Calculation of Cluster Geometries with the Help of Hellmann-Feynman Forces

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The equilibrium geometries of Na_n clusters ($n \leqslant 7$) are calculated by letting randomly generated clusters relax under the action of the Hellmann-Feynman forces. We find that clusters with five atoms or less have a planar structure whereas larger clusters have closely packed three-dimensional geometries. The calculated adiabatic ionization potentials are in good agreement with the experimental appearance potentials.

Introduction

The geometrical structure of relatively large metallic clusters, having more than about 300 atoms, has been experimentally determined for several metals [1]. It is in particular known that Ag and Au clusters have a typical five-fold symmetry whereas Pt, Pd and Al clusters seem to retain the crystallographic structure of the bulk. However in the case of very small metallic clusters, of the order of 10 atoms, not even the symmetries are known. One is forced, in order to calculate their physical properties, either to choose a reasonable structure or to predict the geometry from theoretical calculations. In the first case one usually assumes that the cluster has the same high symmetry as the bulk and that it is built from bulk unit cells, which is most unlikely to be true for very small metallic clusters. In the second case one tries to minimize the total energy respect to the parameters describing the cluster structure. Since there are $3N$-6 such parameters for a cluster of N atoms, this is a very difficult task, and in most cases the energy minimization is only carried out with respect to a couple of parameters, the others being kept constant.

For metallic dimers and trimers it is possible to compute the whole energy surface [2, 3], but for larger aggregates other approaches must be used to obtain the equilibrium geometry of the cluster without an a priori assumption on their geometry.

We have developed an approach in which we start from an initial cluster geometry chosen at random, we then calculate the forces on the atoms and make use of these forces to relax the initial geometry till it reaches an equilibrium structure. The process is repeated with different initial cluster geometries until a true minimum is found. We have applied this scheme to determine the equilibrium structure of the sodium clusters Na_n and Na_n^+ with $n \leqslant 7$.

Computational Method

The details of the computational method that we have used are reported elsewhere [2], we only here briefly mention its main characteristics:

i) the core electron effects on the valence electrons are treated within the pseudopotential approximation. We have chosen an l-dependent ab initio pseudopotential calculated by Bachelet et al. [4].

ii) the exchange and correlation effects are treated self-consistently within the local spin-density approximation of the density functional formalism. We have used the interpolation formulas of Perdew and Zunger [5].

iii) the forces on the atoms are obtained by applying the Hellmann-Feynman theory [6] to the pseudopotential local spin density scheme [7].

To obtain the equilibrium geometries we start with a randomly generated cluster structure and we calculate its electronic structure, its energy, and the forces on the atoms. The cluster structure is then relaxed in the direction of the forces to give a new cluster structure. The whole procedure of self-consistent calculation of the energy and forces followed by the relaxation of the structure is repeated until an equilibrium geometry is reached. Since the initial cluster geometry is obtained by a random process, there is no a priori geometry assumption in the calculation of the energy minimum. The traps of the local minima are avoided by performing several calculations with different starting geometries for each cluster size. This relaxation method corresponds to a steepest descent minimization method in the Born-Oppenheimer energy hypersurface.

Results

The calculated equilibrium geometries of Na_n and Na_n^+ clusters with $n \leqslant 7$ are represented in Figs. 1 and 2 respectively.

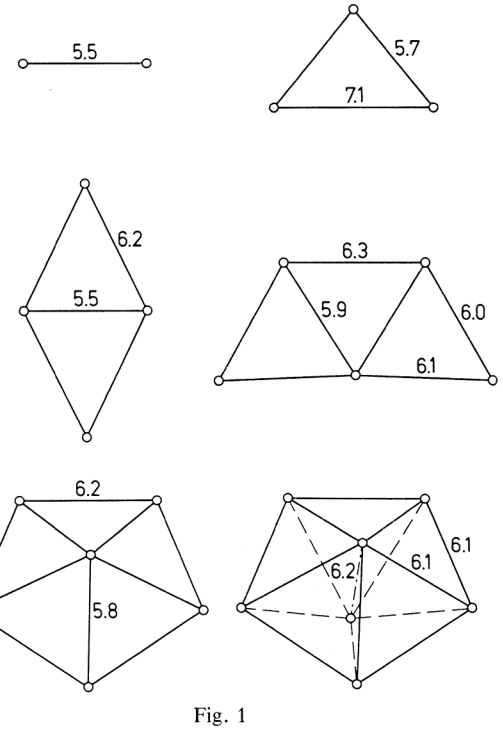

Fig. 1
Equilibrium geometries of Na_n clusters. For $n \leqslant 5$ all atoms are in the same plane, Na_6 is a pentagonal pyramid and Na_7 a pentagonal bipyramid. The distances are given in atomic units

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The species with less than 5 atoms have plane equilibrium geometries, with distorted equilateral triangles as the basic building block. The equilibrium geometries of the hexamers and septamers are 3-dimensional with a five-fold symmetry axis present in Na_6, Na_7 and Na_7^+ clusters, Na_6^+ has a rather irregular shape. There is a general agreement in the literature with respect to the theoretical equilibrium geometries of the alkali trimers [2, 3, 8, 9] and tetramers [8, 10, 11]. However, our calculated equilibrium geometries for the Na_5, Na_6 and Na_7 clusters are different from those obtained by Flad et al. [8] with a pseudopotential Hartree-Fock plus local correlation method. In their work, Flad et al. concluded that structures with Na_2 units were a characteristic feature of the small sodium clusters. In this work we have not found any tendency for dimerization, unstead there is a preference for closely packed structures, either plane or three-dimensional. Several symmetrical geometries of the Li_6 molecule [12] have been calculated with a configuration interaction method. It is found that a pentagonal pyramidal geometry is the most stable configuration, which is similar to our result for the structure of Na_6.

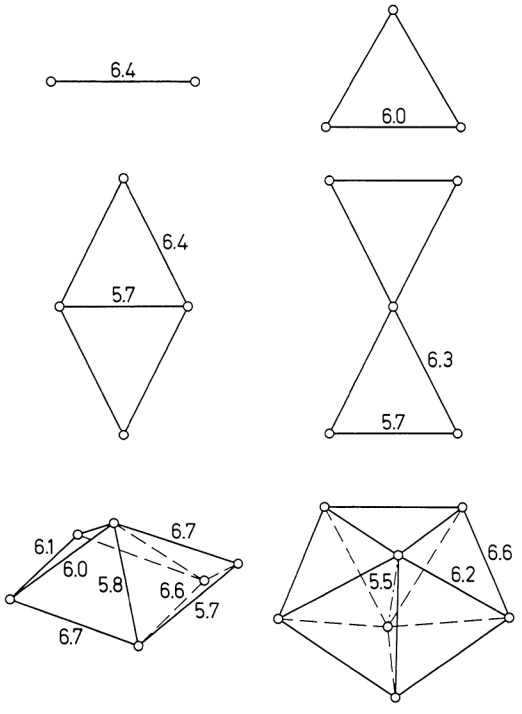

Fig. 2
Equilibrium geometries of Na_n^+ clusters. For $n \leqslant 5$ all atoms are in the same plane, Na_6^+ has a C_s symmetry, Na_7^+ is a pentagonal bipyramid. The distances are given in atomic units

The appearence potentials of Na_n clusters produced in a molecular beam have been measured by photoionization followed by mass spectroscopy. In a clean experiment, where no fragmentation or multiphoton processes occur [13] and where the distribution of the excited states is roughly Boltzmanian, the appearance potential of the clusters is equal to the adiabatic ionization potentials. We show in Fig. 3 calculated adiabatic ionization potentials of Na_n and two sets of experimental photoionization values, those of Herrmann et al. [14] and Peterson et al. [15]. The agreement between the experimental values is not very good for the Na_5, Na_6 and Na_8 clusters. Our calculated values, and in particular their trend, are in better agreement with the results of Herrmann et al. [14]. Previous calculations of the ionization potentials of Na clusters have been reported by Flad et al. [8], they have however calculated vertical ionization potentials of selected cluster structures, which can not be directly compared with the experimental appearance potentials.

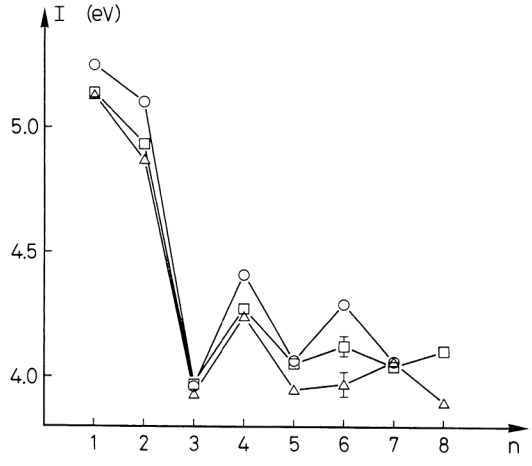

Fig. 3
Ionization potentials of Na_n clusters. The circles are the calculated adiabatic ionization potentials, the squares and the triangles are respectively the photoionization appearance potentials of Refs. [14] and [15]. We have only reported the experimental error bars for Na_6

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