Vibronic Emission Spectrum of \textit{p}-Xylyl Radical

\textsc{Myeong H. Suh,}\textsuperscript{1} \textsc{Sang K. Lee}\textsuperscript{2} \textsc{and Terry A. Miller}

Laser Spectroscopy Facility
Department of Chemistry
The Ohio State University
Columbus Ohio 43210
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\textbf{ABSTRACT}

We have obtained high resolution Fourier transform emission spectra of the $\tilde{A} \leftrightarrow \tilde{X}$ transition of the jet-cooled \textit{p}-xylyl radical in the 450nm spectral region. The band contours of several vibronic bands are examined. By using the rotational constants obtained from previous high resolution LIF spectra and information about the torsional constants from dispersed fluorescence experiments, both \textit{a}-type and \textit{b}-type band contours are simulated. Based on symmetry arguments and the results of the simulation, we have reassigned the 6\textit{a} and 6\textit{b} vibrational mode frequencies of the ground electronic state of the \textit{p}-xylyl radical.

\textsuperscript{1}\textit{Present address: Department of Chemistry, Texas A\&M University, College Station, Texas 77843}

\textsuperscript{2}\textit{Present address: Department of Chemistry, Pusan National University, Pusan 609-735, Korea}
I Introduction

The electronic structure of benzyl and the three isomeric methyl substituted benzyl radicals (xylyls) have been the subject of much experimental and theoretical work\(^{(1,2,3)}\). The effects of methyl substitution in the ortho, meta and para positions have been studied by many different groups\(^{(4,5,6,7,8,9,10,11)}\). Para substitution is especially interesting as the symmetry axis does not change from the benzyl radical, thus preserving closely the lineage of the benzyl. Cossart-Magos and Cossart\(^{(12)}\) extended their benzyl rotational contour analysis to the \(p\)-xylyl radical emission spectra by examining the \(\tilde{A} \rightarrow \tilde{X}\) transition in a room temperature discharge. They concluded that the \(\tilde{A}\) state symmetry of \(p\)-xylyl is \(^2\!A_2\), analogous to benzyl itself. Miller and coworkers confirmed their conclusion in their high resolution, rotationally resolved analysis\(^{(3)}\). By comparing band contours, Cossart-Magos and Cossart\(^{(12)}\) also assigned the \(6a^0_1\) and \(6b^0_1\) transitions. They, however, found that the assignments were somewhat unexpected in that the \(6a\) mode has higher frequency (637 cm\(^{-1}\)) than that (458 cm\(^{-1}\)) of the \(6b\) mode in the ground electronic state of \(p\)-xylyl. The opposite case was found in the parent molecule, \(p\)-xylene, in which the \(6a\) mode has lower (454 cm\(^{-1}\)) frequency than \(6b\) (646 cm\(^{-1}\)) mode.

Selco and Carrick\(^{(2)}\) reexamined \(p\)-xylyl radical in a supersonic expansion, but at relatively low resolution (~1 cm\(^{-1}\)). They were able to assign many new vibronic bands and also concluded that the \(6a\) and the \(6b\) vibrations in the ground state of \(p\)-xylyl are interchanged in frequency with respect to \(p\)-xylene. The band shapes they observed however were somewhat different from the simulation predicted by Cossart-Magos and Cossart
at a similar temperature.

The previous assignments are not totally unambiguous because most of the earlier work was performed at either relatively high temperature or low resolution conditions. Furthermore, the xylyl radicals have a methyl rotor which contributes internal torsional transitions to the spectrum which, in turn, may complicate the spectra. It is the purpose of this work to reexamine p-xylyl spectra for unambiguous assignments of the vibration modes by taking spectra at relatively low temperature (50K) and relatively high resolution (0.2 cm$^{-1}$).

## II Experimental

The experimental conditions are similar to our previous work\cite{13}, hence only a brief description is given here. The xylyl radicals are generated and excited by a corona discharge and their emission is probed by a Fourier transform spectrometer. The parent compound, p-xylene, is mixed with helium carrier gas and expanded into the vacuum chamber through a small pinhole in a glass nozzle. Typically the power supply for the discharge is operated at about 1000V. Higher voltages increase the production of C$_2$. When the anode position inside the nozzle is well adjusted so as to produce a green jet, the fluorescence spectrum of the p-xylyl radical is clearly observed. However we found that optimization of the position of the anode and the value of the discharge electrode voltage are very important for producing a strong p-xylyl signal.

Initially, survey scans were obtained at low, 2 cm$^{-1}$ instrumental resolution and subsequently, higher resolution scans were obtained at or near
0.2 cm\(^{-1}\) instrumental resolution. The Doppler-limited, highest resolution scans (0.01 cm\(^{-1}\)) did not produce any significant improvement for the rotational contour compared to the previous spectral resolution, only serving to decrease the signal to noise ratio. For the final, high resolution spectra, usually 150 scans, taken over an hour period, were averaged.

III Theory

The general electronic structure of the \(p\)-xylyl can be simply described by \(\pi\) electron theory. The \(\pi\) molecular orbitals can be written in terms of the seven \(p\)-atomic orbitals. The \(C_{2v}\) approximation, treating the methyl group as a structureless ball, is reasonable when one is dealing with the electronic properties, and in this way the electronic configuration of the ground state of the \(p\)-xylyl can be written in the form

\[
(1b_2)^2(2b_2)^2(1a_2)^2(3b_2)^1 \quad \tilde{X}^2B_2\quad [1]
\]

Miller’s group (3) as well as Cossart-Magos and Cossart (12) found that the first electronic excited state has \(^2A_2\) symmetry for \(p\)-xylyl. Fig. 1 shows the molecular-fixed axis system of \(p\)-xylyl showing the moment of inertia axis in the \(C_{2v}\) symmetry approximation. (There is a nearby \(B^2B_2\) state which interacts with the \(A^2A_2\) state, but as this study pertains to the \(\tilde{X}\) state, we need not go into the details of these interactions, which have been discussed extensively before. (12,3))

For an allowed transition, the transition moment matrix element must be nonvanishing. If we neglect nuclear and electronic spin wave functions, the allowed transitions must satisfy the following equation,
\[ < E', V', R', T' | M_k | E'', V'', R'', T'' > \neq 0 \]  \hspace{1cm} [2]

where \( E, V, R, \) and \( T \) refer to the corresponding electronic, (non-torsional) vibrational, rotational and torsional wave functions. \( M_s \) refers to the electric dipole moment in laboratory coordinates; it can be written as a linear combination of its components \( (k) \) along the molecular fixed axes by using a rotational matrix, \( D_{sk} (\omega) \) where \( \omega \) denotes the Euler angles relating the molecule - and space-fixed coordinate systems.

By assuming the eigenfunction is separable one can rewrite Eq.2 to obtain

\[ \sum_{i,k} < T' | T'' > < R' | D_{sk}^{-1}(\omega) | R'' > < V', E' | M_k | E'', V'' > \neq 0 \]  \hspace{1cm} [3]

Eq. 3 implies that the symmetry of \( | T > \) cannot change in the transition.

For the \( p \)-xylyl radical, if the torsional motion of the methyl group is taken into account, one should use the molecular symmetry group \( G_{12} \). In \( G_{12} \) symmetry group notation, the observable, allowed torsional transitions are

\[
\begin{align*}
0a' & - 0a' \\
1e'' & - 1e'' \\
2e' & - 2e'
\end{align*}
\]

In the same way (in \( C_{2v} \) notation) one can easily derive the allowed vibronic transition from Eq. 3, i.e., \( < V', E' | M_k | E'', V'' > \neq 0 \).
predicts that the $6a_1^0$ (in Wilson notation as in ref.\cite{15}) must be $b$-axis polarized while $6b_0^1$ should be $a$-axis polarized. Therefore, the $6a_1^0$ transition is expected to have a similar lineshape as the $b$-axis polarized $0_0^0$ transition.

The rotational Hamiltonian of an asymmetric rotor can be written in the form

$$H_R = AJ_z^2 + BJ_x^2 + CJ_y^2$$ \[4\]

where $J_x, J_y$ and $J_z$ are the components of the rotational angular momentum $\mathbf{J}$ along the corresponding molecule-fixed axes, and $A, B$ and $C$ denote the rotational constants. Interaction terms caused by the unpaired electron, such as spin-orbit or spin-rotation couplings, are not included in the Hamiltonian as these types of splittings are not resolved experimentally. For the same reason we do not need to distinguish between the rotational angular momentum $\mathbf{N}$ and the total angular momentum $\mathbf{J}$. Higher order centrifugal distortion terms also can be neglected within experimental error for the present low-temperature experiments.

If molecules have an internally rotating methyl group, as in xylyl, the torsional energy terms need to be included for the high resolution contour analysis. The complete torsion-rotational Hamiltonian for $p$-xylyl can then be written\cite{16}

$$\mathcal{H} = \mathcal{H}_T + \mathcal{H}_R + \mathcal{H}_{RT}$$ \[5\]

$$\mathcal{H}_R = A_F J_z^2 + B J_x^2 + C J_y^2$$ \[6\]

$$\mathcal{H}_T = F p^2 + \frac{1}{2} V_6 (1 - \cos 6 \alpha)$$ \[7\]

$$\mathcal{H}_{RT} = -2 A_F p J_z$$ \[8\]

where $\mathcal{H}_R$ represents the (modified) rotational Hamiltonian, $\mathcal{H}_T$ the tor-
sional Hamiltonian and $H_{RT}$ contains the rotational-torsional coupling terms. The $p$ represents the angular momentum of the methyl group internal rotation; $\alpha$ is the internal rotation angle; $F$ is the reduced rotational constant of the methyl group about its symmetry axis; and $V_6$ is the sixfold torsional barrier height which hinders the internal rotation of the methyl group. $A_F$ is the rotational constant of the frame (the “benzyl” part) about the a-axis. The rotational terms are defined in terms of the moments of inertia as follows:

$$A_F = \frac{\hbar^2}{2(I_z - I_\alpha)} \quad [9]$$

$$B = \frac{\hbar^2}{2I_y} \quad [10]$$

$$C = \frac{\hbar^2}{2I_x} \quad [11]$$

$$F = \frac{\hbar^2}{2(I_z - I_\alpha)} \left(\frac{I_z}{I_\alpha}\right) \quad [12]$$

where the terms have their usual meaning. The coordinates $(x, y, z)$ are shown in Fig. 1.

The Hamiltonian matrix of $H$ can be constructed using the rotational-torsional, $|J, K,m>$, basis set, where $|J, K>$ are symmetric top wave functions and $|m>$ are the free rotor wave functions for the methyl group. Since the free rotor quantum number $m$ has no finite limit, the Hamiltonian matrix is infinite. This can be overcome by using a matrix truncated at a given $m$ which will give the desired energy convergence. However, the truncated matrix is still large when including the higher $J$ needed to simulate our experiment spectra. (The $J$ and $m$ required are about 50 and 10 respectively for $p$-xylyl at $T=45K$). Because $J$ is a good quantum number,
one may reduce the matrix into individual $J$ blocks, which gives a matrix of order $2J+1$. Each $J$ block can be further reduced into an even $K$ block and odd $K$ block, which have $J$ and $J+1$ possible $K$ values. Inclusion of the $m$ quantum number increases the size of matrix by $2m_{MAX} + 1$. In our example, this means that the dimension of the matrix to be solved by the full diagonalization method is about 1000 x1000. To simulate an observed spectrum with this method, one must diagonalize large matrices of this size hundreds of times; even today this is computationally challenging. We have found that for the simulation purposes, we can choose an approximate formulation (corresponding in this case to a 51x51 matrix), described below, which can proceed much faster.

In our jet experiment, only the first few low-lying torsional levels of the $\tilde{A}$ state appear to be populated. The rotational structure of $p$-xylyl associated with each of these torsional levels can be described by an effective rotational Hamiltonian. The following effective Hamiltonian can be obtained,

$$\mathcal{H} = \mathcal{H}_T + \mathcal{H}_R + \mathcal{H}_{RT} = \mathcal{H}_T + \mathcal{H}_{eff}$$ [13]

with

$$\mathcal{H}_{eff} = A_T J_z^2 + B J_x^2 + C J_y^2 + D_z J_z$$ [14]

where

$$A_T = A_F + 4A_F^2 \sum_{T' \neq T} \frac{<T | p | T'>^2}{E_T - E_{T'}}$$ [15]

$$D_z = -2A_F <T | p | T>$$ [16]

The eigenvalues of the effective Hamiltonian of Eq. 14 within the rotational
basis | R > for a given torsional level | T > are used for the simulation of the spectra. By symmetry, the matrix element < T | p | T > becomes zero for nondegenerate torsional levels (0a' 1, for example); hence D_z vanishes. Thus in this particular case we are left with the standard asymmetric top Hamiltonian, except the effective A_T constant is different for each torsional level.

The torsional Hamiltonian, \( H_T \), can now be treated separately to give the eigenenergies of the torsional levels. It has the following non-zero matrix elements in the free rotor | m > basis

\[
\delta_{m,m'} = Fm^2 + \frac{1}{2}V_6 \quad [17]
\]
\[
\delta_{m,m\pm6} = -\frac{1}{4}V_6 \quad [18]
\]

for the sixfold symmetry potential. The matrix is diagonalized for both ground and excited electronic states as a function of the rotor constant, F, and barrier height, V_6, to obtain the corresponding torsional levels. The transition frequencies are calculated from the eigenenergies with the aid of the selection rules. The eigenfunctions |T> are used to calculate A_T and D_z via Eqs. 15 and 16.

Each electronic transition, \( \tilde{A}^2A_2 \leftrightarrow \tilde{X}^2B_2 \), has several subbands due to the torsional transitions. The subbands, depending on the torsional states involved, are hereafter referred as A (for 0a' 1 − 0a' 1), E'' (for 1e'' − 1e'') and E' (for 2e' − 2e') subbands.
IV  Result and Discussion

A part of the low resolution (2 cm\(^{-1}\)) spectrum of \(p\)-xylyl is shown in Fig. 2. The spectrum shows several transitions including the 0\(_0^0\) band and several other vibronic bands. Our low resolution spectrum clearly shows a strong 0\(_0^0\) band at 21700 cm\(^{-1}\) and three other strong peaks at 460 cm\(^{-1}\) ("460 band"), 640 cm\(^{-1}\) ("640 band") and 830 cm\(^{-1}\) respectively to the red of the 0\(_0^0\) band. The assignments of these peaks by Selco and Carrick can be found in ref. (2) and are partially reproduced in Table 1 for comparison.

The low resolution rotational contours of the "460 band" and the peak at 830 cm\(^{-1}\) are similar to that of the 0\(_0^0\) band while the "640 band" is rather different, suggesting that the previous assignments of the 6\(_a\) and 6\(_b\) bands may not be correct. To further investigate the possibility, high resolution spectra were taken at 0.2 cm\(^{-1}\) instrumental resolution.

Fig. 3 shows high resolution spectra of the several bands. It is unmistakable that the 0\(_0^0\) band and the 830 cm\(^{-1}\) band are comparable. The "460 band" looks slightly different from the 0\(_0^0\) band, but still it is much more similar to the 0\(_0^0\) band than the "640 band" is, which has a quite different and narrower overall contour. Therefore we believe it is more reasonable to assign the "460 band" as a b-type transition (i.e. 6\(_a^0\)) and the "640 band" as an a-type (i.e. 6\(_b^0\) band).

To confirm our hypothesis, both a-type and b-type bands for the \(p\)-xylyl radical were simulated including torsional structure. We chose the 0\(_0^0\) band and "640 band" as models of b-type and a-type transitions respectively as these bands are both very prominent in the observed spectra. The rotational constants for the 0\(_0^0\) band (b-type transition) are taken from the high
resolution study by Miller’s group (3). Simulation of the spectra has been performed by using the effective Hamiltonian given in Eq. 14. The separation between the subbands was determined from the eigenvalues of \( \mathcal{H}_T \) using the values of the potential parameters from Lin, et al. (17) These parameters are all summarized in Table 2. The calculated energy levels and the center frequencies of the allowed transitions are given in Table 3.

The simulation of the observed bands involved the following major steps:

(a) Calculate the torsional energy level shift from 0\( a'_1 \), \( \Delta E_T \), by finding the eigenvalues of \( \mathcal{H}_T \). The torsional quantum number \( m \) is truncated at 40 for this calculation. Any further increase of the value \( m \) did not improve our calculation significantly.

(b) Calculate the effective rotational constants \( A_T \) and \( D_Z \), Eqs. 15 and 16, using the torsional eigenfunctions from step (a) and the constants from Table 2. As only the vibrationless levels of the \( \bar{X} \) and \( \bar{A} \) states were examined in the high resolution spectrum, (very) small adjustments were made to the rotational constants for the other vibrational levels. The parameters are summarized in Table 4.

(c) Calculate the rotational structure of each torsional level by finding the eigenvalues of \( \mathcal{H}_{\text{eff}} \). The process of simulating rotational structure of each level is facilitated by use of the SpecSim program (18).

(d) Combine the rotational spectra of the three torsional transitions (0\( a'_1 \) − 0\( a'_1 \), 1\( e'' \) − 1\( e'' \) and 2\( e' \) − 2\( e' \)) after adjusting their frequencies using the \( \Delta E_T \) values from Table 3.

The relative intensities (see Table 3) of the three torsional bands were chosen to best match the observed spectra. Lin and coworkers (17) observed that the torsional intensity patterns in \( p \)-xylyl could not be well described
by torsional “Franck-Condon” factors. The first few torsional state stacks should be all metastable, as the transitions between the different (symmetry) torsional states are not allowed by selection rules. Therefore, one might expect somewhat arbitrary populations and resulting intensity patterns in the observed spectra depending on the efficiency of the relaxation, oscillator strength, etc.

The simulations of the bands shown in Figs. 4-6 show that the \( A \) subband contributes the most intensity to the overall band contour. Even without including the \( E'' \) and \( E' \) torsional subbands, it is not too difficult to determine the transition types of the observed bands after comparing them with the simulation. In both \( a \) and \( b \) types of transitions, the \( E'' \) subband appeared between the P and R branches of the \( A \) subband as relatively strong sharp peaks and the \( E' \) subband appeared as a small hump at about 6 cm\(^{-1}\) to the low frequency side of the \( A \) subband origin. The effective rotational constants derived from the work of Miller’s group\(^{(2)}\) for the \( 0^0\) transition produced a good simulation for the \( 0^0 \) band (\( b \) type) and, with minor adjustment, the “640 band” (\( a \) type) as well, which supports the assignment of the “640 band” or the \( 6b_0^0 \) band. The rotational constants used in all the simulations are given in Table 4.

### IV.1 Perturbation of the \( 6a_1^0 \) band.

Even though our simulation reproduced the observed spectra quite reasonably, there initially were some significant differences in the “460 band” simulation. In particular, the central peak, observed as a strong line in the \( 0^0 \) band, is not so obvious. We have tried to vary the torsional barrier as well as the rotational constants to reproduce the observed “460 band”. It appears
however, that the “460 band” is not well reproduced for any reasonable values of the potential barrier $V_6$, nor does the overall appearance of the simulation seem to improve. We are however able to satisfactorily reproduce the rotational contour of the “460 band” by introducing a small adjustment to the molecular constants given in Tables 3 and 4: The following describes the adjustment performed.

1) For the $A$ subband, a small distortion constant $D''_{jk} = 3 \times 10^{-6} \text{ cm}^{-1}$ was introduced. While not changing the contour dramatically, the distortion constant improved the band shapes, especially the small hump at higher frequency side. The magnitude of the $D''_{jk}$ seems not unreasonable. For the case of cyclopentadienyl, a value of $D''_{jk} = 2.5 \times 10^{-6} \text{ cm}^{-1}$ was obtained (19).

2) The separation between the $A$ subband and $E''_{00}$ subband was adjusted to 0.86 cm$^{-1}$, compared to the value in Table 3 of $\Delta E_T = 1.22 \text{ cm}^{-1}$. The shift of 0.36 cm$^{-1}$ is too large to be explained by a change of the torsional potential since only 0.03 cm$^{-1}$ shift is expected for potential barrier change of about 20 cm$^{-1}$.

Fig. 6 shows the rotational contour of the “460 band” and the resulting, rather good simulation, when the above modifications are included. The relatively large shift between the $A$ and $E''_{00}$ subband may be explained by a Fermi resonance type interaction between the torsional stacks built upon the other vibrations. In $p$-xylyl molecules, several low frequency vibrations are expected. For instance, Leach and coworkers reported the $16b$ ($b_2$ symmetry) mode to have a frequency of 389 cm$^{-1}$ (20). The torsional stack of $16b$ (or other low frequency modes) can interact with the torsional stack of the $6a_1$ mode, via Fermi resonance type perturbation. Fig. 7 illustrates how this type of interaction results in the relative shifts of the subbands. The Fermi
resonance must occur between levels of the same (overall) symmetry and the 
resonance perturbation is greatest when the energy separation of the same 
symmetry levels are small. As illustrated in Fig. 7, the (overall) symmetry 
of the torsional stacks built on the non-totally symmetric vibrational states 
can be the same as those built on the totally symmetric vibrational state, re-
sulting in an interaction. Each torsional state may be differently perturbed, 
which could result in “pushing together” the \( e'' \) and \( a'_1 \) torsional states. This 
picture, while difficult to prove, may give a qualitative explanation for the 
observed \( E'' \) subband shift.

It may also be partially the reason that the previous studies had dif-
ficulties identifying these bands correctly. The “460 band” does not have 
precisely the same appearance as the \( 0_0^0 \) band in overall contour, especially 
because it misses the central peak (\( E'' \) subband) which is overlapped with 
the \( A \) subband. On the other hand, the “640 band” does have a small 
central peak, which, when it is observed at low resolution, looks similar to 
the central peak in the \( 0_0^0 \) band. These effects would have made it difficult 
to correctly assign the low resolution or high temperature spectrum, but 
the bands are clearly recognizable in our high resolution, low temperature 
experiment system.

V  Conclusion

We have obtained high resolution Fourier transform emission spectra of the 
\( A^2 \text{A}_2 - \widetilde{X}^2 \text{B}_2 \) transition of the jet-cooled \( p \)-xylyl radical in the 450nm spec-
tral region. The band contours of several vibronic bands are examined. By 
using the rotational constants and torsional parameters obtained from pre-
vious work, both \( a \)-type and \( b \)-type rotational transitions including torsional structure are simulated. Based on the results of the simulations, we have reassigned the \( 6a \) and \( 6b \) vibrational modes of the ground electronic state of the \( p \)-xylyl radical.

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REFERENCES


Table Legends

Table 1: Vibrational Bands of $p$-xylyl Emission Spectrum. Frequencies are given in cm$^{-1}$ below the origin.

Table 2: Molecular constants$^a$ in units of cm$^{-1}$.

Table 3: Calculated Torsional Energy levels in units of cm$^{-1}$.

Table 4: Rotational Constants$^a$ in units of cm$^{-1}$ for $\tilde{A}(1a'_1)$ and $\tilde{X}(1a'_1)$. 
Table 1: Vibrational Bands of $p$-xylyl Emission Spectrum. Frequencies are given in cm$^{-1}$ below the origin.

<table>
<thead>
<tr>
<th>$\tilde{X}$ State Level</th>
<th>Symmetry</th>
<th>$p$-xylene$^a$</th>
<th>$p$-xylyl$^b$</th>
<th>$p$-xylyl$^c$</th>
<th>$p$-xylyl$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0$_0$</td>
<td>a$_1$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6a$_1$</td>
<td>a$_1$</td>
<td>454.3</td>
<td>637.3</td>
<td>636.7</td>
<td>458.57(3)$^e$</td>
</tr>
<tr>
<td>6b$_1$</td>
<td>b$_1$</td>
<td>646.3</td>
<td>458.3</td>
<td>457.0</td>
<td>636.77(3)$^e$</td>
</tr>
<tr>
<td>1$_1$</td>
<td>a$_1$</td>
<td>824.3</td>
<td>831.2</td>
<td>829.9</td>
<td>829.87(3)</td>
</tr>
</tbody>
</table>

a. Ref. (21)
b. Ref. (2)
c. Ref. (12).
d. This work
e. Statistical error only.
Table 2: Molecular constants$^a$ in units of cm$^{-1}$

<table>
<thead>
<tr>
<th></th>
<th>$A_F$</th>
<th>$B$</th>
<th>$C$</th>
<th>$F$</th>
<th>$V_6$</th>
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<tbody>
<tr>
<td>$\tilde{X}(^2B_2)$</td>
<td>0.18611</td>
<td>0.05044</td>
<td>0.03984</td>
<td>5.300</td>
<td>21</td>
</tr>
<tr>
<td>$\tilde{A}(^2A_2)$</td>
<td>0.17998</td>
<td>0.05023</td>
<td>0.03938</td>
<td>5.163</td>
<td>128.2</td>
</tr>
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a. Ref $(3,17)$
Table 3: Calculated Torsional Energy levels in units of cm$^{-1}$

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\tilde{A}^2A_2$ level</th>
<th>$\tilde{X}^2B_2$ level</th>
<th>$\Delta E_T$ $^a$</th>
<th>Relative Intensity$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0a'_1 - 0a'_1$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>$1e'' - 1e''$</td>
<td>4.050</td>
<td>5.264</td>
<td>-1.214</td>
<td>100</td>
</tr>
<tr>
<td>$2e' - 2e'$</td>
<td>14.605</td>
<td>20.978</td>
<td>-6.366</td>
<td>30</td>
</tr>
<tr>
<td>$3a''_2 - 3a''_2$</td>
<td>22.417</td>
<td>42.667</td>
<td>-20.250</td>
<td>6$^b$</td>
</tr>
</tbody>
</table>

a. Shift in transition frequency relative to the $0a'_1 - 0a'_1$.
b. Not included in the contour because it is sufficiently displaced. However, almost all the spectra show a weak feature at this position.
c. Estimated for simulation.
Table 4: Rotational Constants\textsuperscript{a} in units of cm\textsuperscript{-1} for $\tilde{A}(1a'_1)$ and $\tilde{X}(1a'_1)$.

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>$A_T$</th>
<th>$B$</th>
<th>$C$</th>
<th>$D_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{A}(1a'_1)$</td>
<td>0.17874</td>
<td>0.05023</td>
<td>0.03938</td>
<td>0</td>
</tr>
<tr>
<td>$\tilde{A}(2e'')$</td>
<td>0.17815</td>
<td>0.05023</td>
<td>0.03938</td>
<td>0.27520</td>
</tr>
<tr>
<td>$\tilde{A}(3e')$</td>
<td>0.17304</td>
<td>0.05023</td>
<td>0.03938</td>
<td>0.41566</td>
</tr>
<tr>
<td>$\tilde{X}(1a'_1)$</td>
<td>0.18606</td>
<td>0.05044</td>
<td>0.03984</td>
<td>0</td>
</tr>
<tr>
<td>$\tilde{X}(2e'')$</td>
<td>0.18604</td>
<td>0.05044</td>
<td>0.03984</td>
<td>0.36939</td>
</tr>
<tr>
<td>$\tilde{X}(3e')$</td>
<td>0.18559</td>
<td>0.05044</td>
<td>0.03984</td>
<td>0.73014</td>
</tr>
</tbody>
</table>

\textsuperscript{a} For $\tilde{A}(1a'_1)$ and $\tilde{X}(1a'_1)$ the values of $B$ and $C$ were obtained directly from ref. (2) while $A_T$ and $D_z$ were calculated from data within refs. (2) and (17). Slight adjustments to these values for vibrational variation were permitted to obtain the best simulations for the remaining levels.
Figure Captions

1. Molecular fixed axis system of \( p \)-xylyl. The orientation of the \( x \), \( y \), and \( z \) axis is consistent with Miller’s notation (3), also with the \( I \_) representation. \((x = b, y = c, \text{and } z = a)\)

2. Low resolution Fourier Transform Spectrum of the \( \tilde{A}^2A_2 - \tilde{X}^2B_2 \) transition of the \( p \)-xylyl radical.

3. High resolution Fourier Transform Spectra of several vibronic bands of the \( p \)-xylyl radical. The overall contours of the “460 band” and \( 1^0_1 \) band are similar to that of the \( 0^0_0 \) band, while the contour of the “640 band” is rather different.

4. The observed \( 0^0_0 \) band (above) and the corresponding \( b \)-type simulated band (below) of the \( p \)-xylyl radical. The rotational temperature is 45K and the parameters for the simulation are given in Tables 3 and 4. The prominent features in the spectrum correspond to rotational band heads (\( P \), \( Q \), and \( R \)) or for the \( e \) transitions just \( Q \) as indicated.

5. The observed “640 band” (above) and its simulation by an \( a \)-type band (below). The rotational temperature is 45K and the parameters for the simulation are given in Tables 3 and Table 4. As with Fig. 4 the rotational band heads corresponding to prominent features are indicated.

6. The observed “460 band” (above) and the simulation of the \( b \)-type band (below). The rotational temperature is 45K and the parameters for its simulation are given in Tables 3 and 4. Additional adjustments to
the simulation are described in the text. As with Fig. 4 the rotational band heads corresponding to prominent features are indicated.

7. A diagram demonstrating how Fermi resonance type interactions can cause the shifts of torsional levels with the same symmetry of the total wavefunction, $\Psi_{\text{tot}}$. The strongest interactions are shown by double arrows. The dotted lines indicate the energy level shift caused by the Fermi interaction. The Fermi interaction is greater when the energy difference between the same symmetry levels is smaller, resulting in differential shifts of the torsional levels.
Figure 1: Molecular fixed axis system of $p$-xylyl. The orientation of the $x$, $y$, and $z$ axis is consistent with the traditional choice of axes for these molecules (see Fig. 5, ref. 4) and also with the $I_r$ representation. ($x = b, y = c$, and $z = a$)
Figure 2: Low resolution Fourier Transform Spectrum of the $\tilde{A}^2A_2 - \tilde{X}^2B_2$ transition of the $p$-xylyl radical.
Figure 3: High resolution Fourier Transform Spectra of several vibronic bands of the $p$-xylyl radical. The overall contours of the “460 band” and $1^0_1$ band are similar to that of the $0^0_0$ band, while the contour of the “640 band” is rather different.
Figure 4: The observed $0^0_0$ band (above) and the corresponding $b$-type simulated band (below) of the $p$-xylyl radical. The rotational temperature is 45K and the parameters for the simulation are given in Tables 3 and 4. The prominent features in the spectrum correspond to rotational band heads ($P$, $Q$, and $R$ or for the $e$ transitions just $Q$) as indicated.
Figure 5: The observed “640 band” (above) and its simulation by an $a$-type band (below). The rotational temperature is 45K and the parameters for the simulation are given in Tables 3 and Table 4. As with Fig. 4 the rotational band heads corresponding to prominent features are indicated.
Figure 6: The observed “460 band” (above) and the simulation of the $b$-type band (below). The rotational temperature is 45K and the parameters for its simulation are given in Tables 3 and 4. Additional adjustments to the simulation are described in the text. As with Fig. 4 the rotational band heads corresponding to prominent features are indicated.
Figure 7: A diagram demonstrating how Fermi resonance type interactions can cause the shifts of torsional levels with the same symmetry of the total wavefunction, $\Psi_{tot}$. The strongest interactions are shown by double arrows. The dotted lines indicate the energy level shifted by the Fermi interaction. The Fermi interaction is greater when the energy difference between the same symmetry levels is smaller, resulting in differential shifts of the torsional levels.