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Vibrational spectra and assignment of fundamental vibrational modes of O-Bromobenzoyl chloride based on DFT calculations

S.Sivakumar¹, G.Raja² and M.E.Rajasaravanan¹

¹Department of Physics, Government Arts College, Salem-636 007, India.

²Department of Chemistry, Paavai Engineering College, Namakkal-637 018, India.

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ABSTRACT

The molecular vibrations of O-Bromobenzoyl chloride (OBBC) 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 OBBC. 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.

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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 OBBC 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 OBBC was obtained from Lancaster chemical company, U.K., and used as such for the spectral measurements. The room temperature Fourier transform infrared spectra of OBBC was recorded in the 4000-400cm⁻¹ region at a resolution of ±1cm⁻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 OBBC were performed with the Gaussian 98W 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 (S_i) calculated with the Gaussian 98W program and adjusted during the scaling procedure with Molvib were subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering (Polavarapu, 1990; Keresztury et al., 1993 and Keresztury, 2002).

$$I_i = \frac{f(\nu_o - \nu_i)^4 S_i}{\nu_i [1 - \exp(-hc\nu_i / KT)]}$$

Where ν_o is the exciting frequency (in cm^{-1}), ν_i is the vibrational wavenumber of the i^{th} 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 OBBC belongs to C_s symmetry are shown in Fig.1. The global minimum energy obtained by the DFT structure optimization for OBBC were presented in Table 1. The optimized geometrical parameters obtained by the large basis set calculation (the global minimum energy) in this study for OBBC were presented in Table 2.



Fig. 1. Optimized molecular structure of O-Bromobenzoyl chloride.

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 OBBC 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 1. Global minimum energy of OBBC obtained by DFT structure optimization

Method	Energies (Hartrees)
6-31G**	-1194.734221
6-311+G**	-1194.123027

Vibrational spectra

The 36 normal modes of OBBC were distributed amongst the symmetry species as $\Gamma_{3N-6} = 25 A'$ (in-plane) + 11 A'' (out-of-plane), 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 OBBC along with the observed and calculated frequencies, IR and Raman intensities and normal mode descriptions (characterized by TED) are reported in Table 5. For visual comparison, the observed and simulated FTIR and FT-Raman spectra of OBBC were presented in Fig. 2. & Fig. 3.

Root mean square (RMS) values were obtained in this study using the following expression.

$$RMS = \sqrt{\frac{1}{n-1} \sum_i^n (u_i^{\text{calc}} - u_i^{\text{exp}})^2}$$

Table 2. Optimized geometrical parameters of OBBC 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	177.02600
C6-C5	1.39036	C7-C1-C6	123.11555	O8-C7-C1-C6	-155.47697
C7-C1	1.48014	O8-C7-C1	127.29354	C19-C7-C1-C6	24.830982
O8-C7	1.19036	C19-C7-C1	113.92032	Br10-C2-C1-C6	-178.44099
C19-C7	1.84221	Br10-C2-C1	120.15349	H11-C3-C2-C1	-179.02902
Br10-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 OBBC

No(i)	Symbol	Type	Definition
Stretching			
1-4	r_i	C-H(aro)	C3-H11,C4-H12,C5-H13,C6-H14
5	R_i	C-Br(aro)	C2-Br10
6	R_i	C-Cl (sub)	C7-C19
7	p_i	C-O(sub)	C7-O8
8-13	P_i	C-C(ring)	C1-C2,C2-C3,C3-C4,C4-C5,C5-C6,C6-C1
14	P_i	C-C(sub)	C7-C1
Bending			
15-22	θ_i	C-C-H	C2-C3-H11,C4-C3-H11, C3-C4-H12,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-Br	C1-C2-Br10,C3-C2-Br10
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			
35-38	ω_i	C-H	H11-C3-C2-C4,H12-C4-C3-C5, H13-C5-C4-C6,H14-C6-C5-C1
39	ω_i	C-Br	Br10-C2-C1-C3
40	ω_i	C-C	C7-C1-C2-C6
41	ω_i	C-Cl	C1-C7-O8-C19
Torsion			
42-47	τ_i	rting	C1-C2-C3-C4,C2-C3-C4-C5, C3-C4-C5-C6,C4-C5-C6-C1, C5-C6-C1-C2,C6-C1-C2-C3
48	τ_i	τ C-Cl	C2(C6)-C1-C7-O8(C19)

*for numbering of atom refer Fig. 1

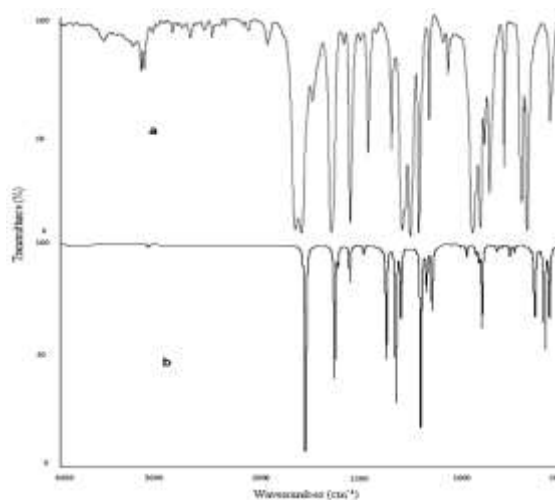


Fig.2. FT-IR Spectra of O-Bromobenzoyl chloride (a) Observed (b) Calculated with B3LYP / 6-311+G**

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

No.(i)	Symbol ^a	Definition ^b	Scale factors used in calculation
1-4	C-H	r _{1,r2,r3,r4}	0.923
5	C-Br(aro)	R5	0.93
6	C-Cl(sub)	R6	0.93
7	C-O	p7	0.921
8-13	C-C	P8,P9,P10,P11,P12,P13	0.905
14	C-C(sub)	P14	0.905
15-18	C-C-H	($\theta_{15}-\theta_{16}$)/ $\sqrt{2}$, ($\theta_{17}-\theta_{18}$)/ $\sqrt{2}$, ($\theta_{19}-\theta_{20}$)/ $\sqrt{2}$, ($\theta_{21}-\theta_{22}$)/ $\sqrt{2}$	0.945
19	C-C-Cl	β_{23}	0.95
20	C-C-Br	($\beta_{24}-\beta_{25}$)/ $\sqrt{2}$	0.95
21	C-C-O	γ_{26}	0.982
22	C-C-C	($\alpha_{27}-\alpha_{28}$)/ $\sqrt{2}$	0.989
23	Bring	($\alpha_{29}-\alpha_{30}+\alpha_{31}-\alpha_{32}+\alpha_{33}-\alpha_{34}$)/ $\sqrt{6}$	0.989
24	Bring	($2\alpha_{29}-\alpha_{30}-\alpha_{31}+2\alpha_{32}-\alpha_{33}-\alpha_{34}$)/ $\sqrt{12}$	0.989
25	Bring	($\alpha_{30}-\alpha_{31}+\alpha_{33}-\alpha_{34}$)/2	0.989
26	C-H	$\omega_{35}, \omega_{36}, \omega_{37}, \omega_{38}$	0.966
27-30	C-Br	ω_{39}	0.968
31	C-C	ω_{40}	0.938
32	C-Cl	ω_{41}	0.966
33	Tring	($\tau_{42}-\tau_{43}+\tau_{44}-\tau_{45}+\tau_{46}-\tau_{47}$)/ $\sqrt{6}$	0.938
34	Tring	($\tau_{42}-\tau_{44}+\tau_{45}-\tau_{47}$)/2	0.938
35	Tring	($-\tau_{42}+2\tau_{43}-\tau_{44}-\tau_{45}+2\tau_{46}-\tau_{47}$)/ $\sqrt{12}$	0.938
36	τ -C-Cl	$\tau_{48}/4$	0.948

^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.

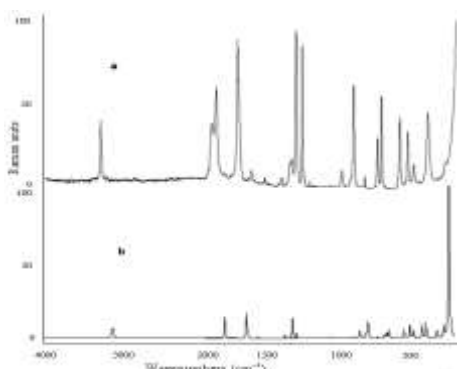


Fig.3. FT – Raman Spectra of O-Bromobenzoyl chloride (a) Observed (b) Calculated with B3LYP/6–311+G **

Discussion

The RMS error of the observed and calculated frequencies (unscaled / B3LYP/6-311+G**) of OBBC was found to be 108 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 7.45 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 1600, 1537, 1466 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).

C–H 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 3195 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 1466, 1370 and 1485, 1310 cm^{-1} in IR and Raman respectively. While the peaks established at 1034 and 980 cm^{-1} are attributed to C-H out-of-plane deformation vibrations. 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 803, 645 cm^{-1} have been assigned to C-Br stretching and bands at 755, 660 cm^{-1} have been assigned to C-Cl stretching in OBBC.

C-O vibrations:

The carbonyl stretching frequency has been most extensively studied by infrared spectroscopy. 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. This multiply bonded group is highly polar ($>\text{C}^{\delta+}=\text{O}^{\delta-}$) 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 electro-negativities 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 $>\text{C}=\text{O} \leftrightarrow \text{C}^+-\text{O}^-$. 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 1919 and 1900 cm^{-1} have been assigned to C=O stretching vibrations for OBBC.

Ring vibrations

Monosubstituted 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

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

No.	Symmetry species Cs	Observed frequency (cm ⁻¹)		Calculated frequency (cm ⁻¹) with B3LYP/6-311+G** force field				TED (%) among type of internal coordinates ^c
		Infrared	Raman	Unscaled	Scaled	IR ^a A _i	Raman ^b I _i	
1	A'			3272	3243	1.214	114.717	CH(99)
2	A''			3265	3236	2.576	197.523	CH(99)
3	A''	3195 w		3256	3227	10.882	147.804	CH(99)
4	A''		3190 s	3253	3224	3.13	91.186	CH(99)
5	A'	1919 vs	1900 vs	1883	1867	31.156	114.911	CO(85),CC(6),bCCl(5)
6	A'			1676	1661	65.086	77.502	CC(66),bCH(19),bring(11)
7	A'	1600 vs		1652	1638	32.565	17.164	CC(73),bCH(10),bring(9)
8	A''	1537 vs		1568	1554	82.314	17.489	bCH(50),CC(40),CBr(9)
9	A'	1466 s	1485 s	1468	1455	21.481	2.327	CC(53),bCH(37)
10	A'	1414 vs	1380 s	1373	1361	2.297	5.655	CC(91)
11	A''	1370 s	1310 w	1341	1329	39.681	4.046	bCH(87),CC(7)
12	A''	1297 vw	1290 s	1307	1296	38.695	19.916	CBr(54),CC(22),bCH(15),bring(10)
13	A'	1237 vw		1239	1228	102.783	33.92	CC(61),bring(16),bCH(12),bCO(5)
14	A'	1197 vw	1200 s	1201	1191	43.38	16.161	bCH(72),CC(21)
15	A'	1168 w	1140 s	1146	1136	27.741	1.948	bCH(66),CC(28)
16	A'	1110 w	1040 s	1043	1034	1.774	28.447	bring(45),CC(38),bCH(16)
17	A'	1034 vs	980 vs	982	974	0.146	0.037	gCH(91),tring(8)
18	A'	1012 vs		977	969	1.484	1.019	gCH(81),tring(16)
19	A'	885 vw	890 vs	905	897	158.565	6.912	CC(47),bCO(24),CCl(11),bring(9)
20	A'			864	857	4.075	5.705	gCH(68),tring(13),gCBr(11),gCC(5)
21	A'	817 vs		839	832	104.543	9.233	gCH(98)
22	A'	803 vw	780 vs	825	818	44.786	1.649	bring(29),bCO(22),CC(18),CBr(14),CCl(10)
23	A'	755 vw		735	729	20.663	1.981	tring(57),gCCl(14),gCC(14),gClO(8),gCH(6)
24	A'	660 w		668	662	64.42	10.618	tring(26),gClO(24),bring(15),gCCl(8),bCC(7),gCH(7)
25	A'	645 vw		646	641	30.18	3.63	bring(35),tring(21),gClO(19),gCBr(9),gCH(6)
26	A''	566 vs		625	620	1.489	10.767	bring(30),bCO(27),CC(10),CCl(10),bCCl(8)
27	A'	540 vs	550 vs	518	514	5.825	1.445	tring(36),gCBr(30),gCC(13),bCCl(6),bring(5)
28	A''	466 s		484	480	4.452	1.071	bCCl(30),bring(16),tring(14),gCBr(10),CCl(8),bCC(8)
29	A'			428	425	49.169	10.679	tring(54),CCl(14),bCBr(13),gCH(12)
30	A''		420 w	426	423	3.919	3.394	tring(54),bCBr(15),gCH(12),CCl(12)
31	A'			393	390	3.123	4.965	bCBr(29),bCO(19),bring(15),CCl(14),CC(10),bCCl(6)
32	A''		270 w	308	306	2.487	4.879	tring(23),gCC(20),bring(13),CC(12),bCCl(7),gCH(6)
33	A''			271	269	0.734	4.466	tring(25),gCC(17),bCCl(15),bCC(11),gClO(6),CCl(6)
34	A'		190 vs	169	168	0.276	0.838	bCC(38),bCCl(32),bCO(16)
35	A'		122 vw	103	103	0.117	6.195	tring(41),gCC(28),gCH(15)
36	A'			54	54	0.282	1.881	tCCl(80),bCCl(6),tring(5)

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.

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.

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 OBBC. Refinement of the scaling factors applied in this study achieved a weighted RMS deviation of 7.45 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.

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