

# Critical influences on the rate of intramolecular vibrational redistribution: A comparative study of toluene, toluene-d<sub>3</sub> and *p*-fluorotoluene.

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## Abstract

The intramolecular vibrational redistribution (IVR) dynamics following the excitation of a mode in the first electronically excited states of toluene, toluene-d<sub>3</sub> and *p*-fluorotoluene that has predominantly C-CH<sub>3</sub> stretching character and an internal energy of  $\sim 1200$  cm<sup>-1</sup> have been compared using picosecond time-resolved photoelectron imaging spectroscopy as a probe. Temporal changes in the intensities of spectral features in each molecule have enabled IVR lifetimes of 12, 15 and 50 ps, respectively, to be determined. Our measurements show that doorway states are critical in mediating the IVR dynamics in toluene and toluene-d<sub>3</sub>, and we deduce that these doorway states, which are assigned in the course of this work, are also instrumental in reducing the IVR lifetimes of these molecules relative to *p*-fluorotoluene.

## 1. Introduction

One of the goals in studies of intramolecular dynamics is to investigate the respective roles of (a) density of states and (b) the activation of particular degrees of freedom on the rate and mechanism of energy redistribution. For this reason, it is valuable to study closely-related systems that are prepared in comparable vibrational states, and/or with comparable excitation energy. Classic examples of this are the studies by Lehmann, Scoles and coworkers of molecules containing carbon triple bonds [1,2], and the studies of Parmenter and coworkers of small fluorobenzenes with and without attached methyl groups [3-5]. In recent work, we have studied intramolecular vibrational energy redistribution (IVR) in the first electronically excited states of toluene and *p*-fluorotoluene (pFT), and have published some selected results [6-8]. In the present work, we compare the dynamics that result subsequent to the preparation of one quantum in a near-isoenergetic ( $\sim 1200$  cm<sup>-1</sup>), predominantly C-CH<sub>3</sub> stretching mode, in the S<sub>1</sub> electronic states of toluene, toluene-d<sub>3</sub> and pFT.

An interesting feature of the chosen molecules is the degree of freedom associated with the methyl rotor. Evidence that torsional motion of the methyl group in substituted toluenes affects the IVR lifetime has been discussed in the literature by a number of authors [3,5-7,9-11]. A study by Perry et al. [12] has suggested that when excitation occurs in a vibrational mode associated with a center

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of flexibility (i.e. a bond about which internal rotation occurs), the IVR lifetime increases with torsional barrier height. For toluene derivatives, the C-CH<sub>3</sub> bond represents such a center, and a motivation for our comparative study is to see if this relationship holds true. In Table I it can be seen that the barrier heights ( $V_6$ ) in the first excited electronic state for toluene and toluene-d<sub>3</sub> are very similar, but the barrier height for pFT is around 35% higher due to the influence of the fluorine substituent [11,13-15]. Furthermore, it can be seen that the energies of the internal rotation levels are comparable for toluene and pFT but, as expected, are significantly lower for toluene-d<sub>3</sub>.

Moss and Parmenter have compared the IVR lifetimes following the preparation of a CF stretching vibration at  $\sim 1230\text{ cm}^{-1}$  in the  $S_1$  excited states of pFT and pFT-d<sub>3</sub> [5], and also of pFT and *m*-fluorotoluene (mFT) [4]. In their work, it was found that the IVR lifetime of pFT-d<sub>3</sub> was about a factor of two shorter than that of pFT. However, the IVR lifetime of mFT was a factor of twelve shorter than that of pFT. Moss and Parmenter rationalized this by postulating that the increased interaction between the methyl rotor and the aromatic ring for the *meta* structure, consistent with the fact that in  $S_1$  the torsional barrier in mFT is four times larger than that in pFT, serves to promote IVR. However, this is inconsistent with the relationship proposed by Perry et al. [12]. Borst and Pratt [11] have suggested that the IVR dynamics are not controlled directly by barrier height, but by the hyperconjugative interaction between the benzene ring and the methyl group, which in turn influences the barrier height. The role of hyperconjugation in IVR has been explored by a number of authors [16-19] and is expected to lead to an inhibition of IVR in pFT relative to toluene, assuming an equivalent density of states.

The mode of interest in the present work is  $\nu_{13}$  according to Varsanyi [20]; this same mode is labelled  $\nu_8$  in Ref. [21], and has recently been redesignated  $\mathcal{M}_6$  in Ref. [22] as part of a rationalization of the vibrations of monosubstituted benzenes. In the present work, we use one-photon excitation from the vibrational origin in  $S_0$  to prepare one quantum in this mode in  $S_1$  in each of toluene, toluene-d<sub>3</sub> and pFT. The resulting dynamics are then probed through time-resolved photoelectron spectroscopy. In common with some of our recent work, we use the slow electron velocity map imaging (SEVI) method [6,7], which provides superior resolution to that obtained in our earlier time-resolved studies [23,24]. The higher quality data allows quantum beats and exponential decays associated with coupled vibrational states in  $S_1$  to be characterized. Our results are also discussed in light of resonance-enhanced multiphoton ionization (REMPI) and zero-electron-kinetic-energy (ZEKE) photoelectron spectra which have been measured with nanosecond laser pulses [25-27].

## 2. Experiment

The picosecond laser system (Coherent), velocity-map imaging (VMI) photoelectron spectrometer, experimental procedures and data analysis techniques used in the picosecond experiments have been described elsewhere [6,7] and are not reproduced in detail here. Briefly, the two UV outputs from the laser system have pulse durations of 1 ps and bandwidths of  $\sim 13 \text{ cm}^{-1}$ . The co-propagating laser beams are focused into the VMI chamber using a 1.0 m focal length lens, resulting in typical pump and probe pulse intensities of  $5 \times 10^9 \text{ W/cm}^2$  and  $1 \times 10^{11} \text{ W/cm}^2$  respectively. The wavelength of the pump beam is tuned to be resonant with the absorption maximum at  $\sim 1192 \text{ cm}^{-1}$  (toluene),  $\sim 1225 \text{ cm}^{-1}$  (toluene- $d_3$ ) and  $\sim 1195 \text{ cm}^{-1}$  (pFT) above the  $S_1$  origin; the probe wavelength is chosen to access the cation internal states of interest. The samples (toluene, toluene- $d_3$  and pFT) are seeded in 3 bar He and expanded through a pulsed nozzle (General Valve) operating at a repetition rate of 40 Hz. The supersonic expansion is skimmed leading to a molecular beam with a rotational temperature of  $\sim 10 \text{ K}$ . Inside the spectrometer chamber, the laser beams are spatially and temporally overlapped with the pulsed molecular beam; the typical operating pressure is  $4 \times 10^{-8} \text{ mbar}$ . A delay stage enables the selection of chosen time intervals between the pump excitation pulse and the probe ionization pulse in order to monitor time-dependent behaviour. A three-element electrostatic lens focuses the electrons onto a vacuum imaging detector (VID, Photek) to create a two-dimensional image, which is captured using a CCD camera and recorded using IFS32 software (Photek). Using this technique we are able to record photoelectron images as a function of both pump-probe time delay and probe wavelength. These images are converted to give photoelectron spectra as discussed in earlier work [6]. Photoelectron angular distributions were also obtained from the images but they showed no significant changes with time delay and will not be discussed further. The imaging detector is also operated in ion detection mode to measure mass-resolved REMPI spectra via the  $S_1$  state of each molecule.

The nanosecond REMPI and ZEKE experiments, some of whose results are discussed in the present work, are fully described in Refs. [25,26].

### 3. Results and Discussion

#### 3.1 REMPI and photoelectron spectra

Figure 1 shows one-colour REMPI spectra measured via  $S_1$  in toluene, toluene- $d_3$  and pFT using picosecond laser pulses (bandwidth  $\sim 13 \text{ cm}^{-1}$ ). In each case the peaks are assigned according to Varsanyi notation [20]. The peak corresponding to excitation of the mode of interest ( $13^1$  in Varsanyi notation) appears at  $\sim 1192 \text{ cm}^{-1}$  for toluene, at  $\sim 1225 \text{ cm}^{-1}$  for toluene- $d_3$  and at  $\sim 1195 \text{ cm}^{-1}$  for pFT. The assignment of the peak in toluene- $d_3$  contradicts previous work in the literature [28,29] and has been established by reference to the time-resolved photoelectron spectra measured in the present work in combination with supporting quantum chemistry calculations. Figure 2 shows nanosecond REMPI spectra measured via  $S_1$  in the region of the transition of interest in toluene, toluene- $d_3$  and pFT. Also shown in each plot is the idealized

Gaussian spectral profile of the picosecond pump laser pulse, which indicates the spectral region that is accessed in the time-resolved experiments. In the case of toluene, the nanosecond REMPI spectrum reveals that three partially resolved peaks lie within the Gaussian profile; these are centered at 1184, 1192 and 1197  $\text{cm}^{-1}$  and will be denoted  $|1\rangle$ ,  $|2\rangle$  and  $|3\rangle$  respectively. For toluene- $\text{d}_3$  two close-lying peaks at 1222 and 1225  $\text{cm}^{-1}$  lie within the Gaussian profile, with a less intense peak at 1215  $\text{cm}^{-1}$  at the edge of the profile.<sup>3</sup> For pFT a peak at 1195  $\text{cm}^{-1}$  dominates the spectral region contained within the Gaussian profile, with additional minor peaks appearing at 1203 and 1208  $\text{cm}^{-1}$ .

Nanosecond ZEKE spectra have been recorded for toluene and pFT, and picosecond time-resolved photoelectron spectra have been recorded for all three molecules. Before discussing these results, we briefly outline the information they can provide. In the nanosecond experiments the resolution of the excitation step is  $\sim 0.1 \text{ cm}^{-1}$ , enabling a narrow portion of each absorption profile to be selectively excited. Although true eigenstate resolution (selection of all relevant quantum numbers) is not achieved, for the purposes of this discussion we can assume that a stationary “vibrational eigenstate” has been prepared. The wavefunction of the prepared state, which has no time-dependence, is given by:

$$\mathcal{Y} = |I\rangle = a_{Ib}|b\rangle + \sum_n a_{Id_n}|d_n\rangle, \quad (1)$$

where  $|I\rangle$  denotes the vibrational eigenstate prepared,  $|b\rangle$  denotes the zero-order bright state ( $13^1$  in this case) and  $\{d_n\}$  is the set of dark zero-order states to which the bright state is coupled. The coefficients  $a_{I\gamma}$  express the relative contributions of the bright and dark states to the prepared eigenstate. The photoelectron spectrum that results following the ionization of the prepared wavefunction represented by Eq. (1) will be the photoelectron spectrum characteristic of  $|I\rangle$  which will consist of a superposition of the photoelectron spectra that are characteristic of the contributing bright and dark states. If the bright state is not coupled to any dark states it will be equivalent to a vibrational eigenstate, and so the photoelectron spectrum will simply reflect the bright state in that case. For molecules such as toluene, photoelectron spectra generally show a strong  $\Delta v = 0$  peak, along with a series of weaker  $\Delta v \neq 0$  peaks. Thus, a photoelectron spectrum characteristic of the  $13^1$  bright state is expected to show a strong peak corresponding to the  $13^1$  cation state. If, however, the bright state is strongly coupled to a single dark state (Fermi resonance) then the characteristic photoelectron spectrum will contain two strong features corresponding to  $\Delta v = 0$  for each of the bright and dark states, along with weaker  $\Delta v \neq 0$  peaks for both states. If the bright state is coupled to many dark states, designated “bath states”, then a highly congested photoelectron spectrum is expected. In the case of toluene, the excitation of a narrow spectral region centered on each of the REMPI peaks denoted  $|1\rangle$ ,  $|2\rangle$  and  $|3\rangle$  in Fig. 2a

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<sup>3</sup>In the case of toluene- $\text{d}_3$  the intensities of the peaks at 1222 and 1225  $\text{cm}^{-1}$  are suppressed in the nanosecond REMPI spectrum by a factor of  $\sim 4$ , as determined from the ratio of the peak intensities in the nanosecond and picosecond REMPI spectra. This suppression could conceivably be attributed to mode-specific internal conversion or intersystem crossing. We can estimate a lower limit of 3 ns for such non-adiabatic dynamics from our picosecond studies of all three molecules and therefore conclude that this relatively slow process can be neglected in the present IVR studies.

gives rise to the ZEKE spectra shown in Fig. 3a-c, respectively. Clear congestion can be seen in all three cases, particularly for  $|1\rangle$ ; the assignment of the peaks that appear above the congestion is discussed in Ref [25]. In Fig. 3d the ZEKE spectrum measured following excitation of a narrow portion of the absorption profile in pFT is shown. The congestion observed in this ZEKE spectrum is more prominent than that seen in previous work [27,30], as a consequence of the adoption of different background subtraction procedures, but significant structure still remains. For both toluene and pFT, nanosecond ZEKE spectra therefore provide evidence of IVR following the excitation of the bright state, with the IVR being apparently more significant in the case of toluene.

In the picosecond time-resolved experiments the  $\sim 13 \text{ cm}^{-1}$  bandwidth of the excitation pulse coherently excites vibrational features lying within a relatively broad spectral region in  $S_1$ ; see the Gaussian profiles superimposed on the REMPI spectra in Fig. 2. A time-evolving wavepacket (superposition of eigenstates) is prepared, which can be represented by:

$$\psi(t) = \sum_I c_I |I\rangle \exp\left(\frac{iE_I t}{\hbar}\right) = \sum_I c_I a_{Ib} |b\rangle \exp\left(\frac{iE_I t}{\hbar}\right) + \sum_{I,n} c_I a_{Id_n} |d_n\rangle \exp\left(\frac{iE_I t}{\hbar}\right), \quad (2)$$

where the  $c_I$  coefficients weight the contribution of each eigenstate,  $|I\rangle$ , in the prepared superposition. In the limit where the bandwidth encompasses all dark states to which a single bright state is coupled, the wavepacket at zero time will resemble the zero-order bright state:

$$\psi(0) = \hat{A} \sum_I c_I |I\rangle = |b\rangle, \quad (3)$$

whereas at later times it will resemble multiple zero-order states. The photoelectron spectrum that results following the ionization of the wavepacket given in Eq. (2) will be time-dependent. At time zero it is expected to be dominated by a  $\Delta v = 0$  peak characteristic of the bright state, and its structure is then expected to change with pump-probe time delay. If the bright state is coupled to many dark states then its signature will become progressively weaker at long time delays. If it is strongly coupled to a limited number of dark states then oscillations in the time-dependent intensity (i.e., quantum beats) are expected, as observed in our earlier work [6-8].

Picosecond time-resolved photoelectron spectra, measured at selected time delays, are compared in Figs. 4 and 5 for toluene and pFT, and in Fig. 6 for toluene and toluene- $d_3$ . These spectra were measured using the SEVI technique described in Ref. [6], which enables us to optimize the resolution in the photoelectron spectra. In Fig. 4a it can be seen that the toluene photoelectron spectrum shows distinct changes in structure over only a few picoseconds, with the intensity of the  $13^1$  cation peak at  $1234 \text{ cm}^{-1}$  gradually decreasing from 0 to 3 ps and then increasing from 3 to 5 ps. By contrast, the pFT photoelectron spectra shown in Fig. 4b remain very similar over the same range of time delays. In Fig. 5 the photoelectron spectra measured at 0 ps and at 500 ps are compared for toluene and pFT. Over this timescale the intensity in the sharp peaks is almost entirely lost for toluene, leading to a relatively featureless spectrum at 500 ps. This indicates that almost all of the population has been transferred from the bright state to a multitude (bath) of

weakly coupled dark states. In contrast, the sharp peaks in the pFT photoelectron spectrum only decrease in intensity by approximately a factor of two, and the broad continuum below the sharp peaks shows an increase in intensity, which indicates that only part of the bright state population is redistributed (see Section 3.4). In Fig. 6 the early time behaviour of the toluene and toluene- $d_3$  photoelectron spectra are compared. The photoelectron spectrum measured at time zero for toluene- $d_3$  is strikingly similar to that recorded for toluene. Spectra at increasing time delays for both molecules show significant changes in structure, with the  $13^1$  cation peaks initially decreasing in intensity and then reappearing again at 6 ps for toluene and at 12 ps for toluene- $d_3$ . As observed in our earlier work [7], this initial oscillation in intensity is characteristic of the influence of strongly-coupled dark states [31] in the IVR dynamics. These states, known as doorway states, mediate the coupling between the prepared bright state and a weakly-coupled bath of dark states and have maximum population at intermediate stages of the IVR process. To summarize, these preliminary observations suggest that in the case of toluene and toluene- $d_3$  the IVR dynamics are dominated by a limited number of doorway states. In the case of pFT there is no evidence for doorway states, and the weakly coupled states only remove part of the bright state population. Thus it appears that the relatively well-structured ZEKE spectrum observed for pFT results from this substantial remaining bright state population. In the following sections we quantify and discuss the IVR dynamics further, including the likely coupling mechanisms giving rise to the observed behaviour. We focus our discussion on anharmonic and torsion-vibration coupling which are likely to be the dominant mechanisms at the temperatures and  $S_1$  internal energies studied. We note that we see no evidence for vibronic coupling (loss of population from  $S_1$ )<sup>3</sup> on the timescale of our experiments.

### 3.2 Time profiles

The time-dependent behaviour can be characterized by plotting the integrals of peaks in the photoelectron spectra as a function of time delay. These peak integrals are determined by using the trapezium rule across cation internal energy ranges that are specified in Table II. Examples of these time profiles are shown in Figs. 7 to 10; the solid lines represent fits that are described below. In Fig. 7 the peak integrals correspond to regions of photoelectron intensity encompassing the  $13^1$  ion state in toluene, toluene- $d_3$  and pFT. This ion state reflects the behaviour of the initially prepared bright state in  $S_1$  because of the  $\Delta v = 0$  propensity on ionization. In the present work, the resolution is not sufficient to determine the intensity due to a single ion vibrational state uniquely, and the spectra show an increasing contribution from the broad continuum underneath the sharp peaks as the time delay increases. As a consequence, we refrain from commenting on the absolute intensity values that are determined from the time profiles of the peak integrals. Instead, we use the time profiles to determine IVR timescales (lifetimes and oscillation periods), and we obtain quantitative information on individual ion peak intensities directly from the picosecond photoelectron spectra. First we discuss each of Figs. 7-10 in turn.

In Fig. 7 it can be seen that the photoelectron intensity corresponding to the  $13^1$  ion state decays over a 200 ps timescale for all three molecules, signifying the transfer of population away from the bright state and into the bath states. However, differences in the time profiles for the three molecules are clear, with oscillatory structure observed at early time delays for toluene and toluene- $d_3$  but not for pFT. As discussed above, these oscillations reflect the transfer of population between the bright state and one or more doorway states.

In Fig. 8 we compare the toluene time profiles for peak integrals corresponding to three distinct regions of photoelectron intensity, one of which ( $1200\text{-}1260\text{ cm}^{-1}$ ) reflects the behaviour of the bright state and the other two of which ( $1260\text{-}1320\text{ cm}^{-1}$  and  $1400\text{-}1530\text{ cm}^{-1}$ ) reflect the behaviour of two doorway states. Strong oscillations are observed in all three cases, with the photoelectron intensity maximized at 0 ps for the bright state region and minimized at 0 ps for the doorway state regions. It is clear that the oscillation patterns are too complicated to describe with a single cosine function. In Fig. 9 we compare the early time behavior of the toluene- $d_3$  peak integrals that correspond to regions of photoelectron intensity reflecting bright ( $1160\text{-}1350\text{ cm}^{-1}$ ) and doorway ( $1350\text{-}1450\text{ cm}^{-1}$ ) state behaviour. As noted in Section 3.1, the oscillation period has roughly doubled on moving from toluene to toluene- $d_3$ . The plot in Fig. 9b is approximately a mirror image of the plot shown in Fig. 9a, providing a particularly clear signature of the transfer of population between the bright and dark states. In Fig. 10 we compare the early time behaviour of peak integrals representing bright ( $1180\text{-}1275\text{ cm}^{-1}$ ) and dark ( $1370\text{-}1550\text{ cm}^{-1}$ ) state behaviour for pFT. In this instance, the time profiles are devoid of any strong or regular oscillatory components, and reflect the gradually increasing population of bath states with time that is characteristic of statistical IVR.

Oscillation periods and decay times can be extracted from the data shown in Figs. 7-10 by fitting the time-dependent peak intensities to the empirical equation

$$I(t) = A + B \exp\left(\frac{-t}{\tau_1}\right) + \exp\left(\frac{-t}{\tau_2}\right) \left[ C \cos\left(\frac{2\pi t}{\tau_C}\right) + D \cos\left(\frac{2\pi t}{\tau_D}\right) \right]. \quad (4)$$

This empirical equation is based on the physical situation in which a bright state is strongly coupled to two doorway states and weakly coupled to a bath of other dark states; it contains the same ingredients used in our earlier work [7] and yields the fits that are plotted as solid lines in Figs. 7-10. Relating Eq. (4) to our earlier work reveals that the coefficients  $A$ ,  $B$ ,  $C$  and  $D$  are collections of the coupling coefficients,  $a_{I_j}$ , which were introduced in Eq. (1). Because the cosine terms in Eq. 4 only appear when doorway states are involved in the dynamics,  $C$  and  $D$  can be set to zero in the case of pFT. Table II lists the values of the parameters in Eq. (4) that are obtained from the fits of the time profiles of selected regions of the photoelectron spectra for toluene, toluene- $d_3$  and pFT. The values obtained for the lifetimes  $\tau_1$  and  $\tau_2$  are discussed in Section 3.3 and the oscillation periods  $\tau_C$  and  $\tau_D$  are discussed in Section 3.5.

### 3.3 IVR lifetimes

The exponential decay time constants in Eq. (4) provide information on the overall IVR lifetime. When oscillations are observed in the time profiles, as occurs for toluene and toluene-d<sub>3</sub>, two lifetimes are deduced [see Eq. (4)] with the  $\tau_1$  value representing the overall exponential lifetime and the  $\tau_2$  value indicating the decay time of the beating behaviour; in principle these two values should be equal in most circumstances. Values for the IVR lifetimes have been determined from the average of the  $\tau_1$  and  $\tau_2$  values given in Table II for each molecule, where available. However, the poorly determined  $\tau_1$  value for the toluene-d<sub>3</sub> doorway state region has been excluded from this average because the uncertainty of  $\pm 15$  ps is much larger than the uncertainties in the other  $\tau_1$  and  $\tau_2$  values determined for toluene-d<sub>3</sub>. This procedure leads to values of the IVR lifetime,  $\tau_{IVR}$ , of  $12 \pm 7$  ps,  $15 \pm 4$  ps and  $50 \pm 6$  ps for toluene, toluene-d<sub>3</sub> and pFT, respectively (see Table II). In what follows we discuss these values by reference to the density of states in each molecule, and to the barrier to internal rotation (see Table I). In particular, we seek to explain (i) why the  $\tau_{IVR}$  values are so similar for toluene and toluene-d<sub>3</sub> and (ii) why the  $\tau_{IVR}$  value for toluene (and hence for toluene-d<sub>3</sub>) is so much shorter than that for pFT.

The overall density of states at the S<sub>1</sub> bright state energy for the three molecules has been estimated with a simple counting algorithm using the scaled harmonic vibrational frequencies given in Ref. [26], and the calculated torsional energies listed in Table I. The vibrational frequencies corresponding to the same modes in toluene and toluene-d<sub>3</sub> are very similar in most cases (Table III), however, the torsional energies are strongly affected by deuteration (Table I). As a consequence, the average density of states in the region of the bright state energy is approximately a factor of two greater for toluene-d<sub>3</sub>. Although toluene and pFT have the same number of modes with frequencies below 1000 cm<sup>-1</sup>, nine of those modes have frequencies that are more than 7% lower in pFT than in toluene. As a consequence, despite the similarity of the torsional energies, the average density of states in pFT in the region of the bright state is approximately a factor of two higher. Thus, pFT and toluene-d<sub>3</sub> have similar average densities of states at the bright state energy, whereas toluene has a significantly lower density of states. An increased density of states at a given excitation energy might be expected to lead to a shorter IVR lifetime. However, in the present work, similar  $\tau_{IVR}$  values have been determined for toluene and toluene-d<sub>3</sub>, with a much longer  $\tau_{IVR}$  value determined for pFT, indicating poor correlation with the density of states. The comparable IVR lifetimes for toluene and toluene-d<sub>3</sub> can be rationalized by noting that the additional states that contribute to the density of states for toluene-d<sub>3</sub> at a given excitation energy are caused by the availability of lower lying torsionally excited levels in the deuterated molecule, which suggests that these torsionally excited levels do not play a key role in the dynamics. This in turn would imply that in the case studied here torsion-vibration interactions do not play a major role in the IVR dynamics in toluene or toluene-d<sub>3</sub>. However, we cannot find a way to rationalize the relative IVR lifetimes in toluene and pFT on the basis of the densities of states and conclude that the total average density of states is not a good predictor of the relative IVR lifetimes at these excitation energies.



A substantial barrier to internal rotation is caused by an interaction of the ring with the methyl group, which could be expected either to (a) facilitate IVR, as concluded by Moss and Parmenter in their comparison of pFT and mFT [4], or (b) hinder IVR as concluded by Perry and coworkers [12]. In the case of toluene and toluene- $d_3$  the barriers are very similar, consistent with the observation of a similar IVR lifetime in the two molecules. Although our observed relative IVR lifetimes for toluene and pFT lend support to the Perry and coworkers hypothesis (see the barrier heights listed in Table I) and are inconsistent with that of Moss and Parmenter, this assumes that the same IVR mechanism operates in each molecule. The Borst and Pratt hyperconjugation hypothesis [11], in which the motion of the methyl group modulates the structure of the ring thus disrupting its conjugation, would also lead to a longer lifetime for pFT relative to toluene because the fluorine atom acts to stabilize the hyperconjugated structure.

In general it is expected that IVR lifetimes decrease with excitation energy. In the case of pFT, reference to our earlier work [7] shows that this is not always observed. In that work an IVR lifetime of only 17 ps was measured at an excitation energy of 845  $\text{cm}^{-1}$ , compared with the lifetime of 50 ps measured at an excitation energy of 1195  $\text{cm}^{-1}$  in the present work. In Ref. [7] doorway states were observed to mediate the IVR dynamics at 845  $\text{cm}^{-1}$ ; their presence may therefore be invoked to explain this observation. In corroboration of this, we have found in the present work that shorter IVR lifetimes are determined for the molecules (toluene and toluene- $d_3$ ) in which doorway states are observed to operate than are determined for pFT in which no doorway states contribute. Thus, in both the present work and the work presented in Ref. [7], the availability of doorway states appears to serve to reduce the IVR lifetime. Our observations to date are therefore consistent with the idea that the presence of doorway states is a critical determinant of IVR lifetimes. The availability or otherwise of such doorway states is a coincidental consequence of the presence of dark states that (i) have an  $S_1$  internal energy approximately equal to that of the bright state, (ii) have the same overall symmetry as the bright state, and (iii) are strongly coupled to the bright state. The presence of doorway states cannot be predicted on the basis of arguments concerning the total density of states, the torsional barrier height, or hyperconjugative interactions.

### **3.4 Comparison of IVR dynamics in toluene and *p*-fluorotoluene**

As discussed in our earlier work on toluene and pFT [6,7], a molecular beam temperature of  $\sim 10$  K is used in the picosecond time-resolved experiments. Owing to the different nuclear spin symmetries of the torsional levels [13], the bright state prepared at time zero will contain roughly equal populations of two incoherently prepared torsional components, characterized by values of the internal rotation quantum number of  $m = 0$  and  $m = 1$ , and there will be  $< 5\%$  population in levels with  $m > 1$ . For each molecule, the various torsional components may exhibit different dynamics if torsion-vibration coupling plays a significant role in the IVR process; this is because symmetry selection rules dictate that different dark vibrational states will couple to each of the

torsional components of the bright state [32]. In contrast, in anharmonic coupling the torsional quantum number is conserved and the same set of vibrational dark states can couple to all torsional components of the bright state.

As discussed in Section 3.1, the time-resolved photoelectron spectra shown in Fig. 5 show that almost all of the intensity of the sharp peaks observed at 0 ps is lost at 500 ps for toluene, whereas only half of the intensity is lost for pFT at 500 ps. From this we conclude that half of the bright state population is “trapped” in the case of pFT, which is consistent with an IVR pathway existing for one of the initially prepared torsional components but not for the other. Such a situation can only occur if torsion-vibration coupling mediates the IVR process. In the case of toluene, the substantial decrease in bright state intensity indicates that both torsional components undergo IVR. These interpretations are consistent with the ZEKE spectra shown in Fig. 3. For pFT, the strong  $13^1$  ZEKE peak at  $1230\text{ cm}^{-1}$  together with the congestion observed at higher ion internal energies (see Fig. 3d) suggests that only part of the bright state population undergoes IVR. In the case of toluene, the high degree of congestion visible in the ZEKE spectra in Figs. 3a-c supports the conclusion that both prepared torsional components undergo IVR.

### 3.5 Comparison of IVR dynamics in toluene and toluene- $d_3$

As discussed in Sections 3.1 and 3.2, the time evolution of the wavepackets in toluene and toluene- $d_3$  is analogous to some previous observations we have made [7], and is characteristic of IVR that is facilitated by doorway states. The early time dynamics is dominated by the interaction of the bright state with these doorway states and is relatively unaffected by other interactions which will increasingly contribute at later times. In the present work, the doorway states for toluene give rise to oscillations in the time profiles with periods of  $\tau_C = 6.5\text{ ps}$  and  $\tau_D = 4.9\text{ ps}$  which are consistent for all the ion energy ranges studied (see Table II). These oscillation periods correlate with eigenstate energy separations of  $\Delta E_C = \hbar / \tau_C \equiv 5.1\text{ cm}^{-1}$  and  $\Delta E_D = \hbar / \tau_D \equiv 6.8\text{ cm}^{-1}$ , which are approximately consistent with the separations  $\Delta E_{23} = 5\text{ cm}^{-1}$  and  $\Delta E_{12} = 8\text{ cm}^{-1}$  between the three peaks ( $|1\rangle$  at  $1184\text{ cm}^{-1}$ ,  $|2\rangle$  at  $1192\text{ cm}^{-1}$  and  $|3\rangle$  at  $1197\text{ cm}^{-1}$ ) in the nanosecond REMPI spectrum (see Fig. 2a). This suggests that the  $S_1$  vibrational eigenstates responsible for the three REMPI peaks contain contributions from the bright state and the coupled doorway states. Therefore we conclude that two doorway states dominate in toluene.

For toluene- $d_3$ , oscillations with a period of  $\tau_C = 10.6\text{ ps}$  are observed in the time profiles which are consistent for all the ion energy ranges studied (see Table II). This period corresponds to an energy separation of  $\Delta E_C = \hbar / \tau_C \equiv 3.1\text{ cm}^{-1}$ , which is in excellent agreement with the spacing between the peaks at  $1222$  and  $1225\text{ cm}^{-1}$  present in the nanosecond REMPI spectrum in Fig. 2b. The close-lying peak at  $1215\text{ cm}^{-1}$  does not appear to be involved in the IVR dynamics, as evidenced by the absence of oscillations with periods of either 5 or 3 ps that would be consistent with peak separations of 7 and  $10\text{ cm}^{-1}$  between the  $1215\text{ cm}^{-1}$  peak and the peaks at  $1222$  and

1225  $\text{cm}^{-1}$ , respectively. The deduced values of 15.4 ps, 20.1 ps and 26.1 ps for  $\tau_D$  in the three ion energy ranges studied (Table II) are not consistent within error bars. Although this might suggest that the bright state couples to more than one doorway state, only one ion peak characteristic of a doorway state appears in the time-resolved photoelectron spectra for toluene- $\text{d}_3$  (see below), indicating that a single doorway state is involved in the dynamics. The variation in the deduced values for  $\tau_D$  can be explained, however, if the four observed oscillation periods ( $\tau_C$  plus the three values found for  $\tau_D$ ) are caused by energy differences between four or more eigenstates,[33] each containing contributions from the bright state and a single doorway state, as well as from multiple bath states.

In order to provide assignments for the doorway states in toluene and toluene- $\text{d}_3$ , we consider the cation internal energies of peaks observed in the photoelectron spectra at times when the contribution of the doorway states is maximized;  $t = 3$  ps for toluene and  $t = 6$  ps for toluene- $\text{d}_3$ . In the case of toluene we find that two characteristic photoelectron peaks with cation internal energies of 1290 and 1460  $\text{cm}^{-1}$  appear at 3 ps (see Fig. 6a) and these can be attributed to the  $\Delta v = 0$  ionization of two doorway states; we label these states Doorway A and Doorway B. These peaks can also be seen in the toluene ZEKE spectrum shown in Fig. 3b. In the case of toluene- $\text{d}_3$ , a cation peak characteristic of a doorway state appears at an internal energy of 1391  $\text{cm}^{-1}$ , as observed in the 6 ps spectrum in Fig. 6b. We label the equivalent  $S_1$  state Doorway C.

With this information we can begin a search for candidates for the doorway states that (i) have  $S_1$  energies close to that for the  $S_1$   $13^1$  bright state, (ii) have cation internal energies consistent with the experimental observations, and (iii) fulfill the selection rules allowing coupling to one or more of the torsional components of the  $13^1$  bright state. The procedure used for the doorway state search is outlined in Ref. [7] and has been updated to make use of the selection rule for torsion-vibrational coupling,  $\Delta m = \pm 3n$  (where  $n = 1, 2, \dots$ ), discussed by Gascooke and Lawrance [32], with the caveat that the total symmetry of the bright and doorway states in the  $G_{12}$  point group must be the same. In order to perform such a search it is necessary to have a consistent set of vibrational frequencies for  $S_1$  and the ion. For this purpose the calculated scaled harmonic values listed in Table III were adopted; these values approximate the uncoupled anharmonic frequencies. The TD-B3LYP/aVTZ method was used for the  $S_1$  calculation, with UB3LYP/aVTZ used for the cation; in both cases a scaling factor of 0.97 was applied. The use of the scaled harmonic values in  $S_1$  is consistent with a search for zero-order states that can couple to the bright state [7]. The energies of the torsional levels,  $E_F$ , were taken from the calculated values listed in Table I. Because of incomplete available information, the energies of the torsional levels in the ion were assumed to be the same as those in  $S_1$ ; for known cases this is a reasonable approximation [34]. Torsion-vibrational states were accepted as plausible doorway candidates if their  $S_1$  energy lay within  $\pm 40$   $\text{cm}^{-1}$  of the relevant torsional component of the  $13^1$  bright state, and if their cation energy lay within  $\pm 25$   $\text{cm}^{-1}$  of the energy of the photoelectron peaks deemed to be characteristic of the ionization of a doorway state (see above). The wider energy window in  $S_1$  reflects the fact

that the calculated frequencies are less accurate for excited electronic states than for ion ground states. The resulting candidates are listed in Table IV for toluene and in Table V for toluene-d<sub>3</sub>. These Tables list the doorway state candidates first according to whether they are anharmonic or torsion-vibration candidates, and then in order of increasing  $\Delta N$ , which represents the difference in the number of vibrational quanta between the bright state and the candidate; the coupling strength is expected to depend inversely on  $\Delta N$ . The value assigned for  $\Delta N$  is further increased if a change in torsional state is also required, by assigning  $\Delta N = 1$  for  $\Delta m = \pm 3$  or  $\pm 6$ ,  $\Delta N = 2$  for  $\Delta m = \pm 9$  or  $\pm 12$ , .... In Tables IV and V we only list candidates with a total  $\Delta N \leq 4$ .

Before discussing the candidates listed in Tables IV and V we consider the torsional level dependence of the observed dynamics in toluene and toluene-d<sub>3</sub>. As discussed in Section 3.4, at  $\sim 10$  K the prepared bright state in toluene contains two torsional components ( $0a_1'$  and  $1e''$ ) with almost equal population. In the case of toluene-d<sub>3</sub>, the lower energies of the torsional levels mean that prior to excitation significant population ( $\sim 12\%$ ) resides in the  $2e'$  (*ortho*) state, in addition to  $\sim 47\%$  in the  $0a_1'$  (*para*) state and  $38\%$  in the  $1e''$  (*ortho*) state. Therefore in this case IVR channels involving three torsional levels of the bright state need to be considered. In principle, IVR dynamics can be associated with any or all of the torsional components prepared in each molecule. In the data shown in Fig. 6 the intensity of the  $13^1$  ion peak, which directly reflects the  $S_1$  bright state population, decreases by at least 75% between 0 and 3 ps for toluene and between 0 and 6 ps for toluene-d<sub>3</sub>, where this change in intensity corresponds to the transfer of vibrational population to the doorway states. Our results therefore suggest that more than one torsional component of the bright state must be coupled to doorway states in toluene and in toluene-d<sub>3</sub>. This in turn implies that either the same anharmonic coupling route exists for each component, or coincidental torsion-vibration coupling routes exist for each component. This observation will be used when discussing the plausibility of the candidates listed.

#### (a) Doorway A (toluene)

Possible candidates for Doorway A, which has an ion energy of  $1290 \text{ cm}^{-1}$ , are given in the upper part of Table IV. It can be seen that there are four states that (i) satisfy the selection rules for coupling to one or both torsional components of the bright state, (ii) are energetically plausible and (iii) give rise to  $\Delta N \leq 4$ . Only one of these candidates,  $|1^1 16b^1 10b^1\rangle$ , satisfies the selection rules for coupling to both  $|13^1, 0a_1'\rangle$  and  $|13^1, 1e''\rangle$  through anharmonicity. Two of the other states ( $|3^1, 3a_1''\rangle$  and  $|6a^1, 12a_1'\rangle$ ) satisfy the selection rules for coupling to the  $m = 0$  component only, through a torsion-vibration interaction. The final state, ( $|4^1 6b^1, 7e''\rangle$ ) satisfies the selection rules for coupling to the  $m = 1$  component only, again through a torsion-vibration interaction. Because an IVR route must be available to both torsional components (see discussion above) the  $|1^1 16b^1 10b^1\rangle$  state is superficially the most likely, but we also allow for the possibility that a combination of two torsion-vibration states, each giving an IVR route for one of the

torsional components of the bright state, could give rise to doorway A. The plausibility of the candidate states can be tested by using the experimentally determined ion vibrational frequencies presented in Ref. [26]. These frequencies, when combined with the calculated torsional energies, enable the prediction of ion peak positions of 1295, 1258 and 1305  $\text{cm}^{-1}$  for the  $|1^{11}6b^{11}0b^{11}\rangle$ ,  $|6a^1, 12a_1'\rangle$  and  $|4^{16}b^1, 7e''\rangle$  candidates, respectively. The observed ion peak at 1290  $\text{cm}^{-1}$  lies significantly closer to the predicted value for  $|1^{11}6b^{11}0b^{11}\rangle$  than the values for  $|6a^1, 12a_1'\rangle$  and  $|4^{16}b^1, 7e''\rangle$ , and therefore the latter states can be dismissed on energetic grounds. An experimentally based ion energy for the final possible candidate,  $|3^1, 3a_1''\rangle$ , is not available, but this state could only contribute in coincidental combination with the  $|4^{16}b^1, 7e''\rangle$  state, which has been discounted. Therefore we conclude that the  $|1^{11}6b^{11}0b^{11}\rangle$  state is the most likely candidate for Doorway A.

*(b) Doorway B (toluene)*

There are seven candidates listed in the lower part of Table IV that could give rise to the ion peak near 1460  $\text{cm}^{-1}$ . Three of these candidates ( $|11^2\rangle$ ,  $|6a^{14}16b^1\rangle$  and  $|17a^110b^115^1\rangle$ ) satisfy the selection rules for coupling to both torsional components of the bright state through anharmonicity. Two of the remaining states ( $|6a^110a^1, 6a_2'\rangle$ , and  $|17b^115^1, 6a_2'\rangle$ ) satisfy the selection rules for coupling to  $m = 0$  only, through a torsion-vibration interaction. The  $|17b^1, 10e'\rangle$  state satisfies the selection rules for coupling to  $m = 1$  only, through a torsion-vibration interaction. The two components of the final state,  $|6a^117b^1, 3a_2''\rangle$  and  $|6a^117b^1, 2e'\rangle$ , respectively satisfy the selection rules for coupling to the  $m = 0$  and  $m = 1$  components of the bright state, but because they are separated by 25  $\text{cm}^{-1}$  they cannot simultaneously lie within the laser bandwidth on excitation.

Based on predicted coupling strength alone the  $|11^2\rangle$  state (for which  $\Delta N = 3$ ) is the most likely candidate, and its calculated ion frequency is very close to the position of the observed ion peak at 1460  $\text{cm}^{-1}$ . However, the calculated frequency of  $|11^2\rangle$  in  $S_1$  is 30  $\text{cm}^{-1}$  away from the experimental energy of the bright state. Because experimental ion frequencies are not available for modes  $\nu_{11}$ ,  $\nu_{10a}$  and  $\nu_{17b}$ , the plausibility of most of these doorway state candidates cannot be further assessed. The exceptions are  $|6a^{14}16b^1\rangle$  and  $|17a^110b^115^1\rangle$ . The former has an energy in the ion which, using experimentally derived vibrational frequencies [26], is predicted to be 21  $\text{cm}^{-1}$  lower than the observed peak at 1460  $\text{cm}^{-1}$ , whilst the latter has an energy in  $S_1$  which is predicted on the basis of experimentally derived vibrational frequencies [21,26] to be 25  $\text{cm}^{-1}$  lower than that of the bright state. These relatively large discrepancies do not lend support to either of these candidates.

Instead, we consider the hypothesis that Doorway B is in fact related to Doorway A. Such a relationship might be expected if Doorway A and Doorway B are part of a Fermi resonance. In the  $S_1$  electronic state the  $|1^1\rangle$  state that contributes to Doorway A is known to be in Fermi resonance with  $|4^{16}b^1\rangle$  [21]. Therefore it is expected that any state of the form  $|1^1Y^1\rangle$  will be

in Fermi resonance with  $|4^1 16b^1 Y^1\rangle$ . In addition, the state  $|16b^1 10b^1\rangle$  is known to be strongly coupled to  $|6a^1\rangle$  (and weakly coupled to  $|16a^2\rangle$ ) [6,26,32]; therefore any state of the form  $|X^1 16b^1 10b^1\rangle$  will be in Fermi resonance with  $|X^1 6a^1\rangle$ . Based on this, we could expect the  $|1^1 16b^1 10b^1\rangle$  state to be strongly coupled to the states  $|1^1 6a^1\rangle$ ,  $|4^1 16b^1 6a^1\rangle$  and  $|4^1 16b^2 10b^1\rangle$ , forming states that can couple to both torsional components of the bright state. Because the two Fermi resonances have been well-characterized, we know the energies of the relevant ion states; these are listed in Table VI. Two of these zero order states have experimental ion energies that lie within  $11\text{ cm}^{-1}$  of a doorway state; these are  $|1^1 16b^1 10b^1\rangle$ , already found as the most plausible candidate for Doorway A, and  $|4^1 16b^2 10b^1\rangle$  which has an ion energy of  $1471\text{ cm}^{-1}$ , close to that required for Doorway B. It is interesting to note that the state  $|1^1 6a^1\rangle$  only requires  $\Delta N = 3$  and might be expected to be a bright state. However, if this state were significantly populated (either on excitation or through IVR) then an ion peak at  $1263\text{ cm}^{-1}$  would be observed in between the ion peaks at  $1234\text{ cm}^{-1}$  and  $1290\text{ cm}^{-1}$  which correspond to the bright state and Doorway A respectively. No such peak is seen in the time-resolved spectra in Fig. 4(a). In conclusion, we assign Doorway B to  $|4^1 16b^2 10b^1\rangle$  based on the evidence presented, although we note that five vibrational quanta have to change in order for it to couple to the bright state. Figure 11 illustrates the deduced tier structure for the coupled vibrational states and indicates how the progression of the IVR process is reflected in the time-resolved photoelectron spectra.

(c) Doorway C (toluene- $d_3$ )

In the case of toluene- $d_3$  (see Table V) there are eight plausible doorway state candidates. Of these, the  $|(\delta_{as}^-)^1 4^1\rangle$  and  $|10b^1 6b^1 10a^1\rangle$  states satisfy the selection rules for anharmonic coupling to the bright state and therefore provide an IVR route for all three torsional components of the bright state. In addition, two torsional components of the  $|16a^1 18b^1\rangle$  state provide an IVR route for each of the  $m = 0$  and  $m = 1$  bright state components through a torsion-vibration coupling mechanism. These are  $|16a^1 18b^1, 3a_2''\rangle$ , which is coupled through  $\Delta m = \pm 3$  to  $|13^1, 0a_1'\rangle$ , and  $|16a^1 18b^1, 2e'\rangle$  which is coupled through  $\Delta m = \pm 3$  to  $|13^1, 1e''\rangle$ . The separation of  $11\text{ cm}^{-1}$  between these two components means that both can lie within the bandwidth on excitation, lending plausibility to this assignment. Although the  $|16a^1(\delta_{as}^+)^1 3a_1''\rangle$  and  $|16a^1(\delta_{as}^+)^1 2e'\rangle$  states also provide a route for each of the  $m = 0$  and  $m = 1$  bright state components, in this case their separation ( $23\text{ cm}^{-1}$ ) means that they cannot both lie within the bandwidth. We further note that combination bands involving the Fermi resonance between  $|1^1\rangle$  and  $|4^1 16b^1\rangle$ , which were identified as doorway states for toluene, are out of range of the bright state in the case of toluene- $d_3$ .

The  $|(\delta_{as}^-)^1 4^1\rangle$  state gives rise to the lowest  $\Delta N$  and seems on this basis to be the most likely candidate. The experimental ion energy of  $528\text{ cm}^{-1}$  for  $4^1$  given in Ref [26] is  $8\text{ cm}^{-1}$  higher than the calculated value, which brings the estimated ion energy for  $|(\delta_{as}^-)^1 4^1\rangle$  to within  $12\text{ cm}^{-1}$  of the observed ion peak energy. For the  $|10b^1 6b^1 10a^1\rangle$  state, an experimental ion energy value of  $477$

cm<sup>-1</sup> for 6b<sup>1</sup> [26] brings the estimated ion energy to within 8 cm<sup>-1</sup> of the observed ion peak energy. Either of these states is therefore possible and the anharmonic mechanism would be consistent with the comparable IVR rates in toluene and toluene-d<sub>3</sub> (see Section 3.3). However, for toluene-d<sub>3</sub> the torsion-vibration mechanism involving  $|16a^1 18b^1, 3a_2''\rangle$  and  $|16a^1 18b^1, 2e'\rangle$  cannot be dismissed. The calculated ion energies of 1400 and 1411 cm<sup>-1</sup> for these two components are within 9 and 20 cm<sup>-1</sup>, respectively, of the observed peak in the photoelectron spectrum. The experimental ion energy of 334 cm<sup>-1</sup> for 16a<sup>1</sup> [26] is 7 cm<sup>-1</sup> lower than the calculated value, which would bring the estimated ion energy closer to that of the observed peak. Therefore we conclude that Doorway C could be assigned to  $|(\delta_{as}^-)^{14^1}\rangle$ ,  $|10b^1 6b^1 10a^1\rangle$ , or the combination of  $|16a^1 18b^1, 3a_2''\rangle$  and  $|16a^1 18b^1, 2e'\rangle$ .

#### (d) Summary

We thus deduce that two doorway states dominate the IVR dynamics in toluene, and that these can be assigned to  $|1^1 16b^1 10b^1\rangle$  (Doorway A) and  $|4^1 16b^2 10b^1\rangle$  (Doorway B). These states satisfy the selection rule for anharmonic coupling to both  $|13^1, 0a_1'\rangle$  and  $|13^1, 1e''\rangle$ . The interaction of the bright state with the two doorway states gives rise to the two oscillation periods  $\tau_c = 6.5$  ps and  $\tau_D = 4.9$  ps observed in the time profiles shown in Fig. 8, and to the three peaks observed in the REMPI spectrum in Fig. 2a. Ionization of Doorway A and Doorway B gives rise to the peaks at 1290 and 1460 cm<sup>-1</sup> respectively, as seen in the photoelectron spectrum measured at 3 ps (see Fig. 6a). We thus deduce that the early time dynamics is dominated by anharmonic coupling to two doorway states. However, torsion-vibration coupling is still expected to play a role in the longer time dynamics as a consequence of indirect interactions involving bath states.

In the case of toluene-d<sub>3</sub>, one doorway state (Doorway C) drives the IVR dynamics. This state could be assigned to  $|(\delta_{as}^-)^{14^1}\rangle$ ,  $|10b^1 6b^1 10a^1\rangle$  or the combination of  $|16a^1 18b^1, 3a_2''\rangle$  and  $|16a^1 18b^1, 2e'\rangle$ . In all three cases IVR from both the  $|13^1, 0a_1'\rangle$  and  $|13^1, 1e''\rangle$  components could occur; in the former two cases IVR from the  $|13^1, 2e'\rangle$  component could also occur. The influence of Doorway C at early stages of the IVR process is manifested by strong oscillations in the time profiles with a period of  $\tau_c = 10.6$  ps (see Fig. 9), and is further supported by the observation of two peaks at 1222 and 1225 cm<sup>-1</sup> in the nanosecond REMPI spectrum in Fig. 2b. Ionization of this Doorway C gives rise to the peak at 1391 cm<sup>-1</sup> seen in the photoelectron spectrum measured at 6 ps (see Fig. 6b).

## 4. Conclusions

We have examined the IVR dynamics that result following the preparation of the S<sub>1</sub> 13<sup>1</sup> vibrational level in toluene, toluene-d<sub>3</sub> and pFT, where mode 13 is predominantly a C-CH<sub>3</sub> stretching motion at ~1200 cm<sup>-1</sup> in each molecule. Similar IVR lifetimes of 12 and 15 ps are observed for toluene

and toluene- $d_3$ , whereas the IVR lifetime for pFT is approximately four times longer. These lifetimes are listed in Table VII, along with some comparators. In the measurements conducted using chemical timing by Parmenter and coworkers [4,5] the sample was at room temperature; this may explain the large discrepancies in the determined lifetimes (see Table VII). In our work, the significantly shorter IVR lifetimes observed for toluene and toluene- $d_3$  when compared with pFT are attributed to the role played by doorway states, which are observed to mediate the IVR process in the case of toluene and toluene- $d_3$  but not in pFT. Tentative assignments for these doorway states have been made in the course of this work. In contrast to the interpretations given elsewhere [4,9], we find no consistent role for the methyl rotor in mediating the IVR dynamics, and in fact in pFT, where torsion-vibration coupling is deduced to dominate the dynamics, the IVR lifetime is relatively long. We conclude that, at these relatively low excitation energies, IVR lifetimes are largely determined by details of the energy level structure and the availability of doorway states.

### **Acknowledgements**

We are grateful to Warren Lawrance for helpful discussions. This work was supported by EPSRC grant EP/E046150.



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## Tables

Table I: Internal rotor barrier heights ( $V_6$ ) and energy levels in  $S_1$  taken from the specified references, or calculated\* and quoted to one decimal place.

Barrier height	Toluene energy/cm <sup>-1</sup>		Toluene-d <sub>3</sub> energy/cm <sup>-1</sup>		pFT energy/cm <sup>-1</sup>	
$V_6$	-26.4 [11]		-24.5 [11]		-33.7 [15]	
Torsional level	calc*	exp [11,13]	calc*	exp	calc*	exp [14,15]
$0a'_1$	0	-	0	-	0	-
$1e''$	5.3	5.2	2.7	-	4.9	4.9
$2e'$	21.2	20.6	11.0	-	19.5	13.7
$3a''_2$	41.0	41.0	18.5	-	35.5	-
$3a''_1$	54.2	53.5	30.8	-	52.3	52.9
$4e'$	84.6	84.2	43.8	-	78.1	74.3
$5e''$	132.3	130.8	68.5	-	122.0	108.4
$6a'_2$	190.4	-	98.6	-	175.7	-
$6a'_1$	190.4	-	98.6	-	175.7	172.0

\*The internal rotor energies are calculated from the internal rotor constant  $F$ , assuming that the energies are given by  $Fm^2$ . The internal rotor constants are:  $F = 5.29 \text{ cm}^{-1}$  (toluene [11]),  $F = 2.74 \text{ cm}^{-1}$  (toluene-d<sub>3</sub> [11]),  $F = 4.88 \text{ cm}^{-1}$  (pFT [14,15]). The degeneracy of the  $3a''_1$  and  $3a''_2$  internal rotation states is lifted through interaction with the torsional potential such that their energies are separated by half the torsional barrier height [11]. The degenerate  $6a'_2$  and  $6a'_1$  states lie above the barrier.

Table II: Parameters given by fitting the time profiles for chosen regions of the photoelectron spectra to Eq. 4 (see text).

	<b>tol-h<sub>8</sub></b>			<b>tol-d<sub>3</sub></b>			<b>pFT</b>	
	Bright 1200- 1260 <sup>a</sup>	Doorway 1260- 1320 <sup>a</sup>	Doorway 1400- 1530 <sup>a</sup>	Bright 1160- 1350 <sup>a</sup>	Doorway 1350- 1450 <sup>a</sup>	Bath 1500- 1650 <sup>a</sup>	Bright 1180- 1275 <sup>a</sup>	Dark 1370- 1550 <sup>a</sup>
A	51 ± 4	55 ± 3	116 ± 4	207 ± 6	107 ± 3	141 ± 4	16.4 ± 0.3	12.0 ± 0.2
B	32 ± 5	<sup>b</sup>	-10 ± 6	106 ± 13	-30 ± 3	-52 ± 7	7.4 ± 0.3	-6.4 ± 0.3
C	71 ± 7	-10 ± 4	-33 ± 7	111 ± 14	-16 ± 3	-26 ± 7	-	-
D	<sup>b</sup>	-12 ± 4	-17 ± 6	44 ± 12	-29 ± 3	-28 ± 3	-	-
$\tau_C$ /ps	6.4 ± 0.2	6.3 ± 0.3	6.8 ± 0.2	10.8 ± 0.2	10.6 ± 0.2	10.4 ± 0.3	-	-
$\tau_D$ /ps	<sup>b</sup>	4.9 ± 0.2	4.9 ± 0.3	20.1 ± 2.1	15.4 ± 0.6	26.1 ± 3.2	-	-
$\tau_1$ /ps	20 ± 7	<sup>b</sup>	10 ± 12	19 ± 6	58 ± 15	17 ± 5	55 ± 6	45 ± 5
$\tau_2$ /ps	5 ± 1	17 ± 12	8 ± 3	12 ± 3	15 ± 3	11 ± 2	-	-
$\tau_{IVR}^c$ /ps	12 ± 7			15 ± 4			50 ± 6	

<sup>a</sup> Region of ion internal energy in cm<sup>-1</sup> over which the photoelectron intensity is integrated

<sup>b</sup> Term makes a negligible contribution in this case

<sup>c</sup> Taken from the average of the  $\tau_1$  and  $\tau_2$  values but omitting the value of  $\tau_1$  determined for the toluene-d<sub>3</sub> doorway state because of its large uncertainty. The average uncertainty is also given.

Table III: Calculated scaled harmonic frequencies for toluene and toluene-d<sub>3</sub> taken from Ref [26]. Only those modes whose S<sub>1</sub> fundamental frequencies are ≤ 1192 cm<sup>-1</sup> in toluene and/or ≤ 1225 cm<sup>-1</sup> in toluene-d<sub>3</sub> are included.

Mode <sup>a</sup>	Mode <sup>b</sup>	Mode <sup>c</sup>	Sym <sup>d</sup>	toluene		toluene-d <sub>3</sub>	
				S <sub>1</sub> <sup>e</sup>	ion <sup>f</sup>	S <sub>1</sub> <sup>e</sup>	ion <sup>f</sup>
$\mathcal{M}_6$	8	13	$A_1'$ ( $A_1$ )	1184	1220	1210	1240
$\mathcal{M}_7$	9	9a		1142	1181	1143	1185
$\mathcal{M}_8$	10	18a		945	958	944	952
$\mathcal{M}_9$	11	12		960	979	962	974
$\mathcal{M}_{10}$	12	1		745	753	718	727
$\mathcal{M}_{11}$	13	6a		452	504	436	476
$\mathcal{M}_{12}$	14	17a	$A_2'$ ( $A_2$ )	697	996	697	993
$\mathcal{M}_{13}$	15	10a		562	784	562	783
$\mathcal{M}_{14}$	16	16a		210	340	210	340
$\mathcal{M}_{15}$	20	5	$A_2''$ ( $B_1$ )	797	1008	806	1008
$\mathcal{M}_{16}$	21	17b		695	919	675	952
$\mathcal{M}_{17}$	22	11		581	731	576	681
$\mathcal{M}_{18}$	23	4		437	564	417	520
$\mathcal{M}_{19}$	24	16b		312	374	308	366
$\mathcal{M}_{20}$	25	10b		146	147	138	139
$S_7$	18	$\delta_{as}^+$		1345	1439	1011	1039
$S_8$	19	$\delta_{as}^-$	967	979	796	853	
$\mathcal{M}_{26}$	33	3	$A_1''$ ( $B_2$ )	1140	1258	1140	1259
$\mathcal{M}_{28}$	35	18b		1027	1052	995	1052
$\mathcal{M}_{29}$	37	6b		522	485	520	492
$\mathcal{M}_{30}$	38	15		329	336	293	299
$S_4$	30	$\delta_{as}^+$		1427	1384	1030	1002
$S_5$	36	$\delta_{as}^-$		927	944	765	777

<sup>a</sup> Notation for the vibrations of the aromatic ring from Ref. [22]. Notation for the methyl group vibrations from Ref. [32].

<sup>b</sup> Notation used in Ref. [21]

<sup>c</sup> Notation used in Ref. [20]

<sup>d</sup> Irreducible representation using the G<sub>12</sub> (C<sub>2v</sub>) point group.

<sup>e</sup> TD-B3LYP/aVTZ with a scaling factor of 0.97.

<sup>f</sup> UB3LYP/aVTZ with a scaling factor of 0.97.

Table IV: List of vibrational states in toluene with suitable symmetry for coupling to  $|13^1, 0 a'_1\rangle$  or  $|13^1, 1e''\rangle$ , with a total  $\Delta N \leq 4$ , with calculated  $S_1$  energies within  $\pm 40 \text{ cm}^{-1}$  of the bright state absorption maximum ( $1192 \text{ cm}^{-1}$ ) and with calculated ion energies within  $\pm 25 \text{ cm}^{-1}$  of the observed cation states at either  $1290 \text{ cm}^{-1}$  (top) or  $1460 \text{ cm}^{-1}$  (bottom). The calculated energies are taken from Tables I and III, and the IVR mechanism is either anharmonic (a) or torsion-vibration (t-v) coupling (see text). The level in bold is the deduced most likely assignment for one of the observed doorway states.

Bright state component	Vibrational state of doorway candidate	Torsional state of doorway candidate	mechanism	$\Delta N$	$S_1$ energy <sup>a</sup> / $\text{cm}^{-1}$	Ion energy <sup>b</sup> / $\text{cm}^{-1}$	$\Delta E_{S_1}$ / $\text{cm}^{-1}$	$\Delta E_{\text{ion}}$ / $\text{cm}^{-1}$
$13^1 0 a'_1$ $13^1 1e''$	<b><math>1^1 16b^1 10b^1</math></b>	<b><math>0a'_1</math></b> <b><math>1e''</math></b>	a	4	1203	1274	11	-16
$13^1 0 a'_1$	$3^1$	$3a''_1$	t-v	3	1194	1312	2	22
$13^1 1e''$	$4^1 6b^1$	$7e''$	t-v	4	1213	1303	21	13
$13^1 0a'_1$	$6a^1$	$12a'_1$	t-v	4	1214	1266	22	-24
$13^1 0a'_1$ $13^1 1e''$	$11^2$	$0a'_1$ $1e''$	a	3	1162	1462	-30	2
$13^1 0a'_1$ $13^1 1e''$	$6a^1 4^1 16b^1$	$0a'_1$ $1e''$	a	4	1201	1442	9	-18
$13^1 0a'_1$ $13^1 1e''$	$17a^1 10b^1 15^1$	$0a'_1$ $1e''$	a	4	1172	1479	-20	19
$13^1 0a'_1$	$6a^1 10a^1$	$6a'_2$	t-v	4	1204	1478	12	18
$13^1 0a'_1$	$17b^1 15^1$	$6a'_2$	t-v	4	1214	1445	22	-15
$13^1 0a'_1$ $13^1 1e''$	$6a^1 17b^1$	$3a''_2$	t-v	4	1188	1464	-4	4
		$2e'$			1163	1439	-29	-21
$13^1 1e''$	$17b^1$	$10e'$	t-v	4	1219	1443	27	-17

<sup>a</sup> Relative to  $S_1 v = 0, 0 a'_1$  (for the  $13^1 0 a'_1$  torsional component) or  $S_1 v = 0, 1e''$  (for the  $13^1 1e''$  torsional component).

<sup>b</sup> Relative to  $D_0 v = 0, 0 a'_1$  (for the  $13^1 0 a'_1$  torsional component) or  $D_0 v = 0, 1e''$  (for the  $13^1 1e''$  torsional component).

Table V: List of vibrational states in toluene-d<sub>3</sub> with suitable symmetry for coupling to  $|13^1, 0a'_1\rangle$ ,  $|13^1, 1e''\rangle$ , or  $|13^1, 2e'\rangle$ , with a total  $\Delta N \leq 4$ , with calculated S<sub>1</sub> energies within  $\pm 40$  cm<sup>-1</sup> of the bright state absorption maximum (1225 cm<sup>-1</sup>) and with calculated ion energies within  $\pm 25$  cm<sup>-1</sup> of the observed cation states at 1391 cm<sup>-1</sup>. The calculated energies are taken from Tables I and III, and the IVR mechanism is either anharmonic (a) or torsion-vibration (t-v) coupling (see text). The states in bold are the deduced most likely assignments of the observed doorway state.

Bright state component	Vibrational state of doorway candidate	Torsional state of doorway candidate	mechanism	$\Delta N$	S <sub>1</sub> energy <sup>a</sup> /cm <sup>-1</sup>	Ion energy <sup>b</sup> /cm <sup>-1</sup>	$\Delta E_{S_1}$ /cm <sup>-1</sup>	$\Delta E_{ion}$ /cm <sup>-1</sup>
13 <sup>1</sup> 0a' <sub>1</sub> 13 <sup>1</sup> 1e'' 13 <sup>1</sup> 2e'	<b>(<math>\delta_{as}^-</math>)<sup>1</sup>4<sup>1</sup></b>	<b>0a'<sub>1</sub></b> <b>1e''</b> <b>2e'</b>	a	3	1213	1373	-12	-18
13 <sup>1</sup> 0a' <sub>1</sub> 13 <sup>1</sup> 1e'' 13 <sup>1</sup> 2e'	<b>10a<sup>1</sup>10b<sup>1</sup>6b<sup>1</sup></b>	<b>0a'<sub>1</sub></b> <b>1e''</b> <b>2e'</b>	a	4	1220	1414	-5	23
13 <sup>1</sup> 0a' <sub>1</sub>	18a <sup>1</sup> 16a <sup>1</sup>	6a' <sub>2</sub>	t-v	4	1253	1391	28	0
13 <sup>1</sup> 0a' <sub>1</sub> 13 <sup>1</sup> 1e'' 13 <sup>1</sup> 2e'	16a <sup>1</sup> ( $\delta_{as}^+$ ) <sup>1</sup>	3a'' <sub>1</sub> 2e' 1e''	t-v	4	1252 1229 1213	1410 1387 1371	27 4 -12	19 -4 -20
13 <sup>1</sup> 0a' <sub>1</sub> 13 <sup>1</sup> 1e'' 13 <sup>1</sup> 2e'	<b>16a<sup>1</sup>18b<sup>1</sup></b>	<b>3a''<sub>2</sub></b> <b>2e'</b> <b>1e''</b>	t-v	4	1224 1213 1197	1411 1400 1384	-1 -12 -28	20 9 -7
13 <sup>1</sup> 0a' <sub>1</sub>	5 <sup>1</sup> 15 <sup>1</sup>	6a' <sub>2</sub>	t-v	4	1198	1406	-27	15
13 <sup>1</sup> 1e''	12 <sup>1</sup> 16a <sup>1</sup>	5e''	t-v	4	1238	1380	13	-11
13 <sup>1</sup> 2e'	( $\delta_{as}^-$ ) <sup>1</sup> 4 <sup>1</sup>	4e'	t-v	4	1246	1406	21	15

<sup>a</sup> Relative to S<sub>1</sub> v = 0, 0 a'<sub>1</sub> (for the 13<sup>1</sup> 0 a'<sub>1</sub> torsional component), S<sub>1</sub> v = 0, 1e'' (for the 13<sup>1</sup> 1e'' torsional component), or S<sub>1</sub> v = 0, 2e' (for the 13<sup>1</sup> 2e' torsional component).

<sup>b</sup> Relative to D<sub>0</sub> v = 0, 0 a'<sub>1</sub> (for the 13<sup>1</sup> 0 a'<sub>1</sub> torsional component), D<sub>0</sub> v = 0, 1e'' (for the 13<sup>1</sup> 1e'' torsional component), or D<sub>0</sub> v = 0, 2e' (for the 13<sup>1</sup> 2e' torsional component).

Table VI: Ion energies of the states expected to be strongly coupled to  $|1^16b^110b^1\rangle$  in the  $S_1$  electronic state of toluene. The states given in bold have experimental ion energies closest to the peaks observed at 1290 and 1460  $\text{cm}^{-1}$  in the photoelectron spectrum at 3 ps.

Zero order state	Ion energy* / $\text{cm}^{-1}$ (calculated [26])	Ion energy / $\text{cm}^{-1}$ (experimental [25,26])
$ 1^16a^1\rangle$	1257	1263
<b><math> 1^116b^110b^1\rangle</math></b>	<b>1274</b>	<b>1295</b>
$ 4^116b^16a^1\rangle$	1442	1439
<b><math> 4^116b^210b^1\rangle</math></b>	<b>1459</b>	<b>1471</b>

\*Scaled Harmonic; see Table III

Table VII: Measured IVR lifetimes.

Excitation energy	toluene <sub>a</sub>	toluene-d <sub>3</sub> <sub>a</sub>	pFT		pFT-d <sub>3</sub> <sub>b</sub>	mFT <sub>c</sub>
			a	b		
$\sim 1200 \text{ cm}^{-1}$	12 ps	15 ps	50 ps	15.2 ps	3.4 ps	1.2 ps
$\sim 2000 \text{ cm}^{-1}$	-	-	-	3.4 ps	1.5 ps	-

- a. This work.  
 b. D.B. Moss and C.S. Parmenter, J. Chem. Phys. 98, 6897 (1993).  
 c. P.J. Timbers, C.S. Parmenter and D.B. Moss, J. Chem. Phys. 100, 1028 (1994).



## Figures

1. Comparison of (1 + 1) picosecond REMPI spectra measured via the  $S_1$  excited state in (a) toluene, (b) toluene- $d_3$  and (c) pFT, with selected vibrational states labelled.
2. (1 + 1) nanosecond REMPI spectra measured in the vicinity of the  $13_0^1$  transition in  $S_1$  for (a) toluene, (b) toluene- $d_3$  and (c) pFT. In each plot, a Gaussian profile represents the idealized spectral profile of the picosecond laser pulse and indicates the spectral region excited in the time-resolved experiments.
3. Comparison of ZEKE spectra following excitation of a narrow portion of the  $S_1$   $13^1$  absorption profile. (a), (b) and (c) are measured following excitation at the centre of the regions labelled ( $|1\rangle$ ,  $|2\rangle$  and  $|3\rangle$ , respectively, in the toluene absorption profile shown in Fig. 2a. (d) is measured following excitation at the centre of the pFT absorption profile shown in Fig. 2c (see text for details).
4. Comparison of picosecond time-resolved SEVI spectra at early time following preparation of the  $13^1$  bright state in  $S_1$ : (a) toluene, (b) pFT.
5. Comparison of SEVI spectra at time delays of 0 ps and 500 ps: (a) toluene, (b) pFT.
6. Comparison of time-resolved SEVI spectra illustrating recurrence behaviour: (a) toluene, (b) toluene- $d_3$ .
7. Time profiles for a region of the photoelectron spectrum dominated by signal from the  $13^1$  cation state: (a) toluene, (b) toluene- $d_3$  and (c) pFT (see text). The intensity scale is zero at the point where it crosses the abscissa. The data points are indicated by solid circles; the solid line results from fitting the data to Eq. (4).
8. Time profiles for toluene for selected regions of the photoelectron spectrum: (a) 1200-1260  $\text{cm}^{-1}$ , (b) 1260-1320  $\text{cm}^{-1}$  and (c) 1400-1530  $\text{cm}^{-1}$  (see text). The intensity scale is zero at the point where it crosses the abscissa. The data points are indicated by solid circles; the solid line results from fitting the data to Eq. (4).
9. Time profiles for toluene- $d_3$  for selected regions of the photoelectron spectrum: (a) 1160-1350  $\text{cm}^{-1}$  and (b) 1350-1450  $\text{cm}^{-1}$  (see text). The intensity scale is zero at the point where it crosses the abscissa. The data points are indicated by solid circles; the solid line results from fitting the data to Eq. (4).
10. Time profiles for pFT for selected regions of the photoelectron spectrum: (a) 1180-1275  $\text{cm}^{-1}$  and (b) 1370-1550  $\text{cm}^{-1}$  (see text). The intensity scale is zero at the point where it crosses the abscissa. The data points are indicated by solid circles; the solid line results from fitting the data to Eq. (4).
11. Schematic diagram illustrating the proposed tier structure for the scenario discussed in Section 3.5(b), which has been created following the assignment of the two doorway states that operate in toluene. The upper section indicates how the hierarchy of the coupled vibrational states is reflected in the time-resolved photoelectron spectra.