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Vibrational Spectroscopic Studies and *ab initio* Calculations of Pyridine-3-sulfonic Acid

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FT-Raman and FT-IR spectra of pyridine-3-sulfonic acid were recorded and analyzed. The molecular geometry and vibrational wave numbers of pyridine-3-sulfonic acid have been calculated using the Hartree-Fock method with different basis sets. Comparison of the observed fundamental vibrational wavenumbers of pyridine-3-sulfonic acid with calculated results by Hartree-Fock method is found in agreement with the experimental data.

Key Words: Pyridine-3-sulfonic acid, FT-Raman, FT-IR, Hartree-Fock *ab initio* calculation.

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 fields[1]. Pyridine has the intrinsic interest of being the azine nearest to benzene. Aromatic sulfonation is an important industrial process which is used for the manufacture of detergents and surfactants from alkyl benzene[2]. Sulfones are useful intermediates in a wide range of fields such as agrochemicals[3], pharmaceuticals[4] and polymers[5,6]. The sulfonyl group is widely used by synthetic organic chemists and sulfones have many industrial applicatons[7,8]. Pyridine-3-sulfonic acid is found to inhibit the growth of micro organisms[9]. In the present study, the FT-Raman, FT-IR and theoretical calculations of the wave numbers for the pyridine-3-sulfonic acid are reported.

EXPERIMENTAL

Pyridine-3-sulfonic acid was purchased from Sigma-Aldrich, USA. The FT-IR and FT-Raman spectra were recorded using a Bruker IFS 66 V FT-IR/FT-Raman spectrometer.

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Computational details

Ab initio quantum chemical computations were performed at the HF/6-31G(d), HF/6-31C(d,p) and HF/6-311G(d,p) levels of theory to obtain the vibrational wave numbers of normal modes of pyridine-3-sulfonic acid using the Gaussian03 program package[10]. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. All optimized structures were confirmed to be minimum energy conformations. Harmonic vibrational wave numbers were calculated using analytic second derivatives to confirm the convergence to minima on the potential surface. The inclusion of 'd' polarization and double-zeta function in the split valence basis set is expected to produce a marked improvement in the calculated geometry[11]. At the optimized structure of the examined species no imaginary frequency modes were obtained, proving that a true minimum on the potential energy surface was found. The optimum geometry was determined by minimizing the energy with respect to all geometric parameters without imposing molecular symmetry constraints. As suggested by Scott and Radom[12] for a better comparison with experiment, the calculated wave numbers are scaled by an empirical factor of 0.9045. This scaling factor accounts for systematic error caused by basis set incompleteness, neglect of electron correlation and vibrational anharmonicity[13]. The vibrational assignments are given in Table 1.

TABLE-1
CALCULATED VIBRATIONAL WAVENUMBERS, MEASURED INFRARED AND RAMAN BAND POSITIONS (CM^{-1}) AND ASSIGNMENTS FOR PYRIDINE-3-SULFONIC ACID

HF/6-31 G(d)	HF/6-311 G(d,p)	HF/6-311 G(d,p)	υ_{IR}	υ_{Raman}	Assignment
3654	3719	3720			υOH
3091	3073	3055	3120 m	3117 w	υCH
3086	3064	3042	3091 m	3092 w	υCH
3077	3059	3038	3046 mbr	3070 m	υCH
3057	3036	3015	3004 mbr	3047 w	υCH
			2937 mbr	2936 w	υOH
			2786 mbr		Combination/overtone
			2082 mbr		Combination/overtone
			1969 mbr		Combination/overtone
			1740 m		Combination/overtone
1625	1623	1610	1628 m	1629 m	υPy
1615	1613	1601	1617 m	1618 w	υPy
			1551 m		υPy
1488	1483	1472	1470 m		υPy
1432	1428	1419			υPy
1366	1362	1361	1360 m		$\upsilon_a SO_2$
1342	1336	1329	1318 m		$\upsilon_a SO_2$
			1255 s	1263 wbr	δCH

HF/6-31 G(d)	HF/6-311 G(d,p)	HF/6-311 G(d,p)	υ_{IR}	υ_{Raman}	Assignment
1216	1210	1203	1203 s		δCH
1188	1184	1156	1186 s	1185 m	$\upsilon_s SO_2$
1154	1148	1136	1141 s	1144 m	δCH
1135	1120	1102	1116 m	1118 w	$\delta_s OH$
1106	1105	1098			δCH
1083	1080	1063		1048 vs	δCH
1034	1033	1026	1035 s	1034 m	υS-O(H)
1033	1032	1025	1022 s	1020 vvs	υPy
1011	1010	1007			γCH
1010	1009	1003	1010 sh		γCH
978	978	973	957 m	950 w	γCH
854	855	854	927 m	902 w	γCH, γSOH
824	820	818	820 m	821 m	γCH
741	740	738	742 m	742 s	δPy(X), υC-S
696	696	695	681 m	670 w	γPy
			633 m	630 w	δPy, δSO_2
618	618	619	608 m	607 w	δPy, δSO_2
593	592	596	568 m	571 w	δPy(X), δSO_2
554	555	553	552 m	52 w	ωSO_2
470	470	474		481 w	γPy, τSO_2
450	453	449			γPy(X)
408	407	407		405 w	γPy, τSO_2
360	356	364		380 w	δPy, τSO_2
313	313	312		317 w	ρSO_2
286	288	285			ρSO_2
184	183	184		173 vs	τPy
140	132	136			τPy
121	117	121		129 vvs	τPy
27	27	25			τPy

RESULTS AND DISCUSSION

Band assignments are made referring to reported data on selected organic structures[14], Colthup *et al.*[15], Silverstein and Webster[16], Urena *et al.*[17], Klots[18] and Philip *et al.*[19].

The pyridine C-H stretching vibrations[14,18,20,21] are usually observed in the range 3100-3000 cm^{-1}. We have observed four νCH modes of 3-X substituted pyridine at 3120, 3091, 3046, 3004 cm^{-1}, in the IR spectrum and at 3117, 3092, 3070, 3047 cm^{-1} in the Raman spectrum. The calculated values (HF/6-31G(d) for this mode are 3091, 3086, 3077 and 3057 cm^{-1}. The band at 2937 cm^{-1} in the IR spectrum and 2936 cm^{-1} in the Raman spectrum can be typically seen in the spectra of sulfonic acid due to OH stretching[15]. Overtones/combinations of hydrogen bonded OH bending modes are observed in the IR spectrum in the range 2786-1740 cm^{-1} due to proton tunneling and Fermi resonance interactions[22-26]. Ring stretching vibrations[14,16] occur in the region 1600-1300 cm^{-1}. These modes involve stretching and contraction of all the bonds in the ring and interaction between the stretching modes. The bands 1628, 1617, 1551, 1470 cm^{-1} in the IR spectrum and 1629, 1618 cm^{-1} in the Raman spectrum are asigned as ring stretching vibrations. The calculated values after scaling (HF/6-31G(d)) are 1625, 1615, 1488 and 1432 cm^{-1}. According to Bellamy[27] the band at 1600 cm^{-1} may show a double maximum and Cook and Church[28] suggest that for 3-mono substituted pyridine the average seperaton of these bands is 20 cm^{-1}. The band at 1033 cm^{-1} (calculated), 1022 cm^{-1} (IR) and 1020 cm^{-1} (Raman) is assigned to the pyridine ring breathing mode[14,17]. The δCH bands are expected[14,17] in the range 1263-1048 cm^{-1} in both IR and Raman spectra.

The out-of-plane CH deformation vibrations[14,17] are observed in the range 1010-820 cm^{-1}. The bands at 1010, 957, 927 and 820 cm^{-1} in the IR spectrum and 950, 902 and 821 cm^{-1} in the Raman spectrum are assigned to γCH modes. The calculated values are 1011, 1010, 978, 854 and 824 cm^{-1} (HF/6-31G(d)) which are in agreement with the observed values. As seen from Table-1, the *ab initio* calculation shows that γCH mode at 854 cm^{-1} is not pure but contain significant contribution of the mode γSOH[19]. The in plane deformation modes of pyridine are observed at 742, 633, 608 and 568 cm^{-1} in the IR spectrum and at 742, 630, 607, 571 and 380 cm^{-1} in the Raman spectrum. The calculated values are 741, 618, 593, 360 cm^{-1} and these modes are not pure but contain contributions from other substituent sensitive modes[14]. The C-S stretching vibration appears moderately to strongly in the region 760 ± 25 cm^{-1} for majority of investigated molecules[14]. The band observed at 742 cm^{-1} is assigned to νC-S vibration. As seen from Table-1, the *ab initio* calculations also show that the νC-S vibration is not pure and contain significant contributions of other modes. The out-of-plane deformations are assigned at 696, 470, 450, 408 cm^{-1} (calculated) and 681 cm^{-1} (IR) and 670, 481, 405 cm^{-1} (Raman) and some of these modes also contain contributions from other modes[14].

The spectra of esters of sulfonic acids are dominated by three absorptions with a moderate to strong intensity, due to both SO_2 stretching vibrations and a S-O stretching. Usually esters of sulfonic acids absorb at 1385 ± 35 cm^{-1} due to asymmetric SO_2 stretching vibrations[14,16]. The calculated values are 1366 and 1342 cm^{-1}. Sulfonic acid complexes show symmetric SO_2 stretching vibrations[14] at 1200 ± 35 cm^{-1}. The symmetric SO_2 stretching vibration appears around 1186 cm^{-1} in both IR and Raman spectra[14,16,29] with a theoretical value of 1188 cm^{-1}. By comparison with OH bending frequencies in sulfuric acid and other sulfonic acids the band at around 1118 cm^{-1} is assigned to SOH bend[30]. The νS-O(H) mode is reported at 1026 cm^{-1} for sulfamic acid[19] at around 1020 cm^{-1} for amino benzene sulfonic acids[31] and at 1040 cm^{-1} for *p*-toluene sulfonic acid[32]. For pyridine-3-sulfonic acid, the νS-O is observed as a strong band at 1035 cm^{-1} in the IR spectrum, as a medium intense one at 1034 cm^{-1} in the Raman spectrum and the calculated value is 1034 cm^{-1} [33].

Usually the SO_2 deformations absorb with a weak to moderate intensity. The SO_2 scissors[14] absorb in the range 565 ± 45 cm^{-1} and observed at 633, 608 cm^{-1} in the IR spectrum and at 630, 607 cm^{-1} in the Raman spectrum. A second SO_2 deformation, often assigned as a wagging mode is found at 552 cm^{-1}, clearly separated from the scissors. The SO_2 twisting and rocking vibrations[14,34] are seen in the range 425 ± 85 cm^{-1} and 345 ± 55 cm^{-1}. The calculated values in the range 408-286 cm^{-1} contain contributions from these two modes. The low frequency modes are assigned to the torsion of the pyridine ring[14].

Conclusion

In this work, we have performed the experimental and the theoretical vibrational analysis of pyridine-3-sulfonic acid. A comparison of the result of the experimental and theoretical study gave us a description of the vibrational properties of pyridine-3-sulfonic acid. The calculated vibrational wave numbers obtained with Hartree-Fock basis are in good agreement with the experimental values obtained for the investigated molecule. The observed disagreement between the theory and experiment could be a consequence of the anharmonicity and of the general tendency of the quantum chemical moethods to overestimate the force constants at the exact equilibrium geometry[35].

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