

# DFT Study of Properties of HCl Trimer

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**Abstract**—DFT reveals structural and vibrational properties of HCl trimer by using basis set 6-311++g\*\* with various functionals. For PBEPBE functional, bond length ( $H-Cl=1.312 \text{ \AA}$ ) increases with intermediate frequency value  $2.668.10 \text{ cm}^{-1}$  as compared to other functionals. Also the intermolecular stretching modes are higher for WB97XD. The variation is observed in density of states (DOS) for occupied and unoccupied orbitals for different functionals. The negative electron affinity (EA) for WB97XD ( $-11.7207 \text{ eV}$ ) is observed due to high LUMO energy. For all functionals, values of global hardness interpret expected results and approximately equal.

**Keywords:** DFT, Basis set and Functional, Molecular Dynamics, Energy gap, DOS, Simulation and Modelling

## I. INTRODUCTION

The properties of (HCl) trimer are studied by using density functional theory (DFT). We discussed the structural properties, vibrational properties, orbital energies and some global descriptors of the (HCl)<sub>3</sub>, with the help of hydrogen chloride bond cooperativity. These properties are studied with the help of quantum mechanical density functional theory (DFT). Now a days, Hydrogen bonding is most widely investigated class of non-covalent interactions due to its importance in the chemical and physical properties of molecules as well as its impact on the structure and functions of molecules [1]. Also the hydrogen bonding in clusters plays an important role in molecular orbital energies and hence for hydrogen chloride it is expected that change in energy gap is observed with respect to different functionals. Clusters of hydrogen-bonded molecules are extremely important as model systems in the study of intermolecular interactions and chemical reactivity [2]. The structures, energies and vibrational spectra of dimer, trimer and tetramer of HX (X=Cl,Br,I) are analyzed by Latajka and Scheiner [3]. Chandler et al. also studied optimized (HCl)<sub>1-4</sub> clusters at the second-order Moller–Plesset (MP2) theoretical level [4]. Several experimental [5]-[15] and theoretical studies [16-20] are analysed for HCl clusters.

The hydrogen-bonding cooperativity in X-H clusters (X=F,Cl,Br, . . . ) can also be studied with the help of shift to low frequencies ( $\Delta\nu$ ) and the increase in the intensity of the fundamental X-H stretching vibration relative to the monomer [21]. It is also seen that, the range selection with DFT and other fast approximate theories, such as semi empirical methods based on the neglect of differential diatomic overlap integral approximation [22], [23] should take into account the expected error margin in frequencies. The present study is concerned with vibrational excitation of the high frequency stretching modes of (HCl)<sub>3</sub> which also affects the geometry as well as orbital energies of the structure.

The highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are the most important orbitals to study stability and reactivity of a molecule. The energy gap values may show a big variation even at the same size of the cluster due to the complexity in the molecular structure [24]. The HOMO-LUMO energy gap explains the concluding charge transfer interaction within the molecule and is useful in determining molecular electrical transport properties [25]. A molecule with a high energy gap (HOMO-LUMO energy gap) has low chemical reactivity and the high kinetic stability [26], because it is energetically unfavourable to add an electron to the high-lying LUMO in order to remove electrons from the low-lying HOMO. During molecular interactions, the Lowest Unoccupied Molecular Orbital (LUMO) accepts electrons and its energy is related to the electron affinity (EA), whereas the Highest Occupied Molecular Orbital (HOMO) donates electrons and its energy corresponds to the ionization potential (IP) [27], [28].

## II. COMPUTATIONAL DETAILS

In recent studies, clusters of the various molecules can be studied by using different methods in molecular dynamic (MD) simulations. HCl trimer has been studied at different theoretical levels with common basis set 6-311++g\*\*. In many studies, Density functional theory (DFT) calculations have

been carried out with several hybrid functionals including the Becke three-parameter [29] (B3) with the Perdew and Wang[30] (PW91) and Lee, Yang, and Parr [31] (LYP) correlation functionals. Also the calculations with the Adamo and Barone [32] Becke style one-parameter functional using a modified Perdew–Wang exchange and PW91 correlation [33], (MPW1PW91) have been carried out. In this report, the geometries of HCl trimer have been fully optimized with exchange and correlation functional (PBEPBE) [34], hybrid functional (B3LYP) [35], standalone functional (HCTH) [36], exchange functional (TPSSTPSS) [37] and functional including dispersion (WB97XD) [38]. Also the frequency calculations of the optimized

structures have been characterized as local minima. The calculations have been carried out with the GAUSSIAN 16 [39]. All the optimized structures gave no negative vibrational modes showing that all structures were stationary points in the geometry optimization procedures.

### III. RESULTS AND DISCUSSIONS:

#### 1. Structural Properties

The optimized structures of HCl trimer are presented in figure 1 and some structural parameters (bond length and bond angles) are calculated at different levels with basis set 6-311++g\*\*, are shown in Tables 1.

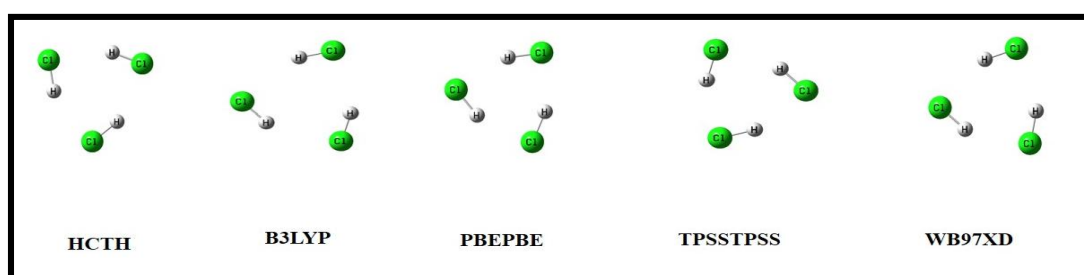


Figure 1. Optimized Structures of HCl trimer at different functional with basis set 6-311++g\*\*.

Table 1: Bond length (H-Cl and Cl-Cl) of optimized structures of (HCl)<sub>3</sub> for different functionals

Bond Length (Å <sup>0</sup> ) / Bond Angles (°)	HCTH	B3LYP	PBEPBE	TPSSTPSS	WB97XD
H-Cl	1.285	1.295	1.312	1.303	1.291
Cl-Cl	4.023	3.7878	3.6158	3.6785	3.7472
H-Cl-H	89.19	87.8	85.01	85.91	88.11

The HCTH functional optimizes (HCl)<sub>3</sub> to its precise bond length (1.285 Å<sup>0</sup>) is in quite good agreement with experimental HCl monomer (1.275 Å<sup>0</sup>) but for PBEPBE, it increases up to 1.312 Å<sup>0</sup>. The Cl-Cl internuclear distance for all the functionals is high compared to experimental value reported by Ohashi and Pine (3.566 Å) at MPW1PW91/aug-cc-pVDZ level. But deviation is seen quite minimum for the Cl-Cl bond from the experimental value approximately by 0.049 Å<sup>0</sup> at PBEPBE level. We also observed that Cl-H-Cl angle shows a tendency towards rectangle at the HCTH level ( $\approx 89.193^\circ$ ). Our findings strongly indicate that cooperative effects arising from hydrogen bonding play a significant role in the behaviour of (HCl)<sub>3</sub>. They also provide some evidence that these effects seem to reach a limit for a relatively small number of HCl clusters. In

addition, our results also show that the magnitude of these effects is more important for HCl clusters.

#### 2. Vibrational Properties

The Detailed studies of hydrogen halide clusters are often conducted in condensed phases, typically within inert gas matrices. Interactions with the matrix atoms may influence the vibrational structure of the hydrogen-bonded complex [40]. Table 2 represents H-Cl stretching frequencies of (HCl)<sub>3</sub> and average frequency shift relative to the experimental value (2889 cm<sup>-1</sup>) of monomer ( $\Delta\nu_1$  in cm<sup>-1</sup>) and average experimental value (2778 cm<sup>-1</sup>) of trimer ( $\Delta\nu_2$  in cm<sup>-1</sup>).

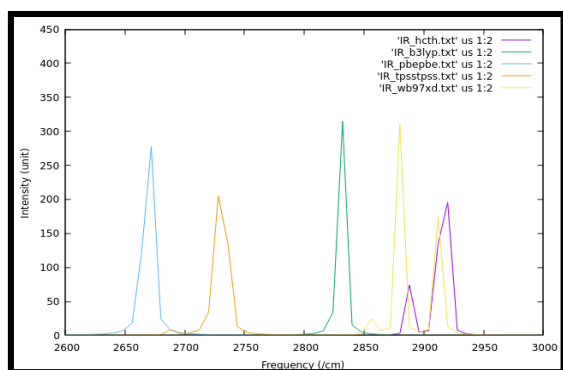


Figure 2: IR-spectrum of HCl trimer for different functional with basis set 6-311++g\*\*

It is observed that the average frequency at TPSSTPSS/6-311++g\*\* level (2715.41 cm<sup>-1</sup>) is in good agreement with the experimental value (2778 cm<sup>-1</sup>). As can be seen in table 2, for PBEPBE level, the high vibrational shifts are observed by 240.01

cm<sup>-1</sup> and 129.01 cm<sup>-1</sup> with respect to average experimental HCl monomer and average HCl trimer respectively. Also PBEPBE/6-311++g\*\* results high intensity (667.69 unit) in frequency range 2669.64 cm<sup>-1</sup> with high polarity prediction as shown in Fig 2. In contrast B3LYP gives almost zero intensity (0.26 unit) at frequency 2805.49 cm<sup>-1</sup> with the lowest frequency shift relative to the experimental trimer value which is the indication of low energy of radiation. As shown in figure 2, at HCTH level, stretching vibrations require more energy and show absorption bands in higher frequency region (2919.61 cm<sup>-1</sup>) which is similar for alkane functional group. Our results of stretching vibrations for various functionals are in agreement with the results for larger HCl clusters which also indicate that hydrogen-bond cooperativity increases for (HCl)<sub>3</sub>.

Table 2: H-Cl stretching frequencies of (HCl)<sub>3</sub> and the average frequency shift relative to the experimental value (2889 cm<sup>-1</sup>) of monomer ( $\Delta v_1$  in cm<sup>-1</sup>) and average experimental value (2778 cm<sup>-1</sup>) of trimer ( $\Delta v_2$  in cm<sup>-1</sup>).

Frequency (cm <sup>-1</sup> )	Experimental frequency <sup>13</sup> (cm <sup>-1</sup> )	HCTH	B3LYP	PBEPBE	TPSSTPSS	WB97XD
$\nu_1$	2787	2888.26	2805.49	2609.23	2686.79	2858.10
$\nu_2$	2787	2911.92	2829.97	2668.10	2725.99	2880.19
$\nu_3$	2760	2919.61	2830.83	2669.64	2733.45	2913.16
$\langle \nu \rangle$	2778	2906.59	2822.09	2648.99	2715.41	2883.81
$\Delta v_1$	-	17.59	66.91	240.01	173.59	5.19
$\Delta v_2$	0	128.59	44.09	129.01	62.59	105.81

### 3. Molecular Orbitals (HOMO-LUMO)

The values of the HOMO-LUMO energy gap reflect the chemical activity of the molecule. The decrease in the HOMO-LUMO energy gap explains the

eventual charge transfer interaction taking place within the studied HCl trimer because of the strong electron-accepting ability of the electron acceptor group [41]. The computed HOMO, LUMO and band gap energies of HCl trimer are listed in Table 3.

Table 3: HOMO, LUMO and Band gap energies for various functionals with basis set 6-311++g\*\* of HCl trimer.

Energy (eV)	HCTH	B3LYP	PBEPBE	TPSSTPSS	WB97XD
E <sub>HOMO</sub>	-8.5177	-9.4965	-8.3329	-8.4330	-11.7207
E <sub>LUMO</sub>	-1.6610	-0.9494	-1.3110	-1.0988	0.8234
$\Delta E$	6.8567	8.5417	7.0219	7.3343	12.5442

For WB97XD, (HCl)<sub>3</sub> with a high orbital gap (HOMO-LUMO energy gap) ( $\Delta E=12.5442$  eV) has low chemical reactivity and high kinetic stability because it is energetically unfavorable to add an electron to the high-lying LUMO (0.8234 eV) in

order to remove electrons from the low-lying HOMO (-11.7207 eV) [42], [43]. Hence at WB97XD level, (HCl)<sub>3</sub> is said to be stable and chemically harder than that of having a small HOMO-LUMO energy gap at HCTH level [44]. But

at HCTH level, smaller gap (6.8567 eV) shows variation about 53.27% with respect to WB97XD which indicates maximum stretching between H and Cl atoms. As can be seen in Table 3, it is assumed that the electron-withdrawing substituents lead to a decrease in the energy levels of the molecular orbitals whereas electron-donating groups have the opposite effect.

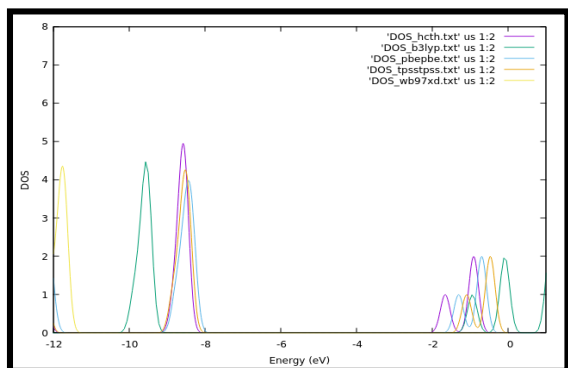


Figure 3: Density of states for HOMO-LUMO energies of HCl trimer

The peaks of DOS are studied between HOMO and LUMO energies for the given functional with common basis set 6-311++g\*\* are shown in figure 3. At energy -8.58 eV, the high peak of DOS (4.9464) is observed at HCTH which shows that many states are available for occupation with approximately closer to high value of HOMO (-8.5177 eV). In contrast, peak of DOS (3.9829) at energy (-8.44 eV) is seen for PBEPBE within the HOMO energy range (-8.3329 eV). It is observed that, for LUMO energies at HCTH, B3LYP,

PBEPBE, TPSSTPSS levels, the DOS is approached almost unity ( $\approx 0.99$ ) which shows that the states are not available for occupation.

#### 4. Global Reactivity Descriptors

During molecular interactions, the LUMO accepts electrons and its energy corresponds to the electron affinity (EA) while the HOMO represents electron donors and its energy is associated with the ionization potential (IP). The global electrophilicity index ( $\omega$ ), introduced by Parr et al.<sup>45</sup> is based on thermodynamic properties and measures the favourable change in energy when a chemical system attains saturation by the addition of electrons. Global reactivity descriptors calculated for (HCl)<sub>3</sub> using basis set 6-311++g\*\* at different levels of DFT calculations are shown in Table 4.

HOMO-LUMO energies also play an important role in determining the chemical reactivity (global electrophilicity) of a system which is defined as follows,

$$\omega = \frac{\mu^2}{2\eta} \quad (1)$$

Where,  $\eta$  denotes the global chemical hardness and  $\mu$  represents the electronic chemical potential which describes the charge transfer within a system in the ground state as follows

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \quad (2)$$

$$\mu = \frac{E_{HOMO} + E_{LUMO}}{2} \quad (3)$$

Table 3: Global reactivity descriptors for various functionals with basis set 6-311++g\*\* of HCl

Global reactivity descriptors (eV)	HCTH	B3LYP	PBEPBE	TPSSTPSS	WB97XD
I	8.5177	9.4965	8.3329	8.4331	11.7208
A	1.6610	0.9494	1.3110	1.0988	-0.8234
$\eta$	3.4284	4.2735	3.5110	3.6671	6.2721
$\mu$	-5.0893	-5.2230	-4.8220	-4.7659	-5.4487
$\omega$	1.8888	1.5958	1.6557	1.5485	1.1833

At B3LYP, structure has greater value of chemical potential ( $\mu = -5.2230$  eV) and more reactive than that with small electronic chemical potential ( $\mu = -4.7659$  eV) at TPSSTPSS level. It is noted that high electron affinity (EA) approaches high electrophilicity ( $\omega = 1.8888$  eV) and low global hardness ( $\eta = 3.4284$  eV) at HCTH level. Because

of the larger HOMO-LUMO energy gap, the global hardness increases and chemical reactivity (global electrophilicity) decreases for WB97XD. The calculated results show that the structure at WB97XD and at HCTH has the highest and lowest stabilities respectively.

## IV. CONCLUSION

Hence our results illustrate the importance of hydrogen-bond (HB) co-operativity in the determination of the structural and vibrational properties of HCl trimer. In addition, from HOMO-LUMO energies, we are also providing evidence by using DFT calculation, that for WB97XD, (HCl)<sub>3</sub> has low chemical reactivity and high kinetic stability. Along with it, for HCTH/6-311++g\*\* level, it is seen that within (HCl)<sub>3</sub> there is a strong electron-acceptance from Cl. The satisfactory variation is observed in density of states (DOS) for occupied and unoccupied orbitals for different functionals. The Global reactivity descriptors analysis showed that for HCTH, there is the lowest Global hardness ( $\eta=3.4284$  eV) which indicates the low resistance of a structure towards deformation. In summary, PBEPBE/6-311++g\*\* results high intensity (667.69 unit) in frequency range 2669.64 cm<sup>-1</sup> with high polarity prediction. In contrast B3LYP gives almost zero intensity (0.26 unit) at frequency 2805.49 cm<sup>-1</sup> with the lowest frequency shift relative to the experimental trimer value which is the indication of low energy of radiation. The theoretical results show the cooperative effects of H-bonds is more important for HCl clusters. This report revealed the structure at WB97XD and at HCTH has the highest and lowest stabilities respectively. This work is complemented and discussed within the scope of quantum chemical calculations with DFT.

## V. ACKNOWLEDGEMENT

Authors would like to thank HOD, Department of Physics, Principal and Management of M. M. College of Arts, N. M. Institute of Science, H. R. J. College of Commerce, Bhavan's College (Autonomous), Andheri (W), India for providing the research facilities and their constant encouragement and support.

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