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EFFECT OF META SUBSTITUTION OF METHYL GROUP ON 2-HYDROXYPYRIDINE: SPECTROSCOPIC INVESTIGATION

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We have reported here the detailed investigation of the effect of methyl group substitution on the meta-position of the 2-hydroxypyridine molecule. Resonance enhanced multiphoton ionization (REMPI), FT-IR and Raman spectroscopic techniques have been used for the experimental study of the molecules. *Ab initio* calculations were used for theoretical investigations of the molecules. The origin band of the molecules 3-methyl-2-hydroxypyridine (3M2HP) and 5-methyl-2-hydroxypyridine (5M2HP) was observed at 33830 and 34105 cm^{-1} in their REMPI spectroscopy, and the bands assigned as a $\pi\pi^*$ transition state. The vibronic coupling of $n\pi^*$ and $\pi\pi^*$ transition states took place in 3M2HP, thus some low intense bands near the origin band of the molecule were observed in the REMPI spectrum. However, there was no such kind of bands in 5M2HP. The π^*–σ^* hyperconjugation is responsible for the conformational change of the methyl group in 3M2HP upon excitation ($S_0 \rightarrow S_1$).

Keywords: methyl torsion, REMPI, *ab initio*, hyperconjugation, HOMO, LUMO

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1. Introduction

The nitrogen heterocyclic molecules are very important in different kind of biological processes as well as in industrial applications, thus it needs attention to understand the photophysical and photochemical properties of these molecules. However, the fluorescence yield for these molecules is very low due to the close-lying excited states. In these molecules, there is a possibility of a close proximity of having another excited state ($n\pi^*$), that arises due to the presence of lone pairs, with the $\pi\pi^*$ excited state. In many heterocyclic molecules, these closely placed states result in strong mixing of the vibronic (vibrational and electronic) levels and thus affect the radiative as well as non-radiative energy decay properties of the excited states. Bickel et al. [1] reported that the difference between the position of these two transition states ($\pi\pi^*$ and $n\pi^*$) can be changed by substitution of a chemical group on any position of the molecule. Thus, the photophysical properties of these kinds of molecular systems depend on the electronic states and can be changed by any suitable substitution. Hence this kind of a molecular system can be used as modelled molecules to study the vibronic coupling of these transition states as well as the nature of molecular systems.

The methyl group can affect the photophysical and photochemical properties of molecules and can also act as a probe for investigations. The coupling of the methyl group torsional motion with low frequency vibrations leads to the concept of mixing of two closely spaced electronic states. Lim and team [2] studied the energy states $n\pi^*$ and $\pi\pi^*$ of nitrogenous heterocyclic molecules and they concluded for the molecules quinoline and isoquinoline that the lowest energy state is an $n\pi^*$ state [2, 3]. Fischer [4, 5] worked on the spectroscopic study of isoquinoline vapour and found that the $n\pi^*$ singlet state is slightly below the lowest energy $\pi\pi^*$ singlet state. The fluorescence excitation and dispersed fluorescence excitation spectroscopy of supersonic jet cooled isoquinoline and its methanol complex have been carried out by Felker and Zewail [6] and the coupling of $\pi\pi^*$ and $n\pi^*$ states was observed for the molecules and its complexes [3, 6, 7]. The methylisoquinolines were studied previously using laser induced fluorescence (LIF) and dipersed fluorescence (DF) excitation spectroscopic techniques [8]. The vibronic mixing of $n\pi^*$ and $\pi\pi^*$ excited states was observed in methylated isoquinoline molecules and it was also reported that the $n\pi^*$ state possessed longer life time than the $\pi\pi^*$ state.

The objective of this study is to understand the mechanism of the methyl torsional potential of the molecule in the ground electronic state as well as in the excited electronic states. However, the effect of methylation in the ground electronic state has been previously studied [9]. The focus is on the study of close-lying electronic states and the interactions due to the methyl group substitution on different positions in these methylated 2-hydroxypyridines. However, the interest is to understand the effect of different electronic environment on the methyl torsional behaviour and thus on the barrier potential of the molecule.

2. Experimental section

The resonance enhanced multiphoton ionization (REMPI) experiment was performed using a tunable dye laser which was pumped by a second harmonic of a pulsed Nd:YAG laser (*Litron* Nano Series Lasers, UK). For the ionization of 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 a stepper motor which was controlled by the developed LabVIEW program. The angle tuning of the second harmonic crystal was done manually, and then this final output was made to cross through a supersonic chamber, where the interaction with the sample takes place. The laser pulse and molecular jet were synchronized in time using two pulsed nozzle drivers (IOTA ONE Pulsed Driver from *Parker* Instrumentation) and a self-made microsecond pulsed delay generator. The opening of the pulsed nozzle is optimized for the cold molecular beam and maximum ionization signal. A convex lens of 8.0 cm focal length was used to focus the frequency doubled laser pulse inside the chamber, where the interaction takes place. The ionization signal, which was reflected by a plate termed as a repulser plate (R), was collected in the direction perpendicular to both laser and molecular beams with the help of a channel electron multiplier (DR. SJUTS KBL 25RS). The signal from the channel electron multiplier is averaged (typically 128 pulses) and digitized using an optically triggered digital oscilloscope (TDS 1012B), and stored in a computer. The molecules 3-mehtyl-2-hydroxypyridine and 5-methyl-2-hydroxypyridine were purchased from *Sigma Aldrich* and *Alfa-Aesar* chemical companies, respectively, and used without further purification. IR and Raman spectroscopy were performed using a FTIR-Imaging System (3000 Hyperion Microscope with Vertex 80 FT-IR System, *Bruker*, Germany) with a spectral resolution of FT-IR 0.2 cm^{-1} and a HR800-UV confocal micro-Raman spectrometer (*Horiba Jobin Yvon*, France), respectively.

3. Theoretical background

Ab initio calculations have been used for the theoretical investigation of the molecules in the ground (S$_0$) as well as in the excited (S$_1$) electronic states. The geometry optimization has been performed along with the calculating barrier potential. The torsional potential in one dimension is given by $V(\tau)=\frac{V_3}{2}(1-\cos 3\tau)+\frac{V_6}{2}(1-\cos 6\tau)$, where τ is the torsional angle. All the *ab initio* calculations for the ground as well as the excited electronic states were performed in Gaussian’09 [10] and the visualization of the molecular geometry and the molecular orbitals was carried out in the Gabedit software [11]. The procedure used for the theoretical study of the molecules in their ground (S_0) and excited (S_1) electronic states has been discussed in detail in our previous article [9, 12].

4. Results and discussion

4.1. REMPI spectroscopy

4.1.1. 3-Methyl-2-hydroxypyridine

The REMPI spectrum of supersonic jet-cooled 3-methyl-2-hydroxypyridine (3M2HP) is shown in Fig. 1. The spectrum was recorded after 30 min of the release of argon gas. Broad as well as sharp spectral bands were observed in a range of 33800 to 33500 cm^{-1}. The transition at 33830 cm^{-1} is assigned to the origin of the spectrum as there is no more low frequency below this. There is no appreciable change in the intensity of the peak whenever pressure of the gas increases. The excitation spectrum for the parent molecule 2-hydroxypyridine arises due to the $\pi\pi^*$ excitation [13] and no sign of $n\pi^*$ transition states arises in the spectrum. In a similar manner we assign the origin band at 33830 cm^{-1} to $\pi\pi^*$ transition. The origin band is red-shifted by 2294 cm^{-1} relative to the parent molecule indicating a change in excitation energy whenever the methyl group substitution takes place. There are several vibronic bands near the origin showing intense low frequency transitions. On the other hand, in the case of 2-hydroxypyridine no such weak band is observed in this region [13].

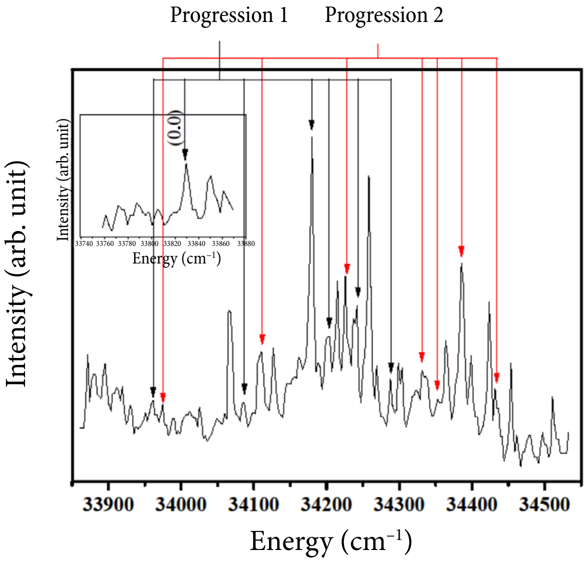

Fig. 1. REMPI spectrum of 3M2HP after 30 min of release of argon gas. The spectrum is normalized with the laser intensity.

The possible reason for appearing of many low frequency bands near the origin could be the methyl internal rotational transitions, as it shows low frequency bands. But all the bands cannot be possible only because of the torsional transitions. Nimlos et al. recorded the excitation spectra for 2-hydroxypyridine and observed a number of transitions which cannot be assigned to any vibrational band which is associated with $\pi\pi^*$ transitions [14]. Such transitions were also reported by Felker et al. [6] and explained with the mixing of $\pi\pi^*$ and $n\pi^*$ vibrational states which do not have a spacing characteristic of $\pi\pi^*$ transitions. The possible reason for appearing of many low frequency bands near the origin band could be the existence of a nearby $n\pi^*$ state, and the vibronic coupling between the levels of $\pi\pi^*$ and $n\pi^*$. Table 1 shows the observed bands and their assignment.

Table 1. Assignment of the bands in the REMPI of 3M2HP.

Energy, cm^{-1}	$\Delta\nu$, cm^{-1}	Assignment
33830	0	Origin ($\pi\pi^*$)
33961	131	2e
33974	144	ν_0^1
34084	254	3a1
34108	278	ν_0^1 2e
34179	349	5e
34202	372	6a2
34226	396	ν_0^1 3a1
34239	409	6a1
34286	456	7e
34331	501	ν_0^1 5e
34351	521	ν_0^1 6a2
34383	553	ν_0^v 6a1
34421	591	ν_0^1 7e

Close to the origin transition, a band at a separation of 21 cm^{-1} is observed. Assigning this band to the 2e torsional transition of the methyl group proclaimed the 3a1 and 4e bands around 53 and 83 cm^{-1}, respectively. But there is no well-resolved band near the predicted value. Hence the second peak cannot be assigned to a torsional band. Also, assigning 21 cm^{-1} to a 2e band produces a barrier of a very low magnitude. But the barrier potential in the ground as well as in the excited states will be of the same order as there is no splitting of 0a1, 0a1 and 1e, 1e transitions for the origin band. Similar bands were reported for 1 MPY [15] in which it was assumed that this could be some anomalous band associated with the $n\pi^*$ transition.

The bands at 131 and 254 cm^{-1} from the origin band in the spectrum may be assigned to 2e and 3a1 torsional transitions, respectively. The potential parameters in the excited state can be obtained by fitting these bands. The excited state torsional parameters ($V'_3 = 464$ cm^{-1}, $V'_6 = 2$ cm^{-1}, $F' = 5.3$ cm^{-1}) were obtained by the best fit of these observed bands. The calculated as well as experimentally observed torsional frequencies are presented in Table 2. The bands at 349, 372, 409 and 456 cm^{-1} can be assigned to 5e, 6a2, 6a1 and 7e torsional transition bands. There was no 4e band in the spectrum. The band at 278 cm^{-1} from the origin band could be due to the mixing of two vibrational modes. Hence, the band at 144 cm^{-1} was assigned to the second lowest vibrational mode (ν_0^1) in the excited state and can explain the presence of the band at 278 cm^{-1}. There are many other vibrational modes 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 Table 2 as progression 2. The bands at 396, 501, 521, 553 and 601 cm^{-1} are assigned to 3a1, 5e, 6a2, 6a1 and 7e torsion and vibration combination bands. The potential parameters used for the assignments of these combination bands are $V'_3 = 472$ cm^{-1}, $V'_6 = 1$ cm^{-1} and $F' = 5.3$ cm^{-1}.

4.1.2. *5-Methyl-2-hydroxypyridine*

The obtained REMPI spectrum of jet-cooled 5-methyl-2-hydroxypyridine (5M2HP) is shown in Fig. 2. The spectrum is recorded after 30 min of the release of the gas. One intense peak with few other peaks was observed in a spectral range of 33900 to 34550 cm^{-1}. The observed spectrum was then normalized using the dye laser profile. The transition band at 34105 cm^{-1} has been defined as the origin band of the molecule. This is the $\pi\pi^*$ transition band. The characteristic of this band and the intensity pattern in the spectrum indicates an unchanged molecular conformation in the excited state compared to the ground state. The other bands are either vibrational bands or methyl torsional bands of the molecule. These bands are at 169, 267, 291, 316, 348 and 384 cm^{-1} from the assigned origin (34105 cm^{-1}). The assignment of the torsional band transitions 169, 267 and 291 cm^{-1} was identified as 3a1, 6a2 and 6a1 using the potential parameters $V_3 = 276$ cm^{-1}, $V_6 = -50$ cm^{-1} and $F = 5.3$ cm^{-1}. Meanwhile, the band at 316 cm^{-1} matched with the band

Table 2. Assignment of the torsional transitions in the REMPI spectrum. Comparison between the experimentally observed and the calculated frequencies of a methyl group ($V_3' = 464$ cm^{-1}, $V_6' = 2$ cm^{-1}, $F' = 5.3$ cm^{-1}; $V_3' = 472$ cm^{-1}, $V_6' = 1$ cm^{-1}, $F' = 5.3$ cm^{-1}).

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	136.2	131	1e–2e	137.2	134
0a1–3a2	136.4	–	0a1–3a2	137.4	–
0a1–3a1	254	254	0a1–3a1	257	252
1e–4e	257	–	1e–4e	259	–
1e–5e	349	349	1e–5e	353	357
0a1–6a2	369	372	0a1–6a2	372	377
0a1–6a1	410	409	0a1–6a1	414	409
1e–7e	451	456	1e–7e	455	457

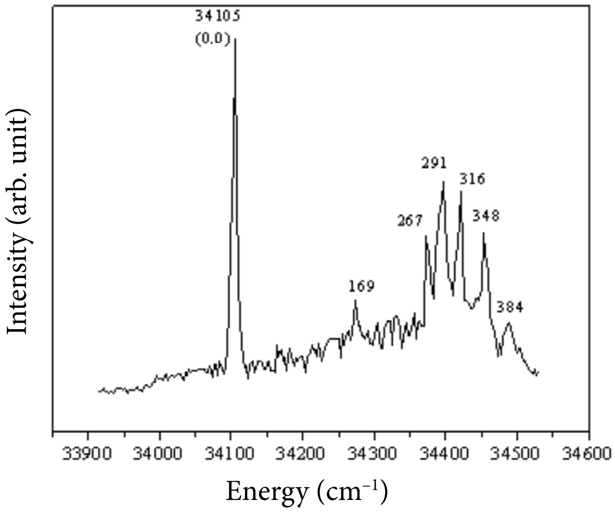

Fig. 2. REMPI spectrum of 5M2HP after 30 min of the release of helium gas. The spectrum is normalized with the laser intensity.

transitions for 3-methyl-2-hydroxypyridine. Hence, this band can be assigned to the vibration corresponding to the 3-methyl-2-hydroxypyridine molecule. The other bands at 348 and 384 cm^{-1} are assumed as some other vibration.

Table 3. Assignments of the bands in 5-methyl-2-hydroxypyridine (V'_3 = 276 cm^{-1}, V'_6 = −50 cm^{-1} and F' = 5.3 cm^{-1}).

Energy, cm^{-1}	$\Delta\nu$, cm^{-1}	Assignment
34105	0	Origin ($\pi\pi^*$)
34274	169	3a1
34372	267	6a2
34396	291	6a1
34421	316	–
34453	348	–
34489	384	–

4.2. IR and Raman spectrum

4.2.1. 3-Methyl-2-hydroxypyridine

For the assignments of the obtained vibrational as well as torsional bands in the ground electronic state, infrared (IR) and Raman spectroscopic techniques were analysed. The FT-IR and Raman spectrum of the molecule in the condensed phase is shown in Figs. 3 and 4, respectively. The spectral resolution in the far IR region is very high compared to that in the mid IR region, thus there is a minimum discrepancy in few of the band positions and their relative intensity such as 490 and 557 cm^{-1} in Fig. 3(a). However, the main interest is to observe the low frequency bands near the origin due to the methyl torsion motion. The calculated frequencies with their relative IR intensity and Raman activity are listed in Table ST1 as supplementary material (Appendix 1) under the harmonic approximation with the optimized geometry in the B3LYP/TZVP level of theory. Few of the calculated low frequency bands are in close proximity with the experimentally observed bands in Raman and FT-IR. The band at 126 cm^{-1} is the pure torsional band of the molecule in the ground state which can also be seen in the Raman spectrum at 107 cm^{-1}. While the bands

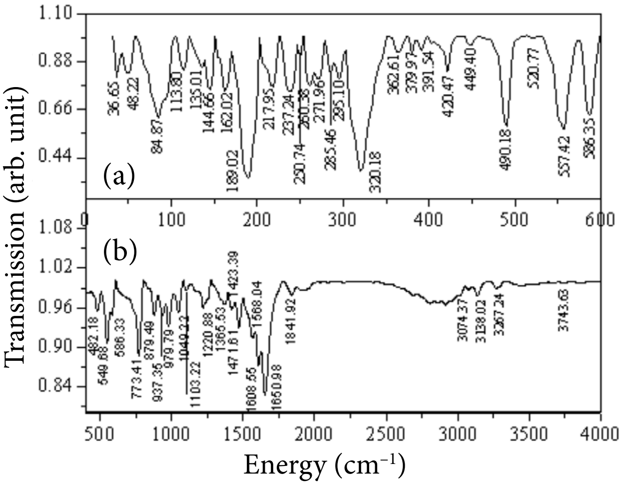

Fig. 3. IR spectra of 3M2HP in (a) the far IR and (b) the mid IR region.

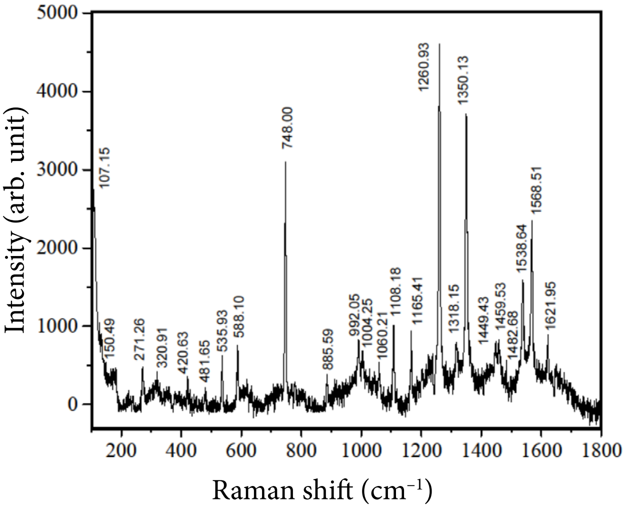

Fig. 4. Raman spectrum of 3-methyl-2-hydroxypyridine.

at 150 and 271 cm^{-1} in the Raman spectrum can also be seen in the FT-IR spectrum at 162 and 272 cm^{-1}, respectively. These low frequency bands are obtained due to the torsional motion of the ring frame and close to the theoretically obtained bands at 163 and 273 cm^{-1}, respectively. The molecule has 15 atoms hence 39 fundamental frequencies are present. Among these 39 fundamental frequencies, 11 are in-plane and 28 are out-of-plane vibrational modes. For all the bands strong mixing of various vibrational modes was observed. However, the first three low frequency vibrations show torsional characteristics.

Figure 5 shows six low frequency vibrations in the ground electronic state of the molecule in which arrows represent the atomic displacements. The lowest frequency was at 126 cm^{-1}. This is because of the torsional motion of the methyl group. The next two calculated low frequencies are at 163 and 273 cm^{-1}. 163 cm^{-1} is observed as a mixture of various torsional motions of the ring frame with the C_3C_8 torsion, while 273 cm^{-1} is obtained because of the mixing of the torsional motion and the bending/wagging motion of the ring frame. These two frequencies are identified in the observed bands in IR and in Raman spectra. However, there was no band at 349 cm^{-1} in the Raman or the IR spectrum as it was present in the REMPI spectra of the molecule. There was no analogous frequency in the calculation. On the basis of these observations, this band was assigned to the torsional 'e' progression (5e).

4.2.2. *5-Methyl-2-hydroxypyridine*

The FT-IR and Raman spectrum of 5-methyl-2-hydroxypyridine is shown in Figs. 6 and 7, respectively. The discrepancy, as discussed previously, is also observed in Fig. 6(a) for 500 and 527 cm^{-1} due to the spectral resolution. The B3LYP/TZVP level of theory has been used to calculate the fundamental frequencies, their relative IR intensity and Raman activity under the harmonic approximation with the optimized geometry, and it is listed in Table ST2 as supplementary material (Appendix 2).

39 fundamental frequencies were obtained for the molecule in which mixing of various vibrational bands was observed as in 3M2HP. There

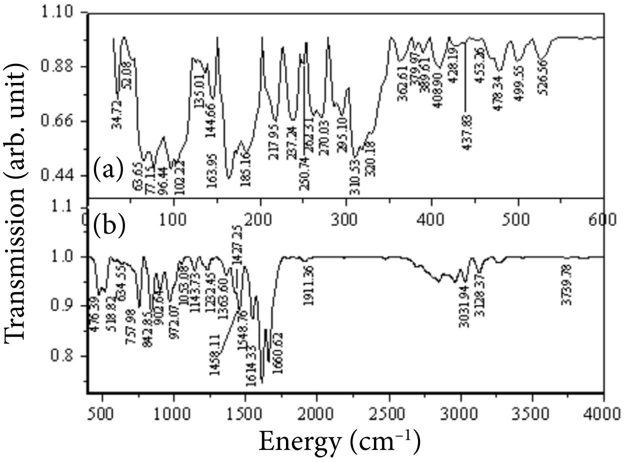

Fig. 6. IR spectra of 5M2HP in (a) the far IR and (b) the mid IR region.

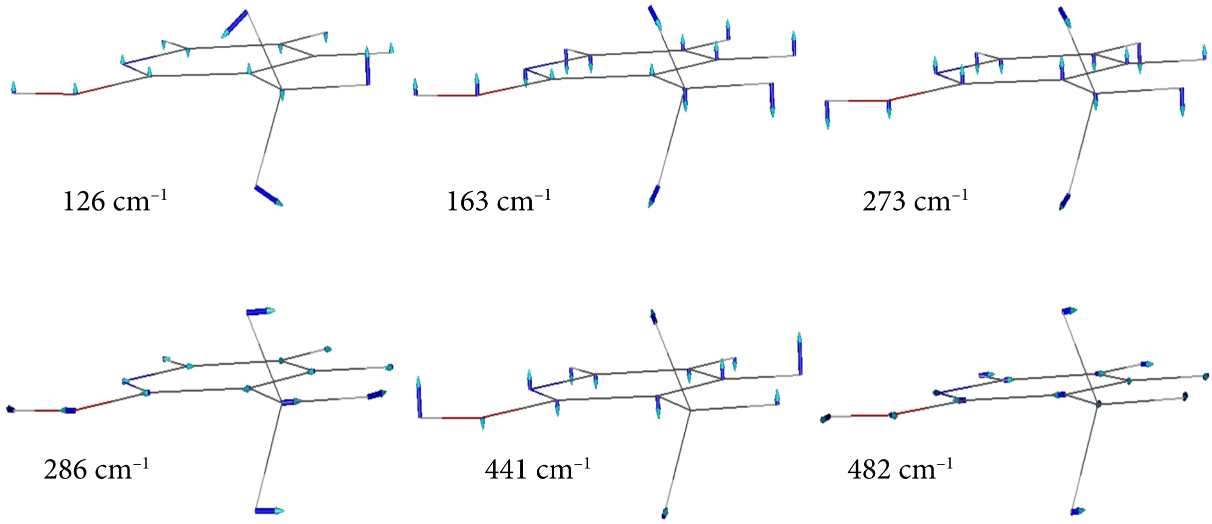

Fig. 5. First six low frequency vibrations in the ground electronic state of 3M2HP.

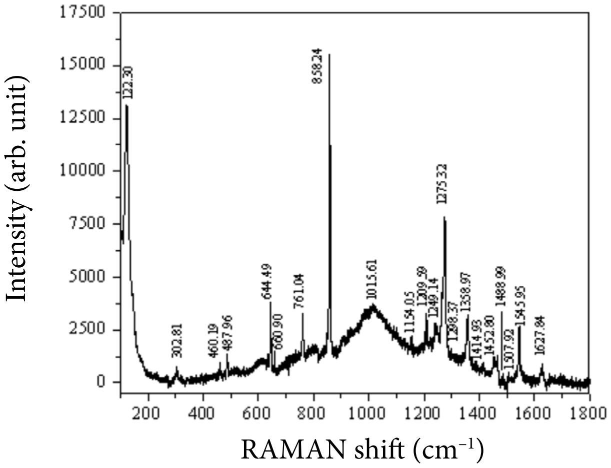

Fig. 7. Raman spectrum of 5-methyl-2-hydroxypyridine.

were no such low frequency vibrational bands as in 3-methyl-2-hydroxypyridine. The first two calculated frequencies were obtained as mixing of the vibrational motions. A low frequency at 74 cm^{-1} was observed as mixing of the torsional characteristic of the methyl group and the out-of-plane wagging/bending motion of the ring frame, while the band at 141 cm^{-1} was due to the mixing of the torsional motion of the ring as well as its out-of-plane wagging/bending motion.

4.3. Theoretical study: Ab initio calculations

4.3.1. 3-Methyl-2-hydroxypyridine

The intensity pattern observed from the REMPI spectrum suggests the change in the methyl group position upon excitation from the ground electronic state to the excited electronic state ($\pi\pi^*$). The torsional potential due to the methyl group internal motion was estimated with the observed 5e band. Further investigation for the conformational study and the torsional potential in the excited state was carried out using the B3LYP/TZVP level of theory. The optimized geometry in the excited state is shown in Fig. 8(a). In the obtained minimum energy conformation of the molecule, the ring frame is always planar and the internal rotation of the methyl group was observed. The torsional angle dependence of the potential energy curve for the excited state (S_1) is shown in Fig. 8(b).

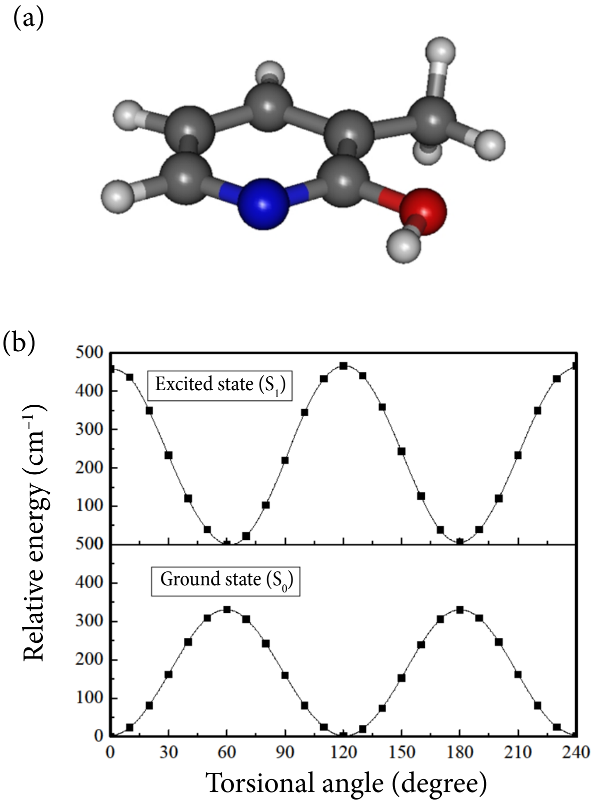

Fig. 8. (a) The optimized geometry and (b) the torsional angle dependence of the potential barrier curve for 3-methyl-2-hydroxypyridine using the B3LYP/TZVP level of theory.

The curve was extracted from the ground state potential energy and the calculated excitation energies for every torsional angle. The calculated value of the three-fold potential term V_3 was found to be 464 cm^{-1} and matched with the experimentally observed value. It can also be seen from the potential curve that the potential minimum has been shifted by 60° in the excited state relative to the ground state. This is in agreement with the result obtained from the optimized geometry and from the observed REMPI spectrum. The change in the methyl group conformation and the magnitude of the torsional potential barrier in 3-methyl-2-hydroxypyridine upon excitation ($S_0 \rightarrow S_1$) were explained using the π^*–σ^* hyperconjugation [15]. The π^*–σ^* hyperconjugation in the LUMO at the top of the barrier conformation stabilizes these in the ground as well as in the excited states. The orbital contour diagram for 3-methyl-2-hydroxypyridine in the HOMO and LUMO in the minimum and top of the barrier conformation is shown in Fig. 9. The π^*–σ^* hyperconjugation was observed only in the 0 degree conformation in the LUMO. This signifies the change in conformation of the methyl group

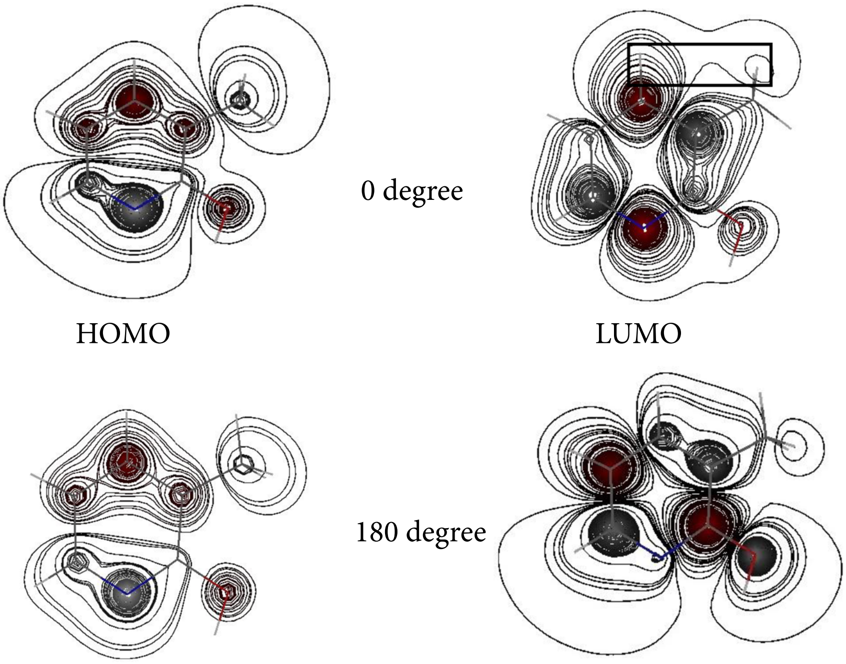

Fig. 9. Contour diagrams of the HOMO and LUMO of 3M2HP in the minimum energy conformation (0 degree) and top of the barrier conformation (180 degree). The contour diagrams are plotted with the same sensitivity.

in the excited state, i.e. rotation of the methyl group upon excitation from the ground electronic state to the excited electronic state ($S_0 \rightarrow S_1$).

4.3.2. 5-Methyl-2-hydroxypyridine

As observed from the obtained REMPI spectrum, there is no such change in the conformation of the methyl group obtained in 5M2HP as in 3M2HP when excitation took place from the ground electronic state to the excited electronic state. The B3LYP/TZVP level of theory has been taken into account for the further investigation of the conformation and torsional potential of the molecule in the excited state (S_1). The optimized geometry of 5-methyl-2-hydroxypyridine in the S_1 state is shown in Fig. 10(a). The ring frame is always planar whenever geometry optimization

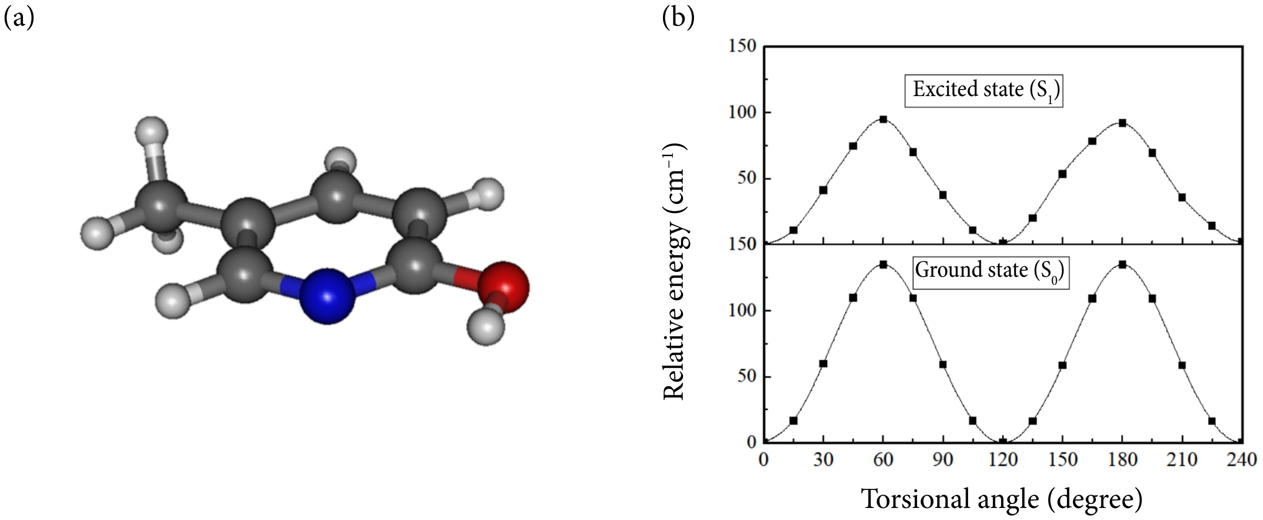

Fig. 10. (a) The optimized geometry and (b) torsional angle dependence of the potential barrier curve for 5M2HP using the B3LYP/TZVP level of theory.

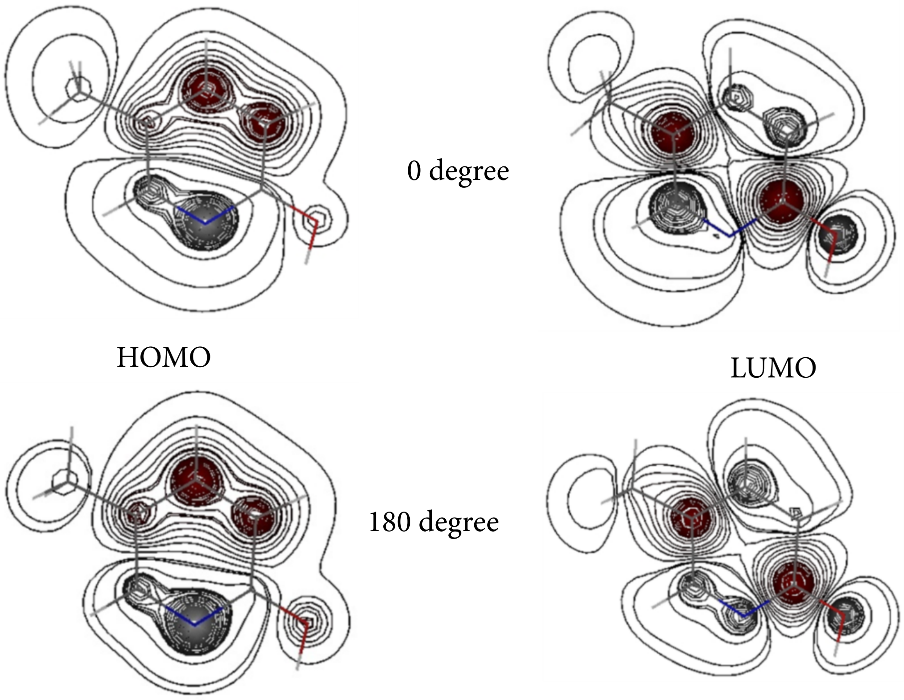

Fig. 11. Contour diagrams of the HOMO and LUMO of 5M2HP in the minimum energy conformation (0 degree) and top of the barrier conformation (180 degree). The contour diagrams are plotted with the same sensitivity.

in the minimum energy conformation has been performed. The torsional angle dependence of the potential energy curve for the excited state (S_1) is shown in Fig. 10(b). The calculated three-fold potential term V_3 was found to be 92 cm^{-1}. The obtained potential curve for the optimized geometry is in agreement with the REMPI spectrum of the molecule.

As discussed previously, the observed π^*–σ^* hyperconjugation explained the changes in the methyl group conformation and in the magnitude of the torsional potential barrier in 3M2HP upon excitation ($S_0 \rightarrow S_1$). But in the case of 5M2HP, there is no change of methyl group conformation (as in the REMPI spectrum) hence no π^*–σ^* hyperconjugation is involved. The orbital contour diagram for 5-methyl-2-hydroxypyridine in the HOMO and LUMO in the minimum energy conformation and top of the barrier energy conformation is shown in Fig. 11.

5. Conclusions

The obtained REMPI spectrum shows an internal rotation of the methyl group in 3-methyl-2-hydroxypyridine upon excitation from the ground state to the excited state which can also be observed from the obtained results from the *ab initio* calculations as well as from the intensity pattern calculation. The band at 33830 and 34105 cm^{-1} was assigned as the $\pi\pi^*$ transition state and named as the origin band for 3M2HP and 5M2HP, respectively. Many low frequency vibrational bands were near the origin band which could be because of the vibronic coupling of the $n\pi^*$ and $\pi\pi^*$ transition states in the 3-methyl-2-hydroxypyridine molecule. The π^*–σ^* hyperconjugation is responsible for the conformational change in the methyl group in 3-methyl-2-hydroxypyridine, while there was no hyperconjugation in 5-methyl-2-hydroxypyridine.

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Appendix 1

Table ST1. Band position in the IR and Raman spectra of 3M2HP along with the theoretically calculated frequencies using the B3LYP/TZVP level of theory.

Calculated frequencies, cm^{-1}	Relative IR intensity	Raman activity	IR, cm^{-1}	Raman, cm^{-1}	Assignments
In-plane vibrations					
286	3.46	0.63	285		ν_{11}
462	7.49	0.61	490	482	ν_{10}
543	7.47	4.64	550		ν_9
607	1.36	7.45	586	588	ν_8
759	2.32	20.95			ν_7
1082	12.42	16.48			ν_6
1359	78.39	7.19	1366	1350	ν_5
3166	7.98	116.64	3138		ν_4
3171	17.16	66.91			ν_3
3203	12.47	182.62	3267		ν_2
3755	81.10	121.32	3744		ν_1
Out-of-plane vibrations					
126	0.13	0.46	135	107	ν_{39}
163	0.13	1.20	162	150	ν_{38}
273	8.88	1.79	272	271	ν_{37}
441	8.64	0.01	449	421	ν_{36}
526	77.60	2.53	521	536	ν_{35}
564	14.76	0.81	557		ν_{34}
741	10.39	0.36		748	ν_{33}
796	44.91	0.03	773		ν_{32}
886	11.34	1.27	879	886	ν_{31}
943	0.01	0.25	937		ν_{30}
957	1.59	0.09			ν_{29}
1013	13.61	4.51		1004	ν_{28}
1063	1.38	0.09	1049	1060	ν_{27}
1122	88.64	1.11	1103	1108	ν_{26}
1191	53.34	4.10		1165	ν_{25}
1235	53.26	4.96	1221	1261	ν_{24}
1306	13.05	1.32			ν_{23}
1319	26.98	16.56		1318	ν_{22}
1426	3.22	10.12	1423		ν_{21}
1466	87.23	5.40	1472	1460	ν_{20}
1481	7.67	10.51		1483	ν_{19}
1501	58.66	3.16		1539	ν_{18}
1509	39.28	2.00		1569	ν_{17}
1631	73.49	11.85		1622	ν_{16}
1641	18.99	23.85			ν_{15}
3034	22.91	211.57			ν_{14}
3084	12.23	80.28	3074		ν_{13}
3111	16.25	61.48			ν_{12}

Appendix 2

Table ST2. Band position in the IR and Raman spectra of 5M2HP along with the theoretically calculated frequencies using the B3LYP/TZVP level of theory.

Calculated frequencies, cm^{-1}	Relative IR intensity	Raman activity	IR, cm^{-1}	Raman, cm^{-1}	Assignments
In-plane vibrations					
306	0.95	0.28	311	303	ν_8
438	19.34	0.29	438		ν_7
492	0.22	8.84	500		ν_6
666	4.77	5.18		661	ν_5
759	3.84	1.65	758	761	ν_4
877	8.88	32.44		858	ν_3
3210	3.12	135.99			ν_2
3756	80.28	131.05	3740		ν_1
Out-of-plane vibrations					
74	0.09	0.60	77		ν_{39}
141	0.60	0.12	145		ν_{38}
322	0.37	1.83	320		ν_{37}
430	0.02	0.28	428		ν_{36}
486	100.16	1.71	478	488	ν_{35}
546	23.35	1.28			ν_{34}
731	4.59	1.11			ν_{33}
828	32.86	0.22			ν_{32}
923	3.24	0.25			ν_{31}
972	0.02	0.11	972		ν_{30}
1006	0.06	1.84		1016	ν_{29}
1045	9.14	0.58	1053		ν_{28}
1063	2.38	0.04			ν_{27}
1151	19.12	1.86	1144	1154	ν_{26}
1188	200.04	3.06			ν_{25}
1241	1.74	9.88	1232	1249	ν_{24}
1309	15.26	8.65		1298	ν_{23}
1319	84.00	9.75			ν_{22}
1368	38.60	3.82	1364	1359	ν_{21}
1425	1.12	17.24	1427	1415	ν_{20}
1438	14.88	3.05		1453	ν_{19}
1490	7.20	11.85		1488	ν_{18}
1505	11.85	11.49			ν_{17}
1526	209.95	0.16	1549	1546	ν_{16}
1626	35.94	7.98	1614	1628	ν_{15}
1652	76.15	27.84	1661	1656	ν_{14}
3028	34.27	239.38	3032		ν_{13}
3075	17.36	91.46			ν_{12}
3104	14.97	59.82			ν_{11}
3152	24.05	102.11	3128		ν_{10}
3168	10.02	83.36			ν_9

References

[1] G.A. Bickel, G.W. Leach, D.R. Demmer, J.W. Hager, and S.C. Wallace, The torsional spectra of jet-cooled methyl substituted indoles in the ground and first excited states, J. Chem. Phys. **88**, 1–8 (1988), https://doi.org/10.1063/1.454636

[2] W.A. Wassam and E.C. Lim, 'Proximity effect' and radiationless transitions in aromatic molecules with non-bonding electrons, J. Mol. Struc. **47**, 129–198 (1978), https://doi.org/10.1016/0022-2860(78)87184-1

[3] A. Hiraya, Y. Achiba, K. Kimura, and E.C. Lim, Identification of the lowest energy $n\pi^*$ states in gas-phase polycyclic monoazines: Quinoline and isoquinoline, J. Chem. Phys. **81**(7), 3345–3347 (1984), https://doi.org/10.1063/1.447998

[4] G. Fischer and A.E.W. Knight, Narrow band laser excited fluorescence as a probe of the near-resonance vibronic coupling in isoquinoline vapour, Chem. Phys. **17**(3), 327–342 (1976), https://doi.org/10.1016/S0301-0104(76)80035-3

[5] G. Fischer and R. Naaman, Near resonance vibronic coupling. Isoquinoline, Chem. Phys. **12**(4), 367–379 (1976), https://doi.org/10.1016/0301-0104(76)87075-9

[6] P.M. Felker and A.H. Zewail, Jet spectroscopy of isoquinoline, Chem. Phys. Lett. **94**(5), 448–453 (1983), https://doi.org/10.1016/0009-2614(83)85030-1

[7] A.K. Jameson, B.E. Forch, K.T. Chen, S. Okajima, H. Saigusa, and E.C. Lim, Electronic and vibrational relaxations in van der Waals complexes of isoquinoline with argon and nitrogen: energetics and dynamics of photodissociation leading to S_1 ($n\pi^*$) isoquinoline, J. Phys. Chem. **88**(21), 4937–4943 (1984), https://doi.org/10.1021/j150665a029

[8] R.K. Sinha, B.P. Singh, and T. Kundu, Effect of electronic states coupling on methyl torsion in 3-methylisoquinoline, Indian J. Phys. **86**(3), 187–194 (2012), https://doi.org/10.1007/s12648-012-0040-3

[9] A.K. Srivastava, R.K. Sinha, S. Saxena, and T. Kundu, Effect of methylation on 2-hydroxypyridine in ground state: Theoretical study, Int. J. Chem. Sci. **16**(2), 270(1–13) (2018), https://doi.org/10.21767/0972-768X.1000270

[10] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, et al., *Gaussian09 Revision E.01* (Gaussian Inc., Wallingford, CT, 2009).

[11] A.R. Allouche, Gabedit – A graphical user interface for computational chemistry softwares, J. Comp. Chem. **32**(1), 174–182 (2011), https://doi.org/10.1002/jcc.21600

[12] R.K. Sinha, B.P. Singh, and T. Kundu, Origin of threefold methyl torsional potential in methylindoles, Theo. Chem. Acc. **121**(1), 59–70 (2008), https://doi.org/10.1007/s00214-008-0450-7

[13] Y. Matsuda, T. Ebata, and N. Mikami, IR–UV double-resonance spectroscopic study of 2-hydroxypyridine and its hydrogen-bonded clusters in supersonic jets, J. Phys. Chem. A. **105**(14), 3475–3480 (2001), https://doi.org/10.1021/jp003272x

[14] M.R. Nimlos, D.F. Kelley, and E.R. Bernstein, Spectroscopy, structure, and proton dynamics of 2-hydroxypyridine and its clusters with water and ammonia, J. Phys. Chem. **93**(2), 643–651 (1989), https://doi.org/10.1021/j100339a030

[15] B. Pradhan, R.K. Sinha, B.P. Singh, and T. Kundu, Origin of methyl torsional barrier in 1-methyl-2(1H)-pyridinimine and 3-methyl-2(1H)-pyridone: II. Ground state, J. Chem. Phys. **126**(11), 114313(1–8) (2007), https://doi.org/10.1063/1.2566602

[16] H. Nakai and M. Kawai, π^*–σ^* hyperconjugation mechanism on the rotational barrier of the methyl group (I): Substituted toluenes in the ground, excited, and anionic states, J. Chem. Phys. **113**(6), 2168–2174 (2000), https://doi.org/10.1063/1.482029

METILO GRUPĖS META PAKEITIMO 2-HIDROKSIPIRIDINE POVEIKIS: SPEKTROSKOPINIS TYRIMAS

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