Research Paper :

Numerical simulation of the internal vibrations of NH_2 in amino-benzoic acids

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ABSTRACT

Our present work reports the IR spectra of amino substituted Benzoic Acids recorded by FTIR spectrometer and also simulated theoretically. The simulation was performed using GF matrix and AM1, PM3, DFT method. In this work 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 benzoic acid, m-amino benzoic acid, p-amino benzoic acid, FTIR spectra, vibrational spectra, AM1, PM3, DFT,G-F Matrix

Carboxylic acids (RCOOH) are a common and important functional group and provide the point of success to the carboxylic acids derivatives (acetyl chlorides, esters, amides etc.). Carboxylic acids are the most acidic of the common organic functional groups. Amino benzoic acid is used by topical application as a sunscreen agent. Amino benzoic acid and its derivatives effectively absorb light throughout the UVB range but absorb little or no UVA light. Amino benzoate sunscreen agents, therefore, may be used to prevent sunburn[7].

Molecular structures and inter/intra molecular interactions have a direct influence on the type of structural framework that biomolecules can adopt. Understanding of fundamental processes, dynamics, molecular-orbital studies and force constant calculations are, thus, main objectives of spectroscopists. Intramolecular force field helps us by identifying fundamental frequencies, assigning fundamental frequencies to correct mode of vibrations, determining reliable force constants and designing the drug as input parameters and to predict vibrational frequencies of related molecules. Theoret[8] studied the IR spectra of o-, m- and p-amino benzoic acids in different crystalline forms

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 (or even more) are now within reach. Vibrational spectra of small molecules of biological or pharmaceutical relevance are routinely treated combing DFT electronic structure calculations with a harmonic analysis[9]. Due to deficiencies of the quantum chemical calculations and/or due to the neglect of anharmonic effects, these frequencies are typically a few per cent higher than the observed ones.

We compared experimental results with calculated frequencies of amino benzoic 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.

MATERIALS AND METHODS

Amino Benzoic acid were purchased from Sigma Chemical Co (USA). I.R. Spectrum has been recorded in the liquid phase in the range 400-4000cm^{-1} on Perkin-Elmer spectrometer Model 397.

Preparation of KBr Pallets: 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 finally grounded mixture was than pressed under very high pressure in a press (about 10/cm^2) to form a small pallet (about 1-2 mm thick and 1cm in diameter).

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

Computational and theoretical details :

In noncomplex molecules, the G F Matrix [13] is given by:

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

where t, t' = 1,2,3,……, 3N-6

In 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 ξ_i as :

$$S_t = \sum\nolimits_{i=1}^{3N} B_{ti}\, \xi_i$$

where t = 1,2,3….., 3N-6

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

$$G_{tt'} = \sum\nolimits_{\alpha=1}^{3N} \mu_\alpha\, S_{t\alpha} \cdot S_{t'\alpha}$$

Where dot represents the scalar product of two vectors and $\mu_\alpha = 1/m_\alpha$, the reciprocal of the mass of atom α.

The AM1 and PM3 semi empirical approaches were performed as implemented in MOPAC program [10] and the PRECISE keywords were used. DFT calculations were performed using HYPER CHEM program [11] at the B3LYP [12] levels of theory with 6-31G* basis set [13]. The vibrational IR specra 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)[14]. Contributions greater than 10% are given.

RESULTS AND DISCUSSION

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 2. Due to anharmonicity, the harmonic vibrational frequencies were found to be lowered by1 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 NH_2 has 6 modes of vibrations. These modes are as : two stretching vibrations (one symmetric and one asymmetric) both belonging to a' species, two angle deformations (scissoring and rocking), one out-of-plane wagging of NH_2 and one torsion vibration of NH_2

There are three major differences between the C-H and N-H stretching frequencies. First, the force constant for N-H stretching is stronger, there is a larger dipole moment associated with the N-H bond, and finally,

the N-H bond is usually involved in hydrogen bonding. The stronger force constant leads to a higher frequency for absorption. The N-H stretching frequency is usually observed from 3500-3200 cm^{-1}. The larger dipole moment leads to a stronger absorption and the presence of hydrogen bonding has a definite influence on the band shape and frequency position. The presence of hydrogen bonding has two major influences on spectra. First, its

Table 1 : Internal Vibrations of NH$_2$ group			
Mode of vibration	o-Amino Benzoic Acid (in cm^{-1})	m-Amino Benzoic Acid (in cm^{-1})	p-Amino Benzoic Acid (in cm^{-1})
a' N-H	3622 (E)	3432(E)	3460(E)
Asymmetric	3601.6(GF)	3490.1(GF)	3521.3(GF)
Stretching	3530.9(AM1)	3492.4(AM1)	3512.2(AM1)
	3567.4(PM3)	3504.1(PM3)	3528.9(PM3)
	3611.8(DFT)	3447(DFT)	3481.5(DFT)
CN-H	3325(E)	3363(E)	3462(E)
Symmetric	3342.9(GF)	3207.6(GF)	3487.2(GF)
Stretching	3539.9(AM1)	3464.6(AM1)	3490.0(AM1)
	3516.3(PM3)	3428.4(PM3)	3502.7(PM3)
	3336.7(DFT)	3348.9(DFT)	3448.1(DFT)
NH$_2$ In-Plane	1156(E)	1110(E)	1132(E)
Bending	1162.3(GF)	1123.5(GF)	1140.1(GF)
	1219.5(AM1)	1217.7(AM1)	1143.9(AM1)
	1203.8(PM3)	1192.5(PM3)	1159.4(PM3)
	1169.3(DFT)	1119.4 (DFT)	1121.3(DFT)
NH$_2$ Rocking	541(E)	525(E)	523(E)
	527.1(GF)	531.3(GF)	529.3(GF)
	558.1(AM1)	537.2(AM1)	539.3(AM1)
	568.3(PM3)	547.4(PM3)	535.6(PM3)
	537.1(DFT)	531.8(DFT)	518.1(DFT)
a" Wagging	459(E)	432(E)	412(E)
	441.8(GF)	441.8(GF)	408.3(GF)
	440.5(AM1)	497.4(AM1)	380.2(AM1)
	432.6(PM3)	475.2(PM3)	387.8(PM3)
	447.9(DFT)	427.6(DFT)	411.5(DFT)
Torsion	--	--	--
	284.7(GF)	280.2(GF)	300.1(GF)
	281.7(AM1)	251.2(AM1)	326.0(AM1)
	296.9(PM3)	256.8(PM3)	338.1(PM3)
	291.4(DFT)	279.4(DFT)	294.7(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

presence causes a shift toward lower frequency of all functional groups that are involved in hydrogen bonding and second, the peaks are generally broadened.

The NH_2 stretching modes appear in the region 3500 – 3100 cm^{-1} and the asymmetric component has slightly higher magnitude than the symmetric component. D.N. Singh[15] observed asymmetric modes at 3465 cm^{-1} and symmetric mode at 3360 cm^{-1}. However, A.K.Tiwari [16] observed them at 3449 cm^{-1} and 3367 cm^{-1}, respectively.

He observed in-plane bending and rocking mode at 1630 cm^{-1} and 1055 cm^{-1}, respectively. A.K. Tiwari got in-plane bending mode at 1621 cm^{-1} and rocking mode at 952 cm^{-1}.

D.N. Singh[15] observed wagging vibration at 592 cm^{-1} and he didn't get torsion mode. A.K.Tiwari observed these vibrations at 626 cm^{-1} and 274 cm^{-1}, respectively. In present study we get frequencies for them as :

Conclusion:

Theoretical semi-empirical quantum mechanical AM1, PM3, DFT and GF matrix calculations of the

Fig. 3 :   **FT-IR Spectra of p-amino benzoic acid**

geometry and vibrational frequencies of the o-,m-,p- amino benzoic 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, anharmonicity and computational basis set. The results indicate that, the exchange functional proposed by Becke and the correlation functional of Lee, Yang and

Fig. 1 :   **FT-IR Spectra of 0-amino benzoic acid**
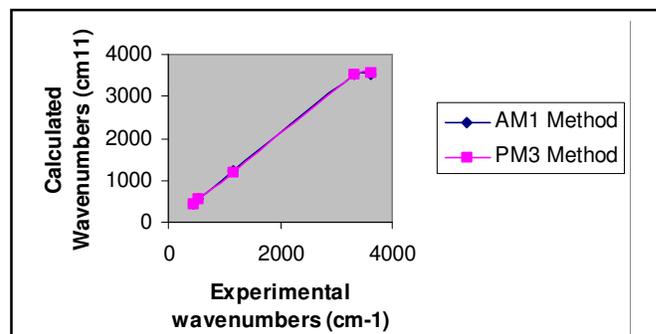
Fig. 4 :   **Correlation Diagram for Experimental Vs Calculated Frequencies (AM1 andPM3 method) for o-aminobenzoic acid**

Fig. 2 :   **FT-IR Spectra of m-amino benzoic acid**
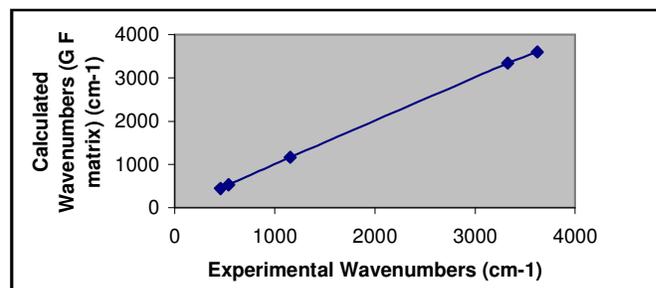
Fig. 5 :   **Correlation Diagram for Experimental Vs Calculated Frequencies (G-F matrix method) for o-amino benzoic acid**
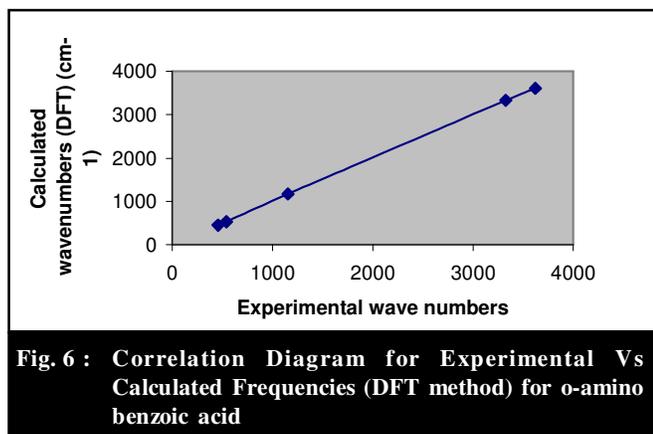
Fig. 6 : Correlation Diagram for Experimental Vs Calculated Frequencies (DFT method) for o-amino benzoic acid

Parr with 6-31G* basis set is the optimal model for studying o-,m-,p- amino benzoic acids. Fig. 4, 5 and 6 shows agreement 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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REFERENCES

1. WWW.Chemicalland21.com, Nov.(2005).

2. **Wilson** and Gisvolds (1998). *Textbook of Organic, Medicinal and Pharmaceutical Chemistry*, Lippincott Williams & Wilkins; 10th edition, ISBN 987-0397515837,

3. **Wong,M.W.** (1996). *Chem Phys. Letters*, **256**: 391-399

4. **Ibrahim, M.** and Koglin, E. (2004). *Acta Chim*, **51**: 453-460

5. **Florio, G.M.**, Zwier, T.S., Myshakin, E.M., Jordan, K.D. and Sibert III, E.L. (2003). *J. Chem. Phys.*, **118** : 1735

6. **Wilson, E.B.**, Decius, J.C. and Cross, P.C. (1955). Molecular Vibrations, Mc Graw-Hill Book Co.

7. **Foye, W.O.,** Williams, D.A. and Lemke, T.L. (2002). Principle of Medicinal Chemistry, 5th edition, Lippincott Williams and Wilkins, New York

8. **Theoret, A.** (1971). *Spectrochim Acta A*, **27**: 11.

9. **Bakker, J.M.**, Meyer, G., Kabelac, M. and M.S. de Vries, (2004). *Phy. Chem. Chem. Phys.*, **6** : 2810.

10. Win MOPAC- Molecular Orbital Program, Fujitsu Limited.

11. Hyperchem Package 7 for molecular modeling, Hypercube Inc.

12. **Becke, A.D.** (1993). *J. Chem. Phys.*, **98**:5648.

13. **Here, W.J.**, Random, L., Schlyer, P.V.R. and Pople, J.A. (1989). Ab initio Molecular- Orbital Theory, Wiley, New York.

14. **Florio, M.,** Sibert, E.L. and Zwier, T.S. (2001). *Faraday Discuss*, **118** : 315.

15. **Singh, D.N.** (1980). Ph.D. Thesis, B.H.U., India.

16. **Tiwari, A.K.** (2004). Ph.D.Thesis, Dr. H.S.Gaur University, Sagar.

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