## **Equilibrium Geometries and Electronic Structures of Small Sodium Clusters**

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We report self-consistent local-spin-density calculations which provide, for the first time, the equilibrium geometries of the sodium clusters  $Na_n$  and  $Na_n^+$  with  $n \le 8$  and n = 13, without making any *a priori* assumptions. Our results are in excellent agreement with recently obtained photoionization appearance potentials and electron-spin-resonance spectra. We find rapid formation of the metallic bond with a dominance of closely packed structures in two and three dimensions, and propose a simple model to account for it.

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Understanding the nature of the chemical bond and the electronic properties of small metallic clusters is a topic of increasing interest in many branches of physics and chemistry, particularly for its implications in such important fields as nucleation, heterogeneous catalysis, and photochemical reactions.<sup>1</sup> Recently the development of the molecular-beam technique and improvements of the matrix-isolation method have made possible new experiments that provide important information on the electronic and structural properties of small metallic aggregates, ranging from alkali to transition and noble metals. Despite this progress, some fundamental physical aspects of metal clusters, such as their geometrical and electronic structures, remain largely unknown and open to conjecture, even for alkali-metal clusters, which are perhaps the best understood microclusters.

Theoretically an accurate determination of the equilibrium geometries of the clusters using ab initio total-energy methods has been possible only for dimers and trimers, since the number of parameters describing the energy surface becomes unmanageably large for clusters of four atoms or more. Investigations on larger clusters have been performed either with use of semiempirical methods such as extended Hückel or complete neglect of differential overlap (CNDO), which prove quite unreliable when compared with experiment,  $^2$  or by making some a priori assumptions about the nuclear geometries when using parameter-free methods. For instance, some symmetrical configurations of the clusters Na<sub>2</sub> to Na<sub>8</sub> have been studied with a Hartree-Fock-based method.<sup>3</sup> After analyzing a few selected geometries, the authors suggested that dimerization effects play an important role in small metallic clusters. If confirmed, this conclusion would imply a rather slow formation of the metallic bond as a function of the particle size.

In this Letter we report a first-principles calculation of the equilibrium geometries of the sodium clusters  $Na_n$  and  $Na_n^+$  with  $n \le 8$  and n = 13. Our results provide an unambiguous interpretation of the measured photoionization appearance potentials of Na clusters in vacuum and are in excellent agreement with the electron spin resonance (ESR) spectra of matrix-isolated sodium clusters. We find no sign of dimerization effects, but the presence of delocalized metallic electrons appears in our calculations for the whole range of sizes studied.

Our computational method is based on the localspin-density and pseudopotential approximations and has been described in detail elsewhere.<sup>4,5</sup> In the present application we use the first-principles Hamann-Schlüter-Chiang nonlocal pseudopotentials as given by Bachelet, Hamann, and Schlüter<sup>6</sup> and the Perdew-Zunger<sup>7</sup> interpolation for the exchange and correlation energies and potentials. We use the Hellmann-Feynman theorem<sup>8</sup> to compute the forces acting on the atoms, which permits us to determine the equilibrium configuration without imposing any symmetry constraint. We showed in a previous publication<sup>9</sup> that, contrary to the general result of all-electrons calculations, the pseudopotential scheme makes it possible to obtain accurate and reliable Hellmann-Feynman forces with a relatively small number of basis functions. We notice that analytical derivatives of the total energy (gradient forces) have been used in quantum chemistry to optimize molecular geometries in all-electrons calculations,<sup>10</sup> and that the Hellmann-Feynman forces were used in pseudopotential calculations in solids, for instance to optimize the surface geometry.<sup>11</sup>

In this work we compute the equilibrium geometries starting from randomly generated configurations and use the Hellmann-Feynman forces to follow the steepest descent path to a minimum of the energy surface. Several precautions were taken in order to avoid the problem of local minima and to reach the absolute minimum with the smallest effort. Details of the method will be published elsewhere.<sup>12</sup>

The absolute minimum of the energy surface was obtained for all the clusters studied, except for  $Na_{13}$  and  $Na_{13}^+$  where we limited ourselves to an analysis of some Jahn-Teller distortions of the highly symmetric icosahedral and cubo-octahedral configurations. Here we will present only the results which are more relevant to a comparison with experiment and describe the general picture that emerges from our calculations, referring to a future publication<sup>12</sup> for a more detailed account of all our results.

The equilibrium geometries for the neutral clusters are displayed in Fig. 1. We can see that the geometries are planar for the clusters with up to five atoms, the six-atom cluster is quasiplanar, and real three-dimensional ground-state geometries only appear when the number of atoms is larger than or equal to seven. In general, the first local minima are well separated from the absolute minimum by more than 0.2 eV, with the only notable exception being the hexamer, where we find a truly planar isomer at an energy 0.04 eV higher than the absolute minimum.

How well our calculated ground-state geometries provide a realistic description of the electronic structure of the Na microclusters can be seen by comparing our results with experiment. There are, in particular, two experiments that can be directly related to our calculations, namely (i) the measurement of the appearance potential of Na<sub>n</sub> clusters in a molecular beam by means of photoionization followed by mass spectroscopy,<sup>2, 13</sup> and (ii) the measurement of the ESR spectra of alkali clusters trapped in a frozen inert-gas matrix.<sup>14, 15</sup>

In a careful appearance-potential experiment, where no fragmentation or multiphoton processes occur and where the distribution of the excited states is approximately Boltzmannian, the measured appearance potentials of the clusters are equal to the adiabatic ionization potentials and are therefore sensitive to the equilibrium geometries of both the neutral and the ionized clusters.<sup>16</sup> We show in Fig. 2 our calculated adiabatic ionization potentials for the Na<sub>n</sub> clusters and the experimental values of Herrmann, Schumacher, and Wöste<sup>2</sup> and of Peterson *et al.*<sup>13</sup> Our calculated ionization potentials and



FIG. 1. Equilibrium geometries of  $Na_n$  clusters. The internuclear distances are given in atomic units.

their trend show good agreement with the experimental data, particularly with those of Herrmann, Schumacher, and Wöste<sup>2</sup> for the larger clusters. With use of our equilibrium geometries and vertical rather than adiabatic ionization potentials, no agreement with experiment would have been found.

The information on the equilibrium geometries contained in the ionization potentials is only indirect. More direct information is provided by the ESR spectra of alkali clusters trapped in a matrix.<sup>14,15</sup> A comparison of the calculated and measured isotropic spin populations<sup>17</sup> is reported in Table I. A few remarks are in order here: (i) The measured features appear to be quite independent of the matrix used.<sup>15</sup> (ii) In our calculation we compute pseudospin densities, rather than real spin densities, at the nuclear sites. This should affect only minimally the calculated isotropic spin popula-



FIG. 2. Ionization potentials of  $Na_n$  clusters. The clusters. The circles are the calculated adiabatic ionization potentials; the squares and the triangles are, respectively, the photoemission appearance potentials of Refs. 2 and 13. We have only shown the experimental error bars for the  $Na_6$  and  $Na_9$  cases. The broken line is the result of a simple electrostatic model (Ref. 2).

tions, since both the real and the pseudoisotropic spin populations are normalized to their corresponding atomic values. (iii) Experiments have not been able to identify the spectral features associated with the pentamers. Our calculated values could help in identifying this spectrum. (iv) The ESR spectra show the presence of two inequivalent atoms in the trimers only for temperatures lower than 20K. At higher temperatures the ESR spectra indicate the presence of three equivalent atoms. This behavior has been previously attributed to a pseudorotation<sup>5, 18</sup> (a particular dynamic Jahn-Teller effect).

The evolution of the cluster geometries as a function of the cluster size can be interpreted in terms of a simple model that also sheds some light on the bonding mechanisms in metallic microclusters. The dominant features of our calculated geometries are close packing and the presence of delocalized "metallic" electrons. Close packing is already indicated by the fact that our smaller planar clusters are made from distorted equilateral triangles, i.e., the building blocks of close packing in two dimensions. The presence of delocalized valence electrons shows up in our calculated charge densities, and is reflected in the evolution of the equilibrium geometries as a function of the cluster size. These geometries nowhere show the presence of dimerization, i.e., covalent effects, indicated as a possibility for the very small clusters  $(n \leq 4)$  on the basis of qualitative theoretical arguments.<sup>19</sup>

The delocalized valence electrons fill molecular

TABLE I. Experimental isotropic spin populations and calculated "pseudo" isotropic spin populations. The multiplicity of each value is indicated in parentheses.

	Experimental	Calculated
Na	1.0	1.0
Na <sub>3</sub>	$0.47^{a}(2 \times)$	$0.48(2 \times)$
	$-0.07^{a}$	- 0.04
Na <sub>5</sub>	<sup>b</sup>	0.19(2×)
		$0.17(2 \times)$
		0.06
Na <sub>7</sub>	$0.37^{\circ}(2 \times)$	$0.32(2 \times)$
	$-0.02^{\circ}(5 \times)$	$-0.02(5 \times)$

<sup>a</sup>Ref. 14.

<sup>b</sup>The ESR spectrum of Na<sub>5</sub> has not been observed.

<sup>c</sup>Ref. 15.

orbitals having "s-like," "p-like," "d-like," etc., character according to their global shape. The ordering of these levels is s,p,d for the clusters under consideration. Jahn-Teller distortions will occur in the presence of a partially filled shell, and therefore the most compact geometries, that maximize the number of nearest neighbors, will not always be favored. Trimers, quadrimers, pentamers, and hexamers correspond to the successive filling of  $p_x$  and  $p_{v}$  levels and are planar or quasiplanar. Real threedimensional structures begin to occur only when n = 7, which corresponds to the filling of the  $p_z$  levels in addition to the  $p_x$  and the  $p_y$ . Indeed the clusters with seven and eight electrons, whose "p-like" orbitals are all occupied, have very regular threedimensional configurations with their nearestneighbor distances almost identical.

For the thirteen-atom cluster we find that the cubo-octahedron (fcc) and its tetragonal distortion have lower energy than the icosahedron and its small distortions. This result is interesting since molecular-dynamics calculations using additive two-body potentials always favor the most compact structures, i.e., icosahedral structures for small clusters.<sup>19</sup> Experiments have also shown the presence of a fivefold symmetry axis in clusters of rare gases and of noble metals<sup>19</sup> having fewer than 1000 atoms. Our result is not an indication that bulklike (fcc) structures are already attained with thirteen atoms for alkali-metal clusters, but rather suggests a manifestation of the Jahn-Teller effect. The icosahedron has a half-filled degenerate "d-like" molecular orbital shell and the cubo-octahedron is a particular distortion of the icosahedron that partially lifts the orbital degeneracy while still maintaining a very compact geometrical configuration. The importance of the incompletely filled molecular shells will decrease as a function of the cluster size and we cannot exclude the dominance of icosahedral structure for larger clusters.

In conclusion, we have seen that the geometrical structures of very small sodium clusters having up to thirteen atoms follow from the presence of delocalized electrons combined with Jahn-Teller distortions. These effects completely dominate the ground-state configurations of the very small alkali clusters, which show a very peculiar behavior quite different from, e.g., rare-gas clusters. There is, however, a whole range of intermediate sizes, not considered in the present investigation, where Jahn-Teller distortions are expected to be less important but the high surface-to-volume ratio could still give rise to peculiar small-particle effects.

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