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Experimental and Theoretical Vibrational Study of Isatin

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Abstract: The FT-IR vibrational spectra of Isatin have been recorded in the range 4000–100 cm⁻¹. A detailed vibrational spectral analysis has been carried out and assignments of the observed fundamental bands have been proposed on the basis of peak positions and relative intensities. The optimized molecular geometry, vibrational frequencies, atomic charges, dipole moment, rotational constants and several thermodynamic parameters in the ground state were calculated using *ab initio* Hartree–Fock (HF) methods with different basis sets. The observed vibrational wave numbers in FT-IR and FT-Raman spectra were analyzed and assigned to different normal modes of the molecule. Most of the modes have wave numbers in the expected range.

Keywords: FTIR, Hartree-Fock, Isatin.

1. INTRODUCTION

Isatin or 1H – indole-2, 3-dione is an indole derivative. The compound was first obtained by Erdman¹ and Laurent² in 1841 as a product from the oxidation of indigo dye by nitric acid and chromic acids. The compound is found in many significance due to their wide spectrum of biological activities³. The synthetic versatility of isatin has led to the extensive use of this compound in organic synthesis. In nature, isatin is found in plants of the genus *Isatis*, in *Calanthe discolor* LINDL. Isatin is the biologically active chemical produced by an *Altermones* sp. strain inhibiting the surface of embryos of the cardiac shrimp *palaemon macrodactylus*, which protect them from the pathogenic fungus *Lagenidium callinectes*⁴. Isatin ring system consists of pyrrole ring fused with benzene ring. Pyrrole ring is a five-member ring containing one nitrogen in the ring system. Isatin moiety shows biological activities like antimicrobial, CNS depressant, anti-HIV, cytotoxicity, anti-inflammatory, analgesic, antianxiety and many other activities.

2. Method of Calculation

The compound under investigation namely Isatin is purchased from M/S Aldrich chemicals; USA with spectroscopic grade and it is used as such without any further purification. The FT-IR Spectrum of the compound has been recorded in Perkin-Elmer 180 spectrometer in the range of 4000–400 cm⁻¹. The spectral resolution is ± 2 cm⁻¹. The FT-Raman spectrum of the compound is also recorded in the same instrument with FRA 106 Raman module equipped with Nd-YAG laser source operating in the region 100–4000 cm⁻¹ at Indian Institute of Technology Chennai.

3. Results and Discussion

3.1 Vibrational Analysis of Isatin

The molecular structure of the Isatin is optimized and the optimized structure is shown in fig.1. The maximum number of potentially active observable fundamentals of a non-linear molecule which contains N atoms is equal to (3N-6), apart from three translational and

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three rotational degrees of freedom. Hence Isatin molecule which was planar has 16 atoms with 42 modes of vibrations. Vibrational analysis of isatin calculated in table no.1 Ring C-C stretching vibrations normally occur in the region $1590-1430\text{ cm}^{-1}$ [9]. In the present case, the C-C stretching vibrations have been assigned at 1488 cm^{-1} . Generally C=C stretching vibrations in aromatic compounds form a band in the region of $1430-1650\text{ cm}^{-1}$ [10, 11]. Accordingly, in the present study, the C=C stretching vibrations of Isatin are observed at 1632 & 1615 cm^{-1} . When compared to the literature range cited above, there is a considerable decrease in frequencies which is also worsening with the increase of mass of substitutions. In the present work, three strong bands found at $735, 706, 653$ are assigned to CCC in plane bending and three supplementary bands are assigning at $549, 332, 167\text{ cm}^{-1}$ to CCC out of plane bending. These assignments are in line with the assignments proposed by the literature [12, 13]. The aromatic structure shows the presence of C-H stretching vibrations in the region $3100-3000\text{ cm}^{-1}$. Which is the characteristic region for ready identification of C-H stretching vibrations. The bands appeared at $3071, 3105$ and 3035 cm^{-1} in the Isatin have been assigned to C-H ring stretching vibrations. C-H in plane bending vibrations are normally occurred as a number of strong to weak intensity bands in the region $1300-1000\text{ cm}^{-1}$. In the present case, C-H in plane bending vibrations of the present compound are identified at $1190, 1151, 1145, 1093$ & 1015 cm^{-1} . The C-H out of plane bending vibrations are observed in the region $1000-809\text{ cm}^{-1}$. The four C-H out of plane bending vibrations are observed at $949, 944, 883$ & 817 cm^{-1} . These in plane and out of plane vibrational frequencies are found to be well within their characteristic region. Generally C=O stretching vibrations in aromatic compounds form a band in the region of $1790-1720\text{ cm}^{-1}$. Accordingly, in the present study, the C=O stretching vibrations of Isatin are observed at 1734 & 1730 cm^{-1} . In Isatin usually the N-H stretching vibrations occur in the region $3500-3300\text{ cm}^{-1}$. In the present study, the asymmetric and symmetric vibrations of N-H stretching are assigned to the bands at 3444 & 3183 cm^{-1} respectively. These assignments are in the line with the literature. The N-H in plane bending vibrations (Scissoring) are usually observed in the region $1610-1630\text{ cm}^{-1}$. The C-N stretching vibration is always mixed with other bands and is usually assigned in the region $1266-1382\text{ cm}^{-1}$. The C-N stretching is observed strongly in at 1270 cm^{-1} and is mixed with C-H in plane bending vibration. This frequency is also at the lower end of the expected range which may be also due to the interaction of C-C vibration, whose frequency extends up to this value. This view supported by the literature. The C-N vibration in this work is observed strongly and coupled with C-C vibration.

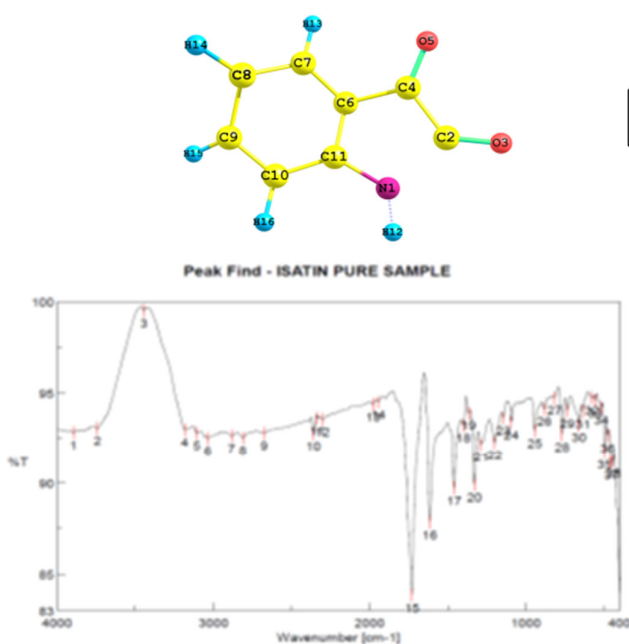


Fig.1 Molecular Structure of Isatin

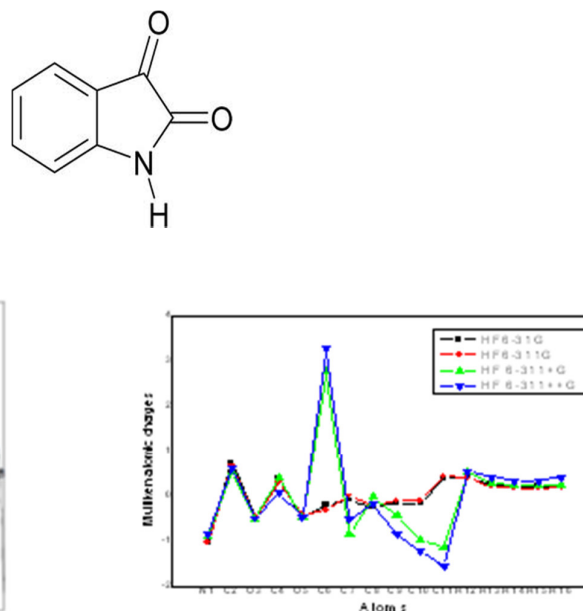


Fig.2 Plot of graph between Mulliken atomic charges Vs Atoms

3.2. Mulliken atomic Charges

The total atomic charges of Isatin are obtained by Mulliken population analysis with different HF basis set HF 6-31G, 6-311G, 6-311++G, HF/6-311++G basis sets were listed in table 4. The negative values of in the of higher basis set such as HF/6-311++G (d, p). The negative values of N_1 O_3 C_7 C_8 C_9 C_{10} C_{11} atoms in the aromatic ring lead to a redistribution of electron density. Due to this negative charges C_6 accommodate higher positive charge and becomes more acidic the charges obtained from HF/6-31G (d, p), HF/6-311G (d, p) basis sets show that carbon atom is more acidic due to more positive charge the better represented graphical form of the results has been done in figure 2.

Conclusions

The FT-IR, spectral measurements have been made for Isatin. The equilibrium geometry, vibration frequencies, and thermodynamic properties of the title compound was performed on the basis of HF and levels of theory utilizing HF 6-31G, 6-311G, 6-311+G, HF/6-311++G basis sets. Comparison between the calculated vibrational frequencies & intensities and experimental values indicates the FTIR spectra of the title compound well. The shift in frequencies with benzene, toluene, and water also investigated.

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Table 1 Detailed assignment of theoretical wave numbers of Isatin

IR	Experimental Raman	HF 6-31G Scaled	HF 6-311G Scaled	HF 6-311+G Scaled	HF 6-311++G Scaled	Vibrational Assignment
3444 s	-	3243	3211	3218	3218	δ N-H
3183 vs	-	3147	3106	3105	3105	δ N-H
3105 vs	3071	3140	3099	3098	3098	ν C-H
3035 vs	-	3126	3083	3082	3082	ν C-H
-	-	3114	3072	3071	3071	ν C-H
1944 w	-	1912	1872	1863	1863	ν C=C
1730 w	1734	1840	1797	1789	1789	ν C=O
1615 vs	1632	1663	1649	1646	1645	ν C=C
-	-	1612	1596	1592	1592	δ N-H
-	1488	1558	1549	1545	1545	ν C-C
-	-	1527	1515	1512	1511	ν C-C
1401 vs	1424	1463	1457	1452	1451	ν C-N
1366 vs	-	1392	1382	1379	1378	ν C-N
1287 vs	1207	1291	1284	1281	1281	ν C-N
1200 vs	-	1258	1251	1248	1248	ν C-N
-	-	1209	1209	1204	1204	δ C-H
-	1190	1197	1183	1182	1182	δ C-H
-	-	1176	1169	1166	1166	δ C-H
1145 vs	1151	1132	1122	1120	1120	δ C-H
1093 vs	-	1114	1100	1099	1099	δ C-H
-	1015	1078	1069	1067	1067	δ C-H
-	-	1004	997	995	995	δ C-H

944.36	949	949	945	942	942	ϕ_{C-H}
883.36	-	897	896	891	891	ϕ_{C-H}
-	-	895	893	889	889	ϕ_{C-H}
817 m	-	840	840	833	832	ϕ_{C-H}
744.36	735	804	802	799	798	(CCC) δ
-	-	783	777	766	765	(CCC) δ
706.36	-	728	726	720	720	(CCC) δ
653 m	-	693	689	687	686	(CCC) δ
-	-	635	634	631	631	(CCC) δ
-	-	610	608	606	605	(CCC) δ
-	-	581	584	584	583	(CCC) δ
-	549	546	547	547	547	(CCC) δ
-	-	476	478	477	477	(CCC) ϕ
-	-	454	455	454	453	(CCC) ϕ
-	-	397	398	398	398	(CCC) ϕ
-	-	378	379	377	377	(CCC) ϕ
-	332	314	313	311	311	(CCC) ϕ
-	167	232	234	233	233	(CCC) ϕ
-	-	172	175	174	174	(CCC) ϕ
-	-	-258	-270	-273	-273	(CCC) ϕ

TABLE 2: Mulliken Atomic Charges of Isatin

Atoms	HF6-31G	HF6-311G	HF 6-311+G	HF 6-311++G
N1	-1.0236	-1.0180	-0.8818	-0.8390
C2	0.7520	0.6655	0.5235	0.6082
O3	-0.5094	-0.4524	-0.4948	-0.4840
C4	0.3859	0.3225	0.4064	0.0735
O5	-0.4676	-0.4023	-0.4784	-0.4700
C6	-0.1928	-0.3028	2.8014	3.3021
C7	-0.0853	-0.0052	-0.8497	-0.5181
C8	-0.2382	-0.2156	-0.0138	-0.1687
C9	-0.1696	-0.1023	-0.4381	-0.8206
C10	-0.1695	-0.0952	-0.9655	-1.2211
C11	0.3879	0.4480	-1.1399	-1.5432
H12	0.4075	0.3953	0.5440	0.5558
H13	0.2590	0.2073	0.2810	0.4270
H14	0.2164	0.1775	0.2277	0.3493
H15	0.2184	0.1745	0.2255	0.3349