

Full Length Research Paper

Numerical simulation of the internal vibrations of COOH group in amino-salicylic acids

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Our present work reports the IR spectra of amino substituted salicylic acids recorded by FTIR spectrometer and also simulated theoretically. The simulation was performed using GF matrix and AM1, PM3, DFT method. In this work, the following steps were taken: optimizing the geometry, computing the IR spectra and comparing it with experimental spectra. Assuming C_s point symmetry, vibrational assignments for the observed frequencies have been proposed. The spectra exhibit distinct features originating from low frequency vibrational modes caused by intra-molecular motion.

Key words: o-amino salicylic acid, m-amino salicylic acid, p-amino salicylic acid, FTIR spectra, vibrational spectra, AM1, PM3, DFT, G-F Matrix.

INTRODUCTION

Salicylic acid contains both a hydroxyl and a carboxyl group, which react with either an acid or an alcohol. Salicylic acid has strong antiseptic and germicidal properties because it is a carboxylated phenol. The presence of the carboxyl group appears to enhance the antiseptic property. Many hair tonics and remedies for athlete's foot, corns and warts employ the keratolytic action of salicylic acid.

Volvo et al. (1983) calculated normal coordinates for salicylic acid molecule and proposed the assignment of the observed Raman and IR spectra. They found that C=O stretching modes are accounted for by specific interactions due to the symmetry characteristics and possible conformational changes in the solution.

With the availability of powerful computers and the advent of efficient density functional theory (DFT) methods implemented in standard codes, structure and dynamics of systems containing a few tens of atoms (even more) are now within reach. Vibrational spectra of small molecules of biological or pharmaceutical relevance are routinely treated combining DFT electronic structure calculations

with a harmonic analysis (Bakker et al., 2004). Due to deficiencies of the quantum chemical calculations and/or due to the neglect of an anharmonic effect, these frequencies are typically a few percent higher than the observed ones.

Marck et al. (2002) studied theoretical simulation of the ν_s stretching band for salicylic acid taking into account adiabatic couplings between the high-frequency O-H stretching and the low-frequency intermolecular O.....O stretching modes. Jadrijevic et al (2004) analyzed the structures and the spectral properties of salicylic acid and benzoic acids by means of FT-IR (Figures 1-3 and NMR spectroscopy).

We compared experimental results with calculated frequencies of amino-salicylic acids using force matrix method and AM1, PM3 and DFT method. These methods were able to account breadth of spectrum as well as description of vibrational modes to encourage the application of a similar procedure to a larger and more complex group.

EXPERIMENTAL

Amino salicylic acids were purchased from Sigma Chemical Company (USA). I.R. Spectra has been recorded in the liquid phase in

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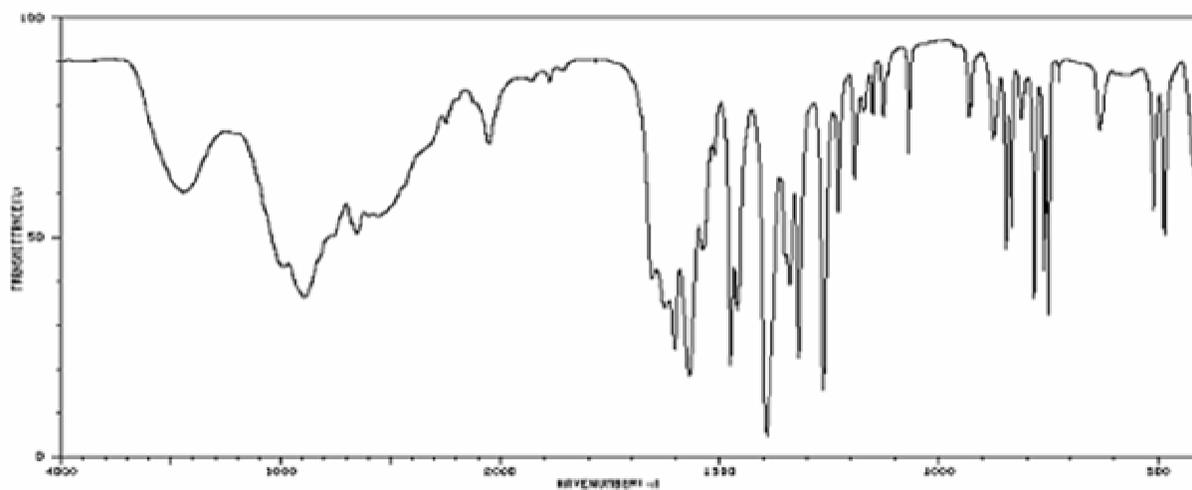


Figure 1. FT-IR Spectra of 3-amino salicylic acid.

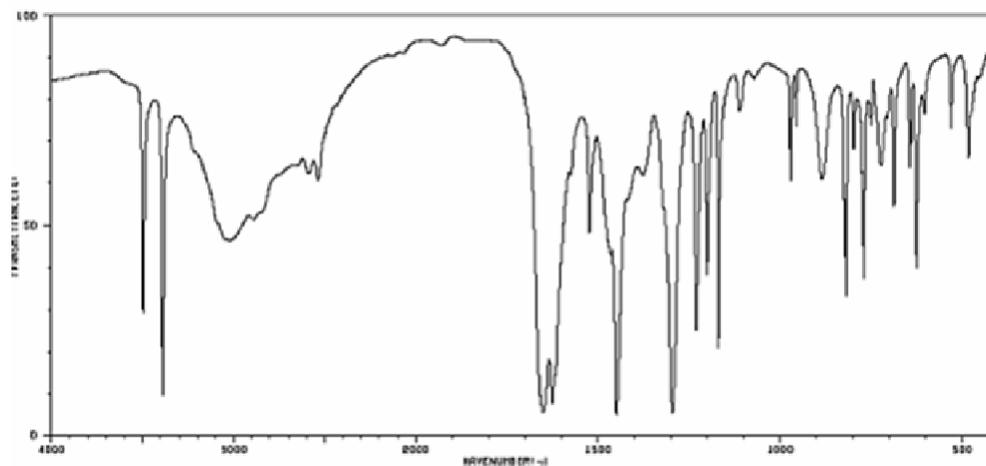


Figure 2. FT-IR Spectra of 4-amino salicylic acid.

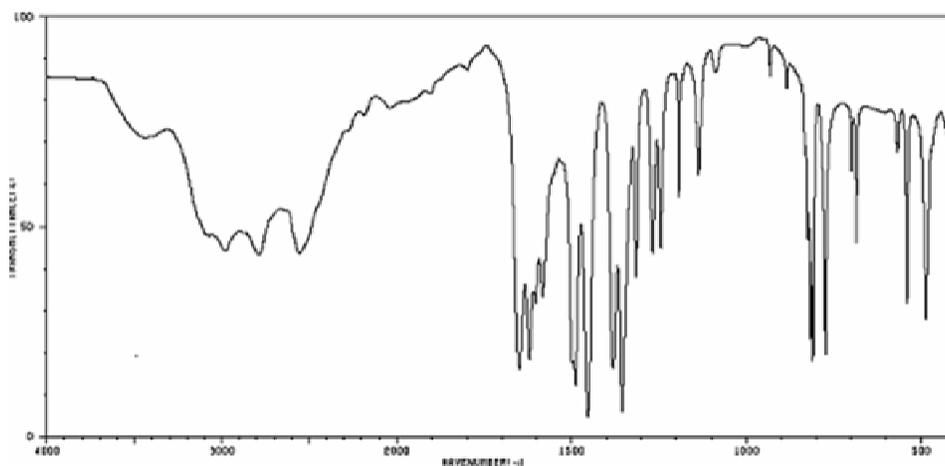


Figure 3. FT-IR Spectra of 5-amino salicylic acid.

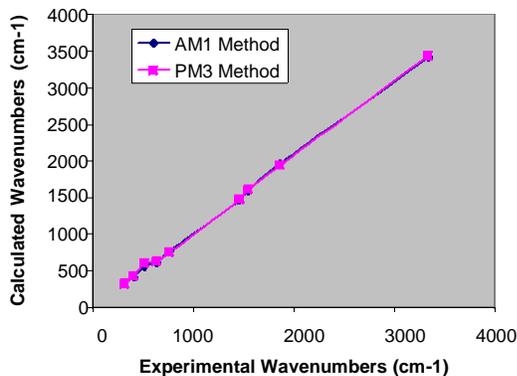


Figure 4. Correlation diagram for experimental Vs calculated frequencies (AM1 and PM3 method) for 3-aminosalicylic acid.

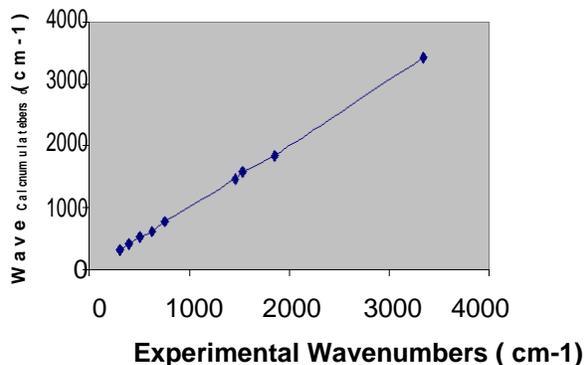


Figure 5. Correlation diagram for experimental Vs calculated frequencies (G-F matrix method) for 3-amino salicylic acid.

the range 400 – 4000 cm^{-1} on Perkin-Elmer spectrometer Model 397.

Preparation of KBr discs

A small amount of finally grounded solid sample was intimately mixed with about 100 times or more than its weight of potassium bromide powder. The finely grounded mixture was then pressed under very high pressure in a press (about $10/\text{cm}^2$) to form a small pallet (about 1 - 2 mm thick and 1 cm in diameter).

The accuracy of the measurements was estimated to be within 3 cm^{-1} and the resolution was better than 2 cm^{-1} through the entire range for both the spectra.

Computational and theoretical details

In noncomplex molecules, the G F Matrix is given by:-

$$G_{tt'} = \sum_{i=1}^{3N} (B_{ti} B_{t'i}) / m_i \quad \text{where } t, t' = 1, 2, 3, \dots, 3N-6$$

which m_i is the mass of the atom to which the subscript i refers and B_{ti} , $B_{t'i}$ are constants determined by geometry of molecule.

Internal coordinate S_t are related with Cartesian displacement coordinate s_i as:

$$S_t = \sum_{i=1}^{3N} B_{ti} s_i \quad \text{where } t = 1, 2, 3, \dots, 3N-6$$

On solving G.F. matrix for any atom s_i is obtained as:

$$G_{tt'} = \sum_{i=1}^{3N} B_{ti} B_{t'i} / m_i$$

Where dot represents the scalar product of two vectors and $m_i = 1/m$, the reciprocal of the mass of atom.

The AM1 and PM3 semi empirical approaches were performed as implemented in MOPAC program (1997) and the precise keywords were used. DFT calculations were performed using HYPERCHEM program (2002) at the B3LYP (1993) levels of theory with 6-31G* basis set (1989). The vibrational IR spectra were calculated at the B3LYP/ 6-31G* levels of theory. We have transformed the harmonic force fields, determined initially in the cartesian coordinates, were transformed to the force fields in the internal local coordinates. The force fields obtained were used to calculate the potential energy distribution (PED, 2001). Contributions greater than 10% are given.

RESULTS AND DISCUSSIONS

We had employed a very large basis set for the computational of the frequencies. First infrared frequencies were calculated for the amino benzoic acids (C_s Symmetry) at the DFT (B3LYP), AM1, PM3 and G F Matrix level of theory. We can get information from computational vibrational spectra only when we compare it with experimental spectrum. Our results are given in Table 1. Due to an harmonicity, the harmonic vibrational frequencies were found to be lowered by 1 to 3% in almost all cases except AM1 method.

The number of internal vibrations for a group is given by $3m-3$, where m is the number of atoms in the group. Thus COOH has 9 modes of vibrations. These modes are as follow; O-H Stretching, C-O Stretching, C=O Stretching, in-plane-rocking, in-plane bending of C-O, in-plane-bending of C=O, in-plane -bending of OH, out-of-plane wagging, and out- of-plane torsion. Antony et al. (2005) studied vibrational spectra of benzoic acid and got C=O Stretching at 1745 cm^{-1} , C-O stretching at 1050 cm^{-1} , C-O in-plane bending at 594 cm^{-1} , C=O in-plane bending at 1804 cm^{-1} , OH stretch at 3785 cm^{-1} , rocking mode at 554 cm^{-1} , torsion mode at 594 cm^{-1} and wagging mode at 441 cm^{-1} . Florjo et al. (2003) observed C=O Stretching at 1752 cm^{-1} , C-O stretching at 1347 cm^{-1} , C-O in-plane bending at 628 cm^{-1} , OH stretch at 3785 cm^{-1} , rocking mode at 628 cm^{-1} , and wagging mode at 160 cm^{-1} . In pre-sent study we get frequencies as shown in Table 1.

Conclusions

Theoretical semi-empirical quantum mechanical AM1, PM3, DFT and GF matrix calculations of the geometry and vibrational frequencies of the o-,m-,p- amino salicylic acids are presented in this paper and compared with infrared spectra. The calculated geometries and frequencies agree well (for DFT and G.F. Matrix) with the experimental ones, but there are some differences between frequencies mainly due to intermolecular interactions, an harmonicity and computational basis set. The results indicate that, the exchange functional proposed by Becke and the correlation functional of Lee, Yang and Parr with 6-31G* basis set is the optimal model for studying o-,m-,p- amino benzoic acids. Figures 4 to 6 shows agreement

Table 1. Internal vibrations of COOH group.

	Mode of vibration	3-amino salicylic acid (cm ⁻¹)	4-amino salicylic acid (cm ⁻¹)	5-amino salicylic acid (cm ⁻¹)
a'	O-H Stretching	3338(E)	3397(E)	3409(E)
		3438.9(GF)	3416.5(GF)	3400.3(GF)
		3417.9(AM1)	3423.3(AM1)	3418.7(AM1)
		3432.8(PM3)	3432.6(PM3)	3434.7(PM3)
		3347.8(DFT)	3390.7(DFT)	3385.1(DFT)
	C-O Stretching	1856(E)	1845(E)	1823(E)
		1846.3(GF)	1863.2(GF)	1799.9(GF)
		1959.2(AM1)	2075.5(AM1)	1801.2(AM1)
		1938.4(PM3)	1973.5(PM3)	1874.8(PM3)
		1863.7(DFT)	1852.6(DFT)	1849.2(DFT)
	C=O Stretching	1538(E)	1592(E)	1584(E)
		1581.4(GF)	1581.1(GF)	1570.2(GF)
1590.9(AM1)		1583.6(AM1)	1580.2(AM1)	
1603.7(PM3)		1611.8(PM3)	1601.6(PM3)	
1542.7(DFT)		1581.9(DFT)	1574.8(DFT)	
Bending C-O	401(E)	450(E)	465(E)	
	408.3(GF)	431.3(GF)	448.8(GF)	
	414.5(AM1)	437.2(AM1)	418.2(AM1)	
	421.6(PM3)	431.6(PM3)	438.1(PM3)	
	409.1(DFT)	412.8(DFT)	418.7(DFT)	
Bending C=O	310(E)	374(E)	327(E)	
	311.8(GF)	371.6(GF)	313.2(GF)	
	318.2(AM1)	357.5(AM1)	311.8(AM1)	
	322.5(PM3)	328.5(PM3)	325.6(PM3)	
	312.4(DFT)	367.3(DFT)	335.1(DFT)	
Bending OH	1461(E)	1450(E)	1454(E)	
	1460.6(GF)	1445.3(GF)	1445.6(GF)	
	1467.6(AM1)	1451.8(AM1)	1451.7(AM1)	
	1471.6(PM3)	1470.1(PM3)	1462.7(PM3)	
	1458.1(DFT)	1452.7(DFT)	1459.1(DFT)	
a''	Rocking	633(E)	641(E)	686(E)
		612.4(GF)	639.2(GF)	665.3(GF)
		614.5(AM1)	632.9(AM1)	656.3(AM1)
		623.6(PM3)	627.5(PM3)	641.8(PM3)
		629.6(DFT)	638.1(DFT)	672.3(DFT)
	Wagging	510(E)	525(E)	568(E)
		521.5(GF)	531.5(GF)	548.8(GF)
		556.0(AM1)	535.4(AM1)	532.8(AM1)
		549.1(PM3)	538.5(PM3)	541.2(PM3)
		514.8(DFT)	518.4(DFT)	553(DFT)
	Torsion	761(E)	775(E)	774(E)
		771.4(GF)	768.2(GF)	770.1(GF)
769.4(AM1)		769.9(AM1)	776.5(AM1)	
751.7(PM3)		753.79PM3)	761.9(PM3)	
758.3(DFT)		765.1(DFT)	779.2(DFT)	

E:- Experimental frequencies; GF:- Theoretical frequencies calculated by GF Matrix method; AM1:- Theoretical frequencies calculated by quantum mechanical AM1 MOPAC method; PM3:- Theoretical frequencies calculated by quantum mechanical PM3 MOPAC method; DFT:- Theoretical calculations were performed using HYPER CHEM program at the B3LYP levels of theory with 6-31G* basis set

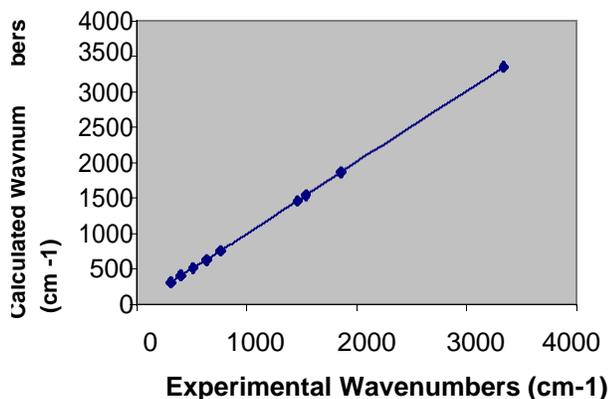


Figure 6. Correlation diagram for experimental Vs calculated frequencies (DFT method) for 3-amino salicylic acid.

between the experimental and calculated wave numbers. The graph is linear which shows that theoretical and experimental results are in good agreement. Similar graphs were obtained for m- and p- amino benzoic acids.

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