

Molecular Structure, Vibrational Spectroscopic and HOMO- LUMO Studies of *m*-Bromoacetophenone by Quantum Chemical Investigations

KHULOOD O. KAZAR

Chemistry Department, College of Science
Kerbala University, Kerbala, Iraq

MOHAMMED ALAA ABDUL ZAHRA

Chemistry Department, College of Education of Pure Sciences
Kerbala University, Kerbala, Iraq

NASEER K. SHREEF

Chemistry Department, College of Science
Kerbala University, Kerbala, Iraq

LOAY G. ABD ALI

Chemistry Department, College of Science
Kerbala University, Kerbala, Iraq

MANAL ABED MOHAMMED

Chemistry Department, College of Education of Pure Sciences
Kerbala University, Kerbala, Iraq

KHLOWD M. JASEM

Chemistry Department, College of Science
Kerbala University, Kerbala, Iraq

Abstract:

Quantum chemical calculations of energies, geometries and vibrational wave numbers of m-bromoacetophenone were carried out by DFT levels of theory using CEP-121G basis set. The study is extended to calculate the HOMO- LUMO energy gap, ionization potential, electron affinity, global hardness, chemical potential, global electrophilicity, polarizability and thermodynamic properties of m-bromoacetophenone. A complete vibrational assignment aided by the theoretical harmonic frequency analysis has been proposed. The calculated HOMO and LUMO energies show the charge transfer occurs in the molecule. The harmonic vibrational frequencies calculated have

been compared with experimental FTIR spectra. The observed and the calculated frequencies are found to be in good agreement.

Key words: DFT, Ionization potential, electron affinity, energy gap, and IR spectrum.

Introduction

Aromatic ketones such as acetophenone, propiophenone and their derivatives have great analytical and pharmaceutical applications. m-bromoacetophenone is used as an intermediate product for the preparation of fenoprofen which is an anti-inflammatory, analgesic and antipyretic drug [1,2]. Chemically it is called as 1-(3-bromophenyl)-ethanone. Alzheimer's disease (progressive form of percentile dementia) is treated with the drug which was invented from 3-bromoacetophenone [3]. It is used as a reaction initiator with organopolysiloxane, which is the base polymer to prepare silicone rubber [4]. It is also used as a coupling partner in microwave accelerated cross-coupling of a range of aryl boronic acids with aryl chlorides [5].

Substituted bromoacetophenone are used to synthesis dicationic diarylpyridines which are used as nucleic acid binding agents [6]. The title compound is used as an antibacterial agent [7]. It is also used as a photo radical polymerization initiator to provide a cross linkable silyl group terminated vinyl polymer [8]. DFT calculations of vibrational spectra of many organic systems [9,10], have shown promising conformity with experimental results. Therefore, in these present investigation DFT techniques is employed to study the complete vibrational spectra of the title compound and to identify the various normal modes with greater wave number accuracy. Several other investigations have been carried out on the title compound and its derivatives [11-15]. Literature

survey reveals that to the best of our knowledge no DFT/B3LYP/CEP-121G frequency calculations of 3-bromoacetophenone have been reported so far. It may be due to difficulty in interpreting the spectra of these molecules because of their complexity and low symmetry. Due to the absence of vapour phase infrared spectra, a complete vibrational assignment is not available in the literature. Hence the present investigation was undertaken to study the vibrational spectra of this molecule completely and to identify the various normal modes with greater wave number accuracy. Assuming C₁ point group symmetry the band assignments have made.

Density Functional Theory (DFT) calculations have been performed to support our wave number assignments. The theoretically predicted IR intensities is well in agreement with that of experimental spectral data.

2. Computational Details

The entire calculations conducted in the present work were performed at B3LYP level included in the Gaussian 03W package [16] program together with the CEP-121G basis set function of the density functional theory (DFT) utilizing gradient geometry optimization [17]. All the geometries were optimized using CEP-121G basis sets using density functional theory (DFT) [18] employing the Becke's three-parameter hybrid functional [19] combined with Lee-Yang-Parr correlation [20] functional (B3LYP) method. The DFT partitions the electronic energy as $E = E_T + E_V + E_J + E_{XC}$, where E_T , E_V , and E_J are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms respectively. The electron correlation is taken into account in DFT via the exchange correlation term E_{XC} , which includes the exchange energy arising from the antisymmetric of the

quantum mechanical wave function and the dynamic correlation in the motion of individual electrons [21].

The optimized structural parameters were used in the vibrational frequency calculations at the DFT level to characterize all stationary points as minima. Then vibrational averaged nuclear positions of m-bromoacetophenone is used for harmonic vibrational frequency calculations resulting in IR frequencies together with intensities. The DFT hybrid B3LYP functional also tends to overestimate the fundamental modes in comparison to the other DFT methods; therefore, scaling factors have to be used to obtain considerably better agreement with experimental data. Thus according to the work of Rauhut and Pulay [22], a scaling factor of 0.963 has been uniformly applied to the B3LYP calculated wavenumbers.

Finally, calculated normal mode vibrational frequencies, provide thermodynamic properties by way of statistical mechanics. By combining the results of the Gaussview program [23] with symmetry considerations, vibrational frequency assignments were made with high degree of accuracy. There is always some ambiguity in defining internal coordination. However, the defined coordinate form complete set and matches quite well with the motions observed using the Gaussview program. To achieve a close agreement between observed and calculated frequencies, the least square fit refinement algorithm was used. For the plots of simulated IR and Raman spectrum, pure Lorentzian band shapes were used with a bandwidth of 10 cm^{-1} . HOMO-LUMO energy gaps has been computed and other related molecular properties are calculated.

3. Results and Discussion

3.1. Molecular Geometry

The optimized structure parameters of m-bromoacetophenone calculated by DFT-B3LYP level with the CEP-121G basis set are listed in the Table 1 in accordance with the atom numbering scheme given in Fig.1. The molecular structure, XRD studies have been studied for the compound m-chloroacetophenone and m-nitroacetophenone. Since the compound chosen for the present study has close structural relation with the above-mentioned compounds, the molecular parameters have been taken from m-chloroacetophenone and m-nitroacetophenone [24,25]. Table 1 compares the calculated bond lengths and angles for m-bromoacetophenone with those experimentally available from X-ray diffraction data [24, 25]. From the theoretical values, we can find that most of the optimized bond angles are slightly larger than the experimental values, due to the theoretical calculations belong to isolated molecules in gaseous phase and the experimental results belong to molecules in solid state. In spite of the differences, calculated geometric parameters represent a good approximation and they are the bases for calculating other parameters, such as vibrational frequencies and thermodynamic properties.

3.2 Energies

Table 2 shows the values of the total energy and electronic states for the analyzed structures and the energy gap of the m-bromoacetophenone. The total energy for studied molecule as a linear function of bromine substituted to the acetophenone molecule. It is clear that from table 2, the total energy is increase and depending on the atomic number of halogen atom, and it is observed that substitution of bromine (electron-accepting) causes decreasing the HOMO and LUMO energy, it is known that the electron accepting substituents decreasing

the LUMO and HOMO energies [26], and energy gap decreased. The frontier orbital (HOMO and LUMO) of the chemical species are very important in defining its reactivity[27] The LUMO-HOMO energy gaps of m-bromoacetophenone is small than that of the original molecule, with decreasing energy gap, electrons can be easily excited from the ground state. The table 2 shows these energies of studied molecule, the molecule has C_1 symmetry.

B3LYP functional used in this study has a high efficient to calculate the electronic properties for the organic studied molecules, such as ionization potentials (IP), electron affinities (EA), chemical potential (K), absolute hardness (η), absolute softness (S), electrophilic index (ω). The properties are computed by the way that is based on the differences between the HOMO and the LUMO energies of the neutral molecule and is known as orbital-vertical (Koopmans' theorem).The calculated properties for each variable clearly reveal that the ionization potential for the m-bromoacetophenone is higher than that for the original molecule, this indicates that this molecule needs high energy to become cation comparing with the acetophenone. The strength of an acceptor is measured by its electron affinity (EA) which the energy released when adding one electron to LUMO. An acceptor must have a high EA, adding the Br atom to acetophenone molecule leads to increasing the ability of the electron affinity for the molecule, as we see in table 4. The Koopmans' theorem is a crude but useful and fast approach [26,28]. The behavior of electronegativity, softness and electrophilic index for the studied molecules shows the magnitude larger than for the original molecule, adding the Br atom gives the molecules more softness. The larger the HOMO-LUMO orbital energy gap, the harder the molecule. The hardness has been associated with the stability of the chemical system[27]. In the present study, HOMO-LUMO gap and hardness of the acetophenone molecule is larger than those for

m-bromoacetophenone as shown in table 2 and table 4, which clearly indicates that the molecule is the most stable .

3.4 Molecular polarizability and the Dipole moment

One of the objectives of the present investigation is to study the effect of the basis sets B3LYP/ CEP-121G levels on molecular polarizability of acetophenone and its m-bromoacetophenone derivative using the Gaussian03W program. In this study, the computation of the molecular polarizability $\langle \alpha \rangle$ was reported, m-Bromoacetophenone molecule has polarizability larger than that in acetophenone. The calculated dipole moment values show that the acetophenone molecule is highly polar and more than m-bromoacetophenone. The calculated dipole moment and polarizabilities by DFT method are summarized in Table 3.

3.5 Thermodynamic properties

On the basis of vibrational analysis at B3LYP/ CEP-121G level, several thermodynamic parameters are calculated and are presented in Table 5. Table 5 showed that acetophenone compound less entropy ΔS° and larger in the ΔU° , ΔH° , ΔA° and ΔG° properties than those of its m-bromoacetophenone derivative, this because Br substituent effect.

3.6 Electronic densities

The electron densities for acetophenone molecule and its m-bromoacetophenone derivative were listed in (Table 6) . Electron densities are different between them because the Br substituent effect .

3.7 Vibrational assignments

3.7.1 C-H Vibrations

The aromatic structure shows the presence of C-H stretching vibrations in the region 3250 cm^{-1} - 2950 cm^{-1} which is

characteristic region for the ready identification of C-H stretching vibrations and particularly the regions 3250 cm^{-1} - 3100 cm^{-1} for asymmetric stretching and 3100 cm^{-1} - 2950 cm^{-1} for symmetric stretching modes of vibration [29]. For most cases, the aromatic compound C-H vibration absorption bands are usually weak; in many cases it is too weak for detection. In this region, the bands are not affected, appreciably by the nature of substituents. In the present work, for the m-bromoacetophenone, the FTIR bands observed at 3238 cm^{-1} , 3220 cm^{-1} and 3197 cm^{-1} have been assigned to C-H stretching vibration. The B3LYP level at CEP-121G gives slightly different frequency values at 3211 cm^{-1} , 3201 cm^{-1} and 3164 cm^{-1} as indicated in Table 7. In general the aromatic C-H stretching vibrations calculated theoretically are in good agreement with the experimentally reported values [30,31] for di substituted benzene in the region $3200 - 2900\text{ cm}^{-1}$. The out of plane bending mode of C-H vibration is found well in agreement with the experimentally predicted in the region $1000-600\text{ cm}^{-1}$ [32]. At B3LYP/ CEP-121G , 982 and 834 cm^{-1} , is calculated . The observed FTIR value of 996 cm^{-1} is in excellent agreement with 982 cm^{-1} of B3LYP/ CEP-121G results. The out of plane C-H deformation vibrations of m-bromoacetophenone is experimentally predicted in the region 636 and 996 cm^{-1} coincides satisfactorily with the calculated values in the same region. The aromatic C-H in-plane bending modes of benzene and its derivatives are observed in the region $1300-1000\text{ cm}^{-1}$ [33]. The C-H in plane bending vibrations assigned even though found to be contaminated by C-CH₃ stretch are found in literature [34,35], while the experimentally observed values for m-bromoacetophenone is at 1268 cm^{-1} . The C-H in-plane bending vibration of m-bromoacetophenone coincides satisfactorily with the experimentally observed values in this region.

3.7.2 C-Br Vibrations

The compound under consideration m-bromoacetophenone has a bromine substitution. The heavier mass of bromine obviously makes the C-Br stretching mode to appear in longer wavelength region. Bellamy has assigned the region 700-600 cm^{-1} for the C-Br stretching [36,37]. Based on this, the band observed at 660 cm^{-1} in FTIR is assigned to C-Br stretching. The theoretically calculated value for m-bromoacetophenone 662 cm^{-1} is well agreed with the experimental value.

3.7.3 Methyl group Vibrations

The m-bromoacetophenone compound under consideration possess a CH_3 group in the side substitution chain. There are nine fundamentals one can expect to a CH_3 group, namely the symmetrical stretching in CH_3 (CH_3 sym. stretch) and asymmetrical stretching (in plane hydrogen stretching mode); the symmetrical (CH_3 sym. deform) and asymmetrical (CH_3 asym. deform) deformation modes; in-plane rocking, out-of-plane rocking, twisting and bending modes [38]. Each methyl group has three stretching vibrations, one being symmetric and other two asymmetric. The frequencies of asymmetric vibrations are higher than the symmetric one [39].

The theoretically computed values 3016 cm^{-1} for CH_3 symmetric stretching and 3091 cm^{-1} , 3137 cm^{-1} for CH_3 asymmetric stretching shows an excellent agreement with the range allotted by Williams and Fleming [40]. CH_3 asymmetric and symmetric in-plane bending are observed at 1470 and 1315 cm^{-1} in FTIR, respectively [41]. The torsion vibrations are not observed in the FTIR because these appear at very low frequency. The observations at 41 cm^{-1} in m-bromoacetophenone is in agreement with theoretical results of similar compounds, table 7.

3.7.4 C=O Vibrations

The C=O stretching vibration in acetophenone and m-bromoacetophenone has a main contribution in the mode, with B3LYP/ CEP-121G) predicted frequencies at 1624 cm^{-1} (Table 7), this is in agreement with the very strong experimental frequencies at 1635 cm^{-1} in FTIR spectrum. The out of plane C=O bending vibration mode of m-bromoacetophenone with the experimental frequency of 140 cm^{-1} found to be in excellent agreement. The above conclusions are in agreement with the literature value [42].

3.8 Isodesmic reaction

The stabilizing effect of a substituent is often assessed by using isodesmic reactions (conserved bond type). A positive energy difference (Δ) (scheme 1) indicates stabilization of the reactant by substituent [43], so the negative Δ refers to more reactivity for reactants (m-bromoacetophenone) than those for products (acetophenone).

4. Conclusion

The results of the study lead to the following conclusions. (i) The proper frequency assignments for the compounds is performed for the first time from the FTIR. The experimental FTIR spectra for m-bromoacetophenone was compared with the theoretical DFT calculations of the vibrational spectra of the molecule. (ii) The equilibrium geometries of compounds were determined and analyzed both at DFT level utilizing CEP-121G basis set, Geometry optimization for m-bromoacetophenone has been found in a good agreement with experimental data. (iii) The HOMO-LUMO energy gap and other related molecular properties were discussed and reported. The presence of the Br substituent decreases the energy gap of the molecule, this is one of the important properties obtained in this work, and a

small energy gap means small excitation energies of manifold of the excited states. (iv) molecular polarizability was calculated and the results were discussed, the results showed that the Br substitution leads to increase the average polarizability and cause to more reactive than original molecule. (v) The electronic properties (IP, EA, K, η , S, ω) were calculated by using DFT.

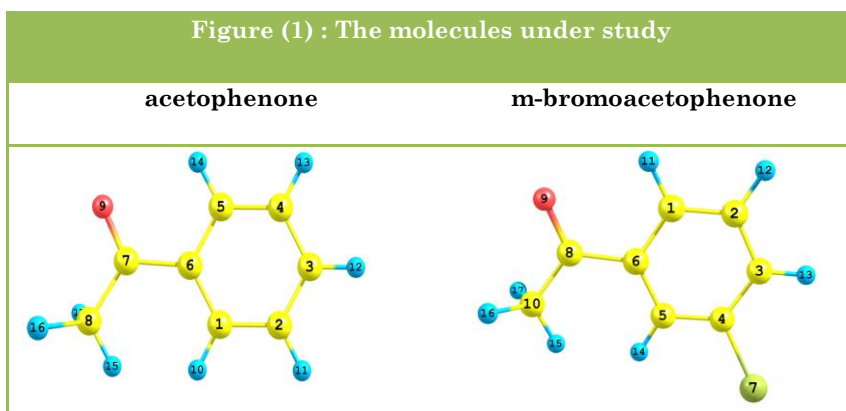


Table 1: Optimized geometrical parameters of acetophenone and bromoacetophenone isomers, bond length(Å), Interaxial angles(°)

Molecules	bond length	Our data	Expt.[24,25]	bond angles	Our data	Expt.[24,25]
Acetophenone	C8-H17	1.097	-	H12-C3-C4	120.085	-
	C6-C7	1.510	-	C5-C4-C3	120.021	-
	C10-C8	1.532	-	H14-C5-C6	121.310	-
	C4-H13	1.087	-	C6-C1-C2	120.388	-
	C7-O9	1.265	-	C6-C7-O9	119.795	-
	C5-C4	1.408	-	H10-C1-C2	118.855	-
	C2-C3	1.413	-	C8-C7-C6	121.716	-
C1-C6	1.420	-	H11-C2-C1	120.076	-	
m-Bromo Acetophenone	C10-H15	1.097	1.113	H13-C3-C4	120.578	120.000
	C6-C8	1.514	1.351	C5-C4-C3	122.021	121.000
	C10-C8	1.531	1.512	H14-C5-C6	121.538	120.000
	C4-Br7	1.972	1.881	C6-C1-C2	120.492	120.200
	C8-O9	1.264	1.208	C6-C8-O9	119.634	118.900
	C5-C4	1.409	1.395	H11-C1-C2	121.365	120.000
	C2-C3	1.417	1.395	C10-C8-C6	121.819	120.000
	C1-C6	1.422	1.395	H12-C2-C1	120.076	119.000

Table 2: Total energy, Electronic states and Energy gap for molecules calculated by DFT with B3LYP system and CEP-121G basis set .

Molecule	Symmetry	Energy (a.u)	Electronic States(a.u)		Energy Gaps (a.u)
			HOMO	LUMO	
acetophenone	C ₁	-65.8964	-0.2597	-0.0728	0.1869
m-Bromoacetophenone	C ₁	-78.6637	-0.2638	-0.0843	0.1757

Table 3: calculated dipole moment μ (debye), components of α_i (i = xx,yy,zz) an average of the dipole polarizability $\langle \alpha \rangle$ in atomic units for molecules.

Molecule	μ	α_{xx}	α_{yy}	α_{zz}	$\langle \alpha \rangle$
acetophenone	3.4867	126.317	98.521	45.104	89.98
m-Bromoacetophenone	1.4260	155.397	116.150	47.160	106.23

Table 4 Comparison of related molecular properties of acetophenone with its bromoacetophenone isomers calculated by DFT with B3LYP system and CEP-121G basis set .

Molecule	IP	EA	K	S	η	χ
acetophenone	0.2597	0.0728	-0.1663	5.348	0.0934	0.1663
m-Bromoacetophenone	0.2638	0.0843	-0.1741	5.571	0.0897	0.1741

Table 5 : Comparison of Thermodynamic properties of acetophenone with its bromo -acetophenone isomers calculated by DFT with B3LYP system and CEP-121G basis set .

Molecule	ΔU° (kcal/mole)	ΔH° (kcal/mole)	ΔS° (cal/mole K)	ΔA° (kcal/mole)	ΔG° (kcal/mole)
acetophenone	90.406	90.99842	85.330	64.96486	65.55728
m-bromo acetophenone	84.845	85.43742	95.579	56.34812	56.94054

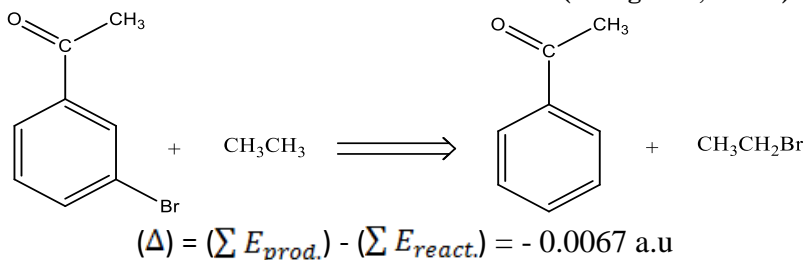
Table 6. Electronic densities for molecules calculated by DFT with B3LYP system and CEP-121G basis set

Atom	Acetophenone	Atom	m-Bromoacetophenone
C ₁	4.185615	C ₁	4.258151
C ₂	4.16965	C ₂	4.112427
C ₃	4.14233	C ₃	4.119201
C ₄	4.143278	C ₄	4.393534
C ₅	4.254717	C ₅	4.131932
C ₆	3.651727	C ₆	3.638567
C ₇	4.128597	Br ₇	6.851167
C ₈	4.592329	C ₈	4.122377
O ₉	6.132994	O ₉	6.125523
H ₁₀	0.819933	C ₁₀	4.591251
H ₁₁	0.843527	H ₁₁	0.776626
H ₁₂	0.842802	H ₁₂	0.833219
H ₁₃	0.83968	H ₁₃	0.807417
H ₁₄	0.783683	H ₁₄	0.782089
H ₁₅	0.845938	H ₁₅	0.84146
H ₁₆	0.811585	H ₁₆	0.807518
H ₁₇	0.811614	H ₁₇	0.807542

Table 7: Vibrational wavenumbers obtained for 3-bromoacetophenone at B3LYP/ CEP-121G [harmonic frequency (cm⁻¹)] IR intensities (km mol⁻¹).

acetophenone		3-Br.acetophenone			Characterization of Normal modes
v _{cal} cm ⁻¹	IR int.	v _{cal} cm ⁻¹	IR int.	v _{exp} cm ⁻¹	
22	0.899	41	0.782	-	τCH3 torsion
45	4.88	59	0.943	-	lattice vibration
160	0.077	140	7.97	-	γ C=O + γCH
231	6.10	144	2.54	-	CH3 torsion
369	0.791	154	0.020	-	CH3 torsion+ βCH
-	-	186	0.597	-	γ C-Br
-	-	276	3.19	-	β C-Br
468	2.088	295	6.355	-	β C-H
570	27.29	371	0.638	430	γ C-H
616	9.66	432	0.473	-	γ C-H
628	0.672	472	4.09	538	γ C-C-C
710	38.67	478	1.41	590	β C-C-O
-	-	576	30.37	636	CH3 twisting+ u C-Br
-	-	662	0.119	660	u C-Br
889	0.475	661	14.32	683	ring breathing
972	3.531	701	16.47	785	β C-C-C
979	20.32	768	26.97	838	γ C-H
1002	1.763	834	59.53	901	γ C-H
1020	0.978	919	13.70	960	γ C-H
1033	5.536	975	1.18	987	γ C-H
1048	2.96	982	16.66	996	γ C-H
1069	0.682	998	6.85	1020	δ ring + γC-H
1086	1.639	1044	4.16	1064	CH3 twisting
1103	7.002	1067	38.80	1091	γ C-H + β C-C
1192	0.576	1068	0.78	1101	β C-H
1210	18.23	1096	0.40	1124	u C-C+ β C-H
1280	214.85	1116	6.16	1186	δ C-H
1338	6.290	1199	6.10	1268	u C-C+ βC-H
1355	4.183	1270	269.04	1315	ρ C-H
1421	37.03	1319	18.10	1357	γ C-C
1462	16.94	1340	2.19	1405	CH3 wagging
1495	9.92	1427	39.15	1450	u C-C
1497	11.32	1483	0.53	1470	δ C-H3
1518	6.805	1494	10.54	1494	u C-C
1586	106.13	1509	17.24	1516	u C-C
1618	62.59	1573	143.7	1566	u C-C
1629	16.28	1607	29.16	1592	u C-C
1612	6.988	1624	50.93	1635	u C=O
3090	11.90	3016	5.28	3066	u _s CH3
3133	21.39	3091	10.08	3127	u _{as} CH3
3147	0.504	3137	20.60	3153	u _{as} CH3
3160	13.76	3164	10.99	3197	ring (u C-H)+ u C-H ₃
3174	36.89	3201	14.79	3220	ring (u C-H)+ u C-H ₃
3194	9.68	3211	2.19	3238	ring (u C-H)

Scheme 1. Evaluation of substituted effects (energies Δ , in a.u)



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