Computational study of 2-bromo-4-chloroacetophenone

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ABSTRACT

The vibrational frequencies of 2-Bromo-4-chloroacetophenone were calculated using Gaussian 03 software package and the fundamental modes are assigned. The predicted infrared intensities and Raman activities are reported. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of non linear optics.

Key words: HF calculations, hyperpolarizability, nonlinear optical activity.

INTRODUCTION

2-Bromo-4-chloroacetophenone is one of the new organic nonlinear crystal having good second harmonic generation efficiency[1]. The organic non linear optical materials play an important role in second harmonic generation, frequency mixing , electro optic modulation, optical parametric oscillation and optical bi-stability[2]. Organic crystals have parameters superior to widely used crystals like KDP[3,4]. Chenthamarai *et al.*[5] reported the growth of good quality of 4-hydroxy acetophenone and nitro doped 4-hydroxy acetophenone crystals from the saturated methanol solution by slow cooling method. *Ab initio* quantum mechanical method is at present widely used for simulating the IR spectrum. Such simulations are indispensable tools to perform normal coordinate analysis so that modern vibrational spectroscopy is unimaginable without involving them. In the present study, the theoretical calculations of the wavenumbers and first hyperpolarizability of the title compound are reported.

Computational details

Calculations of the title compound were carried out with Gaussian 03 program[6] using the HF/6-31G* basis set to predict the molecular structure and wavenumbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using the analytic second derivatives to confirm the convergence to minimum on the potential surface. The wavenumber values computed at the Hartree-Fock level contain known systematic errors due to the negligence of electron correlation[7]. We therefore, have used the scaling factor value of 0.8929 for HF/6-31G* basis set.[7] The geometrical parameters corresponding to the optimized structure (Fig. 1) are given in table 1. The absence of imaginary wavenumber on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

RESULTS AND DISCUSSION

The calculated wavenumbers, infrared intensities and Raman activities and the corresponding assignments are given in table 2. The vibrations of the CH_2 group, the asymmetric stretch $\upsilon_{as}CH_2$, symmetric stretch $\upsilon_s CH_2$, scissoring vibration δCH_2, appear in the region 2945 ± 45, 2885 ± 45 and 1445 ± 35 cm^{-1}, respectively[8,9]. The HF calculations give these modes at 3038, 2963 and1446 cm^{-1}. The upshift of the stretching mode is due to the presence of halogen atom in the structure. Bands of hydrocarbons due to CH_2 twisting and wagging vibrations, are observed in the range[9,10] 1180-1390 cm^{-1}. These bands are generally appreciably weaker than those resulting from CH_2 scissoring vibrations. The CH_2 wagging and twisting modes are assigned at 1325 and 1242 cm^{-1}. The band calculated at 877 cm^{-1} is assigned as the rocking mode of CH_2 which is expected in the region[8] 805 ± 30 cm^{-1}. The C=O stretching vibration provides a strong absorption in the region[8] 1740 ± 90 cm^{-1} and in the present case the band at 1686 cm^{-1} is assigned as this mode. The in-plane and out-of-plane C=O deformations[8] are expected in the regions 585 ± 115 cm^{-1} and 520 ± 90 cm^{-1} and these bands are also identified (Table 2). Arslan *et al.*[11] reported υCCl at 683 (experimental) and at

Table 1: Geometrical parameters of the title compound

Bond lengths (A)							
1.3856	C1-C6	1.3797	C1-H7	1.0701	C2-C3	1.3915	
1.0695	C3-C4	1.3932	C3-C12	1.4836	C4-C5	1.3837	
1.0710	C5-C6	1.3816	C5-H10	1.0702	C6-Cl11	1.8042	
1.5052	C12-C14	1.2195	C13-H15	1.0731	C13-H16	1.0746	
1.9956							
Bond angles(°)							
118.9	A(2,1,7)	120.7	A(6,1,7)	120.4	A(1,2,3)	120.5	
119.0	A(3,2,8)	120.4	A(2,3,4)	119.3	A(2,3,12)	122.4	
118.3	A(3,4,5)	120.6	A(3,4,9)	119.1	A(5,4,9)	120.3	
118.8	A(4,5,10)	120.8	A(6,5,10)	120.4	A(1,6,5)	121.9	
119.1	A(5,6,11)	119.1	A(3,12,13)	120.4	A(3,12,14)	121.2	
118.4	A(12,13,15)	109.3	A(12,13,16)	113.4	A(12,13,17)	110.6	
111.8	A(15,13,17)	105.5	A(16,13,17)	105.6			

711 , 736, 687, 697 cm^{-1} theoretically. In the present study the band at 619 cm^{-1} is assigned as stretching mode of CCl . As expected the CBr stretching mode[12] is assigned at 515 cm^{-1}. The benzene ring possesses six ring stretching vibrations, of which the four with the highest wavenumbers (occurring respectively near 1600, 1580, 1490 and 1440 cm^{-1}) are good group vibrations. The fifth ring stretching vibration is active near 1335 ± 35 cm^{-1}, a region which overlaps strongly with that of the CH in-plane deformation and the intensity is in general low, or medium high[8]. For the para substituted phenyl ring the δPh modes are expected in the region[8]1280-1620 cm^{-1}. The δPh modes are given in table 2. The ring breathing mode for the paradisubstituted benzenes with entirely different substitutions[13] have been reported to be strongly IR active with typical bands in the interval 780-840 cm^{-1}. For the title compound, the HF calculation give the band at 747 cm^{-1} with a strong IR activity. For paradisubstituted benzenes, the in-plane CH deformations are seen in the range 995-1315 cm^{-1} and the out-of-plane CH deformations are below 1000 cm^{-1}. Generally, the CH out-of-plane deformations with the highest wavenumbers have a weaker intensity than those absorbing at lower wavenumbers. The substituent in-plane and out-of-plane ring modes are also identified and assigned (Table 2).

The CCl bond length in the present case is 1.8042 A and that of CBr is 1.9956 A which is in agreement with the previous reported values[14,15] . Chlorine is highly electronegative and tries to obtain additional electron density. It attempts to draw it from

Table 2: Calculated vibrational wavenumbers and band assignments

$\upsilon_{(HF)}$ cm^{-1}	IR Intensity (KM/Mole)	Raman activity (A**4/AMU)	Assignments
3058	1.18	122.60	υCH
3052	1.34	76.21	υCH
3045	0.41	75.11	υCH
3041	0.52	48.88	υCH
3038	0.27	27.74	$\upsilon_{as}CH_2$
2963	5.40	89.22	$\upsilon_s CH_2$
1686	216.71	80.50	υC=O
1609	96.78	127.06	υPh
1580	19.43	9.39	υPh
1503	27.31	8.41	υPh
1446	36.58	15.04	δCH_2
1398	22.20	2.89	υPh
1325	2.31	1.86	ωCH_2
1279	164.74	39.02	υPh
1242	31.55	14.89	τCH_2
1210	16.35	1.48	δCH
1192	8.66	6.23	δCH
1134	7.40	21.42	υCX(X)
1108	0.17	2.57	δCH
1075	81.54	12.92	υCX(X)
1057	0.35	3.70	υC(=O)C
1050	0.22	5.94	δCH
1018	27.13	7.62	υCC
1015	51.07	1.13	γCH
910	46.27	0.76	γCH
887	0.25	2.90	γCH
877	16.13	5.80	ρCH_2
784	10.35	4.55	γCH
747	32.14	21.40	Ring breathing
712	6.00	5.92	γPh
638	0.14	7.29	δC=O
619	28.60	16.65	υCCl
529	45.21	6.87	γPh(X)
515	32.78	8.79	υCBr
459	11.72	11.73	γC=O
427	3.63	3.39	γPh(X)
423	4.24	1.86	δPh(X)
301	0.79	4.06	δPh(X)
295	3.30	4.58	δPh(X)
255	2.30	2.17	δCBr
165	7.30	1.02	γPh(X)
133	3.48	2.15	tCH_2
90	4.34	0.52	tCCl
69	1.07	4.25	tCBr
41	0.25	5.95	tPh

υ-stretching; δ-in-plane deformation; γ-out-of-plane deformation; τ-twisting; rocking; ω -wagging; t- torsion; X-substituent sensitive; Ph-Phenyl; subscripts: as – asymmetric, s- symmetric.
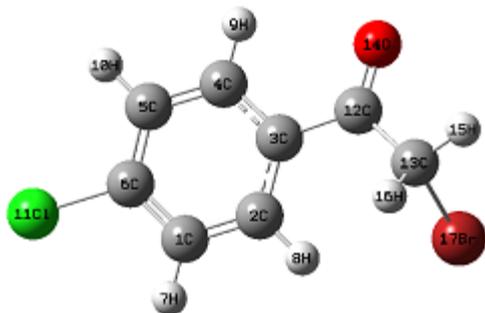
the neighbouring atoms, which moves closer together in order to share the remaining electrons more easily as a result. Due to this, the bond angle A(1,6,5) is found to be 121.9° and the exocyclic angles A(5,6,11), A(1,6,11) become 119.1°.

Analysis of organic molecules having conjugated π-electron systems and large hyperpolarizability using infrared and Raman spectroscopy has evolved as a subject of research[16]. The potential application of the title compound in the field of non linear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement, by analyzing the vibrational modes using the IR and Raman spectrum. The calculated first hyperpolarizability of the title compound is 3.50×10^{-30} esu, which is comparable with the reported values of similar derivates[15].We conclude that the title compound is an attractive object for future studies of non linear optical properties.

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