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Origin of methyl torsional barrier in 1-methyl-2-(1H)-pyridone

B. Pradhan and Bhanu P. Singh
Department of Physics, Indian Institute of Technology Bombay, Mumbai-400076, India

Chayan K. Nandi and T. Chakraborty
Department of Chemistry, Indian Institute of Technology Kanpur, UP-208016, India

T. Kundu
Department of Physics, Indian Institute of Technology Bombay, Mumbai-400076, India

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The laser induced fluorescence excitation and single vibronic excitation dispersed fluorescence spectra have been studied for supersonic jet cooled 1-methyl-2(1H)-pyridone. The methyl torsional bands and some low frequency vibrational transitions were assigned for both ground and excited states. The torsional parameters $V_3=244$ cm$^{-1}$ and $V_6=15$ cm$^{-1}$ for the ground state and $V_3=164$ cm$^{-1}$ and $V_6=40$ cm$^{-1}$ for the excited state were obtained. To get the insight into the methyl torsional barrier, ab initio calculations were performed and compared with the experimental results. Origin of potential barrier was traced by partitioning the barrier energy into changes in bond–antibond interaction, structural, and steric energies accompanying methyl rotation using natural bond orbital analysis. The role of local interactions in ascertaining the barrier potential reveals that its nature cannot be understood without considering the molecular flexing. The hyperconjugation between CHσ* and ring π* observed in lowest unoccupied molecular orbital (LUMO) stabilizes the methyl group conformer that undergoes a 60° rotation in the excited state with respect to that of the ground state, and it is the change in LUMO that plays important role in the excited state barrier formation.

I. INTRODUCTION

Internal rotation of methyl group has been studied extensively to understand the basic interactions giving rise to the barrier to its rotation, and also for its importance in intramolecular and photochemical dynamics. This hindered motion manifests in potential barrier of varying magnitudes depending on local chemical structure and electronic state. Due to its sensitivity to any structural and electronic perturbation, many methylated molecules exhibit dramatic change in barrier height and methyl group conformation upon electronic excitation and ionization. Substantial efforts have been devoted to ascertain the barrier using various experimental techniques and to provide accurate explanation for its origin using quantum chemical calculations. Lister, MacDonald, and Owen’s monograph and Reed and Weinhold’s review provide basic references on internal rotation. Payne et al. and Villard et al. have presented in-depth review of ab initio barrier calculations. Nature of methyl rotation in aromatic compounds has been reviewed by Ito, while Spangler and Pratt have focused on the internal rotation dynamics in their paper. Liljefors and Allinger proposed that the methyl torsional barrier in the aromatic molecules originate from the difference in the π bond order between the two ring C–C bonds vicinal to methyl group. This idea has been extended by George et al. for toluene and several other aromatic hydrocarbons. Lu et al. proposed that if the steric effect is absent, the barrier height is proportional to the calculated bond order with a slope of 950 cm$^{-1}$ per bond. Nakai et al. showed that the in-plane C–H eclipses the higher order C–C bond due to the attractive donor–acceptor interaction between them. Based on theoretical investigations, a new mechanism involving π* and σ* hyperconjugation in the lowest unoccupied molecular orbital was proposed to explain the variation of torsional barrier in substituted toluenes, such as fluorotoluene, cresol etc. Barrier energy partitioning in terms of structural, steric, and hyperconjugative charge transfer during methyl rotation allowed deeper understanding of this problem. However, the role of dominant interactions causing the barrier even in case of the simple textbook molecule Ethane is still under scrutiny.

Nitrogen containing heterocycles are of central importance in diverse areas of biochemical processes and industrial applications. 2-pyridone, the tautomer of 2-hydroxy pyridine has been the subject of much spectroscopic investigations for the understanding of hydrogen transfer reaction leading to keto-enol tautomerization. The electronic spectra of 2-pyridone and its clusters have been studied in supersonic jet by several workers. Nilmos et al. have performed detailed analysis of the $S_0\rightarrow S_1$ electronic transition of jet cooled 2-pyridone and its hydrogen bonded clusters by using laser induced fluorescence and mass-resolved resonance enhanced multiphoton ionization spectroscopic techniques. Two intense transitions observed in the excitation spectrum were assigned to electronic origins arising from two stable conformers in the ground state. Later, Held and co-workers investigated these bands further by analyzing rotational fine structure to conclude that these bands are as-

Email address: tkundu@phy.iitb.ac.in

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associated with the transitions originating from the same ground state but terminating at electronic excited states having slightly different structures. From rotational constant measurement it was found that these two conformers mainly arise from the two displaced positions of amine hydrogen and nitrogen. Using Fluorescence dip infrared spectroscopy, Matsuda et al. have demonstrated that the NH stretching vibration of the ground state associated with the transitions originating from the same electronic excited states, thus giving further evidence for the two bands originating from the same zero point vibrational level. With an intuition that spectroscopic investigation of the species having imine hydrogen atom replaced by a heavy methyl group will provide insight into the structure, we have investigated 1-methyl-2(1H)-pyridone (1MPY) both theoretically and experimentally. Due to high sensitivity of methyl torsional barrier height to electronic distributions, 1-methyl-2(1H)-pyridone presents an opportunity to explore (i) methyl internal rotation properties in ground and excited states, (ii) basic interactions causing this barrier, and (iii) the effect of methyl substitution on these two origins and other low frequency vibrations.

In this paper we present the fluorescence excitation and dispersed emission spectra of 1MPY. Observed methyl torsion and some other low frequency modes in ground ($S_0$) and excited ($S_1$) states have been assigned with the help of ab initio calculation. From the observed transitions methyl torsional frequencies and its potential barrier have been estimated and compared with corresponding theoretical values. The contributions of different interactions present in the molecule have been analyzed using natural bond orbital (NBO) analysis. It is found that the contributions to barrier energetics cannot be understood without taking into account the molecularflexing. The preferential conformation of methyl group in the excited state was explained by $\pi^* \cdot \sigma^*$ hyperconjugation mechanism.

II. EXPERIMENTAL SECTION

For spectroscopic investigations, 1-methyl-2(1H)-pyridone purchased from Aldrich was used without further purification. The fluorescence excitation experiments were performed using a free jet expansion system under vacuum $\sim 3 \times 10^{-5}$ to $1 \times 10^{-4}$ Torr. The sample was heated to $\sim 60^\circ$C–$70^\circ$C to provide sufficient vapor pressure. The vapor stream entrained in He at 2–3 atm was expanded into the vacuum chamber through pulsed nozzle valve of 0.4 mm diameter orifice. A frequency doubled dye laser (~1 mJ, 6 ns) using DCM dye in DMSO solvent pumped by second harmonic of Nd:YAG (YAG, yttrium aluminum garnet) laser was employed as the tunable excitation source. The laser pulse and jet (opening time 320 $\mu$s) interactions were temporally synchronized by digital delay to maximize the fluorescence. The fluorescence emanating from the interaction zone was imaged into a photomultiplier tube. Schott glass filter was used to eliminate the scattering below 350 nm. Signal from PMT was acquired by digital storage oscilloscope interfaced with a computer. The dispersed fluorescence spectra were recorded using 0.75 m spectrophotometer with the typical resolution of $5 \sim 7 \text{ cm}^{-1}$.

III. THEORETICAL BACKGROUND

The Hamiltonian for hindered internal rotation of methyl group is expressed by $H(\tau) = Fp^2 + V(\tau)$, where $F$ is the reduced internal rotational constant of methyl rotor, $p$ is the torsional angular momentum and one-dimensional torsional potential $V(\tau) = (1/2)[V_3(1 - \cos 3\tau) + V_6(1 - \cos 6\tau)]$ in terms of torsional angle $\tau$. The eigenvalues of Hamiltonian are obtained by expanding the hindered rotor wave function in terms of 21 free rotor wave functions and by diagonalizing the Hamiltonian matrix. The parameters $F$, $V_3$, and $V_6$ are adjusted to reproduce the experimentally observed torsional energies.

Point group symmetry is not adequate to describe the molecules exhibiting internal rotation. Molecular symmetry group developed by Longuet-Higgins is more appropriate for such cases where the molecular Hamiltonian can be defined in terms of all symmetry allowed energetically feasible permutations and permutation inversion of equivalent nuclei. As a finite potential barrier exists for internal rotation of methyl group and tunneling through the barrier is possible in

<table>
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<tr>
<th>Peak</th>
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<th>$\Delta \nu$ (cm$^{-1}$)</th>
<th>Assignment</th>
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<td>origin</td>
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<tr>
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<td></td>
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<tr>
<td>3</td>
<td>29 908.2</td>
<td>86</td>
<td>2e</td>
</tr>
<tr>
<td>4</td>
<td>29 942.6</td>
<td>120</td>
<td>3a_1</td>
</tr>
<tr>
<td>5</td>
<td>29 994.5</td>
<td>172</td>
<td>3a_0</td>
</tr>
<tr>
<td>6</td>
<td>30 018.8</td>
<td>196</td>
<td></td>
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<td>15</td>
<td>30 128.5</td>
<td>306</td>
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</table>
the experimental time scale, molecular states of 1MPY can be classified according to irreducible representations of the molecular symmetry group $G_6$. Under $G_6$ symmetry group, the in-plane and out-of-plane vibrational modes are categorized as $a_1$ and $a_2$ symmetry, respectively, and the torsional levels are classified into $a_1$, $a_2$, and $e$ symmetry species. Internal rotation levels are denoted by a combination of the rotational quantum number $m$ of a one-dimensional free rotor and the symmetry species of permutation inversion group, such as $0_1$, $1e$, $2e$, $3a_2$, $3a_1$, $4e$ etc. in the ascending order of the torsional energy levels. There are 39 normal modes for 1MPY out of which 26 are in-plane ($a_1$) and 13 out-of-plane ($a_2$) modes. Since all vibrionic transitions in the jet cooled molecules are from totally symmetric zero point energy vibrational state, the Condon approximation leads to a vibrionic selection rules that only $a_1$ modes are allowed. The fluorescence excitation spectrum and dispersed emission spectra are expected to exhibit only $a_1$ type fundamentals or even combinations of $a_2$ modes. For $G_6$ symmetry the allowed torsional transitions are $a_1 \leftrightarrow a_1$, $a_2 \leftrightarrow a_2$, and $e \leftrightarrow e$. Methyl internal rotation being extremely anharmonic is treated separately from other normal mode vibrations.

IV. SPECTRA AND ASSIGNMENTS

A. Fluorescence excitation spectrum

The laser induced fluorescence excitation (FE) spectrum of jet cooled 1-methyl-2(1H)-pyridone in the first 500 cm$^{-1}$ region of the $S_0 \rightarrow S_1$ system is shown in Fig 1. Table I summarizes the observed positions and separations from the lowest frequency band. The spectrum shows well-resolved vibronic structure. The band appeared at 29 822 cm$^{-1}$ is assigned to origin ($\pi \rightarrow \pi^*$) transition as our search for frequencies below this revealed no new features. Increasing backing pressure does not bring any appreciable change in intensity, which ruled out the possibility of first band to be hot band. The origin band is only 10 cm$^{-1}$ redshifted with respect to that of 2-pyridone$^{13}$ indicating a small change in excitation energy by the introduction of methyl group. There is a strong vibronic activity near origin showing several intense low frequency transitions. On the other hand, in case of 2-pyridone, very few weak bands are seen in this region.

Appearance of these bands with methyl substitution can be attributed to methyl group motions. Another interesting feature of the FE spectrum is the spectral congestion with increasing energy and abrupt disappearance of vibronic structure beyond 500 cm$^{-1}$. In 2-pyridone, the transition at 100 cm$^{-1}$ is described as another origin arising from a different equilibrium structure of the molecule.$^{13,14}$ One can easily speculate this separation to be reduced in 1MPY due to the substitution of methyl group and likewise the band at 22 cm$^{-1}$ (Fig. 1) could be another origin. The other possibilities for its assignment could be the methyl torsion or other low frequency vibrations.

As methyl group exhibits large amplitude torsional vibration and often show characteristic low frequency transitions below 100 cm$^{-1}$, the band at 22 cm$^{-1}$ can also be assigned to methyl torsion. Assignment of this band as $2e$ torsional transition of methyl group predicts the $3a_1$ and $4e$ levels near 50 cm$^{-1}$ and 85 cm$^{-1}$, respectively. The observed 86 cm$^{-1}$ band can be well assigned to $4e$ but the spectrum lacks any band near 50 cm$^{-1}$. Total absence of $3a_1$ band in the spectrum questions the assignment of the second peak as a torsional band. The fact that the origin band does not show any splitting of $0a_1$ and $1e$ level within the resolution of laser wavelength indicates that the magnitude of torsional po-

TABLE II. Assignments of observed bands in dispersed fluorescence spectrum.

<table>
<thead>
<tr>
<th>Excitation at 0.0</th>
<th>Excitation at 22 cm$^{-1}$</th>
<th>Excitation at 86 cm$^{-1}$</th>
<th>Excitation at 120 cm$^{-1}$</th>
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</thead>
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<td>Assignment</td>
<td>(\Delta \nu) cm$^{-1}$</td>
<td>Assignment</td>
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<td>0_0</td>
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<td>177</td>
</tr>
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</tr>
<tr>
<td>238</td>
<td>5_0</td>
<td>349</td>
<td>37_1</td>
</tr>
<tr>
<td>271</td>
<td>6_0</td>
<td>490</td>
<td>37_1</td>
</tr>
<tr>
<td>285</td>
<td>7_0</td>
<td>565</td>
<td>32_0</td>
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<td>309</td>
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<td>38_1</td>
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<tr>
<td>389</td>
<td>9_0</td>
<td>35_1</td>
<td>38_1</td>
</tr>
</tbody>
</table>
| 492 | 10_0 | 35_1 | 38_1 | 445 | 34_0 | }
potential barrier in ground and excited states are comparable. The third and fourth bands in the excitation spectrum appearing at 86 cm\(^{-1}\) and 120 cm\(^{-1}\) are assigned as 2\(e\) and 3\textit{a}\(_1\) torsional transitions, respectively. These bands are fitted to obtain the potential barrier in the excited state with \(V_3 = 164\) cm\(^{-1}\), \(V_6 = 40\) cm\(^{-1}\), \(F = 5.2\) cm\(^{-1}\). The calculated energy levels are 85.0 (2\(e\)), 92.0 (3\textit{a}2), 121.8 (3\textit{a}1), 142.7 (4\(e\)), and 185 cm\(^{-1}\) (5\(e\)). However the predicted 4\(e\) and 5\(e\) bands are not observed in the FE spectrum. This could be the effect of mixing of other low frequency vibrations with torsional motion (discussed later). The fifth band in the FE spectrum at 172 cm\(^{-1}\) is assigned to \(ν_{34}\) ring deformation mode because its emission spectrum (following section) exhibits a strong peak at 440 cm\(^{-1}\) which corresponds to \(ν_{34}\) mode in ground state. The above observation shows that the \(ν_{34}\) mode undergoes a 268 cm\(^{-1}\) reduction in going from ground to excited state.

### B. Dispersed fluorescence spectra

The dispersed fluorescence (DF) spectrum obtained by exciting 0,0 band (29 822 cm\(^{-1}\)) is shown in Fig. 2. Several low frequency activities seen within 300 cm\(^{-1}\) are attributed to methyl torsional motion and out-of-plane vibrations of ring frame. The transitions and their assignments are listed in Table II. The intensity of origin band is found to be weak, and the strongest feature appears at 162 cm\(^{-1}\). The weak 0,0 transition implies that the excited state potential is shifted with respect to that of the ground state. The bands at 99, 162, 175, 223, 271 cm\(^{-1}\) are assigned as methyl torsional progression 2\(e\), 3\textit{a}2, 4\(e\), 5\(e\), and 6\textit{a}1, respectively, in the ground state. Because the 0\textit{a}1 and 1\(e\) bands are nearly degenerate within laser linewidth, progression for transitions to both \(a\)1 and \(e\) levels are observed, thereby confirming this excitation band as origin. This assignment is in agreement with the observed torsional fundamental (101 cm\(^{-1}\)) in the Raman spectrum of neat liquid.\(^{13}\) The observed bands are fitted with torsional parameters \(V_3 = 244\) cm\(^{-1}\), \(V_6 = 15\) cm\(^{-1}\), \(F = 5.2\) cm\(^{-1}\) and the comparison of experimental with calculated frequencies are illustrated in Table III. The DF spectra upon exciting 86 cm\(^{-1}\) (2\(e\)) and 120 cm\(^{-1}\) (3\textit{a}1) bands of the excited state presented in Fig. 3 also show the \(e\) progression at 100, 177, 225 cm\(^{-1}\) for the former and \(a\)1 progression at 271 cm\(^{-1}\) for the later.

The potential energy surface of molecules in the excited state often found to be different from the ground state, and the relative intensity distribution of transitions in dispersed fluorescence spectra provides the information regarding the relative shift of potential between ground and excited states. The displacement of the minima of internal rotational potential between ground and excited states can be obtained by the Frank–Condon overlap calculation. The Frank–Condon factor\(^{20}\) is expressed by \(I = |\langle ψ_{m,α}(τ) | ψ_{m′,α′}(τ + θ) \rangle|^2\), where \(ψ_{m,α}(τ)\) and \(ψ_{m′,α′}(τ + θ)\) are the methyl rotor wave functions in the ground and excited states, respectively, and \(θ\) is the displacement angle corresponding to the shift in the potential minima between \(S_0\) and \(S_1\). The methyl rotor wavefunctions, obtained from the calculation to fit the torsional energy levels for ground and excited states, were used for the intensity calculation. The value of \(θ\) was adjusted to give best fit between the calculated and observed intensity distributions. As can be seen in Fig. 4(a) the calculated intensity distribution is qualitatively in agreement with observed intensities except for

![Fig. 3. Dispersed fluorescence spectra obtained by excitation into 0+22, 0+86, 0+120, 0+172 cm\(^{-1}\) bands.](image3)

![Fig. 4. Comparison between calculated (white column) and observed (black column) intensity distributions in dispersed fluorescence spectra (a) exciting at 0\textit{a}1, 1\(e\) band (0,0), (b) exciting at 2\(e\) band (86 cm\(^{-1}\)), and (c) exciting at 3\textit{a}1 (120 cm\(^{-1}\)). The calculated intensities are obtained with phase difference (θ=60°) and normalized with respect to one of the torsional bands intensity.](image4)
for 162 cm\(^{-1}\) band corresponding to 60° phase shift. The 162 cm\(^{-1}\) band exhibits unusually large intensity and this one-dimensional model of torsional motion does not reproduce its observed intensity. The intensity distribution of torsional transitions in emission spectra obtained upon excitation of 86 and 120 cm\(^{-1}\) bands also show a mismatch with the calculated values [Figs. 4(b) and 4(c)]. These discrepancies may be due to Duschinsky effect leading to the mixing of torsion with other normal mode vibrations which results in the transfer of oscillator strength between the modes. Calculation of normal modes for ground and excited states at HF/6-31G\( (d,p) \) and CIS/6-31G\( (d,p) \) levels, respectively, reveal that vector displacements of atoms in the lowest frequency of ground state is a purely torsional mode of the methyl group, whereas in excited state this mode involves out-of-plane ring vibration along with dominant torsional motion (Fig. 5). Hence the wavefunctions including only torsional coordinate are somewhat inadequate to account for relative intensity distribution. Though intensities determined from these approximate wavefunctions are in quantitative disagreement with observed intensity, however, it does provide a qualitative description of the intensity pattern.

The emission spectrum of 22 cm\(^{-1}\) band (Fig. 3) exhibits transitions at 98, 177, and 224 cm\(^{-1}\) which are 2\( e \), 4\( e \), and 5\( e \) torsional transitions, respectively. Unlike emission spectrum of 0,0 band, no a\( _1 \) symmetry torsional bands are seen. The absence of torsional transitions of a\( _1 \) symmetry and other dissimilarities in vibrational structure with respect to 0,0 emission spectrum do not ascertain the 22 cm\(^{-1}\) band as another electronic origin. Possibly this band could then be some other low vibrational frequency strongly mixed with torsional motion of e symmetry giving rise to emission of e torsional species only.

Fujimoto et al.\(^{19}\) had measured the infrared and Raman spectrum of 1MPY and carried out vibrational band assignment with normal coordinate analysis by \textit{ab initio} calculation at HF/6-31G level. Here we have assigned vibrational bands in the emission spectra upto 500 cm\(^{-1}\) facilitated mainly by \textit{ab initio} frequency calculation using density functional theory at B3LYP/6-31+\(+\)G\( (d,p) \) level (Table IV). The dispersed emission spectrum of 0,0 band is expected to be dominated by a\( _1 \) modes and even combinations of a\( _2 \) modes according to symmetry rule. The calculated lowest frequency (104 cm\(^{-1}\)) attributed to the torsional mode of methyl group is in good agreement with that observed experimentally (99 cm\(^{-1}\)). The calculated value of the next mode (\( \nu_{38} \)) is 139 cm\(^{-1}\). A very weak band found at 288 cm\(^{-1}\) in DF spectrum of 0,0 band, which appears prominently in emission spectra of 86 cm\(^{-1}\) and 172 cm\(^{-1}\) band (Fig. 3) can be assigned to 38\( b_2 \) leading to 38\( b_1 \) fundamental at 144 cm\(^{-1}\). Appearance of a very weak band at 145 cm\(^{-1}\) (Table II) in the emission from the above two bands confirms this assignment. In Raman spectrum\(^{19} \) this band is assigned to \( \nu_{37} \) mode, but \textit{ab initio} calculation (Table IV) predicts 214 cm\(^{-1}\) for this mode. We assign it to be a 38\( b_1 t_{2e} \) torsion-vibration combination band. Considering \( \nu_{37} \) mode frequency to be 214 cm\(^{-1}\), the observed 309 cm\(^{-1}\) band can be reasonably assigned as 37\( b_1 t_{2e} \) combination band. The medium intense 492 cm\(^{-1}\) band, appearing as very strong feature in 22 cm\(^{-1}\) and 120 cm\(^{-1}\) excited emission spectra, can be tentatively assigned as 35\( b_1 t_{2e} \) combination band. Alternatively, this can also be assigned to \( \nu_{31} \) mode fundamental frequency (calculated value 505 cm\(^{-1}\)).

### V. METHYL GROUP INTERNAL ROTATION: POTENTIAL BARRIER AND CONFORMATION

In order to investigate theoretically the internal rotation of the methyl group in 1MPY, \textit{ab initio} electronic structure calculations were carried out for the ground state (\( S_0 \)) and the excited state (\( S_1 \)) using Hartree–Fock (HF) and single excitation configuration interaction methods, respectively. The torsional barrier heights and shapes were evaluated from potential energy curves calculated as a function of the rotational angle (\( \tau \)) between the methyl group and the frame. The rotational angle with respect to in-plane hydrogen of the methyl group (\( \tau=0 \)) is defined for the stable conformation in the \( S_0 \) state. The potential energy curve is obtained by constraining the rotational angle (\( \tau \)) of methyl rotor to local frame and then by optimizing the rest of the geometry to minimize energy. All the calculations were carried out using GAUSSIAN98.\(^{21} \)

#### A. Ground state

The minimum energy configuration in ground state is shown in Fig. 6. The in-plane hydrogen of the methyl group (\( H_{13} \)) is placed away from the carbonyl oxygen (staggered conformation). The highest energy conformation in course of rotation is eclipsed one where in-plane hydrogen eclipses the C==O bond. The potential parameters (\( V_2 \) and \( V_6 \)) calculated using different levels of theory are summarized in Table V.
functions predicts barrier lower than the observed one. Addition of diffuse functions to basis set [6-311+ +G(d,p)] which is necessary to properly describe the lone pair, yields the barrier (239 cm\(^{-1}\)) that is close to experimentally determined value (244 cm\(^{-1}\)). The effect of electron correlation on the barrier height calculated using MP2/6-31G(d,p) shows that second-order correlation correction to the Hartree–Fock energy describes the potential barrier adequately. Barrier calculated using density functional theory (B3LYP) always predicts a lower barrier irrespective of the basis set used.

To understand the origin of potential barrier and the structure in the ground state, we analyzed the energetic consequences of natural bond orbital (NBO) decomposition of the barrier for methyl rotation. NBO’s are the localized set of Lewis like (\(\sigma\) and \(\pi\) bond, lone pair, and core) and non-Lewis (\(\sigma^*\) and \(\pi^*\) antibond and Rydberg) orbitals formed by transformation of molecular wavefunctions into one-center (lone pair) and two-center (bond) representations. This analysis, in a way provides deeper understanding of local interactions causing the torsional barrier in such big molecules. In the NBO representation, the diagonal elements of the Fock matrix represent the energies of localized bonds, antibonds, and lone pairs, and off diagonal elements represent bond–antibond, lone pair–antibond, and negligibly small antibond–antibond interactions. The NBO calculations were performed using NBO 3.1 module of GAUSSIAN98.\(^{21}\)

In NBO scheme, it is possible to partition the barrier using an energy decomposition expressed in terms of Lewis and delocalization energy changes

![Graph](https://via.placeholder.com/150)

**TABLE V.** *Ab initio* calculated potential parameters for methyl torsion using different levels of theory.

<table>
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<th>Level of theory</th>
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<th>(V_d(\text{cm}^{-1}))</th>
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<td>B3LYP/6-311++G(d,p)</td>
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</tr>
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<td>15</td>
</tr>
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</table>

\[\Delta E_{\text{barrier}} = \Delta E_{\text{lewis}} + \Delta E_{\text{deloc}},\]

where \(\Delta E_{\text{lewis}}\) represents the energy of doubly occupied NBOs comprising the core, lone pairs, and localized set of Lewis structure. The \(\Delta E_{\text{deloc}}\) represents the contribution of hyperconjugative stabilization to torsional barrier arising from bond-antibond and lone pair-antibond interactions. We calculated \(\Delta E_{\text{lewis}}\) by eliminating the non-bonding orbitals (using NOSTAR option) and the \(\Delta E_{\text{deloc}}\) was derived using Eq. (1). The barrier energy \(\Delta E_{\text{barrier}}\), \(\Delta E_{\text{lewis}}\), and \(\Delta E_{\text{deloc}}\) energies are shown in Fig. 7. It is evident from the figure that the delocalization energy change is clearly the barrier forming term in accordance with the observation of small molecules like ethane,\(^{22}\) methanol,\(^{23}\) dimethyl ether,\(^{24}\) etc. However, this positive energy change is largely canceled by the opposite \(\Delta E_{\text{lewis}}\) term to produce a small barrier for methyl torsion. To get further insight, it is essential to partition these interaction energies into contributions arising from specific bond–antibond interactions.

1. Delocalization energy change

The bond–antibond and lone pair–antibond interaction energies were calculated by the procedure suggested by Reed and Wienhold.\(^{2}\) The difference between eclipsed and staggered conformer energies was calculated by deleting a particular interaction as

\[\Delta E[F_{ij}^{\text{del}}] = E[D] - E[F_{ij}^{\text{del}}].\]

The contributions of bond-antibond interactions to the barrier energy were derived from \(\Delta^2E[F_{ij}^{\text{del}}] = \Delta E_{\text{barrier}} - \Delta E[F_{ij}^{\text{del}}]\) and are shown in Fig. 8 for various major interactions. We first concentrate on the local hyperconjugative interactions of methyl group with the surroundings. The interactions CNvicinal–CH\(_{ip}\) and CH\(_{ip}\)–CN\(_{vicinal}\) are always barrier forming terms, whereas the CH\(_{ip}\)–CN\(_{vicinal}\) is the antibarrier term. However, the magnitude of the later is large enough to almost cancel the effect of the former. The interactions of lone-pair [N(\(\pi\)), O(\(\sigma\)), and O(\(\pi\))] with antibonding orbitals of the methyl group are always attractive and favor the in-plane hydrogen eclipsing the C=O bond.
nonmethyl interactions shows that the other delocalization energies are also important factors to get a clearer picture of the overall effect during methyl rotation. The contributions from $C_2C_3C_4C_5, C_2C_5C_6O_7, C_6O_7N_1C_2$, and $O(\pi)N_1C_6$ overwhelm the antibarrier effect produced by the local methyl group interactions and generate the overall positive delocalization term. These nonmethyl interactions are due to the effect of molecular flexing during methyl rotation process. The geometry analysis [HF/6-31G(d,p)] shows the angle opening of $C_6N_1O_7$ by 2.5° (116.4° in staggered and 118.9° in eclipsed) in going from staggered to eclipsed conformer. This angle opening brings about a substantial change in hyperconjugative interactions within the molecular frame as well. Thus the overall contribution of delocalization energy change, the barrier forming term, cannot be understood without the effect induced by molecular relaxation.

2. Structural energy change

The change in Lewis energy, $\Delta E_{\text{lewis}}$, represents energy changes in the Fock matrix elements of doubly occupied bond orbitals and is described as

$$\Delta E_{\text{lewis}} = \Delta E_{\text{struc}} + \Delta E_{\text{steric}},$$

where $\Delta E_{\text{struc}}$ describes the energy changes due to all the interactions within and between bonds and $\Delta E_{\text{steric}}$ is the change in steric exchange repulsion. Since $\Delta E_{\text{struc}}$ corresponds to the change of the Fock matrix elements of the Lewis structure, the reasonable approximation is

$$\Delta E_{\text{struc}} \approx \Delta E_{\text{bonds}} = \Delta \omega,$$

where $\Delta \omega$ is the pNBO energy change corresponding to individual bond energy change accompanying rotation. $\Delta \omega$ can be obtained from

$$\Delta \omega = \epsilon_e n_e - \epsilon_s n_s,$$

where $\epsilon_e$ and $\epsilon_s$ represent the bond energy of the eclipsed and staggered conformations, respectively, and $n_e$ and $n_s$ indicate the charge occupation of the corresponding conformers. Table VI contains the major bond energy changes due to methyl rotation. Total bond energy change for methyl group (C8–H13, C8–H14, and C8–H15) only is 719 cm$^{-1}$ which implies that the local structural energy is higher in eclipsed conformer than in staggered one, thus giving positive contribution to barrier. The energy difference due to total structural energy change was found to be 1255 cm$^{-1}$ when all the bonds and lone-pairs were considered. However, the total $\Delta E_{\text{lewis}}$ was found to be negative in going from staggered to eclipsed conformer. Thus, the overwhelming contribution from the steric interaction ($\Delta E_{\text{steric}}$) brings out $\Delta E_{\text{lewis}}$ to be antibarrier term. Hence, in this theoretical framework, methyl torsional barrier in eclipsed conformer arises from positive contribution of $\Delta E_{\text{deloc}}$ and $\Delta E_{\text{struc}}$, whereas steric exchange repulsion provides the opposing force resulting in a lower barrier for this rotation.

B. Excited state

In this section, we present the investigation of the origin of methyl torsional barrier and conformational preference of methyl group in excited state using ab initio method. Many aromatic and heterocyclic methyl-containing molecules were found to exhibit profound change in barrier height and a 60° rotation of methyl group upon excitation. To explain this behavior, Nakai et al. have pointed out a new type of interaction, namely, $\pi^* - \sigma^*$ hyperconjugation using molecular orbital theory. By considering such an interaction they were able to successfully interpret the variation of barrier magnitude and methyl group conformation for substituted tolenes, naphthalenes, and azabenzenes in excited state. While conventional hyperconjugation appears between an occupied bond orbital and lone pair and unoccupied antibond orbital, the $\pi^* - \sigma^*$ hyperconjugation appears between unoccupied ring $\pi^*$ orbital and an unoccupied CH $\sigma^*$ orbital. This hyperconjugation leads to a weak intramolecular bonding between the out-of-plane methyl hydrogen and the ring. We also find that this $\pi^* - \sigma^*$ hyperconjugation mechanism is well applicable to 1Mpy in explaining methyl group behavior. In this scheme, the focus is on the excitation energy instead of total energy to obtain potential energy surface for the excited state. Although, absolute excitation energy of
1MPY calculated by CIS/6-31G(d,p) method (~4.7 eV) is somewhat overestimated than the experimental value (3.7 eV), only relative change in excitation energy during methyl rotation was considered for dynamical nature of the barrier. To determine the potential energy curve for the excited state, we calculated the single CI vertical excitation energy using ground state optimized geometry at discrete torsional angles of methyl group and subtracted ground state potential energies from the excitation energies. The variation of these energies with respect to minimum energy was plotted against torsional angle. The barrier height is found to be 256 cm⁻¹ as compared to the observed value of 164 cm⁻¹. It is apparent from the potential curve (Fig. 9) that in excited state, potential minima is 60° shifted with respect to ground state. This confirms the shift obtained from relative intensity calculation. While the spectroscopic results are inadequate to specify the energetically preferred conformation of methyl group relative to ring frame, this certainly predicts change in orientation accompanying electronic excitation. 

**Ab initio** calculation predicts the absolute conformer in the ground state to be staggered conformation. A 60° shift in potential indicate that the stable conformation attained by methyl group in excited state is eclipsed conformer. Geometry optimization at CIS/6-31G(d,p) level also shows the preference of eclipsed form as minimum energy conformer. The molecular orbital picture gives better understanding as regard to conformational preference adopted by methyl group in both the electronic states. Figure 10 shows the orbital contour plot of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 1MPY at τ=0° and τ=60° displaying the relative stability of corresponding orbital energies. In 1 MPY, \(\pi^*-\sigma^*\) hyperconjugation between methyl C–H antibond and ring \(\pi^*\) stabilizing this configuration in ground state. Eclipsed conformer is stabilized in excited state due to hyperconjugation exhibited by LUMO. The contour diagrams are plotted with same sensitivity.

To comprehend the nature of barrier, torsional angle dependence of orbital energies were plotted. In the first-order treatment, the excitation energy variation is expressed by \(\Delta E_{S_0-S_1} = e_{LUMO} - e_{HOMO} - J_{HOMO,LUMO} + K_{HOMO,LUMO} - e_{HOMO,LUMO} + K_{HOMO,LUMO}\). Here, \(\Delta E_{S_0-S_1}\) is the excitation energy, \(e\) is the orbital energy, and \(J\) and \(K\) are coulomb and exchange integrals, respectively. Figure 11 shows the dependence of eclipsed conformer in the excited state. To comprehend the nature of barrier, torsional angle dependence of orbital energies were plotted. In the first-order treatment, the excitation energy variation is expressed by

\[
\Delta E_{S_0-S_1} = e_{LUMO} - e_{HOMO} - J_{HOMO,LUMO} + K_{HOMO,LUMO} - e_{HOMO,LUMO} + K_{HOMO,LUMO}.
\]

Here, \(\Delta E_{S_0-S_1}\) is the excitation energy, \(e\) is the orbital energy, and \(J\) and \(K\) are coulomb and exchange integrals, respectively. Figure 11 shows the dependence of
$\varepsilon_{\text{HOMO}}$, $\varepsilon_{\text{LUMO}}$, and $\Delta \varepsilon_{\text{HOMO- LUMO}}$ on $\tau$. The variation of HOMO energy with respect to torsional angle is feasible compared to LUMO. Thus, LUMO plays key role in determining the barrier in excited state as compared to HOMO.

VI. CONCLUSION

From the excitation spectrum and dispersed fluorescence spectra of 1MPY, the internal rotational levels of methyl group and some of the low frequency vibrational bands have been assigned in ground and excited states. The spectral analysis reveals considerable mixing of methyl torsion with low frequency vibrational modes, such as ring out-of-plane in the excited state. As a consequence, instead of one-dimensional description of methyl rotor, torsion–vibration coupling should also be included to describe the intensity pattern of torsional transitions and appearance of many features in observed spectra. The barrier height undergoes reduction in excited state as compared to the ground state. Unlike many ortho substituted aromatic molecules that show many fold decrease of barrier height and undergo conformational change in excited state, the barrier decrease for 1MPY is much less pronounced, wherein the methyl group rotates 60° in the excited state with respect to the ground state.

The experimental results are substantiated by ab initio calculations performed to obtain potential parameters and conformations for methyl rotation in both the electronic states. The calculation at HF level predicts the barrier adequately for higher basis set with diffuse functions. On the other hand, the barrier calculated using density functional theory yields value lower than the observed one. The CIS calculation overestimates the barrier height in the excited state, but predicts the 60° change of methyl group conformer. Considering the total contributions from various parts of the molecule to the barrier, NBO analysis shows that the torsional barrier predominantly arises from delocalization and structural energy changes while steric exchange repulsion forms the anti barrier. However, the local hyperconjugation interactions with methyl group alone are not decisive in barrier formation. It is the skeletal relaxation during methyl rotation that plays an important role in strengthening the contribution of hyperconjugation and is a key factor in determining the origin of the barrier. For the excited state, the $\pi^* - \sigma^*$ hyperconjugation interaction model explains reasonably the switching of methyl group conformation from staggered to eclipsed conformer. In this picture, LUMO seems to play more dominant role than HOMO for the variation of excited state barrier energy.

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