

## Electronic structure of calcium clusters

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The electronic structure of calcium clusters containing up to 13 atoms is studied within the general gradient approximation (GGA) of the density-functional formalism. For the calcium dimer it is observed that the exchange functional in GGA overestimates the binding energy, while a hybrid approach including Hartree-Fock exchange gives a better agreement with the experimental results. Binding energies, optimized geometries, vibrational frequencies, and thermodynamic properties have been calculated for several isomers at each cluster size. Various structures corresponding to saddle points of the energy curve are reported, along with the isomerization reaction path for  $\text{Ca}_5$ ,  $\text{Ca}_6$ , and  $\text{Ca}_7$ . It was found that  $\text{Ca}_{12}$  undergoes a structural transition as a function of temperature, changing structure at  $T=318$  K. A comparison of the minimum energy isomer geometry and binding energy obtained for each cluster size with those obtained from the Murrell-Mottram empirical potential shows that this potential overestimates the binding energies and does not adequately predict the optimized structures for several cluster sizes.

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### I. INTRODUCTION

Calcium is a very abundant element that plays an important role in a variety of compounds, mechanisms, and processes. This element is of interest because of its potential use in excimer lasers, carbon-chemical engineering, and ion deposition. Despite its popular chemical usages, only a limited number of experimental observations for pure calcium clusters [1] have been reported. Calcium belongs to the group-IIA alkaline-earth metals with closed-shell electronic configuration  $[\text{Ar}]4s^2$ . The bonding in the bulk quasimetal is quite strong with a cohesive energy of 1.825 eV. In contrast, the  $\text{Ca}_2$  molecule presents a weakly bound ground state with a dissociation energy of only 0.14 eV and strongly bound excited states [2,3]. The discrepancy in the bonding behavior at the two size limits (bulk and dimer) suggests that a change in the bonding must take place as a function of cluster size.

Metallic clusters have been the subject of intense interest in recent years [4,5]. One property of small metallic clusters that has received little attention is their vibrational spectra. Recently we have reported a detailed theoretical investigation of the harmonic vibrational frequencies of  $\text{Rh}_2$  through  $\text{Rh}_6$  using density functional and large basis sets [6]. For small calcium clusters there have been very few *ab initio* calculations that include electron correlation effects or report vibrational frequencies:  $\text{Ca}_2$  [7–10],  $\text{Ca}_3$  [11],  $\text{Ca}_4$  [9–13], and  $\text{Ca}_5$  [9]. For larger calcium clusters there are no first-principles calculations, although there have been attempts to model the cluster geometries with the empirical potential of Murrell and Mottram (MM) [14,15] that has two- and three-body interactions.

In this paper we perform an exhaustive all-electron study within the density-functional theory (DFT) framework and the generalized gradient approximation (GGA) of Ca clusters

containing up to 13 atoms. Results are presented in Sec. II for the calcium dimer including a thorough comparison between various calculation methods. The energetics and vibrational frequencies for  $\text{Ca}_3$  through  $\text{Ca}_{13}$  are described in Secs. III and IV. These sections also discuss several isomerization reaction paths and report several cluster structures corresponding to saddles of the energy surface. Section V contains a discussion on the thermodynamic properties obtained in the harmonic approximation and their role in the relative stability of the clusters as a function of size and temperature. A thermally induced structural transition for  $\text{Ca}_{12}$  is highlighted in this section. Concluding remarks are given in the last section of this paper.

### II. METHODS AS APPLIED TO THE CALCIUM DIMER

The Kohn-Sham equations [16] were solved self-consistently using the GGA representation of the correlation functional. Becke's three-parameter functional [17] is a hybrid method that includes a combination of Hartree-Fock (HF) exchange with DFT correlation energies. The hybrid Becke-Perdue-Wang 1991 (B3PW91) method used throughout this paper includes Perdue and Wang local and non local correlation functionals [18,19]. A triple valence basis set (6-311G) containing  $8s,7p,1d$  Gaussians contracted as (62111111,3311111,3) and augmented with one *d* polarization function [20] was used in all calculations. We found this basis set to be sufficiently large to give good results at a reasonable computational effort. Adding an additional diffuse function produced insignificant changes in both the energy and bond length of  $\text{Ca}_2$ . The basis set superposition error (BSSE) [21] was negligible for both calculations with the triple valence basis set including one or two polarization functions.

Based on the dimer results, all calculations reported in this paper were performed with the triple valence basis set including one *d* polarization function. Results in forthcoming sections do not include the BSSE correction. However, we

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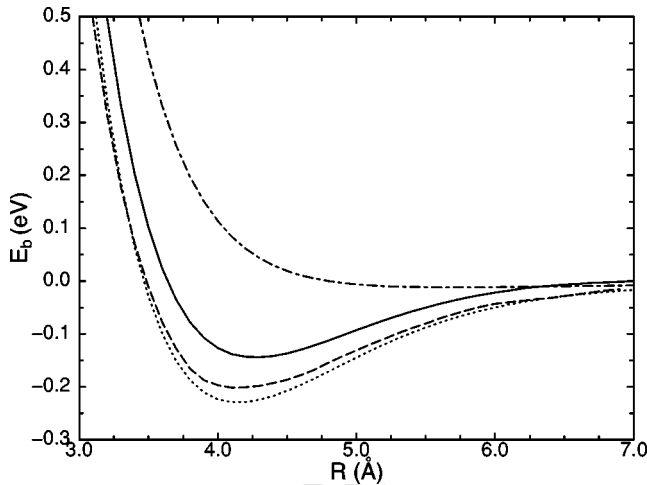


FIG. 1. Binding energy of  $\text{Ca}_2$  as a function of interatomic distance with various methods: B3PW91 (solid line), PW91PW91 (dotted), NRLMOL (dashed), and MP4 (dashed-dotted).

did test for BSSE with calculations up to  $\text{Ca}_4$  and found an insignificant decrease in the total energy for these cluster sizes. Worth noting is that BSSE is important when the basis set is small, and our basis set is large.

Since  $\text{Ca}_2$  is a closed-shell system, it demands a good representation of the electron correlation energy to obtain reasonable total energies. We performed an analysis of various methods on the calcium dimer, which are summarized in Fig. 1, where the binding energy ( $E_b$ ) is displayed as a function of interatomic distance ( $R$ ). The binding energy is computed as the value of the total energy of two isolated Ca atoms (with the BSSE correction) minus the total energy of the dimer. The solid line shows results with the hybrid B3PW91 method. The dot-dashed line represents the Moller-Plesset results with up to four excitations (MP4) [22]. The dotted line illustrates results within GGA in which both exchange and correlation functionals [18,19] are provided (PW91PW91) and the same basis set as in B3PW91 was used. All calculations were done using GAUSSIAN-98 [23]. The accuracy attained in the self-consistent field (SCF) process assures eight decimal places in the energies. The dashed line pertains to the same level of approximation than PW91PW91 but results were obtained with the NRLMOL package. [24] In this case we used a basis set of 19 noncontracted Gaussians augmented by three floating Gaussians [25] to expand each of the  $s$ ,  $p$ , and  $d$  orbitals that were optimized on the calcium atom. The accuracy in the SCF was the same as that obtained with the GAUSSIAN package. The small discrepancies between results obtained from using PW91PW91 (dotted line) and the NRLMOL (dashed lines) are due to the difference in the basis sets.

The MP4 calculation (dashed-dotted line) significantly underestimates the electron correlation, while GGA (both PW91PW91 and NRLMOL) overestimates the binding energy (dotted and dashed lines). The dissociation energy found with B3PW91 (solid line) is 0.147 eV, in very good agreement with the experimental result of 0.136 eV [2,3]. In addition, we found a value of 4.269 Å for the equilibrium bond length, which compares well to the experimental value of

TABLE I. Comparison of different calculations of the binding energy, interatomic distance, and harmonic frequency of  $\text{Ca}_2$ .

	Method basis set	$E_b$ (eV)	$R_e$ (Å)	$\nu$ ( $\text{cm}^{-1}$ )
This work	B3PW91 6-311g(d)	0.144	4.27	72.3
This work	NRLMOL	0.201	4.30	76.0
Ref. [3]	Experimental	0.136	4.277	65.07
Ref. [2]	Experimental	0.133	4.28	64.93
Ref. [9]	CI [4s2p]	0.007	6.509	
Ref. [10]	CI [4s2p1d]	0.029	5.080	
Ref. [8]	LDA [4s3p]	0.012	5.503	
Ref. [7]	LDA	0.2	4.30	80

4.277 Å. Our predicted harmonic frequency is  $72.3 \text{ cm}^{-1}$ , also in good agreement with the experimental results. The zero-point energy correction to the binding energy is very small (0.2 kcal/mole). The first and second ionization potentials of  $\text{Ca}_2$  calculated with B3PW91 are 4.950 and 9.118 eV, respectively.

Additionally, we performed a fit of the Morse potential parameters to the B3PW91 energy curve of Fig. 1 in the range of interatomic distances  $3.3 \text{ Å} \leq R \leq 5.3 \text{ Å}$ . The values obtained are:  $D_e = 0.139140 \text{ eV}$ ,  $\beta = 1.093$ , and  $r_0 = 4.261 \text{ Å}$ . The error of the fit was 0.01 eV (twice the standard deviation). The harmonic frequency and anharmonic constant obtained from this Morse potential are  $\nu_e = 68.85 \text{ cm}^{-1}$  and  $x_e \omega_e = 1.06 \text{ cm}^{-1}$ , respectively. These values are in excellent agreement with those obtained from spectroscopic measurements [2,3,26]. A fit of the long-range portion of the binding energy as a function of interatomic distance to expressions of the type  $R^{-6}$  was not successful, indicating that the dimer attractive tail carries components other than dispersive force contributions.

The PW91PW91 and the NRLMOL results are very close to the early local-density approximation (LDA) results of Jones [7]. Other calculations for the dimer have reported significantly different binding energies and interatomic distances. A summary of all results is given in Table I. We have shown that MP4 configuration interaction calculation does not include a large enough set of configurations to account for the electron correlation energy in the calcium dimer. The HF description of the electron exchange energy in  $\text{Ca}_2$  provided by B3PW91 is superior to the functional representation of that energy in both PW91PW91 and NRLMOL. The agreement between the B3PW91 calculations and the experimental values of the binding energy, bond distance, and harmonic frequency for the calcium dimer led us to use the hybrid method B3PW91 in our investigation of larger calcium clusters.

### III. ENERGETICS AND VIBRATIONAL FREQUENCIES OF CALCIUM TRIMER, TETRAMER, AND PENTAMER

Table II lists the binding energy per atom  $E_b$ , average bond length  $R_{ave}$ , energy difference between the (LUMO) and (HOMO) one-electron levels  $\Delta_{HL}$ , and normal mode frequencies. In this table, as well as in the rest of this paper,

TABLE II. Binding energy per atom, HOMO-LUMO energy gap, average bond length, and harmonic frequencies of stable isomers of  $\text{Ca}_3$ ,  $\text{Ca}_4$ , and  $\text{Ca}_5$ .

	Sym	$E_b$ (eV/atom)	$\Delta_{HL}$ (eV)	$R_{ave}$ (Å)	$\nu$ ( $\text{cm}^{-1}$ )
$\text{Ca}_3$	$D_{3h}$	0.220 (B3PW91)	1.926	3.933	98.8( $E'$ ), 107.7( $A'_1$ )
		0.247 (NRLMOL)		4.171	95( $E'$ ), 85( $A'_1$ )
		0.009 Ref. [9]		6.033	
	$D_{\infty h}$	0.162 Ref. [11]	1.657	4.172	83.0( $E'$ ), 94.0( $A'_1$ )
		0.114 (B3PW91)		4.202	6.7( $\Pi_u$ ), 56.2 ( $\Sigma_g$ ), 98.1( $\Sigma_u$ )
		0.149 (NRLMOL)		4.200	
$\text{Ca}_4$	$T_d$	0.014 Ref. [9]	1.990	6.403	
		0.444 (B3PW91)		3.767	103.6( $E$ ), 122.7( $T_2$ ), 142.0( $A_1$ )
		0.445 (NRLMOL)		3.906	91( $E$ ), 111( $T_2$ ), 130( $A_1$ )
		0.021 Ref. [9]		5.345	
		0.151 Ref. [10]		4.286	
	$D_{4h}$	0.198 Ref. [12]	1.350	4.159	
		0.199 Ref. [13]		4.138	
		0.341 Ref. [11]		4.017	86.0( $E$ ), 105.0( $T_2$ ), 127.0 ( $A_1$ )
	$D_{4h}$	0.075 Ref. [9]		5.874	
	$D_{\infty h}$	0.139 (B3PW91)	0.299	4.166	4.5, 4.5, 9.3, 46.1, 82.1, 114.0
		0.176 (NRLMOL)		4.452	
$D_{2h}$	0.020 (B3PW91)	0.299	3.506, 3.921		
	0.046 Ref. [9]		5.980		
$\text{Ca}_5$	$D_{3h}$	0.479 (B3PW91)	1.451	3.822	69.7( $E'$ ), 87.5( $E''$ ), 91.2( $A'_1$ ), 103.4( $A'_2$ ), 132.9( $E'$ ), 157.5( $A'_1$ )
		0.483 (NRLMOL)		4.025	63( $E'$ ), 76( $E''$ ), 90( $A'_1$ ), 102( $A'_2$ ), 117( $E'$ ), 145( $A'_1$ )
		0.142 Ref. [9]		5.398	
	$C_{4v}$	0.087 Ref. [9]		5.715	
	$C_{2v}$	0.065 Ref. [9]		5.926	
	$D_{5h}$	0.033 Ref. [9]		6.191	

binding energies at the minima are reported as positive values. In all calculations, the self-consistent-field results (SCF) convergence was attained up to eight decimals. The optimization of the bond lengths is accurate up to four decimals. The ground-state configurations are the equilateral triangle ( $D_{3h}$ ) for  $\text{Ca}_3$ , the tetrahedron ( $T_d$ ) for  $\text{Ca}_4$ , and the trigonal bipyramid ( $D_{3h}$ ) for  $\text{Ca}_5$ . Other geometries of the trimer and tetramer were also studied, as listed in Table II. For comparison this table contains all other published results for these cluster sizes. Previous calculations performed on  $\text{Ca}_3$  (equilateral triangle) and  $\text{Ca}_4$  (tetrahedron) [11] revealed a binding energy of 0.162 eV/atom and 0.341 eV/atom, respectively. Both values underestimate the binding energy as compared to our results by 30% and 26%, respectively. Reported bond lengths for the trimer and tetramer from Ref. [11] are 4.172 and 4.016 Å, respectively. These bond lengths are higher than our values of 3.933 and 3.767 Å. The pentamer is the characteristic trigonal bipyramid of close-packed structures. Reported binding energies in Ref. [9] are much lower than our results, and the corresponding bond lengths longer than our values (see Table II). Even though there are reported calculations for other geometries of  $\text{Ca}_4$  and  $\text{Ca}_5$  [9] as listed in Table II, none of those structures was found to be a minimum of the energy surface. In fact, we found that most

of these structures are associated with saddle points of the energy surface.

In summary, it is apparent that for the trimer and tetramer, a good treatment of both correlation and exchange energies is crucial. Not only binding energies are higher in our paper than previously reported in the literature, but also the bond lengths are significantly smaller. The HOMO-LUMO gap in the most stable isomers of  $\text{Ca}_3$  through  $\text{Ca}_5$  is high (1.9 to 1.4 eV), indicating that these clusters are far from presenting a metallic character. However, the gap decreases in the higher-energy isomers of these cluster sizes, as can be seen from data in Table II. When we compare our results between B3PW91 and NRLMOL (Table II), we see that the binding energies tend to have the same value, although the interatomic distances are slightly longer in NRLMOL than in B3PW91. We attribute this effect to the differences in the exchange energy between the two methods.

#### IV. ENERGETICS AND VIBRATIONAL FREQUENCIES OF LARGER CALCIUM CLUSTERS

The search of stable structures of  $\text{Ca}_6$  through  $\text{Ca}_{13}$  was initialized from numerous geometries in our database. Optimization of all cluster structures was performed without

TABLE III. Binding energy per atom, HOMO-LUMO energy gap, average bond length of stable isomers of Ca<sub>6</sub> through Ca<sub>13</sub> using B3PW91 and NRLMOL (when explicitly mentioned).

	Sym	$E_b$ (eV/atom)	$\Delta_{HL}$ (eV)	$R_{ave}$ (Å)
Ca <sub>6</sub>	$C_{2v}$	0.514	1.217	3.852
	$C_{2v}$	0.520 (NRLMOL)		3.986
Ca <sub>7</sub>	$D_{5h}$	0.623	1.416	3.805
	$D_{5h}$	0.604 (NRLMOL)		3.954
	$C_2$	0.563	1.283	3.851
	$C_s$	0.547	1.336	3.864
	$C_{3v}$	0.515	1.139	3.923
Ca <sub>8</sub>	$C_s$	0.638	1.192	3.828
	$C_s$	0.629 (NRLMOL)		3.921
Ca <sub>9</sub>	$C_{2v}$	0.687	1.048	3.830
	$C_s$	0.658	1.053	3.829
Ca <sub>10</sub>	$C_{4v}$	0.752	1.636	3.868
	$C_s$	0.693	1.019	3.841
	$C_s$	0.659	0.835	3.865
Ca <sub>11</sub>	$D_{4d}$	0.751	0.846	3.789
	$C_1$	0.733	1.026	3.842
Ca <sub>12</sub>	$C_1$	0.756	0.900	3.848
	$C_1$	0.748	0.766	3.884
	$C_1$	0.742	0.714	3.867
Ca <sub>13</sub>	$C_1$	0.781	0.772	3.848
	$C_i$	0.755	0.723	3.934

symmetry constraints. The ground state of all clusters were singlets. Accuracy in the SCF ensures eight decimal places in the energies, whereas optimization of geometries are accurate up to the fourth decimal. In Table III we report the geometry, point group, binding energy, energy gap between the LUMO and HOMO ( $\Delta_{HL}$ ), and average bond length for

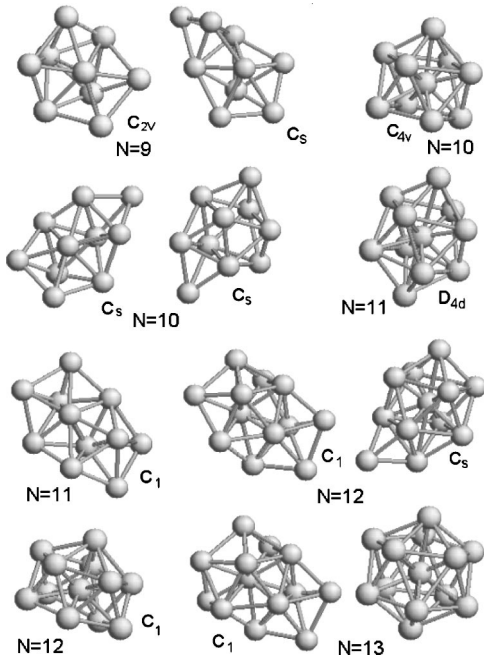


FIG. 2. Low-energy stable isomers of Ca<sub>9</sub> through Ca<sub>13</sub>.

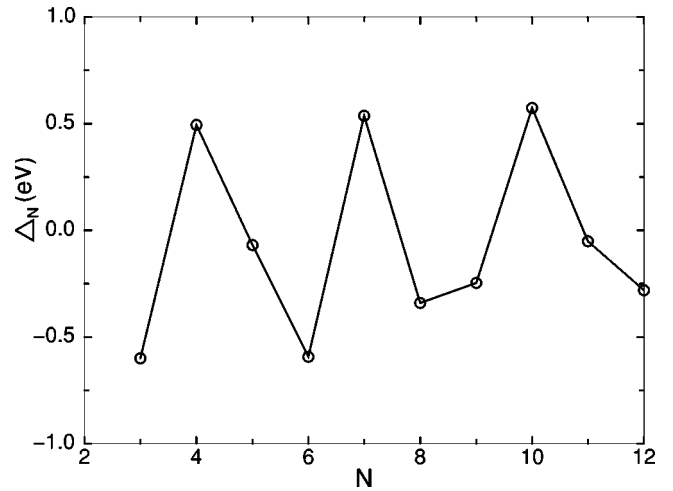


FIG. 3. Energy stability pattern of calcium clusters at zero temperature.

the investigated cluster structures of Ca<sub>6</sub> through Ca<sub>13</sub>. The geometry of these clusters is visualized in Fig. 2. The close-packed growth sequence leading to fivefold symmetry clusters is obtained from Ca<sub>4</sub> through Ca<sub>9</sub>, namely, decorating a face of the tetrahedron (Ca<sub>4</sub>) with one atom leads to Ca<sub>5</sub> (trigonal bipyramid), Ca<sub>6</sub> is the pentamer with one decorated face, the pentagonal bipyramid is the geometry for Ca<sub>7</sub>, the heptamer with one decorated face becomes Ca<sub>8</sub>, and Ca<sub>9</sub> is the heptamer with two decorated faces. However, this sequence changes at Ca<sub>10</sub>, which is the anticube with one central atom and one extra atom decorating a square face. A fourfold axis of rotation is preserved at Ca<sub>11</sub> as can be seen in Fig. 2. It is also apparent from this figure that from Ca<sub>11</sub> and up, a secondary structure with twinned pentagonal bipyramids is close in energy to the global minimum structure. The pentagonal bipyramid is a possible building block for larger cluster sizes. In fact the lowest-energy structure of Ca<sub>12</sub> is composed of two of these building blocks with one decorated face, and the lowest structure we found for Ca<sub>13</sub> is that of two twinned pentagonal bipyramids with two decorated faces. An icosahedrallike Ca<sub>13</sub> ( $C_1$  structure, not perfect icosahedron) is 0.336 eV above this twinned structure. Calculations with the NRLMOL package were also carried out for sizes up to  $N=8$ . The results are given in Table III. It is seen that the binding energies tend to coincide between the two calculations as the size of the cluster increases, although structures calculated with NRLMOL are systematically more expanded.

Figure 3 illustrates the second differences of the cluster binding energy,  $\Delta_N = 2E_b(N) - E_b(N-1) - E_b(N+1)$ , for the lowest-energy structures reported in Tables II and III. This function is a measure of the relative stability of clusters at zero temperature with respect to their neighboring sizes. Peaks of this function indicate when a cluster with  $N$  atoms is relatively more stable than clusters with either  $N+1$  or  $N-1$  atoms. In this size range 4, 7, and 10 display an enhanced energy stability at zero temperature.

As is seen in Tables II and III, the HOMO-LUMO energy gap decreases with increasing cluster size from 1.9 for the

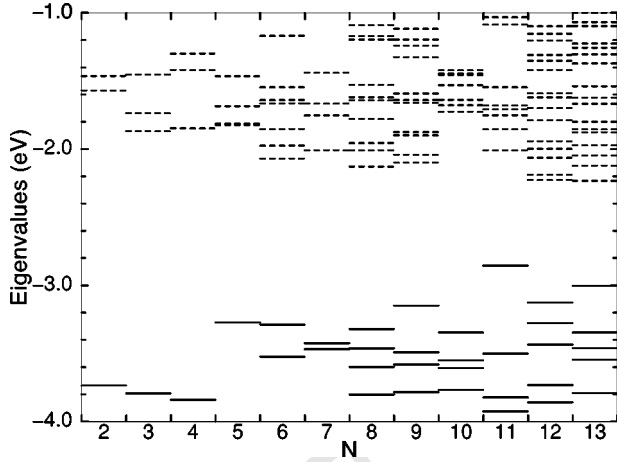


FIG. 4. One electron eigenvalues versus cluster size. Solid lines are the occupied states and dashed lines represent the virtual states.

trimer to 0.8 eV for  $\text{Ca}_{13}$ . This energy gap gives an indication of how metallic the system is, since the Fermi energy lays in it. We conclude that small clusters up to  $\text{Ca}_{13}$  are not metallic because the energy gap is an order of magnitude larger than thermal energies attainable in experiments. Figure 4 is a representation of the one-electron energies around this gap. The plot gives a visual description of how the conduction band builds up as a function of size. It is to be noted that the density-of-states of bulk fcc calcium, calculated with equivalent methods [27], indicates that the Fermi level is located in a region of low density almost edging a small gap of 0.029 eV. Tables II and III report also the average bond distance in each cluster. With the exception of  $\text{Ca}_4$ , which is more tightly bound, these averaged bond distances are slowly increasing and will eventually reach the nearest-neighbor distance of 3.94 Å of bulk fcc calcium. For a given cluster size this average bond length changes with the symmetry of the isomer, as indicated in Table III.

Tables V, VI, and VII of the Appendix contain the harmonic frequencies for all the structures listed in Tables II and III. A pictorial representation of the vibrational spectrum as a function of cluster size is provided in Fig. 5. In this figure the height indicates the degeneracy of each frequency and the dashed spikes denote vibrational modes that are infrared inactive. The spectrum becomes more dense in the center of the band as the size of the cluster is increased. There is also an increase in the width of the band with cluster size. In this size range only  $\text{Ca}_{10}$  presents a very low-frequency mode.

In the search of the structures with lowest total energy we found several structures associated with saddles of the energy surface (one or multiple imaginary frequencies). Relevant data for these structures is provided in Table IV including the order of the saddle point. These structures are interesting because they might be good candidates for intermediate structures in isomerization reactions. For example, we have determined the reaction path that connects the energy surfaces of two degenerate  $\text{Ca}_5$  ( $D_{3h}$ ) isomers. We also found the reaction path in the isomerization of  $\text{Ca}_6$  ( $C_{2v}$ ). These reaction paths are depicted in Figs. 6(a) and 6(b) where the reported energy is relative to the binding energy of

TABLE IV. Binding energy per atom, order of saddle point, and average bond length of structures at saddle points found for  $\text{Ca}_4$  through  $\text{Ca}_{10}$  using B3PW91.

	Sym	Order	$E_b$ (eV/atom)	$R_{\text{ave}}$ (Å)
$\text{Ca}_4$	$D_{2h}$	1	0.257	3.988
	$D_{4h}$	2	0.152	4.234
$\text{Ca}_5$	$C_{4v}$	1	0.339	3.965
$\text{Ca}_6$	$D_{2h}$	1	0.495	3.823
	$D_{4h}$	3	0.458	3.762
	$O_h$	5	0.354	4.071
	$D_{6h}$	6	0.178	4.182
$\text{Ca}_7$	$C_s$	1	0.549	3.824
	$O_h$	9	0.293	3.7
$\text{Ca}_8$	$C_{2v}$	1	0.607	3.862
	$C_s$	1	0.601	3.818
	$D_{6h}$	1	0.541	3.856
	$D_{4d}$	2	0.533	3.900
$\text{Ca}_9$	$D_{4h}$	6	0.390	3.826
	$C_s$	1	0.641	3.715
	$C_{4v}$	1	0.630	3.873
$\text{Ca}_{10}$	$D_{3h}$	2	0.751	3.809
	$D_{4d}$	2	0.640	3.899
$\text{Ca}_{13}$	$C_1$	1	0.774	3.872

the degenerate minima. The Arrhenius-type energy barriers in the two isomerization reactions are the difference between the binding energies of the transition structures ( $C_{4v}$  for the pentamer and  $D_{2h}$  for the hexamer reported in Table IV) minus the binding energy of the minimum structures from Tables II and III. In the case of the hexamer, the octahedron ( $O_h$ ) is the stable geometry obtained under several empirical potentials including the MM potential. We have found that this geometry corresponds to a saddle point of order 5. For larger isomers, various other geometries corresponding to saddles of different orders were detected. These are illustrated in Fig. 7. The binding energies of these saddle structures (see Table IV) allow for determination of the barriers in isomerization reactions. However, these saddles do not necessarily connect the lowest-energy isomer of a given size with another isomer of higher energy. For example, one of the low-energy isomers of  $\text{Ca}_7$  is  $\text{Ca}_6$  with one decorated face ( $C_2$ , two intertwined trigonal bipyramids with one decorated face). There are three equivalent ways to decorate  $\text{Ca}_6$  and therefore three equivalent isomers. In order to go from one of these isomers to the other, the reaction path needs to overcome a barrier of about 0.1 eV and the intermediate structure corresponding to the saddle point is given in Fig. 7.

For comparison purposes we reproduced the lowest-energy geometries of isomers obtained from the MM potential parametrized for calcium [15]. It was found that this potential gives the right geometry of the global minimum structure (but not the bond lengths) of  $\text{Ca}_3$  through  $\text{Ca}_5$  and  $\text{Ca}_7$  through  $\text{Ca}_9$ . However, the lowest-energy isomers obtained with the MM potential for  $\text{Ca}_6$  and  $\text{Ca}_{10}$  through  $\text{Ca}_{13}$  were different than those obtained in our work. Additionally,

TABLE V. Normal-mode frequencies for the isomers of  $\text{Ca}_6$  through  $\text{Ca}_9$  reported in Table III.

	Sym	$\nu$ ( $\text{cm}^{-1}$ )
$\text{Ca}_6$	$C_{2v}$	48.0( $A_1$ ), 68.5( $A_2$ ), 69.0( $B_1$ ), 86.4( $A_1$ ), 92.8( $B_2$ ), 97.0, 100.0( $B_2$ ), 100.9, 104.1( $B_1$ ), 119.1( $B_2$ ), 124.4( $A_1$ ), 157.6( $A_1$ )
$\text{Ca}_7$	$D_{5h}$	74.6( $E_2''$ ), 77.8( $E_1'$ ), 95.8( $A_2''$ ), 105.1( $E_2'$ ), 107.3( $E_1''$ ), 111.0( $A_1'$ ), 116.8( $E_2'$ ), 137.6( $E_1'$ ), 167.8( $A_1'$ )
	$C_2$	41.8( $B$ ), 48.1( $A$ ), 62.3( $A$ ), 82.2, 82.7, 91.3( $A$ ), 98.7( $B$ ), 101.6( $A$ ), 105.4( $B$ ), 114.8( $A$ ), 117.9( $B$ ), 123.3, 123.3, 140.9( $B$ ), 143.3( $A$ )
	$C_s$	43.3, 43.4, 60.5, 80.7, 80.9, 88.2, 89.7, 89.9, 99.5, 105.6, 121.3, 121.4, 127.1, 127.2, 150.0
	$C_{3v}$	12.2( $E$ ), 51.4( $A_2$ ), 58.0( $E$ ), 81.3( $A_1$ ), 94.7( $E$ ), 108.1( $E$ ), 122.5, 122.7( $E$ ), 129.7( $A_1$ ), 156.2( $A_1$ )
$\text{Ca}_8$	$C_s$	43.6( $A''$ ), 60.3( $A'$ ), 70.2( $A'$ ), 72.5( $A''$ ), 88.0( $A'$ ), 93.4( $A'$ ), 94.4( $A''$ ), 99.7( $A''$ ), 101.5( $A'$ ), 104.9( $A'$ ), 107.7( $A'$ ), 110.7( $A''$ ), 116.1( $A''$ ), 120.3( $A'$ ), 121.7( $A'$ ), 133.4( $A''$ ), 146.1( $A'$ ), 151.9( $A'$ )
$\text{Ca}_9$	$C_{2v}$	48.7( $B_2$ ), 53.2( $A_1$ ), 59.0( $A_2$ ), 80.8( $A_1$ ), 83.0( $B_1$ ), 84.3( $A_2$ ), 87.0( $B_2$ ), 93.4( $A_1$ ), 100.6, 100.6, 102.1( $A_2$ ), 103.9( $B_1$ ), 108.9( $A_1$ ), 113.1( $A_1$ ), 115.5( $B_1$ ), 119.4( $B_2$ ), 124.6( $A_2$ ), 128.6( $A_1$ ), 142.8( $A_1$ ), 149.8( $B_2$ ), 165.1( $B_1$ )
	$C_s$	37.1( $A'$ ), 49.4( $A''$ ), 53.7( $A''$ ), 69.5( $A'$ ), 75.4( $A'$ ), 83.0( $A''$ ), 84.9( $A'$ ), 90.4( $A''$ ), 92.4( $A'$ ), 100.4( $A'$ ), 102.9( $A'$ ), 104.2( $A''$ ), 111.4( $A'$ ), 114.7( $A''$ ), 120.5, 120.5, 127.3( $A'$ ), 134.8( $A''$ ), 136.7( $A'$ ), 147.1( $A'$ ), 158.2( $A'$ )

we found that some of the MM lowest-energy geometries are associated to saddle points. Such is the case of  $\text{Ca}_6$  ( $O_h$ ). The MM  $\text{Ca}_{10}$  structure was not stable and relaxed into the  $D_{3d}$  saddle geometry. The MM binding energies for all sizes are systematically higher than our results as is illustrated in Fig. 8(a), where the binding energy from MM structures (crosses) are compared to our calculation (circles). Figure 8(b) shows a comparison of the trend of our average bond distance of the lowest-energy structures as a function of size when compared to those obtained from the MM structures. It is evident that the empirical potential predicts slightly more expanded structures in this size range. We calculated the normal-mode frequencies with the MM structures obtaining spectra very different to ours shown in Fig. 5. For example, the normal frequencies for  $\text{Ca}_3$  are 101 and 144  $\text{cm}^{-1}$ ,<sup>1</sup> which are higher than our results in Table II. The discrepancy of MM frequencies with our B3PW91 results indicates that this model potential tends to stiffen the cluster structures.

## V. HIGHER-ENERGY ISOMERS AND STRUCTURAL TRANSITIONS

A harmonic analysis of several thermodynamic functions was carried out based on the normal-mode frequencies. For example, the free-energy, internal energy, and vibrational specific heat were calculated for all the known isomers re-

ported in Tables II and III of  $\text{Ca}_3$  through  $\text{Ca}_{13}$ . Figures 9(a) and 9(b) depict the size dependence of the free energy per atom and specific heat at 300 and 500 K (circles and crosses, respectively).

We found in this size range that the second to lowest-energy isomer of  $\text{Ca}_{12}$  ( $C_s$ ) becomes more stable at a transition temperature  $T_S = 317$  K. This structural transition temperature was defined as the temperature where there is a crossing of the free energy associated to two of the three  $\text{Ca}_{12}$  isomers (see Table III and Fig. 2). Figure 10(a) depicts the free energy of these three isomers as a function of temperature and the crossing point where the transition occurs. Additionally, we calculated the internal energy and the specific heat for  $\text{Ca}_{12}$ . Figures 10(b) and 10(c) show the behavior of these quantities at temperatures near  $T_S$ . In producing these two plots a broadening algorithm was used to smooth the abrupt change of the functions at the transition temperature. Below  $T_S$  the decorated twinned pentagonal bipyramid structure is preferred, and above  $T_S$  the decorated antcube structure prevails. Notice, that there is no temperature driven transition to the third-to-lowest isomer (incomplete icosahedron) within the harmonic frequency approach. This would mean that the icosahedral growth is not favored by temperature, but instead elements of cubic symmetry that span around a central atom ( $\text{Ca}_{10}$  through  $\text{Ca}_{12}$ ) are more favorably enhanced at temperatures slightly above room tempera-

TABLE VI. Normal-mode frequencies for the isomers of Ca<sub>10</sub> through Ca<sub>12</sub> reported in Table III.

	Sym	$\nu$ (cm <sup>-1</sup> )
Ca <sub>10</sub>	$C_{4v}$	10.0( $B_1$ ), 35.7( $E$ ), 68.2( $A_2$ ), 74.5( $E$ ), 75.8( $B_1$ ), 81.0( $E$ ), 89.4( $E$ ), 98.3( $A_1$ ), 101.9( $B_1$ ), 112.2( $E$ ), 122.0( $A_1$ ), 126.2( $B_1$ ), 126.3( $A_1$ ), 128.8( $E$ ), 134.6( $B_2$ ), 197.9( $A_1$ ), 215.5( $E$ )
	$C_s$	38.4, 42.1, 56.9, 61.7, 78.7, 80.8, 82.3, 89.2, 91.0, 91.3, 96.9, 97.9, 99.4, 108.0, 109.3, 112.7, 114.5, 116.4, 123.3, 124.7, 135.3, 141.0, 146.6, 153.4
	$C_s$	21.5, 26.2, 32.1, 52.8, 63.3, 74.8, 75.0, 81.6, 82.6, 86.4, 86.6, 92.6, 95.6, 97.6, 108.3, 110.6, 114.0, 117.7, 120.8, 124.8, 127.2, 138.7, 138.9, 150.9
Ca <sub>11</sub>	$D_{4d}$	48.7( $E$ ), 50.9, 55.8, 56.1, 62.4( $E$ ), 65.6, 71.3, 71.5, 74.8( $E$ ), 77.7, 88.9( $E$ ), 102.8, 103.0( $E$ ), 112.0, 126.0, 128.5( $E$ ), 130.8( $E$ ), 198.9, 219.4( $E$ )
	$C_1$	41.0, 47.2, 52.9, 67.8, 74.4, 81.4, 83.0, 83.9, 88.3, 90.7, 91.0, 95.6, 99.6, 103.2( $E$ ), 106.6, 109.6, 111.5, 114.3, 117.9, 120.9, 131.8, 138.3, 140.2, 143.6, 147.0, 148.4
Ca <sub>12</sub>	$C_1$	43.2, 47.0, 52.9, 59.5, 63.8, 73.8, 80.4, 81.3, 84.6, 86.9, 87.4, 90.3, 94.8, 97.3, 98.6, 100.9, 101.7, 102.6, 104.3, 105.9, 112.4, 117.6, 119.3, 127.8, 131.2, 136.9, 140.4, 147.4, 150.5, 164.8
	$C_1$	16.9, 34.3, 37.0, 42.4, 49.6, 54.4, 60.5, 62.2, 64.2, 73.0, 75.5, 78.7, 81.3, 84.4, 88.5, 90.4, 93.7, 104.1, 107.6, 108.9, 116.5, 118.3, 124.4, 125.9, 128.5, 129.8, 133.1, 180.1, 209.9, 211.0
	$C_1$	25.4, 28.2, 46.5, 57.4, 57.7, 66.4, 69.4, 75.3, 75.5, 80.5, 84.4, 87.4, 87.5, 89.3, 94.0, 97.5, 106.5, 107.5, 111.0, 111.9, 112.2, 120.6, 129.3, 131.8, 134.0, 136.3, 147.9, 161.7, 173.9, 192.8

ture. No structural transition was detected for Ca<sub>13</sub>, or for clusters smaller than Ca<sub>12</sub>. Similar structural transitions might take place for cluster sizes larger than  $N=13$ .

## VI. CONCLUSION

In this paper we have presented an analysis of small calcium clusters up to Ca<sub>13</sub> using the hybrid DFT approach that includes HF calculation of the exchange energy and local and nonlocal correlation energy functionals provided by Perdue-Wang. We have determined the structure, binding en-

ergies, and harmonic frequencies of vibration for several isomers at each cluster size up to Ca<sub>13</sub>. The lowest-energy structures of Ca<sub>6</sub> and Ca<sub>10</sub> through Ca<sub>13</sub> had not been reported before as global geometries for calcium clusters. We predict that there are two paths of cluster growth. At almost zero temperature, clusters grow by twinning pentagonal bipyramids as the building block, while at temperatures closely above room temperature, clusters grow building shells of atoms around a central atom with local cubic symmetry. For Ca<sub>12</sub>, instead of the icosahedron-minus-one-atom expected structure, we found that this structure is not reachable within

TABLE VII. Normal-mode frequencies for the isomers of Ca<sub>13</sub> reported in Table III.

	Sym	$\nu$ (cm <sup>-1</sup> )
Ca <sub>13</sub>	$C_1$	20.5, 37.3, 51.7, 55.5, 57.0, 64.4, 75.0, 76.3, 82.2, 84.0, 86.3, 89.1, 89.9, 92.8, 93.9, 96.6, 99.0, 101.3, 103.6, 105.4, 107.9, 111.3, 111.7, 117.5, 119.8, 122.8, 128.0, 132.3, 138.9, 144.7, 159.8, 161.9, 180.3
	$C_i$	23.7, 25.6, 35.0, 35.6, 66.9, 67.2, 67.5, 68.0, 68.2, 68.7, 70.8, 71.2, 72.7, 83.0, 89.4, 89.9, 94.5, 94.7, 97.2, 97.6, 115.0, 119.2, 119.4, 122.9, 124.4, 124.4, 130.3, 132.8, 133.0, 146.4, 147.4, 187.3, 187.7

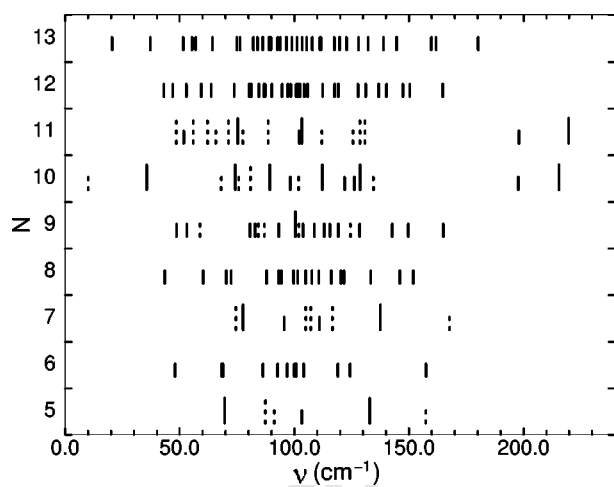


FIG. 5. Normal-mode frequencies of vibration for  $\text{Ca}_5$  through  $\text{Ca}_{13}$ . The height of the spikes indicate the degeneracy of the mode. Solid lines are infrared active modes and dashed lines are inactive.

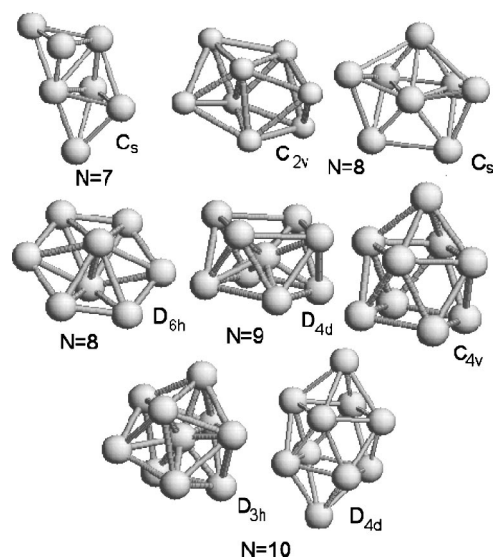


FIG. 7. Several structures of  $\text{Ca}_7$  through  $\text{Ca}_{10}$  corresponding to saddle points of the energy surfaces.

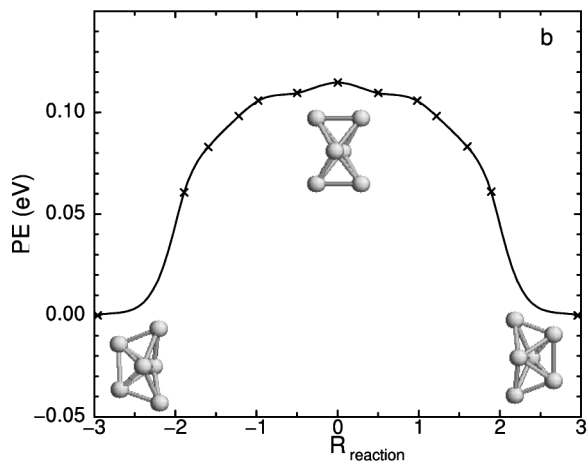
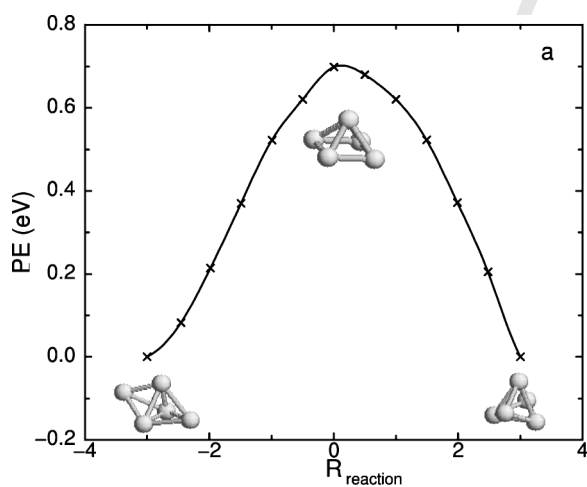


FIG. 6. Isomerization reaction paths for (a)  $\text{Ca}_5$  and (b)  $\text{Ca}_6$ . The intermediate structure is depicted at the barrier point. Energies are relative to the energy of the corresponding reactant. The reaction coordinate is dimensionless.

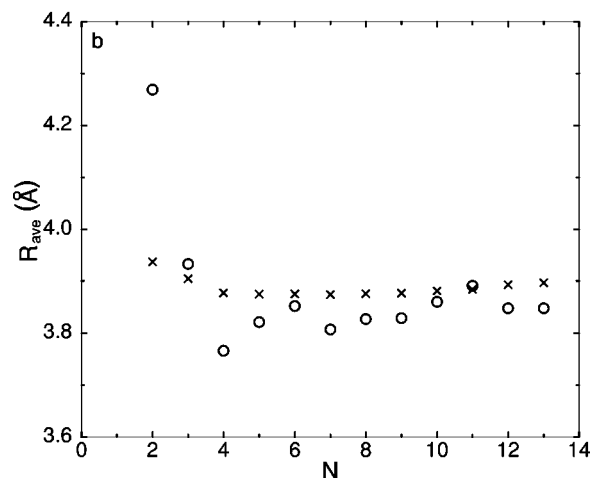
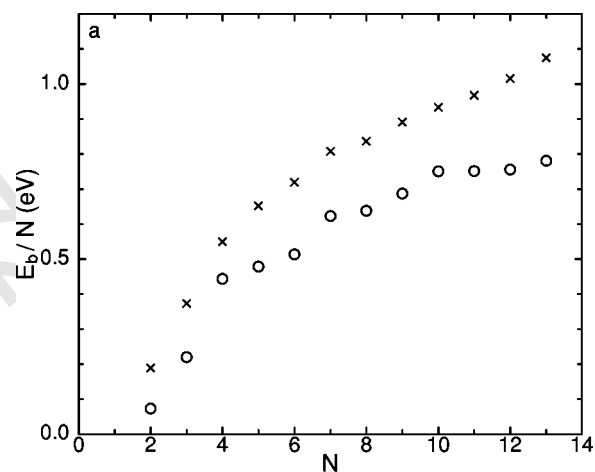


FIG. 8. Comparison of B3PW91 (circles) and Murrell-Mottram potential (crosses) of (a) binding energy per atom versus cluster size and (b) average bond length versus cluster size.



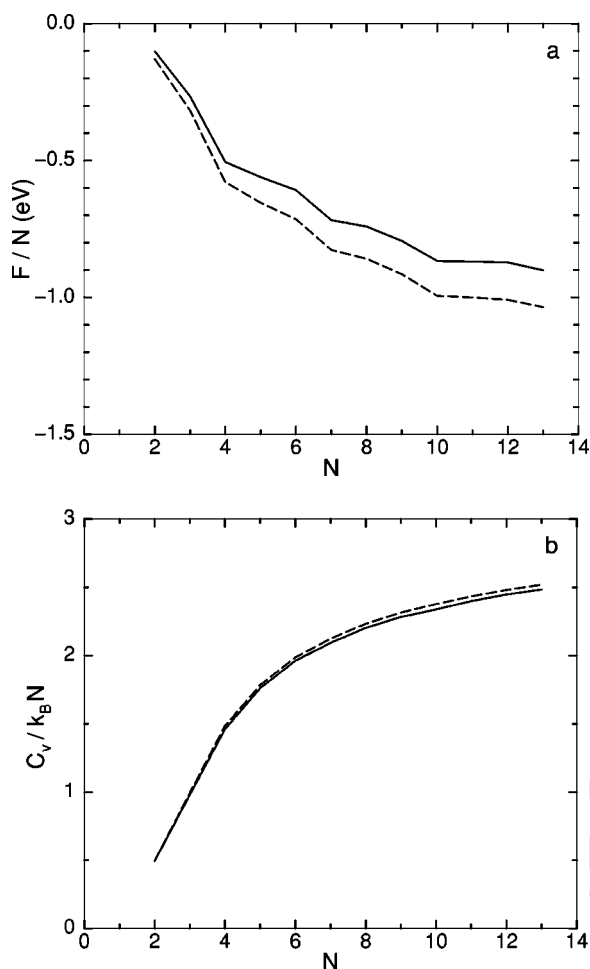


FIG. 9. (a) Free energy per atom versus cluster size; (b) specific heat versus cluster size.  $T=300$  K (full line) and  $T=500$  K (dashed line).  $k_B$  is Boltzmann's constant.

the temperature range studied here (below 500 K). Instead the  $\text{Ca}_{12}$  lowest-energy isomer is a structure with two twinned pentagonal bipyramids that has a decorated face. We also found that this isomer undergoes a structural transition at about 317 K and becomes an isomer with local cubic symmetry elements as depicted in Fig. 2 ( $C_s$  because of slight distortions). The metallic character of calcium is far from being attained at  $\text{Ca}_{13}$  because the HOMO-LUMO energy difference is 0.8 eV, a value that is very large when compared to the small gap of 0.03 eV observed in bulk fcc calcium. The average nearest-neighbor interatomic distances for calcium clusters with  $N > 4$  vary between 3.82 and 3.89 Å, just slightly less than the 3.92 Å found in the fcc crystal.

Calcium is a very reactive element and combines readily with oxygen. Therefore studies of pure calcium clusters are challenging systems for experimental findings. In this direction the predictive content of this paper should be helpful. The energy barriers of various isomerization reaction paths are reported, indicating that for very small clusters, these reactions will not take place at room temperature, favoring instead oxidation mechanisms.

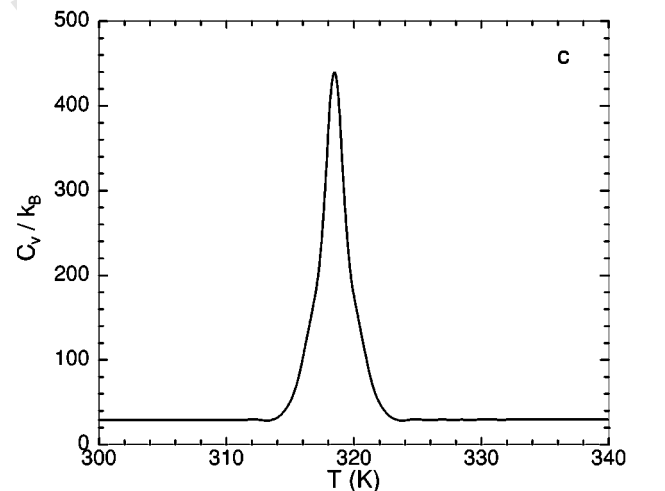
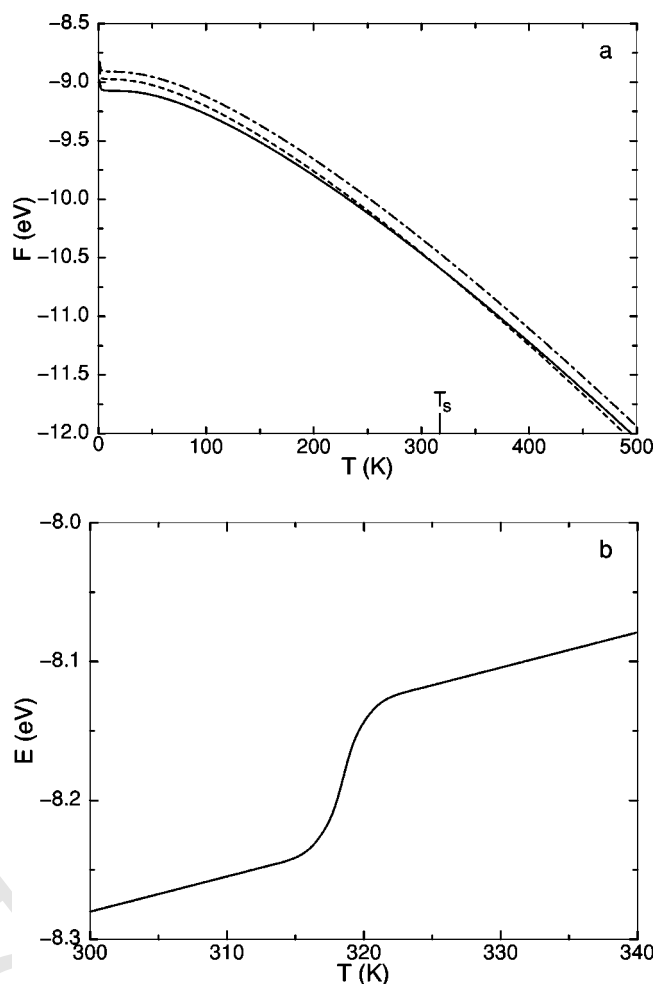


FIG. 10.  $\text{Ca}_{12}$ : (a) free energy as a function of temperature; (b) internal energy near the structural transition temperature; and (c) specific heat near the structural transition temperature.  $k_B$  is Boltzmann's constant.

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#### APPENDIX: VIBRATIONAL FREQUENCIES OF $\text{Ca}_6$ THROUGH $\text{Ca}_{13}$

Determination of vibrational frequencies and its symmetry identification is a lengthy calculation. It is important to

report these frequencies because they can be used in further quasiharmonic analysis of properties not studied in this paper. These frequencies might also be used to develop model potentials to represent calcium clusters. The three Tables V, VI, and VII contain the harmonic frequencies of vibration for all the stable isomers reported in Table III. A visual representation of the frequency spectrum as a function of cluster size is provided in Fig. 5 giving the trend for the formation of the phonon band in the bulk calcium.

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