



Origin of Three Fold Torsional Potential in Methylated 2-Hydroxypyridine

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ABSTRACT

In this paper, the detailed study of methylated 2-hydroxypyridine molecule has been carried out using resonance enhanced multiphoton ionization (REMPI) spectroscopic technique. However, the theoretical investigations have been performed using ab initio calculations. The origin band of the molecules 4-methyl-2-hydroxypyridine (4M2HP) and 6-methyl-2-hydroxypyridine (6M2HP) was observed at 34987 cm^{-1} and 35405 cm^{-1} in their REMPI spectrum and the bands assigned as $\pi\pi^*$ transition state. The vibronic coupling of the $n\pi^*$ and $\pi\pi^*$ transition states took place in 4M2HP, thus some low intense bands near the origin band of the molecule were observed in the spectrum. However, no such kind of bands observed in 6M2HP. The $\pi^*-\sigma^*$ hyperconjugation is responsible for the conformational change of the methyl group in 4M2HP upon excitation ($S_0 \rightarrow S_1$).

Keywords: Ab initio calculation, Hyperconjugation, Methyl torsion, REMPI.

1. Introduction

The torsion motion can be defined as the twisting or pseudo rotation of a group of atoms or a part of molecule with respect to the whole molecule over a multiminima potential. Biphenyl is an example with torsion motion between the two rings. It has twisted angle of 420° (Suzuki, 1959) while in solid state it is a planar molecule (Hargreaves & Rizvi, 1962). The molecule has been studied in supersonic jet cooled condition by Im and Bernstein in 1988 (Im & Bernstein, 1988). The electronic spectroscopy of the molecule was studied by Phillips (Phillips, 1997) while Lewis (Lewis et. al, 1972) provided a model to calculate the torsional energy barrier of the molecule. However, methyl group internal rotation draws a lot of attention from many scientific groups to explore its role in physical and chemical properties of molecules. The study of methyl torsion in methylated molecules is the area of interest from many years using experimental along with the



theoretical investigation using ab initio calculations. Many scientific groups (Lister et. al, 1978; Reed & Weinhold, 1991; Payne & Allen, 1977; Villard, 1974; Pitzer, 1983) have presented basic as well as deep reviews on this topic of interest. The steric repulsion, some electrostatic models, valence bond theory, hyperconjugation and some other concepts have been used to explain the origin of the torsional interactions. Srivastava et. al (Srivastava et. al, 2018) studied the effect of methyl group on different position of 2-hydroxypyridine molecule.

2. Theoretical Background

The geometrical optimization of the molecules was performed using ab initio calculations in the excited (S_1) electronic state. The torsional barrier potential parameters have been obtained using the one dimension equation of torsional potential which is given by $V(\tau) = (1/2)V_3(1 - \cos 3\tau) + (1/2)V_6(1 - \cos 6\tau)$ where τ is torsional angle. All the ab initio calculations for excited electronic states were performed in Gaussian'09 (Frisch et. al, 2009) and the visualization of the molecular geometry and the molecular orbitals were carried out in Gabedit software (Allouche, 2011). The procedure used for the theoretical study of the molecules in their ground (S_0) and excited electronic state (S_1) has been discussed in details in our previous articles (Srivastava et. al, 2018; Sinha et. al, 2008).

3. Experimental details

The resonance enhanced multiphoton ionization (REMPI) experiment was performed using a tunable dye laser which was pumped by a second harmonic of the pulsed Nd:YAG laser (Litron nano series lasers, UK). For the ionization of the molecules, the output from the tunable dye laser was frequency doubled using another second harmonic crystal, while the scanning of the dye laser frequency was done by using stepper motor which was controlled by the developed LabVIEW program. The chemicals (4M2HP and 6M2HP) were purchased from alfa-aesar chemical company and used without further purification.

4. Results and discussion

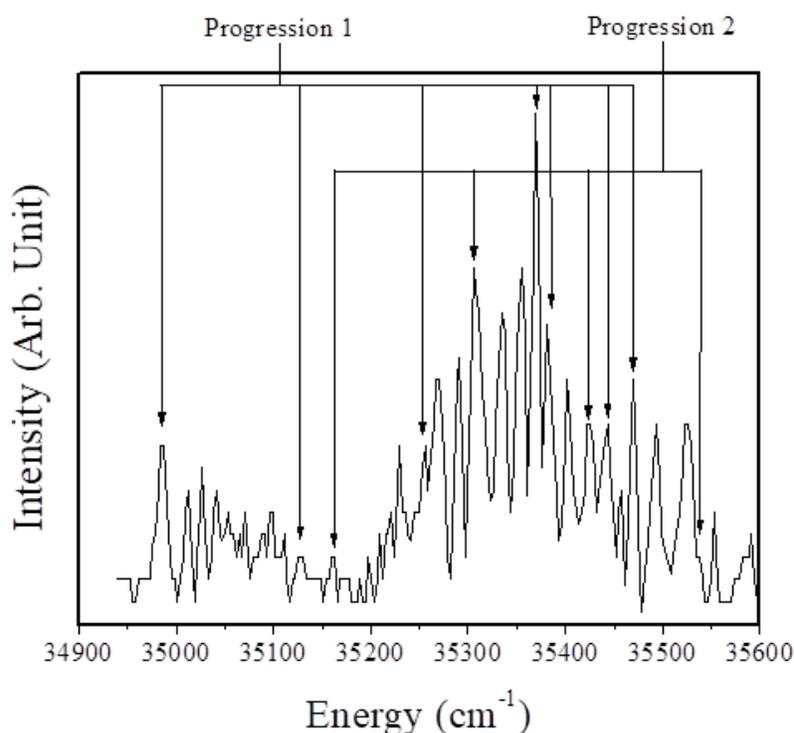
4.1 4-methyl-2-hydroxypyridine

The REMPI spectrum of 4-methyl-2-hydroxypyridine in jet-cooled condition is shown in Fig. 1. The spectrum was recorded just after the release of the carrier gas. Many broad as well as sharp spectral bands were observed in the range of 34900 cm^{-1} to 35600 cm^{-1} . The transition at 34987 cm^{-1} is assigned as the origin band of the molecule. Increasing the pressure of the carrier gas, does not provide any appreciable change in the intensity of the observed peak. Matsuda et. al (Matsuda et. al, 2001) showed the excitation spectrum of 2-hydroxypyridine in which the $\pi\pi^*$ transition band observed as the origin band. Thus, the origin band for 4-methyl-2-hydroxypyridine at 34987 cm^{-1} is assigned as $\pi\pi^*$ transition in a similar manner. 1136 cm^{-1} red shift observed for the origin band of 4-methyl-2-hydroxypyridine relative to the 2-hydroxypyridine molecule from the excitation



spectrum. The plausible reason for this change could be the change in the electronic environment adjacent to the methyl group. In the obtained REMPI spectrum of 4M2HP, some other low frequency bands were observed near to origin band with less intensity. While in case of 2-hydroxypyridine no such weak bands were reported near to origin band (Matsuda et. al, 2001). It may be due to the methyl internal rotational transitions. Though methyl torsional transitions show characteristic low frequency, presence of all these low frequency bands cannot be because of only methyl group internal motion. There could be the existence of $n\pi^*$ transition state involving

Figure 1: REMPI spectrum of 4M2HP after 30 minutes of release of helium gas. The spectrum is normalized with the laser intensity.



vibronic coupling with $\pi\pi^*$ transition state and because of that the low frequency vibration bands appear near to origin band.

At a separation of 26 cm^{-1} , there observed a band with low intensity relative to the origin band. This band could be assigned as 2e torsional transition of methyl group which predicts the 3a1 and 4e torsional bands near to 57 cm^{-1} and 87 cm^{-1} respectively. Though there observed bands at 54 cm^{-1} and 83 cm^{-1} which can be assigned as 3a1 and 4e torsional bands, assignment of other bands will not be possible. Also, assigning 26 cm^{-1} as 2e band, produces a potential barrier of low magnitude. But the barrier potential in excited state was calculated with higher values of the potential parameters. Hence, this band at 26 cm^{-1} could also be assigned as some other band which



associated with the $n\pi^*$ transition state. The 2e and 3a1 torsional transitions were assigned for the bands observed at 144 cm^{-1} and 269 cm^{-1} respectively. The potential parameters in the excited state were obtained by fitting these bands. The excited state torsional parameters ($V'_3 = 536\text{ cm}^{-1}$; $V'_6 = -10\text{ cm}^{-1}$; $F' = 5.3\text{ cm}^{-1}$) were obtained by the best fit of these observed bands. The bands observed at a separation of 383 cm^{-1} , 395 cm^{-1} , 459 cm^{-1} and 483 cm^{-1} from the origin band can be assigned as 5e, 6a2, 6a1 and 7e torsional transitions. The other observed bands were also assigned while the 4e band was not observed from the spectrum. While assigning the observed bands from the spectrum it was found that the band at 318 cm^{-1} could be observed due to the mixing of two vibrational modes. Thus the band at 173 cm^{-1} was assigned as the second lowest vibrational mode (v^1_0) in the excited state and can explain the presence of band at 318 cm^{-1} . The different vibrational bands and their assignments are tabulated in Tab. 1.

There are many other vibrational modes observed in the spectrum due to the methyl torsional transitions which can be easily explained by the combination of the other vibrational modes as listed in Tab. 2 as progression 2. The bands obtained at 439 cm^{-1} and 551 cm^{-1} are assigned as 3a1 and 5e and the torsion and vibration combination bands.

Table 1: Assignment of methyl group torsional transitions in REMPI spectrum of 4M2HP.

Energy (cm^{-1})	$\Delta\nu$ (cm^{-1})	Assignment
34987	0	Origin
35131	144	2e
35163	173	v^1_0
35256	269	3a1
35305	318	v^1_0 2e
35370	383	5e
35382	395	6a2
35426	439	v^1_0 3a1
35446	459	6a1
35470	483	7e
35538	551	v^1_0 5e

Table 2: Assignment of methyl group torsional transitions in REMPI spectrum of 4M2HP.

Progression 1			Progression 2		
($S_0 \rightarrow S_1$)	Cal. (cm^{-1})	Obs. (cm^{-1})	($S_0 \rightarrow S_1$)	Cal. (cm^{-1})	Obs. (cm^{-1})
1e – 2e	143	144	1e – 2e	143	145
0a1 – 3a2	143	---	0a1 – 3a2	143	---
0a1 – 3a1	272	269	0a1 – 3a1	270	266



1e – 4e	274	---	1e – 4e	272	---
1e – 5e	382	383	1e – 5e	378	378
0a1 – 6a2	394	---	0a1 – 6a2	391	393
0a1 – 6a1	455	439	0a1 – 6a1	448	---
1e – 7e	488	483	1e – 7e	483	---

The change in the conformation of methyl group upon excitation from the ground state to excited state as observed in the excitation spectrum can be explained using the Frank-Condon factor calculation between these two states. This calculation of Frank-Condon factor reveals the information regarding the shift of the conformation of the methyl group while excitation. The observed REMPI spectrum of 4-methyl-2-hydroxypyridine suggests change in the conformation due to the internal rotation of methyl group upon excitation from ground electronic state (S_0) to excited electronic state (S_1). The observed 5e transition band has been taken in account to estimate the torsional potential due to methyl group motion. B3LYP/TZVP level of theory has been used for further investigation of the conformational change and torsional potential in excited state (S_1). The optimized geometry of 4M2HP is shown in Fig. 2 (a). In minimum energy conformation of the molecule, the ring frame is always planar. The potential curve for the excited state (S_1) is shown in Fig. 2 (b). The calculated three fold potential term (V_3) was 517 cm^{-1} . The obtained potential curve shows an internal rotation of methyl group upon excitation from ground state (S_0) to excited state (S_1). This is in agreement with the observed results from the optimized geometry of ground state and from the obtained REMPI spectrum. The change in methyl group conformation and magnitude of torsional potential barrier in 4M2HP upon excitation were explained using the $\pi^*-\sigma^*$ hyperconjugation (Nakai & Kawai, 2000). The $\pi^*-\sigma^*$ hyperconjugation in LUMO at the top of the barrier conformation stabilizes these in ground as well as in excited states. The orbital contour diagram for 4M2HP in HOMO and LUMO in minimum and top of the barrier conformation is shown in Fig. 3. $\pi^*-\sigma^*$ hyperconjugation was observed only in 180 degree conformation in LUMO. This signifies the change in conformation of methyl group in excited state i.e. rotation of methyl group upon excitation.



Figure 2: (a) The optimized geometry and (b) torsional angle dependence of potential barrier curve for 4M2HP using B3LYP/TZVP level of theory.

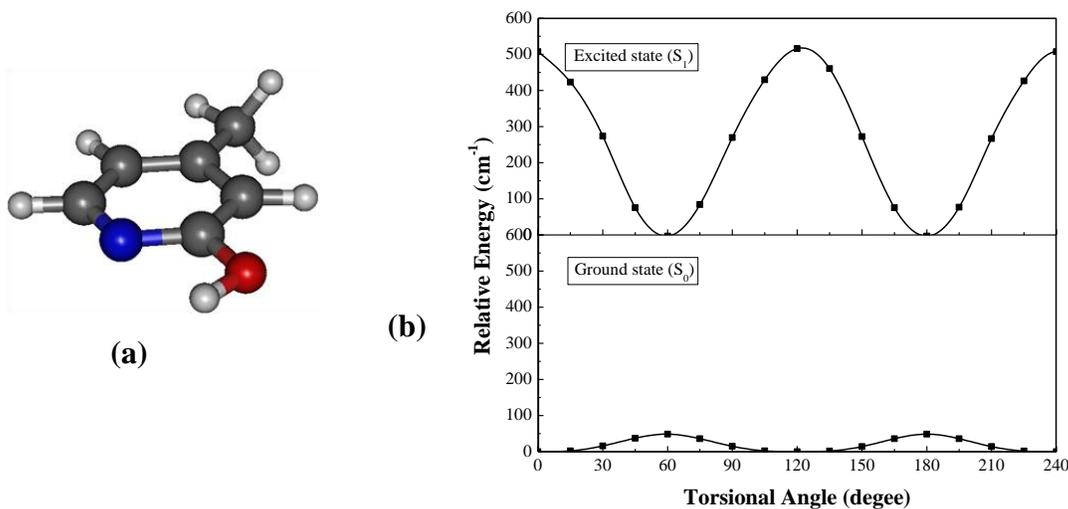
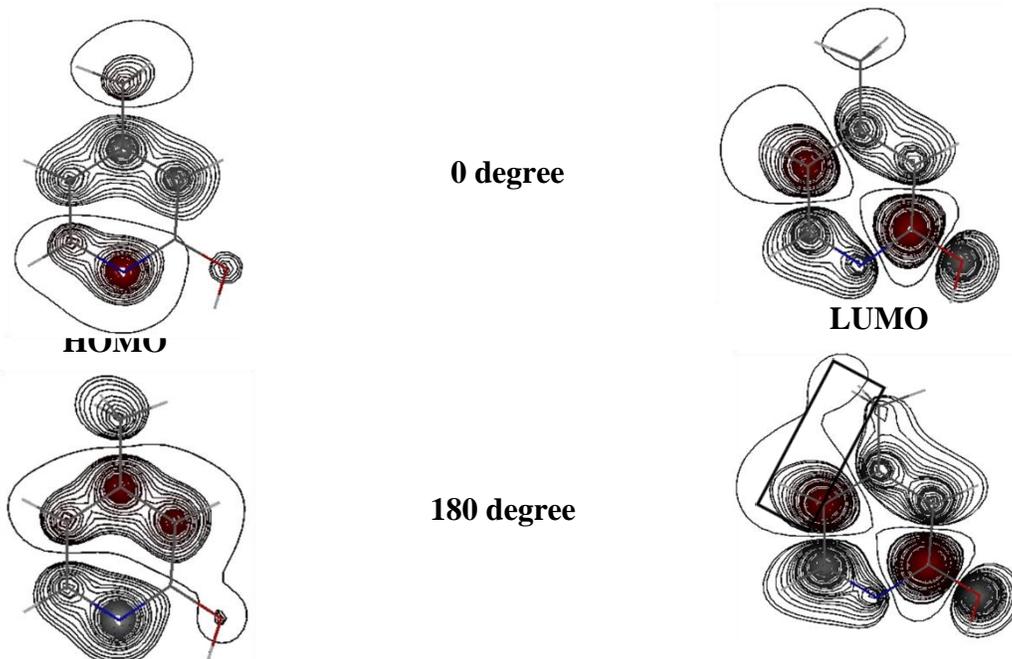


Figure 3: Contour diagrams of HOMO and LUMO of 4M2HP in minimum energy conformation (0 degree) and top of the barrier conformation (180 degree). The contour diagrams are plotted with same sensitivity.



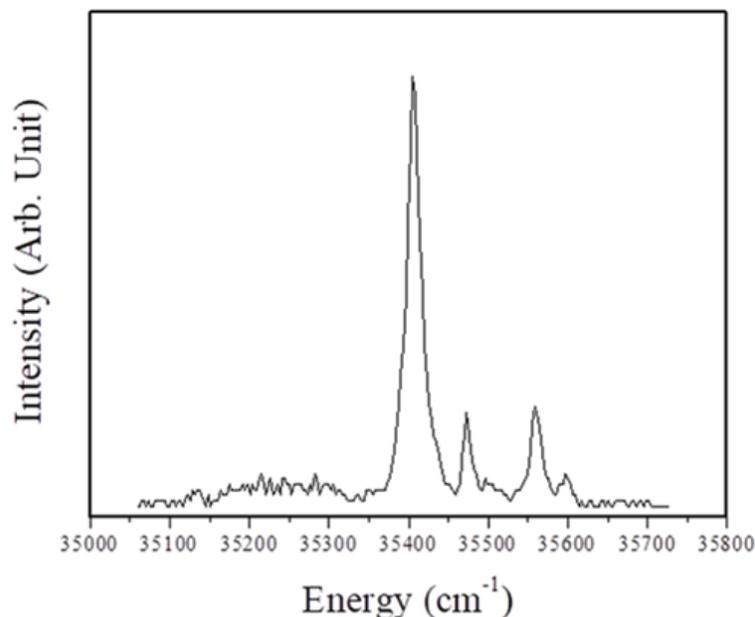
4.2 6-methyl-2-hydroxypyridine

The REMPI spectrum of jet-cooled 6-methyl-2-hydroxypyridine is shown in Fig. 4. The spectrum recorded after 30 minutes of release of the gas. One intense peak with few other peaks



was observed in the spectral range of 35000 cm^{-1} to 35800 cm^{-1} . The observed spectrum then normalized using the dye laser profile. The obtained transition band at 35405 cm^{-1} has been

Figure 4: REMPI spectrum of 6M2HP after 30 minutes of release of helium gas. The spectrum is normalized with the laser intensity.



assigned as the origin band of the molecule. This assigned origin band is observed as $\pi\pi^*$ transition state. The characteristic of this band and the intensity pattern observed in the spectrum indicates unchanged molecular conformation in the excited state compared to the ground state.

The other bands obtained in the excitation spectrum of the molecule can be either vibrational bands or methyl torsional bands of the molecule. These bands are observed at a separation of 68, 153 and 192 cm^{-1} from the assigned origin band (35405 cm^{-1}). The transition bands observed at 68 and 153 cm^{-1} were assigned as 3a2 and 3a1 transition bands with the experimentally obtained potential parameters $V'_3 = 265\text{ cm}^{-1}$; $V'_6 = -84\text{ cm}^{-1}$ and $F' = 5.3\text{ cm}^{-1}$. The other band observed at 192 cm^{-1} is assumed as some other vibration.

Table 3: Absolute and relative spectral positions of observed bands in the REMPI spectrum of 6M2HP.

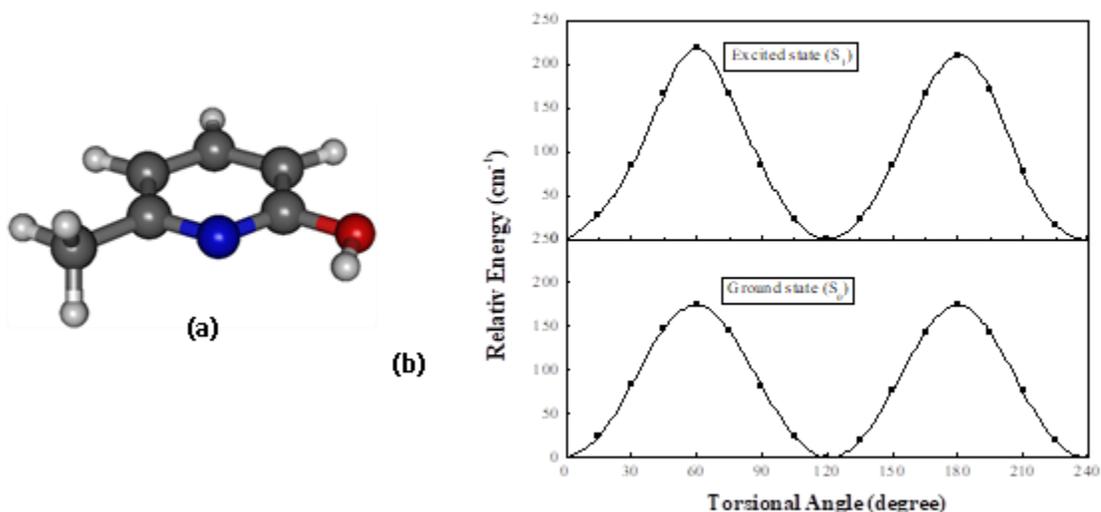
Energy (cm^{-1})	$\Delta\nu$ (cm^{-1})	Assignment
35405	0	Origin
35473	68	3a2
35558	153	3a1
35597	192	----

As observed from the obtained REMPI spectrum, there is no such conformational change due to the internal rotation of methyl group observed when excitation takes place from the ground electronic state (S_0) to the excited electronic state (S_1). B3LYP/TZVP level of theory have been



taken in account for the further investigation of the conformation and torsional potential of the molecule in excited state (S_1). The optimized geometry of 6M2HP in excited state is shown in Fig. 5 (a). The ring frame is always planar whenever geometry optimization in minimum energy conformation has been performed. The calculated intensity pattern, using the obtained potential parameters for ground as well as for excited state from the theoretical study, is in match with the result obtained from the excitation spectrum. Hence, there is no change in conformation of methyl group observed. The torsional angle dependence of the potential energy curve for the excited state (S_1) is shown in Fig. 5 (b).

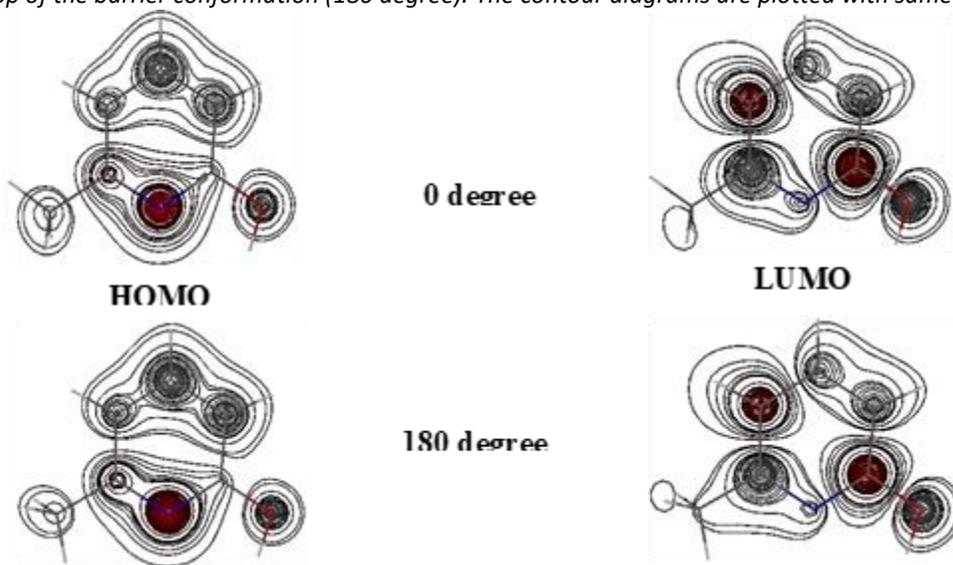
Figure 5: (a) The optimized geometry and (b) torsional angle dependence of potential barrier curve for 6M2HP using B3LYP/TZVP level of theory.





The calculated three-fold potential term V_3 was found to be 212 cm^{-1} . The obtained potential curve for the optimized geometry is in agreement with the observed REMPI spectrum of the molecule. There is no change of methyl group conformation observed in REMPI spectrum, hence no $\pi^*-\sigma^*$ hyperconjugation involves. The orbital contour diagram for 6M2HP in HOMO and LUMO in minimum and top of the barrier conformation is shown in Fig. 6.

Figure 6: Contour diagrams of HOMO and LUMO of 6M2HP in minimum energy conformation (0 degree) and top of the barrier conformation (180 degree). The contour diagrams are plotted with same sensitivity.



5. Conclusion

The ab initio calculation as well as the intensity pattern shows the conformational change in the methyl group in 4M2HP upon excitation from ground state to excited state. The band observed at 34987 and 35405 cm^{-1} was assigned as $\pi\pi^*$ transition state and named as origin band for 4M2HP and 6M2HP respectively. Many low frequency vibrational bands were observed near the origin band in 4M2HP which could be because of the vibronic coupling of the $n\pi^*$ and $\pi\pi^*$ transition states. The $\pi^*-\sigma^*$ hyperconjugation is responsible term for the conformational change in methyl group in 4M2HP while no hyperconjugation observed in 6M2HP.



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