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RESEARCH ARTICLE

SIMULATING RAMAN SPECTRA OF $C_{60}BR_6$ AND $C_{60}CL_6$.

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Abstract

The Ab Initio method is used to simulate both Raman spectrum of $C_{60}Br_6$ and $C_{60}Cl_6$. Each chloride atom as ($C_{60}Cl_6$) well as bromide atom ($C_{60}Br_6$) connected with fullerene perturbed in a small fullerene cage separately. This makes small frequency shifts demonstration in the fullerene derivative spectrum. There are three main groups of range are seen in simulated Raman peaks of $C_{60}Br_6$. The three principal regions of its vibrational spectrum namely the first range from 100 to 800 cm^{-1}, the second range from 800 to 1300 cm^{-1}, the third range from 1300 to 2000 cm^{-1}. It is appearing that no peaks are coming out after 1800 cm^{-1} in $C_{60}Br_6$. The high peaks intensities are appear in the lower region of spectrum of $C_{60}Br_6$ while the low intensities are seen in case of $C_{60}Cl_6$. The numbers of peaks in spectrum of $C_{60}Br_6$ are more than $C_{60}Cl_6$. This is due to bromide atoms are heavier than chloride atoms and thus this giving greater momentum to fullerene cage.

Introduction:-

The discovery of superconductivity of alkali-atom doped fullerenes leads to great efforts for new kind of doped fullerenes, especially hole-doped ones. The doping of fullerenes with boron and nitrogen atoms has been investigated by both experimental and theoretical calculations [1]. These theories revealed that acceptor and donor impurity states may be introduced into the energy gap respectively. Theoretically the halogen doped fullerenes have also been studied in the case when Cl atom which is trapped at the center of the C, cage [2]. Other halogen doped fullerenes where Br atom is placed at the octahedral or the tetrahedral interstitial site of solid C, with face-centered cubic (fcc) lattice structure [3]. These above two cases, are the open shell structure and the metallic bands have been deduced respectively.

It is reported that new compounds $C_{60}Br_6$, $C_{60}Br_8$ and other bromide compound with fullerene have been derived from the solutions of C, with bromine [4, 5]. Their molecular structures have been determined by single-crystal X-ray diffraction exactly [4, 5]. As halogenated C, species are important synthetic intermediates. Thus the halogenated C proved new milestones in promoting the development of the systematic chemistry and physics of the fullerenes.

Raman vibrational is a unique sensitivity spectroscopy to molecular structure in various. We report that comprehensive IR spectroscopic studies of $C_{60}Br_6$ and $C_{60}Cl_6$ with the help of Ab Initio method.

Computational Details:-

The simplest structure of $C_{60}Br_6$ and $C_{60}Cl_6$ molecule model has sixty carbon nuclei reside on a sphere six bromide atoms and six chloride atoms attached with six carbon atoms of C_{60}as shown in figure – 1 (a) and 1(b) respectively. Both the structures, named $C_{60}Br_6$ and $C_{60}Cl_6$ have C_1 symmetry and the bond length of each carbon-carbon is 1.35 Å. The bond length of carbon- bromide and carbon-chloride atoms are 2.07 Å and 2.08 Å respectively. The two different C-C bond lengths in C indicate that the л electrons are evenly delocalized over all bonds. The green colour, brown colour and blue colour represent the carbon, bromide and chloride atoms respectively.

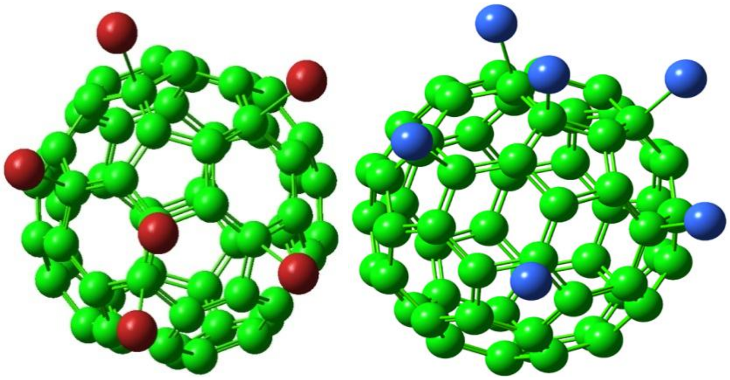

Figure (a) and 1(b) show $C_{60}Br_6$ and $C_{60}Cl_6$ structure configurations

Calculation:-

All calculations of this paper have been done according to Rashid Nizam et al [6]

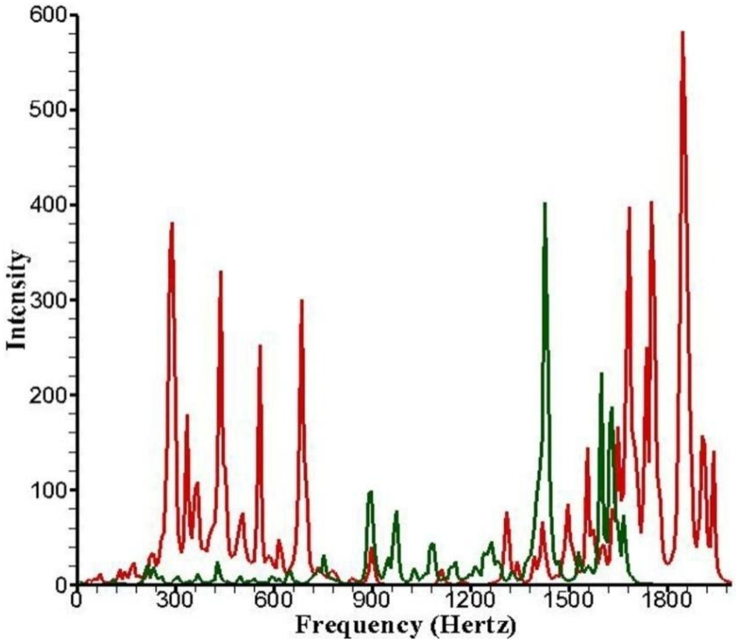

Figure 2 the Raman spectra of $C_{60}Br_6$ and $C_{60}Cl_6$

Result & Discussions:-

Both $C_{60}Br_6$ and $C_{60}Cl_6$ molecules have C_1 symmetry. The Raman spectra of $C_{60}Br_6$ and $C_{60}Cl_6$ are shown in figure 2. The red color lines are Raman spectra of $C_{60}Br_6$ and the green color lines are Raman spectra of $C_{60}Cl_6$ in the figure. It takes 128 and 396 steps to converge the simulated Raman spectrum of $C_{60}Br_6$ and $C_{60}Cl_6$ molecule respectively. The most significant change in the Raman spectrum induced by addition of extra atoms bromide/chloride is in fullerene. The redistribution with new Raman spectrum intensity among the normal modes of fullerene is as given in the table. Fullerene derivatives: both $C_{60}Br_6$ and $C_{60}Cl_6$ molecules have 192 degrees of freedom which is slightly greater than C_{60} normal degrees of freedom because of addition of six atoms (Br and Cl atoms) in the fullerene to form fullerene derivative. The rotational constants in x, y, z axis in the fullerenes derivative $C_{60}Br_6$ and $C_{60}Cl_6$ are 0.050, 0.04, 0.04 and 0.06, 0.05, 0.05 (GHz) respectively. The $C_{60}Br_6$ has 408 symmetry adapted basis functions, 1242 primitive gaussians, 414 cartesian basis functions, 285 alpha electrons and 285 beta electrons with the nuclear repulsion energy 18390.92 Hartrees. The fullerenes derivative ($C_{60}Cl_6$) has done SCF E (RHF) = -17510.87 A.U. after 26 cycles with convergence density matrix= 0.2144D-08. Similarly 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 Raman spectrum of $C_{60}Br_6$ and $C_{60}Cl_6$ are as follows:-

1) The Ab Initio method is used to simulate both Raman spectrum of $C_{60}Br_6$ and $C_{60}Cl_6$ and is shown in figure 2.
2) Each chloride atom as ($C_{60}Cl_6$) well as bromide atom ($C_{60}Br_6$) connected with fullerene perturbed in a small fullerene cage. This makes small frequency shifts demonstration in the fullerene derivative spectrum.
3) There are three main groups of range are seen in simulated Raman peaks of $C_{60}Br_6$. The three principal regions of its vibrational spectrum namely the first range from 100 to 800 cm^{-1}, the second range from 800 to 1300 cm^{-1}, the third range from 1300 to 2000 cm^{-1}. It is appearing that no peaks are coming out after 1800 cm^{-1} in $C_{60}Br_6$.
4) The high peaks intensities are appear in the lower region of spectrum of $C_{60}Br_6$ while the low intensities are seen in case of $C_{60}Cl_6$. The numbers of peaks in spectrum of $C_{60}Br_6$ are more than $C_{60}Cl_6$. This is due to bromide atoms are heavier than chloride atoms and thus this is giving greater momentum to fullerene cage. The lower peaks in the $C_{60}Br_6$ spectrum from 0 to 250 hertz are due to the movement of bromide atoms. The other peaks from 251 to 500 hertz due to movement of carbon atoms in the fullerene cage.
5) The total combination of carbon atoms in $C_{60}Br_6$ spectrum other than bromides gives peaks from 500 to 1000 hertz. These included shaking, breathing, up and down, stretches and bends, twisting of fullerene cage etc.
6) Similarly in Raman peaks of $C_{60}Cl_6$ there are exist three main groups of range. In the first 100–700 cm^{-1} range, the chlorine-atoms motion are observed in the Raman spectrum of $C_{60}Cl_6$. In the second range 700–1250 cm^{-1} carbon and the chlorine atoms equally take part in the vibrations of $C_{60}Cl_6$. The lower peaks are seen in this range when compared with other ranges. In the third range 1250-2000 cm^{-1} the vibrations of $C_{60}Cl_6$ are restricted on the carbon skeleton of the molecule without a significant chlorine atoms motion. Very high peaks are observed in this range than any two other ranges.
7) 17 main peaks of $C_{60}Br_6$ are observed while 8 main peaks of $C_{60}Cl_6$ in the Raman spectra.

Conclusion:-

The $C_{60}Br_6$ and $C_{60}Cl_6$ structures are very sensitive to basis set that are employed. That is why the proper electron correlation level and basis set play a significant role in calculating given accurate structure. It is interesting to note that the number of peaks of $C_{60}Br_6$ are greater than $C_{60}Cl_6$ structure due to bromide atoms are heavier than chloride atoms. Thus this gives greater momentum to fullerene cage.

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