

AB INITIO CALCULATIONS AND VIBRATIONAL SPECTROSCOPIC STUDIES OF 2-CHLORO-6-METHOXYPYRIDINE

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ABSTRACT

A complete vibrational spectral analyses of 2-chloro-6-methoxypyridine is performed. The wavenumbers are calculated on the basis of ab initio force fields using Hartree-Fock 6-31G and B3LYP/6-31G* basis sets. Assignments of all vibrational bands has been performed taking into account the results of ab initio vibrational analysis. Predicted infrared and Raman intensities are reported.*

Keywords : DFT, HF ab initio calculations, pyridine, methoxy

INTRODUCTION

Pyridine has been extensively studied spectroscopically, due to its applications in many chemical structures of high interest in a variety of biomedical and industrial fields¹. Pyridine has the intrinsic interest of being the azine nearest to benzene. The spectroscopic study of N-heterocyclic molecule including substituted pyridines have become quite interesting as they are the constituent of DNA and RNA and hence play a central role in the structure and properties of nucleic acids²⁻⁴. Yadav et. al.⁵ reported the IR and Raman analysis of 2-Chloro-6-methoxypyridine. In this work, we have calculated the vibrational wavenumbers of 2-chloro-6-methoxypyridine using the Hartree-Fock method and compared it with IR and Raman bands observed by Yadav et al.⁵. These calculations are valuable for providing insight into the vibrational spectrum and related molecular parameters. Ab initio quantum mechanical method is at present widely used for simulating IR spectra. Such simulations are indispensable tools to perform normal coordinate analysis, so that modern vibrational spectroscopy is unimaginable without involving them. In the present study, we wish to report the assignment of complete IR spectrum of the title compound supported by Hartree-Fock ab initio and DFT calculations of all fundamental vibrations.

EXPERIMENTAL (COMPUTATIONAL DETAILS)

Calculations of the title compound were carried out with Gaussian03 program⁶ using the HF/6-31G* and B3LYP/6-31G* basis sets to predict the molecular structure and vibrational wavenumbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wave numbers were calculated using the analytic second derivatives to confirm the convergence to minima on the potential surface. The wavenumber values computed at the HF level contain known systematic errors due to the negligence of electron correlation⁷. We therefore, have used the scaling factor value of 0.8929

for HF/6-31G* and 0.9613 for B3LYP/6-31G* basis set. Parameters corresponding to optimized geometry (HF) of the title compound (Fig.1) are given in Table 1. The absence of imaginary wavenumbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The assignments of the calculated wavenumbers is aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes^{8,9}. The resulting vibrational wavenumbers for the optimized geometry and proposed assignments are given in Table 2.

RESULTS AND DISCUSSION

The wavenumbers of the vibrational modes of methoxy group are known to be influenced by a variety of interesting interactions such as electronic effects, inter-molecular hydrogen bond and Fermi resonance¹⁰. Electronic effects such as back donation and induction, mainly caused by the presence of oxygen atom adjacent to methyl group, can shift the position of CH stretching and bending modes^{11,12}. The asymmetric and symmetric stretching are expected in the region 2935-3005 and 2830-2860 cm^{-1} . The computed wavenumbers of modes corresponding to $\nu_{\text{as}}\text{Me}$ and $\nu_{\text{s}}\text{Me}$ are at 2983, 2929 cm^{-1} and 2871 cm^{-1} .

Two bending vibrations can occur within a methyl group. The first of these, the symmetric bending vibration $\delta_{\text{s}}\text{Me}$ involves the in-phase bending of the CH bonds. The second, $\delta_{\text{as}}\text{Me}$ the asymmetrical bending mode involves out-of-phase bending of CH bonds¹³. With methyl esters the overlap of the regions in which methyl asymmetric deformation are active (1465 ± 10 , $1460 \pm 15 \text{ cm}^{-1}$), is quite strong, which leads to many coinciding wavenumbers¹⁴. This is obvious, not only for the asymmetric deformation but also for the symmetric deformations¹⁴ mostly displayed in the range $1450 \pm 20 \text{ cm}^{-1}$. The HF calculations give 1481, 1478 as $\delta_{\text{as}}\text{Me}$ and 1476 cm^{-1} as $\delta_{\text{s}}\text{Me}$ for the title compound. The methyl rock¹⁴ ρCH_3 has been observed in the region 1120-1220 cm^{-1} . The O-C stretching of the O-CH₃ group, coupled with the methyl rock, appears in the wide region $975 \pm 125 \text{ cm}^{-1}$, with an intensity varying from weak to strong¹⁴.

Pazdera et al.^{15,16} reported the CCl stretching mode at 890 cm^{-1} . For the title compound the ab initio calculation give ν_{CCl} band at 851 cm^{-1} whereas Yadav et al.⁵ reported a band $\sim 982 \text{ cm}^{-1}$ as this mode experimentally.

The ring stretching vibrations of pyridine¹³ occur in the general region between 1600 and 1300 cm^{-1} . The absorption involved stretching and contraction of all of the bonds in the ring and interaction between these stretching modes. The band pattern and relative intensities depend on the substitution pattern and the nature of the substituents. The pyridine ring deformation bands¹⁴ are also identified and assigned (Table 2). The linear regression equations are $\nu_{(\text{Raman})} = 8.007 + 0.994 * \nu_{(\text{HF})}$, (R=0.999), $\nu_{(\text{IR})} = 7.194 + 0.997 * \nu_{(\text{HF})}$, (R=0.999) for HF and $\nu_{(\text{Raman})} = 38.411 + 0.968 * \nu_{(\text{DFT})}$, (R=0.999), $\nu_{(\text{IR})} = 57.279 + 0.966 * \nu_{(\text{DFT})}$, (R=0.999) for DFT calculations.

CONCLUSION

In this work, we have performed the theoretical vibrational analysis of 2-chloro-6-methoxypyridine. The theoretical study gave a description of the geometry and vibrational frequencies of the title compound. The calculated vibrational frequencies are in good agreement with the experimental values obtained for the investigated molecule. The observed discrepancies between the theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum mechanical methods to overestimate the force constant at the exact equilibrium geometry.

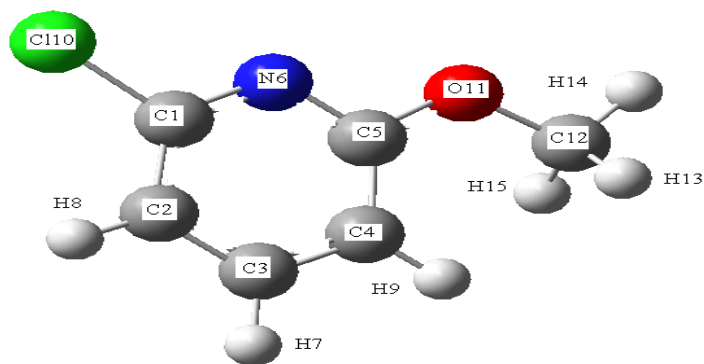


Fig-1 Optimized geometry of 2-chloro-6-methoxy pyridine

Table 1: Geometry parameters of 2-Chloro-6-methoxy pyridine (HF), atom labeling is according to Fig.1

Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)	
C ₁ -C ₂	1.3840	A(2,1,6)	125.1	D(6,1,2,3)	0.0
C ₁ -N ₆	1.3022	A(2,1,10)	118.6	D(6,1,2,8)	180.0
C ₁ -Cl ₁₀	1.7412	A(6,1,10)	116.2	D(10,1,2,3)	180.0
C ₂ -C ₃	1.3814	A(1,2,3)	116.0	D(10,1,2,8)	-0.0
C ₂ -H ₈	1.0711	A(1,2,8)	121.4	D(2,1,6,5)	-0.0
C ₃ -H ₇	1.3832	A(3,2,8)	122.6	D(10,1,6,5)	180.0
C ₄ -C ₅	1.0751	A(2,3,4)	120.4	D(1,2,3,4)	-0.0
C ₄ -H ₉	1.3917	A(2,3,7)	119.9	D(1,2,3,7)	180.0
C ₅ -N ₆	1.0706	A(4,3,7)	119.6	D(8,2,3,4)	-180.0
C ₅ -O ₁₁	1.3192	A(3,4,5)	117.5	D(8,2,3,7)	0.0
O ₁₁ -C ₁₂	1.3312	A(3,4,9)	120.6	D(2,3,4,5)	0.0
C ₁₂ -H ₁₃	1.4022	A(5,4,9)	122.0	D(2,3,4,9)	180.0
C ₁₂ -H ₁₄	1.0843	A(4,5,6)	122.6	D(7,3,4,5)	-180.0
C ₁₂ -H ₁₅	1.0787	A(4,5,11)	124.0	D(7,3,4,9)	0.0
	1.0843	A(6,5,11)	113.3	D(3,4,5,6)	-0.0
		A(1,6,5)	118.4	D(3,4,5,11)	180.0
		A(5,11,12)	120.3	D(9,4,5,6)	180.0
		A(11,12,13)	111.4	D(9,4,5,11)	-0.0
		A(11,12,14)	105.9	D(4,5,6,1)	0.0
		A(11,12,15)	111.4	D(11,5,6,1)	-180.0
		A(13,12,14)	109.3	D(4,5,11,12)	-0.0
		A(13,12,15)	109.6	D(6,5,11,12)	180.0
		A(14,12,15)	109.3	D(5,11,12,13)	-61.3
				D(5,11,12,14)	180.0
				D(5,11,12,15)	61.4

Table 2. Calculated wavenumbers (cm⁻¹) of the fundamental vibrations of 2-Chloro-6-methoxypyridine

$\nu_{(HF)}$	$\nu_{(DFT)}$	$\nu_{(IR)}$	$\nu_{(Raman)}$	IR intensity (HF)	Raman activity (HF)	Assignments
3062	3122	3104	3082	2.97	137.45	ν_{CH}
3060	3117			4.16	44.28	ν_{CH}
3018	3078		3013	12.47	87.07	ν_{CH}
2983	3045	2956	2951	32.74	116.83	$\nu_{as}Me$
2929	2975			51.03	45.98	$\nu_{as}Me$
2871	2916			41.96	105.03	ν_sMe
1604	1580	1602		326.55	23.39	ν_{Py}
1586	1559	1566	1568	191.98	7.85	ν_{Py}
1481	1474			1.31	9.39	$\delta_{as}Me$
1478	1466	1476		99.40	9.12	$\delta_{as}Me$
1476	1460			5.28	23.55	δ_sMe
1439	1417			93.99	3.27	ν_{Py}
1425	1405	1418		210.63	1.52	ν_{Py}
1306	1304	1305	1298	275.79	6.52	ν_{Py}
1207	1270			13.89	2.93	ν_{C-O}
1187	1169			2.25	5.55	ρ_{Me}
1156	1153	1149		3.29	4.64	ρ_{Me}
1142	1139		1148	23.50	1.36	δ_{CH}
1084	1132			227.59	4.18	$\nu_{OC(Me)}$
1077	1075			38.87	4.75	δ_{CH}
1068	1056		1069	36.64	1.48	δ_{CH}
1003	958	1026		0.53	0.96	γ_{CH}
966	950	986	982	6.78	23.32	γ_{CH}
868	840	879	862	0.56	0.17	γ_{CH}
851	835		847	37.45	1.73	ν_{CCl}
793	760	787	766	92.47	0.25	ring breath
735	709	731		2.92	0.83	γ_{CH}
671	669	690	678	17.18	9.24	$\delta_{Py(X)}$
641	618		629	0.22	0.19	$\gamma_{Py(X)}$
554	550			5.27	1.62	$\delta_{Py(X)}$
496	497		522	2.07	1.88	δ_{Py}
452	440		467	0.13	0.57	$\gamma_{Py(X)}$
398	388	416	410	8.41	8.39	δ_{CCl}
300	302			1.64	2.406	$\delta_{Py(X)}$
262	262		278	0.27	0.42	γ_{CCl}

213	213			0.16	1.16	tMe
201	202			1.14	1.35	tMe
173	164		185	0.15	2.46	tPy
76	87			7.15	0.48	tPy

ν -stretching; δ -in-plane deformation; γ -out-of-plane deformation; ρ -rocking; X-substituent sensitive; t-torsion; Py-pyridine; Me-methyl; subscripts: as-asymmetric; s:symmetric; IR intensity (HF) in KM/Mole and Raman activity (HF) in A^{**4}/AMU ; IR and Raman bands from reference [5].

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(Received: 21March 2008

Accepted:26 April 2008

RJC-163)

"Nature has sufficient resources to fulfill everyone's Need, but not has sufficient to fulfill everyone's Greed."

-Mahatma Gandhi