

Stability of As_n [$n = 4, 8, 20, 28, 32, 36, 60$] cage structures

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Abstract

We present all-electron density functional study of the geometry, electronic structure, vibrational modes, polarizabilities as well as the infrared and Raman spectra of fullerene-like arsenic cages. The stability of As_n cages for sizes 4, 8, 20, 28, 32, 36, and 60 wherein each As atom is threefold coordinated is examined. We find that all the cages studied are vibrationally stable and while all the clusters are energetically stable with respect to isolated arsenic atoms, only As_{20} is energetically stable against dissociation into As_4 . We suggest that the Raman spectra might be a means for observing the As_{20} molecule in gas phase.

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Highly symmetric molecular cages are of great interest due to their inherent symmetry and bonding [1]. The highly studied carbon fullerenes [2–4] are prime examples of this class of materials. Apart from their symmetry they also show unusual properties such as superconductivity in the solid phase [5] and storage capacity which can have potential applications in nanotechnology. For more than a decade considerable effort has been paid to the possibility of creating fullerene-like structures with elements other than carbon. Some studies have shown Si and Ge clusters in the gas phase [6–10] form cages but their structures are still controversial. Recently Moses et al. [11] have successfully synthesized a highly symmetric onion-like cage formed by an icosahedral $As@Ni_{12}$ cluster with an As atom at the center. The resulting 13-atom cluster is further encapsulated by a dodecahedral fullerene-like As_{20} . This report opens up the possibility of formation of other possible cage-like As_n clusters in the laboratory. In the present study, we examine the possibility for obtaining stable As cages for sizes upto 60 atoms.

The clusters of other isoelectronic elements nitrogen and phosphorus are well studied. Nitrogen clusters are

studied primarily because of their high energy density. It may be pointed out that although small N clusters are stable, the higher size clusters tend to break up into smaller clusters. Owens [12] has studied N_4 , N_8 , N_{10} , N_{12} and N_{20} clusters theoretically using density functional theory (DFT). He has shown that all the nitrogen clusters have high-energy density and will decompose into N_2 releasing a large amount of energy with highest release for N_8 . A number of phosphorus clusters with closed-shell structure are proposed to be more energetic than P_4 [13–16] theoretically. While the N_{20} clusters are highly unstable, the P_{20} clusters are found to have higher stability. The prediction for P_{20} and the experimental existence of the $As@Ni_{12}@As_{20}$ are indicative of the possible existence of large As clusters.

The stability of the As_n clusters were theoretically studied by Shen and Schaefer [17] for sizes 2, 4, 12, and 20. However, they concluded that As_{20} would be energetically competitive with five As_4 clusters. Our recent calculations done on $As@Ni_{12}@As_{20}$ and As_{20} indicates that As_{20} is stable both electronically and vibrationally. Its most favored dissociation channel is the As tetramer as predicted by Shen and Schaefer [17]. In this work we report our study of other possible As cages and their electronic and vibrational stability. It is possible that the ground state structure of the As clusters considered here

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may not conform to a cage-like structure. However, we have restricted our study only to cage structures and also to the ones which may break up into integral number of tetramers. The focus is on finding vibrationally stable symmetric cages and the energy of dissociation into tetramers. Also we have restricted the cage structures in which the As atoms are in threefold coordination as seen in the experimentally obtained As shell of the $[\text{As}@\text{Ni}_{12}@\text{As}_{20}]^{-3}$ cluster. In this case, the As atoms are sp^3 hybridized with a lone pair and 3 half-filled orbitals which form σ bonds with its nearest neighbors. Shen and Schaefer have shown that the tetrahedral As_4 is a very stable cluster. This follows directly from the considerations that As atoms are sp^3 hybridized and prefer threefold coordination with lone pairs. A similar feature was also seen in $\text{As}@\text{Ni}_{12}@\text{As}_{20}$ cluster [18]. Moreover, the 20 valence electrons associated with the As_4 molecule is known to correspond to a magic number in metallic clusters and this aspect may further contribute to the stability of the tetramer [19].

Our density functional theory [20,21] based calculations were performed at the all-electron level within the generalized gradient approximation (GGA) [22] to describe the exchange-correlation effects. The calculations have been performed using the NRLMOL package [23–25] which employs a Gaussian basis set where the exponentials are optimized for each atom [26]. The basis for the As contains 7s, 6p, and 4d type contracted Gaussians along with a d-type polarization function. The package also employs a variational mesh to calculate the integrals accurately and also efficiently. The Hartree potential is calculated analytically. The self-consistency cycle was carried out till the energies converged to 1.0×10^{-6} Hartree. The symmetry restricted geometry optimization was carried out using the LBFGS scheme till the forces were smaller than 0.001 a.u. The vibrational frequencies are calculated by introducing small perturbation to the equilibrium geometry in the Cartesian directions for all atoms and calculating forces. From these, the dynamical matrix is calculated by finite difference method, diagonalization of which yields the frequencies [27].

We present the optimized structures of the $\text{As}_{4,8,20,28,32,36,60}$ fullerene-like cages in Figs. 1 and 2. The range of nearest neighbor As–As bond lengths, the bond angles, and the symmetry of the molecules are listed in Table 1. The bond lengths of the cages lie between 2.43 and 2.74 Å. The As–As bond length in the experimentally observed $\text{As}@\text{Ni}_{12}@\text{As}_{20}$ cluster is 2.75 Å which is close to the largest bond-length seen in the As cages. The bond angles for the smallest cluster is 60° which increases to the range 104° – 130° for the larger cages. The As_4 and As_8 clusters have T_d and O_h point symmetry. The bond lengths and angles do not vary in these structures due to their symmetry. The As_{20} has a dodecahedron structure made up of 12 pentagons. The

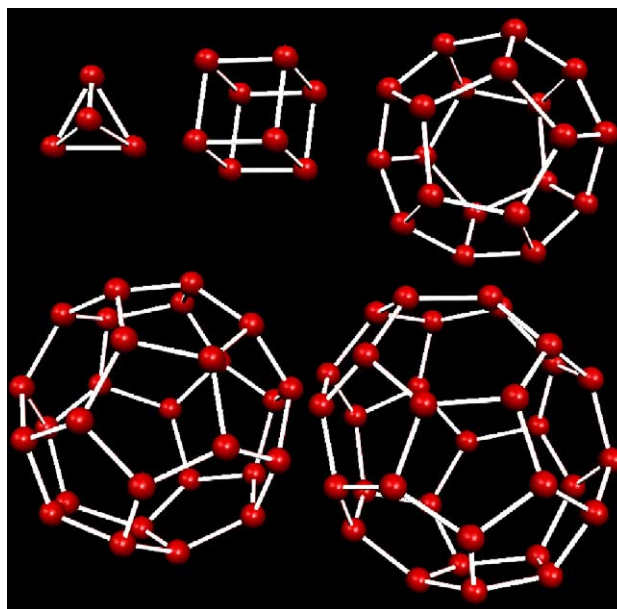


Fig. 1. Structures of As_4 , As_8 , As_{20} , As_{28} , and As_{32} .

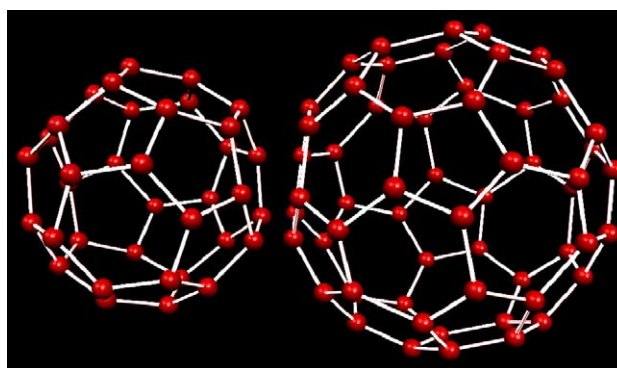


Fig. 2. Structures of As_{36} and As_{60} .

28-atom cluster also has T_d symmetry and has three inequivalent atoms. The 32-atom cluster has an unusual cage-like structure which has an elongated structure. The symmetry for the As_{32} cluster allows for cyclic permutations plus non cyclic permutations followed by inversion. The As_{36} has D_{6h} symmetry while the 60-atom cluster has a structure similar to the C_{60} structure. However, the As_{60} cluster is much larger than the C_{60} in size. Apart from the As_{32} , all the clusters from $n = 20$ onward are spherical in shape. While As_{20} is made up of pentagons, the 28-, 32-, 36-, 60-atom clusters have both pentagonal and hexagonal faces. From Table 1, it becomes evident that beyond As_{20} , the bonds of the clusters are not of equal length and some the bonds become stretched in the larger clusters.

The energetics of the clusters are shown in Table 2. The atomization energy, gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO), and the energies of dissociation into

Table 1

Range of values of bond lengths, angles between inequivalent atoms and symmetry groups for the optimized As_n cages

Cage	As–As (Å)	θ (°)	Symmetry
As_4	2.469	60.0	T_d
As_8	2.547	90.0	O_h
As_{20}	2.497	107.9–108.2	I_h
As_{28}	2.462–2.524	105.4–120.9	T_d
As_{32}	2.441–2.536	104.0–124.4	D_3
As_{36}	2.444–2.538	107.2–130.4	D_{6h}
As_{60}	2.427–2.737	108.0–120.0	I_h

Table 2

The atomization energies (AE), HOMO–LUMO gaps and dissociation energies (DE) for the tetramer channel with and without zero-point energy (ZPE) are presented for As_n where $n = 4, 8, 20, 28, 32, 36,$ and 60

Cage	AE (eV)	HOMO–LUMO gap (eV)	DE (eV)	DE including ZPE (eV)
As_4	2.76	4.10	0.00	0.00
As_8	2.62	1.38	1.12	1.17
As_{20}	2.79	1.44	–0.54	–0.48
As_{28}	2.70	1.50	1.68	1.75
As_{32}	2.69	1.41	2.23	2.34
As_{36}	2.67	1.31	3.14	3.24
As_{60}	2.57	1.28	11.29	11.30

All values are in eV.

As_4 are presented in Table 2. The binding energies per atom of the As clusters are centered around 2.7 eV. All the clusters considered here have close shell structures with a relatively large HOMO–LUMO gap and are Jahn–Teller stable. We have also confirmed that all the clusters studied are local minima in the potential energy landscape. The most striking aspect of these clusters is their dissociation energies with respect to As_4 . Although the atomization energies and vibrational frequencies indicate the clusters to be stable, apart from the As_{20} cluster, all the other cages are unstable with respect to As_4 . It may be pointed out that Shen and Schaefer have predicted that As_{20} to be competitive with As_4 clusters. On the other hand, the experimental mass spectrum of the $As@Ni_{12}@As_{20}$ clusters show peaks for all As_xNi_{12} clusters where $x = 1, 21$ indicating that in this cluster the dissociation channel is As monomers rather than tetramers. This was shown due to the unusual change in bonding of the As_{20} in the encapsulated form [18]. The stability of the As_{20} cage compared to all the other cage structures is still surprising.

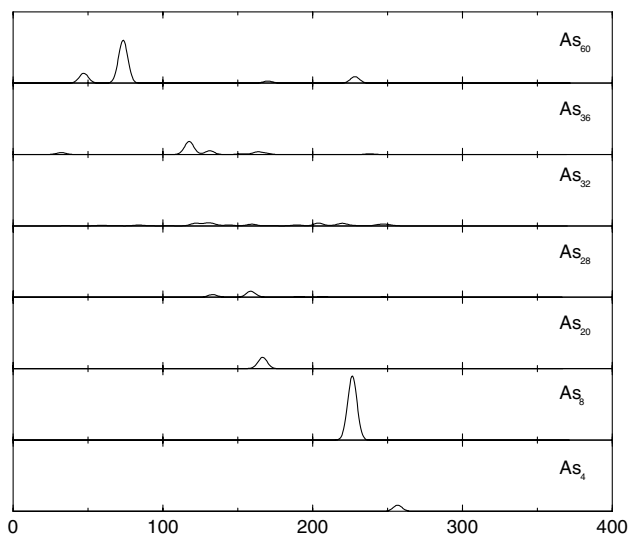
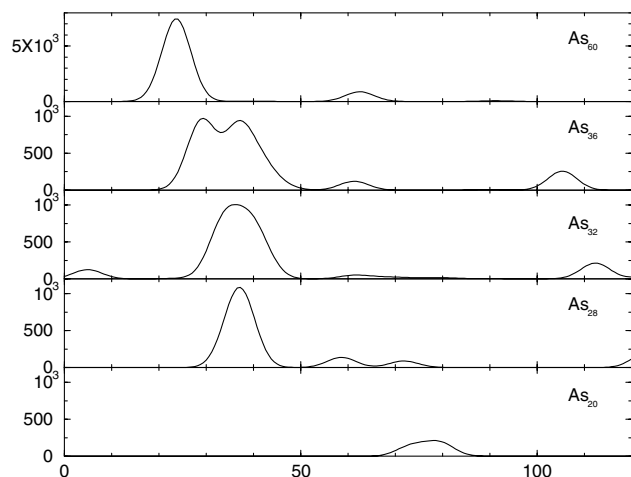
The binding energy of the As_{20} is slightly higher than the As_4 cluster. The As_4 clusters are highly unreactive as evident from the large HOMO–LUMO gap. The atomization energy for As_4 is larger than other clusters while the HOMO–LUMO gap of As_4 is large which indicates the special structural and chemical stability of the As_4 . The As_{20} is characterized by even larger atomization energy which indicates its stability with respect to As_4 . The dissociation energy for the tetramer

channel for all the other clusters are large and positive. The instability of the clusters increases towards the larger sizes. One possible explanation can be the stretching of the bond-angle in the larger clusters. As can be seen from Table 1, the bond angles in the larger clusters of size $n = 28$ onward are twice as large as those in the tetramer.

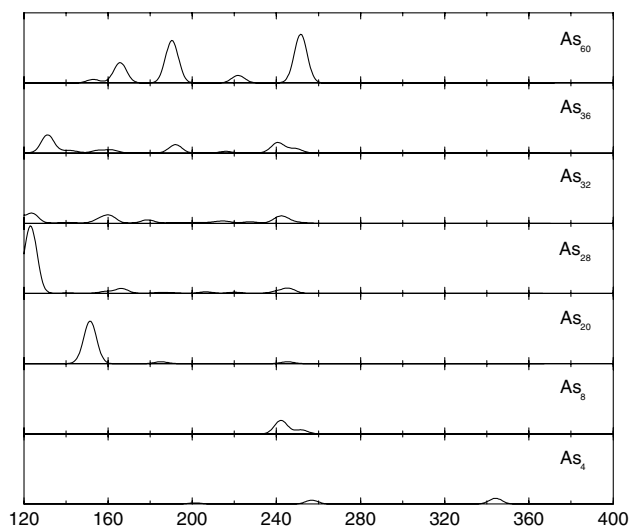
The dissociation of all the As cages except As_{20} is exothermic with respect to As_4 units and the energy released lies between 1 and 11.3 eV. This is by no means large as in the case of nitrogen cages [12] which dissociates into N_2 units. Although N and As occur in the same group, N_2 is more stable due to the formation of triple bond than the As_4 . It may be mentioned here that dissociation of nitrogen cages of size 4 to 20 are found to release energy of the order of 3.0–3.8 Kcal/gm [12].

The predicted infrared (IR) and Raman spectra are presented in Figs. 3–5. These spectra may help in experimental characterization of such cages. The As_4 , As_8 and As_{20} show only one IR active mode each at 257, 227 and 167 cm^{-1} . The larger cages have more dispersion in their bond-lengths and hence in the spring constant resulting in more IR active modes. One noticeable feature is that for the more symmetric cages the IR active frequency goes down across the series. Also while the peaks are high for As_4 and As_8 , the intensities are much diminished for the higher size clusters.

The Raman spectra of the As cages are plotted in the frequency ranges of 0–120 and 120–400 cm^{-1} in Figs. 4 and 5, respectively. The larger clusters show high peaks

Fig. 3. IR spectra of As_4 , As_8 , As_{20} , As_{28} , As_{32} , As_{36} , and As_{60} clusters.Fig. 4. Raman spectra of As_{20} , As_{28} , As_{32} , As_{36} , and As_{60} clusters in the frequency range 0–120 cm^{-1} . The Raman spectra of the As_4 and As_8 clusters do not have any peak in this range. The Raman intensity of the As_{60} is much larger compared to the other clusters and therefore is plotted in a different scale.

in the low frequency region which are several order of magnitude larger than that of the As_4 cluster. The Raman active modes are the ones which change the polarizability of the cages. The frequency of the highest Raman peak decreases as the number of atoms and the radius of the cage increases. The polarizability of the As_{60} is 43.4 per bohr³ per atom and its radius is 6.27 Å. Due to the larger radii of the higher order clusters, the polarizability and its derivative increases which in turn influences the Raman intensity. This trend is seen across the series. The polarizabilities and the average radii of the clusters are shown in Table 3. Since the polarizability is proportional to the volume R^3 , the larger clusters have higher polarizabilities. A comparison with C_{60} fullerene

Fig. 5. Raman spectra of As_4 , As_8 , As_{20} , As_{28} , As_{32} , As_{36} , and As_{60} clusters in the frequency range 120–400 cm^{-1} . All the panels show Raman intensity in the same scale.Table 3
The average radii (Å) and average polarizabilities in Å³ of the As cages

Cage	Radius (Å)	Polarizability (Å ³)
As_4	1.51	18.05
As_8	2.21	35.69
As_{20}	3.50	96.01
As_{28}	4.20	145.19
As_{32}	4.49	170.18
As_{36}	4.76	196.67
As_{60}	6.29	386.41

shows [28] that in the As_{60} the polarizability is about 4–5 times larger. This is consistent with the radii of the two cages – the As_{60} cage is about 2 times larger than the C_{60} cage. The As_{60} shows an intense Raman peak at 24 cm^{-1} corresponding to a H_g mode of vibration which is several times larger than those for As_{28} , As_{32} , and As_{36} . Unlike the IR spectra, the intensity of the highest peaks gets larger as the cluster size grows. For a plane polarized incident light and under the condition that the direction of incident beam, the polarization direction of the incident light and the direction of observation are perpendicular to each other, the Raman scattering cross-section is given by the following equation [29]:

$$\frac{d\sigma_i}{d\Omega} = \frac{(2\pi\nu_s)^4}{c^4} \frac{h(n_i + 1)}{8\pi^2\nu_i} \frac{I_{Ram}}{45}, \quad (1)$$

where ν_s is the frequency of scattered light, n_i is Bose–Einstein statistical factor, ν_i is frequency of the i th mode of vibration, and

$$I_{Ram} = 45 \left(\frac{d\alpha}{dQ} \right)^2 + 7 \left(\frac{d\beta}{dQ} \right)^2 = 45\alpha''^2 + 7\beta'^2, \quad (2)$$

where

$$\alpha'' = \frac{1}{3}(\alpha'_{xx} + \alpha'_{yy} + \alpha'_{zz}),$$

$$\beta'^2 = \frac{1}{2}[(\alpha'_{xx} - \alpha'_{yy})^2 + (\alpha'_{xx} - \alpha'_{zz})^2 + (\alpha'_{yy} - \alpha'_{zz})^2] + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2). \quad (3)$$

Here, α'' and β' are the mean polarizability tensor derivative and the anisotropy of the polarizability tensor derivative, respectively. I_{Ram} is the Raman scattering activity and Q is the normal mode coordinate. The scattering cross section is inversely proportional to the frequency of the vibrational mode and therefore at low frequencies the Raman intensity increases as can be seen from Fig. 4.

The Raman scattering intensities in the frequency range 120–400 cm^{-1} are shown in Fig. 5. All the modes of As_4 show Raman activity since they are, respectively, of A_1 , T_2 and E symmetry. The highest peak for As_4 occurs at 344 cm^{-1} in good agreement with experimental value of 356 cm^{-1} [30]. The experimental Raman spectra of As vapor shows a strong peak at this frequency [30]. The As_4 shows other peaks at 201 and 257 cm^{-1} . The experimental spectrum displays a broad peak at around 250 cm^{-1} which becomes much broader at high temperature. A weighted Raman spectra of the most stable species, namely As_4 and As_{20} shows an asymmetric peak around 250 cm^{-1} similar to the experimental profile. Another peak at 200 cm^{-1} is less intense but is still visible in the experimental spectrum. The calculated As_{20} Raman spectrum shows prominent peaks at frequencies 185, 152, and 79 cm^{-1} . Since the experimental Raman spectrum is measured between 120 and 450 cm^{-1} , the large signatures of the As_{20} can not be discerned from the experimental spectrum. In the high density limit, the peaks of the weighted spectrum shows small peaks at 152 and 79 cm^{-1} whereas around 250 a somewhat broad peak is observed. In the low density limit, the peaks below 152 becomes much more prominent than the peaks at higher frequencies. An experimental measurement of the Raman spectra in the low frequency region can be helpful in identifying the existence of As_{20} .

In conclusion, we have studied the geometry, vibrational stability, energetics and IR and Raman spectra of As cages of size $n=4, 8, 20, 28, 32, 36,$ and 60 to examine the possibility of existence of As cages. We find that all the clusters except As_{20} are unstable against dissociation into As_4 units. The energy released in the exothermic dissociation is significantly smaller than that associated with the isoelectronic nitrogen clusters. We determine the vibrational stability of the clusters and also predict the IR and Raman spectra. The polariz-

ability increases with cluster size. We expect our study will inspire experimental search for such metastable clusters and suggest that the Raman peak at roughly 80 cm^{-1} could be used to identify the existence of As_{20} .

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