



# Movement of Ng<sub>2</sub> molecules confined in a C<sub>60</sub> cage: An ab initio molecular dynamics study



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## ARTICLE INFO

### Article history:

Received 12 May 2014

Received in revised form 25 June 2014

In final form 26 June 2014

Available online 8 July 2014

## ABSTRACT

An ab initio molecular dynamics study on Ng<sub>2</sub>@C<sub>60</sub> (Ng = He–Kr) systems is performed to analyze the movement of Ng<sub>2</sub> molecules inside a C<sub>60</sub> cage. Within 500 fs time window, the He<sub>2</sub> undergoes precession encompassing translation, vibration and rotation readily whereas other Ng<sub>2</sub> molecules show usual vibration but the degrees of translation and rotation decrease with an increase in size of the Ng atoms. Increase in interaction between the Ng centers and cage carbons and an increased distortion of cage in moving from He to Kr seem to be responsible for this. During the movement, the Ng<sub>2</sub> units behave as single entity.

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## 1. Introduction

The long-established chemical principle that noble gases (Ng) are inert and do not take part in chemical bonding was abandoned after the synthesis of Xe<sup>+</sup>[PtF<sub>6</sub>]<sup>−</sup> by Bartlett [1,2]. Prompted by this synthesis within a short duration, a good number of Kr–Rn compounds [3,4] were synthesized, which further raised the interest of the researchers in this developing arena named Ng chemistry. The contributions of Räsänen and co-workers [3–5] in synthesizing successfully a series of compounds of type H(Ng)Y (Ng = Ar, Kr, Xe; Y = electron-withdrawing group) and that of Feldman et al. [6] in preparing Ng hydrides and other related Ng compounds are considered as significant in enriching this field. The Ng-compounds were also investigated theoretically by different researchers [7–14].

The study of chemical systems under unusual conditions like the endohedrally confined one has been a matter of great interest to the scientists. Ever since the discovery of fullerenes in 1985 [15], several methods were developed for producing endohedrally doped fullerenes since the space inside could hold atoms and even small molecules. Methods such as ion bombardment and high pressure/high-temperature techniques [16–22] were used but the yield was low (<1%) and so the ‘molecular surgery’ method was used where a hole is chemically opened on the surface of the fullerene cage, and a gas molecule is inserted reversibly through the orifice [23–30]. Komatsu et al. added groups to C<sub>60</sub> to create a

13-membered ring in the carbon cage [27] large enough to permit H<sub>2</sub> and He to enter [28,29]. They then devised a sequence of reactions that closed the hole, trapping H<sub>2</sub> inside to produce H<sub>2</sub>@C<sub>60</sub> in high yield [30]. Several theoretical and experimental [16,31–34] studies were also carried out on the endohedrally trapped Ng compounds like Ng<sub>n</sub>@C<sub>60</sub> and Ng<sub>n</sub>@C<sub>70</sub>. These unusual endohedrally trapped compounds are stable with a van der Waals type of interaction in most cases in that there is no chemical bond between the trapped atom and the carbon cage. Yet, they are very stable, since several C–C bonds must break to allow the atom to escape. In addition to the fullerene cages, inclusion of Ng atoms in much smaller cages like C<sub>10</sub>H<sub>16</sub>, C<sub>20</sub>H<sub>20</sub> and Mo<sub>6</sub>Cl<sub>8</sub>F<sub>6</sub> was also studied [35–38].

From a theoretical perspective, noble gas dimers (Ng<sub>2</sub>) confined in a C<sub>60</sub> and other cages have revealed how the valence electrons of atoms, which have a fully occupied valence shell, change when they are confined to strong interatomic interactions at equilibrium geometry. The theoretical data suggest of a possible new type of inter-atomic interaction, which would provide material for further stimulating discussions about the nature of a chemical bond. Certain quantum-chemical studies about the endohedrally confined Ng dimers i.e. Ng<sub>2</sub> (Ng = He–Xe) in C<sub>60</sub> fullerene cage [39–41] revealed that the Ng–Ng distances in Ng<sub>2</sub>@C<sub>60</sub> are considerably shorter than those in free Ng dimers. All these Ng<sub>2</sub>@C<sub>60</sub> systems are thermodynamically unstable toward the loss of Ng atoms. Krapp and Frenking [40] investigated whether the bonds in between two Ng atoms or in between Ng and C atoms in Ng<sub>2</sub>@C<sub>60</sub> systems could be called a chemical bond. With the help of detailed bonding analysis and IUPAC definition of a chemical bond, they termed the Ng–Ng and Ng–C bonds for Ng = Ar–Xe as genuine chemical bonds whereas those in He<sub>2</sub>@C<sub>60</sub> and Ne<sub>2</sub>@C<sub>60</sub> are just weakly bonded

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**Table 1**

The Ng–Ng distance ( $r_{\text{Ng–Ng}}$ , Å), shortest Ng–C distance ( $r_{\text{Ng–C}}$ , Å) of the  $D_{3d}$  symmetric  $\text{Ng}_2@C_{60}$  (Ng = He, Ne, Ar and Kr) systems at the M05-2X/6-311G(d) and BP86/TZVPP level and the distance ( $r_{\text{cg}}$ , Å) along the centers of  $C_6$  rings along the Ng–Ng axis and along the centers of  $C_5$  rings perpendicular to the Ng–Ng axis.

Systems	M05-2X/6-311G(d)		BP86/TZVPP		M05-2X/6-311G(d)	
	$r(\text{Ng–Ng})$	$r(\text{Ng–C})$ shortest	$r(\text{Ng–Ng})$	$r(\text{Ng–C})$ shortest	$r_{\text{cg}}(C_6)$	$r_{\text{cg}}(C_5)$
$\text{He}_2@C_{60}$	2.035	2.640	1.953	2.696	6.488	6.613
$\text{Ne}_2@C_{60}$	2.091	2.638	2.099	2.657	6.536	6.599
$\text{Ar}_2@C_{60}$	2.357	2.620	2.364	2.630	6.736	6.553
$\text{Kr}_2@C_{60}$	2.449	2.630	2.460	2.637	6.837	6.533

van der Waals interactions. Further, based on the very small energy differences between differently oriented  $\text{Ng}_2$  units inside the  $C_{60}$  cages, they argued about a nearly free precession movement of  $\text{Ng}_2$  around its midpoint in the  $C_{60}$  cage, except for the  $\text{Xe}_2$  dimer. They particularly put stress on the  $\text{He}_2@C_{60}$  for such a precession to occur. In an earlier study it was shown through the ab initio simulation that the He–He unit undergoes translation, rotation and vibration inside the cavity of  $\text{B}_{12}\text{N}_{12}$  and  $\text{B}_{16}\text{N}_{16}$  cages [42]. The ab initio simulation also revealed that although Ng entrapped  $\text{B}_{12}\text{N}_{12}$  and  $\text{B}_{16}\text{N}_{16}$  cages are thermodynamically unstable, they are kinetically stable at room temperature except  $\text{Ne}_2@B_{12}\text{N}_{12}$ . However,  $\text{Ne}_2@B_{12}\text{N}_{12}$  was found to be kinetically stable at low temperature.

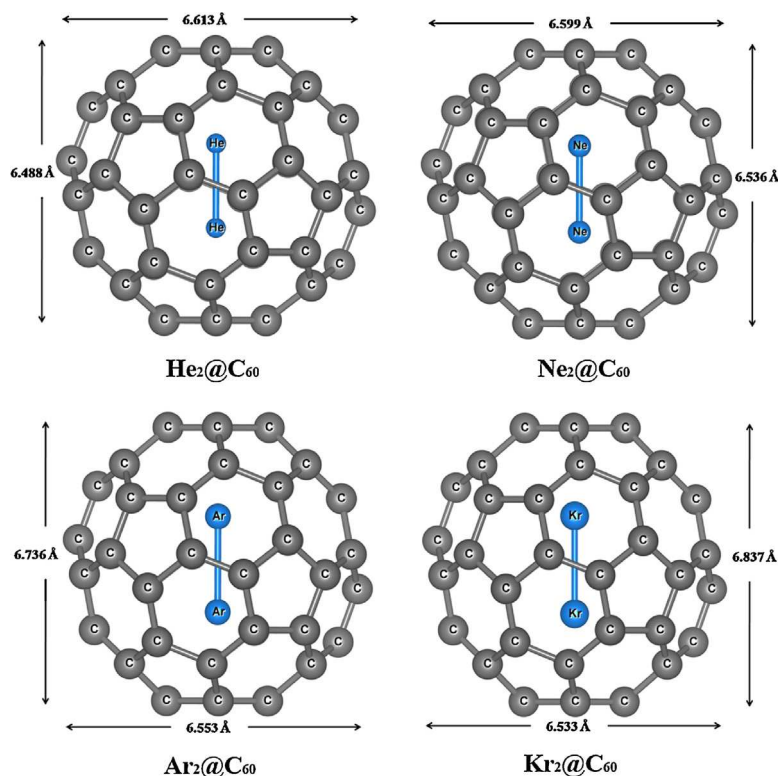
Our objectives toward the present study include:

- (1) To check the kinetic stability of these systems through ab initio molecular dynamics study since they are thermodynamically unstable.
- (2) Frenking et al. [40] argued about the free precession of the  $\text{Ng}_2$  units inside the cage on the basis of the very small energy differences between differently oriented  $\text{Ng}_2$  units. We need to check whether these  $\text{Ng}_2$  units really precess inside the  $C_{60}$  cage at room temperature and if yes then by what extent, up to 500 fs time scale.

- (3) To check whether these weakly interacting  $\text{He}_2$  and  $\text{Ne}_2$  systems can be termed as molecules we would like to analyze the Ng–Ng bond distance values at different time steps.
- (4) In order to check the applicability of maximum hardness principle and minimum electrophilicity principle during time evolution of these endohedrally trapped systems the variation of hardness and electrophilicity with time during simulation and their correlation with the change in energy of the systems are studied.

## 2. Computational details

We have considered the  $D_{3d}$  symmetric  $\text{Ng}_2@C_{60}$  (Ng = He, Ne, Ar and Kr) systems since  $D_{3d}$  point group structures have lower energy than the other symmetric structures as shown by Frenking et al. [40], except for  $\text{He}_2@C_{60}$ . In case of  $\text{He}_2@C_{60}$ , the other symmetric structures are slightly lower in energy (0.02 kcal/mol) than that with  $D_{3d}$  symmetry. We have optimized these systems at the M05-2X/6-311G(d) level using GAUSSIAN 09 program package [43]. The dynamics of all the  $\text{Ng}_2@C_{60}$  (Ng = He, Ne, Ar and Kr) systems are investigated by using ab initio molecular dynamics [44], atom-centered density matrix propagation (ADMP) [45–47] technique as included in GAUSSIAN 09 suite of program [43]. The dynamics



**Figure 1.** Optimized geometries of the  $D_{3d}$  symmetric  $\text{Ng}_2@C_{60}$  (Ng = He, Ne, Ar and Kr) systems at the M05-2X/6-311G(d) level. (The Ng–C bonds are not shown for clarity of the structures; the distance along the centers of  $C_6$  rings along the Ng–Ng axis and along the centers of  $C_5$  rings perpendicular to the Ng–Ng axis are also shown.)

are performed at the DFT-D-B3LYP/6-311+G(d,p) level taking the optimized geometries at the M05-2X/6-311G(d) level. Boltzmann distribution is used to generate the initial nuclear kinetic energies of the systems. The temperature is maintained by using a velocity scaling thermostat throughout the simulation. Here all the simulations are carried out at 298 K. Default random number generator seed is used as implemented in GAUSSIAN 09 to initiate the initial mass weighted Cartesian velocity. For all the cases, trajectories up to 500 fs are generated (within the time gap of 1 fs). The electronegativity ( $\chi$ ) [48,49], hardness ( $\eta$ ) [50,51] and electrophilicity ( $\omega$ ) [52] of the systems are calculated as:

$$\chi = -\mu = \frac{I + A}{2} \quad (1)$$

$$\eta = I - A \quad (2)$$

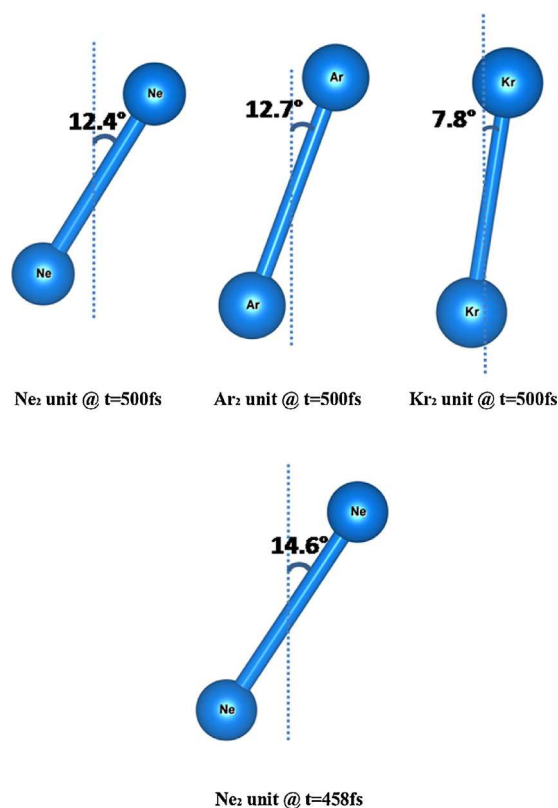
and

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \quad (3)$$

where  $I$  and  $A$  are the ionization potential and electron affinity of the system, respectively. Here  $I$  and  $A$  are computed using Koopmans' theorem [53]. Note that although Koopmans' theorem is strictly valid within the Hartree–Fock theory; however one may use the same in Kohn–Sham calculation with the help of Janak's theorem [54]. It is worth mentioning that the electron affinities computed from the LUMO energies would be even more approximate than the ionization potentials from HOMO energies [55].

### 3. Results and discussion

Table 1 shows the key structural parameters of the  $D_{3d}$  symmetric  $\text{Ng}_2@\text{C}_{60}$  systems at the M05-2X/6-311G(d) level and those at the previously considered BP86/TZVPP level. The Ng–Ng bond distances and the shortest Ng–C bond distances are very much comparable at these two levels of theory. In case of  $\text{He}_2@\text{C}_{60}$ , the differences in the corresponding parameters are slightly more than that in the other systems. Figure 1 shows the optimized geometries of the  $D_{3d}$  symmetric  $\text{Ng}_2@\text{C}_{60}$  systems at the M05-2X/6-311G(d) level. Now, the dynamical behavior of all these  $\text{Ng}_2@\text{C}_{60}$  systems can be well understood by an ab initio molecular dynamics study. Since we are particularly interested in knowing the nature of movement of  $\text{Ng}_2$  units at room temperature, we perform the dynamics study at 298 K. We have found that among these systems only  $\text{He}_2@\text{C}_{60}$  undergoes almost free precession encompassing translation, rotation and vibration throughout the simulation time essentially due to the smaller size of  $\text{He}_2$ . But in the remaining systems, the  $\text{Ng}_2$  units only undergo usual vibration with slight rotation and translation. In the  $D_{3d}$  point groups, each Ng centers in the  $\text{Ng}_2$  unit are orientated toward the centers of the two oppositely faced  $\text{C}_6$  rings. If we look at the movement of  $\text{Ng}_2$  units through one face of the  $\text{C}_6$  ring, the  $\text{Ng}_2$  units are found to move mostly within the region made through connecting each C centers of the  $\text{C}_6$  ring with the same of the oppositely faced  $\text{C}_6$  ring. The  $\text{Ng}_2$  units prefer to stay within this region to avoid severe steric repulsion caused when approached closer to the cage atoms. After 500 fs, the  $\text{Ne}_2$  unit is found to make a  $12.4^\circ$  clock-wise rotation with respect to the Z-axis connecting the midpoint of  $\text{Ng}_2$  unit and center of the  $\text{C}_6$  ring whereas the same are found to be  $12.7^\circ$  and  $7.8^\circ$  for the  $\text{Ng}_2$  units in  $\text{Ar}_2@\text{C}_{60}$  and  $\text{Kr}_2@\text{C}_{60}$ , respectively as shown in Figure 2. Although after 500 fs,  $\text{Ne}_2$  moves through an angle nearly equal to that of  $\text{Ar}_2$  in intermediate time say after 458 fs, this angle is  $14.6^\circ$  (Figure 2) indicating its higher ability to rotate than  $\text{Ar}_2$ . Therefore,  $\text{Ng}_2$  units other than  $\text{He}_2$  cannot rotate easily. A longer time may be required for a significant rotation. Note that although here we see a net clock-wise rotation for  $\text{Ng}_2@\text{C}_{60}$  cases (Ng = Ne–Ar) after 500 fs giving a sense about the unidirectional rotation of  $\text{Ng}_2$  units



**Figure 2.** Orientation of the  $\text{Ng}_2$  units (Ng = Ne, Ar and Kr) with respect to the Z-axis connecting the midpoint of  $\text{Ng}_2$  unit and center of the  $\text{C}_6$  ring (dotted line) of the  $\text{C}_{60}$  cage along the Ng–Ng axis at  $t = 500$  fs and 458 fs (for  $\text{Ne}_2$  unit only).

inside the  $\text{C}_{60}$  cage one does not expect an unidirectional rotation in presence of thermal energy. It seems that after the current simulation time it shows the rotation in a particular direction but with a longer simulation time, it may show the rotation in different directions similar to  $\text{He}_2@\text{C}_{60}$ . [56] In fact, here we may connect this with the study of Alexandrova et al. [57] in which they controlled the direction of rotation of inner  $\text{B}_3$  ring in  $\text{B}_{13}^+$ , a Wankel-motor, by applying an external circularly polarized infrared laser. Otherwise, the  $\text{B}_3$  ring rotates in both clockwise and anti-clockwise directions. Therefore, here also to facilitate a unidirectional rotation of  $\text{Ng}_2$  units an external driving force at a particular direction will be needed. Note that although the precession of  $\text{Ng}_2$  units in  $\text{C}_{60}$  cage and the fluxional behavior of the inner units in those so-called molecular Wankel-motors are quite different they have similarities due to the fact that in both cases the presence of strong bonds between the rotating unit and peripheral atoms will hinder such rotation. In Wankel-motors, the presence of multicenter- $2e^-$  bond favors such fluxionality [58]. In cases of  $\text{Ng}_2@\text{C}_{60}$ , the  $\text{He}_2$  and  $\text{Ne}_2$  are interacting with the  $\text{C}_{60}$  cage only through weak van der Waals interaction but the interaction gets stronger for the Ar and Kr cases [40]. This is due to the larger separation between two trapped Ng atoms in moving from He to Kr, the Ng atoms become closer to the cage C atoms producing stronger interaction. In fact Frenking et al. [40] termed the Ar/Kr–C bonding as some sort of true chemical bonds. This seems to be responsible for the fact that  $\text{He}_2$  can rotate freely whereas the rotation gradually becomes hindered in moving from Ne to Kr. Another factor, which will have some effect in restricting the rotation of  $\text{Ng}_2$  units, is the distortion of  $\text{C}_{60}$  cage in accommodating  $\text{Ng}_2$  inside. It is found that in  $\text{Ng}_2@\text{C}_{60}$  cages, the cage diameter expands along the Ng–Ng axis and contracts perpendicular to the Ng–Ng axis. This type of distortion is negligible in case of He but it gradually increases in moving

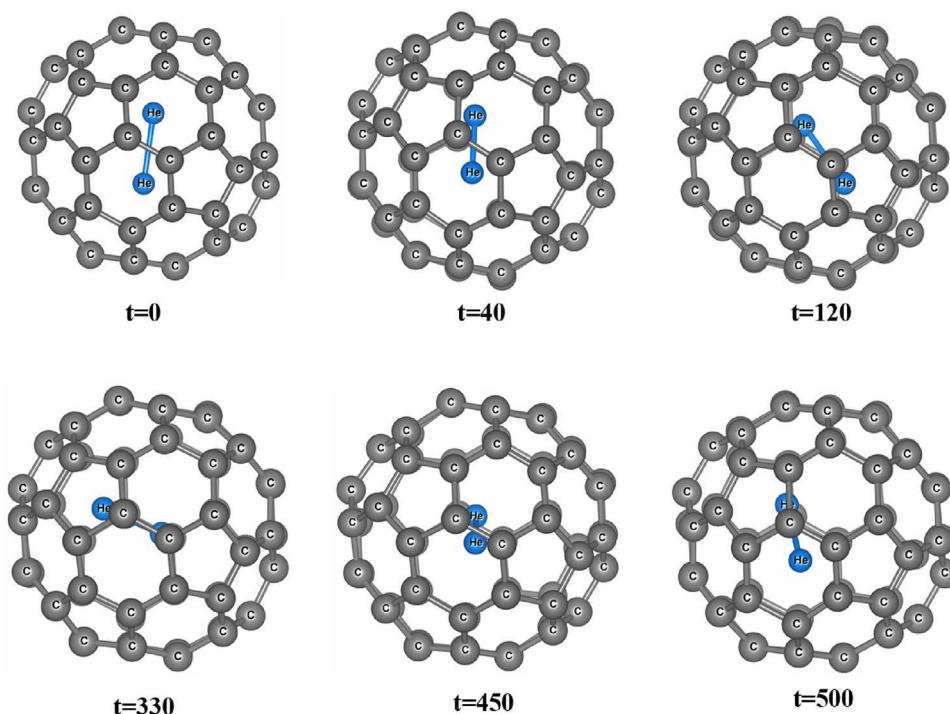


Figure 3. Snapshots at different time steps of  $\text{He}_2@C_{60}$  system (time in fs).

from Ne to Kr. In  $C_{60}$  cage, the distance between the centers of two oppositely faced  $C_6$  rings is 6.470 Å and the same between two oppositely faced  $C_5$  rings is 6.619 Å. Note that in  $\text{Ng}_2@C_{60}$ , the distance ( $r_{cg}$ ) along the centers of  $C_6$  cages represents the diameter along the Ng–Ng axis and that along the centers of  $C_5$  rings represents the diameter perpendicular to the Ng–Ng axis. The  $r_{cg}$  values in Table 1 clearly show the changes in diameters in the  $\text{Ng}_2$  trapped cages. In fact, in  $\text{Kr}_2@C_{60}$  the diameter gets elongated by almost 0.4 Å along the Kr–Kr axis and contracted by  $\sim 0.1$  Å perpendicular to the Kr–Kr axis. Such distortion of  $C_{60}$  cage can also be understood by the preparation energy calculated by Frenking et al. [40] where they found very low preparation energy in cases of He (0.02 kcal/mol) and Ne (0.79 kcal/mol) which is considerably high for Ar (11.48 kcal/mol) and Kr (23.68 kcal/mol) cases. Therefore, in  $\text{Ng}_2@C_{60}$ , the rotation of  $\text{Ng}_2$  units has to be accompanied by the rearrangement of such structural distortion. It is another reason behind the small rotation angle found in  $\text{Ng}_2@C_{60}$  cases in 500 fs time window other than  $\text{He}_2@C_{60}$ . For these systems in much longer time we may find a considerable rotation.

Figure 3 presents the snapshots at different time steps of the  $\text{He}_2@C_{60}$  system, which clearly depict the movement of  $\text{He}_2$  units throughout the simulation. The occurrence of such precession movement within the cavity was also concluded by Krapp and Frenking [40], based on their study regarding the geometry and energy calculations of  $\text{Ng}_2@C_{60}$  systems. Cerpa et al. [59] also referred to this free precession of  $\text{He}_2$  inside the  $C_{20}H_{20}$  cage owing to the very low energy difference between the isomers having different He–He orientations. In another study [42] the precession of  $\text{He}_2$  units within the  $B_{12}N_{12}$  and  $B_{16}N_{16}$  cages was reported. Therefore, here we have demonstrated that  $\text{He}_2$  indeed undergoes precession encompassing translation, rotation and vibration. From the movie files provided in the electronic supplementary material one can see the movement of the  $\text{Ng}_2$  units inside the cage. As previously mentioned by Frenking et al. [40] such free movement of  $\text{He}_2$  unit inside the cage further justifies the observation from the experimental [60] and theoretical studies [41] on the  $^3\text{He}$  NMR of  $\text{He}_2@C_{60}$  that  $\text{He}_2@C_{60}$  almost has the same  $^3\text{He}$  chemical shift as

that of the  $\text{He}@C_{60}$ . The snapshots at different time steps of the  $\text{Ne}_2@C_{60}$ ,  $\text{Ar}_2@C_{60}$  and  $\text{Kr}_2@C_{60}$  systems are presented in Figures S1, S2 and S3, respectively, in the supplementary material.

From the previous study [40], it is clear that the  $\text{He}_2$  and  $\text{Ne}_2$  are just weakly bonded species. Now, the question is whether they can be called a molecule or just a couple of atoms trapped in a cage. In fact Cross et al. [35] termed them as artificial molecule. Note that to bring two Ng atoms at a distance as that in the  $\text{Ng}_2@C_{60}$  complexes, one has to pay energy. It is 2.07 kcal/mol for  $\text{He}_2$  and 6.38 kcal/mol for  $\text{Ne}_2$  [40]. Therefore, if there is a scope then they should stay apart. But during the whole simulation process we have observed that the  $\text{Ng}_2$  units move as a single entity within the cage which is clear from the movies provided in the supplementary material. The  $\text{He}_2@C_{60}$  case will be the best example to understand this since

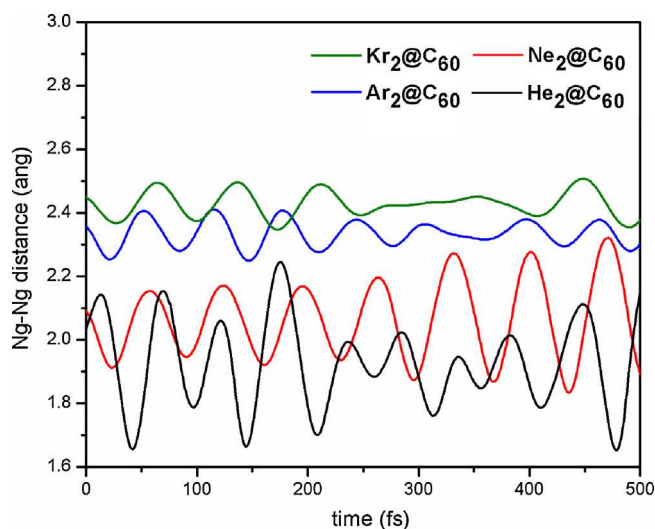
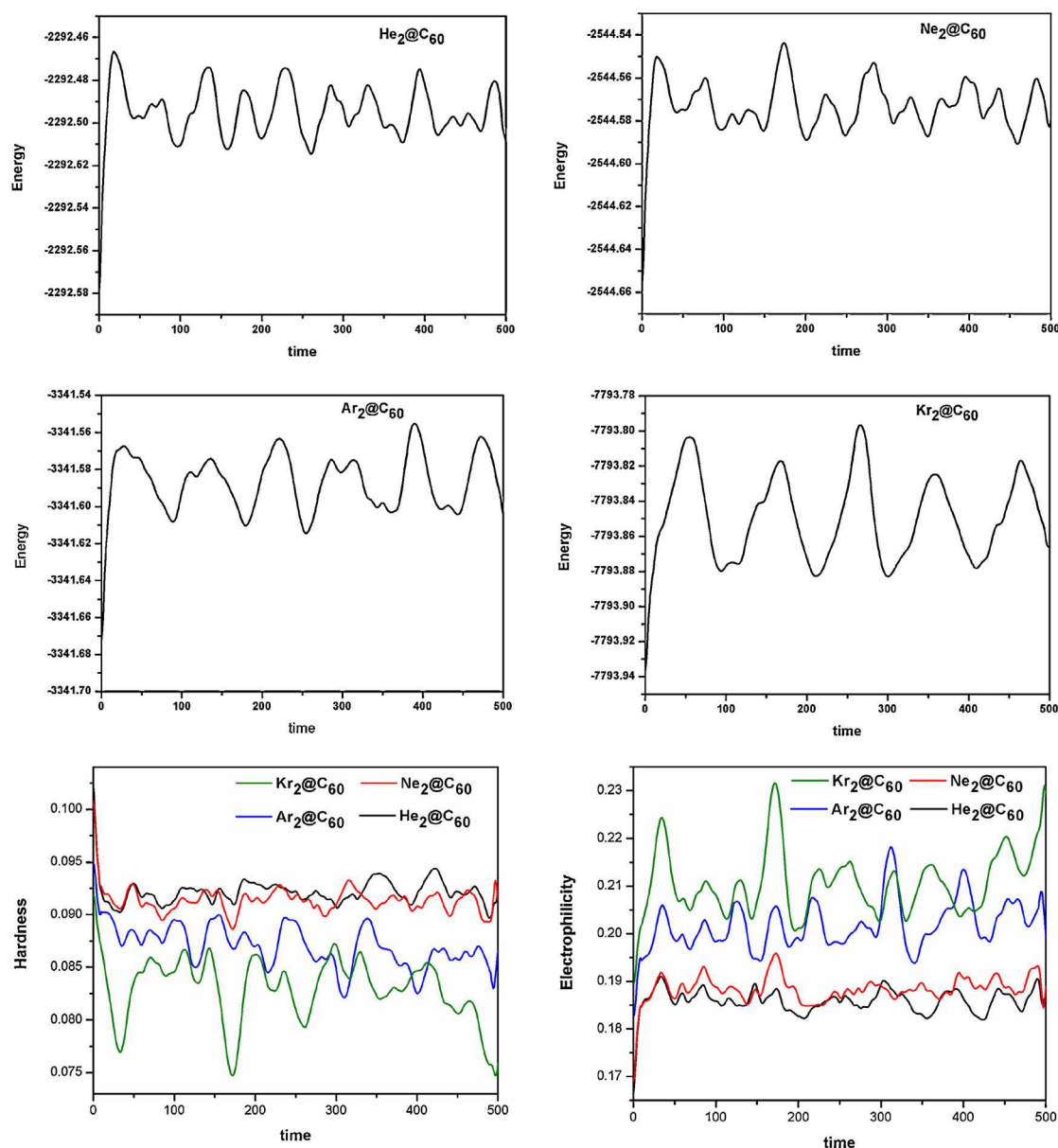


Figure 4. Plot of Ng–Ng distance (in Å) vs. time (in fs) for  $\text{Ng}_2@C_{60}$  systems (Ng = He, Ne, Ar, Kr).





**Figure 5.** Time evolution of Energy (in a.u.), Hardness (in a.u.) and Electrophilicity (in a.u.) for  $\text{Ng}_2@C_{60}$  systems ( $\text{Ng} = \text{He}, \text{Ne}, \text{Ar}, \text{Kr}$ ) (time in fs).

there is maximum space available inside the cage to move around. The two He atoms are correlated to each other and follow each other and there seems to be no random movement. It is also evident from Figure 4 which presents the plots of Ng–Ng distances with time. Except the usual stretching and compression of He–He bonds not much abruptness appears in the plot. The equilibrium He–He bond distance in  $\text{He}_2@C_{60}$  is 2.035 Å. It is found to vary within 2.2–1.6 Å. Therefore, they are not just two He atoms rather a single  $\text{He}_2$  molecule. It is also interesting to note from the natural population analysis (NPA) that the net NPA charges on the Ng atoms in the  $C_{60}$  cage are zero or close to zero and therefore no transfer of electron from the Ng atoms to the cage atoms takes place. The total Wiberg Bond Index (WBI) for each He atoms in  $\text{He}_2@C_{60}$  is 0.0, for each Ne atoms in  $\text{Ne}_2@C_{60}$  is 0.0003, for each Ar atoms in  $\text{Ar}_2@C_{60}$  is 0.0146 and for each Kr atoms in  $\text{Kr}_2@C_{60}$  is 0.0357.

The time evolution of energy, hardness and electrophilicity of the  $\text{Ng}_2@C_{60}$  systems is presented in Figure 5. Oscillations in the energy plots of the  $\text{Ng}_2@C_{60}$  systems are observed. The confined Ng atoms move within the  $C_{60}$  cage and when they come near the walls of the cage distortion in the cage occurs. The oscillations

in the energy curves are due to these distortions, resulting in the increase in the nuclear kinetic energy. For smaller Ng atoms the distortion is less than the larger Ng atoms. However the energy oscillates within a fixed range for all the  $\text{Ng}_2@C_{60}$  systems. It has already been established [40] that the endohedral confinement of Ng atoms is thermodynamically unstable toward the release of both the Ng atoms from the  $C_{60}$  cage. But we can see that throughout the simulation process all the structures remain intact and thus we can say that all the structures are at least kinetically stable. In the time evolution of hardness and electrophilicity plots (Figure 3) oscillations similar to energy plots are observed. According to maximum hardness principle (MHP) [61–64] and minimum electrophilicity principle (MEP) [65,66], an increase in hardness [50,51] and a decrease in electrophilicity [52] imply the increased stability of the system. In most of the cases, when energy increases, the hardness decreases and electrophilicity increases during simulation and vice versa. Comparing the hardness and electrophilicity of the  $\text{Ng}_2@C_{60}$  systems in Figure 3, it is clear that the hardness decreases and electrophilicity increases in going from He to Kr entrapped systems i.e., stability of the systems decreases in the same order. With an

increase in size of Ng atoms, the system becomes less stable with respect to dissociation into empty cages and Ng atoms [41]. Therefore, very good correlation is found between the nature of changes in hardness and electrophilicity values and those in energy of the systems.

#### 4. Conclusion

Through ab initio molecular dynamics study we have verified the conclusion drawn by Frenking et al. [40] regarding the nearly free precessional movement of Ng<sub>2</sub> inside the C<sub>60</sub> cage based on the low energy difference in different geometries of Ng<sub>2</sub>@C<sub>60</sub> in which the Ng<sub>2</sub> are in different orientations. We have found that the He<sub>2</sub> unit indeed undergoes translation, vibration and rotation very readily. However, the degree of such movements is restricted with an increase in the size of Ng atoms. After 500 fs, Ne<sub>2</sub>, Ar<sub>2</sub> and Kr<sub>2</sub> are found to have a net clock-wise rotation of only 12.4°, 12.7° and 7.8°, respectively, with respect to the Z-axis connecting the midpoint of the Ng<sub>2</sub> unit and center of the C<sub>6</sub> ring. Therefore, in these cases, longer time period is needed to have a significant rotation. With an increase in size of the Ng atoms, the interaction with the Ng and cage carbon atoms increases. This seems to be one of the reasons which restrict such movements for the heavier analogs. Another reason is the distortion of the C<sub>60</sub> cage in accommodating Ng atoms. The distortion is large for the larger Ng atoms whereas it is negligible for the He case. The rotation of Ng<sub>2</sub> units has to be accompanied by the elongation along the Ng–Ng axis resulting in a slower rate of rotation for the larger Ng-analogs. During the simulation, the Ng<sub>2</sub> units are found to move as single entities rather than two separate individual Ng atoms. This fact is even more transparent in case of He<sub>2</sub>@C<sub>60</sub> in which there is enough space to stay apart from each other. Further, nice correlation is found among the nature of changes in hardness and electrophilicity values and those in energy of the systems during simulation.

#### Acknowledgements

PKC would like to thank DST, New Delhi for the J. C. Bose National Fellowship. MK and SP thank CSIR, New Delhi for their fellowships.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cplett.2014.06.052](https://doi.org/10.1016/j.cplett.2014.06.052).

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