetry \( S_1 m^0 = 0 \) level. It is possible to form localized e symmetry orbitals from the methyl H 1s orbitals,\(^{29} \) and so it may be that such orbitals might give a mechanism for the activity of this band via torsion-electronic coupling.

Another explanation is a movement away from \( G_6 \) molecular symmetry, as has been discussed in relation to the precessing of the methyl group around the \( G_5 \) axis as it rotates.\(^{28,30} \) Such geometric distortions have been termed "torsional flexing" and been shown to be described by the \( V_6 \) parameter.\(^{3} \) This would move the symmetry away from \( G_6 \), but if the methyl C–H bond lengths remained the same length, then the symmetry would become \( G_5 \), which would still retain e symmetry (with \( a_1 \) and \( a_2 \) combining to form a single \( a \) symmetry class, as mentioned in Subsection IV B).

A viable explanation requires the height of the torsional barrier to be sufficient to "lock" the torsional motion such that it is best described as a vibration of a \( C_2 \) symmetry molecule. In these circumstances, the methyl C–H bond lengths would not be expected to be the same—as indeed they are not [Fig. 9(c)]. Then, the "torsions" could be described as \( a \) symmetry vibrations, which could gain an activity via vibronic or intrachannel coupling, as described in Sec. IV B. We agree that it is strange that we only see \( \tilde{m}^5 \), but this could be an intensity effect.

We also note that in the ZEKE spectra recorded via e symmetry levels in Figs. 3(d)–3(g), we see a band at \( \sim 292 \) cm\(^{-1} \). One possible assignment of this is to \( \tilde{m}^5 \), but it is also possible that this could be \( m^{6\text{e}} \)—see Fig. 10(b). If the latter were the case, then this would be an \( a_2 \) symmetry band observed via an e symmetry level, again breaking the \( a/e \) selection rule, and again being consistent with a geometric distortion away from \( G_6 \) symmetry. (Interestingly—see Fig. 1—the \( m^5 \) and \( m^{6\text{e}} \) levels are the two levels that converge as \( V_5 \) increases, to form the third quantum of the torsion vibration.) We also comment that the \( \tilde{m}^5 \) band was seen in the ZEKE study of mFT by Takazawa et al.,\(^{3} \) although it was not commented upon—indeed, in their Appendix, they specifically note that no \( a \leftrightarrow e \) symmetry transitions were observed even though this band is clearly in their spectrum.

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FIG. 10. (a) Overlay of the ZEKE spectrum via \( m^5 \) with that via \( m^0 \)—the former spectrum has been scaled so that the \( m^5 \) bands have approximately the same intensity in both spectra. See text for discussion. (b) ZEKE spectrum via \( m^5 \) showing the band at \( \sim 292 \) cm\(^{-1} \) that can be assigned to \( 29 \) m\(^{6\text{e}} \) or \( m^{6\text{e}} \). The preceding superscripted "\( * \)" used in the text is omitted in the labels for clarity. See text for further discussion.
In summary, there are two plausible explanations for the appearance of the \( ^1m^4 \) band when exciting via \( m^6 \): an overlap with the \( ^{13}\text{C}-m\text{FT} \) \( ^1m^4 \) band or a significant geometric distortion away from \( G_0 \) symmetry. Although not definitive, the significant magnitude of \( V_3 \) and no definitive evidence for the expected \( ^1m^4 \) band in Fig. 10(a) lead us tentatively to favor the latter explanation. A mass-analyzed threshold ionization (MATI) experiment would be useful in deciding between the two interpretations discussed.

D. Interactions involving the \( ^{30}_1 \) and \( ^{30}_2 \) vibtor levels

One aspect of the ZEKE spectra that stands out is the activity of the \( D_{2g} \) vibration via various vibtor levels, including both the fundamental and the first overtone. (The expectation that such a structure would be seen was expressed in Ref. 22.) This covers general activity as well as several unusually intense or weak bands. Because of this activity, we have been able to ascertain the band positions of many vibtor levels involving this vibration (see Table II). In so doing, we conclude that the torsional potential appears to be modified when this vibration is excited—see below.

In Fig. 3, it may be seen that there is the activity of \( ^{30}_1 \) \((\pm)\) when exciting via \( m^6 \) and a weak \( ^{30}_1 \) \((\pm)\) band when exciting via \( m^4 \); there is also a weak \( ^{29}_0 \) \( 30^m_6 \) band observed when exciting via \( m^6 \). A series of \( e \) symmetry vibtor bands involving \( ^{30}_1 \) are seen when exciting via the four \( e \) symmetry torso-torsional levels \( m^1, m^2, m^3, \) and \( m^4 \). Particularly noticeable is the abnormally intense \( ^{30}_1 m^3 \) band when exciting via \( m^1 \) [see Fig. 3(f)]; the activity of this band is echoed by the unexpectedly intense \( ^{30}_1 m^4 \) band, seen when exciting via \( 30^m_4 \) [Fig. 4(b)]. We also see a number of vibtor bands involving both \( ^{30}_1 \) and \( ^{30}_2 \) when exciting via \( 21^m_1 \) [Fig. 6(b)]; this richness in structure can be contrasted with the very simple spectrum observed via \( 21^m_0 \). Also, such a \( ^{30}_1 \) activity is not seen when exciting via the \( 29^0_0 \) bands, except for \( 29^0_0 30^m_1 \) [Fig. 8(b)]. We also see weak \( 21^m_1 \) vibtor bands when exciting via the \( 32^0_2 \) levels—see Fig. 5.

In Fig. 11, we show portions of ZEKE spectra showing the \( a_1/a_2 \) torsional levels when exciting via \( m^4 \), together with the corresponding \( ^{30}_1^0 \) and \( ^{30}_2^0 \) vibtor levels, obtained when exciting through the \( 30^m_0 \) \((\pm)\) and \( 30^m_0 \) intermediate levels. (Ideally, we would have recorded a ZEKE spectrum via the \( 30^m_0 \) level; however, this transition is not seen in the REMPI spectrum.) The \( 30^m_1 \) spectra have been offset to align the \( ^{30}_1^0 \) and \( ^{30}_2^0 \) bands with the \( m^0 \) band. It may be seen that there is a slight shift in the \( ^{30}_1 \) vibtor bands to lower wavenumber with respect to the corresponding torsional ones and somewhat more so for the \( ^{30}_1 \) ones. In a similar way, in Fig. 12, we show portions of ZEKE spectra that show the \( e \) torsional levels when exciting via \( m^4 \), together with the corresponding \( ^{30}_1 \) and \( ^{30}_2 \) vibtor levels, obtained when exciting through the \( 30^m_0 \) and \( 30^m_0 \) intermediate levels. (Similar to the above comment, it would have been useful to have recorded a ZEKE spectrum via the \( 30^m_0 \) level; however, this transition is not seen in the REMPI spectrum.) The \( 30^m_1 \) and \( 30^m_2 \) spectra have been offset to align the \( ^{30}_1^0 \) and \( ^{30}_2^0 \) bands with the \( m^0 \) band. The \( ^{30}_1 \) vibtor bands appear to have shifted with respect to the corresponding torsional ones, with the \( 30^m_0 \) bands having shifted more so. It is also noticeable that the \( ^{30}_1^0 \) and \( ^{30}_2^0 \) bands appear to be shifted from the expected position—see Table II and comments below. We interpret these observations as suggesting that the torsional potential is modified from that of the vibrationless case; however, to gain quantitative information on this, a full analysis including anharmonicity, vibration-torsional coupling, and variation of the torsional parameters would be required—this is in progress by Lawrance and Gascooke (Flinders University, Adelaide) and will be the subject of a forthcoming publication. A vibration-modified potential can be rationalized by looking at the calculated vibrational mode diagram for \( D_{2g} \) in Fig. 13. We can see that the motion involves the two \( \text{ortho} \) hydrogen atoms to the methyl group moving out of plane in sync, while the methyl group moves out-of-phase with this. In addition, it is clear that there is torsional motion of the methyl group also.

The significant activities of \( ^{30}_1^0 m^4 \) when exciting via \( m^4 \) and of \( ^{30}_0 m^4 \) when exciting via \( 30^m_4 \) [see Figs. 3(f) and 4(b)] are in contrast to the corresponding \( ^{29}_1 \) vibtor bands. It may be seen from Fig. 13 that \( D_{2g} \) also contains an element of torsional motion. Furthermore, \( m^4 \) is closer in wavenumber to \( ^{29}_1 \) than to \( ^{30}_1 \). Together, this suggests that the coupling of the vibrational and torsional motions is very specific. Indeed, in the \( S_1 \) state, it was also concluded that the \( D_{2g} \) vibration coupled to the torsions more efficiently than did \( D_{2g} \). In the case of \( m^0 \), the \( D_{30} \) motion appears to be key in coupling to the torsional motion although other vibrations such as \( D_{2g} \) are also involved. In previous work, it has been noted that vibrations that involve motions close to the coordinate that demonstrates high-amplitude motion \( ^{30}_1 \) are expected to show increased coupling. However, we have noted in very recent work...
that it is important to look at the whole motion of a vibration. The present work demonstrates that even then, there are subleties as to which vibrations couple most efficiently.

Previous workers have discussed the precession of the methyl group and variations in geometric parameters as a function of the torsional angle. Indeed, it has been shown that such precession may be equated with an altered \( V_6 \) contribution to the potential. However, we have noted in the above that, for example, the observation of \( ^+m^1 \) when exciting via the origin is inconsistent with the main-
torsional transitions are aligned with \( ^m^1 \). Different spacings between the corresponding torsional levels are evident. The preceding superscripted \( ^+ \) used in the text is omitted in the labels for clarity. See text for further discussion.

FIG. 12. Sections of ZEKE spectra recorded via the following \( e \) symmetry inter-
mediate \( S_1 \) levels: (a) \( 0^0m^1 \), (b) \( 30^0m^1 \), and (c) \( 30^2m^1 \). The spectra in (b) and (c) have been shifted so that their respective \( ^m^1 \) torsion transitions are aligned with \( ^m^1 \). Different spacings between the corresponding torsional levels are evident.

![Figure 12](image_url)

![Figure 13](image_url)

FIG. 13. Calculated vibrational mode diagrams for \( m \)-fluorotoluene. For the three out-of-plane \((a_2 \) symmetry) vibrations at the bottom of the figure, the motion of the CH3 group is indicated, as viewed along its \( C_3 \) axis.

ZEKE spectrum in Fig. 4(b). Interestingly, \( m \) is seen in emission in Ref. 22 although the \( m^1 \) band is not seen in the present REMPI, nor the fluorescence spectra of that work.

It can also be seen that the \( ^+30^2m^4 \) level has been pushed below the \( ^+30^3m^3(-) \) level. Although we do not see the \( ^+30^1m^1 \) band, a possible \( ^+30^3m^4 \) ... \( ^+30^2m^4 \) interaction is plausible, as a counterpart to the \( ^+30^3m^4 \) ... \( ^+m^1 \) interaction. It is likely that there are other weak vibtor interactions occurring throughout the region.

E. Other vibrations

In Table II, the relative wavenumbers of the torsional levels associated with a number of vibrations are tabulated. These have been extracted from our ZEKE spectra and cross-checked where possible. We have commented on the \( ^+30^1 \) and \( ^+30^2 \) levels in Sub-
section IV D and implied that there are shifts for the \( ^+29^2 \) levels but that these are small. We also see small shifts for the \( ^+29^2 \) and \( ^+29^3 \) levels and note that all of these involve out-of-plane vibra-
tions. On the other hand, no noticeable shifts are seen for the in-
plane vibrations, \( ^+18^1 \) and \( ^+21^4 \). It can be seen from their mode diagrams (Fig. 13) and symmetry that there is no torsional aspect to their motions, which may underlie the lack of interaction between these vibrations and the torsion. Interestingly, there also seems to be no interaction between \( ^+28^2 \) and the torsion, despite this being an out-of-plane mode; this is not unexpected when looking at its motion (Fig. 13), which also does not contain any obvious torsional motion.


TABLE III. Calculated and experimental wavenumbers for the vibrations pertinent to the present study.

| Symmetry | S1     |        | D0<sup>+</sup> |        |
|----------|--------|--------|----------------|--------|
|          | Calculated<sup>a</sup> | Experimental | Calculated<sup>a</sup> | Experimental |
| α<sub>1</sub> | 18     | 459    |               | 509    | 510    |
|          | 21     | 281    | 284<sup>b</sup> | 290    | 296    |
| α<sub>2</sub> | 28     | 241    | 258<sup>c</sup> | 373    | 372    |
|          | 29     | 184    | 173<sup>d</sup> | 190    | 194<sup>d</sup> |
|          | 30     | 122    | 127<sup>d</sup> | 167    | 167    |

<sup>a</sup>TD-B3LYP/aug-cc-pVTZ, scaled by 0.97. Note that these values replicate those at an essentially identical level of theory published in Ref. 22.

<sup>b</sup>UB3LYP/aug-cc-pVTZ, scaled by 0.97; ⟨S<sup>2</sup>⟩ = 0.76.

<sup>c</sup>Present work.

<sup>d</sup>From Ref. 22.

<sup>e</sup>From Ref. 24.

<sup>f</sup>The fundamental value for +29<sup>f</sup> is tentative.

In Table III, we give the experimental and calculated wavenumbers for the vibrations discussed in the present work. Generally, the agreement between the two sets of values is good; similarly good agreement was found for the vibrations in the S<sub>0</sub> and D<sub>0</sub><sup>+</sup> states. Ongoing work in our group is focusing on higher-wavenumber vibrations.

F. Discussion of the origin of the barriers

Lu et al.<sup>28</sup> have discussed the barriers in various methyl-substituted benzenes, concentrating on the S<sub>0</sub> and D<sub>0</sub><sup>+</sup> states. They calculated the equilibrium geometries and barrier heights, finding relatively good agreement for the latter between calculated and experimental values; the calculations thus identified the sign of the V<sub>3</sub> barrier in many cases. In discussing the V<sub>3</sub> barriers in the S<sub>0</sub> state, it was the steric interaction between the methyl hydrogen atoms and the ortho hydrogen atoms that was key, and this was also the case for the V<sub>4</sub> barrier in molecules that belonged to the G<sub>12</sub> MSG, which has been discussed previously.<sup>28,29</sup> When V<sub>3</sub> was large, the barrier was discussed in terms of asymmetry in the two C–C bonds that neighbored the C–CH<sub>3</sub> bond, with a relationship being found between the difference in bond order of the two C–C bonds and the barrier height. Furthermore, it was found that for mFT<sup>+</sup>, the geometry was pseudo-cis in the cation, as we find—Fig. 9(c). As far as we can see, there was no explicit rationale as to the link between the bond order difference and the barrier height; however, it was implied that it was to do with the location of the positive charge following ionization of mFT. This charge is concentrated in one of the aforementioned C–C bonds neighboring the methyl group, with the other concentration being in a C–C bond neighboring the C–F bond; this is embodied in those bond lengths, as can be seen in Fig. 9(c). The pseudo-cis geometry has the in-plane methyl hydrogen on the opposite side to the C–C bond with the localized positive charge, thus reducing the Coulombic repulsion between the 6+ methyl H atoms and the positive charge localized in one of the adjoining C–C bonds; furthermore, it is then intuitively clear then why the bond order difference of the two C–C bonds neighboring the methyl group, being linked to the difference in charge density, is explicitly linked to the barrier height.

It is an interesting conclusion from previous work from Weisshaar’s group<sup>30</sup> that for both mFT<sup>+</sup> and mCIT<sup>+</sup>, the equilibrium geometry was pseudo-cis and the barriers were very similar. It was concluded that the type of substituent determined the π electron density structure and this in turn dominated the sign and value of the V<sub>3</sub> parameter. It would be useful to explore this conclusion further.

Considering the interaction between some out-of-plane vibrations and the torsional motion, we note that in the cation, this lowers the barrier slightly for D<sub>0</sub><sup>+</sup> vibtor levels. Since the barrier appears to originate predominantly from the asymmetry in the interaction with the π-electron charge density, it appears logical that moving the methyl group out of plane lowers this interaction somewhat.

V. CONCLUSIONS

In the present work, we have recorded ZEKE spectra via many of the S<sub>1</sub> levels below 350 cm<sup>-1</sup>. These consist of torsions, low-frequency vibrations, and vibtor levels. The activity we see, which confirms the assignments deduced in Ref. 22 from 2D-LIF spectra, allows the largest number of torsion and vibtor levels to be observed for a single molecule to date. This has allowed detailed information to be deduced on the torsional and vibration-torsional levels in the cation. This provides persuasive evidence that the torsional potential itself is altered by particular vibrational motions. In addition, a number of vibtor levels are likely involved in more localized interactions, and this will be explored further in future work with the Lawrance group at Flinders University and will form part of a future publication. We also have discussed the possibility that the spectroscopy may be indicating a definitive shift away from G<sub>6</sub> molecular symmetry and that the molecule is starting to behave more like a C<sub>6</sub> molecule. We have also reported values for five cationic vibrational wavenumbers.

Future ZEKE and 2D-LIF work will look at higher-lying vibrations, where we hope to gain insight into the explicit levels involved.
in the switch to dissipative IVR and, by comparison to our work on pFT, the differences that underpin the more-rapid IVR that occurs for mFT than pFT, as investigated by Timbers et al. This comparison should provide further illumination into the substituent positional effect.

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