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Systematic *ab initio* configuration-interaction study of alkali-metal clusters. II. Relation between electronic structure and geometry of small sodium clusters

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The quantum-chemical investigation of the electronic and geometrical structure of neutral sodium clusters carried out with the all-electron Hartree-Fock (HF) or effective-core-potential HF followed by multireference double-excitation configuration-interaction (MRD-CI) procedure demonstrates the complete analogy to the electronic properties of Li_n clusters. The general rules determining the electronic properties of small alkali-metal clusters are again clearly confirmed. Under experimental conditions which do not allow strong cluster fragmentation the large abundances of Na_8 and Na_4 can be expected.

I. INTRODUCTION

Some very characteristic properties of small alkali-metal clusters have been found in the previously published contributions employing various theoretical methods for the investigation of lithium and sodium clusters. For the majority of small Li_n clusters,[1-3] Hartree-Fock (HF) and configuration-interaction (CI) treatments give qualitatively similar optimal shapes as the methods based on the local-spin-density[4] approach (LSD) yield for the Na clusters of the same nuclearity. A characteristic feature of the electronic and geometric structure of small Li clusters as function of cluster size is the transition from planar toward three-dimensional cluster shapes. The reason for this geometry change has been explained in detail earlier[5] and has been rediscovered by Rao *et al.*[6] The multireference double-excitation configuration-interaction (MRD-CI) work has demonstrated the special stability of some small neutral and cationic Li_n clusters in a rough agreement with the Knight's shell model[7] of clusters. Nevertheless, some additional preferential abundances ("magic numbers") appear in the *ab initio* MRD-CI treatment,[1-3] mainly due to the change of the cluster shape from the planar forms to the three-dimensional ones. Further, some qualitative discrepancies exist between the LSD results for Na clusters and all-electron HF-MRD-CI results for the Li clusters: For example, the LSD approach combined with the geometry optimization carried out using Hellmann-Feynman forces yields for Na_8 a less symmetrical optimal geometry than that obtained from the MRD-CI procedure for the Li octamer. The elucidation of this discrepancy is not without interest since eight is a "magic number" for the neutral alkali-metal clusters. Evidently, one can ask if these discrepancies are due to the differences in the electronic structure of Li and Na atoms or if they are caused by the differences in the theoretical approaches.

The far-reaching agreement between the theoretical predictions of the alkali-metal–cluster abundances based on the HF-CI investigation of Li clusters and the experiments carried out for Na and even for K clusters[7-9] is striking and suggests a profound similarity among clusters of alkali metals. On the other hand, the fact that different computational methods do not perfectly agree upon prediction of optimal cluster geometries can be an indication that the differences in stability of cluster isomers are too small to be evaluated by some theoretical procedures. However, the qualitative agreement among various methods supports the assumption that the quantum-mechanical methods are basically reliable and suitable also for indication of small energy differences if they are due to some general cluster properties. Theoretical studies on Li and Na clusters can show the capability of various quantum-mechanical methods to describe characteristic specific cluster properties built from atoms with larger numbers of valence electrons. The reliability of the most important results obtained from various methods for Na clusters should be systematically examined. Consequently, a systematic investigation of Na clusters with the *ab initio* HF-CI procedures applied already to small Li clusters is desirable.

The aim of the present work is to demonstrate the far-reaching similarities between the properties of Na and Li clusters when their electronic structure is investigated at the same level of theory. Because the all-electron *ab initio* methods can be applied to the higher-nuclearity clusters generally only with some difficulties, also the "valence-only" effective-core-potential (ECP) method has been used for the investigation of Na clusters. The comparison of the ECP results for Na clusters with the all-electron treatment of these clusters with relatively large numbers of electrons can prove the general reliability of this simplified procedure for the investigation of alkali-metal clusters with even larger numbers of electrons.

II. METHODS USED

In the present work the geometry of neutral Na clusters has been optimized employing the analytical gradient method[10] in the case of all-electron Hartree-Fock (AE-HF) treatment and a numerical algorithm has been used for the effective-core-potential Hartree-Fock (ECP-HF) approximations. The electron correlation effects are taken into account in the framework of the MRD-CI method[11,12] for the optimized AE-HF and ECP-HF cluster geometries. In addition, for Na_n ($n<6$) clusters the best energy–optimal-geometry search has been carried out for the CI energy according to the numerical algorithm of Ref. 13 in the framework of the ECP approximation.

The comparison of the results obtained from the direct CI method[14,15] and those obtained from the extrapolation technique of the MRD-CI procedure has been carried out in the case of Na_6 isomers, for which a very small energy difference has been found.

The atomic-orbital (AO) basis set used for an AE calculation is $(9s,4p)$ contracted to $(3s,1p)$,[16,17] and augmented by one diffuse p function with the exponent $\alpha_p=0.065$, which has been optimized for the Na_2 dimer at the CI level (basis A). For HF-ECP calculations the definition of the effective core local potential and the basis set for valence $3s$ orbital are taken from Ref. 18. The basis is augmented by the same diffuse p function used in the AE treatment. In addition, three other AO basis sets[17]—$(9s, 5p/4s, 3p)$, $(14s, 8p/6s, 5p)$, and $(14s, 8p\ 1d/6s, 5p, 1d)$ labeled B, C, and D, respectively—have been used for the tetramer in the D_{2h} symmetry.

III. RESULTS AND DISCUSSION

A. The geometries of Na clusters

The AE-HF, and ECP-HF, as well as ECP-CI geometry optimizations, yield qualitatively the same Na cluster topologies, which are, moreover, nearly identical with the optimal cluster shapes found for small neutral Li clusters. The resulting topologies as well as the minimum-energy interatomic distances determined by AE-HF, ECP-HF, and ECP-CI methods are shown in Fig. 1. One can observe generally very good agreement among the results of the three approaches, the AE-HF interatomic distances are larger than the corresponding ECP-HF ones, which, in turn, are still slightly larger than the distances obtained from the ECP-CI optimization. The interatomic distances reported in this work are consistently larger than the corresponding distances quoted in the paper of Martins *et al.*[4] The difference can already be noticed for the bond length of the Na_2 molecule: the LSD approach yields 5.5 a.u. for the Na_2 bond length, whereas the values reported in this work are around 6.1 a.u. The experimental value lies in between (5.8 a.u.).[19] A comparison of AE-HF optimized distances for Na_4 in the D_{2h} symmetry employing AO basis sets A–D shows that basis sets B and D yield only slightly shorter distances than basis sets A and C. The smallest and largest values for the rhombus side are 3.69 and 3.74 Å, and for the shorter rhombus diagonal, 3.23 and 3.26 Å, respectively. These results prove that basis set A employed throughout this study yields reliable distances.

It is remarkable that the shapes of small Na clusters developing with increasing nuclearity are parallel in detail with the shapes of Li clusters: Na_4 and Na_5 are slightly distorted segments of the (111) plane of the fcc crystal lattice. The ground-state energy of the pentagonal pyramidal C_{5v} form of Na_6 is practically degenerate with the ground-state energy of the planar Na_6 D_{3h} form, which can be again considered a segment of the fcc crystal lattice. Na_7 can be taken as a step in the pentagonal cluster growth. Na_8 has a highly symmetric T_d shape with four pyramids built on the four faces of an inner tetrahedron. Martins *et al.*[4] have obtained a D_{2d} geometry for the Na_8 cluster as the most stable geometry. The search for the optimal geometry of the neutral Na octamer starting from the D_{2d} Na_8 geometry of Martins *et al.*[4] also gave rise to the more symmetrical T_d form of Na_8.

Since a general orientation about the favorable shapes of the alkali-metal clusters has been obtained in the study of small Li clusters, it is sufficient to use stronger constraints in the choice of variable parameters for the energy optimization of the Na cluster geometries than for Li clusters. The constraints are indicated in the figure caption of Fig. 1. We do not believe that any important geometries have been missed, mainly because the results in the present work exhibit regularities parallel to those valid for Li clusters.

The only larger difference between the Li and Na geometries appears for the heptamers: Both Na_7 and Li_7 have favorable shapes of the D_{5h} pentagonal bipyramid, but the distance between the apical atoms in the D_{5h} Na_7 cluster (4.1 Å) is larger than the sides of its pentagon (3.7 Å). In the D_{5h} Li_7 cluster the height of the bipyramid (3.10 Å) is nearly the same as the side length of the pentagon (3.15 Å), so that the Li_7 pentagonal bipyramid is, quite precisely, five condensed tetrahedra.[3] It is, nevertheless, necessary to emphasize that the computed energy of Na_7 changes very little with the changes of the bipyramidal height.

The ratio of experimental distances for Na and Li dimers is 1.15 and, for Na and Li (bcc) lattices, 1.23. This can be rationalized in terms of a larger promotion energy for Na (2.10 eV) than for Li (1.85 eV) atoms.[20] Correspondingly, the participation of p functions is always larger for Li_n than for Na_n stable clusters if comparable AO basis sets are employed.

B. The Na cluster stability

Figure 2 shows the atomization energy per atom (or binding energy per atom, E_b/n) as a function of the num-

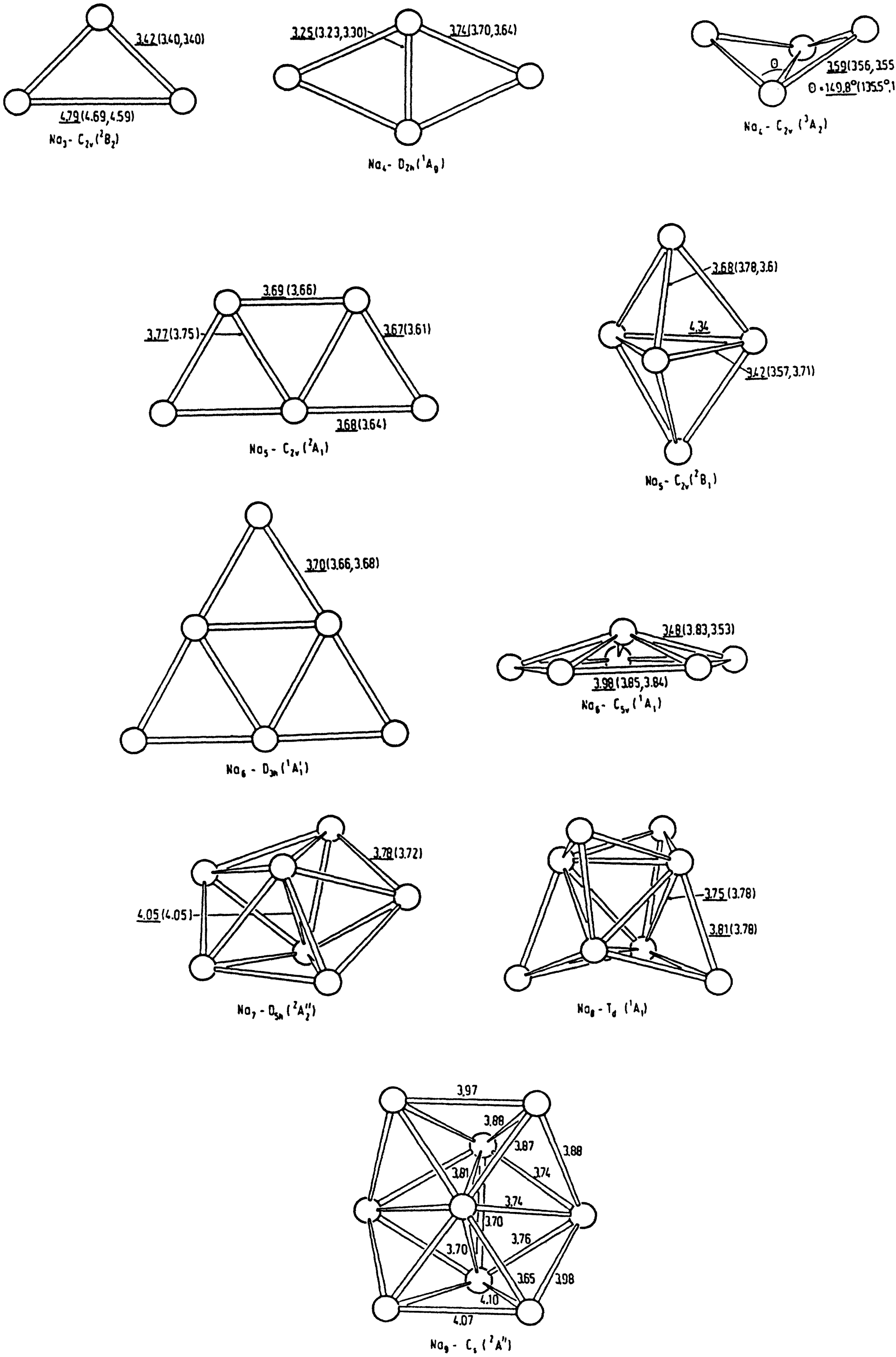

FIG. 1. Topologies and geometries of optimized Na clusters. The first (underlined) number means the AE-HF bond length. The first and second numbers in the parentheses correspond to the ECP-HF and ECP-CI values, respectively. In the conjugated-gradient energy-minimization procedure, the following constraints, given in parentheses, have been imposed: Na_3 and Na_4 (no constraints); ${}^2A_1$ Na_5 (planar C_{2v}); ${}^2B_1$ Na_5 (C_{2v}); Na_6 (planar D_{3h}, only the common interatomic distance is varied); Na_6 (C_{2v}); Na_7 (D_{5h}); and Na_8 [D_{2d} with D_{2d} geometry of Martins *et al.* (Ref. 4) and a T_d structure as starting points]; Na_9 (C_s bicapped pentagonal bipyramid). Bond lengths are in angstroms.

ber of atoms n in the Na clusters:

$$E_b/n = E_1 - E_n/n \ , \tag{1}$$

where E_n is the energy of a cluster with n Na atoms. The detailed results of calculation are given in Table I. The analogy between E_b/n curves for Li and Na clusters is evident.[3] In Fig. 2 the E_b/n calculated with the all-electron MRD-CI method for the AE-HF optimized geometries are compared with the ECP-MRDCI method for the ECP-HF optimized geometries. For comparison, the dependence of the atomization energy calculated with the LSD procedure from Ref. 4 is also shown in Fig. 2.

The following features of the E_b/n can be pointed out: First, the overall behavior of E_b/n as a function of n is similar for all the three approaches. Second, the AE-CI and ECP-CI methods give numerically very similar results, whereas the LSD approach yields, in general, larger values for the E_b/n. In the latter case the E_b/n curve is steeper, with increasing cluster size, than in the former case. This can be connected with generally observed overestimation of the bond strength by the LSD approximation. Third, the slope of the E_b/n function between $n=6$ and 7 is relatively small. This circumstance can be due to the difficult determination of the optimal geometry for the Na heptamer since the minimum seems to be very shallow. Such a behavior exhibits neither the E_b/n for Li clusters nor the E_b/n for Na clusters of Martins *et al.*[4]

The second difference of the cluster energy $\Delta^2 E_n$ as a function of the cluster size is shown in Fig. 3. The quan-

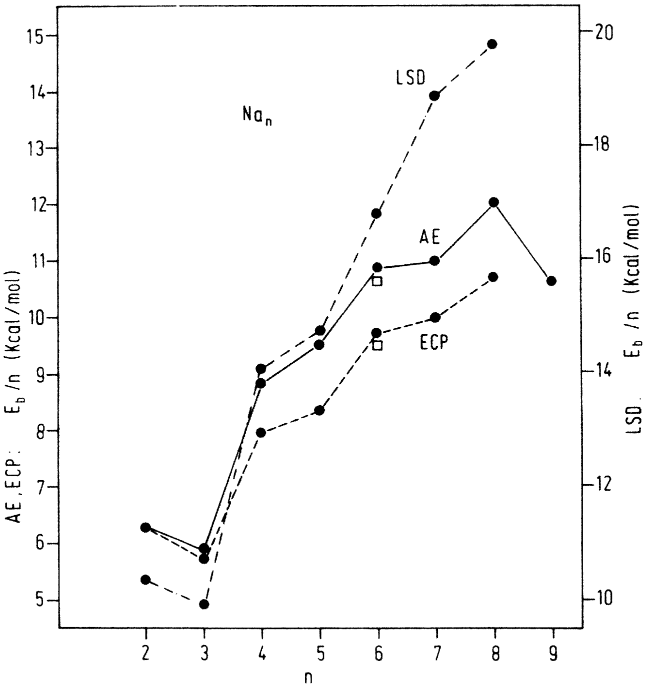

FIG. 2. The atomization energy E_b/n as a function of the number of atoms in the Na clusters. The solid (——) and dashed (— — —) lines label the all-electron MRD-CI and effective potential MRD-CI results, respectively. The energies are determined for the corresponding HF optimal geometries. The results of this work are compared with the E_b/n values of the LSD method (—·—·—·) (Ref. 4). The ECP-MRDCI energies obtained for the ECP-CI optimized geometries differ so little from the ECP-MRDCI energies for the ECP-HF optimized geometries that they cannot be distinguished from the latter on the scale used in Fig. 2. The scale on the left-hand side is valid for the E_b/n curves obtained from AE and ECP molecular-orbital methods. The scale on the right-hand side is for the LSD results of Martins *et al.* (Ref. 4).

TABLE I. Energies E_n^{CI} (a.u.) for the neutral Na$_n$ clusters obtained from the MRD-CI procedure for geometries optimized with various procedures [all-electron CI (AE-CI), all-electron Hartree-Fock (AE-HF), the pseudopotential Hartree-Fock (ECP-HF), and the pseudopotential-CI (ECP-CI)]. Energies obtained from the Hartree-Fock approximation E_n^{SCF} (a.u.) are also given. (SCF denotes self-consistent field.)

n	Symm. state	Geometry optimization	E_n^{SCF}	$E_n^{\mathrm{CI}\,a}$
2		AE-CI		−323.3176
		ECP-CI		−0.3841
3	C_{2v} $^2B_2$	AE-HF	−484.9413	−484.9729
		ECP-HF	−0.5395	−0.5720
		ECP-CI		−0.5721
4	D_{2h} ^1A_g	AE-HF	−646.5984	−646.6494
		ECP-HF	−0.7269	
		ECP-CI		−0.7765
4	T shape $^1A_1$	AE-HF	−646.5951	−646.6416
		ECP-HF	−0.7259	
		ECP-CI		−0.7715
4	C_{2v} $^3A_2$	AE-HF	−646.5947	−646.6393
		ECP-HF	−0.7245	
		ECP-CI		−0.7690
5	$C_{2v}{}^{b}$ $^2B_1$	AE-HF	−808.2454	−808.3093
		ECP-HF	−0.9017	−0.9635
		ECP-CI		−0.9638
5	C_{2v} $^2A_1$	AE-HF	−808.2595	−808.3174
		ECP-HF	−0.9186	−0.9741
6	C_{5v} $^1A_1$	AE-HF	−969.9109	−969.9899[c]
		ECP-HF	−1.1027	−1.1805
		ECP-CI		−1.1805
6	D_{3h} $^1A_1'$	AE-HF	−969.9193	−969.9884[c]
		ECP-HF	−1.1097	−1.1822
		ECP-CI		−1.1822
7	D_{5h} $^2A_2''$	AE-HF	−1131.5682	−1131.6610
		ECP-HF	−1.2908	−1.3821
8	T_d $^1A_1$	AE-HF	−1293.2346	−1293.3395
		ECP-HF	−1.4864	−1.5803
9	C_s $^2A_1$	AE-HF	−1454.8737	−1454.9871

[a] MRD-CI extrapolated energies.

[b] AE-HF geometry optimization yields a C_{2v} geometry, whereas the ECP-HF procedure has been performed for D_{2h} geometry.

[c] The direct CI values of E_6 are −969.9912 and −969.9938 a.u. for the Na$_6$ C_{5v} and Na$_6$ D_{3h} geometries, respectively.

tity $\Delta^2 E_n$ is defined as

$$\Delta^2 E_n = E_{n+1} + E_{n-1} - 2E_n \ , \tag{2}$$

where E_k is the energy of the cluster with k Na atoms. Let us point out here the possible interpretation of the quantity $\Delta^2 E_n$ as the difference between the fragmentation energies of the Na_n and Na_{n+1} clusters:

$$\Delta^2 E_n = (E_{n-1} + E_1 - E_n) - (E_n + E_1 - E_{n+1}) \ . \tag{3}$$

The general character of the $\Delta^2 E_n$ dependence on n for Na clusters is similar to the analogous function $\Delta^2 E_n$ for Li clusters: The sharp maxima for the tetramer and octamer, and minima for the clusters with odd number of atoms, as well as less pronounced maxima for the hexamer, are common features of $\Delta^2 E_n$ functions for both Li and Na clusters. However, the minimum of $\Delta^2 E_n$ for Na_7 is very pronounced, whereas the minimum for Li_7 is quite shallow. This difference might be connected with the questionable geometry of the Na_7 clusters obtained from our calculations and should be considered with some caution.

C. Vertical ionization potentials of Na clusters

The energies of cationic Na clusters for the same geometries of neutral Na clusters have been calculated with AE MRD-CI methods using the same AO basis set as for the neutral Na clusters. The corresponding vertical ionization potentials (IP's) are shown in Fig. 4. The IP's dependence on the cluster size shows an oscillation between the cluster with even and odd nuclearity, and the maxima for Na_4 and Na_8 are noticeable. The vertical ionization potential for the sodium heptamer represents a minimum, as does the IP for Li_7. Nevertheless, the oscillations in the values of the IP's for different cluster sizes are less pronounced in this work than in the analogous curve calculated with the LSD method. The agreement between the general trend of the IP's dependence upon nuclearity, and the experimentally determined IP's (Refs. 21 and 22) can be considered satisfactory in view of differences in the experimental results for small sodium clusters. The systematic underestimation of the ionization potentials can be due to the lack of intershell correlation and/or noninclusion of d-type basis functions in the AO basis set. For the stable rhombic structure of Na_4, vertical ionization potentials have been calculated using AO basis sets A, B, and D. Inclusion of the d functions (basis set D) slightly increases the value of the IP's to 4.09 eV, in comparison with 4.03 and 4.01 eV for basis sets A and B, respectively. A further careful investigation of the influence of the intershell correlation on the ionization potentials and, more generally, on the strength of the interactions in Na clusters is in progress.

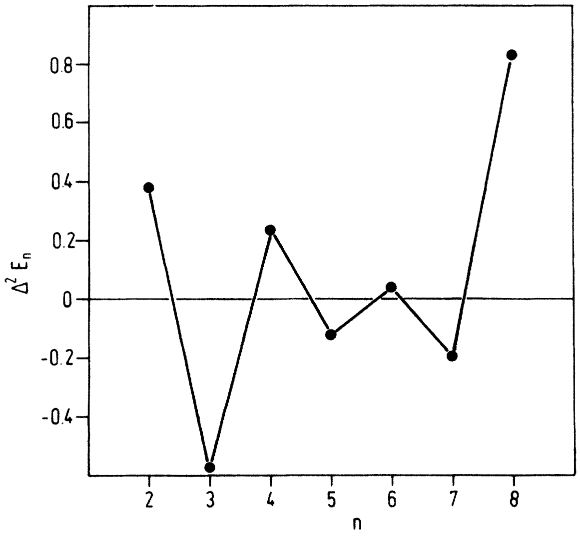

FIG. 3. The second difference $\Delta^2 E_n$ as a function of the number of Na atoms in clusters. The results are derived from the AE MRD-CI energies calculated for the AE-HF optimized geometries.

IV. SUMMARY

The HF and multireference double-excitation CI in both all-electron and pseudopotential versions show that the most important electronic properties of sodium clusters are in full accordance with the corresponding properties of the lithium clusters. Evidently, the similarity between the valence-electron shells of the Li and Na atoms plays here the most important role. The same simple general rules determining the electronic and geometric structures of Li and Na (and probably of K, Rb, and Cu) clusters are responsible for the fact that the results are fairly independent of the quantum-mechanical methods applied.

According to the stability criterion $\Delta^2 E_n$, the "closed-shell" Na_8 T_d and the planar rhombic Na_4 forms should exhibit relatively large abundances in the detection devices if the experimental conditions do not lead to cluster fragmentation. The prediction of two stable structures of comparable energies for Na_5 and Na_6 can be useful for experimentalists, although the barriers among these structures have not been determined yet and might deserve attention in the future.

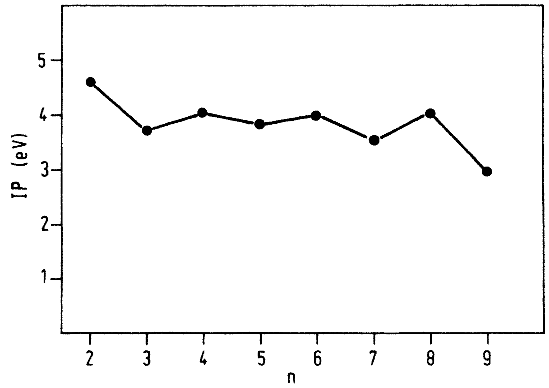

FIG. 4. Vertical ionization potentials (IP's) (in eV) for Na_n clusters obtained from the MRD-CI calculations.

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