# POTENTIAL ENERGY SURFACE SCAN OF $Al_9Cu_3Fe_1$ I COSAHEDRAL CLUSTERS USING DFT

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## *Abstract*

*Quasicrystals are material with perfect long-range order, but no three-dimensional translational periodicity. They are typically binary and tenary metallic alloys. Although progress has been made in deciphering their atomic structure, the understanding of their physical properties remains a challenging and fascinating problem. Potential energy surface (PES) are procedure used in determine the lowest and transition state of molecules or clusters. PES enable us to understanding how computational physics and chemistry programs locate and characterize structures of interest. In this work Fritz Haber Institute Code together with Basin-Hopping Monte Carlo algorithms were used to performed potential energy surface scan on $Al_9Cu_3Fe_1$ icosahedral cluster. It was observed that the global minimum and highest transition state were found at MC_Step 353 and MC_Step 168 with energy of -22340531524 eV and -22340479167 eV respectively. IR-spectra revealed stretching, scissoring, wagging, twisting vibrational modes and are in agreement with literature.*

**Key**: Potential Energy Surface (PES), Metroplis Monte Carlo, IR-spectra and Quasicrystals.

## 1.0    Introduction

Quasicrystals [1] are long-range-ordered structures that lack lattice periodicity. Although progress has been made in deciphering their atomic structure, the understanding of their physical properties remains a challenging and fascinating problem, because the Bloch theorem can no longer be applied. For example, icosahedral quasicrystals exhibit diffraction patterns with fivefold symmetry axes, while diffraction patterns of decagonal quasicrystals exhibit tenfold symmetry axes. This particular character of the structure raises the question of how the dynamics of quasilattices are best described

and whether the aperiodicity implies that the vibration spectra of quasicrystals are similar to those of amorphous materials [2].

Clusters containing a few to several thousands of atoms occupy an intermediate size range between individual atoms and condensed matter. Clusters properties are strongly dependent on the size. One of the most fundamental problems in the field of cluster science is to describe the structural and electronic properties of these intermediate systems and understand how these determine the physical and chemical properties of the cluster [3]. Increased attention has been given to transition metal clusters. Part of this interest is due to the potential utility of these clusters in nanotechnology applications and heterogeneous catalysis. There is also interest in these clusters at a fundamental level, since they display unique physical and chemical properties due to the partly filled d-shells[3].

Potential energy surface (PES) are important because they aid us in visualizing and understanding the relationship between potential energy and molecular geometry and understanding how computational physics and chemistry programs locate and characterize structures of interest [4]. Potential energy surfaces, allows determination of energy minima and transition states. Once a reasonable PES is constructed, vibrational spectra and reaction rate can be calculated and predicted. PES can be constructed based on Born-Oppenheimer approximation which regards electrons run much faster than nucleus and rests on the fact the nucleus are much more massive than electrons, and allows us to say that the nucleus are nearly fixed with respect to electron motion.Besides application in spectroscopy [5] and reaction dynamics PES is involved in cross section which is used to study theories of molecular collision due to molecular beams applied widely. Furthermore, it's also applied in in-depth study for themophysical properties in the case of statistical mechanics to solve the problem of macroscopic coefficients.

The determination of the global minima for a cluster was found to be very interested in both physics and chemistry. Several method for the determination of global minima were available. In this work Fritz Haber Institute Code together with Basin-Hopping Monte Carlo algorithm was used to performed potential energy surface scan on $Al_9Cu_3Fe_1$ icosahedral cluster. Four hundred Monte Carlo steps were performed and five valid geometry were selected. The selectedminimum was then verified by the calculation of its vibrational frequency.

## 2.0    Potential Energy Scan
In a modern quantum mechanical approach, the potential energy surface scan was started based on the approximation [6];

i.    The motion of electrons is considered in a field of fixed nuclei in space at distances R. If the nuclei do not move, their kinetic energy is zero and the total Hamiltonian is reduced to the electronic Hamiltonian.

ii.    Defining an electronic eigenfunction for a molecule and solving the electronic Schrodinger Equation at fixed nuclear distances gives the electronic eigenvalue.

iii.    The PES is created by calculating the electronic energy of a molecule as a function of R by varying the positions of the nuclei.

The time-independent Schrödinger equation describing the many-body system is[6]:

$$H(r,R)\Psi(r,R) = E\Psi(r,R) \tag{1}$$

where the Hamiltonian is a function kinetic energy and potential energy of the system:

$$H(r,R) = T(r,R) + V(r,R) \tag{2}$$

Heitler and London[7] used Born and Oppenheimer Approximation (BOA) to consider that the electrons are moving in a field of fixed nuclei at coordinate R, and thus their kinetic energy is zero:

$$H_{ele} = T_{ele}(r) + V_{ele-ele}(r) + V_{nucl-nucl}(R) + V_{elec-nucl}(r,R) \tag{3}$$

The electronic eigenfunction $\psi_{ele}^n(r,R)$ that satisfy the electronic Schrödinger equation is;

$$H_{ele}(r,R)\psi_{ele}^n(r,R) = E_{ele}^n(R)\psi_{ele}^n(r,R) \tag{4}$$

with n as electronic quantum number

BOA did not solve the electronic eigenvalue problem explicitly but presuppose that it is solved, and so it is not known how to calculate $\psi_{ele}^n(r,R)$ and $E_{ele}^n(R)$ based on the BOA. In particular, BOA stressed that Hamiltonian cannot be freely adjusted. For consistency in the series expansion, BOA had to use a single point in the space of all possible nuclear positions that must correspond to the minimum of the electronic energy. Therefore, the series expansion does not lead to a PES on which the nuclei move.

Condon [8] proposed that the total wave function of a vibrating molecule $\psi_{ele,vi}(r,R)$ can be expanded as a product of electronic $\psi_{ele}^n(r,R)$ wavefunction at fixed nuclear position and nuclear vibrational wave function $\chi_{vi}^{n,v}(R)$:

$$\psi_{ele,vi}(r,R) = \psi_{ele}^n(r,R)\chi_{vi}^{n,v}(R) \tag{5}$$

known as adiabatic approximation. IUPAC harmonize Condon's and BOA to calculate the eigenvalue and eigenfunction of clusters and molecule. The effective potential $U_n(R)$ that is generated is dependent on the level of approximation. Henry, Walter and Kimbal [9] use equation (1) and (5) as :

$$H(r,R)\psi_{ele}^n(r,R)\chi_{vi}^{n,v}(R) = E\psi_{ele}^n(r,R)\chi_{vi}^{n,v}(R) \tag{6}$$

In the equation, the nuclear kinetic energy affect both $\psi_{ele}^n(r,R)$ and $\chi_{vi}^{n,v}(R)$, so we have

$$\left(\frac{\partial^2}{\partial R^2}\right)\psi_{ele}^n(r,R)\chi_{vi}^{n,v}(R) = \psi_{ele}^n(r,R)\left(\frac{\partial^2}{\partial R^2}\right)\chi_{vi}^{n,v}(R) + 2\left(\frac{\partial}{\partial R}\right)\psi_{ele}^n(r,R)\cdot\left(\frac{\partial}{\partial R}\right)\chi_{vi}^{n,v}(R) +$$
$$\chi_{vi}^{n,v}(R)\left(\frac{\partial^2}{\partial R^2}\right)\psi_{ele}^n(r,R) \tag{7}$$

whereas $\left(\frac{\partial^2}{\partial R^2}\right)$ affect $\psi_{ele}^n(r,R)$

$$\left(\frac{\partial^2}{\partial R^2}\right)\psi_{ele}^n(r,R)\chi_{vi}^{n,v}(R) = \chi_{vi}^{n,v}(R)\left(\frac{\partial^2}{\partial R^2}\right)\psi_{ele}^n(r,R) \tag{8}$$

Thus, the total Schrödinger becomes;

$$\left[-\sum \frac{1}{2M}\psi_{ele}^{n}(r,R)\left(\frac{\partial^{2}}{\partial R^{2}}\right)\chi_{vi}^{n,v}(R)\right.$$
$$-\sum \frac{1}{M}\left(\frac{\partial}{\partial R}\right)\psi_{ele}^{n}(r,R)\cdot\left(\frac{\partial}{\partial R}\right)\chi_{vi}^{n,v}(R)$$
$$\left.-\sum \frac{1}{2M}\chi_{vi}^{n,v}(R)\left(\frac{\partial^{2}}{\partial R^{2}}\right)\psi_{ele}^{n}(r,R)-\sum \frac{1}{2m}\chi_{vi}^{n,v}(R)\left(\frac{\partial^{2}}{\partial R^{2}}\right)\psi_{ele}^{n}(r,R)\right]$$
$$+\left[V_{ele-ele}(r)+V_{nucl-nucl}(R)+V_{ele-nucl}(r,R)\right]\psi_{ele}^{n}(r,R)\chi_{vi}^{n,v}(R)$$

$$= E\psi_{ele}^{n}(r,R)\chi_{vi}^{n,v}(R) \tag{9}$$

multiplying from the left by $\psi_{ele}^{*n}$ and integrate over the electronic coordinate leads

$$\left[-\sum \frac{1}{2M}\left(\frac{\partial^{2}}{\partial R^{2}}\right)-\int \sum \frac{1}{2M}\psi_{ele}^{*n}\left(\frac{\partial^{2}}{\partial R^{2}}\right)\psi_{ele}^{n}(r,R)dr\langle M-\rangle \int \sum \frac{1}{M}\psi_{ele}^{*n}\left(\frac{\partial}{\partial R}\right)\psi_{ele}^{n}(r,R)\left(\frac{\partial}{\partial R}\right)+E_{ele}^{n}(R)\right]\chi_{vi}^{n,v}(R)=$$
$$E_{v}^{n,v}(R)\chi_{vi}^{n,v}(R) \tag{10}$$

neglecting the second and third term (i.e by applying BOA assumption), equation (10) becomes;

$$\left[-\sum \frac{1}{2M}\left(\frac{\partial^{2}}{\partial R^{2}}\right)+E_{ele}^{n}(R)\right]\chi_{vi}^{n,v}(R)=E_{v}^{n,v}(R)\chi_{vi}^{n,v}(R) \tag{11}$$

based on the adiabatic approximation, the equation (11) represent the nuclear Schrödinger equation for which the effective potential in which the nuclei moves is generated by the electronic energy $E_{ele}^{n}(R)$ as a function of R;

$$U^{n}(R)=E_{ele}^{n}(R) \tag{12}$$

known as the adiabatic potential energy surface and it can be used to calculate $E_{ele}^{n}(R)$ by using any appropriate quantum mechanical method. Fritz Haber Institute Density function theory code was used to search for the global minima.

## 3.1 Computational Method

## 3.2 FHI-Aims Code
Fhi-aims(Fritz Haber Institute ab-initio molecular simulation) is a computer program package for computational material science based on quantum-mechanical first principles. The main production method is Density Functional Theory(DFT) to compute the total energy and derived quantities of molecular, cluster or solid condense matter in its electronic ground state. In addition FHI-aims allows to describe electronic single quasiparticle excitations in molecules using different self-energy formalisms, and wave-function base molecular total energy calculation based on Hartree-Fock and manybody perturbation theory[10].
The focus here is on Density Functional Theory(DFT) in the local and semi-local (generalized gradient) approximations. However, an extension on hybrid functional, Hartree-Fock theory, and MP2/GW electron self-energies for local energies and excited states is possible with the same underlying algorithms. An all electron/full-potential treatment that is both computationally efficient and accurate is achieved for periodic and cluster geometries on equal footing, including relaxation

and ab initio molecular dynamics [11]. The construction of transferable, hierarchical basis set is demonstrated, allowing the calculation to range from qualitative tight-binding like accuracy to meV-level total energy convergence with basis set. Together with scalar-relativistic treatment, the basis sets provide access to all elements from light to heavy. Both low-communication parallelization of all real-space grid based algorithms and a scalapack-based, customized handling of the linear algebra for all matrix operations are possible, guaranteeing efficiencient scaling (CPU time and memory) up to massively parallel computer system with thousands of CPUs [11].

### 3.2    Procedure

Fritz Haber Institute Code together with Basin-Hopping Monte Carlo algorithms script were used to scan for the global minima using PBE exchange functional. Total of 400 Basin-Hopping steps were set for the icosahedral cluster $Al_9Cu_4Fe_1$ and this was done to allow enough visibility of minima. For each time the total energy and new geometry were recorded from the algorithms (i.e the algorithms will compared the relative energy and that of the new and evaluated that; if the initial relative energy is larger than the new one then the algorithms will take the new and further optimized until all the steps were done). However, valid minima were selected and kept separately as designed in the algorithms. The global minimum from the selected geometries was confirmed by further optimizing the geometry of the valid minima. Vibrational frequencies, zero point energy were calculated and used as criteria for the selection.

### 3.3 JMOL

J Mol is a Molecular viewer; used to visualize the molecular structure of an atom, molecule, clusters and crystals. The code can runs on both Linux base and windows and was designed to calculate some properties of the structure at semi-empherical level. However the code can displayed the vibrational frequency of the structure at semi-empherical level.

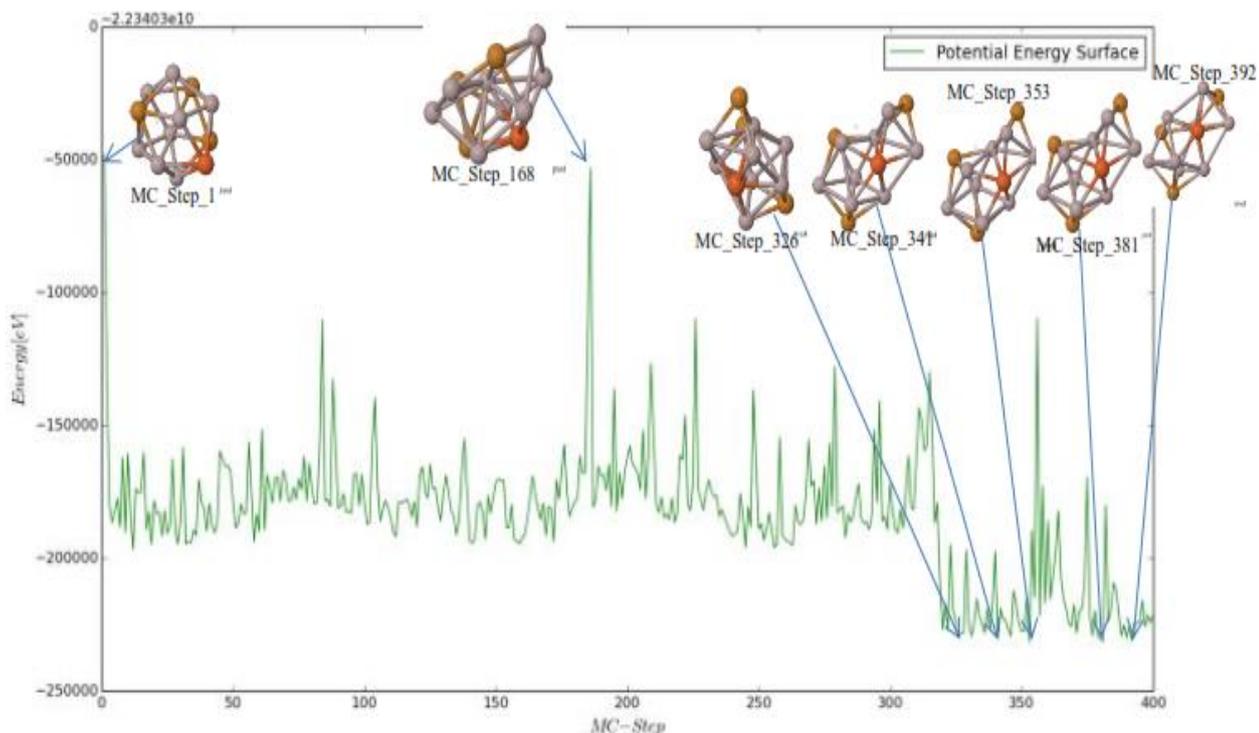## 4.0 Result and Discussion

## 4.1 Potential Energy Surface Scan



Figure.1 Basin-Hopping Monte Carlo Steps: (i) MC_Step_1 initial geometry (ii) MC_Step_168 highest transition state (iii) MC_Step_326, MC_Step_341, MC_Step_353, MC_Step_381 and MC_Step_392 lowest minima
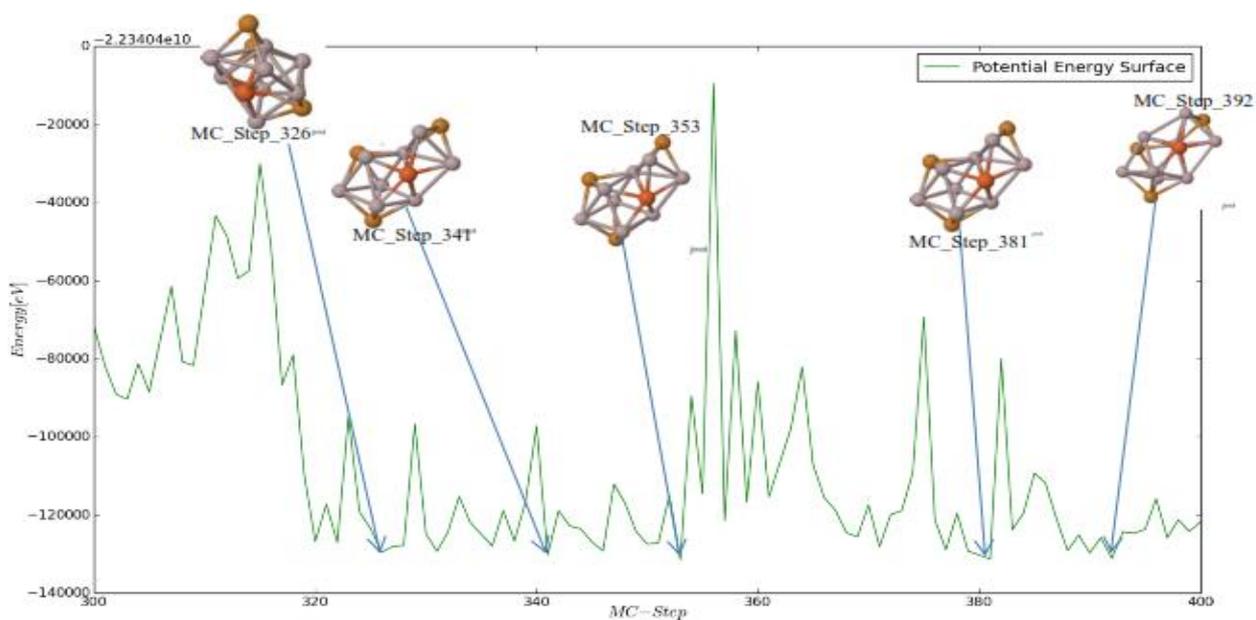


**Figure 2: Expected local minima area zooming to display the global minima**

**Table 1: Basin-Hopping Monte-Carlo search, total energy and description of the geometry**

| S/N | MC_Step | Energy [eV] | |
|---|---|---|---|
| 1 | 1 | -22340348129 | Initial structure |
| 2 | 168 | -22340479167 | Highest Transition State |
| 3 | 326 | -22340529536 | Expected minimum |
| 4 | 341 | -22340530214 | Expected minimum |
| 5 | **353** | **-22340531524** | **Expected minimum** |
| 6 | 381 | -22340531247 | Expected minimum |
| 7 | 392 | -22340531104 | Expected minimum |

Figure 1 shows Basin-Hopping Monte-Carlo search for 400 steps. It was found that the lowest minima were identified to be found at MC_step; 326, 341, 353, 381 and 392. The final geometry of the local minima were found to be non-icosahedron and this was due to the bond between iron and copper as reported in [12]. However, table 1 shows the energy of each MC_Step and it was found that MC_Step 353 was the global minimum with energy of -22340531524eV. Also it was found that the highest transition state was at MC_step 168 with energy of -22340479167eV. The difference between the transition state and the local minimum was found to be −52357eV. For better visualization since the lowest minima were found to be at range between 326 step to 400 steps .Figure 2 shows the magnified section of the localminima and it was observed that step 353 was the global minimum of the structure.

## 4.2    IR-Spectra of $Al_9Cu_3Fe_1$ Icosahedral quasicrystal Clusters



The
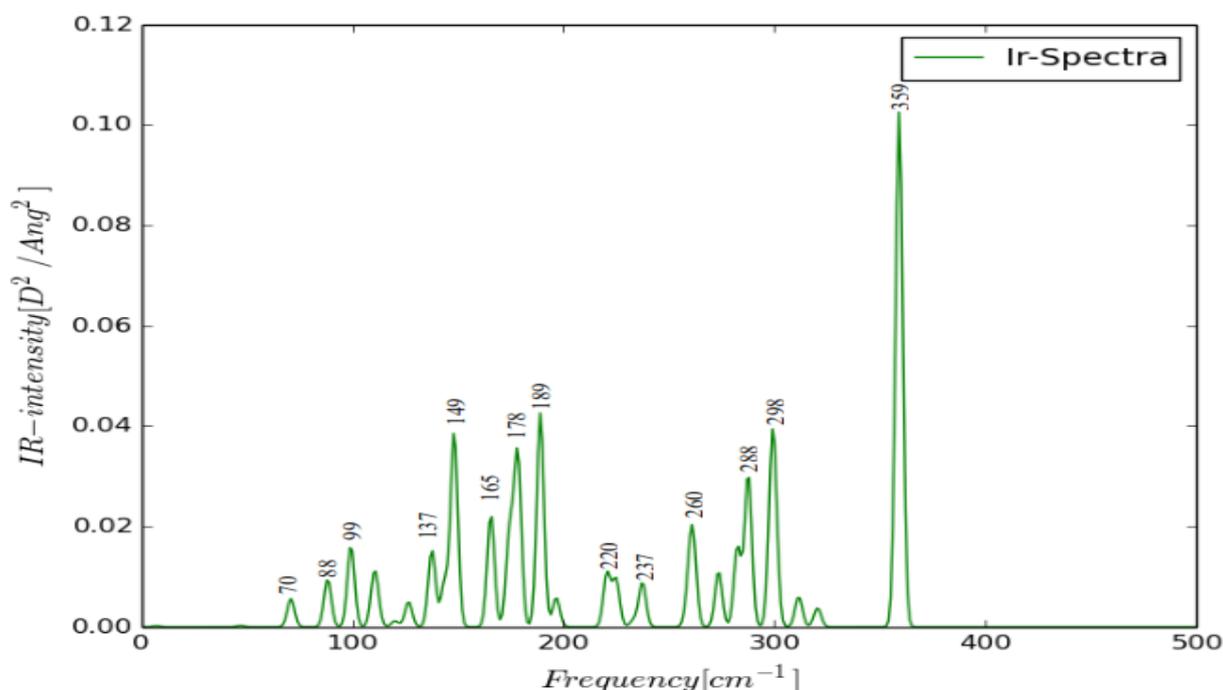
**Figure 3: IR spectra of $Al_9Cu_3Fe_1$ Cluster with Icosahedral**

stationary point was found by geometry optimization. It was desirably checked whether it is a minimum, transition state or a hilltop. Vibrational frequency calculation was performed, normal mode frequencies and zero point energy were recorded. Figure 3 shows the IR-spectra of

$Al_9Cu_3Fe_1$ modes of vibrations; Stretching (both Symmetric, and Asymmetric), Rocking, Wagging, Twisting and scissoring vibrations were observed. ***Jmol*** molecular builder was used to visualize the normal modes. It was found that there are Symmetric Stretching vibration at frequencies 137.723 $cm^{-1}$ between $Al_{atom\,4} - Al_{atom\,10} - Al_{atom\,7}$ and at 300.00 $cm^{-1}$ between $Cu_{atom\,2} - Al_{atom\,10} - Al_{atom\,4}$. There are Asymmetric stretching vibration at frequencies 149.90 $cm^{-1}$, 220.00 $cm^{-1}$, 237.00 $cm^{-1}$, and 288.00$cm^{-1}$ between $Al_{atom\,7} - Al_{atom\,9} - Cu_{atom\,1}$, $Al_{atom\,9} - Cu_{atom\,1} - Al_{atom\,12}$, $Al_{atom\,10} - Al_{atom\,7} - Al_{atom\,9}$, $Al_{atom\,4} - Al_{atom\,11} - Al_{atom\,12}$ respectively. There is also a rocking vibration at frequency 260cm-1 between $Cu_{atom\,1} - Al_{atom\,12} - Al_{atom\,9}$, then there is a Wagging vibration at frequency 165.651cm-1 between $Cu_{atom\,3} - Al_{atom\,10} - Cu_{atom\,1}$ respectively. And finally there are two Twisting vibrations at frequencies 99.383cm-1, 178.00cm-1 and 189.09cm-1 between $Cu_{atom\,2} - Al_{atom\,7} - Al_{atom\,11}$ $Al_{atom\,8} - Fe_{atom\,5} - Al_{atom\,6}$ and $Al_{atom\,9} - Fe_{atom\,5} - Al_{atom\,11}$ respectively. However 0.36982535 eV was found to be the zero point energy. The Ir-spectra obtained was in agreement with the work of Sa'id and Babaji 2016[12]


## 5.0    Conclusion

In this work we reported the potential energy scanning using Fhi-aims Metropolis Monte Carlo and IR-spectra of $Al_9Cu_3Fe_1$ Icosahedral cluster using Mackay model. Total of 400 Fhi-aims Metropolis Monte Carlo steps were performed. The global minimum was found at 353 MC_steps. The IR-spectra found to have the description of vibrational modes for the global minimum was found to be in agreement with the work reported by Sa'id and Babaji, 2016 [12].

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