Vibrational frequency analysis of CH_3Cl molecule; ab initio study

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Abstract: *First-principles calculations implemented by Gaussian 09 sets of programs has been performed in order to study the stability, electronic properties, nature of bonding and vibrational frequency assignments for* CH_3Cl *molecule using QCISD levels of approximation with the choice of basis set 6-31G(d, p). Quantum Theory of Atoms In Molecule (QTAIM) approach has been adopted for bonding analysis and HOMO, LUMO energies were taken as the central aspects for discussing the chemical reactivity of the studied system. The vibrational frequency shift due to isotopic substitution of C-atom and Cl-atom in title molecule has been discussed.*

Keywords: First-principles calculations, Basis sets, electron density, HOMO-LUMO energy gap, Vibrational frequencies etc.

1. Introduction:

Chlorinated compounds, which are the constituents of hazardous wastes, have long been recognized as hampering hydrocarbon combustion [1,2]. Several investigations have reported the results of experimental measurements made in flows burning chlorinated hydrocarbons or mixtures of conventional hydrocarbons and chlorine containing compounds [3-6]. Earlier work from our laboratories investigated the effect of the addition of chloromethanes to the feed-stream for the partial oxidation of methane with metal oxygen cluster compounds (heteropoly oxometalates) as catalysts [7-9]. The investigation involves the burning of methane/ methyl chloride mixtures in air, the study being motivated by the need of understand the influence of varying amounts of hydrocarbon-bonded chlorine on hydrocarbon burning. Experimental measurements are conducted in premixed counter flowing flames burning chlorine containing fuel mixtures. The burning velocities are determined following established methodology [10-12]. The present work reports the study for the stability, isotopic variation of vibrational frequency of CH_3Cl and corresponding force constant including bonding analysis followed by the quantum theory of atoms in molecules (QTAIM) approach.

This paper have been organised as follows, in chapter 2 we discuss briefly computation methodology, in chapter 3 results have been discussed and chapter 4 contains its conclusions and outlook.

2. Methodology

We have performed first-principles calculation implemented by Gaussian 09 [13] set of programs in QCISD levels of approximation with the choice of basis set 6-31G(d,p). First we optimized the studied structure without any symmetry restriction. Thus obtained optimized geometry was used to run the frequency calculation. The global minima of the structure was confirms by obtaining all positive frequencies. Taking the stable structure, bonding analysis has been performed using QTAIM approach.

3. Results and Discussion

3.1 Stability and electronic properties

We have performed the frequency optimization calculations for CH_3Cl molecule at QCISD levels of approximation with the basis set 6-31G(d,p) implemented by Gaussian 09 set of programs. For calculating the binding energy of CH_3Cl we have taken the reference energy of C, H and Cl atoms to be (-37.68940), (-0.49823) and (-459.56901) amu respectively at the same levels of calculation. The calculated value of binding energy for CH_3Cl is 17.801 eV, showing that the studied system is stable in nature. We have also observed different values of bond lengths; C-H bond and C- Cl bond with values 1.09Å and 1.78Å respectively. These estimated values of bond lengths are exactly equal to the corresponding experimental values [14]. Two types of bond angle is observed in this system, i.e. bond angle H-C-H and H-C-Cl having values 110.09°and 108.84°respectively. The estimated value of dipole moment of CH_3Cl is about 2 Debye, this value of dipole moment shows the studied molecule is highly polar in nature.

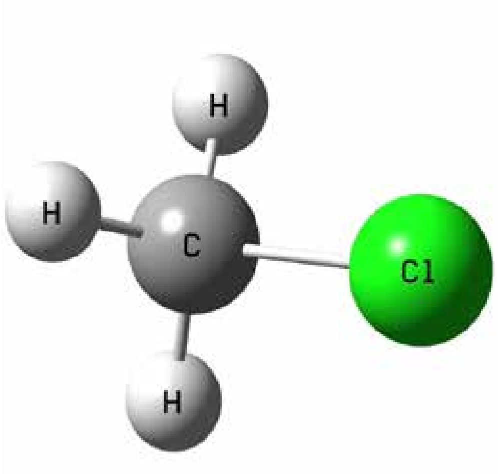

Fig.1 : The optimized structure of CH_3Cl molecule at the QCISD levels of approximation with basis set 6-31G(d,p).

Molecular orbitals (HOMO and LUMO) and their properties are very useful for physicist and chemist and are very important parameters for quantum chemistry. This is also used by the frontier electron density for predicting the most reactive position in π- electron systems and explains several types reaction in conjugated systems[15] The central aspect of electronic properties of the system is its H-L gap [16,17]. The greater the H-L gap indicates larger stability with lesser chemical reactivity and vice versa. Thus, the study of the H-L gap is very important for solid state community, and with this regard we have calculated the HOMO, LUMO energies and its related parameters for CH_3Cl molecule. The energy difference between HOMO and LUMO called as H-L gap for CH3Cl is 17.100 eV. Using the HOMO LUMO energies, we obtained the related parameters such as ionization energy ($I_E = -E_{HOMO}$) 11.820 eV, electron affinity ($E_A = -E_{LUMO}$) -5.280 eV, hardness ($H = E_g/2$) 8.550 eV, softness ($\eta = 1/H$) 0.116 eV^{-1}, chemical potential ($\mu = E_H+E_L/2$) -3.269 eV and global electrofillicity index ($\omega = \mu^2/2H$) 0.625 eV respectively.

3.2 Bonding analysis

Electron density ρ(r), its gradient vector, its Laplacian $\nabla^2\rho(r)$ and characteristics of the critical points [the points where ρ(r) = 0] provide a quantitative description of bonding in molecules and crystals in terms of quantum mechanical topological theory [18]. The pairs of gradient lines in the $\rho(r)$ originated at the saddle critical point between atoms and terminated at two neighbouring nuclei, along which the electron density (ED) is maximal with respect to any other line, are the most important for characterization of the atomic interactions. They form the atomic interaction lines named the bond paths in an equilibrium system. Corresponding bond critical points are denoted as (3, -1): they are characterized by three non-zero eigenvalues of the curvature or Hessian matrix, λ_i, and the sum of the algebraic signs of λ_i is -1. Values $\lambda_1 < 0$ and $\lambda_2 < 0$ measure the degree of the ED contraction towards the bond critical point, while $\lambda_3 > 0$ measures the degree of the ED contraction towards each of the bonded nuclei. The sign of the Laplacian at the bond critical point $\nabla^2\rho(r) = \lambda_1 + \lambda_2 + \lambda_3$ depends on the relationship between the λ_i values at this point. If the electrons are locally concentrated around the bond critical point [$\nabla^2\rho(r) < 0$], the electrons are shared by both nuclei: this is typical for shared or covalent atomic interactions.

Otherwise the electrons are concentrated in each of the atomic basins [$\nabla^2\rho(r) > 0$] and the atomic interaction belongs to the closed shell type. The latter is typical for ionic, hydrogen and van der Waals bonds [19]. Thus, $\nabla^2\rho(\mathrm{r})$ reflects the character of the atomic interactions [20]. If two or more bonds are of the same nature then greater the electron density at corresponding BCP represents greater strength. In case of our system, same approach for analysing the bond (C-H and C-Cl) in CH_3Cl molecule. The value of ρ and $\nabla^2\rho$ at BCP for both types of bonds has been tabulated as follows,

Table 3 : The density of electron (ρ) and its Laplacian $\nabla^2\rho$) at specified BCP of CH_3Cl obtained by QCISD/6-31G(d,p) calculations.

C-H		C-Cl	
ρ	$\nabla^2\rho$	ρ	$\nabla^2\rho$
0.292	-1.086	0.183	-0.251

From the Table 3 the negative sign of $\nabla^2\rho$ at both BCP indicates the open shell type (covalent) of bond in CH_3Cl molecule. Furthermore, the larger value of ρ at BCP C-H than that of C-Cl shows the greater strength of C-H bond than C-Cl bond in the studied molecule.

3.3 Vibrational frequency analysis

For the molecules, if energy is increased then the oscillation will become more vigorous. An elastic bond, like a spring has a certain vibrational frequency, dependent on the mass of the system and the force constant, but is independent of the amount of distortion. The energy of the harmonic oscillator can be expressed as

$$E_n = (n + ½)\,\hbar\omega \tag{1}$$

Where, E_n is the energy of the nth quantum state, n is the vibrational quantum number and is equal to zero or an integer, ω is the vibrational frequency of oscillator. For lowest possible quantum state, n = 0. So, equation (1) becomes

$$E_o = ½\ \hbar\omega \tag{2}$$

This implication is that any molecule can never have zero vibrational energy i.e. the atoms can never have zero be completely at rest relative to each other. The zero-point energy, E_O depends on the vibrational frequency and strength of the chemical bond and atomic masses. One can estimate the zero-point energy using Gaussian 09 set of programs for studied system. We have estimated frequency of vibration of the CH_3Cl molecule using the relation

$$\omega = \sqrt{\frac{k}{\mu}} \tag{3}$$

where, μ is the reduced mass of the system and k is the force constant. When we changed the reduced mass by changing the atomic mass of individual atoms in the molecule,then the frequency is also changed resulting the diffrernt value of force constant. The isotopic variation of frequency of the studied system is presented in Table 2 and Table 3, where the value inside the bracket is the percentage of the frequency shift from the stable geometry.

Table 2: Isotopic variation of vibrational frequency and corresponding force constant for CH_3Cl using isotopes of Chlorine obtained by QCISD/ 6-31G(d,p) calculations.

Cl= 35		Cl = 37	
Frequency (cm^{-1})	Force Constant (mDyne/ Å)	Frequency (cm^{-1})	Force Constant (mDyne/ Å)
767 (s)	2.3961	761 (0.78%)	2.3185 (3.23 %)
1074 (d)	0.7968	1073 (0.09%)	0.7955 (0.16%)
1456 (s)	1.4216	1456 (0.00%)	1.4216 (0.00%)
1539 (d)	1.4725	1539 (0.00%)	1.4725 (0.00%)
3148 (s)	6.0036	3147 (0.03%)	6.0036 (0.00%)
3255 (d)	6.9192	3255 (0.00%)	6.9192 (0.00%)

Table 3: Isotopic variation of vibrational frequency and corresponding force constant for CH_3Cl using isotopes of Carbon obtained by QCISD/ 6-31G(d,p) calculations.

C= 12		C = 13		C = 14	
Frequency (cm^{-1})	Force Constant (mDyne/ Å)	Frequency (cm^{-1})	Force Constant (mDyne/ Å)	Frequency (cm^{-1})	Force Constant (mDyne/ Å)
767 (s)	2.3961	749 (2.34%)	2.5577 (6.74%)	732 (4.56%)	2.7178 (13.42%)
1074 (d)	0.7968	1068 (0.55%)	0.7848 (1.50%)	1063 (1.02%)	0.7739 (2.87%)
1456 (s)	1.4216	1450 (0.41%)	1.3931 (2.00%)	1444 (0.82%)	1.3700 (3.62%)
1539 (d)	1.4725	1536 (0.19%)	1.4625 (0.67%)	1534 (0.32%)	1.4538 (1.27%)
3148 (s)	6.0036	3145 (0.09%)	5.9840 (0.32%)	3143 (0.15%)	5.9673 (0.60%)
3255 (d)	6.9192	3242 (0.39%)	6.8203 (1.42%)	3232 (0.71%)	6.7363 (2.64%)

Where, s stands for singlet and d stands for doublet. We observed nine (3N-6) modes of vibration for CH3Cl among them three are doublet and three are singlet. From the table isotopic contribution of chlorine is significant only on the lower band. The corresponding deviation of the frequency as well as force constant is near about two times on increasing the isotopic mass of C =13 to C = 14.

4.Conclusion and Outloooks

In the present work, we have studied the stability of the CH_3Cl molecule using first principle calculations. Our calculation shows that the studied molecule is highly stable with binding energy 17.801 eV.. The studied HOMO-LUMO energy gap 17.100 eV also helps to analyse the properties of the CH_3Cl molecule. We also study the bonding analysis of the studied molecule and determined open shell type bonding with C-H bond (1.09 Å) more strength than that of C-Cl bond (1.78Å). Further we study the isotropic contribution of Chlorine and Carbon on the studied system and found nine modes of vibrations. Out of which three are observed doublet and three are singlet but all the frequencies obtained are real value. The shift of the frequencies have observed maximum in the isotopic contribution of carbon than that of the Chlorine i.e. the isotopic contribution of chlorine is not significant without lower band but isotopic contribution of carbon is about twice times deviation of frequency as well as force constant on increase the isotopic mass of chlorine.

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