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Static dipole polarizabilities of Sc_n ($n \leq 15$) clusters*

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The static dipole polarizabilities of scandium clusters with up to 15 atoms are determined by using the numerically finite field method in the framework of density functional theory. The electronic effects on the polarizabilities are investigated for the scandium clusters. We examine a large highest occupied molecular orbital — the lowest occupied molecular orbital (HOMO–LUMO) gap of a scandium cluster usually corresponds to a large dipole moment. The static polarizability per atom decreases slowly and exhibits local minimum with increasing cluster size. The polarizability anisotropy and the ratio of mean static polarizability to the HOMO–LUMO gap can also reflect the cluster stability. The polarizability of the scandium cluster is partially related to the HOMO–LUMO gap and is also dependent on geometrical characteristics. A strong correlation between the polarizability and ionization energy is observed.

Keywords: Sc_n cluster, static dipole polarizability, electronic property, density functional theory
PACC: 3640, 3520M, 3640C, 7115M

1. Introduction

Polarizability represents one of the most important observables for understanding the electronic properties of clusters, since it is very sensitive to the delocalization of valance electrons, as well as cluster structure and shape. The polarizabilities of atoms and free clusters have been extensively studied both theoretically and experimentally during the past few years.[1−4] Furthermore, polarizability is one of the characteristic properties of clusters that can be obtained in experiments, and it can provide information on the bonding and geometrical features of the clusters. A thorough understanding of the polarizabilities from theoretical calculations is therefore important in cluster science.

The jellium model has been successfully used to study the polarizability of large metallic clusters. However, for semiconductor and some transition metal (TM) clusters, bonding and geometrical effects cannot be incorporated into the jellium model. In addition, Yang and Jackson[5] have confirmed that there exists a large difference in the polarizability of a small copper cluster between calculated and observed values.[5] This arises from the uncertainty in the correct ground state structure with the atomic structures obtained by using an empirical potential. Alternatively, *ab initio* calculations based on quantum chemistry are needed. In connection to this it would be very useful to obtain cluster structures at a more reliable level of theory, such as density functional theory (DFT).

However, only Torrens[6,7] has calculated the molecular dipole–dipole polarizabilities of Sc_n, C_n and endohedral $Sc_n@C_m$ (n = 1–7, 12) clusters by using a polarization model based on interacting dipoles. He has concluded that a calibration of the *ab initio* calculations is needed as a primary standard to reduce the large difference between POLAR and PAPID programs. To date there has been no systematic theoretical investigation on the polarizabilities of scandium clusters by using DFT. The structural, electronic and magnetic properties of Sc clusters with up to 16 or 18 atoms obtained from density functional DMol calculations were recently reported.[8,9] We have also recently studied the stability, the electronic and the magnetic properties of Sc_n, Y_n and La_n (n=2–10) clusters by using DFT.[10] Although by using different calculation programs and the DFT method, our results are close to those of previous studies[8,9] on the stability, the structural, and the magnetic prop-

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erties of scandium clusters, the significant properties of static dipole polarizabilities of scandium clusters, which are strongly related to the electronic structure property and the measurable experiment results, have not yet been studied. We now extend our studies on the polarizabilities of noble-metal clusters[11,12] to scandium clusters with up to 15 atoms. Thus, in the present paper, the static dipole polarizability properties of Sc_n ($n \leq 15$) clusters, including the dipole moment, static polarizability, polarizability anisotropy, size-dependence of polarizability and the effect of electronic structure on polarizability are investigated by using the numerically finite field (FF) method in the framework of DFT.

2. Computational details

2.1. Geometrical optimization

It is well known that electron correlation plays a primary role in determining molecular polarizabilities. In connection with this, the DFT method has shown significant improvement on Hartree–Fock results in the calculations of molecular polarizabilities and hyperpolarizabilities.[13,14] However, the geometries, the electronic properties and polarizabilities of molecules or clusters are quite sensitive to the exchange-correlation functional used in the DFT method. For these reasons the DFT level necessary to give reliable results first needs to be determined. Therefore we calculate the spectroscopic constants for a Scandium dimer and trimer by using several different exchange-correlation functionals combined, respectively, with the LANL2DZ and with CEP-121G basis set. Comparing the calculated results of Sc_2 and Sc_3, separately, with the measurements and the previous theoretical calculations, shows that the selected BP86/CEP-121G DFT level can be reliably used to predict the properties of the larger Sc_n clusters. The detailed calculations can be found in Ref.[10]. Therefore, in the present work, all geometry optimization and vibrational frequency calculations for the Sc_n ($n \leq 15$) clusters are performed by using the DFT at the BP86/CEP-121G level. The CEP-121G basis set is a compact effective potential[15] in which the dependence of spin-orbit effects is averaged out, and the valence electrons of Sc are considered to be $3s^2 3p^6 3d^1 4s^2$.

Since there is controversy about the geometrical shape of TM clusters containing a few atoms, the total energy has been calculated and the geometrical structure with the lowest energy is chosen as the ground state geometry. When the cluster has less than six atoms, a default SCF convergence of 10^{-8} is used. For the larger clusters ($n \geq 6$), the computation cannot converge, but to a 10^{-6} tolerance. The thresholds for convergence are 0.00045 a.u. and 0.0003 a.u. for the maximum force and root-mean-square force, respectively. All of the calculations are performed under spin-unrestricted conditions. The ground states of pure Sc clusters have the lowest possible multiplicity that can be obtained for a given number of unpaired electrons. And all isomers are confirmed to be the local minima by the harmonic vibrational frequency calculations.

2.2. Finite field treatment

The static response properties of a molecule can be defined in two different ways. The field-dependent energy $E(\boldsymbol{F})$ can be expanded in a series

$$E(\boldsymbol{F}) = E(0) - \sum_i \mu_i F_i - \frac{1}{2}\sum_{ij} \alpha_{ij} F_i F_j - \ldots, \quad (1)$$

where $E(0)$ is the total energy of the molecular system in the absence of the electric field, the quantities F_i are components of the applied field in different directions ($i, j = x; y; z$), and μ_i and α_{ij} are components of the static dipole moment and polarizability tensor, respectively.

Alternatively, the static response properties of a molecule can be defined by expanding the field-dependent dipole moment, calculated from the field-induced charge distribution, as a series of the external electric field

$$\mu_i(\boldsymbol{F}) = -\frac{\partial E(\boldsymbol{F})}{\partial F_i} = \mu_i(0) + \sum_j \alpha_{ij} F_j + \ldots. \quad (2)$$

The equivalence of these two definitions for a field-independent basis set accords with the Hellmann–Feynman theorem.[16] We have used the dipole moment expansion in our density functional calculation. The polarizability is defined by

$$\alpha_{ij} = \frac{\partial \mu_i(\boldsymbol{F})}{\partial F_j} = -\frac{\partial^2 E(\boldsymbol{F})}{\partial F_i \partial F_j}, \quad i, j = (x, y, z). \quad (3)$$

Using the finite difference expressions for the first and second derivatives, we find the diagonal elements of the polarizability tensor α_{ii} from the dipole moment $\mu_i(F)$, or from the total energy $E(\boldsymbol{F})$ at $\boldsymbol{F} = 0$, and $\boldsymbol{F} = \pm\delta F_i$ applied along the i-th axis.

In the present work, the external field is applied along the x, y, z axes with a magnitude of 0.005 a.u and a tighter self-consistent field (SCF) convergence of 10^{-8} Hartree is adopted as a criterion. These values have been found to yield well-converged results for the polarizability. The measured data in the experiment are usually the mean polarizabilities ($\langle\alpha\rangle$), which can be obtained by the trace of the polarizability tensor to be

$$\langle\alpha\rangle = \frac{1}{3}\mathrm{tr}(\alpha_{ij}) = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad (4)$$

and the polarizability anisotropy ($|\Delta\alpha|$) can be calculated to be

$$\begin{aligned} |\Delta\alpha|^2 &= \frac{3\,\mathrm{tr}\,\alpha^2 - (\mathrm{tr}\,\alpha)^2}{2} \quad \text{(general axes)} \\ &= \frac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 \\ &\quad + (\alpha_{yy} - \alpha_{zz})^2] \quad \text{(principal axes)}. \end{aligned} \qquad (5)$$

The FF approach[17] implemented within the GAUSSIAN 03 package[18] is used to calculate the dipole moment and static electric polarizability components at the BP86/CEP-121G level. In the DFT framework, BP86 functionals combined with the CEP-121G basis set can give a good description of the bonding as well as the geometrical and electronic features of TM clusters. Thus, BP86/CEP-121G methods are expected to describe the scandium clusters polarizabilities well at a level of acceptable computational time.

3. Results and discussion

3.1. Equilibrium geometry and relative stability

The equilibrium geometries are obtained at the BP86/CEP-121G level of DFT for Sc_n ($n \leq 15$) clusters. Based on the optimized geometries, the static polarizabilities of scandium clusters are investigated by using the FF method. The static polarizability is a ground state property that is close to the geometrical characteristic and can vary significantly between different isomers with nearly the same energies. Therefore it is important to identify the correct ground-state structure. The optimized structures of these ground-state clusters with the energy minima, composed of 3–15 atoms, are illustrated in Fig.1. For all Sc_n ($n > 3$) clusters, both the lowest-energy structure and their isomers which are not depicted here are all closed compact arrangements. The detailed geometrical parameters for the lowest-energy structures of Sc_n ($n \leq 15$) clusters are listed in Table 1.

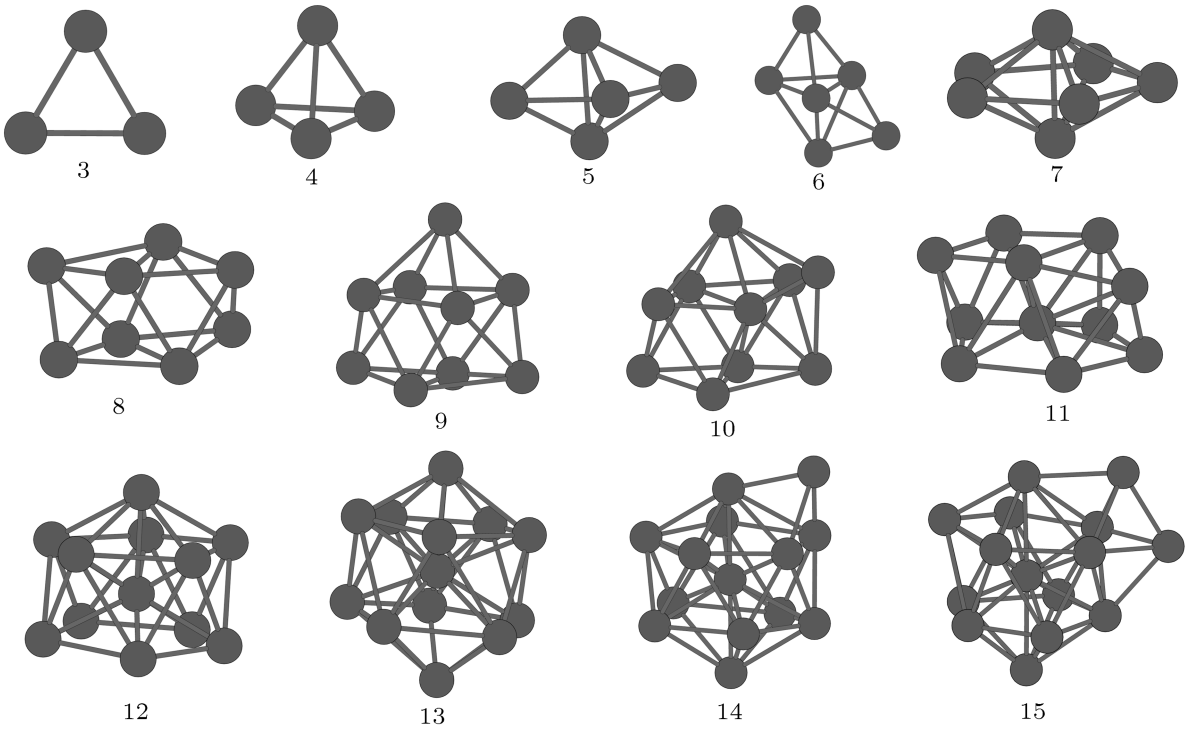


Fig.1. The optimized lowest-energy structures of Sc_n ($n = 3$–15) clusters.

Table 1. The calculations of symmetry (sym.), ground state, average bond length (R), binding energy (E_b), static dipole moments (μ), mean static polarizabilities per atom ($\langle\alpha\rangle/n$), polarizability anisotropy ($|\Delta\alpha|$), HOMO–LUMO gap (E_{gap}), and ionization energy (V_{IP}) of the lowest-energy structures for the Sc_n ($n \leq 15$) clusters.

n	sym.	state	R/Å	E_b/eV	μ/Debye	$\langle\alpha\rangle/n$/Å^3	$\lvert\Delta\alpha\rvert$/Å^3	E_{gap}/eV	V_{IP} /eV
1		^2D			0.000	17.190	1.354	0.586	2.631
2	$D_{\infty h}$	$^5\Sigma u$	2.64	1.376	0.000	17.248	19.296	0.268	5.320
3	D_{3h}	$^2A_1'$	2.84	3.442	0.157	14.731	12.455	0.513	5.493
4	S_4	^3A	2.79	6.343	0.097	11.535	2.160	0.490	5.205
5	C_{3v}	^2A	2.88	8.918	0.051	11.915	10.197	0.431	4.814
6	C_{2v}	$^5A_1$	2.97	11.520	0.031	12.511	10.455	0.358	4.716
7	D_{2h}	^2A	2.86	14.873	0.058	10.097	11.211	0.369	4.751
8	C_{2v}	^5A	3.04	17.469	0.495	11.200	21.092	0.397	4.562
9	C_s	^2A	2.99	20.112	0.151	11.412	15.410	0.257	4.653
10	C_{3v}	^3A	3.10	23.031	0.453	9.571	10.469	0.309	4.602
11	C_2	$^2A'$	3.15	25.552	0.469	11.213	17.257	0.350	3.738
12	C_1	$^5A_1$	3.19	28.037	0.204	9.027	9.718	0.286	4.235
13	C_{2h}	^{20}A	3.05	31.991	0.438	8.165	8.249	0.418	4.507
14	C_1	$^9A_1$	3.21	34.422	0.287	9.257	11.367	0.238	3.968
15	C_1	^4A	3.28	37.533	0.386	8.962	18.846	0.292	3.901

In order to analyse the stability and the size-dependent physical properties of Sc clusters, we calculate the total binding energy (E_b), binding energy per atom (E_b/n), fragmentation energy [$D(n, n-1)$], and second-order difference in total cluster energy [$\Delta_2 E(n)$]. Figure 2 shows that the binding energy per atom of the ground-state generally increases with increasing cluster size. Figures 2 and 3 show $D(n, n-1)$ and $\Delta_2 E(n)$ of the Sc clusters, respectively. The values of the magic number (n) for the local stability maxima are found to be 4, 7, 10 and 13, i.e. $n = 4$, 7, 10, and 13, implying that these clusters are obviously more stable than their neighbouring clusters. The behaviour of the variations is different from that of alkali or noble metal clusters, which exhibit characteristic shell oscillations with respect to cluster size. The properties of the geometrical structures cannot be understood in terms of the electronic shell jellium model, but they can be understood by the model of geometry dense gather. Both figures 2 and 3 show that the maximal magic number for the relative stability is 13, i.e. $n = 13$ among the Sc_n ($n \leq 15$) clusters. Our results for ground-state structures and relative stability agree fairly closely with those presented by two recent papers on the study of Sc clusters using DFT within the DMol3 package.[8,9]

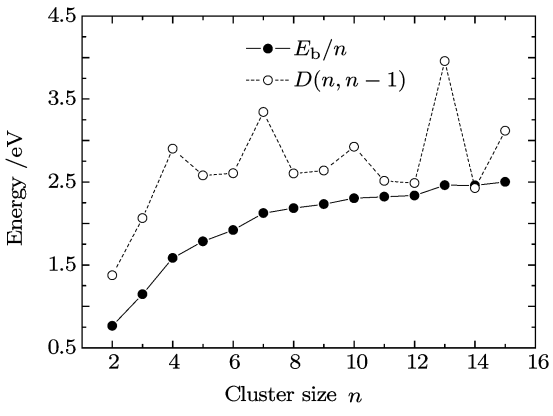


Fig.2. The size dependences of the calculated binding energy per atom (E_b/n) and fragmentation energies [$D(n, n-1)$] of the lowest-energy Sc_n ($n \leq 15$) clusters.

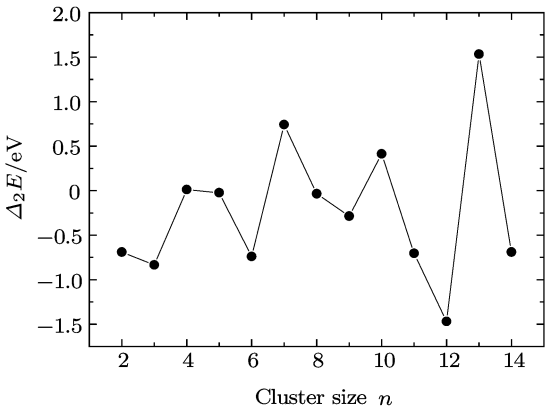


Fig.3. The second-order difference in total energy ($\Delta_2 E$) of the lowest-energy Sc_n ($n \leq 15$) clusters versus cluster size.

3.2. Static dipole polarizability

Table 1 gives the calculated data of dipole moments, mean static polarizabilities and polarizabil-

ity anisotropy for Sc_n ($n = 1 - 15$) clusters. In order to explore the relationship between the electronic effect and polarizability, we also calculate the energy gap between the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) gap, as well as the ionization energy (Table 1). Our calculated static dipole polarizability for atomic Sc is 115.463 a.u. (17.190 Å^3) (1 Å=0.1 nm). In another theoretical study, a linear response time-dependent density functional theory (TDDFT) method gives 105.88 a.u. (15.763 Å^3),[19] Torrens[7] found 16.893 Å^3 (113.468 a.u.) for the polarizability of the free Sc atom. Nonrelativistic calculation and Douglas–Kroll relativistic corrections gave 123.60 a.u. (18.401 Å^3) and 121.22 a.u. (18.047 Å^3), respectively.[20] Thus our calculated value for the Sc atom agrees with other calculations.

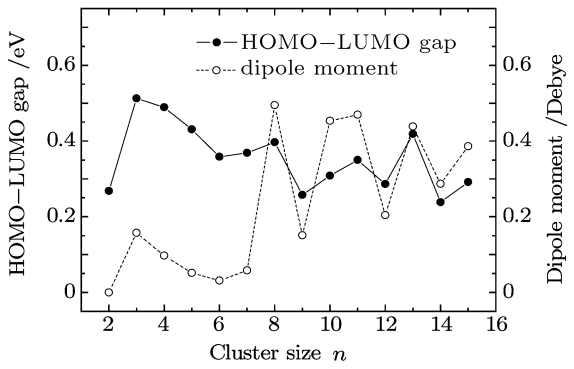


Fig.4. The HOMO–LUMO gap and the dipole moments of Sc_n ($n \leq 15$) clusters, each as a function of cluster size.

The dipole moments calculated by using the FF method are generally too small in those optimized structures. Furthermore, our results are generally lower than those of Torrens's using the POLAR and PAPID program, which is an interaction-induced dipole polarization model for Sc_n (n = 1–7, 12) clusters.[6,7] This difference arises from the use of different theoretical methods and different geometric structures. In addition, as discussed by Torrens in his paper, a suitable calculation method requires a calibration standard.[7] The dipole moments may also be influenced by the temperature effect.[5] In our theoretical calculations a temperature of 0 K has been assumed. Because the obtained dipole moments are generally very low, we cannot observe the obvious relationship between the dipole moment and symmetry as the cluster size increases. For some semiconductor or TM clusters, higher symmetry leads to relatively low dipole moments for different geometrical structures.[21−23] However, the dipole moments found from our calculations are closely related to the electronic structure. In Fig.4, the dipole moments are plotted together with the HOMO–LUMO gap as a function of cluster size. For all of the Sc_n ($n \leq 15$) clusters, a large HOMO–LUMO gap corresponds to a large dipole moment. Therefore, useful information on the electronic structures of clusters can be obtained from the dipole moments.

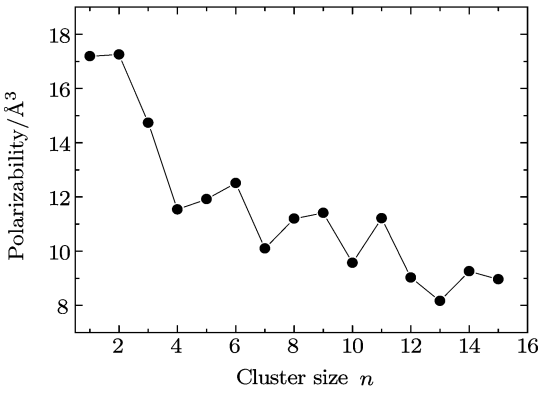


Fig.5. Calculations of the static polarizability per atom of the lowest-energy Sc_n ($n \leq 15$) clusters as a function of cluster size.

We now explore the size-dependent polarizability of the lowest energy structures of Sc clusters. The variation of computed values for polarizabilities with the number of atoms in the cluster is shown in Fig.5. As a reference, we include the bulk limit for the polarizability, estimated from the Clausius–Mossotti relation: $\alpha = \dfrac{3(\varepsilon-1)\nu}{4\pi(\varepsilon+2)}$, in which ν is an elementary volume per atom in the crystalline state, and ε is the bulk relative dielectric constant. For metal, ε approaches infinity and the dependence of α on ε disappears. In this work, the ν value used for Sc is 15.0 Å^3/atom and the polarizability α of the bulk Sc is calculated to be 3.581 Å^3/atom. The present mean polarizability of Sc clusters is larger than the bulk value. The clusters are more polarizable than their bulk counterparts. Our conclusion is consistent with Torrens' results for the polarizability of the Sc atom.[6,7] The high polarizability of small clusters may be attributed to the dangling bonds in the surface of the cluster. They tend to have higher coordination numbers than the crystalline counterparts.[24] For example, the polarizabilities of alkali metal and some semiconductor clusters have also been shown to significantly exceed the bulk limit and tend to decrease with increasing cluster size.[24−26]

Figure 5 shows that the static polarizability per atom decreases slowly with the increase of cluster size, accompanied with some local oscillations. By increasing the cluster size, the polarizabilities of Sc_n ($n \leq 15$) clusters exhibit local minima to be 4, 7, 10 and 13, i.e. $n = 4$, 7, 10, and 13 which all have small polarizabilities compared with their neighbours in cluster size. The minimum polarizability principle (MPP) states that any system evolves naturally towards a state of minimum polarizability.[27−29] By applying the MPP to chemical reactivity, we conclude that those clusters with the local minimum polarizability are more stable than the neighbouring clusters. This is also consistent with the above discussion on the stability of scandium clusters.

The calculated polarizability anisotropies for Sc clusters are given in Table 1 and are plotted as a function of cluster size in Fig.6. The polarizability anisotropy is similar to the calculated mean polarizability per atom. Local minima are also found to be 4, 10 and 13, i.e. $n = 4$, 10, and 13. This is also accordant with the above discussion on stability. Therefore polarizability anisotropy is also obviously related to cluster stability.

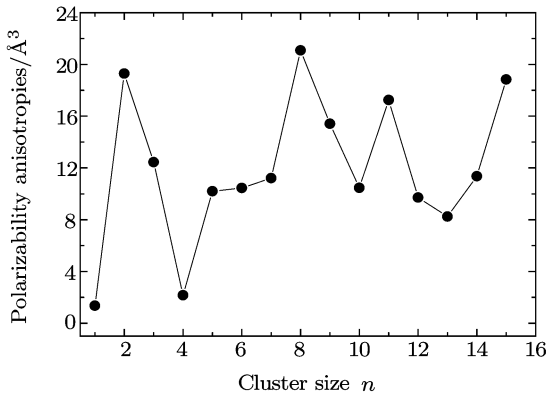


Fig.6. Calculated polarizability anisotropies of the lowest-energy Sc_n ($n \leq 15$) clusters as a function of cluster size.

We discuss further the relationship between the polarizability and the electronic structures of clusters. The electronic properties such as the HOMO–LUMO gap and ionization energy usually have some influence on the cluster polarizability. For example, simple perturbation theory suggests that polarizability should be inversely correlated to the HOMO–LUMO gap.[24] In the perturbation theory, polarizability is expressed as a sum of contributions from all excited states.[30] A clear correlation between polarizability and the HOMO–LUMO gap holds if the dominant excited state is mainly described by the HOMO-to-LUMO transition.[22] In this study, however, such a correlation is not observed obviously for Sc clusters in Table 1. But another simple correlation is observed between the polarizability and the HOMO–LUMO gap for some clusters with special sizes. Figure 7 plots the ratio of mean static polarizability to the HOMO–LUMO gap as a function of cluster size. As shown in Fig.7 and Table 1, the clusters with $n = 2$, 6, 9, and 14 have a much higher ratio than those neighbouring clusters. This arises from a large polarizability and a small HOMO–LUMO gap, respectively.

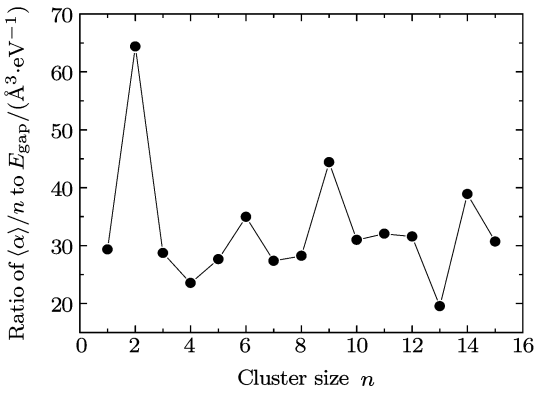


Fig.7. The ratio of polarizability per atom ($\langle\alpha\rangle/n$) to the HOMO–LUMO gap (E_{gap}) of Sc_n ($n \leq 15$) clusters against the cluster size.

The much lower mean static polarizability/HOMO–LUMO gap ratios of the clusters with magic numbers $n = 4$, 7, 10, and 13 cannot be understood by the above correlation, although these clusters have relatively small polarizabilities. Moreover, we find that some clusters with a small (large) HOMO–LUMO gap tend to have small (large) polarizability. For example, the HOMO–LUMO gap of Sc_7 is smaller than that of Sc_8, while the polarizability and the polarizability anisotropies of the Sc_7 are also smaller than those of Sc_8. The same relationships are found for the Sc_{11} and the Sc_{12} clusters. Thus, the Sc_{11} cluster has a larger HOMO–LUMO gap than the Sc_{12} cluster, while the polarizability and the polarizability anisotropies of Sc_{11} are also larger than those of the Sc_{12} cluster. Therefore the polarizability only partially arises from the HOMO-to-LUMO transition, and significant contributions to the polarizability originate from other transitions. This makes the correlation between the HOMO–LUMO gap and the polarizability for Sc clusters unclear. Similar results have also been reported

for silicon, copper and gold clusters.[22,31] This may be attributed to their slight structural difference although the observed structures of the Sc_n ($n > 3$) clusters are all closed compact arrangements. For Sc_7 (Fig.1), the lowest energy structure is the pentagonal bipyramid, which is a more compact geometry than the triangular dodecahedron (bisdisphenoid) structure of Sc_8. Furthermore, for Sc_{11}, the optimized structure is a layered structure composed of two layers: one has six atoms and the other possesses five atoms, while a more compact bell-shaped structure is favourable for Sc_{12}. The polarizability per atom in a cluster is a quantity related to its volume per atom. The more compact structures have relatively few and short bonds, which leads to a more compact cluster and tighter bonding of the valence electrons. Thus, a smaller volume is obtained in the more compact structure, which leads to a smaller polarizability and polarizability anisotropy. Thus the polarizability of the Sc clusters is also closely related to the geometrical characteristics, except for the stability and the HOMO–LUMO gap. In addition, our optimized isomers of Sc clusters do not include planar and other non-compact structures, such as the prolate configuration of Ge clusters and the hollow cage of Au clusters.[21,22] The lowest-energy ground state structures are all compact arrangements for Sc_n ($n > 3$) clusters. Therefore at present we cannot discuss the effects of geometrical arrangements on cluster polarizability.

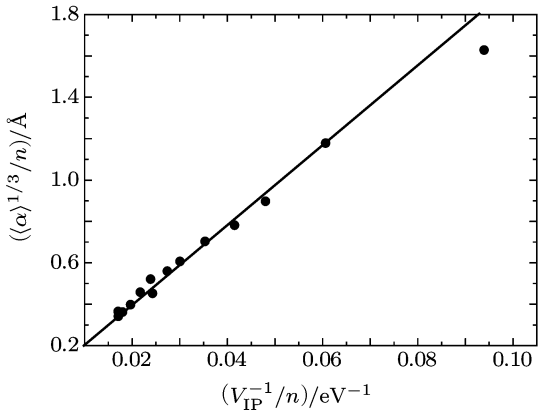


Fig.8. The relationship between polarizability ($\langle\alpha\rangle^{1/3}/n$) and ionization potential ($V_{\rm IP}^{-1}/n$) of the lowest-energy for Sc_n ($n = 2$–15) clusters.

The ionization energy is a quantity indicating the capability of a cluster to lose one valence electron. A recent study by Chandrakumar *et al* [32] has revealed that the cube root of the polarizability per atom ($\langle\alpha^{1/3}/n$) is inversely proportional to the ionization energy per atom ($V_{\rm IP}^{-1}/n$) for both sodium and lithium clusters of $n = 2 - 10$. This relationship means that higher ionization energy leads to a stronger binding of the valence electron and that the static polarizability is a measure of the distortion of the electron density under an external static electric field. In order to explore the correlation between polarizability and ionization energy, the variation of $\langle\alpha\rangle^{1/3}/n$ with $V_{\rm IP}^{-1}/n$ is investigated and displayed in Fig.8. The polarizability of Sc_n clusters is clearly related to the $V_{\rm IP}$, and a strong correlation is observed in which $\langle\alpha\rangle^{1/3}/n$ increases monotonically and linearly with $V_{\rm IP}^{-1}/n$ increasing, except that the ratio of the Sc_2 dimer seems anomalously low with respect to this trend. In addition, the ionization energy is found to be correlated with the static polarizability of the Sc clusters, just like the cases for gold, sodium and lithium clusters.[22,32]

4. Conclusions

The static dipole polarizability properties including the dipole moment, mean static polarizability, and polarizability anisotropy of the lowest-energy structure of Sc_n ($n \leq 15$) clusters in the framework of the DFT and the FF method are studied. Electronic effects on the polarizability such as the HOMO–LUMO gap and ionization energy have also been explored. At the BP86/CEP-121G DFT level, the lowest-energy structures for the Sc_n ($n > 3$) clusters are all found to be closed compact arrangements. An analysis of energetics shows that the Sc_n clusters with $n = 4$, 7, 10, and 13 atoms are more stable. Their stabilities are related to the polarizability properties such as the mean static polarizability per atom, polarizability anisotropy, and the ratio of mean static polarizability to the HOMO–LUMO gap. The calculated dipole moments are related to the electronic structures in which a large HOMO–LUMO gap contributes to a large dipole moment. The static polarizability per atom decreases slowly with the increase of cluster size, accompanied with some local oscillations. Then the MPP is used to characterize the stability of clusters. The polarizabilities of clusters are not only related to the HOMO–LUMO gap but also dependent on geometrical characteristics. The higher ratios of the mean static polarizability to the HOMO–LUMO gap for some clusters arise from a larger polarizability

and a smaller HOMO–LUMO gap than those of the clusters of neighbouring sizes. More compact structures often lead to smaller polarizabilities. The polarizabilities of clusters are clearly related to the ionization energy and strongly correlated monotonically with $\langle\alpha\rangle^{1/3}/n$ and linearly with V_{IP}^{-1}/n for Sc_n ($n > 2$) clusters.

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