

# Theoretical study of the structure of silver clusters

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Neutral silver cluster isomers  $\text{Ag}_n$  ( $n=2$  to 12) were studied by Kohn–Sham density functional theory. There is a strong even-odd oscillation in cluster stability due to spin subshell closing. Nearest-neighbor interatomic distances do not evolve continuously from the diatomic (2.53 Å) to the bulk (2.89 Å). After adding an empirical correction to the calculated values, we estimate that they are always near 2.68 Å for  $3 \leq n \leq 6$ , and near 2.74 Å for  $7 \leq n \leq 12$ . We find several low-energy isomers at all cluster sizes larger than seven atoms with one exception:  $\text{Ag}_{10}$  has a  $D_{2d}$  twinned pentagonal bipyramid isomer predicted to be 0.20 eV more stable than any other isomer. The ellipsoidal jellium model predicts rather well the shapes of stable silver clusters. Other models (extended Hückel, empirical potential) fail to reproduce the energy ordering of cluster isomers. The structural attributes of low-energy silver cluster isomers  $\text{Ag}_n$  ( $n \geq 7$ ) are, in decreasing order of importance: a high mean coordination; a shape that conforms to the ellipsoidal jellium model; and uniformity in atomic coordinations. © 2001 American Institute of Physics.  
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## I. INTRODUCTION

There is continued interest in making and studying small atomic clusters. Many series of elemental clusters have been characterized in detail with a variety of experimental techniques. Properties that have been measured include: binding energies,<sup>1,2</sup> ion mobilities,<sup>3–5</sup> ionization potentials,<sup>6,7</sup> and more generally, electron binding energies,<sup>8,9</sup> magnetic moments,<sup>10</sup> electron spin densities,<sup>11</sup> UV-visible photoabsorption spectra,<sup>12</sup> vibrational modes characterized by Raman,<sup>13,14</sup> infra-red photodissociation,<sup>12,15,16</sup> and zero electron kinetic energy (ZEKE) spectroscopy,<sup>17</sup> and chemical reactivity towards small molecules.<sup>18–20</sup> Cluster properties vary with size and differ, sometimes dramatically, from those of the bulk,<sup>6,10,21</sup> but it is very hard to organize and understand the data accumulated about clusters without knowing their *geometrical structure*, as was pointed out many times (see, for example, Ref. 20). Structure is the basic model chemists use, yet very little is known about the structure of clusters in general. Elucidating the structure of atomic clusters is a challenging problem that requires piecing together information from different experiments and theory. There are only a few elements for which we currently have reliable structural information over a significant size range: carbon,<sup>22,23</sup> silicon,<sup>5,14</sup> and, to a lesser degree, niobium<sup>24</sup> and silver (see the following). Indirect information about the structure of many clusters has been derived from adsorption experiments<sup>20,25,26</sup> (for Fe, Co, and Ni), and ion mobilities.<sup>27</sup>

Silver clusters are particularly interesting for a number of reasons. First, silver clusters and small particles have practical importance because of their role in photography,<sup>28</sup> in catalysis,<sup>15</sup> and their potential use in new electronic materials.<sup>29</sup> Also, the enhanced Raman effect observed for adsorbates on silver surfaces seems to have a cluster

counterpart.<sup>30</sup> Second, the geometric structures of clusters of silver are among the best known after those of carbon and silicon. The triatomic has a  $D_{3h}$  ground state geometry which undergoes Jahn–Teller (JT) distortion leading to three equivalent  $C_{2v}$  obtuse isosceles triangle minima,<sup>31–33</sup>  $\text{Ag}_4$  is a  $D_{2h}$  symmetry planar rhombus,<sup>34</sup>  $\text{Ag}_5$  is a  $C_{2v}$  planar trapezoid;<sup>35</sup> two isomers of  $\text{Ag}_7$  have been identified, a  $C_{3v}$  tricapped tetrahedron<sup>36</sup> and a  $D_{5h}$  pentagonal bipyramid;<sup>37,38</sup> and there have been tentative structural assignments for  $\text{Ag}_n$  ( $n \leq 9$ ).<sup>39</sup> Third, although the structure of  $\text{Ag}_3$ ,  $\text{Ag}_4$ ,  $\text{Ag}_5$  and  $\text{Ag}_7$  are fairly well established, *structureless* theoretical models that ignore the precise positions of nuclei reproduce quite well the size variation of the stabilities and ionization potentials of group IA and IB clusters.<sup>40</sup> One of them, the ellipsoidal jellium model (EJM), gives predictions of the shape of coinage (Cu, Ag, Au) and alkali metal clusters.<sup>41</sup> This raises a number of questions. *Are silver clusters nonrigid?* This is a difficult question<sup>42</sup> which we cannot address satisfactorily by fixed geometry KS-DFT calculations. However, our calculations suggest that  $\text{Ag}_8$ ,  $\text{Ag}_9$ , and possibly  $\text{Ag}_{12}$ , could be nonrigid at room temperature (208  $\text{cm}^{-1}$ ) if we consider the magnitudes of the lowest harmonic frequencies (20 to 50  $\text{cm}^{-1}$ ), and the mean frequency (120  $\text{cm}^{-1}$ ) in relation to the energy separation between the most stable isomers (150 to 600  $\text{cm}^{-1}$ ). *Do many isomers coexist at larger cluster sizes, and if so, do they all have similar shapes?* Our results (Sec. IV A) indicate that  $\text{Ag}_{10}$  has only one abundant isomer, whereas  $\text{Ag}_n$  ( $n=8,9,11,12$ ) most likely exhibit two or more isomers. However, the low energy isomers that possibly coexist share structural similarities (Sec. V). It is possible that the properties of these isomers are indistinguishable, and that they appear as if they were a single chemical species. *Is it important to know details of the structure of silver clusters?* We show (Sec. V) that many important aspects of structure can be expressed with a number of descriptors that is much smaller than the number of degrees of freedom. However,

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one can not ignore nuclear positions entirely, as in the spherical jellium model, or characterize clusters adequately using only, for instance, the three moments of inertia. Furthermore, one needs the optimized geometries of the lowest energy isomer(s) in order to get quantitative accuracy on some properties, such as the ionization potential (Sec. IV C).

Describing clusters that may be nonrigid by means of a *structure* is not straightforward. One can think in terms of descriptors (e.g., moments of inertia) that are dynamically averaged for an individual cluster, or averaged with Boltzmann weight factors over a collection of rigid isomers. The main results reported here were obtained from standard clamped nuclei electronic structure calculations, so we favor the latter point of view. But other descriptions may be more appropriate. For example, one could sample configurations from a constant temperature simulation, map these configurations to the corresponding local minima by steepest descent, characterize the structure of the minima, and give the number of times each minimum is visited during a simulation.<sup>43</sup>

Here we will look at general aspects of structure and make only tentative predictions about specific silver clusters. We are mainly concerned with the energy distribution of isomers, their shapes, their vibrational frequencies, and principles that govern the energetically favored structures. Our main results come from Kohn–Sham (KS) density functional theory (DFT) calculations. We also used simple models in trying to explain different aspects of the *first-principles* results.

The rest of the paper is organized as follows: the next section gives details of the calculations. In Sec. III, we review the literature relevant for us with comparisons to our KS-DFT calculations. The main results of the calculations are in Sec. IV (relative isomer energies, atomization energies, electronic structure, and harmonic frequencies). Section V describes cluster geometry by means of descriptors and tries to account for the KS-DFT structures with simple ideas and models. A summary and conclusions are in Sec. VI.

## II. COMPUTATIONAL DETAILS

We did KS-DFT calculations with the program deMon-KS3p2<sup>44</sup> using the basis sets and scalar relativistic model core potential developed by Andzelm *et al.*<sup>45</sup> The innermost orbitals are described by a model potential and projectors that enforce orthogonality between core and valence, and 17 electrons per silver atom (nominally  $4p^6 4d^{10} 5s^1$ ) are treated explicitly. The grid for numerical evaluation of exchange-correlation terms had 64 radial shells of points, and each shell had 50, 110, or 194 angular points depending on the distance to the nucleus (“FINE” option in deMon). Gradients of the energy were calculated analytically, except for the usual numerical handling of exchange-correlation. Trial geometries were optimized by a standard quasi-Newton method until the norm of the gradient was typically  $5 \times 10^{-5}$  atomic units (a.u.) or less for the lowest energy isomers; for isomers that were clearly high in energy, we stopped optimization when the norm of gradient was about  $5 \times 10^{-4}$  a.u. or even earlier. Even in those cases, the energy is almost certainly within 0.05 eV of the local minimum.

We decided to use the local spin density (LSD) approximation implemented via the Vosko–Wilk–Nusair exchange-correlation functional<sup>46</sup> instead of one of the more recent functionals. The VWN functional has a modest but well-documented accuracy. Newer functionals are in closer agreement with experiment for geometries and binding energies in organic molecules, but they do not give systematic improvements for solids, and very little is known about their performance for metallic systems. The meta-GGA functionals are promising,<sup>47</sup> but there are many different versions of them, they are not all readily available, and they have not been tested sufficiently for a meaningful study of trends in metal clusters. Semi-empirical functionals used in quantum chemistry are not a good choice for metal clusters because they are parametrized by fitting to databases where there are no metal–metal bonds. They are also unsatisfactory for theoretical reasons explained in Ref. 47. In particular, the B3LYP hybrid functional gives disappointing results for transition metal dimers.<sup>48,49</sup> It does not seem significantly better or worse than LSD for metals. The B3LYP functional includes some Hartree–Fock exchange, and Hartree–Fock theory always gives a zero density of states at the Fermi level. The use of Hartree–Fock or B3LYP is problematic for metal clusters whose properties should converge to the bulk metal with increasing size.

We did calculations on Ag<sub>2</sub> with two local and four gradient-corrected functionals and found that, compared to experiment, VWN gives the best bond length (2.504 Å versus 2.53096),<sup>50</sup> a harmonic frequency of 206 cm<sup>-1</sup> (expt. 192 cm<sup>-1</sup>),<sup>51</sup> which is nearly as good as the best gradient-corrected functional, and a dissociation energy of 2.22 eV (expt. 1.66),<sup>51</sup> which overestimates the true value. Local spin density calculations almost always overestimate binding energies (by up to 100%) and harmonic frequencies (typically by 10% to 20%), they under estimate bond lengths (typically by 1% to 2%), and give good energy differences between systems with equal number of bonds. We found that, for silicon, a simple shift of the atom’s energy brings VWN cluster atomization energies<sup>52</sup> in excellent agreement with experiment and high-level calculations.<sup>53</sup> Accordingly, we shifted the silver atom’s energy down by  $(2.22 - 1.66)/2 = 0.28$  eV before calculating the atomization energies of Table I.

Gradient-corrected functionals are more sophisticated and more costly in computer time, but they appear to be less reliable than LSD for silver cluster structures and energies. We report gradient-corrected results for some of the most important silver cluster isomers in Sec. VI, and contrast them with LSD results. Except for Sec. VI, we discuss only LSD results.

We did a thorough search for the lowest energy structures, but we cannot claim to have found the global minima. For Ag<sub>n</sub> clusters with  $n < 9$ , we did calculations on structures already reported in the literature<sup>39</sup> and a few additional ones. Our strategy in searching for the global minima of Ag<sub>n</sub> for  $n \geq 9$  was to take as candidate structures all those derived by capping the most stable Ag<sub>(n-1)</sub> isomer, the ten (or so) lowest  $n$ -atom cluster isomers obtained with a Lennard-Jones (LJ) potential, and a few more structures with high-

TABLE I. Atomization energy (eV) and structural descriptors (see Sec. V) for the most stable silver cluster isomers. See Sec. IV A for the notation and abbreviations used.

Cluster	$A$ (eV)	$\rho$	$\gamma$	$\delta$	$\zeta$	$\eta$
2.1	1.662					
3.1 $C_{2v}$ isosceles tri	2.582	2.67	2.00	0.00	0.36	-0.25
4.1 $D_{2h}$ rhombus	4.875	2.63	2.50	0.25	0.57	0.31
5.1 $C_{2v}$ trapezoid	6.806	2.62	2.80	0.56	0.51	0.18
6.1 $D_{3h}$ triangle	9.477	2.61	3.00	1.00	0.33	-0.49
7.1 $D_{5h}$ PBP	11.547	2.70	4.57	0.82	0.13	-0.34
7.2 $C_{3v}$ TCT	11.379	2.67	4.29	1.35	0.10	-0.30
8.1 $D_{2d}$ DD	14.243	2.67	4.50	0.25	0.06	0.28
8.2 $T_d$ TT	14.228	2.67	4.50	2.25	0.00	0.00
9.1 $C_s$ B-DD	15.895	2.68	4.67	0.67	0.19	0.42
9.2 $C_{2v}$ 12-PBP	15.875	2.68	5.11	1.65	0.10	-0.08
9.3 $C_{2v}$ 11'-PBP	15.845	2.69	4.89	2.32	0.07	0.28
9.4 $C_1$ A-DD	15.842	2.67	4.67	0.89	0.07	-0.02
10.1 $D_{2d}$ twinned PBP	18.501	2.69	5.20	2.16	0.19	0.46
11.1 $C_1$ 123'4'-PBP	20.610	2.69	5.46	2.07	0.25	0.22
11.2 $C_1$ 11e23-PBP	20.463	2.67	5.46	2.43	0.18	0.06
12.1 $C_s$ 1234'5'-PBP	23.263	2.68	5.67	2.39	0.21	0.08
12.2 $C_1$ irregular	23.188	2.67	5.33	1.56	0.21	0.10
12.3 $C_1$ multic-PBP	23.108	2.67	5.33	1.39	0.18	0.09

symmetry (e.g., bicapped square antiprism at  $n=10$ ) or obtained by removing atoms from a 13-atom  $O_h$  cuboctahedron fragment of fcc crystal. For each of these structures we guessed the optimal Ag–Ag bond lengths from previous calculations, took a few (typically 7) steps with a standard quasi-Newton local optimization algorithm, ranked isomers by increasing energy, and then carried on full optimization of clusters that were roughly within 1.0 eV of the best one (typically about ten structures). We looked at  $Ag_{11}$  last and optimized fewer structures because comparisons with energies of 10- and 12-atom cluster isomers, along with short partial local optimization (3 steps), allowed us to quickly rule out many structures.

We did normal mode analyses by finite difference of gradients only for the most stable clusters of each size. This is required to find whether a stationary point on the potential surface is a minimum. But normal mode analysis is not overly important here for two reasons. First, the harmonic frequencies of all but the smallest silver clusters tend to be very similar from one isomer to another. The low frequencies are the most interesting because they could help identify nonrigid clusters; but low frequencies are notoriously difficult to calculate accurately, and here they should be taken only in a semiquantitative sense. Second, there is an important difference between metal clusters and covalently bonded molecules. In molecules, saddle points on the energy surface often correspond to breaking localized chemical bonds; they are very different from molecules near equilibrium. This is not normally the case in metals. There is a smooth change in the electronic structure of a metal in going from a minimum to a saddle point. Since we are interested in general aspects of the structure of clusters that could be nonrigid, saddle points are almost as relevant as minima.

### III. REVIEW OF THE LITERATURE

There have been very many articles published on silver clusters and we will only review those most relevant to this

work. The spectroscopic parameters that we calculate by VWN, and the experimental ones (in parentheses), for the diatomic molecule are: a bond length of 2.50 Å (2.530 96),<sup>50</sup> a dissociation energy of 2.22 eV (1.623),<sup>54</sup> and a harmonic frequency of 206  $cm^{-1}$  (192).<sup>51</sup> These deviations from experiment for  $Ag_2$  are typical of the VWN method.

The *trimer* has been studied extensively by different techniques.<sup>31–33,55–62</sup> Experiments give strong evidence that  $Ag_3$  is a Jahn–Teller distorted isosceles triangle,<sup>32,33,55,56</sup> likely an obtuse triangle, but we are not aware of any experimental bond length or angle determination. Calculations give values that range from 63° to 84° for the large angle, with the best values close to 68°, and from 2.58 to 2.76 Å for the short bond lengths with the best value probably being close to 2.68 Å (see Ref. 31 and references therein). Our VWN calculation gives 69° and 2.56 Å. It underestimates the bond length, but apparently gives a good value for the angle. Analysis of experimental spectra is greatly complicated by the dynamic Jahn–Teller effect for the ground state, and maybe some excited states, and the presence of isotopomers. There are several conflicting determinations of the fundamental frequencies of the symmetric stretch ( $\omega_s$ ) and doubly degenerate asymmetric stretch ( $\omega_e$ ) modes:  $\omega_s = 161 cm^{-1}$  and  $\omega_e = 96 cm^{-1}$ ,<sup>55</sup>  $\omega_s = 180 cm^{-1}$  and  $\omega_e = 67 cm^{-1}$ ,<sup>56</sup>  $\omega_s = 121 cm^{-1}$  and  $\omega_e = 99 cm^{-1}$ ,<sup>33</sup>  $\omega_s = 158 cm^{-1}$  and  $\omega_e = 140 cm^{-1}$ ,<sup>32</sup> and  $\omega_s = 129 cm^{-1}$  (average of four isotopomers).<sup>59</sup> Resonance Raman spectra in cold matrix showed bands at 120.5  $cm^{-1}$  in Kr<sup>63</sup> and 111  $cm^{-1}$  in Kr and Xe<sup>64</sup> which were assigned to  $Ag_3$ . On the whole, experiments put  $\omega_s$  around 150  $cm^{-1}$  and  $\omega_e$  around 100  $cm^{-1}$ , with both of them being very uncertain. We simply calculated VWN harmonic frequencies for a permanently distorted  $C_{2v}$  triangle and got 209, 142, and 66  $cm^{-1}$ . The smaller frequencies and their average, 104  $cm^{-1}$ , are not inconsistent with the degenerate  $\omega_e$  of fluxional  $Ag_3$  found in most experiments. The highest VWN frequency is surely higher than the true  $\omega_s$ . This is probably due to VWN bond lengths

being too short, but also maybe partly to the harmonic approximation and static  $C_{2v}$  structure that we used, instead of the true dynamic symmetry ( $D_{3h}$ ). In any case, it is unlikely that the higher VWN frequency would be in error by more than 50%, so it gives support to the higher values of  $\omega_s$ .

Dissociation energies have been measured by collision induced dissociation for  $Ag_n^+$  up to  $n=25$ ,<sup>65</sup> and for  $Ag_n^-$  up to  $n=11$ .<sup>66</sup> Dissociation energies of  $Ag_n^-$  ( $n=7$  to 11) were also obtained by analyzing the kinetics of photodecomposition.<sup>67</sup> When combined with vertical ionization potentials (IP)<sup>68,69</sup> and electron affinities (EA),<sup>70-74</sup> they yield dissociation energies of neutral clusters, but these have large uncertainties. The IP's show evidence of electronic shells and strong even-odd oscillations, as do the dissociation energies. The size dependence of the IP's is highly structured and indicates that silver clusters can not be treated as simple jellium spheres, their geometries are nonspherical.<sup>68,69</sup> Photoelectron spectra of the anion clusters have been studied in much detail.<sup>70-74</sup>

The association complexes of  $Ag_n$  with  $NH_3$ ,<sup>12,75</sup>  $CH_3OH$ ,<sup>16</sup>  $C_2H_4$ , and  $C_2H_4O$ <sup>15</sup> have been characterized experimentally. These complexes were used as models for adsorption, diffusion, and reaction on silver surfaces. The binding of  $C_2H_4$  and  $C_2H_4O$  to silver clusters is similar to that observed on silver surfaces.<sup>15</sup> Ammonia bonding to silver clusters shows size-dependent properties: The measured binding entropies indicate that  $NH_3$  is mobile on many silver clusters, but locally bound on some.<sup>12,75</sup>

Optical absorption spectra have been reported for  $Ag_n$  embedded in solid argon<sup>76,77</sup> ( $n=3$  to 40), and for gas-phase  $Ag_n$ <sup>12,78</sup> ( $n=4,7,9,10,12$ ) and a few  $Ag_n^+$  clusters.<sup>79</sup> The spectra of  $Ag_4$  and  $Ag_7$  are very simple, but those of  $Ag_{10}$ ,  $Ag_{12}$ , and especially  $Ag_9$ , have many peaks which suggest low symmetry or multiple isomers. We did find many isomers for  $Ag_9$  (Sec. IV A). Optical absorption<sup>80</sup> and Raman scattering<sup>81</sup> experiments were done for larger clusters embedded in a matrix. Haslett and co-workers reported the Raman spectra of silver clusters isolated in a matrix of solid argon and identified the structure of  $Ag_5$ <sup>35</sup> as the planar trapezoid (5.1 in Fig. 1) and that of  $Ag_7$ <sup>36</sup> as the tetracapped tetrahedron (7.2 in Fig. 1).

On the theoretical side, Bonačić-Koutecký and co-workers did a comprehensive study of structural isomers of  $Ag_n^+$  and  $Ag_n^-$ ,<sup>39</sup> and  $Ag_n^-$ <sup>82</sup> ( $n=3$  to 9) by Hartree-Fock and correlated *ab initio* methods. According to their configuration interaction calculations, the isomers within 0.2 eV of the most stable for each size are (refer to Table IV for the notation, and Fig. 1): 4.1; 5.1 and 5.2; 6.2 and 6.3; 7.1; 8.1 and 8.2; and 9.2. This agrees with our VWN results on many points, but there are discrepancies as well: We find 5.2 to be unstable; for  $Ag_6$  the lowest energy structure is different; and for  $Ag_9$ , we find many more isomers in addition to 9.2. Bonačić-Koutecký *et al.* also studied the absorption spectra of  $Ag_n^+$  and  $Ag_n^-$  ( $n=2$  to 4), showing, in particular, strong evidence for the rhombus geometry of  $Ag_4$ , and calculated the electron impact ionization cross-sections of  $Ag_n$  ( $n=2$  to 7).<sup>83</sup> References to several theoretical studies prior to 1998 can be found in the article by Bonačić-Koutecký and co-

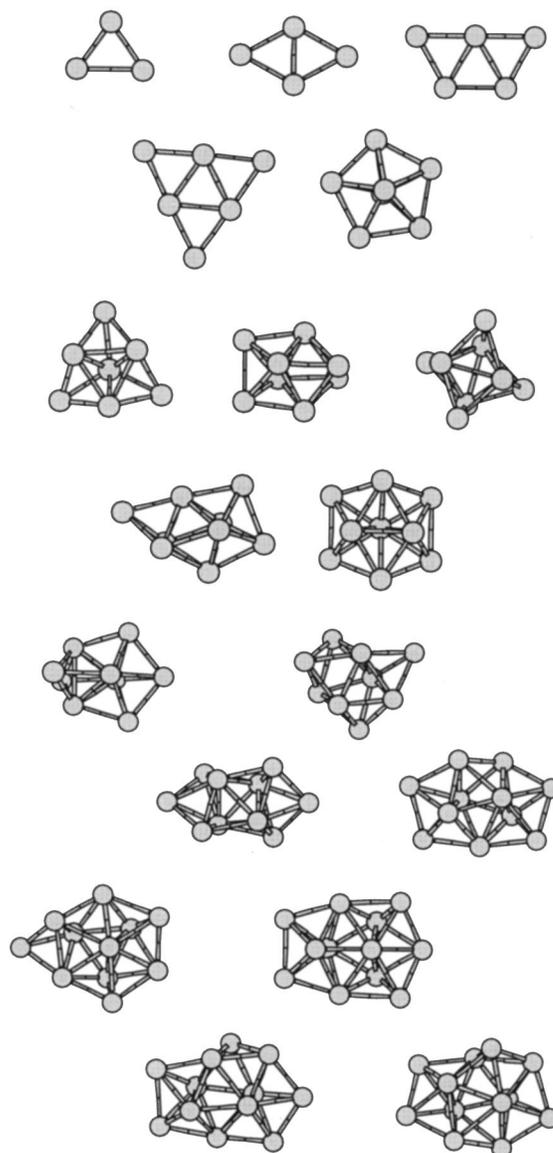


FIG. 1. The lowest energy  $Ag_n$  isomer of each size, and isomers within 0.18 eV of them, ordered (from left to right and top to bottom) by increasing size and energy.

workers (see citations number 10 to 31 in Ref. 34). These studies dealt mostly with small clusters ( $n < 6$ ).

## IV. KOHN-SHAM LOCAL SPIN DENSITY RESULTS

### A. Relative isomer energies

We optimized geometries and calculated energies for 68 isomers of  $Ag_n$  ( $n=3-12$ ). We do not report all the optimized structures here, but their cartesian coordinates are available upon request to the author. Figure 1 shows the lowest energy isomer, and those within 0.18 eV of the lowest, for each size. We assign labels to clusters such as 7.1 or 9.3; the first number indicates the number of atoms and the second gives the rank in increasing energy order. Hence, 9.3 is the third most stable 9-atom cluster. Some structures have special importance because they are building blocks for larger clusters. They are: the 6-atom  $O_h$  octahedron (O); the  $D_{5h}$  pentagonal bipyramid (PBP) 7.1, and  $C_{3v}$  tricapped tetrahe-

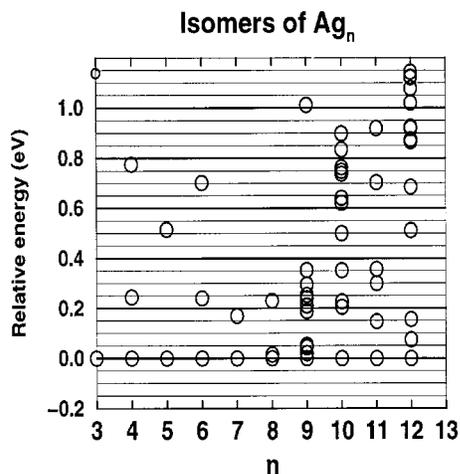


FIG. 2. Relative energy of  $\text{Ag}_n$  cluster isomers (eV).

dron (TCT) 7.2, both of which have been identified experimentally; the  $D_{2d}$  dodecahedron (DD) 8.1, which can also be viewed as a distorted bicapped octahedron; the  $T_d$  tetra-capped tetrahedron (TT) 8.2; the  $D_{2d}$  twinned PBP 10.1; and, the ideal 13-atom  $I_h$  icosahedron and  $O_h$  cuboctahedron from which smaller clusters can be obtained by removing atoms. Many of the larger stable clusters can be obtained by successive cappings of triangular faces or edges of the octahedron (O), PBP, DD, or TT. We denote any of the symmetry equivalent triangular faces of an octahedron or PBP by 1, and we number the other triangular faces in sequence according to their position relative to the first one: On the same side of the equatorial plane are 2 and 3, while 1', 2', etc., are on the other side of the equatorial plane. For example, we denote the five distinct bicapped PBP by 12-PBP, 13-PBP, 11'-PBP, 12'-PBP and 13'-PBP, and the three distinct bicapped octahedra 12-O=11'-O, 13-O=12'-O, and 13'-O. We represent capping of the edge common to 1 and 1' by the symbol "1e." Thus, the  $D_{2d}$  twinned PBP 10.1 can be described as a 11'-PBP with a tenth atom capping the 11' edge of the PBP or, for short, 11'1e-PBP. The DD has two distinct triangular faces: four at the ends which we denote "A" and eight on the sides which we denote "B." Here are some other abbreviations that we use in the tables: for trigonal bipyramid, "TBP"; for square antiprism, "SAP"; to denote a cluster formed by deleting  $n$  atoms from a  $O_h$  cuboctahedron, "cubo- $n$ " likewise, "ico- $n$ " for deleting from the icosahedron; "bic," "tric," "tetrac," and "multic" for bicapped, tri-capped, tetracapped, and multicapped, respectively; to denote capping at a triangular face formed by a previous capping.

Figure 2 shows the calculated isomer energies relative to the most stable of each size. Many isomers that we considered are not shown on this diagram because their energies are too high. We expect these relative energies to be accurate to within roughly 0.2 eV. Taking this as a guideline, our calculations support the previous structure assignments for  $\text{Ag}_3$  (slightly obtuse  $C_{2v}$  triangle),  $\text{Ag}_4$  (rhombus), and  $\text{Ag}_5$  (trapezoid), and predict that  $\text{Ag}_6$  is a planar  $D_{3h}$  triangle and  $\text{Ag}_{10}$  is a  $D_{2d}$  twinned PBP. The structure of  $\text{Ag}_7$  is problematic. The calculations indicate that the  $D_{5h}$  PBP is favored by 0.17

eV over the  $C_{3v}$  TCT, in agreement with electron spin resonance experiments.<sup>37</sup> But a comparison of the observed Raman spectrum to simulated spectra based on DFT calculations clearly favors the  $C_{3v}$  TCT.<sup>36</sup> We favor the latter because the simulated Raman spectrum is very sensitive to structure. However, considering the small calculated energy difference between  $D_{5h}$  PBP and  $C_{3v}$  TCT, it is possible that experimental details can favor the formation of one or the other isomer. The energy difference between 8.1 and 8.2 is very small and does not allow prediction of structure. There are four isomers of  $\text{Ag}_9$  within 0.05 eV of each other obtained by different capping of the PBP and DD. While we cannot predict the structure of  $\text{Ag}_9$ , these energies are a strong indication that many isomers of  $\text{Ag}_9$  are probably observed in experiments. For  $\text{Ag}_{11}$  and  $\text{Ag}_{12}$ , the relative energies suggest that, unlike  $\text{Ag}_9$ , only one or two structures would be seen in low-temperature experiments.

To sum up, the low-energy structures of  $\text{Ag}_n$  evolve from planar for  $n=3$  to 6, to high-symmetry and compact for  $n=7$  and 8, to a coexistence of many bi-capped PBP and capped DD at  $n=9$ , and finally to prolate structures obtained by successive cappings of the PBP for  $n=10, 11$ , and 12. We give a more detailed analysis in Sec. V.

## B. Size dependence of energies

There are different ways to present the size dependence of cluster energies. In Table I and Fig. 3 we report: (a) atomization energies "A" corresponding to  $\text{Ag}_n \rightarrow n\text{Ag} - A$  eV; (b) binding energies "BE" corresponding to  $\text{Ag}_n \rightarrow \text{Ag}_{n-1} + \text{Ag} - \text{BE}$  eV; (c) cohesive energies,  $A/n$ ; and (d) disproportionation energies "D" for  $2\text{Ag}_n \rightarrow \text{Ag}_{n-1} + \text{Ag}_{n+1} - D$  eV. The VWN energy of the single silver atom was shifted so as to reproduce the known dissociation energy of the diatomic, 1.66 eV. All other energies were taken directly from VWN calculations. We calculated vibrational frequencies for some of the clusters, but the energies that we report here *do not include* the zero point energy (ZPE). The ZPE is small for silver clusters and it has a nearly constant value of 0.007 eV ( $60\text{ cm}^{-1}$ ) per degree of freedom.

With the empirical correction to the silver atom energy, we expect that our VWN binding and cohesive energies would both converge to a value close to 2.95 eV, the experimental bulk cohesive energy  $E_c$  (bulk), at large cluster size. The largest binding energy (2.70 eV, for  $\text{Ag}_8$ ) and the binding energy of  $\text{Ag}_{12}$  (2.65 eV) are within 10% of  $E_c$  (bulk); but the largest cohesive energy (1.94 eV,  $\text{Ag}_{12}$ ) is only two-thirds of  $E_c$  (bulk) and the cohesive energy increases only slowly with size. There is an even-odd oscillation in cluster energies which is most obvious when we look at disproportionation [Fig. 3(b)]. The mean absolute value of the disproportionation energy is 0.75 eV. If we look separately at even and odd numbered clusters, for example reactions of the type  $2\text{Ag}_n = \text{Ag}_{n-2} + \text{Ag}_{n+2}$ , we still see appreciable variations (on the order of  $\pm 0.5$  eV) in relative stabilities. If we leave aside the obvious even-odd oscillations and overall increase in binding energies with size, the 7- and 8-atom clusters appear more stable than the rest, whereas  $\text{Ag}_9$  appears the

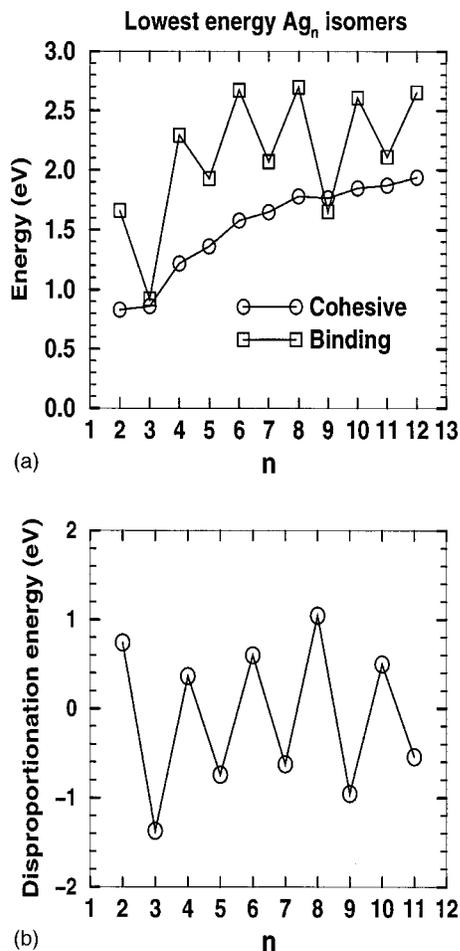


FIG. 3. Energies (eV) of the most stable cluster isomers of each size: (a) cohesive and binding energies, and (b) disproportionation energies.

least stable. The PBP 7.1 and DD 8.1 are also important structural motifs in the larger clusters.

By combining the experimental EA<sup>70</sup> and collision induced dissociation energies of the anions,<sup>66</sup> one can get experimental atom binding energies for the neutral clusters. Unfortunately, the uncertainty on these is large, on the order of 0.2 to 0.5 eV. Bearing this in mind, our calculations and experiments agree on many points: Ag<sub>8</sub> has the largest BE and it is close to 2.7 eV; Ag<sub>9</sub> has the smallest BE and it is close to 1.5 eV; other BEs in the range 4 ≤ n ≤ 11 are between 1.9 and 2.6 eV. There is disagreement about the BE of Ag<sub>6</sub> which we calculate to be 2.67 eV, but is much smaller according to experiment (apparently around 2.0 eV).

### C. Electronic structure

The energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) correlate very well with the relative isomer energies and IP's of the clusters. The HOMO–LUMO gap varies between 0.15 and 0.27 eV among odd-numbered clusters: 7.1 has the largest value (0.27 eV) and is the most stable in that group. The gaps for the isomers N.1 (see Table II) are the largest for every even N with two exceptions: the linear 4.3 (1.2 eV) and tetrahedral 8.2 (2.5 eV). The latter has essentially the same energy as 8.1. The HOMO–LUMO gaps of the various

TABLE II. HOMO–LUMO energy gap, and vertical ionization potential (eV) of the most stable cluster isomers.

Cluster	Gap	Vertical IP			
		Calc.	Expt. <sup>a</sup>	Diff.	
2.1	2.3	8.58	7.60	0.98	
3.1	C <sub>2v</sub> isosceles tri	0.2	6.34	6.20	0.14
4.1	D <sub>2h</sub> rhombus	0.9	7.16	6.65	0.51
5.1	C <sub>2v</sub> trapezoid	0.3	6.74	6.35	0.39
6.1	D <sub>3h</sub> triangle	2.4	7.69	7.15	0.54
6.2	C <sub>1</sub> 1e-TBP	0.7	7.48	"	0.33
6.3	C <sub>3v</sub> pyramid	1.9	7.48	"	0.33
7.1	D <sub>5h</sub> PBP	0.3	6.50	6.40	0.10
7.2	C <sub>3v</sub> TCT	0.2	6.60	"	0.20
8.1	D <sub>2d</sub> DD	1.8	7.24	7.10	0.14
8.2	T <sub>d</sub> TT	2.5	(7.50)	"	0.40
8.3	C <sub>s</sub> 1-PBP	1.4	6.84	"	-0.26
9.1	C <sub>s</sub> B-DD	0.2	6.45	6.00	0.45
9.2	C <sub>2v</sub> 12-PBP	0.2	5.88	"	-0.12
9.3	C <sub>2v</sub> 11'-PBP	0.2	5.73	"	-0.27
9.4	C <sub>1</sub> A-DD	0.2	(5.77)	"	-0.23
10.1	D <sub>2d</sub> twinned PBP	1.0	6.45	6.25	0.20
10.2	C <sub>1</sub> 11e2-PBP	0.8	(6.36)	"	0.11
10.3	C <sub>s</sub> 124'-PBP	0.8	(6.60)	"	0.35
10.4	C <sub>1</sub> 11'3-PBP	0.8	(5.96)	"	-0.29
11.1	C <sub>1</sub> 123'4'-PBP	0.2	6.34	6.30	0.04
11.2	C <sub>1</sub> 11e23-PBP	0.2	6.04	"	-0.26
12.1	C <sub>s</sub> 1234'5'-PBP	0.9	6.66	6.50	0.16
12.2	C <sub>1</sub> irregular	0.9	6.53	"	0.03
12.3	C <sub>1</sub> multi-PBP	0.7	6.35	"	-0.15

<sup>a</sup>Reference 69.

even-N isomers span the range between zero and these maximal values. A few isomers of Ag<sub>10</sub> and Ag<sub>12</sub> have triplet ground states: the most stable among them have energies of +0.90 eV and +0.69 eV relative to 10.1 and 12.1, respectively.

Calculated vertical IP's are given in Table II. The difference between vertical IP and HOMO energy is usually within ±0.02 eV (and always within ±0.07 eV) of the mean for a given cluster size. The (IP–HOMO) for clusters with 2 to 12 atoms are 2.90, 2.34, 2.25, 2.13, 2.08, 2.03, 1.97, 1.81, 1.82, 1.74, and 1.73 eV. The IP's shown in parentheses in Table II are empirical estimates based on the HOMO energy and the mean of (IP–HOMO) for clusters of the same nuclearity. In cases where the structure is known (2.1, 3.1, 4.1, and 5.1), the calculated vertical IP's overestimate experimental values<sup>69</sup> by 0.98, 0.14, 0.51, and 0.39 eV, respectively, while the average of 7.1 and 7.2 overestimates by 0.15 eV. From this, we expect that the calculated IP's for Ag<sub>n</sub> (6 ≤ n ≤ 12) to be within -0.2 eV and +0.4 eV of experiment, provided that the structures are correct. Using this as a guideline, the comparison of IP's does not allow us to say anything about the structure of Ag<sub>7</sub>, Ag<sub>9</sub>, and Ag<sub>12</sub>, but it almost rules out 8.3, 10.4, and 11.2 as possible observed structures. The structure we would predict for Ag<sub>6</sub> on the basis of VWN energies, 6.1, is in doubt; its IP does not agree with experiment, and other calculations do not show 6.1 as particularly stable.<sup>39</sup> We think that VWN is biased toward planar structures and that the true most stable isomer of Ag<sub>6</sub> is *not* 6.1. Many isomers of Ag<sub>9</sub> with nearly equal VWN energies are likely to coexist in experiments. None of them has an IP equal to the

experimental value of 6.00 eV. They are either too high and close to 6.45 eV (9.1, 9.6, and 9.8), or too low and close to 5.80 eV (9.2, 9.3, 9.4, 9.5, 9.7, 9.9, and 9.10). The unusually large drop in IP from Ag<sub>8</sub> to Ag<sub>9</sub> observed by Jackschath *et al.*<sup>69</sup> and Alameddin *et al.*<sup>68</sup> could be due to an averaging effect that includes several isomers of Ag<sub>9</sub> with low IP that are only slightly higher in energy than 9.1.

Bérces *et al.* used an effective IP, defined as the cluster IP plus a polarization energy, to discuss the anticorrelation of IP and reactivity in niobium clusters.<sup>19</sup> Following them, we write the IP of a hypothetical metal sphere, IP<sup>o</sup>, as

$$\text{IP}^{\circ} = \text{WF} + \frac{e^2}{2(R_c + a)}, \quad (1)$$

where WF is the bulk metal work function (4.64 eV for silver),  $R_c$  is the radius of the spherical cluster, and  $a$  is the extent of electron density spillout. In order to calculate  $R_c$ , we assume that atoms pack as closely in a cluster as in a fcc crystal so that we can assign them atomic volumes equal to  $(R_a^3\sqrt{2}/2)$ , where  $R_a$  is half a typical distance between nearest neighbors in the cluster. We take  $R_a = 2.7 \text{ \AA}$  by average over our VWN optimized geometries. We initially took  $a = (R_a/2) = 1.35 \text{ \AA}$ , but after test calculations we modified it to  $a = 1.215 \text{ \AA}$ . The radius of the hypothetical spherical cluster is

$$R_c = R_a n^{1/3} 3\sqrt{2} (8\pi). \quad (2)$$

We calculated IP<sup>o</sup> by Eqs. (1) and (2). Of course IP<sup>o</sup> varies smoothly with size and does not agree very well with experiment. We are interested in the *differences* between IP<sup>o</sup> and the VWN cluster IP because these will show specific effects of size and structure on IP's. The difference (IP–IP<sup>o</sup>), in eV, for isomers N.1 (N=3 to 12) are: –0.44, 0.51, 0.19, 1.22, 0.09, 0.89, 0.14, 0.18, 0.11, and 0.47. With the exception of clusters 3.1 and 10.1, (IP–IP<sup>o</sup>) is close to half the HOMO–LUMO gap which is, itself, relevant to chemical reactivity. Removing the trivial IP<sup>o</sup> from actual cluster IP's gives another way to look at the relation between cluster IP and reactivity.<sup>19</sup>

#### D. Harmonic frequencies

We did a normal mode analysis for the following structures: all N.1 isomers, 7.2, 8.2, 9.2, and 9.4. In all cases, we found  $(3N-6)$  real frequencies, and it seems very likely that structures within a few tenths of an eV of N.1 are minima as well. The lowest, mean, and largest frequencies for each of the N.1 isomers are shown in Table III. There is a noticeable jump in the largest frequency from  $N=6$  to  $N=7$  clearly due to the change from planar to 3D structure. This could be useful in elucidating the structure of Ag<sub>6</sub> because the largest frequency is a breathing mode for which we expect intense Raman activity. We calculated the vibrational contribution to the enthalpy at 298 K.<sup>84</sup> It amounts to about 0.44 kcal/mol per degree of freedom for all clusters at which we looked. All clusters have some very low frequencies, lower than that of Ag<sub>3</sub>. We take this as an indication that silver clusters could be nonrigid at room temperature. The calculated frequencies and relative isomer energies suggest that most silver clusters

TABLE III. Lowest, mean, and largest harmonic frequencies (cm<sup>-1</sup>) for some of the most stable isomers.

Cluster		Frequencies		
3.1	C <sub>2v</sub> tri	66	139	209
4.1	D <sub>2h</sub> rhombus	45	128	216
5.1	C <sub>2v</sub> trapezoid	29	119	224
6.1	D <sub>3h</sub> triangle	31	117	231
7.1	D <sub>5h</sub> PBP	36	115	194
7.2	C <sub>3v</sub> TCT	25	117	194
8.1	D <sub>2d</sub> DD	56	118	196
8.2	T <sub>d</sub> TT	23	118	194
9.1	C <sub>s</sub> B-DD	40	113	202
9.2	C <sub>2v</sub> 11'-PBP	43	111	208
9.4	C <sub>1</sub> A-DD	46	114	195
10.1	D <sub>2d</sub> twinned PBP	35	114	198
11.1	C <sub>1</sub> 123'4'-PBP	44	113	199
12.1	C <sub>s</sub> 1234'5'-PBP	37	112	204

are neither liquidlike nor rigid at room temperature. They probably undergo large amplitude motions along certain modes, but for most cluster sizes, the isomer energy separations seem too large to allow frequent isomer interconversion. Clusters Ag<sub>8</sub>, Ag<sub>9</sub> (and maybe also Ag<sub>12</sub>) look different. They have relative isomer energies of the same order as room temperature and not much larger than typical harmonic frequencies, so frequent isomer interconversion and liquidlike behavior appear possible.<sup>42</sup>

#### V. STRUCTURE OF SILVER CLUSTERS

It is not practical to discuss the structure of N-atom clusters in terms of  $(3N-6)$  (or  $3N$ ) nuclear coordinates. By using, instead,  $m$  shape descriptors ( $m \ll 3N-6$ ), we lose details, but we can gain insight and a convenient way of comparing clusters of different sizes. It is important to select descriptors that are appropriate for the systems and properties under study.<sup>85</sup> Here we use five descriptors which, we think, play an important role for the relative energies of silver clusters. We define the nearest-neighbor distance for a given atom "k"  $\rho_k$  as the average of the two shortest distances from atom k to other atoms in the cluster (or just the shortest distance for some atoms in 4.2 and 4.3), and we define the mean nearest-neighbor distance  $\rho$  as the average of the  $\rho_k$ 's in a cluster. We define the coordination number of an atom,  $c_k$ , as the number of atoms located within a sphere of radius  $1.15\rho$  centered around atom k. Using the  $c_k$ 's in a N-atom cluster, we calculate the mean coordination,  $\gamma$ , and the root-mean-square fluctuation among coordinations,  $\delta$ :

$$\gamma = \sum_{k=1}^N c_k / N, \quad (3)$$

$$\delta = \left[ \sum_{k=1}^N (c_k - \gamma)^2 / N \right]^{1/2}. \quad (4)$$

We derive two descriptors from the three moments of inertia  $I_a \geq I_b \geq I_c$ . We use the following definition of asphericity,  $\zeta$ :

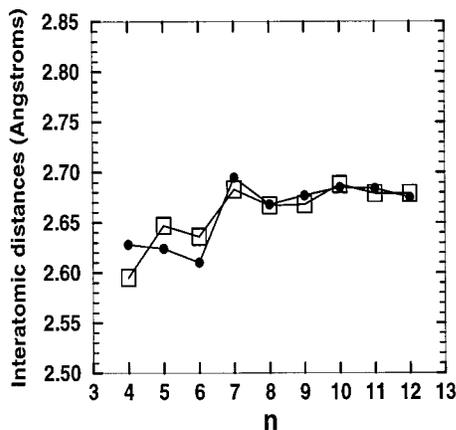


FIG. 4. Nearest-neighbor distance ( $\rho$ ) averaged over all isomers for each size. Filled circles: Boltzmann weight factors with  $\beta=10 \text{ eV}^{-1}$ . Open squares: Simple average (same weight for each isomer).

$$\zeta = \frac{(I_c - I_b)^2 + (I_b - I_a)^2 + (I_a - I_c)^2}{I_a^2 + I_b^2 + I_c^2}. \quad (5)$$

Another descriptor,  $\eta$ , is used to distinguish between prolate and oblate clusters,

$$\eta = (2I_b - I_a - I_c)/I_a. \quad (6)$$

Together, the five descriptors  $\rho$ ,  $\gamma$ ,  $\delta$ ,  $\zeta$ , and  $\eta$ , summarize important aspects of cluster structure:  $N\rho^{1/3}$  scales with the size of the cluster and  $\rho$  approaches the bulk nearest-neighbor distance  $R_{NN}$  at large  $N$ ;  $\gamma$  and  $\delta$  depend on the connectivity between atoms;  $\zeta$  and  $\eta$  describe the shape, they are both zero for a spherical cluster and the sign and magnitude of  $\eta$  tells how much a cluster is prolate (when  $\eta > 0$ ) or oblate (when  $\eta < 0$ ). The values of the descriptors for the most stable clusters are listed in Table I.

In order to allow easier comparisons, we performed averages of descriptors for each cluster size. We do these averages in either of two ways: (a) by assigning equal weights to each isomers; or (b) by assigning unequal Boltzmann weights  $\exp(-\beta(E_j - E_0))$  to each cluster  $j$ , where  $E_j$  and  $E_0$  are the atomization energies of isomer  $j$  and of the most

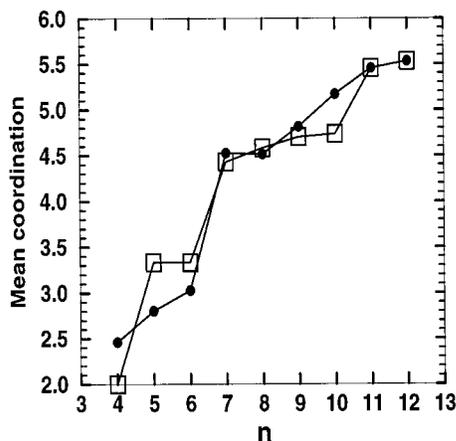


FIG. 5. Mean coordination ( $\gamma$ ) averaged over all isomers for each size. Filled circles: Boltzmann average ( $\beta=10 \text{ eV}^{-1}$ ). Open squares: Simple average.

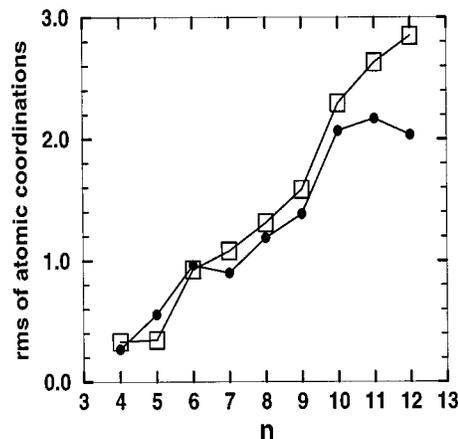


FIG. 6. Root-mean square deviation of atomic coordination around the average value ( $\delta$ ) averaged over all isomers for each size. Filled circles: Boltzmann average ( $\beta=10 \text{ eV}^{-1}$ ). Open squares: Simple average.

stable isomer (“0”) of the same size. We chose  $\beta = 10 \text{ eV}^{-1}$ , not so much to simulate a temperature, but more to smooth out errors that come with VWN energies.

Average (a) depends on the structures (after local optimization) that were considered in the search for the global minimum. To see what characteristics are energetically favorable for silver clusters, one should look mainly at the averages (b), implicitly assuming that we did a good search for the global minimum. To a lesser degree, the difference between averages (b) and (a) also matters, because a poor choice of trial structures could cause an artificial bias in averages (b). Figures 4–8 show the two types of averages for each of the five descriptors.

The nearest-neighbor distance  $\rho$  (Fig. 4) is clearly shorter in the planar clusters  $n=4$  to  $6$  where coordination is smallest (Fig. 5). There is a jump in  $\rho$  (and clearly also in  $\gamma$ ) from  $n=6$  to  $n=7$ . Surprisingly,  $\rho$  changes very little from  $n=7$  to  $n=12$  and it remains much smaller than the experimental bulk value of  $2.89 \text{ \AA}$ . The VWN calculation underestimates the bond length of  $\text{Ag}_2$  by  $0.03 \text{ \AA}$ . Even if VWN underestimated the interatomic distances by  $0.10 \text{ \AA}$ , the true

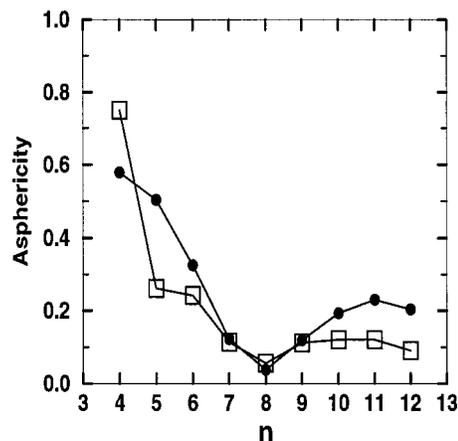


FIG. 7. Asphericity ( $\zeta$ ) averaged over all isomers for each size. Filled circles: Boltzmann average ( $\beta=10 \text{ eV}^{-1}$ ). Open squares: Simple average.

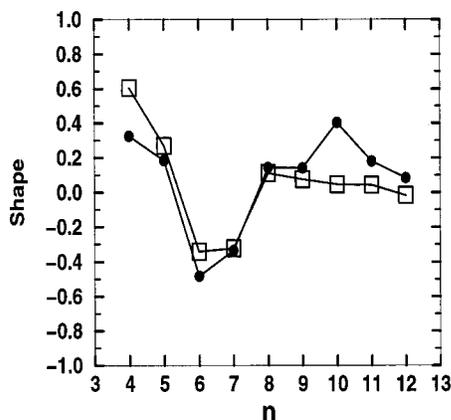


FIG. 8. Shape ( $\eta$ ) averaged over all isomers for each size. Filled circles: Boltzmann average ( $\beta=10$  eV $^{-1}$ ). Open squares: Simple average.

$\rho$  in 7- to 12-atom Ag clusters would still be about 0.10 Å less than the bulk nearest-neighbor distance.

The LJ potential favors structures with maximum coordination, and we expected the same for clusters of a simple metal like silver for  $n \geq 7$ . This is only partly true. The most stable LJ clusters are generally *not* very good structures for  $Ag_n$ . Their relative energies (eV) with respect to the best isomer for  $n=7$  to 12 are as follows: 0.00, 0.23, 0.04, 0.64, 0.70, and 1.12, respectively. The  $Ag_n$  clusters do *not* maximize  $\gamma$ . However,  $\gamma$  tends to be close to maximum. It should be noted that the isomers considered in the search are not random, they are very compact, and that among these, the  $\gamma$  of the lowest energy structures are neither low nor high (compare filled circles and open squares in Fig. 5).

For  $n \geq 7$ , there is a clear preference for structures that minimize  $\delta$  (Fig. 6). Although some clusters have small  $\delta$  for reasons of symmetry (e.g., 7.1 and 8.1), there is in general no more correlation between high symmetry and small  $\delta$  than there is between high symmetry and low energy. Clusters 9.1, 11.1, and 12.1 all have low symmetry, yet small  $\delta$ . Conversely, many high-symmetry structures which we considered have a large  $\delta$  (and a high energy). We suggest that, other things being equal, minimizing  $\delta$  could be a useful heuristic principle for atomic cluster structure.

The descriptor  $\zeta$  has a clear minimum near  $n=8$  (Fig. 7) in very good agreement with the EJM.<sup>41</sup> This could be somewhat coincidental because there are not too many ways of making compact arrangements of a few hard spheres, and structures that maximize  $\gamma$  and minimize  $\delta$  happen to have a small or zero value of  $\zeta$  for  $n=6$  to 9 for geometrical reasons. This is partly why the two kinds of averages are very close at  $n=7$ , 8, and 9 (Fig. 7). Note, however, that low-energy structures of  $Ag_{10}$ ,  $Ag_{11}$ , and  $Ag_{12}$  are on average, more aspherical than the isomers for which we did calculations.

The descriptor  $\eta$  allows a more detailed comparison of the favored shapes. First, we look at the energetically favored structures (filled circles in Fig. 8). We left out  $Ag_3$  because such a small cluster has too few possible isomers for average descriptors like  $\eta$ , or a model like the jellium, to be meaningful, and because the isosceles triangular structure of  $Ag_3$  is well understood from high-level theory. This leaves

nine cluster sizes for judging the validity of the simple EJM against KS-DFT. According to KS calculations, the 6- and 7-atom clusters are oblate ( $\eta < 0$ ),  $Ag_4$  and  $Ag_{10}$  are “strongly prolate” ( $\eta > 0.2$ ), and all other clusters are “weakly prolate.” The shapes predicted by the EJM agree rather well with DFT (Fig. 8 and Ref. 41) with one exception:  $Ag_5$  is strongly oblate in the jellium model but prolate according to DFT. But for very small clusters, there is no reason to expect accurate predictions from the EJM. Indeed, aside from  $Ag_5$ , the EJM can be said to “fail” for  $Ag_4$  because the highly prolate linear structure is much less stable than the moderately prolate rhombus. There are also subtle, but significant, differences between VWN and EJM among larger clusters. According to the EJM, 8.2 is favored over 8.1 by the shape ( $\eta=0.00$  versus  $\eta=0.28$  for 8.1). Despite this, and the fact that 8.1 and 8.2 have the same  $\rho$  and  $\gamma$ , the two isomers are equally stable. We think that the reason for this is that 8.1 has a much smaller  $\delta$  (0.25 compared to 2.25). Also, contrary to EJM predictions, the VWN-stable  $Ag_{10}$  is a lot more prolate ( $\eta=0.46$ ) than  $Ag_{11}$  and  $Ag_{12}$ . We think that this is because 10.1 has the largest  $\gamma$  among the prolate isomers of  $Ag_{10}$ . One isomer has a larger  $\gamma$  than 10.1 but it is oblate ( $\eta=-0.28$ ). Two other isomers have a  $\gamma$  equal to that of 10.1: one is oblate and unstable (0.90 eV), the other is weakly prolate ( $\eta=0.10$ ) and, as one would expect from EJM, it is the second most stable isomer, 10.2 (11e2-PBP). It is not always possible for all descriptors to assume their optimal values simultaneously, because of geometric constraints, and this causes discrepancies between predictions from the EJM and actual optimal cluster structures.

To summarize, the structural attributes of low-energy silver clusters appear to be, in decreasing order of importance: a high mean coordination ( $\gamma$ ); a shape ( $\eta$ ) that conforms to the EJM; and uniformity in atomic coordinations (small  $\delta$ ), whether or not this is accompanied by high symmetry. In general, these isomers also have relatively large HOMO–LUMO gaps, but this is related to having an optimal shape in the EJM.

The EJM is not very useful for structure prediction because it says nothing about the position of the atoms. In order to better understand factors that relate structure and energy, we did fixed geometry calculations on all the VWN-optimized isomers with two very simple theoretical models: Extended Hückel molecular orbital theory and an empirical model for the energy based on the atomic coordinations  $c_k$  of Eq. (3).

The extended Hückel molecular orbital (eHMO) theory is well known.<sup>86</sup> We used a simplified version of it with a single  $s$  atomic orbital, one electron per silver atom, and an empirical calculation of overlap instead of using actual atomic orbitals. We set the diagonal elements of the Hamiltonian matrix  $H_{ii}$  equal to the VWN 5s atomic orbital energy (−4.718 eV) and we take the overlap integrals to be  $S_{ij} = \exp(-\alpha R_{ij})$ . We chose  $\alpha=0.27$  Å $^{-1}$  so as to give an overlap of 0.25 for a typical nearest-neighbor distance (2.70 Å). We use the Wolfsberg–Helmholtz formula  $H_{ij}=0.875 \times S_{ij} \times (H_{ii} + H_{jj})$  for the off-diagonal Hamiltonian matrix elements. With these choices the HOMO–LUMO gaps are reasonable, typically within 0.2 eV of the VWN values (the

latter vary between 0.25 and 2.50 eV among even-numbered clusters). We did not try to optimize the parameters in any way because eHMO structural predictions are not sensitive to the precise values of the parameters, and eHMO theory cannot give reliable quantitative predictions of cluster energies. We take the eHMO energy as the sum, over occupied spin-orbitals, of orbital energies.

The empirical potential that we use is motivated by the observation that, in many metallic systems, cohesive energies scale as the square root of the atomic coordination.<sup>87</sup> We take coordinations  $c_k$  as already defined and calculate the cluster binding energy as a sum of atomic contributions:

$$U = E_c \sum_k (c_k/12)^{1/2}, \quad (7)$$

where  $E_c$  is the bulk cohesive energy of silver (2.95 eV) and 12 is the coordination of a silver atom in a fcc crystal. We will refer to this model as SSAC for “Sum of Square-roots of Atomic Coordinations.” Notice that this simple formula is in error by only 3% when applied to diatomic silver (1.70 eV vs. the experimental 1.66 eV), and that it reproduces the exact cohesive energy in the bulk limit. The SSAC is a crude model, but it is accurate enough for our purpose, and it is probably preferable than more complicated models in trying to find structural principles. We used a more complicated version of the SSAC to calculate surface energies. These results will be reported elsewhere. The main problem with the SSAC and similar models (e.g., the embedded atom method) is that it ignores specific quantum effects caused by symmetry (electronic shells, Jahn–Teller distortion) and spin pairing (even-odd oscillation). Like the LJ potential, the SSAC predicts that the lowest energy structures are those that maximize  $\gamma$  — structures derived from successive capping of the  $D_{5h}$  PBP and  $I_h$  icosahedron. The additive LJ potential and SSAC differ mainly in the size dependence of atomization energies.

The jellium and SSAC models are, in a sense, opposite. In the EJM, the symmetry of delocalized quantum states of  $N$  electrons dictate where the nuclei go in an average sense. The SSAC potential does not explicitly treat electrons, and it predicts specific arrangements of atoms that tend to be as compact and symmetrical as possible. The jellium and eHMO models give similar predictions of cluster shape, although they come from very different physical approximations. The EJM and eHMO theory can be viewed as simple models that try to capture the most important quantum effects.

Table IV gives the relative energy of isomers as calculated by VWN, SSAC, eHMO and the average of SSAC and eHMO. In each case, energies are shifted so that the most stable isomer of each size is assigned a zero energy. The VWN results are certainly the most reliable and they agree with experiment in every known case ( $Ag_3, Ag_4, Ag_5, Ag_7$ ). We believe that VWN generally gives good predictions of the lowest energy structures, so we rate the simple models according to their ability to reproduce VWN results.

It is clear from Table IV that SSAC and eHMO are both very poor at predicting relative isomers energies. Interestingly, the relative energies of the *average* of SSAC and

TABLE IV. Relative energies (eV) of isomers obtained by VWN, SSAC, eHMO, and the average of SSAC and eHMO (Avg). See Sec. IV A for the notation and abbreviations used.

Cluster	VWN	SSAC	eHMO	Avg	
4.1	0.00	0.00	0.79	0.00	
4.2	$C_{2v}$ Y-shaped	0.24	0.62	0.30	0.07
4.3	linear	0.78	1.25	0.00	0.23
5.1	$C_{2v}$ trapezoid	0.00	1.00	0.00	0.00
5.2	$C_{2v}$ TBP	0.52	0.00	1.03	0.02
5.3	$C_{2v}$ TBP	1.20	0.00	1.22	0.11
6.1	$D_{3h}$ triangle	0.00	0.94	0.00	0.01
6.2	$C_{5v}$ pyramid	0.24	0.39	0.54	0.00
6.3	$C_1$ 1e-TBP	0.70	0.00	1.42	0.25
7.1	$D_{5h}$ PBP	0.00	0.00	0.19	0.00
7.2	$C_{3v}$ TCT	0.17	0.46	0.00	0.14
8.1	$D_{2d}$ DD	0.00	0.30	0.17	0.10
8.2	$T_d$ TT	0.02	0.49	0.00	0.11
8.3	$C_s$ 1-PBP	0.23	0.00	0.27	0.00
9.1	$C_s$ B-DD	0.00	0.71	0.30	0.25
9.2	$C_{2v}$ 12-PBP	0.02	0.00	0.52	0.00
9.3	$C_{2v}$ 11'-PBP	0.04	0.46	0.38	0.16
9.4	$C_1$ A-DD	0.05	0.73	0.30	0.26
9.5	$C_s$ 132'-O	0.19	0.81	0.28	0.28
9.6	$C_1$ 13'-PBP	0.19	0.43	0.36	0.13
9.7	$C_1$ 1t1'-O	0.21	0.81	0.42	0.35
9.8	$C_1$ 11e-PBP	0.21	0.40	0.49	0.18
9.9	$C_s$ 13-PBP	0.24	0.44	0.44	0.18
9.10	$C_1$ 1tt'-PBP	0.25	0.81	0.41	0.35
9.11	$C_{2v}$ 11'1e-O	0.30	0.37	0.51	0.18
9.12	$C_1$ 12'-PBP	0.35	0.44	0.58	0.25
9.13	$C_{4v}$ SAP	1.01	3.58	0.00	1.53
10.1	$D_{2d}$ twinned PBP	0.00	0.40	0.93	0.05
10.2	$C_1$ 11e2-PBP	0.21	0.41	0.84	0.00
10.3	$C_s$ 124'-PBP	0.23	0.71	0.85	0.16
10.4	$C_1$ 11'3-PBP	0.35	0.86	0.54	0.08
10.5	$D_{2h}$ AA'-DD	0.50	1.03	0.99	0.39
10.6	$C_s$ 123-PBP	0.62	0.00	1.55	0.15
10.7	$C_1$ 11'2-PBP	0.74	1.35	0.80	0.46
10.8	$C_1$ 12-TT	0.75	0.90	0.81	0.23
10.9	$C_1$ BB'-DD	0.76	0.70	0.99	0.22
10.10	$C_s$ cubo-3	0.84	1.63	0.64	0.52
10.11	$C_s$ 11'2-PBP	0.90	0.44	1.30	0.25
10.12	$C_1$ cubo-3	1.50	2.46	0.63	0.92
10.13	$C_s$ 12'3-PBP	1.65	0.86	1.30	0.46
10.14	$C_s$ bic SAP	2.25	4.96	0.37	2.04
10.15	$D_{4d}$ bic SAP	3.01	6.01	0.00	2.38
11.1	$C_1$ 123'4'-PBP	0.00	0.36	0.06	0.01
11.2	$C_1$ 11e23-PBP	0.15	0.40	0.00	0.00
11.3	$C_s$ 122e3-PBP	0.30	0.43	0.05	0.04
11.4	$C_1$ 11'1e2-PBP	0.36	0.41	0.24	0.13
11.5	$C_s$ 1234-PBP	0.70	0.00	0.49	0.05
11.6	$C_1$ 122'3-PBP	0.92	0.88	0.25	0.36
12.1	$C_s$ 1234'5'-PBP	0.00	0.75	0.11	0.00
12.2	$C_1$ irregular	0.07	1.42	0.00	0.28
12.3	$C_1$ mc-PBP	0.16	1.40	0.15	0.35
12.4	$C_2$ 122'2e3-PBP	0.51	0.80	0.50	0.22
12.5	$C_2$ anti bic-10.1	0.51	0.80	0.53	0.23
12.6	$C_{2v}$ tetrac-TT	0.69	0.80	0.64	0.28
12.7	$C_s$ 1234(23e)-PBP	0.87	0.80	0.51	0.22
12.8	$C_1$ 12342e-PBP	0.88	0.81	0.56	0.25
12.9	$C_s$ 11'-10.1	0.92	1.68	0.25	0.53
12.10	$C_s$ irregular	1.02	1.99	0.04	0.58
12.11	$C_1$ 12342'-PBP	1.08	0.82	0.75	0.36
12.12	$C_s$ ico-1	1.12	1.23	0.86	0.62
12.13	$C_{5v}$ ico-1	1.12	0.00	0.97	0.05
12.14	$C_s$ 11'1e22'-PBP	1.14	0.83	0.74	0.35
12.15	$D_{3h}$ 3-6-3	1.22	1.10	0.99	0.61
12.16	$C_{2v}$ cubo-1	1.30	1.89	0.10	0.56

TABLE V. Spectroscopic parameters calculated for  $\text{Ag}_2$  with the VWN, PVS, BP86, and BLAP functionals.

	$D_e$ (eV)	$R_e$ (Å)	$\omega_e$ ( $\text{cm}^{-1}$ )
VWN	2.22	2.50	206
PVS	1.98	2.49	211
BP86	1.65	2.57	182
BLAP	1.30	2.66	150
Expt. <sup>a</sup>	1.66	2.530 96	192

<sup>a</sup>See Sec. II.

eHMO (rightmost column in Table IV), which we will call “SSAC-eHMO,” is in better agreement with VWN than either SSAC or eHMO. The root-mean-square deviations from VWN isomer energies (eV) are 0.81 for SSAC, 0.63 for eHMO, and 0.43 for SSAC-eHMO, whereas the root-mean-square average of the VWN energies themselves is 0.80 eV. Another comparison we can make is to rank isomers by increasing energy for the various models. Then we form sets of isomers that fall in the lower half, by energy, and count how many isomers are in common between the sets generated by VWN, SSAC, eHMO, and SSAC-eHMO. Comparing to VWN, SSAC gets 16.5 “hits,” eHMO gets 18, and SSAC-eHMO gets 21, out of a possible maximum of 29. Judging from this, SSAC-eHMO has some merits for predicting isomer energies, but SSAC and eHMO have no value. Focusing on the few lowest-energy isomers of each size makes SSAC-eHMO look even better compared to SSAC and eHMO. Of course these numbers would change somewhat if we implemented SSAC and eHMO differently; but SSAC-eHMO is clearly the better of the three models, and its relative energies do correlate with those of VWN. We conclude that the most stable isomers of  $\text{Ag}_n$  represent an optimum compromise between close packing of atoms, as predicted by SSAC (and embedded atom methods), and JT distortion due to orbital symmetry and electron count, which is the essence of structure prediction by eHMO (and the EJM). Although our SSAC and eHMO models are crude, it is doubtful that small changes in these models, or their parameters, would produce a useful method for structural predictions. The SSAC and eHMO models seem to capture different aspects of the physics controlling cluster structure. An empirical method that would combine the two in a nontrivial way (*unlike* a simple average) could be really useful for investigating the structure of metal clusters.

## VI. GRADIENT-CORRECTED FUNCTIONALS

We repeated calculations for some of the lowest energy isomers using the gradient-corrected exchange functional of Becke,<sup>88</sup> combined with the gradient-corrected correlation functional of Perdew,<sup>89</sup> or with the kinetic-energy-density and Laplacian dependent correlation functional developed by Proynov *et al.*<sup>90</sup> We denote these two methods BP86, and BLAP, respectively. We also did some calculations with the gradientless exchange-correlation functional of Proynov *et al.*<sup>91</sup> denoted PVS. Table V shows our results for  $\text{Ag}_2$ ,<sup>92</sup> and Table VI shows relative isomer energies obtained by LSD, PVS, BP86, and BLAP. We use the same labels in

TABLE VI. Relative energies (eV) of isomers obtained with VWN, PVS, BP86, and BLAP functionals.

	VWN	PVS	BP86	BLAP
4.1	0.00	0.00	0.00	0.13
4.2	0.24	0.24	0.05	0.00
4.3	0.78	0.74	0.35	0.10
5.1	0.00	0.00	0.00	0.00
5.2	0.52	0.53	0.70	0.77
5.3	1.20	1.04	1.27	1.28
6.1	0.00	0.00	0.00	0.00
6.2	0.24	0.23	0.37	0.41
6.3	0.70	0.71	0.98	1.17
7.1	0.00	0.00	0.00	0.03
7.2	0.17	0.18	0.07	0.00
8.1	0.00	0.00	0.07	0.10
8.2	0.02	0.00	0.00	0.00
8.3	0.23	0.23	0.22	0.10

Table VI as in Table IV, hence, 7.1 is the pentagonal bipyramid for all functionals, even though it is the lowest energy structure only for LSD and PVS.

The PVS functional gives essentially the same structures and relative isomer energies as VWN (Table VI). It gives smaller binding energies than VWN, but after shifting the Ag atom energies to make  $D_e(\text{Ag}_2)$  equal to the experimental value, VWN and PVS energies become very similar. The BLAP functional does not seem reliable for predicting structures of silver clusters. It gives a diatomic Ag–Ag bond which is too long (by 0.13 Å), too soft and too weak ( $\omega_e$  and  $D_e$  are both 20% smaller than experiment). For  $\text{Ag}_3$ , it is hard to compare to experiment because BLAP gives a very flat potential from which we get only a rough estimate of the short bond length (2.74 Å) and angle (116°). For  $\text{Ag}_4$ , the BLAP relative energies of isomers (see Table VI) are at odds with calculations of Bonačić-Koutecký and co-workers<sup>34</sup> which strongly indicate the rhombus as the most stable structure. Nearest-neighbor interatomic distances generally increase with cluster size. For clusters with ten atoms and more, BLAP gives an average nearest-neighbor distance of about 3.00 Å, already larger than the experimental bulk interatomic distance (2.89 Å). We did BLAP calculations for many isomers not listed in Table VI. The calculated BLAP relative energies (eV) for these isomers are as follows: 9.1 = 0.02, 9.2 = 0.10, 9.3 = 0.11, 9.4 = 0.06, and 9.5 = 0.00; 10.1 = 0.08, 10.2 = 0.10, 10.3 = 0.13, 10.4 = 0.00, 10.6 = 0.71, 10.11 = 0.73, 10.12 = 0.62, and 10.13 = 0.68; 11.1 = 0.00, 11.2 = 0.02, 11.3 = 0.26, 11.6 = 0.63, and 11.7 = 0.97; and 12.1 = 0.00, 12.2 = 0.15, and 12.3 = 0.04. Predictions from BP86 and BLAP calculations regarding structures likely to have a low energy generally agree with VWN. However, the BP86 and BLAP relative energies of planar isomers are smaller by 0.2 to 0.5 eV compared to VWN. The BLAP results differ from VWN in other ways. Most bonds are longer by 0.2 to 0.4 Å compared to VWN, and isomers tend to be closer in energy in BLAP than in VWN. The BP86 optimized structures and relative energies are intermediate between those of BLAP and VWN.

The energetic trends displayed for VWN in Fig. 3 are found to be almost identical with PVS, and qualitatively

similar with BP86 and BLAP. Even-odd energy oscillations are found with all functionals, but they are slightly stronger with BLAP. We shifted the Ag atom energies for PVS and BLAP, as we did for VWN, so that the binding energy of  $\text{Ag}_2$  matches the experiment (1.66 eV). For BP86, there is no need for an energy shift because the calculated  $\text{Ag}_2$  binding energy (1.65 eV) is already essentially equal to the experimental value. These corrected energies are used for comparing the size dependence of energies of various functionals. The BLAP cohesive energy differs from that of other functionals. It does not increase smoothly with size, it has a maximum for planar  $\text{Ag}_6$  (1.09 eV/atom), and it is only 1.06 eV/atom for  $\text{Ag}_{12}$ . We can extrapolate cluster energies to get rough estimates of the bulk cohesive energy  $E_c$  for each functional in the following way. First, we take the ratio of the empirical SSAC cohesive energies for the bulk and for  $\text{Ag}_n$ , for  $n=8$ , the ratio is 1.746. Then we multiply the  $\text{Ag}_8$  cluster cohesive energy by 1.746 to get estimates of  $E_c$  which are, in eV/atom, 3.11 (VWN), 3.07 (PVS), 2.41 (BP86), and 1.85 (BLAP). The experimental  $E_c$  for silver is 2.95 eV/atom. If we use  $n=9, 10, 11$ , or  $12$  instead, VWN gives  $E_c$  estimates that are close to one another and are in slightly better agreement with experiment (2.96, 3.02, 3.00, and 3.06, respectively), while BLAP estimates become worse (1.70, 1.71, 1.65, and 1.68, respectively). These numbers suggest that a simple shift of atomic energies improves cohesive energies obtained with VWN and PVS functionals, but does not improve energies obtained with the gradient-corrected functionals BP86 and BLAP. Note that all calculations were done with a model core potential optimized for the VWN exchange-correlation functional. Results could be slightly different if we used model core potentials and basis sets optimized separately for each functional. But our tentative conclusions regarding silver cluster energies and structures are that PVS gives results similar to VWN, BP86 generally does not seem as reliable as VWN or PVS even though it yields the  $\text{Ag}_2$  binding energy closest to experiment, and the BLAP functional seems the least reliable.

## VII. CONCLUSION

On the basis of VWN energies, and IP's compared to experiment, we tentatively assign the structure of  $\text{Ag}_{10}$  to 10.1 and  $\text{Ag}_{11}$  to 11.1; either 8.1 or 8.2, or both, are possible for  $\text{Ag}_8$ , and there are three possibilities for the structure of  $\text{Ag}_{12}$ , 12.1, 12.2, and 12.3. Ten isomers of  $\text{Ag}_9$  have comparable VWN energies, and IP's that are either too high or too low compared to experiment. We believe that a mixture of isomers of  $\text{Ag}_9$  is formed in experiments.

It is interesting that the least stable cluster,  $\text{Ag}_9$ , is the one with the largest number of possible isomers. We rationalize this as follows: The lowest energy isomers of silver clusters are those that simultaneously fulfill to a high degree many requirements (large  $\gamma$ , small  $\delta$ , EJM shape, may be high symmetry). For certain sizes, there is not a single structure that meets all these requirements. When this happens, first that cluster size appears relatively unstable, and second, there are many ways to meet some, but not all, requirements for structural stability and, correspondingly, several isomers

with near equal energies. In other words, when a cluster size appears unstable relative to others, it points to the possibility of multiple isomers being present.

The picture that comes out of KS-DFT calculations is that silver clusters,  $\text{Ag}_9$  excepted, adopt one or a few specific structures at low temperature. However, silver clusters can appear as if they were liquid metal droplets for a number of reasons. First, the favored isomers have shapes that do conform with EJM predictions. This is not a coincidence. Molecular orbitals in  $\text{Ag}_n$  are delocalized, and everything else being equal, clusters adopt shapes predicted by the EJM. Second, the lowest harmonic frequencies are quite small which implies large vibrational amplitudes. Third, there are most likely two or three isomers at  $n=8$  and  $12$ , and the presence of multiple isomers becomes more likely with increasing size. Clusters like  $\text{Ag}_9$ , with many isomers, could behave as a liquid droplet if atoms can exchange places by successive isomer interconversions. It would be interesting to have measurements of the temperature dependence of properties of  $\text{Ag}_9$  and molecular dynamics simulations to determine an effective melting temperature for  $\text{Ag}_9$ .

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