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Experimental and Theoretical Spectroscopic Properties of Quinazoline

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In the present study, FT-IR and FT-Raman spectra of quinazoline were recorded and the observed vibrational frequencies were completely assigned. The vibrational frequencies, infrared intensities and Raman scattering activities of the quinazoline were computed using DFT (B3LYP) and HF methods with basis set 6-311++G(d,p) and the corresponding results were tabulated. The calculated and scaled wave number shows good agreement with the experimental values. The influence of the presence of N atom in the skeletal ring on the vibrations of the molecules have been discussed. Moreover, the chemical shifts of the compound were calculated from ^{13}C NMR and ^{1}H NMR by using the Gauge Independent Atomic Orbital (GIAO) method. A UV-visible spectra of the molecule was also experimentally recorded and stimulated by HF and DFT methods and analysis on the electronic properties, absorption wavelengths, excitation energy, dipole moment and frontier molecular orbital energies were reported. The calculated HOMO and LUMO energies and the energy gap analysis shows the charge transformation within the molecule. The polarizability and hyperpolarizability of the compound were also calculated and the results indicates that the chosen compound is a good non-linear optical (NLO) material. The thermodynamic properties such as thermal energy, heat capacity and entropy of the quinazoline were calculated in gas phase.

Keywords: Quinazoline, Density functional theory, Hartee-Fock, Gauss view program, Gauge independent atomic orbital.

INTRODUCTION

Quinazoline is a compound made up of two fused six member aromatic rings-benzene and pyrimidine ring. It is a yellow coloured compound, found usually in crystalline form and it was first prepared by Gabriel in 1903 and first isolated from the Chinese plant Aseru. Quinazoline is the main six-membered heterocyclic ring system with multiple pharmacophores [1] and notable for their biological activities. The derivatives of this class includes medicines with different biological actions like soporific, sedative, tranquilizing, analgesic, anticonvulsant, antitussive, myorelexant, antirheumatic, hypotensive, antiallergic, bronchodilating, antidiabetic, cholagogue, diuretic, cystatic, antimalarial, spermicidal, *etc*., [2]. A through literature survey indicates that a complete vibrational analysis of the quinazoline was not been carried so for and the aim of the present investigation is to undertake a complete vibrational and spectroscopic analysis of the quinazoline. The FTIR and FT-Raman spectroscopy combined with quantum chemical computations has been recently used as an effective tool in the vibrational analysis of drug molecules [3], biological compounds [4] and natural products [5]. In addition, among the computational methods available for computing the electronic structure of molecular systems, DFT method has been preferred one due to its great accuracy in predicting values close to the experimental data's on molecular geometry, vibrational frequencies, atomic charges, dipole moment, thermo dynamical properties, *etc*., [6-10]. Thus in this investigation to understand the vibrational properties and structural characteristics of the quinazoline the density functional theory (B3LYP) calculation has been carried out and the observed bands are assigned based on the results of computation and literature [11-13]. Hartree-Fock (HF) computation was also carried out in the analysis or comparison purpose and to revel the capabilities of DFT techniques.

In addition, the gauge-independent atomic orbital (GIAO) method is used to compute the NMR shielding tensors and ^{13}C and ^{1}H NMR chemical shifts computed for the title compounds. For the UV spectroscopic studies excited state calculation using the time-dependent DFT were carried out and the HOMO, LUMO analyses have been used to elucidate information regarding charge transfer within the molecule. In addition to the above said spectroscopic studies many other molecular characteristics such as bond lengths, bond angles and atomic charges based on Mulliken population analysis, dipole moment, mean polarizability, first order hyperpolarizability

and thermodynamic properties of the compound were also computed.

EXPERIMENTAL

Quinazoline sample was purchased from Sigma-Aldrich Company (USA) with a stated purity of 97 % and it was used to record the spectra as such without further purification. The FTIR spectrum of molecule was recorded in the region 3700-400 cm^{-1} on a Burkerr IFS 66 VFTIR-spectrophotometer and because the sample was in solid state the KBr disc technique was employed for sample preparation. The FT-Raman spectrum of the compound was also recorded in the range 4000-100 cm^{-1} using the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source. The frequencies of all sharp bands both in the FTIR and FT Raman spectra are accurate to 2 cm^{-1}. The absorption spectrum of the compound was recorded with the UV-1700 Series UV-visible spectrometer and the band width on half height is 3.0 nm. ^{1}H NMR spectra were recorded in Bruker DPX FT NMR spectrophotometer operated at 400 MHz and 300 K. For the NMR recording the compound was dissolved in $CdCl_3$ and the chemical shifts were reported in ppm relative to tetramethylsilane (TMS) for ^{1}H NMR spectra.

Quantum chemical calculations: The entire quantum chemical calculations have been performed using the Gaussian 09 software package for windows [14] at DFT level theory using B3LYP functional which is a gradient-corrected, hybrid functional [15] employing the correlation function of Govindarajan *et al.* [16] using the 6-311++G(d,p) basis set. The Hartee-Fock computations was also carried out using the same 6-311++G(d,p) basis set employed in DFT. It was an established fact that the frequencies calculated using quantum computational methods generally higher than the experimental values due to several approximations employed in computations. Thus, in order to improve the calculated values in agreement with the experimental values, it is necessary to scale down the calculated harmonic frequencies and in this work, the vibrational frequencies calculated at HF level are scaled and B3LYP level were scaled by multiple scaling factors [17]. After scaled with the scaling factors, the deviation from the experiments is less than 10 cm^{-1} with a few exceptions. All the normal modes of the compound was assigned based on the results of theoretical analysis and the animation option of Gauss view program [15] additionally utilized to verify the atoms involved and the mode of vibration for a thorough and complete assignment. All the assignments were also compared with the good number of established works and most of the assignments were agree with the literature values.

The energy of highest occupied molecular orbit (E_{HOMO}), the energy of lowest unoccupied molecular orbital (E_{LUMO}), dipole moment (μ), ionization potential (I), electronic chemical potential (μ), electro negativity (X) and global hardness (η) were calculated for the molecule. In order to understand the non-linear optical (NLO) activity of quinazoline, the dipole moment, linear polarizability and first hyperpolarizability were obtained. Moreover, the thermodynamic parameters such as the heat capacity, entropy, enthalpy, *etc*., were computed from the vibrational frequencies of quinazoline. The electronic absorption spectra for the molecule was calculated with the time dependent density functional theory (TD-DFT) level at B3LYP/6-311++G(d,p) basis set and the solvent used here was $CdCl_3$ [16]. The ^{13}C and ^{1}H nuclear magnetic resonance (NMR) chemical shifts of the molecule were calculated by the gauge independent atomic orbital (GIAO) method in chloroform and compared with experimental results.

Prediction of Raman intensities: The Raman activities (S_{Ra}) calculated with GAUSSIAN 09 program [17] converted to relative Raman intensities (I_{Ra}) using the following relationship derived from the intensity theory of Raman scattering [15,18]:

$$I = \frac{f_i(\nu_0 - \nu_i)4S_i}{\nu_i[1-\exp(-hc\nu_i / kT)]}$$

where, ν_0 is the laser exciting wave number in cm^{-1} (here ν_0 = 9398.5 cm^{-1}), ν_i vibrational wavenumber of the i^{th} normal mode (cm^{-1}), S_i Raman scattering activity of the normal mode ν_i and f_i is a constant (equal to 10^{12}) and it is a suitably chosen common normalization factor for all peak intensities. Also h, k, c and T are Planck constant, Boltzmann constant, speed of light and temperature in Kelvin, respectively.

RESULTS AND DISCUSSION

Molecular geometry: The optimized molecular structure of quinazoline with the numbering scheme employed for the atoms is shown in Fig. 1 and the optimized structural parameters (bond length, bond angle and dihedral angle) were reported in Table-1. The computed bond lengths and bond angles are in reasonable agreement with the corresponding experimental values. There were some deviations when compared with the experimental data and these differences are probably due to intermolecular or intra molecular interactions in the solid state. The results shows that the bond lengths of C-C were greater than C-H bond lengths. The bond lengths of C-C atoms found to be in the range of 1.3742 to 1.4237 Å whereas the C-H bond values are approximately equal to 1.0891 Å and the C-N bond values is about 1.3139 Å. The bond angles within the two rings are almost same except where nitrogen atoms replaces carbon atoms and this may be due to the presence of heavy

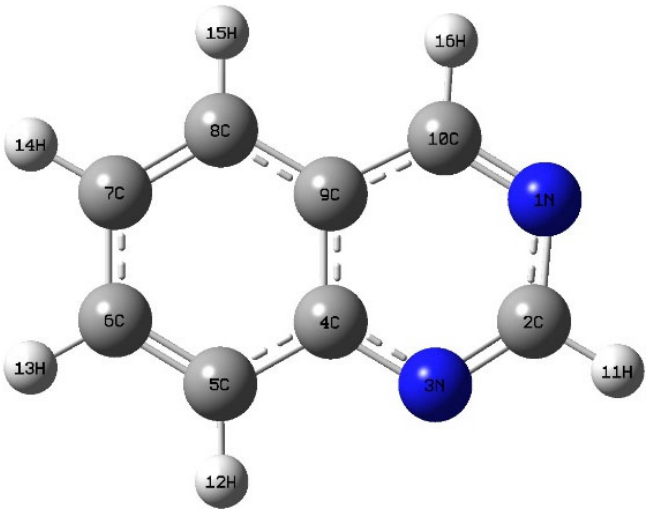

Fig. 1. Optimized molecular structure of quinazoline

TABLE-1
COMPARISON OF THE GEOMETRICAL PARAMETER BOND LENGTHS (Å), BOND ANGLES (°) OF QUINAZOLINE

Atoms involved	Bond length (Å)		Atoms involved	Bond angle (°)	
	DFT(B3LYP) 6-311++G(d,p)	HF 6-311++G(d,p)		DFT(B3LYP) 6-311++G(d-p)	HF 6-311++G(d-p)
1N-2C	1.3621	1.3526	2C-1N-10C	116.1532	116.4337
1N-10C	1.3139	1.2912	1N-2C-3N	127.4467	127.2067
2C-3N	1.3115	1.2877	1N-2C-11H	115.4498	115.368
2C-11H	1.086	1.0755	3N-2C-11H	117.1035	117.4253
3N-4C	1.364	1.3552	2C-3N-4C	116.7686	117.081
4C-5C	1.4167	1.4172	3N-4C-5C	120.0736	120.015
4C-9C	1.4237	1.3993	3N-4C-9C	120.8574	120.856
5C-6C	1.3752	1.3589	5C-4C-9C	119.0689	119.129
5C-12H	1.0832	1.0739	4C-5C-6C	119.7889	119.598
6C-7C	1.4172	1.4193	4C-5C-12H	118.2531	118.4828
6C-13H	1.0843	1.0756	6C-5C-12H	121.958	121.9192
7C-8C	1.3742	1.3573	5C-6C-7C	121.0803	121.2609
7C-14H	1.0839	1.0748	5C-6C-13H	119.7659	119.7555
8C-9C	1.4164	1.4171	7C-6C-13H	119.1538	118.9836
8C-15H	1.0851	1.076	6C-7C-8C	120.3061	120.0262
9C-10C	1.4168	1.4154	6C-7C-14H	119.4748	119.4883
10C-16H	1.0891	1.0789	8C-7C-14H	120.2191	120.4855
			7C-8C-9C	119.7409	119.7042
			7C-8C-15H	120.9115	120.8979
			9C-8C-15H	119.3476	119.3979
			4C-9C-8C	120.0149	120.2817
			4C-9C-10C	115.809	115.6438
			8C-9C-10C	124.1761	124.0745
			1N-10C-9C	122.965	122.7787
			1N-10C-16H	117.2048	117.3803
			9C-10C-16H	119.8302	119.8409

nitrogen atoms connecting the lighter carbon atoms. The angle between 2C-1N-10C, 1N-2C-11H, 2C-3N-4C and 4C-9C-10C were 115° and all the remaining bond angles were almost 120°. All dihedral angles approach ± 180° or 0° and dihedral angles shows that the molecule under study is planar.

Vibrational assignments: The organic compound under study belongs to C_1 point group and it has 16 atoms and hence it must have 42 fundamental normal modes of vibrations. All the 42 fundamental vibrations are not both IR and Raman active but Gaussian computations yields their values. The FTIR and FT Raman spectra of the title compound are shown in Figs. 2 and 3, respectively along with the corresponding stimulated spectra. A detailed spectral assignments of all the fundamental modes are given in Table-2 and the assignments were carried out using established literature and animation option of the Gauss View 5.0 software [19] and Gabedit.

CN/CC vibrations: The identification of C-N vibrations is a difficult task, since the mixing of several bands is possible in this region [20]. In pyrimidine the C=C and C=N ring stretching vibrations are observed in the region 1600-1500 cm^{-1} [21]. In quinazoline the C=N stretching vibrations were observed at 1620, 1575, 1448, 1404 cm^{-1} in FTIR and no CN stretching vibrations could be seen in the FT-Raman spectrum. Likewise C=C stretching vibrations are present in region between 1650-1400 cm^{-1} where CN stretching is identified and these assignments are in line with the literature [21,22]. Moreover most of the CC and CN stretching were identified as mixed modes and this expected because they are occupying the same region as suggested by Silverstein *et al.* [22] and others [20,21]. The bands occurring at 1246, 1129 and 1049

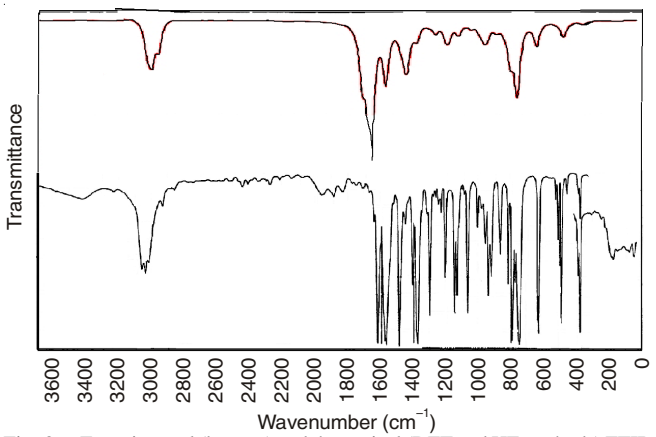

Fig. 2. Experimental (bottom) and theoretical (DFT and HF methods) FTIR spectra of quinazoline

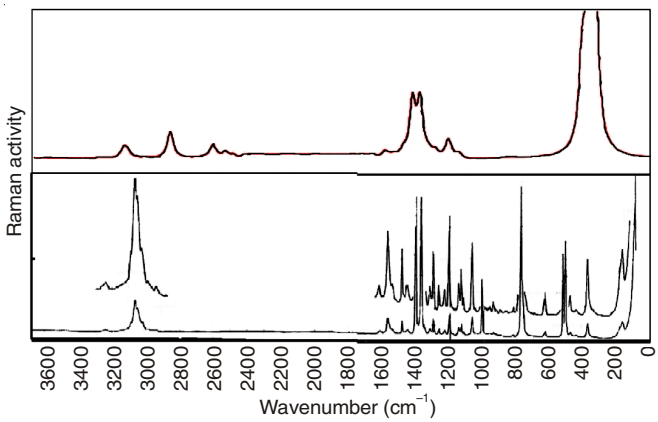

Fig. 3. Experimental (bottom) and theoretical DFT and HF methods (bottom) FT Raman spectra of quinazoline

TABLE-2
COMPARISON OF THE EXPERIMENTAL AND CALCULATED VIBRATIONAL WAVENUMBERS AND PROPOSED ASSIGNMENTS OF QUINAZOLINE

S. No.	Experimental wavenumber		Calculated (DFT) wavenumber		IR intensity	Raman activity	Assignment
	IR	Raman	Unscaled (cm^{-1})	Scaled (cm^{-1})			
1	3190	3195	3221	3189	6.262	204.003	νCH
2	3071		3190	3061	13.415	163.071	νCH
3		3048	3175	3048	8.384	101.398	νCH
4		3016	3165	3007	19.163	161.352	νCH
5	3015		3164	3006	2.389	59.979	νCH
6		2972	3126	2970	18.592	105.386	νCH
7		1566	1658	1575	37.039	7.984	νC-C
8	1620		1618	1618	61.680	2.095	νC=N
9	1575		1599	1567	44.933	27.719	νC-C + νC=N
10	1521		1522	1517	39.792	9.266	νC-C
11	1485		1487	1472	1.384	7.224	νC-C
12	1448		1437	1437	8.868	85.431	νC-C + νC=N
13	1404		1412	1398	18.556	1.608	νC-C + νC-N
14		1396	1395	1395	20.446	83.093	βCH + νC-C
15		1336	1343	1330	10.024	9.282	βCN+ βCH
16	1300	1297	1289	1289	0.100	3.557	βCH + νC-C
17		1265	1266	1253	0.865	2.391	βCH + βCN
18	1246	1233	1237	1237	6.496	10.504	βCH+ βCCC
19		1147	1176	1141	9.168	3.020	βCH + βCCC
20	1134		1158	1123	8.679	4.342	βCNC
21	1129		1132	1120	7.935	7.693	βCCC + βCNC
22	1049		1052	1041	3.611	19.428	βCCC
23	1008	1013	1006	1006	0.065	0.216	γCH
24	979	965	999	979	0.084	0.433	γCH
25		946	982	943	4.082	0.428	γCH
26	963		957	957	7.815	0.625	β-Ringdeformation
27	935		939	930	9.298	0.026	γCH
28	867		883	865	4.454	0.050	γCH
29		829	837	820	2.715	0.267	γCH
30	815	815	805	805	22.801	0.252	γCCC
31	785		787	771	3.513	39.762	Ring breathing
32	749	754	764	749	48.793	0.044	γCCC
33		633	656	640	5.749	0.268	γCCC + γCNC
34	625	630	650	631	10.458	0.932	β-Ring deformation
35		534	541	530	0.267	9.752	Ring triogonal bend
36		518	523	523	0.806	12.888	γCCC
37	491		496	491	10.835	0.242	γCCC
38		457	457	457	0.280	0.023	γCNC + γCCC
39		387	392	384	0.618	1.542	Ring twist
40	373		379	375	1.545	0.113	In-plane ring bend
41		171	179	170	0.191	0.007	Ring twist
42	168		170	167	0.078	0.196	Ring torsion

β = in-plane bending; γ = out of plane bending; ν = stretching; β = in-plane bending; γ = out of plane bending; ω = wagging; τ = twisting/torsion; wavenumbers (cm^{-1}); IR intensities (KM/mol); Raman scattering activities (Å)4/(a.m.u.)

cm^{-1} in the infrared and at 1147 cm^{-1}in Raman spectrum are assigned to the skeletal C-C-C in-plane bending modes of title compound. The in plane bending C-N-C vibrations are assigned to the bands at 1134 and 1129 $cm^{-1}$and the results are in good agreement with the literature values [23-25].

Ring vibrational modes are sensitive to substitutions and in the present study, the bands appearing at 963, 625 cm^{-1} in FT-IR and at 630 cm^{-1} in FT-Raman are assigned to ring deformation vibrations. The bands observed at 387 and 171 cm^{-1} in FT-Raman are assigned to ring twisting modes and no corresponding vibrations were identified in FTIR spectrum of the compound. The ring triogonal bending vibrations are observed at 534 cm^{-1} in FT-Raman spectrum. The other skeleton related vibrations are also identified and presented in Table-2.

C-H vibrations: Aromatic compounds commonly exhibit multiple weak bands in the region 3100-3000 cm^{-1} due to aromatic C-H stretching vibrations [26]. In quinazoline molecule C-H stretching vibrations are observed at 3190, 3071, 3015 cm^{-1} in FTIR spectrum and in FT-Raman at 3195, 3048, 3016 and 2972 cm^{-1}. The theoretically computed frequency were in excellent agreement with the experimental data and also agrees well with the predicted data by Yadav *et al*. [27].

The bands due to the C-H in-plane deformation vibration, which usually occurs in the region 1390-990 cm^{-1} are very useful for characterization and are very strong indeed. In this region, the bands are not affected, appreciably by the nature of the substituents [28]. In this compound C-H in-plane bending was observed at 1300 and 1246 cm^{-1} in FTIR spectrum and in FT-Raman they were identified at 1396, 1336, 1297, 1265, 1233 and 1147 cm^{-1} and it is in excellent agreement with literature values [29]. The C-H out-of-plane bending vibrations generally lies in 950-800 cm^{-1} [30,31]. In FTIR spectrum C-H out-of-plane bending is observed at 1008, 979, 935 and 867 cm^{-1} and in FT-Raman it is observed at 1013, 965, 946 and 829 cm^{-1}.

Mulliken population analysis: The calculation of atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems. The charge distribution on the molecule has an important influence on the vibrational spectra. Mulliken charges are calculated by determining the electron population of each atom as defined in the basis functions and the mulliken atomic charges were listed in Table-3. The total atomic charges of quinazoline obtained by Mulliken population [32] analysis at the HF and DFT level with the 6-311++G(d,p) atomic basis set in gas phase using Gaussian 09.

TABLE-3
MULLIKEN ATOMIC CHARGES OF QUINAZOLINE CALCULATED BY DFT/B3LYP/6-311++G(d,p)

S. No.	Atoms	B3LYP/6-311++G(d,p)	HF/6-311++G(d,p)
1	N	-0.088465	-0.181165
2	C	0.124442	0.237919
3	N	-0.00358	-0.11344
4	C	-1.28684	-1.31205
5	C	-0.32722	-0.32333
6	C	-0.46215	-0.60527
7	C	0.002546	-0.04259
8	C	-0.66762	-0.72002
9	C	2.068445	2.211046
10	C	-0.46523	-0.46424
11	H	0.223766	0.250606
12	H	0.209608	0.250858
13	H	0.168385	0.202157
14	H	0.178096	0.213444
15	H	0.138136	0.172184
16	H	0.187668	0.22388

In quinazoline the results show that substitution of the aromatic ring by N1 and N3 atoms leads to a redistribution of electron density. The C atom attached to the N atom of the ring is positive because of the electron-withdrawing nature of the N atom and other C atoms are negative. As can be seen in Table-3, all the hydrogen atoms have a net positive charge.

Non-linear optical properties: Dipole moment, polarizability and hyperpolarizabilities of organic molecules are important response properties. There has been an intense investigation for molecules with large non-zero hyperpolarizabilities, since these substances have potential as the constituents of non-linear optical (NLO) materials. Non-linear optical materials is at the forefront of modern research because of its importance in providing the significant application such as frequency shifting, optical modulation, optical switching, optical logic and optical memory in areas such as telecommunications, signal processing and optical inter connections [33,34]. Since quantum chemical computations has been extensively used as an effective method to investigate the organic NLO materials [35-37], the polarizabilities and first order hyperpolarizabilities of the compound under study was calculated using DFT-B3LYP and HF methods with 6-311++G(d,p) basis set, based on the finite-field approach. Order hyperpolarizability is a third rank tensor that can be described by $3 \times 3 \times 3$ matrices. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [38] and it can be given in the lower tetrahedral format. It is obvious that the lower part of the $3 \times 3 \times 3$ matrices is a tetrahedral. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes:

$$E = E^\circ - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma + ...$$

where E° is the energy of the unperturbed molecules, F_α is the field at the origin, μ_α, $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first order hyperpolarizabilities, respectively.

In present study, the polarizability and hyperpolarizability tensors (α_{xx}, α_{xy}, α_{yy}, α_{xz}, α_{yz}, α_{zz} and β_{xxx}, β_{xxy}, β_{xyy}, β_{yyy}, β_{xxz}, β_{xyz}, β_{yyz}, β_{xzz}, β_{yzz}, β_{zzz}) were obtained from the frequency job output file of Gaussian. The total static dipole moment (μ), the mean polarizability (α_0), the anisotropy of the polarizability ($\Delta\alpha$) and the mean first order hyperpolarizability (β_0), using the x, y, z components are defined as:

$$\alpha_{total} = \alpha_0 = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)$$

$$\Delta\alpha = \left(\frac{1}{2}\left[\left(\alpha_{xx} + \alpha_{yy}\right)^2 + \left(\alpha_{yy} + \alpha_{zz}\right)^2 + \left(\alpha_{zz} + \alpha_{xx}\right)^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2\right]\right)^{1/2}$$

$$\beta_0 = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2}$$

$$\beta_0 = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yxx} + \beta_{yyy} + \beta_{yzz}\right)^2 + \left(\beta_{zxx} + \beta_{zyy} + \beta_{zzz}\right)^2\right]^{1/2}$$

Polarizability is the property of a species and it is minimum for most stable species and is maximum for least stable species like transition state. The α and β values of the Gaussian 09 output are in atomic units (a.u) and these calculated values converted into electrostatic unit (e.s.u) (for α: 1 a.u = 0.1482×10^{-24} esu; for β: 1 a.u = 8.639×10^{-33} esu) and all the polarizability values of quinazoline are listed in Table-4. The calculated of quinazoline is $1.55153026 \times 10^{-23}$ esu in DFT and $1.434321659 \times 10^{-23}$ esu in HF, respectively.

The dipole moment of a molecule is another important electronic property. The total dipole moment can be calculated using the following equation:

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2}$$

The calculated value of dipole moment was found to be 3.0088 Debye by DFT B3LYP/6-311++G(d,p) and 2.9565 Debye by HF/6-311++G(d,p) methods and the calculated dipole moment values are also given in Table-4. The highest

TABLE-4
CALCULATED ENERGY VALUES OF
QUINAZOLINE IN ITS GROUND STATE

Molecular properties	B3LYP/6-311++G(d,p)
E_{LUMO+1} (eV)	-0.18797
E_{LUMO} (eV)	-0.22281
E_{HOMO} (eV)	-0.35498
E_{HOMO-1} (eV)	-0.35608
$\Delta E_{HOMO-LUMO}$ (eV)	0.13217
$\Delta E_{HOMO-LUMO+1}$ (eV)	0.16701
$\Delta E_{HOMO-1-LUMO}$ (eV)	0.13327
$\Delta E_{HOMO-1-LUMO+1}$ (eV)	0.16811
Global hardness (η) (eV)	0.066085
Chemical softness (S) (eV)	15.13202694
Electronic chemical potential (μ) (eV)	0.288895
Global electrophilicity index (ω) (eV)	0.631461912

value of dipole moment is observed for component μ_x and in this direction, its value is equal to 1.1364 (only magnitude) Debye by DFT and 1.0532 Debye by HF methods. The lowest value of the dipole moment of the compound is μ_z component and its value is -1. 14847395 × 10^{-9} in DFT and -1.35358030 × 10^{-8} by HF method.

The magnitude of the molecular hyperpolarizability is one of important key factors in a NLO system. To study the NLO properties of molecule the value of β of urea molecule which is prototypical molecule is used as threshold value for the purpose of comparison [32]. The β of urea was 0.3728 × 10^{-30} esu obtained by B3LYP/6-311++G(d,p) method [39]. In this study, the calculated β value (8.931493819 × 10^{-31} esu) is nearly three times that of urea and the large β value calculated by the B3LYP method shows that the compound under study is a good NLO material. The theoretical calculation of β components is very useful as this clearly indicates the direction of charge delocalization. The largest β_{xxx} value indicates charge delocalization is perpendicular to the bond axis and the involvement of π orbitals in intra-molecular charge transfer process.

HOMO-LUMO band gap: The frontier molecular orbitals play an important role in understanding the electrical and optical properties. Quantum chemical computations helps to visualize the occupied and unoccupied molecular orbital and in addition the HOMO and LUMO values. The Frontier orbital gap helps to characterize the chemical reactivity, kinetic stability, optical polarizability, chemical hardness and softness of a molecule [40]. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor. The 3D plots of the frontier orbitals, HOMO (highest occupied molecular orbitals) and LUMO(lowest unoccupied molecular orbitals) for quinazoline molecule are shown in Fig. 4.

The energy of the HOMO is directly related to the ionization potential and LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability factor for structures. For the compound under study B3LYP/6-31G++(d,p) calculation shows that the energy band gap of the molecule is about 0.13217 eV. The low value of ΔE is proof enough to show that there is charge transfer within quinazoline proving it to be bioactive [41].

The values of electrophilic index gives an indication about the capacity of the molecule to accept the maximal number of

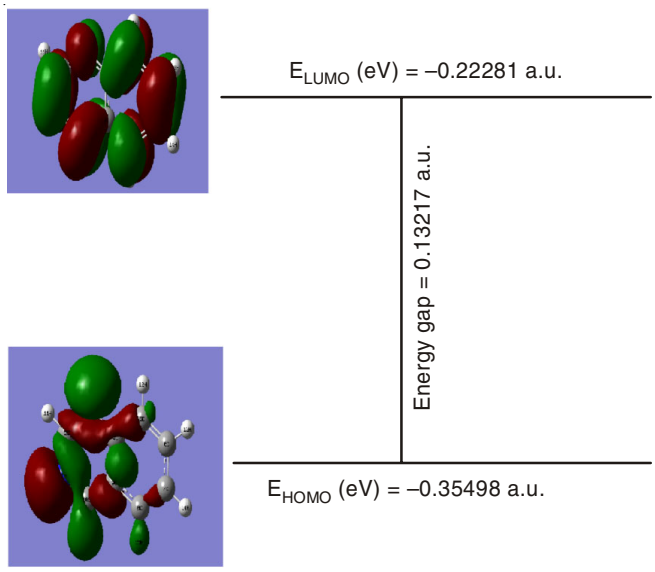

Fig. 4. Patterns of the principle highest occupied and lowest unoccupied molecular orbitals of quinazoline

electrons from the neighboring reservoir of electron. By using HOMO and LUMO energy values for a molecule and the ionization potential the chemical hardness of the molecule were calculated using Koopmans' theorem and are given by

$$\eta = (I_P - E_A)/2$$

or $$\eta = ½ (\varepsilon_{LUMO} - \varepsilon_{HOMO})$$

where I_P = Ionization potential (eV), E_A = electron affinity (eV) and $I_P \sim E_{(HOMO)}$, $E_A \sim E_{(LUMO)}$.

Considering the chemical hardness, large HOMO-LUMO gap means a hard molecule and small HOMO-LUMO gap means a soft molecule. One can also relate the stability of molecule to hardness, which means that the molecule with least HOMO-LUMO gap means it is more reactive.

The electron affinity can be used in combination with ionization energy to give electronic chemical potential, $\mu = ½ (\varepsilon_{LUMO} + \varepsilon_{HOMO})$. Chemical softness (S) = 1/η describes the capacity of an atom or group of atoms to receive electrons and is the inverse of the global hardness [42]. A molecule with a low energy gap is more polarizable and is generally associated with the high chemical activity and low kinetic stability and is termed soft molecule [43]. A hard molecule has a large energy gap and a soft molecule has a small energy gap [44]. It is shown from the calculations that quinazoline has the least value of global hardness (0.066085 eV) and the highest value of global softness (15.13202694 eV) is expected to have the highest inhibition efficiency. The global electrophilicity index is calculated using the relation, $\omega = \mu^2/2\eta$. The HOMO, LUMO and other related Frontier orbital values are listed in Table-5.

Thermodynamic properties: Several thermo dynamical parameters such as zero-point vibrational energy, thermal energy, specific heat capacity, rotational constants, entropy and dipole moment of the molecule under study have been calculated by using DFT B3LYP/6- 311++G(d,p) and HF/6-311++G(d,p) have been given in Table-6. All these thermodynamic data provide helpful information for further study on quinazoline and they can be used to compute the other thermodynamic parameters utilizing the relationships of thermodynamic

TABLE-5
ELECTRIC DIPOLE MOMENT, POLARIZABILITY AND FIRST ORDER HYPERPOLARIZABILITY OF QUINAZOLINE

Parameters	DFT B3LYP	HF
Polarizability (a.u.)		
α_{xx}	149.706835	135.661115
α_{xy}	-0.130711074	-0.104493104
α_{yy}	109.536825	100.802475
α_{xz}	$-1.98590727 \times 10^{-8}$	$0.907954700 \times 10^{-8}$
α_{yz}	$-2.17141262 \times 10^{-8}$	$-3.73318071 \times 10^{-8}$
α_{zz}	54.8312916	53.8845926
α_{tot}	104.6916505	96.78272753
α_{tot}	1.551530×10^{-23} esu	$1.4343216 \times 10^{-23}$ esu
$\Delta\alpha$	$3.865437005 \times 10^{-23}$ esu	$3.565600206 \times 10^{-23}$ esu
Hyperpolarizability (a.u.)		
β_{xxx}	154.659604	-123.186240
β_{xxy}	57.4552124	86.0535957
β_{xyy}	-12.3771781	5.58231344
β_{yyy}	-6.78407348	-18.2586808
β_{xxz}	$-1.03355462 \times 10^{-6}$	$-1.04729747 \times 10^{-6}$
β_{xyz}	$1.77890380 \times 10^{-6}$	$-7.17313944 \times 10^{-7}$
β_{yyz}	$-3.80410944 \times 10^{-6}$	$-3.90257023 \times 10^{-6}$
β_{xzz}	-55.1024479	54.8466355
β_{yzz}	4.90099483	8.58278646
β_{zzz}	$-9.27032778 \times 10^{-7}$	$-3.60124539 \times 10^{-7}$
β_{o}	103.385737	98.85358287
	$8.931493819 \times 10^{-31}$ esu	$8.539961024 \times 10^{-31}$ esu
Diploe moment (Debye)		
μ_x	-1.13640723	1.05322596
μ_y	0.483112734	0.553953910
μ_z	$-1.14847395 \times 10^{-9}$	$-1.35358030 \times 10^{-8}$
μ_{tot}	1.2348360 D	1.190020948 D

TABLE-6
CALCULATED THERMODYNAMIC PARAMETERS OF QUINAZOLINE

Parameters	B3LYP	HF
Zero point energy		
In Joules/mol	323891.0	347141.7
In Kcal/mol	77.41180	82.96886
Rotational temperature (K)		
	0.15546	0.15813
	0.06125	0.06210
	0.04394	0.04459
Rotational constants (GHz)		
	3.23918	3.29499
	1.27624	1.29390
	0.91552	0.92907
Entropy (Cal/mol-Kelvin)		
Total	81.447	79.746
Translational	40.501	40.501
Rotational	28.831	28.786
Vibrational	81.447	79.746
Thermal energy (KCal/mol)		
Total	81.553	86.811
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	79.775	85.033
Molar capacity at constant volume (Cal/Mol-Kelvin)		
Total	26.983	24.682
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	21.021	18.720

functions and to determine the directions of chemical reactions according to the second law of thermodynamics [45,46].

^{1}H and ^{13}C NMR spectral analysis: The combined use of experimental NMR spectroscopy and computer simulation methods offers a powerful way to interpret and predict the structure of large molecules. The isotropic chemical shifts are frequently used as an aid in identification of reactive organic as well as ionic species. It is recognized that accurate predictions of molecular geometries are essential for reliable calculations of magnetic properties [47]. Thus the optimized structure of quinazoline was used to get the NMR spectra using the DFT method with 6-311++G(d,p) level using the GIAO (gauge-independent atomic orbital) method. The theoretical ^{1}H and ^{13}C NMR chemical shifts of quinazoline have been compared with the experimental data [48] as shown in Table-7. Application of the GIAO [49] approach to molecular systems was significantly improved by an efficient incorporation of the method into the *ab initio* SCF calculations, using techniques borrowed from analytic derivative methodologies. The ^{1}H and ^{13}C chemical shifts were measured in $CdCl_3$ and the chemical shifts are reported in ppm relative to TMS for ^{1}H and ^{13}C NMR spectra. The experimental and theoretical ^{1}H and ^{13}C FT NMR spectrum are presented in Figs. 5 and 6. The range ^{13}C NMR chemical shift of typical organic molecule is usually >100 [50,51] and in the present study, signals for aromatic carbons were observed at 70-160 ppm respectively in ^{13}C NMR spectrum for quinazoline. Hydrogen atom is the smallest of all atoms and mostly localized on periphery of molecules. Therefore their chemical shifts would be more susceptible to intermolecular interactions in the aqueous solution as compared to that of other heavier atoms and the signals of the aromatic proton were observed at 7-10 ppm. The nitrogen is much more electronegative than carbon, attracts the bonding pair much more strongly than carbon. It is noted that the values may be slightly shifted due to the solvent used. Since the N atom has more electronegative property it polarizes the electron distribution in its bond and decreases the chemical shifts value. The theoretical peak observed in ^{13}C NMR signals at 160.38 ppm in DFT (161.928

TABLE-7
OBSERVED AND PREDICTED ^{1}H NMR AND ^{13}C NMR ISOTROPIC CHEMICAL SHIFTS (WITH RESPECT TO TMS) FOR QUINAZOLINE

S. No.	Atoms	Chemical shifts (ppm)	
		Experimental	Calculated
1	N	–	331.60540
2	C	160.38	161.92870
3	N	–	319.28810
4	C	155.38	156.65990
5	C	128.59	135.44640
6	C	134.29	137.56200
7	C	128.51	131.50430
8	C	128.08	131.34200
9	C	127.34	129.61060
10	C	160.34	164.91950
11	H	9.410	9.56840
12	H	9.410	8.36740
13	H	9.410	8.06380
14	H	9.410	7.73180
15	H	9.410	7.94170
16	H	9.410	9.47540

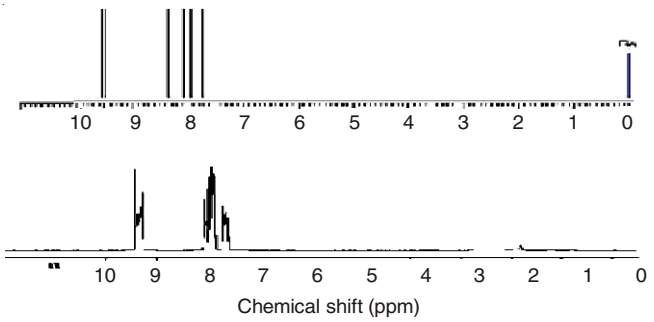

Fig. 5. Experimental (top) and theoretical (bottom) ^{1}H NMR spectrum of quinazoline

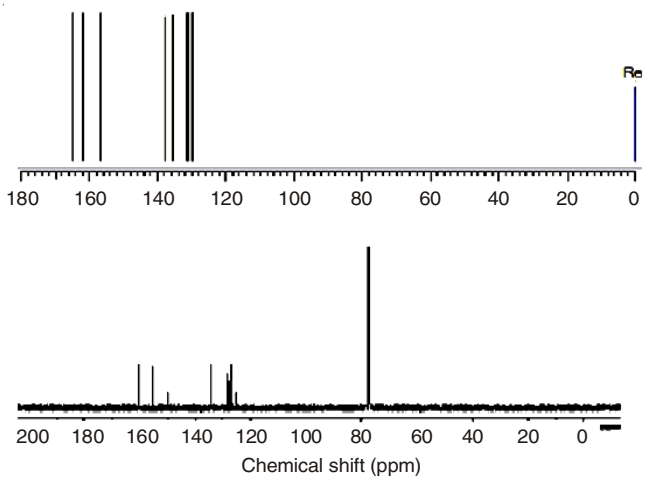

Fig. 6. Experimental (bottom) and theoretical (top) ^{13}C NMR spectrum of quinazoline

ppm in HF) may be assigned to the carbon atom 2C because this ring carbon (2C) attached between two N atoms.

UV-visible spectra and electronic properties: The frontier molecular orbital plays an important role in understanding the electric and optical properties, as well as in the UV-visible spectra and chemical reaction. The UV-visible electronic spectrum of quinazoline in chloroform was recorded in 200-400 nm range and is presented in the Fig. 7. Using the fully optimized ground-state structure, TD-DFT/B3LYP/6-31G++(d,p) calculations [52] have been performed to determine the low-lying excited states of quinazoline. The calculated results including the vertical excitation energies (E), oscillator strength (f) and wavelength along with the measured experimental wavelength and absorbance were listed in Table-8. The simulated spectrum of the compound illustrates one broad band at 295 nm but the experimental visible absorptions which are functions of the electron availability were observed at 269 nm. The difference between the experimental band maxima and TD-DFT values deviates by 33 nm. TD-DFT method predict intense electronic transition at 3.2327 eV (383.53 nm), 4.1048 eV (304.80 nm), 4.3714 eV (283.63 nm) with oscillator strength f = 0.0016, 0.0538 and 0.0007 respectively and is in good agreement with the measured experimental data (exp = 375.00 nm, 304.80 nm and 269.00 nm) shown in Fig. 7. The $\pi \rightarrow \pi^*$ transitions are expected to occur relatively at lower wavelength, due to the consequence of the extended aromaticity of the benzene ring.

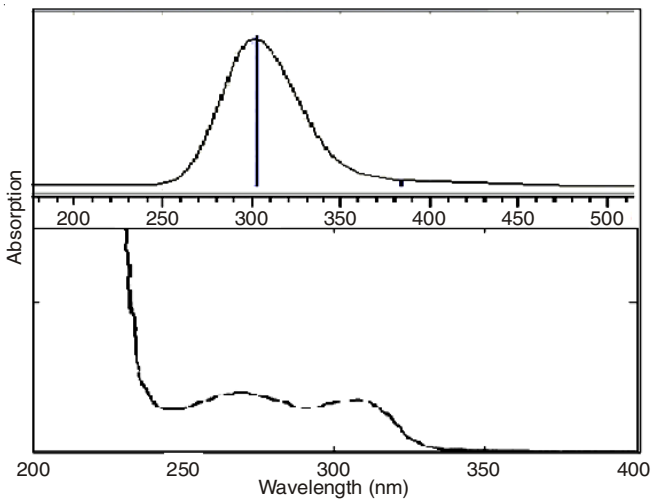

Fig. 7. Experimental (bottom) and simulated (top) UV spectra of quinazoline

TABLE-8
EXPERIMENTAL AND THEORETICAL ELECTRONIC ABSORPTION VALUES OF QUINAZOLINE

Experimental		Theoretical		
Experimental peak positions (nm)	Absorbance	Wavelength (nm)	Excitation energies (eV)	Oscillator strength (f)
375.00	0.007	383.53 (34 → 35)	3.2327	0.0016
304.80	0.346	302.05 (32 → 36) (33 → 35)	4.1048	0.0538
269.00	0.405	283.63 (34 → 36)	4.3714	0.0007

Conclusion

A complete vibrational analysis of quinazoline using experimental and theoretical vibrational data of the molecule based on *ab initio* and DFT method is presented for the first time and found to be in excellent agreement with the available literature. Molecular parameters such as bond lengths, bond angles and Mullikan charges were calculated by using DFT and HF methods and compared with each other. Furthermore, polarizabilities, first-order hyperpolarizabilities and total dipole moment properties of the molecules shows that the title molecules has considerable non-linear optical properties and also found to be greater than exhibited by urea- the standard compound used for comparison. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule. The calculated normal-mode vibrational frequencies and the corresponding force constants yielded thermodynamic properties through computations based on statistical mechanics. Theoretical ^{1}H and ^{13}C chemical shift value (with respect to TMS) were reported and compared with both ^{1}H and ^{13}C experimental NMR spectrum. The electronic properties were also calculated and compared with the experimental UV-visible spectrum. The experimental data and simulations presented helps in a complete characterization of the molecule furthermore these data may be helpful in developing application of quinazoline in pharmaceutical industries and fundamental researches in organic chemistry.

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