Density Functional Theory and
IR Spectroscopic Study of Carboxyl Group

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ABSTRACT

The C=O stretching frequencies of compounds containing carboxylic group are calculated theoretically using Gaussian03 software at the density functional level and compared with experimental values. The C=O bond lengths are also nearly same for all compounds. The nature of substitution in the molecules affect the C=O stretching frequencies. The in-plane OH deformation bands and C-O stretching frequencies are also found to be in agreement with the theoretical results.

Key words: Carboxyl group, DFT calculations, IR.

INTRODUCTION

The study of carboxyl group COOH and its interactions is very important in surface science[1,2], electrochemistry[3] and biology. COOH of both formic and carboxylic acids possess potentially two proton binding sites OH and C=O groups. In environment, carboxyl group plays a crucial role in speciation, transport and deposition of metal ions[4-6]. Proton bounded clusters are known to form hydrogen bounded networks and have been investigated experimentally and theoretically[7-10]. In the present work, infrared spectrum and theoretical calculations are used to study carboxyl group in different molecules.

EXPERIMENTAL

The IR spectra were recorded using a Perkin-Elmer FT-IR spectrometer. The spectral resolution was 4 cm^{-1}.

Computational details

Calculations of the compounds were carried out with Gaussian03 software package[11] using the B3LYP/6-31G* level of theory to predict the molecular structure and frequencies. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational frequencies were calculated using the analytic second derivatives to

confirm the convergence to minimum on the potential surface. The frequency values computed theoretically contain known systematic errors due to the negligence of electron correlation[12]. We therefore, have used the scaling factor value of 0.9613 for B3LYP/6-31G* basis set. The absence of imaginary frequency on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

RESULTS AND DISCUSSION

The –C(=O)OH group is best characterized by the OH stretch, the C=O stretch and the OH out-of-plane deformation as well as the C-O stretch and the OH in-plane deformation. In the present case the DFT calculations give the OH stretch at 3468 cm^{-1}. The most characteristic band of esters arises from the C=O stretching vibration occurring in the range 1650-1750 cm^{-1} with a strong to very strong intensity[13]. Methyl esters of α-unsaturated and aromatic carboxylic acids show the C=O stretching at 1725 ± 20 cm^{-1}. Seth Paul and Van Duyse[14] identified the region 1730 ± 15 cm^{-1} for mono- and di-substituted methyl benozates and

Nyquist[15] proposed 1733 ± 5 cm^{-1} for o-phtalic esters. In the spectra of salicylic acid Volosek *et al.*[16] have reported C=O stretch as intense band at 1637 cm^{-1} (Raman) and 1660 cm^{-1} (IR). For sodium salicylate, Philip *et al.*[17] observed only medium intense bands at 1631 (Raman) and 1652 cm^{-1} (IR). The C=O stretching vibration gives rise to characteristic bands in the IR and Raman spectra and the intensity of these bands can increase due to conjugation or the formation of hydrogen bonds[18]. C=O stretching vibration gives rise to a strong band in the region[9] 1725±65 cm^{-1}. Rippon *et al.*[19] reported a value of 1647 cm^{-1} for the carbonyl stretching mode. The band calculated at 1772 cm^{-1} (DFT) is assigned as υ C=O mode. The OH in-plane deformation, coupled to the C-O stretching vibration is expected in the region 1390 ± 55 cm^{-1}. The C(=O)O stretching vibration, coupled to the OH in-plane deformation, exhibits a moderate to strong band in the region 1250 ± 80 cm^{-1}. The out-of-plane deformation OH[20] exhibits a moderate band in the region 905 ± 65 cm^{-1}. The C=O in-plane deformation is weakly to moderately active in the region 725 ± 95 cm^{-1}. Most carboxylic acid display γC=O in the region 595 ± 85 cm^{-1} in the vicinity of methyl and

Table 1:

Compound	Frequency (DFT) υ (cm^{-1})	IR υ (cm^{-1})	Bond length(Å)
A	1654, 1643	1668, 1650	1.2348
B	1677	1680	1.2350
C	1681	1665	1.2389
D	1747	1692	1.2160
E	1755	1681	1.2154
F	1646	1706	1.2361
G	1777	1617	1.2104

Table 2:

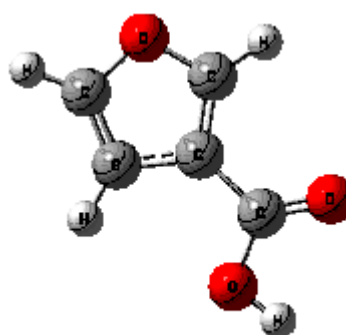| Compound	DFT δOH	IR δOH	DFT υCO	IR υCO
A	1311	1289	1113, 1085	-
B	1365	1344	1243	1235
C	1327	1332	1199	1192
D	1352	1384	1196	1198
E	1370	-	1119	1091
F	1314	-	1090	-
G	1348	1366	1237	1236
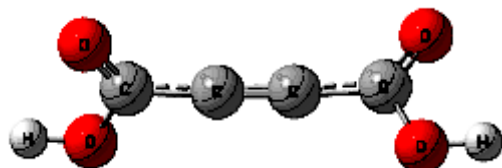
MOLECULE A
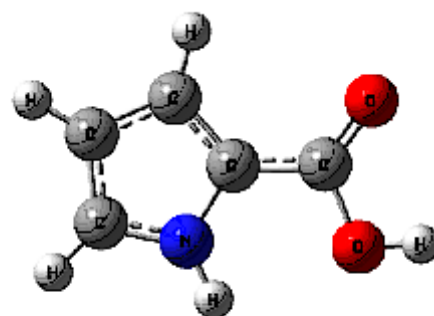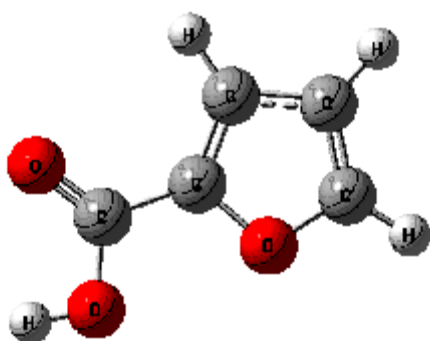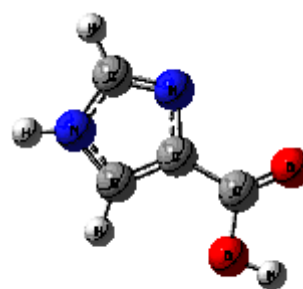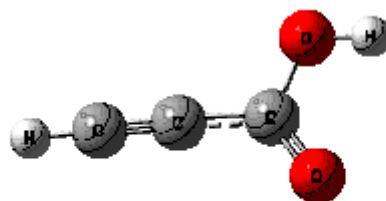
MOLECULE C
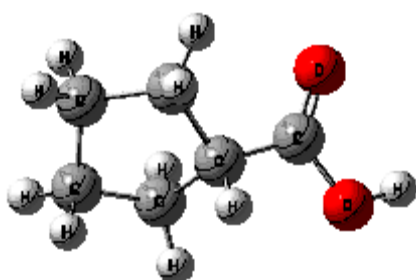
MOLECULE B

MOLECULE E

MOLECULE D

MOLECULE G

MOLECULE F

ethyl esters. The –C(=O)O deformation or rock has a weak to moderate intensity and appears in the region 445 ± 125 cm^{-1}. In the present work, the following compounds are selected for analyzing the C=O stretching frequency: acetylene dicarboxylic acid (A), cyclopentane carboxylic acid (B) 2-pyrrole carboxylic acid (C), 2-furoic acid (D), 3-furoic acid (E), propiolic acid (F), imidazole-4-carboxylic acid (G). The C=O stretching frequencies and the bond lengths are given in the table .

The OH in-plane deformation and C-O stretching frequencies are also tabulated. For most of the compounds, the experimental and theoretical values are in agreement with the reported values in literature.

CONCLUSION

The C=O stretching frequencies of compounds containing carboxylic group are calculated theoretically using DFT methods and compared with experimental values. The C=O bond lengths are also nearly same for all compounds. For compound D and E the substitution change in the ring affects the C=O stretching frequency. In molecule G, the theoretically calculated C=O frequency is found to be greater than experimentally observed value. The in-plane OH deformation bands and C-O stretching frequencies are also found to be in agreement with the theoretical results.

REFERENCES

1. Smith, D.A., Wallwork, M.L., Zhang, J., Kirkham, J., Robinson, C., Marsh, A., and Wond, M., *J. Phys. Chem*. **104B**: 8862 (2000).
2. Kokkoli, E., and Zukoski, C.F., *Langmuir*, **17**: 369 (2001).
3. Boubour, E., and Lennox, R.B., *Langmuir*, **16**: 4222 (2000).
4. Livens, F.R., *Environ. Pollut*. **70**: 183 (1991).
5. Pandey, A.K., Pandey, S.D., and Misra, V., *Ecotoxi. Environ. Safety*, **47**: 195 (2000).
6. Tsutsuki, K., and Kuwatsuka, S., *Soil Sci. Plant Nutr*. **24**: 547 (1978).
7. Zhang, R.Q., Wong, N.B., Lee, S.T., Zhu, R.S., and Han, K.L., *Chem. Phys. Lett*. **319**: 213 (2000).
8. Colomins, C., Teixido, J., Cemeli, J., Luque, F.J., and Orozco, F.L., *J. Phys. Chem*., **102B**: 2269 (1998).
9. Hirata, S., and Iwata, S., *J. Phys. Chem*. **102B**: 8426 (1998).
10. Lifshitz, C., and Feng, W.Y., *Int. J. Mass Spectrom. Ion Proc*. **146**: 223 (1995).
11. Frisch, M.J., *et al*, Gaussian03, Revision C.02, Gaussian Inc., Wallingford CT (2004).
12. Foresman, J.B., and Frisch, E., in E.Frisch (Ed.) Exploring Chemistry with Electronic Structure Methods, A Guide to Using GAussian, Gaussian, Pittsburg PA (1996).
13. Roeges, N.P.G., A Guide to t he Complete interpretation of infrared spectra of organic structures, Wiley, New York (1994).
14. Seth Paul, W.A., and Van Duyse, A., *Spectrochim. Acta* **28A**: 211 (1972).
15. Nyquist, R.A., *Appl. Spectrosc*. **26**: 81 (1972).
16. Volosek, V., Colombo, L., and Furie, K., *J. Raman Spectrosc*. **14**: 347 (1983).
17. Philip, D., John, A., Panicker, C.Y., and Varghese, H.T., *Spectrochim. Acta* **57A**: 1561(2001).
18. Maroulis, G., *J. Mol. Struct. Theochem*. **633**: 177 (2003).
19. Rippon, W.P., Koenig, J.K., and Walton, A.G., *J. Am. Chem. Soc*. **92**: 7455 (1970).
20. Fischmeister, I., *Spectrochim. Acta* **20**: 1071 (1964).