Spectroscopic studies on methyl torsional behavior in 1-methyl-2(1H)-pyridone, 1-methyl-2(1H)-pyridinimine, and 3-methyl-2(1H)-pyridone. I. Excited state

Rajeev K. Sinha, B. Pradhan, S. Wategaonkar, Bhanu P. Singh, and T. Kundu

Citation: J. Chem. Phys. 126, 114312 (2007); doi: 10.1063/1.2566574
View online: http://dx.doi.org/10.1063/1.2566574
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v126/i11
Published by the American Institute of Physics.
Spectroscopic studies on methyl torsional behavior in 1-methyl-2(1H)-pyridone, 1-methyl-2(1H)-pyridinimine, and 3-methyl-2(1H)-pyridone. I. Excited state

Rajeev K. Sinha, B. Pradhan, S. Wategaonkar, a) Bhanu P. Singh, and T. Kundu b)
Department of Physics, Indian Institute of Technology Bombay, Mumbai-400076, India

(Received 16 October 2006; accepted 17 January 2007; published online 21 March 2007)

The laser induced fluorescence excitation and dispersed fluorescence spectra of three nitrogen heterocyclic molecules 1-methyl-2(1H)pyridone (1MPY), 1-methyl-2(1H)pyridinimine (1MPI), and 3-methyl-2(1H)pyridone (3MPY) have been studied under supersonic jet cooled condition. The methyl torsional and some low frequency vibrational transitions in the fluorescence excitation spectrum were assigned for 1MPY. These new assignments modify the potential parameters to the methyl torsion reported earlier. Some striking similarities exist between the torsional and vibrational transitions in the fluorescence excitation spectra of 1MPY and 1MPI. Apart from pure torsional transitions, a progression of vibration-torsion combination bands was observed for both these molecules. The excitation spectrum of 3MPY resembles the spectrum of its parent molecule, 2-pyridone. The barrier height of the methyl torsion in the excited state of 3MPY is highest amongst all these molecules, whereas the barrier in 1MPI is higher than that of 1MPY. To get an insight into the methyl torsional barrier for these molecules, results of the ab initio calculations were compared with the experimental results. It was found that the conformation of the methyl group undergoes a 60° rotation in the excited state in all these molecules with respect to their ground state conformation. This phase shift of the excited state potential is attributed to the π*-ω′ hyperconjugation between the out-of-plane hydrogen of the methyl group and the molecular frame. It has been inferred that the change in lowest unoccupied molecular orbital energy plays the dominant role in the excited state barrier formation. © 2007 American Institute of Physics.

I. INTRODUCTION

Methyl group in a methylated molecule has the ability to undergo large amplitude quantized motion under the influence of the periodic potential arising from the local electronic structure. This hindered motion of the methyl group plays an important role in the intramolecular and the photochemical dynamics of organic molecules. The minimum energy conformation and the barrier to the internal rotation of the methyl group strongly depend on various electronic interactions present in the molecule. In many cases, it was observed that the nature of the torsional potential changed drastically upon electronic excitation.

The azines or azabenzenes constitute a valuable and important series of compounds for both practical and theoretical interests. Since the process of internal rotation has its importance in many chemical and biological processes, studies of the structural and electronic characteristics of azaheterocycles assume great significance. The methyl substitution has a dramatic effect on the photophysics of the molecules, and thus, spectroscopic studies provide an excellent opportunity to explore the effects that the position of the methyl substitution and the electronic structure have on the characteristics of the methyl torsion. A few methyl substituted azabenzenes, both monocyclic as well as polycyclic azines, have been investigated in this regard. The low frequency vibration of the methyl group in 2-methyl pyridine and 4-methyl pyridine was studied by Rudolph and co-workers using microwave spectroscopy. The methyl torsional barrier in 4-methyl pyridine is in correspondence to that of toluene with a nearly free rotor character ($V_0^*=4.75$ cm$^{-1}$) in the ground electronic state, whereas in 2-methyl pyridine the threefold term ($V_0^*=90$ cm$^{-1}$, $V_6^*=-4.13$ cm$^{-1}$) appears due to the symmetry reduction of this molecule. Mass resolved excitation spectroscopic studies of 2-methyl pyridine under jet cooled condition by Seeman et al. did not show any Franck-Condon (FC) activity of the large amplitude motion in the excited state. The ab initio calculated potential barrier ($V_0^*=90$ cm$^{-1}$) by Kawamura et al. was in agreement for the ground state, but the estimated excited state potential using configuration interaction singles (CIS) calculation showed a large increment in the barrier energy ($V_0^*\approx768$ cm$^{-1}$) for this molecule. Caminati et al. had studied monocyclic highly symmetric diazines, namely, 5-methyl pyrimidine and 2-methyl pyrimidine using microwave spectroscopy. Both the molecules show a toluenelike character with $V_0^*\approx1.56$ cm$^{-1}$ for 2-methyl pyrimidine and $V_0^*\approx4.1$ cm$^{-1}$ for 5-methyl pyrimidine in the ground states. Later, Bandy et al. investigated these two molecules using laser induced fluorescence (LIF) excitation and single vibrational level fluorescence spectro-
copy, but failed to observe any low frequency torsional band in the excited state. However, on the basis of the high resolution spectrum of the origin band, a very little change in the excited state potential barrier was predicted. On the other hand, in 4-methyl pyrimidine it was observed that the methyl torsional barrier in the ground state \( V^*_3 = 95 \text{ cm}^{-1} \) increased drastically in the excited state \( V^*_{3} = 740 \text{ cm}^{-1} \), but no conformational change was observed. The \textit{ab initio} calculated barrier heights \( V^*_3 = 87 \text{ cm}^{-1} \) for the ground state and \( V^*_{3} = 746 \text{ cm}^{-1} \) for the excited state are in good agreement with the experiment.5 Another well studied monocyclic diazine, 2-methylpyrazine, was investigated by Tomer \textit{et al.}6 using LIF spectroscopy under jet cooled conditions. In this case also the torsional potential \( V^*_3 = 105 \text{ cm}^{-1} \) increases to \( V^*_{3} = 465 \text{ cm}^{-1} \) upon electronic excitation. The methyl group substituted at different positions in indole, a bicyclic monoazine, was investigated by Bickel \textit{et al.}7 using resonantly enhanced multiphoton ionization spectroscopy. From the positional dependence of the torsional potential studies, it was concluded that the changes in the torsional potential upon electronic excitation could be interpreted as arising from the changes in the electron density adjacent to the methyl rotor. From a systematic theoretical study on several methyl azabenzenes, Kawamura \textit{et al.}8 found a quasilinear correlation between the rotational barrier of the methyl group in the excited state and the splitting between the lowest and the next lowest unoccupied molecular orbitals. Experimental difficulty for these azabenzenes lies in the detection of fluorescence due to its low quantum yield, a consequence of fast nonradiative (internal conversion and intersystem crossing) processes arising from the existence of close lying \( \pi-\pi^* \) and \( n-\pi^* \) states.

In this article, we present the spectroscopic studies of three azines, namely, 1-methyl-2(1H)-pyridinidine (1MPI), 1-methyl-2(1H)-pyridone (1MPY), and 3-methyl-2(1H)-pyridone (3MPY). Molecular structures of these molecules are shown in Fig. 1. 1-methyl-2(1H)-pyridinidine (1MPI) is a stabilized imino form of pyridinidine obtained by substituting a methyl group on a ring nitrogen atom. In both 1MPI and 1MPY, the methyl group is connected to two vicinal single bonds, whereas in 3MPY the methyl group is attached to the ring carbon atom and has one single and one double bond vicinal to it. 1MPI has been studied by UV-visible and infrared spectroscopies. Traore \textit{et al.}12 carried out ultraviolet absorption and fluorescence studies of 1MPI in a solution phase. Inuzuka \textit{et al.}13 studied the IR spectrum of 1-MPI in solution and carried out the normal coordinate analysis for the assignments of the vibrational structures in the ground state. More recently, the laser induced fluorescence spectra of supersonic jet cooled \textit{J. Chem. Phys.} 126, 114312 (2007) facilitated ease of assignments of the ground state normal modes. However, no effort has been made towards the study of methyl internal potential barrier in 1MPI. Features of the IR spectrum of 1-MPI were found to exhibit a similarity with that of 1MPY.16 Recently, Pradhan \textit{et al.}17 studied 1-methyl-2(1H)-pyridone (1MPY) in supersonic jet cooled molecular beam by using fluorescence excitation (FE) and dispersed fluorescence (DF) spectroscopies along with quantum chemical calculations and successfully assigned the observed bands in the ground electronic state and a few bands in the excitation spectrum based on observed DF spectra upon excitation of these bands.

Here, we have investigated the DF spectra of few more bands in the excitation spectrum of 1MPY. On the basis of this experimental result, we have carried out the torsional and vibrational assignments for the transitions observed in the FE spectrum. We also present the FE spectra of supersonic jet cooled 1MPI. In view of the similarities in the spectral features of 1MPY and 1MPI, we have used the excitation spectrum of 1MPY to explain the observed bands in the excitation spectrum of 1MPI. The methyl torsional potential shape and the barrier for 1MPY and 1MPI in both the ground and the first excited states have been extracted and compared with the aid of quantum chemical calculation. Excitation spectrum of 3MPY is also presented here to understand the differences in the excitation spectrum with respect to 1MPY. It has also been examined in the light of excitation spectrum of 2-pyridone.

\section*{II. Experimental Section}

2-pyridinidine, 1MPY, and 3MPY were purchased from Aldrich Chemical Company. 1MPI was prepared from 2-pyridinidine by using the method described by Young \textit{et al.}, whereas 1MPY and 3MPY were used without further purification. The fluorescence excitation experiment was performed using a free jet expansion system under vacuum \( \sim 3 \times 10^{-5} \) to \( 1 \times 10^{-4} \) torr. The sample vapor seeded in He at 1–2 atm was expanded into the vacuum chamber through a pulsed nozzle valve (0.4 mm diameter). A nanosecond Nd:YAG (yttrium aluminum garnet) laser pumped dye laser was used for the excitation of the molecules. Excitation wavelengths in the region of interest were obtained by an appropriate frequency conversion of the dye laser radiation (second harmonic and its mixing with the fundamental of the Nd:YAG laser). Integrated fluorescence of the given molecule was detected by photomultiplier tube in combination with a filter. The signal was digitized and averaged using a digital storage oscilloscope. The dispersed fluorescence was recorded using a monochromator and a cooled charge coupled device detector. The typical resolutions of the dispersed fluorescence spectra were \( 6–7 \text{ cm}^{-1} \).
III. RESULTS AND DISCUSSION

A. FE spectra and assignments

1. 1-methyl-2(1H)pyridone (1MPY)

The molecule 1MPY has 39 normal modes accompanying 26 in-plane \((a_i)\) and 13 out-of-plane \((a_e)\) normal modes under the \(G_6\) molecular symmetry group.\(^{18,19}\) The fluorescence excitation spectrum of 1MPY is shown in Fig. 2(a). In our earlier work,\(^{17}\) the observed band at 29 822.3 cm\(^{-1}\) was assigned as \(S_0 \rightarrow S_1\) \((O_e^0)\) of the \(\pi-\pi^*\) transition. The other bands at 86 and at 120 cm\(^{-1}\) relative to this \(O_e^0\) band were assigned as the methyl torsional transitions to \(2e\) and \(3a_t\) levels, respectively, from the ground zero point energy state, and the band at 172 cm\(^{-1}\) was assigned to the \(34_1\) ring deformation vibrational mode in the excited state. These assignments were based on the observed transitions from these bands allowed to the ground state torsional energy levels \(2e\) at 99 cm\(^{-1}\), \(3a_t\) at 162 cm\(^{-1}\), \(4e\) at 175 cm\(^{-1}\), \(5e\) at 223 cm\(^{-1}\), and \(6a_t\) at 271 cm\(^{-1}\) in the dispersed fluorescence spectra. The potential of the methyl torsion in the excited state was obtained with \(V_e'=164\) cm\(^{-1}\), \(V_a'=40\) cm\(^{-1}\), and \(F=5.2\) cm\(^{-1}\) by fitting these \(2e\) (86 cm\(^{-1}\)) and \(3a_t\) (120 cm\(^{-1}\)) levels. However, the predicted transitions to \(4e\) (142.7 cm\(^{-1}\)) and \(5e\) (185 cm\(^{-1}\)) levels were not observed in the FE spectrum. Although the calculated Franck-Condon (FC) intensity distributions for the transitions from \(0a_t\), \(1e\), and \(2e\) levels of the excited state to the ground state torsional levels were in good agreement with the observed ones, they failed to predict that from the \(3a_t\) band. These discrepancies prompted us to investigate other observed bands in the FE spectrum further. To understand the nature of these bands, we examined the dispersed fluorescence spectra upon excitation of bands located at 203.0, 285.0, 313.0, 351.0, and 359.0 cm\(^{-1}\) with respect to \(O_e^0\), as shown in Fig. 3. Table I presents the assignments of spectral features observed in these DF spectra on the basis of frequency calculations as well as the FC intensity calculations for the torsional levels of this molecule. The DF spectrum obtained by exciting the \(O_e^0+203\) cm\(^{-1}\) band shows a progression of the torsional bands of the \(e\) symmetry along with vibrational bands and their overtones. The intensity of transition to the \(4e\) torsional level is largest, and its intensity distribution bears similarity to that from the \(2e\) band (86 cm\(^{-1}\)) of the excited state in the DF spectrum. The DF spectrum from \(O_e^0+313\) cm\(^{-1}\) and \(O_e^0+359\) cm\(^{-1}\) also show a similar progression of \(e\) symmetry torsional bands and other vibrational bands. This kind of transitions indicates that these bands in the excitation spectrum are either bands of the \(e\) symmetry of torsional mode or a combination of the \(e\) symmetry torsional band with other vibrational modes. The DF spectrum of the band at \(O_e^0+285\) cm\(^{-1}\) shows the progression of the vibrational bands as well as the torsional bands of both \(a\) and \(e\) symmetries. Since \(a\) to \(e\) transition is symmetry forbidden and the linewidth of this band is higher than the other bands, we speculate that there is an overlap of two bands of \(a\) and \(e\) symmetries. The next band at \(O_e^0+351\) cm\(^{-1}\) does not have FC activity with any of the torsional levels of the ground state. The appearance of this band could be due to the vibrational mode in the excited state that is not coupled with the torsional motion.

From the above observations, bands located at 86 cm\(^{-1}\)(2e), 172 cm\(^{-1}\)(3a_t), 261 cm\(^{-1}\)(5e), and 307 cm\(^{-1}\)(6a_t) could be assigned as a progression of methyl torsional transitions building upon \(O_e^0\) electronic origin. These bands were fitted to obtain the excited state torsional parameters \(V_e'=313\) cm\(^{-1}\), \(V_a'=-60\) cm\(^{-1}\), and \(F=5.29\) cm\(^{-1}\). A comparison of the calculated and experimentally observed torsional frequencies is presented in Table II (progression 1). Assignment for most of the bands could fit into this scheme except the 4e band that was not observed. The absorption spectrum of 1MPY in solution\(^{30}\) shows a vibrational band associated with the first \(\pi-\pi^*\) state located at 334 nm, that is, 118 cm\(^{-1}\) away from the observed \(O_e^0\) band at 29 822 cm\(^{-1}\).

In 2-methyl pyridine, although the methyl group activity was not seen in the mass resolved excitation spectrum, the low frequency band observed at 120.6 cm\(^{-1}\) was assigned as a vibronic band.\(^4\) The band at 120 cm\(^{-1}\) in the FE spectrum is...
thus assigned as the second low frequency vibration \((38^1_0)\) of the excited state. The atomic displacements corresponding to this mode shown in Fig. 4a reveal that this vibrational mode includes out-of-plane ring deformation coupled with methyl torsional motion. The optimized geometry with this mode includes out-of-plane ring deformation coupled with the torsional motion. The bands at 203, 285, and 359 cm\(^{-1}\) respectively, most of the out-of-plane vibrations get coupled with the torsional motion. The bands at 203, 285, and 359 cm\(^{-1}\) which are 83, 165, and 239 cm\(^{-1}\) away, respectively, from this vibrational band are assigned as combination bands with torsional progressions \(2e\), \(3a_1\), and \(5e\). Both 203 and 359 cm\(^{-1}\) bands show \(e\) progression, whereas the 285 cm\(^{-1}\) band shows \(a_1\) progression in the DF spectra, as listed in Table I. We have assigned the 203 cm\(^{-1}\) band as a vibration-2e combination band because its FC activity with the ground state torsional bands seen in the DF spectra is in close agreement with the calculated FC intensity pattern for the 2e band. This torsional progression yields the potential parameters \(V'_1=288\) cm\(^{-1}\), \(V'_2=-47\) cm\(^{-1}\), and \(F=5.04\) cm\(^{-1}\). A comparison of the observed and the fitted energy values is given in Table II as progression 2. The band at 233 cm\(^{-1}\) is assigned to the first overtone \((38^2_1)\) of the vibrational band \((38^0_1)\) at 120 cm\(^{-1}\), whereas the 313 cm\(^{-1}\) band is assigned as a combination band \((38^2_0, 2e)\) because it exhibits \(e\) progression in its DF spectrum (Table I). Since the DF spectrum upon excitation of the 285 cm\(^{-1}\) band shows both \(a_1\) and \(e\) torsional progressions, this could originate from the existence of the \(e\) torsional combination band with another vibration. This prompted us to assign the 196 cm\(^{-1}\) band as the third vibrational mode \((37^1_0)\) in the excited state and the transition at 285 cm\(^{-1}\) as a \(37^1_0, 2e\) combination band. The atomic displacements of this vibrational mode [Fig. 4b] also show ring out-of-plane vibration and methyl torsional motion. The DF spectrum of 351 cm\(^{-1}\) did not show any torsional progression, and hence, we assign this band as the fourth vibrational mode \((36^1_0)\) in the excited state. Assignments of these observed bands in the FE spectrum are listed in Table III.

### Table I. Assignments of observed bands in dispersed fluorescence spectra of 1MPY.

<table>
<thead>
<tr>
<th>Excitation at (O^1_2 + 203) cm(^{-1}) (30 025 cm(^{-1}))</th>
<th>Excitation at (O^1_2 + 285) cm(^{-1}) (30 107 cm(^{-1}))</th>
<th>Excitation at (O^1_2 + 313) cm(^{-1}) (30 135 cm(^{-1}))</th>
<th>Excitation at (O^1_2 + 351) cm(^{-1}) (30 174 cm(^{-1}))</th>
<th>Excitation at (O^1_2 + 359) cm(^{-1}) (30 181 cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative separation (cm(^{-1}))</td>
<td>Ground state levels</td>
<td>Relative separation (cm(^{-1}))</td>
<td>Ground state levels</td>
<td>Relative separation (cm(^{-1}))</td>
</tr>
<tr>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>98</td>
<td>2e</td>
<td>96</td>
<td>2e</td>
<td>98</td>
</tr>
<tr>
<td>150</td>
<td>(\nu_{38})</td>
<td>137</td>
<td>(\nu_{38})</td>
<td>235</td>
</tr>
<tr>
<td>173</td>
<td>4e</td>
<td>162</td>
<td>3a_1</td>
<td>305</td>
</tr>
<tr>
<td>203</td>
<td>(\nu_{57})</td>
<td>232</td>
<td>(\nu_{52} 2e)</td>
<td>446</td>
</tr>
<tr>
<td>219</td>
<td>(\nu_{32})</td>
<td>266</td>
<td>6a_1</td>
<td>553</td>
</tr>
<tr>
<td>231</td>
<td>5e</td>
<td>279</td>
<td>2p_{18}</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>(2\nu_{38})</td>
<td>307</td>
<td>(\nu_{52} 2e)</td>
<td></td>
</tr>
<tr>
<td>378</td>
<td>(\nu_{57})</td>
<td>346</td>
<td>(\nu_{57} 2p_{38})</td>
<td></td>
</tr>
<tr>
<td>395</td>
<td>(\nu_{35})</td>
<td>369</td>
<td>2p_{38} 2e</td>
<td></td>
</tr>
<tr>
<td>413</td>
<td>(\nu_{35})</td>
<td>399</td>
<td>(\nu_{35})</td>
<td></td>
</tr>
<tr>
<td>429</td>
<td>(2\nu_{57})</td>
<td>432</td>
<td>(2\nu_{57})</td>
<td></td>
</tr>
<tr>
<td>522</td>
<td>(2\nu_{52} 2e)</td>
<td>460</td>
<td>(\nu_{53})</td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>(\nu_{32})</td>
<td>503</td>
<td>(\nu_{35} 2p_{38})</td>
<td></td>
</tr>
<tr>
<td>553</td>
<td>(\nu_{32})</td>
<td>535</td>
<td>(\nu_{35} 2p_{38})</td>
<td></td>
</tr>
</tbody>
</table>

### Table II. Comparison between calculated and observed torsional frequencies of methyl group in 1MPY.

<table>
<thead>
<tr>
<th>Progression 1</th>
<th>Progression 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torsional energy levels</td>
<td>Calc. (cm(^{-1}))</td>
</tr>
<tr>
<td>2e</td>
<td>86</td>
</tr>
<tr>
<td>3a_{12}</td>
<td>87</td>
</tr>
<tr>
<td>3a_1</td>
<td>175</td>
</tr>
<tr>
<td>4e</td>
<td>181</td>
</tr>
<tr>
<td>5e</td>
<td>253</td>
</tr>
<tr>
<td>6a_{12}</td>
<td>283</td>
</tr>
<tr>
<td>6a_1</td>
<td>312</td>
</tr>
</tbody>
</table>

\(V'_1=313\) cm\(^{-1}\), \(V'_2=-60\) cm\(^{-1}\), \(F=5.29\) cm\(^{-1}\) 
\(V'_1=288\) cm\(^{-1}\), \(V'_2=-47\) cm\(^{-1}\), \(F=5.04\) cm\(^{-1}\)

Downloaded 01 Mar 2012 to 14.139.97.76. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions
To ascertain the above assignments we have calculated the FC factor of only torsional transitions and torsion-vibration (381\textsuperscript{1}) combination band intensities normalized with the observed intensity of the 38\textsubscript{0}\textsuperscript{0} transition. We have used the wave functions obtained from energy level calculations with \(V'_{\text{s}}=313\text{ cm}^{-1}\), \(V'_{\text{o}}=-60\text{ cm}^{-1}\), and \(F=5.29\text{ cm}^{-1}\) for progression 1; \(V'_{\text{s}}=288\text{ cm}^{-1}\), \(V'_{\text{o}}=-47\text{ cm}^{-1}\), and \(F=5.04\text{ cm}^{-1}\) for progression 2; and \(V'_{\text{s}}=244\text{ cm}^{-1}\), \(V'_{\text{o}}=15\text{ cm}^{-1}\), and \(F=5.2\text{ cm}^{-1}\) for the ground state\textsuperscript{17} to calculate the FC factor. The shift of the potential between the excited state and the ground state for both the progressions has been taken to be \(60^\circ\) as observed previously. Using a Lorentzian line shape to model the spectrum we have simulated the excitation spectrum presented in Fig. 2(b) shows very good agreement with the observed one.

2. 1-methyl-2(1H)pyridinimine (1MPI)

The molecule 1MPI has 42 fundamental vibrational modes with 28 in-plane \((\alpha_1)\) and 14 out of plane \((\alpha_2)\) under the \(G_6\) molecular symmetry group.\textsuperscript{18,19} The power normalized FE spectrum of jet cooled 1MPI in the spectral region of the first excited state is shown in Fig. 5(a). Observed transitions and their frequency displacements from the first band in the spectrum are listed in Table \textbf{III}. The first peak at 24 899.9 cm\(^{-1}\) is assigned to the \(S_0 \rightarrow S_1\) \((O'\text{\textsubscript{0}})\) electronic origin transition, which is in good agreement with the earlier reported value (24 899.2 cm\(^{-1}\)). The weak origin transition is apparently due to the shift in the excited state potential energy surface with respect to that of the ground state. As compared to 1MPI, the \(O'\text{\textsubscript{0}}\) band is redshifted by 4922 cm\(^{-1}\) in this case due to the replacement of the oxygen atom by the N-H group. The solution phase study\textsuperscript{12} of 1MPI shows that the \(S_1\) state is of \(\pi\pi^*\) character. Molecular orbital calculation\textsuperscript{21} also confirms the lower electronic excited state to be of \(\pi\pi^*\) character. We, therefore, assign this \(O'\text{\textsubscript{0}}\) band to the \(\pi \rightarrow \pi^*\) transition.

The spectrum exhibits many features common with the excitation spectrum of 1MPY. However, it is less congested. There are 14 clearly observed bands below 400 cm\(^{-1}\), whereas in the case of 1MPI it is more than 30. Both these spectra display a weak origin transition followed by strong vibronic bands. The vibrational structure abruptly disappears beyond 400 cm\(^{-1}\) from the \(O'\text{\textsubscript{0}}\) transition in both cases. There exists a striking similarity between the vibrational bands in

![Image](114312-5)

FIG. 4. Atomic displacements of (a) the \(\nu_{\text{16}}\) vibrational mode and (b) the \(\nu_{\text{17}}\) vibrational mode of 1MPY in the excited state.

![Image](114312-6)

FIG. 5. FE spectra of 1MPI. (a) Experimental and (b) simulated (see text). The \(O'\text{\textsubscript{0}}\) band is at 24 899.9 cm\(^{-1}\).

\begin{table}[h]
\centering
\caption{Assignments of the observed bands in fluorescence excitation spectra of 1MPY and 1MPI.}
\begin{tabular}{|l|l|l|}
\hline
\textbf{Peak positions} & \textbf{Relative separation} & \textbf{Assignment} \\
(cm\(^{-1}\)) & (cm\(^{-1}\)) & \\
\hline
29 822.3 & 0.0 & \text{Origin} \\
29 844.6 & 22 & \\
29 908.2 & 86 & \(\tau_{\text{te}}\) \\
29 942.6 & 120 & \(3\text{8}_1\) \(\nu_{\text{18}}\) \\
29 994.5 & 172 & \(\tau_{\text{te}}\) \(\delta_{\text{e11}}\) \\
30 018.8 & 196 & \(3\text{7}_0\) \(\nu_{\text{20}}\) \\
30 025.7 & 203 & \(3\text{8}_1\) \(\nu_{\text{18}}\) \\
30 030.9 & 209 & \\
30 055.3 & 233 & \(3\text{8}_1\) \(\nu_{\text{18}}\) \\
30 083.1 & 261 & \(\tau_{\text{te}}\) \(\nu_{\text{18}}\) \\
30 107.5 & 285 & \(3\text{8}_1\) \(\nu_{\text{18}}/3\text{7}_1\) \(\nu_{\text{20}}\) \\
30 129.3 & 307 & \(\delta_{\text{e11}}\) \(\nu_{\text{18}}\) \\
30 155.3 & 313 & \(3\text{8}_1\) \(\nu_{\text{18}}\) \\
30 174.0 & 351 & \(3\text{6}_0\) \(\nu_{\text{16}}\) \\
30 181.0 & 359 & \(3\text{8}_1\) \(\nu_{\text{18}}\) \\
30 195.0 & 373 & \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Assignments of the observed bands in fluorescence excitation spectra of 1MPY and 1MPI.}
\begin{tabular}{|l|l|l|}
\hline
\textbf{Peak positions} & \textbf{Relative separation} & \textbf{Assignment} \\
(cm\(^{-1}\)) & (cm\(^{-1}\)) & \\
\hline
24 899.9 & 0.0 & \text{Origin} \\
24 996.0 & 96 & \(\tau_{\text{te}}\) \\
25 025.0 & 125 & \(4\text{1}_0\) \\
25 092.9 & 193 & \(\tau_{\text{te}}\) \(\delta_{\text{e11}}\) \\
25 117.3 & 217 & \(4\text{1}_0\) \(\nu_{\text{18}}\) \\
25 148.1 & 248 & \(4\text{1}_0\) \(\nu_{\text{18}}\) \\
25 286.5 & 386 & \(4\text{1}_0\) \(\nu_{\text{18}}\) \\
25 298.8 & 398 & \(3\text{9}_0\) \(\nu_{\text{18}}\) \\
\hline
\end{tabular}
\end{table}
both the spectra, except for a few. Therefore, taking the spectrum of 1MPY as a basis, we have assigned the bands in the excitation spectrum of 1MPI. The 22 cm\(^{-1}\) band seen in 1MPY is absent in the 1MPI spectrum. Like 1MPY, several transitions in the FE spectrum belong to the methyl torsional mode. Remaining transitions are FC allowed in-plane or out-of-plane vibrations. Torsion-vibration combination bands are also found active in this spectrum. Transition frequencies and their corresponding assignments are presented in Table III. A progression for bands at 96, 193, and 278 cm\(^{-1}\) was identified with the methyl torsional transitions. The potential parameters for the excited state, \(V'_1=358\text{ cm}^{-1}, V'_6=-57\text{ cm}^{-1}\), and \(F=5.31\text{ cm}^{-1}\), were obtained from the best fit to the methyl torsional transitions. A comparison between calculated and the observed frequencies is given in Table IV (progression 1). The threefold potential term here is higher than that of 1MPY, while the sixfold term remains almost similar in magnitude. The 4\(e\) transition is found to be absent in this case as well.

Similar to the 120 cm\(^{-1}\) band in 1MPY, a band is observed at 125 cm\(^{-1}\) in the 1MPI spectrum. This band can also be assigned to another low frequency vibration. \textit{Ab initio} frequency calculation for excited state at the CIS/6-31G\((d,p)\) level predicts four vibrations besides methyl torsion to lie below 400 cm\(^{-1}\). Amongst these, three are out-of-plane vibrations \((\alpha_2\) symmetry under \(G_0)\) and one is an in-plane vibration \((a_1)\). The vector displacements of the first four normal modes with calculated frequencies are shown in Fig. 6. The band at 125 cm\(^{-1}\) could be attributed to the transition to the fundamental of the \(\nu_{41}\) \((41^0)\) mode with its calculated value of 110 cm\(^{-1}\). Though the transitions to \(a_2\) fundamentals have a rigorously vanishing FC factor, such transitions can gain intensity if it is either coupled with the torsion or if the molecular frame undergoes distortion to relax symmetry restrictions. As it is evident in Fig. 6, the vector displacements of atoms for this mode encompass the torsional motion with the out-of-plane ring vibration. Excited state geometry also indicates a heavy distortion in the planarity of the molecular frame\(^{21}\) and thus corroborates our observation. The assignment of band at 125 cm\(^{-1}\) to the \(41^0\) transition allows us to infer that the bands at 217, 310, and 386 cm\(^{-1}\) are the torsion-vibration combination bands. The torsional frequencies of the bands which appear as combinations with \(41^0\) are 92, 185, and 261 cm\(^{-1}\). These frequencies were fitted to obtain the torsional parameters \(V'_1=333.2\text{ cm}^{-1}, V'_6=-45.2\text{ cm}^{-1}\), and \(F=5.04\text{ cm}^{-1}\). Calculated frequencies and the corresponding experimental ones are grouped in Table IV as progression 2. The 248 cm\(^{-1}\) band could be assigned as the first overtone of \(\nu_{41}\) \((41^0)\) or the transition to the fundamental of \(\nu_{40}\) \((40^0)\), and the band at 335 cm\(^{-1}\) could be a \(2e\) combination band with this vibration. The band at 296 cm\(^{-1}\) has been identified as a \(39^0\) transition.

To ascertain the above assignment, dispersed fluorescence spectra for the first few bands near origin were recorded. However, we were unable to capture any distinct bands up to 1000 cm\(^{-1}\) beyond laser excitation within our experimental sensitivity limit. A close inspection reveals few weak features in these spectra. With the help of \textit{ab initio} calculation we derived the ground state torsional potential parameters. Using potential parameters obtained from different levels of theory, torsional energy levels were calculated and matched with the observed transitions. An observed weak feature at 264 cm\(^{-1}\) in the emission spectrum upon excitation of band at 217 cm\(^{-1}\) closely matches with the 3\(a_1\) and 4\(e\) transitions calculated using the potential obtained with the Hartree-Fock (HF)/6-31G\((d,p)\) level (Table V). As the emission originates from the 217 cm\(^{-1}\) band excitation

![FIG. 6. Atomic displacements of four low frequency normal modes of 1MPI in the excited state at the CIS/6-31G\((d,p)\) level of calculation.](image-url)
which is assigned as a $2e$ torsion transition in combination with $41_0^1$, it is unlikely that the 264 cm$^{-1}$ band in the DF spectrum is $3a_1$. The transition from $2e \rightarrow 4e$ is symmetry allowed and the transition to the $4e$ level should be intense, as observed in the case of 1MPy. Therefore, the band at 264 cm$^{-1}$ can be assigned as a $4e$ torsional energy level in the $S_0$ state. However, only this observed band will not be sufficient to extract the torsional potential. We consider the potential to be $V_e^e=454$ cm$^{-1}$ and $V_e^d=31$ cm$^{-1}$ for the ground state as predicted by the HF/6-31G($d,p)$ level calculation for further discussion. With these potential parameters for the ground state along with those obtained experimentally for the excited state, simulated excitation spectrum presented in Fig. 5(b) is obtained with a 60$^\circ$ shift between the minima of the excited and the ground states. Although it shows close agreement with the observed one, a few discrepancies in intensity could be due to the use of pure torsional wave functions for the calculation of FC factors.

It is quite surprising that despite large total fluorescence intensity, dispersed fluorescence spectra lack any prominent features in the low frequency region. Our investigation into this quandary reveals that 70% of the fluorescence was emitted above 450 nm by the excitation of all these bands. Higher quantum efficiency of fluorescence at longer wavelength could be due to the existence of another electronic level below the $\pi\pi^*$ level. Ab initio calculation predicts that there exist three $n\pi^*$ singlet states between the first and second $\pi\pi^*$ singlet states, and these lie close to the $\pi\pi^*$ state. Generally, in the case of $N$-heterocyclic compounds, the singlet excited states $\pi\pi^*$ and $n\pi^*$ are close to each other in energy, and methyl substitution often changes their relative separation. Like 1MPy, where a complicated vibronic structure and anomalous vibronic bands in the excitation spectrum predict the existence of a low lying $n\pi^*$ state, 1MPI may also be containing one of the $n\pi^*$ states below the $\pi\pi^*$. Lack of emission much above the origin due to the activation of radiationless processes gives some evidence to this assignment.

### 3. 3-methyl-2(1H)pyridone (3Mpy)

The fluorescence excitation spectrum of 3Mpy in the 400 cm$^{-1}$ region of the $S_0 \rightarrow S_1$ transition is shown in Fig. 7. The peak positions and relative frequencies of the observed transitions are given in Table VI. The observed bands in the spectrum appear to be broad because of inadequate rotational cooling in the jet. Change in the backing pressure permissible in our experimental setup did not improve the cooling condition. The strong feature at 30 355 cm$^{-1}$ is assigned as the $S_0 \rightarrow S_1 (O_0^0)$ electronic origin transition. This transition is 525 cm$^{-1}$ blueshifted as compared to that in the case of 2-pyridone. While the substitution of the methyl group at the nitrogen atom in the case of 1Mpy does not bring about any change in excitation energy, substitution at ring carbon causes destabilization by raising the electronic energy of the excited state. There are many weak features seen close to the $O_0^0$ band, which may be due to the hot bands resulting from improper cooling. The spectral features resemble more the 2-pyridone than the 1Mpy excitation spectrum. Unlike

### TABLE VI. Assignments of the observed bands in fluorescence excitation spectrum of 3Mpy.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Peak positions (cm$^{-1}$)</th>
<th>Relative separation (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30 355</td>
<td>0.0</td>
<td>Origin (1)</td>
</tr>
<tr>
<td>2</td>
<td>30 441</td>
<td>86</td>
<td>Origin (2)</td>
</tr>
<tr>
<td>3</td>
<td>30 480</td>
<td>125</td>
<td>$r_{11}^1$</td>
</tr>
<tr>
<td>4</td>
<td>30 500</td>
<td>145</td>
<td>$37_0^1$</td>
</tr>
<tr>
<td>5</td>
<td>30 546</td>
<td>191</td>
<td>Origin (2)+$r_{11}^1$</td>
</tr>
<tr>
<td>6</td>
<td>30 566</td>
<td>211</td>
<td>···</td>
</tr>
<tr>
<td>7</td>
<td>30 588</td>
<td>233</td>
<td>$3a_1$</td>
</tr>
</tbody>
</table>
1MPY, here the $O_0^0$ transition is found to be very intense and the spectrum is less congested. An equally strong band is seen at 86 cm$^{-1}$ from the $S_0 \rightarrow S_1 (O_0^0)$ transition. Two similar intense transitions with 100 cm$^{-1}$ separation were also seen in the excitation spectrum of 2-pyridone. These were interpreted as two different electronic origins corresponding to two structural isomers in the excited state. Following this, the band at 86 cm$^{-1}$ is assigned as another electronic origin. We could not record dispersed fluorescence spectra for 3MPY because of its low fluorescence quantum yield. Modest scale \textit{ab initio} calculation often predicts correctly the ground state methyl torsional potential energy barrier as established for several other similar molecules. Hence, further analysis is based on the HF/6-31G(d,p) \textit{ab initio} calculated barrier.

**B. Methyl torsional potential**

In 1MPY, the excited state torsional potential is 60° out of phase with respect to that of the ground state. This phase shift in the torsional potential was explained successfully on the basis of nonconventional $\pi^* - \sigma^*$ hyperconjugation, introduced originally by Nakai \textit{et al.} The FE spectrum of 1MPI also indicates the change in conformation of the methyl group upon excitation. In order to investigate the phase shift as well as the barrier height theoretically, the geometry of this molecule was optimized in both $S_0$ and $S_1$ states using HF and CIS methods, respectively, with the 6-31G(d,p) basis set. The optimized geometries are shown in Fig. 9. The minimum energy conformation of the methyl group in the $S_0$ state is staggered with the in-plane C–H bond placed away from the N–H group. On the other hand, in the $S_1$ state, the methyl group is 60° out of phase with respect to the $S_0$ state and acquires eclipsed conformation with the in-plane C–H bond towards the N–H group. The potential energy curve for the excited state was determined from the excitation energies calculated using CIS/6-31G(d,p) at discrete torsional angles. The variation of these energies relative to the minimum energy was plotted against the torsional angle. The calculated barrier height 250 cm$^{-1}$ is ~100 cm$^{-1}$ lower than the experimentally determined value (358 cm$^{-1}$). The potential energy curve for the excited state is shown in Fig. 10. The conformational preferences of the methyl group in both the electronic states can be understood on the basis of the molecular orbital picture. Figure 11 shows the orbital contour plot of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 1MPI at $\tau_1 = 0°$ and $\tau = 60°$ displaying the relative stability of the corresponding orbital energies. In 1MPI, the $\pi^* - \sigma^*$ hyperconjugation...
tion between the methyl C–H antibond and the ring π antibond is found to be present in both the occupied and unoccupied molecular orbitals. The π⁎-σ⁎ hyperconjugation in HOMO does not appear at τ=60° but rather at τ=0°, giving rise to the energy stabilization for the staggered conformer in the ground state. LUMO shows π⁎-σ⁎ hyperconjugation at τ=60°, thereby stabilizing the eclipsed conformer in the excited state. Figure 12 shows the HOMO energy, LUMO energy, and their difference against torsional angle. It is apparent from the figure that the change in the LUMO energy is a dominant contributor to the change in the excitation energy, while the HOMO energy change of 1MPI has little contribution to \( E_{S_0\rightarrow S_1} \). This trend was also confirmed for 1MPY and other substituted toluene and azabenzenes.

Figure 13 shows the variation of the excitation energy, the torsional potential in the \( S_1 \) state calculated using CIS/6-31G(d,p), and the potential curve for \( S_0 \) calculated by HF/6-31G(d,p) with the potential constants \( V_3=555 \text{ cm}^{-1} \) and \( V_6=6 \text{ cm}^{-1} \) for 3MPY. From the potential curve of \( S_1 \), the barrier height in the excited state was estimated to be 458 cm\(^{-1}\), which is in reasonable agreement with the experimental value of 408 cm\(^{-1}\). Hence, in 3MPY, the barrier to methyl internal rotation undergoes reduction in going from the ground state to the excited state. It is evident in Fig. 13 that the potential minimum in the excited state is 60° shifted with respect to that of the ground state, as in the case of 1MPY, 1MPI, and many other aromatic molecules. In 3MPY also the π⁎-σ⁎ hyperconjugation between the methyl C–H antibond and the ring π antibond was found to be present in LUMO at τ=60°, which is responsible for the stabilization of the eclipsed conformer in the excited state. However, the intense \( O_0^1 \) peaks for 3MPY observed in the FE spectrum do not comply with this conformational change of the methyl group. Probably, it arises due to the oscillator strength borrowed from other nontorsional modes of vibration.

The maximum changes in the HOMO energy, the LUMO energy, and their differences upon methyl rotation for 1MPY, 1MPI, and 3MPY are listed in Table VIII for comparison. The variations of HOMO and LUMO energies are found to be 243 and 818 cm\(^{-1}\), respectively, for 1MPY and 116 and 908 cm\(^{-1}\), respectively, for 1MPI. The potential bar-
rrier in the excited state for 1MPI (358 cm⁻¹) is greater than that for 1MPY (313 cm⁻¹). The possible reason could be due to the smaller change in HOMO energy and the larger change in LUMO energy during methyl rotation for 1MPI compared to those for 1MPY. The LUMO energy change has a dominant contribution in the torsional potential barrier for 3MPY similar to the case of 1MPI and 1MPY.

IV. CONCLUSION

From the fluorescence excitation and dispersed fluorescence spectra of 1MPY, 1MPI, and 3MPY, the internal rotational levels of the methyl group and some of the low frequency vibrations in the excited state have been assigned. The spectral analysis reveals considerable mixing of the methyl torsion with the low frequency vibrational modes such as ring out-of-plane in the excited state. The potential barrier of the methyl group in the excited state is higher in 1MPI than in 1MPY, probably due to the hyperconjugation involving lone pair electrons. Such an interaction is expected to be more in 1MPI than in 1MPY as the lone pair electrons of nitrogen atom is more available for the participation by virtue of smaller electronegativity of nitrogen than oxygen atom. The barrier increases upon electronic excitation in 1MPY, whereas it decreases in the case of 1MPI and 3MPY and the methyl conformer changes by 60° in the excited state. The πω-ω* hyperconjugation interaction model explains this switching of methyl group conformation reasonably well. In this kind of molecules, the change in LUMO energy during the methyl group rotation seems to play a dominant role in the formation of the excited state barrier.

ACKNOWLEDGMENT

This work was supported by the Department of Science and Technology, India.

TABLE VIII. Comparison of HOMO, LUMO, and barrier energy in 1MPY, 1MPI, and 3MPY.

<table>
<thead>
<tr>
<th></th>
<th>ΔE_HOMO (cm⁻¹)</th>
<th>ΔE_LUMO (cm⁻¹)</th>
<th>ΔE_LUMO-HOMO (cm⁻¹)</th>
<th>ΔE_b (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1MPY</td>
<td>243</td>
<td>818</td>
<td>575</td>
<td>313</td>
</tr>
<tr>
<td>1MPI</td>
<td>116</td>
<td>908</td>
<td>792</td>
<td>358</td>
</tr>
<tr>
<td>3MPY</td>
<td>236</td>
<td>959</td>
<td>723</td>
<td>408</td>
</tr>
</tbody>
</table>


