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RESEARCH ARTICLE

Simulating Infrared spectrum of C_{60} Cl_6 through ab initio method

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Abstract

The Infrared spectrum of $C_{60}Cl_6$ has been calculated through ab initio method. It has been observed that the simulated spectrum of $C_{60}Cl_6$ is matching with the available experimental data in literature. It is interested to note that by simple analysis of the normal coordinates of $C_{60}Cl_6$, the four principal regions of its vibrational spectrum 100–130 cm^{-1}, 140–400 cm^{-1}, 400-900 cm^{-1} and 900–1600 cm^{-1} are assigned. In the first 100–130 cm^{-1} range, the chlorine-atom motion predominantly in the infrared spectrum of $C_{60}Cl_6$. In the second range 140–400 cm^{-1}carbon with chlorine atoms equally participate in the vibrations of $C_{60}Cl_6$.The intensities of this range are unusual vibrations are low, and also are observed in the experimental spectra as weak features. In the third range 400-900 cm^{-1} the vibrations of $C_{60}Cl_6$ are restricted on the carbon skeleton of the molecule with insignificant chlorine-atom motion. In the fourth range 900–1600 cm^{-1} the vibrations of the $C_{60}Cl_6$ carbon skeleton have considerable tangential character stretching vibrations in the infrared spectrum.

INTRODUCTION

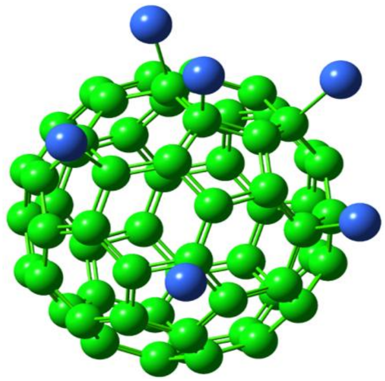
Halogenated fullerenes are of considerable interest because they are prospective originators for the sample preparation of fullerenes derivatives. Chloro-fullerenes were poorly investigated in comparison with other halogenated fullerenes. Single crystal X-ray crystallography has been synthesized and structurally characterized C_{60} chlorinated derivatives such as $C_{60}Cl_{24}$ (T_h), $C_{60}Cl_{28}$ (C_1), $C_{60}Cl_{30}$ (C_2) and $C_{60}Cl_{30}$ (D_{3d}) [1-3].The production of $C_{60}Cl_6$ was reported and this chloride was utilized for the preparation of organic derivatives of C_{60}. [4–8] In the past decade, considerable progress has been made in the understanding of fullerene derivatives.

IR vibrational is a unique sensitivity spectroscopy to molecular structure, so it has an application can assist substantially in structure elucidation, particularly when other commonly used direct methods of structural analysis have failed to provide unambiguous answers. We report that comprehensive IR spectroscopic studies of $C_{60}Cl_6$ with the heip ab initio method.

Computational Details

The simplest structure of $C_{60}Cl_6$ molecule model has sixty carbon nuclei reside on a sphere and six chloride atoms attached with six carbon atoms of as shown in figure -1. The $C_{60}Cl_6$ structure has C_1 symmetry and the bond length of each carbon-carbon is 1.35 Å and the bond length of carbon-chloride atom is 2.08 Å. The two different C-C bond lengths in C indicate that the л electrons are evenly delocalized over all bonds. The green colour and blue colour represent the carbon and chloride atoms respectively.

Figure 1 shows $C_{60}Cl_6$ structure configurations



Calculation

The frequencies are obtained in a frequency analysis based on the time independent Schrodinger equation for the stochastic explanation of the nuclei within the Born-Oppenheimer approximation. This harmonic approximation that replaces the potential $\overline{E}_{el}(R)$ by $\overline{E}_{el}(R) \approx R^{(c)\dagger} F^{(c)} R^{(c)}$, where $R_j^{(c)}$ are Cartesian nuclear coordinates and $F^{(c)}$ is the Cartesian Hessian matrix. Then the nuclear Schrodinger equation in the basis of mass-weighted normal coordinates $R^{(c)}$ within this approximation is given by

$$\left(-\frac{\hbar}{2}\nabla^{(q)\dagger}\nabla^{(q)} + R^{(q)\dagger}F^{(q)}R^{(q)}\right)\left|\upsilon^{tot}\right\rangle = E_{tot}\left|\upsilon^{tot}\right\rangle \qquad (1)$$

where $F^{(q)}$ is the diagonalized Hessian with elements

$$F_{ij}^{(q)} = \left(\frac{\partial^2 \overline{E}_{el}(R^{(q)})}{\partial R_i^{(q)} \partial R_j^{(q)}}\right) \qquad (2)$$

As $F^{(c)}$ is diagonal in eqn. (1) that represents system of 3N decoupled differential equations, one for each normal mode, that is, for a collective motion along an individual normal coordinate.

The infrared spectra intensities of $C_{60}Cl_6$ are calculated through the time dependent perturbation with all SI units quantities dimensions are given in Hartree atomic units. Firstly a specific transition is required to determine the transition rate. So under the first order time dependent perturbation theory and assuming a continuous range of frequencies that can make a transition between the initial state $\left|\upsilon_i\right\rangle$ and the final state $\left|\upsilon_f\right\rangle$.The rate of the transition [10, 11] $\left|\upsilon_f\right\rangle \leftarrow \left|\upsilon_i\right\rangle$ is given by

$$W_{f\leftarrow i} = \frac{1}{\hbar^2}\left\langle H_{fi}^{(1)}\right\rangle^2 \rho_N\left(\upsilon_{fi}\right)\left(\frac{1}{s}\right) \qquad (3)$$

$$\left\langle H_{fi}^{(1)}\right\rangle = \left\langle \upsilon_f^{tot}\middle| H^{(1)} \middle|\upsilon_i^{tot}\right\rangle (J) \qquad (4)$$

where $\rho_N\left(\upsilon_{fi}\right)$ is the density of photon states per frequency range following the Fermi Golden Rule. Neglecting the contributions from magnetic dipole moments and higher order terms in the dipole approximation [12] the perturbation is given by

$$\left\langle H_{fi}^{(1)}\right\rangle = -\left\langle \upsilon_f^{tot}\middle| \overline{\mu}\left(R^{(q)}\right).\varepsilon \middle|\upsilon_i^{tot}\right\rangle$$

$$\approx -\left\langle \upsilon_f^{tot}\middle| \overline{\mu}\left(R^{(q)}\right).\varepsilon \middle|\upsilon_i^{tot}\right\rangle.\varepsilon_0$$

$$= -\langle \mu_{fi} \rangle . \varepsilon_0 (J) \tag{4}$$

Considering that average amplitude ε_0 of the field vector with ε is to be constant all over the molecule. The transition dipole matrix element, $\langle \mu_{fi} \rangle = \langle \upsilon_f^{tot} | \overline{\mu} (R^{(q)}) . \varepsilon | \upsilon_i^{tot} \rangle$, that requires integration over normal coordinates $R^{(q)}$ of the molecule. The total nuclear wave function which include the translation and rotational contribution is given by

$$| \upsilon^{tot} \rangle = | \upsilon \rangle \chi^{rot} . \chi^{trans} \tag{5}$$

Where $| \upsilon \rangle$ is a product of the (3N-6) [or (3N-5) for linear molecules, respectively] vibration of single mode wave functions. Neglecting rotational and translational contributions, the expression in equation (4) gives $\langle H_{fi}^{(1)} \rangle^2 = \langle \mu_{fi} \rangle^2 . \varepsilon_0^2$ such that the electronic dipole moment and have the same direction. As the molecules are randomly oriented in fluids, so to model the spectrum quantum mechanically, an addition over all allowed rotational states would be necessary be included. Thus the classical mean value $\langle \mu_{fi}^{av} \rangle^2 = \langle \mu_{fi} \rangle^2 / 3$ may be applied here.

The classical electromagnetic field energy with frequency υ in volume V is given by $E_\upsilon^{EMF} = 2\varepsilon_0 \varepsilon_0^2 V$, but we may introduce the energy density per frequency range

$$\rho(\upsilon) = \frac{E_\upsilon^{EMF}}{V} \rho_N(\upsilon) \left(\frac{Js}{m^3} \right) \tag{6}$$

And the net transition rate for the transition $| \upsilon_f \rangle \leftarrow | \upsilon_i \rangle$ per unit volume is then given by

$$W_{f \leftarrow i}^{net} = B_{fi} \rho(\upsilon_{fi}) (N_i - N_f) \left(\frac{1}{sm^3} \right)$$ with

$$B_{fi} = \frac{1}{6\varepsilon_0 \hbar^2} \langle \mu_{fi} \rangle^2 \left(\frac{m^3}{Js^2} \right) \tag{7}$$

As the Einstein coefficient for stimulated emission, B_{if}, is equal to $B_{fi}.N_f$, respectively, that denoted the number of molecules per unit volume in the final state. In the case of infrared spectroscopy, the intensity per frequency interval, $I(\upsilon)$ emitted by a radiation source at frequency υ is defined as the energy ΔE that passes through an area A within the time interval t i.e. $I(\upsilon) d\upsilon = \Delta E / (A \Delta t)$. The total of the light source in the finite range of frequencies is given by

$$I_\upsilon := \int_{range} I(\upsilon) d\upsilon = I(\upsilon) \Delta\upsilon \left(\frac{J}{sm^2} \right) \tag{8}$$

Here the intensity per frequency range is assumed to be almost constant, in the range $\Delta\upsilon$ of the line width of the radiation source. If an element of absorbing material of length is dl with cross section $A = V/dl$, so every transition $| \upsilon_f \rangle \leftarrow | \upsilon_i \rangle$ in this element will decrease the energy of the radiation field by an amount of $\Delta E = h\upsilon_{fi}$, such that the number of transition $W_{f \leftarrow i}^{net} V$ in the element of volume V per time interval Δt decreases that decrease in the intensity which is [9] given by

$$-dI_{\upsilon fi} = h\upsilon_{fi} W_{f\leftarrow i}^{net} dl = h\nu_{fi} B_{fi} \rho\left(\nu_{fi}\right)\left(N_i - N_f\right) dl \left(\frac{J}{sm^2}\right) \tag{9}$$

According the eq. (9) in [12] $\rho(\nu) = I(\upsilon)/c = I_{\upsilon}/(c\Delta\upsilon)$ that leads to a homogeneous differential equation with the solution

$$I_{\upsilon fi} = I_{0,fi} \exp[-\kappa\left(\nu_{fi}\right) Cl] \left(\frac{J}{sm^2}\right) \tag{10}$$

Where l is the total length of the sample chamber and the absorption coefficient $\kappa\left(\nu_{fi}\right)$ is given as

$$\kappa\left(\nu_{fi}\right) = \frac{1}{C} \frac{h\nu_{fi}}{c\Delta\upsilon} B_{fi} \left(N_i - N_f\right) \left(\frac{m^2}{mol}\right) \tag{11}$$

Where C is the molar concentration of the absorption material. As the absorption lines always have a finite width, for the integral absorption coefficient A_{υ} such that B_{fi} is constant in the frequency range gives

$$A_{\upsilon} = \int_{line} \kappa(\nu) d\nu = \kappa(\nu) \Delta\nu$$

$$A_{\upsilon} = \frac{1}{C} \frac{h\nu_{fi}}{c} \frac{\left\langle \mu_{fi} \right\rangle^2}{6\varepsilon_0 \hbar^2} \times \left(N_i - N_f\right) \left(\frac{m^2}{smol}\right) \tag{12}$$

The occupation number for the harmonic oscillator from the Boltzmann distribution at the lowest level [9] in thermal equilibrium is given by the above eqn. The expectation value of the electronic dipole moment $\overline{\mu}(R^{(q)})$ in the above equation which enters $\left\langle \mu_{fi} \right\rangle^2$ that depends on $R^{(q)}$ is calculated through a Taylor series expansion. As the higher order terms in the series expansion for the dipole moment directs to the occurrence of over tunes and combination bands in eq. (1).

All fundamental transitions $\left|\upsilon_{p,f}\right\rangle \leftarrow \left|\upsilon_{p,i}\right\rangle$ for a given normal mode p occur at the same frequency $\nu_{fi} = \nu_p$, it is important to add all over absorption coefficients for these transitions. After this addition of transition, the integral absorption coefficient is independent of temperature. Using the eqn. (12), (20), and (21) gives the final result which is calculated with quantum chemical methods.

$$A_{\upsilon} = \frac{1}{4\pi\varepsilon_0} \frac{N_A \pi}{3c} \left(\frac{\partial\overline{\mu}}{\partial R_k^{(q)}}\right)_0^2 \left(\frac{m^2}{smol}\right) \tag{13}$$

The Taylor series expansion of electronic matrix elements used is

$$\overline{\mu} = \overline{\mu}^{(0)} + \sum_k \left(\frac{\partial\overline{\mu}}{\partial R_k^{(q)}}\right)_0 R_k^{(q)} + O\left(R_k^{(q)2}\right) \tag{14}$$

After the evaluation of the total matrix elements, including nuclear wave functions [neglecting quadratic and higher order terms from eqs. (15) and (16)] we get

$$\left\langle \mu_{fi} \right\rangle = \overline{\mu}^{(0)} \left\langle \upsilon_f \middle| \upsilon_i \right\rangle + \sum_k \left(\frac{\partial\overline{\mu}}{\partial R_k^{(q)}}\right)_0 R_k^{(q)} \left\langle \upsilon_f \middle| R_k^{(q)} \middle| \upsilon_i \right\rangle \tag{15}$$

Evaluation of matrix elements $\left\langle \upsilon_f \middle| \upsilon_i \right\rangle$ and $\left\langle \upsilon_f \middle| R_k^{(q)} \middle| \upsilon_i \right\rangle$

$$\left\langle \upsilon_f \middle| \upsilon_i \right\rangle = \prod_{p=1}^{3N-6} \left\langle \upsilon_{p,f} \middle| \upsilon_{p,i} \right\rangle \tag{16}$$

$$\left\langle \upsilon_f \middle| \upsilon_i \right\rangle = \prod_{p=1}^{3N-6} \delta_{\upsilon_{p,f},\upsilon_{p,i}} \tag{17}$$

$$\left\langle \upsilon_f \middle| R_k^{(q)} \middle| \upsilon_i \right\rangle = \left\langle \upsilon_{k,f} \middle| R_k^{(q)} \middle| \upsilon_{k,i} \right\rangle . \prod_{p=1}^{3N-6} \left\langle \upsilon_{p,f} \middle| \upsilon_{p,i} \right\rangle \tag{18}$$

$$\left\langle \upsilon_{k,f} \middle| R_k^{(q)} \middle| \upsilon_{k,i} \right\rangle = \begin{cases} \left(\upsilon_{k,i}+1\right)^{1/2} b_v ; \upsilon_{k,f} = \upsilon_{k,i}+1 \\ \left(\upsilon_{k,i}\right)^{1/2} b_{vk} ; \upsilon_{k,f} = \upsilon_{k,i}-1 \\ 0; otherwise \end{cases} \tag{19}$$

$$b_{vk}^2 = \frac{\hbar}{2\omega_k} = \frac{\hbar}{4\pi\upsilon_k} = \frac{\hbar}{8\pi^2 c\tilde{\upsilon}_k} \tag{20}$$

Summary of the above equations for fundamental transitions $\left|\upsilon_{k,i}+1\right\rangle \leftarrow \left|\upsilon_{k,i}\right\rangle$

$$\left\langle \mu_{fi} \right\rangle = b_{vk} \left(\upsilon_{k,i}+1\right)^{1/2} \left(\frac{\partial \bar{\mu}}{\partial R_k^{(q)}} \right)_0 \tag{21}$$

It is noticed that $\left|\upsilon^{tot}\right\rangle$ is a product of the individual harmonic oscillator wave functions for all normal modes of the molecule in harmonic approximation. The model is arrange in such a way that the incident beam is directed alongside the z-axis of the space fixed Cartesian coordinate system with plane polarized in y direction. The observation of the scattered radiation are detected in plane polarized along the y and z axes without any other analyzer in x-axis (θ=π/2). The amplitude of the induced dipole moment (according 16 eqn.) is given by

$$\left\langle \mu_0^{ind} \right\rangle^2 = \left\langle \mu_{0,y}^{ind} \right\rangle^2 + \left\langle \mu_{0,z}^{ind} \right\rangle^2$$

$$\left\langle \mu_0^{ind} \right\rangle^2 = \left(\left\langle \alpha_{yy,fi} \right\rangle + \left\langle \alpha_{zy,fi} \right\rangle \right) \varepsilon_0^2 \quad (\mathrm{C}^2\mathrm{m}^2) \tag{22}$$

As $\varepsilon_{0,x} = \varepsilon_{0,z} = 0$ however $\varepsilon_{0,y} = \left|\varepsilon_0\right|$. So using this, the expression (15) becomes

$$I\left(\pi/2\right) = \frac{\pi^2 c \left(\bar{\upsilon}_{in} - \bar{\upsilon}_p\right)^4}{2\varepsilon_0} \varepsilon_0^2 \left(\left\langle \alpha_{yy,fi} \right\rangle^2 + \left\langle \alpha_{zy,fi} \right\rangle^2 \right) \tag{23}$$

In classical, all cosine terms averages over in the vibration state converted into the quantum mechanical integration for the scattering volume containing N_i molecules and summation over all allowed rotational levels, gives [13]

$$I\left(\pi/2\right) = \frac{\pi^2 c \left(\bar{\upsilon}_{in} - \bar{\upsilon}_p\right)^4}{2\varepsilon_0} N_i \varepsilon_0^2 \frac{45a^2 + 7\gamma^2}{45} \tag{24}$$

The mean anisotropy γ is introduced by

$$\gamma^2 = \frac{1}{2}\Big[\left(\langle\alpha_{xx,fi}\rangle - \langle\alpha_{yy,fi}\rangle\right)^2 + \left(\langle\alpha_{yy,fi}\rangle - \langle\alpha_{zz,fi}\rangle\right)^2 + \left(\langle\alpha_{zz,fi}\rangle - \langle\alpha_{xx,fi}\rangle\right)^2 + 6\left(\langle\alpha_{xy,fi}\rangle^2 + \langle\alpha_{yz,fi}\rangle^2 + \langle\alpha_{xz,fi}\rangle^2\right) \tag{25}$$

and the mean (isotropic) polarizability a by respectively

$$a = \frac{1}{3}\left(\langle\alpha_{xx,fi}\rangle + \langle\alpha_{yy,fi}\rangle + \langle\alpha_{zz,fi}\rangle\right) \tag{26}$$

The classical polarizability tensor components have been converted into the quantum mechanical matrix elements so the irradiance has to be introduced by

$$\phi = \frac{1}{2}\varepsilon_0 c \varepsilon_0^2 \tag{27}$$

Central differential formula is used to calculate gradients, dipole moments, and polarizability of all three isomeric structures. The data are calculated for 6N different isomeric structures of the $C_{60}Cl_6$ molecule through Bickley formula [14] of 3-point central differences due to every atomic Cartesian coordinate has to be distorted in positive and negative direction. The molecular group symmetry is used to reduce the computational work. Only those distorted structures must be calculated where the displacements for a minimal set of symmetry non redundant are required while the other data are obtained from the symmetric operators calculations.

The isomeric structures molecule exhibit nontrivial point group symmetry, so the symmetry operations of this point group map the position of one nucleus A_1 onto the position of other nucleus A_2. The symmetric operators S are represented by $D_S^{(c)}$ matrices in a basis of Cartesian distortion coordinates. By doing calculation for all Cartesian displacements of atom A_1, the dipole moments, polarizability and gradients for the displacement of the coordinates of atom A_2 are also getting as given by.

$$\mu^{(c)}(2) = D_S^{(c)}\mu^{(c)}(1)$$
$$\nabla E(2) = D_S^{(c)}\nabla E(1) \tag{28}$$

The derivatives are obtained from these transformations

$$\nabla^{(c)}(2)\,\mu^{(c)}(2) = D_S^{(c)}\nabla^{(c)}(1)\,\mu^{(c)}(2) \tag{29}$$

and the corresponding part of the Hessian is

$$F^{(c)}(2) = D_S^{(c)}F^{(c)}(2)\,D_S^{(c)\dagger} \tag{30}$$

The Hessian contains all contributions for rotations and translation. In principle, these modes should have a zero vibration frequency, due to fact that electronic potential energy in which the nuclei move is not affected by these motions. But these motions show absolute values of the frequencies which are slightly greater than zero in absolute value because of the errors in the numerical differentiation procedure. So the percentage of translational and vibration contributions to a normal mode are determined first by comparing the resulting momentum and angular momentum of the normalized mode with the corresponding values for a normalized translational and rotational mode. For a pure vibration normal mode, the momentum and angular momentum ought to be zero occur. The modes with the three largest translational and rotational percentages might be removed.

After the mass weighted Hessian $F^{(m)}$ matrix, the energy eigen value is obtain by diagonalizing the Cartesian Hessian matrix $F^{(q)}$ as given by

$$F^{(q)} = U^{(m)}F^{(m)}U^{(m)}$$
$$F^{(q)} = U^{(m)\dagger}M^{-1/2}F^{(c)}M^{-1/2}U^{(m)} \tag{31}$$

Where M^{-1} is a diagonal matrix which contains $M_{ij}^{-1} = \delta_{ij}/m_i$ and the nuclear mass m_i is the mass of the atom corresponding to the Cartesian coordinate $R_i^{(c)}$. The standard projection operators used to obtain a block diagonalized Hessian is given by

$$P_{\mu}^{(c)} = \frac{n_{\mu}}{h}\sum_{S=1}^{h}\chi_{S,\mu}^{*}D_{S}^{(c)} \qquad (32)$$

Where $\chi_{S,\mu}$ is the character of S in the irreducible representation (irrespective) Γ_{μ} of dimension n_{υ} (h is the order of the group). The matrix of eigenvectors are obtained by diagonalizing the projection operator

$$S_{\mu}^{(c)\dagger}P_{\mu}^{(c)}S_{\mu}^{(c)} = P_{\mu}^{(s)} \qquad (33)$$

which may be used in turn to get the Hessian for irrespectively Γ_{μ} in the symmetry adapted basis $S_{\mu}^{(c)\dagger}F^{(m)}S_{\mu}^{(c)} = F_{\mu}^{(s)}$. It is assumed that mass weighting of the Cartesians coordinates neither affects $P_{\mu}^{(c)}$ nor $S_{\mu}^{(c)}$ so that $S_{\mu}^{(c)} = S_{\mu}^{(m)}$. Thus each block $F_{\mu}^{(s)}$ can be diagonalized separately. It should be noted that the use of projection operators allows clarifying the vibrations according to the irrespectively of the point group.

Result & Discussions

$C_{60}Cl_6$ molecule has C_1 symmetry and it takes 396 steps to converge the simulated infrared of $C_{60}Cl_6$ molecule. The most significant change in the infrared spectrum induced by addition of chloride is in fullerene, and the redistribution with new the infrared intensity among the normal modes of fullerene is as given in the table. Fullerene derivative ($C_{60}Cl_6$) molecule has 192 degrees of freedom which is slightly greater than C_{60} normal degrees of freedom because of addition of six chlorides in the fullerene to form fullerene derivative. The rotational constants in x, y, and z axis in the fullerenes derivative ($C_{60}Cl_6$) is 0.06, 0.05 and 0.05 (GHz) respectively. The $C_{60}Cl_6$ has 354 symmetry adapted basis functions, 1062 primitive gaussians, 354 cartesian basis functions, 321 alpha electrons and 321 beta electrons with the nuclear repulsion energy 12972.07 Hartrees. The fullerenes derivative ($C_{60}Cl_6$) has done SCF E (RHF) = -4970.33 A.U. after 21 cycles with convergence density matrix= 0.4894D-08.

The main results from the calculation of the infrared spectrum of the $C_{60}Cl_6$ is as follows

1) Each chloride atom of $C_{60}Cl_6$ perturbed in a small fullerene cage. So the frequencies of the cage exhibit a small frequency shift that are also found for fullerene-rare gas endo-adducts, which always exhibit a blue shift. 2) The reduced symmetry of the fullerene derivative split the degenerate vibrations of $C_{60}Cl_6$ quite large. This splitting increases vibration which produced by the intermolecular interactions in the crystal. Hence the infrared intensity among the various splitting components is non- uniformly distributed; moreover in some cases the intensity is concentrated in a single component.

3) Analysis of the normal coordinates of $C_{60}Cl_6$ facilitated to assign four principal regions of its vibrational spectrum. 100–130 cm^{-1}, 140–400 cm^{-1}, 400-900 cm^{-1} and 900–1600 cm^{-1}. In the first 100–130 cm^{-1} range, the chlorine-atom motion predominantly in the infrared spectrum of $C_{60}Cl_6$. In the second range 140–400 cm^{-1}carbon with chlorine atoms equally participate in the vibrations of $C_{60}Cl_6$.The intensities of this range are unusual vibrations are low, and also are observed in the experimental spectra as weak features. In the third range 400-900 cm^{-1} the vibrations of $C_{60}Cl_6$ are restricted on the carbon skeleton of the molecule with insignificant chlorine- atom motion. But the internal coordinates associated with chlorine atoms (C– Cl stretches and bends) do contribute to the vibrations of the $C_{60}Cl_6$ molecule. In general, this range may be characterized as particularly rich in the IR spectrum with a large number of strong and medium intensity bands In the fourth range 900–1600 cm^{-1} the vibrations of the $C_{60}Cl_6$ carbon skeleton have considerable tangential character stretching vibrations in the infrared spectrum. The frequencies could not be precisely determined from the experimental spectra in this range due to their low intensities and overlap of the bands

4) The ab initio method is used to calculate many infrared intensities of $C_{60}Cl_6$ which are not observed in experimentally [15]. The calculated infrared spectrum of the fullerene derivative is compared with the available experimental spectrum data at room temperature as explain in table 1.

5) It is worth wise that, the intensity of the infrared-active fundamentals of C_{60} decreases appreciably in the fullerene derivative ($C_{60}Cl_6$). It is found that most of the bands gain assigned as inactive fullerene fundamentals. So it can be taken as evidence that they are indeed fundamentals. In some regions of the simulated spectrum, the overall intensity decreases to an extent that the bands become barely detectable to compare with the available experimental spectrum data.

6) The minimum and maximum simulated infrared of $C_{60}Cl_6$ peak is 122.64 and 1559.32 respectively while experimental available infrared minimum and maximum data are 114.714 and 1572.71 respectively.

Table - I

simul. IR	Experi. IR	simul. IR	Experi. IR	simul. IR	Experi. IR
122.64	114.714	666.32	666.837	1103.59	1096.63
		672.03		1103.27	
131.85	129.592	693.03			
142.14				1108.94	
		694.94	704.857	1109.09	1109.86
162.98	162.653				
164.39		718.2	718.082	1129.93	1121.43
245.38	242	755.1	731.306	1136.91	1128.04
247.59					
		757.47		1136.98	1161.1
275.33	280.02	769.28	764.367	1203.01	
297.88		774.12			
				1204.43	1215.65
327.54	318.041	785.42	785.857	1229.42	
		759.98		1239.87	
374.85	349.449				
		826.15	823.878	1260.26	1253.67
391.18	385.816	826.36		1267.29	
399.74				1270.36	
		832.6	830.49		
404.17	404			1275.29	1278.47
		848.49	851.98		
427.32	425.49			1308.63	1303.27
		860.53	853.633	1322.07	
436.67	440.367				
		861.72		1344.25	1341.29
482.88	498.224	863.66	863.551	1350.52	
501.22		871.42		1368.5	
		878.06		1368.62	
516.86	514.755	880.91		1385.13	
539.01					
		882.76		1399.43	1390.88
540.96	542.857	891.84	891.653	1417.57	
548.03		896.5			
		906.56		1425.79	1438.82
570.95	564.347	909.52		1451.24	
		925.55		1462.63	
579.91	569.306	929.54	929.673		

		933.46		1463.08	1468.57
597.8	585.837			1473.24	
604.02		935.48	941.245		
606.24				1489.52	1485.1
		954.96	956.122		
611.67	615.592			1500.53	
627.4		964.16	975.959	1501.1	
633.86				1510.45	1514.86
634.22		1041.91			
640.94		1042.05		1546.17	1546.27
659.29		1050.43		1548.78	
		1052.22			
		1065.71	1078.45	1559.32	1572.71

Conclusion

The $C_{60}Cl_6$ structures are very sensitive to electron correlation treatment with basis set that are employed. So the proper electron correlation level and basis set play an important role in calculating accurate structure. It is interesting to note that the $C_{60}Cl_6$ structure of matching the available experimental data very much even it is showing other important peaks which are not seen in the experimental data.

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