Available online at www.elixirpublishers.com (Elixir International Journal)

Chemical Physics Letters

Elixir Chem. Phys. Letters 42A (2012) 6573-6577

Vibrational spectra and assignment of fundamental vibrational modes of P-fluorobenzoyl chloride based on DFT calulations

S.Sivakumar¹ and M.E.Rajasaravanan²

¹Department of Physics, Arignar Anna Government Arts College, Attur-636 121,India. ²Department of Physics, Government Arts College, Salem-636 007, India.

ARTICLE INFO

Article history: Received: 22 November 2011; Received in revised form: 19 January 2012; Accepted: 30 January 2012;

Keywords

Vibrational analysis; Infrared spectra; Raman spectra; DFT calculation.

ABSTRACT

The molecular vibrations of P-fluorobenzoyl chloride (PFBC) were investigated in polycrystalline sample, at room temperature, by Fourier transform infrared (FT-IR) and FT-Raman spectroscopies. In parallel, ab initio and various density functional (DFT) methods were used to determine the geometrical, energetic and vibrational characteristics of PFBC. On the basis of B3LYP/6-31G* and B3LYP/6-311+G** methods and basis set combinations, a normal mode analysis was performed to assign the various fundamental frequencies according to the total energy distribution (TED). Simulation of Infrared and Raman spectra, utilizing the results of these calculations led to excellent overall agreement with observed spectral patterns. The scaled quantum mechanical (SQM) approach applying selective scaling of the DFT force fields was shown to be superior to the scaling method in its ability to ensure correct band assignments and successful simulation of IR and Raman spectra including band polarizations and intensity patterns.

© 2012 Elixir All rights reserved.

Introduction

Quantum chemical computational methods have proved to be an essential tool for interpreting and predicting the vibrational spectra. A significant advancement in this area was made by combining semi empirical quantum mechanical method; ab initio quantum mechanical method and density functional theory (DFT), each method having its own advantage. In scaled quantum mechanical (SQM) approach (Pulay et al., 1983; Rauhut et al., 1995 and Baker et al., 1998), the systematic errors of the computed harmonic force field are corrected by a few scale factors which are found to be well transferable between chemically related molecules and were recommended for general use. It requires transformation of the QM force field to internal co-ordinates and applies a limited number of independent scaling that is common within groups of similar internal co-ordinates. Ideally, the number of scale factors applied is kept to a possible minimum to safeguard against arbitrariness in the effective force field produced. Uniform scaling (or frequency scaling) has been criticized by Pulay et al., (1990) pointing out that no scaling and uniform scaling of the force field may often lead to misassignments in case of large molecules, since proper correction for systematic errors of theory is impossible by a single factor. To enhance the utility of the SQM force field method, a set of 11 transferable scaling factors have been proposed for use with the B3LYP/6-311+G^{*} density functional (DFT) force field that seem to be transferable within a wide range of organic molecules containing the atoms C and H (Rauhut et al., 1995 and Baker et al., 1998). The aim of this work is to check the performance of the B3LYP density functional force field for simulation of the FT-IR and FT-Raman spectra of PFBC with the use of the large B3LYP/6-311+G** basis sets, and comparing the effect of simpler and more elaborate versions of scaling, while paying attention to ensuring correct band assignments.

Materials and Methods

Spectroscopically pure PFBC was obtained form Lancaster chemical company, U.K., and used as such for the spectral measurements. The room temperature Fourier transform infrared spectra of PFBC was recorded in the 4000-400 cm⁻¹ region at a resolution of ± 1 cm⁻¹, using BRUKER IFS-66V vacuum fourier transform spectrometer, equipped with an MCT detector, a KBr beam splitter and globar source. The FT-Raman spectrum was recorded on the same instrument with FRA-106 Raman accessories in the region 3500-100 cm⁻¹. Nd:YAG laser operating at 200 mW power with 1064 nm excitation was used as source.

Computational details

Quantum chemical calculations for PFBC were performed with the Gaussian 03W program (Frisch et al., 2002) using the Becke-3-Lee-Yang-Parr (B3LYP) functionals (Becke, 1993) and Lee et al., 1998) supplemented with the 6-311+G^{**} basis sets (referred large basis sets), for the Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry by assuming C_s point group symmetry. Scaling of the force field was performed according to the SQM procedure (Pulay et al., 1983 and Rahght et al., 1995) using selective (multiple) scaling in the natural internal coordinate representation (Fogarasi et al., 1992). Transformations of the force field and the subsequent normal coordinate analysis including the least squares refinement of the scaling factors, calculation of total energy distribution (TED) and IR and Raman intensities were done on a PC with the Molvib program (Version V7.0-G77) written by Sundius (1990 and 2002). The TED elements provide a measure of each internal coordinate's contribution to the normal coordinate. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a band width (FWHM) of 10 cm⁻¹.



Prediction of Raman intensities

The Raman activities (Si) calculated with the Gaussian 03W program and adjusted during the scaling procedure with Molvib were subsequently converted to relative Raman intensities (Ii) using the following relationship derived from the basic theory of Raman scattering (Polavarapu, 1990; Keresztury et al., 1993 and Keresztury, 2002).

$$I_{i} = \frac{f(v_{o} - v_{i})^{4} S_{i}}{v_{i} [1 - \exp(-hcv_{i} / KT)]}$$

Where υ_0 is the exciting frequency (in cm⁻¹), υ_i is the vibrational wavenumber of the ith normal mode; h, c and k are fundamental constants, and f is a suitably chosen common normalization factor for all peak intensities.

Results

Molecular geometry

The molecular structures of PFBC belongs to C_s symmetry are shown in Fig.1.



Fig. 1. Optimized molecular structure of P-fluorobenzoyl chloride.

The global minimum energy obtained by the DFT structure optimization for PFBC were presented in Table 1.

Table 1. Global minimum energy of PFBC obtained by DFT structure optimization

Method	Energies (Hartrees			
6-31G**	-904.41159952			
6-311+G**	-904.63865665			

The optimized geometrical parameters obtained by the large basis set calculation (the global minimum energy) in this study for PFBC were presented in Table 2.

Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose, the full set of 48 standard internal coordinates containing 12 redundancies for PFBC were defined in Table 3.From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combination of internal coordinates following the recommendations of Fogarasi et al., (1985 and 1992) are summarised in Table 4. The theoretically calculated DFT force fields were transformed to this latter set of vibrational coordinates and used in all subsequent calculations.

Table 2. Optimized geometrical parameters of PFBC obtained by B3LYP/ 6–311+G** density functional calculations

Bond length	Value(Å)	Bond angle	Value(Å)	Dihedral angle	Value(Å)
C2-C1	1.40703	C3-C2-C1	121.80356	C4-C3-C2-C1	0.981064
C3-C2	1.38950	C4-C3-C2	119.17003	C5-C4-C3-C2	-0.655061
C4-C3	1.39338	C5-C4-C3	120.34780	C6-C5-C4-C3	-0.289963
C5-C4	1.39799	C6-C5-C4	119.93025	C7-C1-C6-C5	177.026008
C6-C5	1.39036	C7-C1-C6	123.11555	O8-C7-C1-C6	155.476978
C7-C1	1.48014	O8-C7-C1	127.29354	Cl9-C7-C1-C6	24.830982
O8-C7	1.19036	Cl9-C7-C1	113.92032	F10-C2-C1-C6	-178.44099
C19-C7	1.84221	F10-C2-C1	120.15349	H11-C3-C2-C1	-179.02902
F10-C2	1.33812	H11-C3-C2	118.75535	H12-C4-C3-C2	179.567965
H11-C3	1.08470	H12-C4-C3	119.47178	H13-C5-C4-C3	179.971991
H12-C4	1.08617	H13-C5-C4	120.27483	H14-C6-C5-C4	-179.71402
H13-C5	1.08526	H14-C6-C5	120.28770		
H14-C6	1.08349				

^{*}for numbering of atom refer Fig. 1

Table 3. Definition of internal coordinates of PFBCNo(i)symbolTypeDefinition

Streching		C U(ana)	
1-4	r _i	C-H(aro)	СЗ-НП,С4-Н12,С5-Н13,С6-Н14
5	\mathbf{R}_{i}	C-F(aro)	C2-F10
6	R _i	C-Cl (sub)	C7-C19
7	\mathbf{p}_{i}	C-O(sub)	C7-O8
8-13	\mathbf{P}_{i}	C-C(ring)	C1-C2,C2-C3,C3-C4,C4-C5, C5-C6,C6-C1
14	\mathbf{P}_{i}	C-C(sub)	C7-C1
Bending 15-22	$\boldsymbol{\theta}_i$	С-С-Н	C2-C3-H11,C4-C3-H11, C3-C4-12, C5-C4-H12,C4-C5-H13, C6-C5-H13, C5-C6-H14,C1-C6-H14
23	β_i	C-C-Cl	C1-C7-C19
24-25	β_i	C-C-F	C1-C2-F10,C3-C2-F10
26	γ_i	C-C-O	C1-C7-O8
27-28	α_i	C-C-C	C6-C1-C7,C2-C1-C7
29-34	α_{i}	C-C-C (ring)	C1-C2-C3,C2-C3-C4,C3-C4-C5,C4-C5-C6, C5-C6-C1,C6-C1-C2
Out-of-plane			H11-C3-C2-C4,H12-C4-C3-C5,
35-38	ω_i	C-H	H13-C5-C4-C6,H14-C6-C5-C1
39	ω_{i}	C-F	F10-C2-C1-C3
40	ωi	C-C	C7-C1-C2-C6
41	ω _i	C-Cl	C1-C7-O8-C19
Torison			C1-C2-C3-C4,C2-C3-C4-C5,C3-C4-C5-C6,
42-47	τ_i	τring	C4-C5-C6-C1,C5-C6-C1-C2,C6-C1-C2-C3
48	τ	τC-Cl	C2(C6)-C1-C7-O8(Cl9)

^{*}for numbering of atom refer Fig. 1

Table 4. Definiton of local symmetry coordinates and the value corresponding scale factors used to correct the force fields for PFBC

No.(i)	Symbol ^a	Definition ^b	used in calculation
1-4	C-H	r1,r2,r3,r4	0.920
5	C-F(aro)	R5	0.927
6	C-Cl(sub)	R6	0.927
7	C-O	p7	0.918
8-13	C-C	P8,P9,P10,P11,P12,P13	0.902
14	C-C(sub)	P14	0.902
15-18	C-C-H	(015-016) /\12,(017-018) /\12, (019-020) /\12,(021-022) /\12	0.942
19	C-C-Cl	β23	0.947
20	C-C-F	(β24-β25) /√2	0.947
21	C-C-O	γ26	0.979
22	C-C-C	(α27-α28) /√2	0.986
23	bring	(α29-α30+α31-α32+α33-α34)/ √6	0.986
24	bring	(2α29-α30-α31+2α32-α33-α34)/ √12	0.986
25	bring	(a30-a31+a33-a34)/2	0.986
26	C-H	ω35, ω36, ω37, ω38	0.963
27-30	C-F	ω39	0.965
31	C-C	ω40	0.935
32	C-Cl	ω41	0.963
33	tring	$(\tau 42 - \tau 43 + \tau 44 - \tau 45 + \tau 46 - \tau 47)/\sqrt{6}$	0.935
34	tring	$(\tau 42 - \tau 44 + \tau 45 - \tau 47)/2$	0.935
35	tring	(-τ42+2τ43-τ44-τ45+2τ46-τ47)/√12	0.935
36	τC-Cl	τ48/4	0.945

^a These symbols are used for description of the normal modes by TED in Table 5.

^b The internal coordinates used here are defined in Table 3. Vibrational spectra

The 36 normal modes of PFBC were distributed amongst the symmetry species as $\Gamma_{3N-6}=25$ A' (in-plane) + 11 A" (out-ofplane), in agreement with C_s symmetry. All the vibrations are active both in the Raman scattering and infrared absorption. The detailed vibrational assignments of fundamental modes of PFBC along with the observed and calculated frequencies, IR and Raman intensities and normal mode descriptions (characterized by TED) are reported in Tables 5. For visual comparison, the observed and simulated FTIR and FT-Raman spectra of PFBC were presented in Fig. 2. & Fig. 3.Root mean square (RMS) values were obtained in this study using the following expression.



Fig.2. FT-IR Spectra of P-fluorobenzoyl chloride

(a) Observed (b) Calculated with B3LYP / 6-311+G **



Fig.3. FT – Raman Spectra of P-fluorobenzoyl chloride (a) Observed (b) Calculated with B3LYP/6–311+G ** Discussion

The RMS error of the observed and calculated frequencies (unscaled / B3LYP/6-311+G^{**}) of PFBC was found to be 110 cm⁻¹. This is quite obvious; since the frequencies calculated on the basis of quantum mechanical force fields usually differ appreciably from observed frequencies. This is partly due to the neglect of anharmonicity and partly due to the approximate nature of the quantum mechanical methods. In order to reduce the overall deviation between the unscaled and observed fundamental frequencies, scale factors were applied in the normal coordinate analysis and the subsequent least square fit refinement algorithm resulted into a very close agreement between the observed fundamentals and the scaled frequencies. Refinement of the scaling factors applied in this study achieved a weighted mean deviation of 6.73 cm⁻¹ between the experimental and scaled frequencies of the title compound.

C-C vibrations:

The bands between 1650-1480 cm⁻¹ are assigned to C-C stretching modes (Sathyanarayana, 2004). In the present study, the carbon stretching vibrations of the title compound have been observed at 1608,1578,1482 cm⁻¹ in the FT-IR and 1485 cm⁻¹ in FT-Raman spectrum and are presented in Table 5. These assignments are in good agreement with literature (George Socrates, 2001 and Krishna kumar et al., 2003).

Carbon – Hydrogen vibrations

The hetroaromatic structure shows the presence of C-H stretching vibrations in the region 3000-3100 cm⁻¹, which is the characteristic region for ready identification of C-H stretching vibrations. Accordingly, in the present study, the C-H stretching vibrations of the title compound are observed at 3214

 cm^{-1} and 3190 cm^{-1} in the FTIR and Raman spectra respectively.

The bands due to C–H in-plane ring bending vibration interacting with C–C stretching vibration are observed as a number of m-w intensity sharp bands in the region 1500–1300 cm⁻¹. C–H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 900–667 cm⁻¹ (Cohen, 1964). The C-H in-plane bending vibrations of the title compound were identified at 1482, 1382,1307 and 1485,1380 cm⁻¹ in IR and Raman respectively. While the peaks established at 1034,956,794 and 980,780 cm⁻¹ are attributed to C-H out-of– plane deformation vibrations. Among which the peaks at 794 and 780 cm⁻¹ were established both in IR and Raman spectra. These in-plane and out-of-plane vibrational frequencies were found to be well within their characteristic regions.

C-X vibrations:

C-X vibrations are found in the region below 1000 cm⁻¹. The C-X stretching frequency is generally observed in the region 800–600 cm⁻¹ depending on the configuration and conformation of the compound (Lakshmaiah et al., 1989). Based on this, the bands at 817,755,540 cm⁻¹ have been assigned to C-F stretching and bands at 885,660,566 cm⁻¹ have been assigned to C-Cl stretching in PFBC.

C-O vibrations:

The carbonyl stretching frequency is very sensitive to the factors that disturb the nature of the carbonyl group and its precise frequency is characteristic of the type of the carbonyl compound being studied. Particularly detailed correlations have been made for the carbonyl bond stretching frequency. The carbonyl stretching frequency has been most extensively studied by infrared spectroscopy.

This multiply bonded group is highly polar (> $C^{\delta^+}=O^{\delta^-}$) and therefore gives rise to an intense infrared absorption band. The carbon-oxygen double bond is formed by the $p_{\pi}-p_{\pi}$ bonding between carbon and oxygen. Because of the different electronegativities of carbon and oxygen atoms, the bonding electrons are not equally distributed between the two atoms.

The following two resonance forms contribute to the bonding of the carbonyl group $>C=O \leftrightarrow C^+-O^-$ The lone pair of electrons on oxygen also determines the nature of the carbonyl group. The position of the C=O stretching vibration is very sensitive to various factors such as the physical state, electronic effects by substituents, ring strains, etc. (Sathyanarayana et al., 2004).

Consideration of these factors provides further information about the environment of the C=O group. The carbonyl stretching generally occurs as a strong absorption in the region from 1900 to 1600 cm^{-1} .

This portion of the spectrum is most useful because the position of the carbonyl absorption is quite sensitive to substitution effects and the geometry of the molecule. Accordingly, in the present investigation, the peaks identified at 1900 and 1608 cm⁻¹ have been assigned to C=O stretching vibrations for PFBC.

Ring vibrations

Monosubstitued benzoyl, give rise to very strong, strong and weak bands in the region 1025-1000 cm⁻¹, 840-785 cm⁻¹ and 660-615 cm⁻¹ respectively. In the present study, the bands identified at 885,660,566 and 890,420 cm⁻¹ in IR and Raman spectra have been designated to the ring in-plane bending modes. The out-of-plane bending vibrations were identified at 540 and 550 cm⁻¹. Small changes in frequencies observed for these modes are due to the changes in force constant/reduced mass ratio, resulting mainly due to addition of benzoyl group.

No.	Symmetry	Observed frequency (cm ⁻¹)		Calculated frequency (cm ⁻¹) with B3LYP/6-311+G ^{**} force field				TED (%) among type of internal coordinates ^c
	species Cs	Infrared	Raman	Unscaled	Scaled	IR ^a Ai	Raman ^b I _i	
1	A'			3455	3242	1.176	86.907	CH(99)
2	Α″			3442	3230	2.496	149.639	CH(99)
3	A″	3214 w		3430	3218	10.545	111.973	CH(99)
4	Α″		3190 s	3413	3202	3.033	69.080	CH(99)
5	A'	1786 vs	1900 vs	2006	1882	30.190	87.054	CO(85),CC (6),bCCl(5)
6	A'			1773	1664	63.068	58.714	CC(69),bCH(17),bring(10)
7	A'	1608 vs		1739	1632	31.555	13.003	CC(69),bCH(15),bring(10)
8	Α″	1578 vs		1629	1529	79.762	13.249	bCH(44),CC(42),CF(9)
9	A'	1482 s	1485 s	1598	1500	20.815	1.763	bCH(52),CC(37)
10	A'	1382 vs	1380 s	1448	1359	2.226	4.284	CC(87),bCH(7)
11	Α″	1307 s	1310 w	1398	1312	38.451	3.065	bCH(51),CF(19),CC(16),bring(7)
12	Α″	1274 vw	1290 s	1367	1283	37.495	15.088	CF(31),CC(30),bCH(30)
13	A'	1237 vw		1303	1223	99.596	25.697	CC(52),bCH(25),bring(15)
14	A'	1197 vw	1200 s	1268	1190	42.035	12.243	bCH(72),CC(23)
15	A'	1168 w	1140 s	1220	1145	26.881	1.476	bCH(34),CC(33),bring(16),bCC(5)
16	A'	1110 w	1040 s	1137	1067	1.719	21.551	CC(71),bCH(26)
17	A'	1034 vs	980 vs	1060	995	0.141	0.028	gCH(87),tring(13)
18	A'	956 vs		1031	968	1.438	0.772	gCH(91),tring(8)
19	A'	885 vw	890 vs	951	893	153.648	5.236	bring(45),bCO(24),CC (11),CCl(8)
20	A'			936	879	3.949	4.322	gCH(77),tring(13),gCF(6)
21	A'	817 vs		865	812	101.301	6.995	CC (41),bring(18),CF (16),bCO(12),CCl(8)
22	A'	794 vw	780 vs	833	782	43.397	1.249	gCH(88)
23	A'	755 vw		791	743	20.022	1.501	tring(48),gCF(20),gCC(14),gCH(8),gClO(7)
24	A'	660 w		719	675	62.422	8.044	bring(30),bCO(23),CC (12),gClO(10),bCC(8),CCl(7)
25	A'	645 vw		691	649	29.244	2.750	tring(48),gClO(21),gCH(10),gCF(6),bring(5),bCO(5)
26	Α″	566 vs		611	574	1.443	8.157	bring(53),CC (13),tring(9),bCC(7),bCCl(6)
27	A'	540 vs	550 vs	560	526	5.644	1.095	tring(46),gCF(33),gCH(13)
28	Α″	466 s		513	482	4.314	0.811	bCCl(29),bring(18),bCF(14),tring(12),bCC(8),CC(5)
29	Α'			489	459	47.644	8.090	bCF(39),CCl(33),bring(8),bCCl(7),CC (6),bCO(5)
30	Α″		420 w	461	433	3.797	2.571	tring(61),gCC(12),gCH(9),CCl(6)
31	A'			410	385	3.026	3.761	bCO(30),CCl(18),bring(16),tring(15),CC(12)
32	Α″		270 w	297	279	2.410	3.696	bCCl(27),tring(16),bCF(10),CCl(9),CC (8),gCH(7)
33	Α″			254	239	0.711	3.383	tring(43),gCC(16),gCH(11),bCCl(8),gCF(6),bCC(5)
34	A'		190 vs	198	186	0.267	0.635	bCC(49),bCCl(26),bCO(12)
35	A'		122 vw	128	121	0.113	4.693	tring(42),gCC(29),gClO(9),bCCl(8),gCH(5)
36	A'			45	41	0.273	1.425	tCCl(79),bCCl(5)

Table 5. Detailed assignments of fundamental vibrations of PFBC by normal mode analysis based on SQM force field calculation

Abbreviations used: b, bending; g, wagging; t, torsion; s, strong; vs, very strong; w, weak; vw, very weak;

^a Relative absorption intensities normalized with highest peak absorption

^b Relative Raman intensities calculated by Eq.1 and normalized to 100.

^c For the notations used see Table 4.

Conclusion

The SQM force field method based on DFT calculations at the B3LYP/6-311+G** level have been carried out to analyze the vibrational frequencies of PFBC. Refinement of the scaling factors applied in this study achieved a weighted RMS deviation of 6.73 cm⁻¹ between the experimental and scaled frequencies. This close agreement established between the experimental and scaled frequencies obtained using large basis set (6-311+G**) calculations has proved to be more reliable and accurate than the calculations using lower basis sets.

Acknowledgement

The authors are thankful to the Sophisticated Analytical Instrumentation Facility (SAIF), IIT Madras, Chennai, for spectral measurements.

Reference

Baker, J., Jarzecki, A.A., and Pulay, P. 1998. Direct Scaling of Primitive Valence Force Constants: An Alternative Approach to Scaled Quantum Mechanical Force Fields. J. Phys. Chem. A. 102: 1412-1424.

Becke, A.D.1993. Density-functional thermochemistry. III. The role of exact exchange. *J.Chem. Phys.* 98: 5648-5652.

Cohen, H.D., and Miroslav Synek 1964. Accurate Analytical Self-Consistent Field Functions for Atoms. VI. The Ground States of Mo^+ and Mo. *Phys. Rev.* 133: 1263-1266.

Fogarasi, G., and Pulay, P. 1985. In: Durig, J.R., Editor, Vibrational Spectra and Structure vol. 14, Elsevier, Amsterdam, p. 125.

Fogarasi, G., Xhov, X., Taylor P.W., and Pulay, P. 1992. Geometry optimization in redundant internal coordinates. *J. Am. Chem. Soc.* 114: 8191-8201.

Frisch, M.J., Trucks, G.W., Schlega, H.B., Scuseria, G.E., Robb, M.A., Cheesman, J.R., Zakrzewski, V.G., Montgomery Jr., J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K.,Roga, N.,Salvador, N., Dannenberg, J.J., Malick, D.K., Rabuck, A.D., Rahavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Baboul, A.G., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Penng, C.Y., Nanayakkara, A., Challa-Combe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head-Gordon, M., Replogle, E.S., and Pople, J.A. 2002. Gaussian 98, Revision A 11.4, Gaussian Inc., Pittsburgh, PA.

George Socrates. 2001. Infrared and Raman Characteristic Group Frequencies -Tables and Charts (third ed.), John Wiley & Sons, Chichester.

Keresztury, G., Holly, S., Varga, J., Besenyei, G., Wang, A.V., and Durig, J.R. 1993. Vibrational spectra of monothiocarbamates-II. IR and Raman spectra, vibrational assignment, conformational analysis and ab initio calculations of S-methyl-N,N-dimethylthiocarbamate. *Spectrochim. Acta* A. 49: 2007 -2017.

Keresztury, G. 2002. in: Chalmers, J.M., and Griffiths, P.R.(Eds). 2002. Handbook of Vibrational Spectroscopy vol.1, John Wiley & Sons Ltd. p.71.

Krishna kumar, V., and John Xavier, R. 2003. Normal coordinates analysis of vibrational spectra of 2-methylindoline and 5-hydroxyindane. *Indian J. Pure Appl. Phys.* 41: 95-99.

Lakshmaiah, B., and Ramana Rao, G. 1989. Vibrational analysis of substituted anisoles. I-Vibrational spectra and normal

coordinate analysis of some fluoro and chloro compounds. J. Raman Spectrosc. 20: 439-448.

Lee, C., Yang, W., and Parr, R.G. 1998. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B.* 37: 785-789.

Polavarapu, P.L. 1990. Ab initio Raman and Raman optical activity spectra. J. Phys. Chem. 94: 8106-8112...

Pulay, P., Fogarasi, G., Pongor, G., Boggs, J.E., and Vargha, A. 1983. Combination of theoretical ab initio and experimental information to obtain reliable harmonic force constants. Scaled quantum mechanical (QM) force fields for glyoxal, acrolein, butadiene, formaldehyde, and ethylene. *J.Am. Chem. Soc.* 105: 7037-7047.

Pulay, P., Fogarasi, G., Zhou, X., and Taylor, P.W. 1990. Ab initio prediction of vibrational spectra: A database approach. *Vib. Spectrosc.* 1:159-165.

Rauhut, G., and Pulay, P.1995. Transferable Scaling Factors for Density Functional Derived Vibrational Force Fields. *J. Phys. Chem.*99: 3093-3100.

Sathyanarayana, D.N.2004. Vibrational Spectroscopy—Theory and Applications, second ed., New Age International (P) Limited Publishers, New Delhi.

Sundius. T. 1990. Molvib - A flexible program for force field calculations. *J.Mol. Struct.* 218: 321-326.

Sundius, T. 2002. Scaling of ab initio force fields by MOLVIB. *Vib. Spectrosc.* 29: 89-95.

Sundius, T. 2002. MOLVIB (v.7.0), Calculation of harmonic force fields and vibrational modes of molecules, QCPE Program No. 807.