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Static, statistical, and dynamical properties of small sodium clusters

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Abstract. This paper reports results obtained in the study of small alkali metal clusters ($2 \leq n \leq 34$). Properties of interest include static descriptions of the Potential Energy Surfaces (PES) using a Distance-Dependent Tight Binding hamiltonian (DDTB) and new results obtained with the same hamiltonian through a Monte-Carlo Growth Method (MCGM) which is shown to give an efficient way to sample the PES, but may also be helpful to estimate the statistical occurrences of the various isomers (catching areas). The probability for generating a given configuration is proportional to a Boltzmann distribution factor and hence a temperature dependence is introduced in the study of the PES. In section 2, the temperature dependence of the optical response for small clusters (on the example of Na_4) is simulated through *ab initio* calculations of the electronic structure coupled with Monte-Carlo dynamics on the absorbing system in the ground state.

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1. Static and statistical description of the potential energy surfaces

Since we have in mind an exhaustive exploration of the PES of small sodium clusters in the range $n=1-34$, we use a simple mono-electronic hamiltonian of the tight-binding type expressed in a basis of s-only orbitals :

$$\begin{aligned}
 h_{ii} &= \sum_{k \neq i} \rho_{ik}(R_{ik}) \\
 h_{ij} &= t_{ss}(R_{ij}) - \sum_{k \neq i, j} \left[\frac{t_{s\sigma}(R_{ik})t_{s\sigma}(R_{jk})}{\epsilon_{3p} - \epsilon_{3s}} \frac{\vec{R}_{ik} \cdot \vec{R}_{jk}}{|R_{ik}||R_{jk}|} \right] \quad (1)
 \end{aligned}$$

The noticeable improvements with respect to usual tight-binding models is (i) a distance-dependent fit of the matrix elements on accurate *ab initio* calculations for Na_2 and Na_4 , (ii) a perturbative account of s-p mixing via the second term in the right-hand side of eq. (1). This model [1] was shown to provide energy optimized configurations for small clusters (Na_3 - Na_8) in full agreement with the issues of more

sophisticated calculations [2,3]. The search for the minima in ref.1 had been carried on using a usual simulated annealing Monte-Carlo algorithm. However for larger sizes ($n \geq 10$), technical difficulties related with the increase of the degrees of freedom did occur, worsened by the strong degeneracy of the various isomers and the flexible character of metallic clusters. In order to circumvent this problem, we have adapted [4] for sodium clusters a Monte-Carlo technique which is not based on statistical trajectories, but on statistical growth and which was initially developed and checked for biological systems [5].

Let us suppose that the sampling for a given cluster size n is already boltzmanian, e.g., the number of configurations with geometry Q_i^n in the sampling obeys the Boltzmann law :

$$M(Q_i^n) = A_n \exp[-\beta E(Q_i^n)] \quad \text{with} \quad \beta = 1/kT$$

where A_n is a normalization factor and $E(Q_i^n)$ the energy of the configuration Q_i^n . Then, the sampling for size $n+1$ is achieved from the various configurations Q_i^n by adding an atom and so generating a configuration Q_j^{n+1} . This new configuration is replicated according to a conditional probability law of obtaining Q_j^{n+1} from Q_i^n :

$$w(Q_j^{n+1}|Q_i^n) = \exp[-\beta(E(Q_j^{n+1}) - E(Q_i^n))]$$

In practical, since the replication factor must be integer, one uses a replication factor :

$$m_{n+1} = p_{n+1} + r_{n+1}$$

with :

$$p_{n+1} = \text{Int}(w)$$

$$r_{n+1} = \begin{cases} 0 & \text{if } w - p_{n+1} < v \\ 0 & \text{if } w - p_{n+1} > v \end{cases}$$

where v is a random number $0 \leq v \leq 1$. As a consequence, $M(Q_j^{n+1})$ also follows Boltzmann's law. Details about the

control of the algorithm can be found in ref.6. Once the sampling for a given size is achieved, the 150 lowest configurations are submitted to local gradient optimization. Such an optimization pattern not only provides stable isomers, but also the frequencies of obtaining these isomers which depend upon the temperature and of course the catching area of the PES. The reliability was checked on $\text{Na}_2\text{-Na}_9$ clusters for which all known lowest minima were obtained.

Some new low energy stable structures were obtained, not altering the nature of the "absolute" minima until now. Low energy structures were further obtained for all clusters in the range $n=10\text{-}21$ and 34. An exhaustive description of those isomers and a tentative classification of building, emphasizing the role of local five-fold symmetry can be found elsewhere [4], as well as a rationalization of the global shapes of alkali metal clusters obtained in the ellipsoidal jellium model. There have been up to now very few geometry optimisations in this range. Our most stable geometries compare fairly well with the Local Density Car-Parinello results of R othlisberger and Andreoni [2] concerning Na_{10} , Na_{13} , Na_{18} , and Na_{20} . The lowest-energy structures of these clusters are the same in both calculations except in the case of Na_{20} , for which we find a structure slightly more spherical-like, differing from the one found by R othlisberger and Andreoni only through the displacement of a single atom. We present here the lowest-energy geometry of Na_{34} obtained with the MCGM algorithm (fig. 1). This cluster has a very symmetrical geometry (D_{5h}). One can identify a double icosahedron core (19 atoms) surrounded by a 15-atom ring. The global shape of Na_{34} is oblate with two equivalent axial ratios, in agreement with the ellipsoidal jellium model results [7].

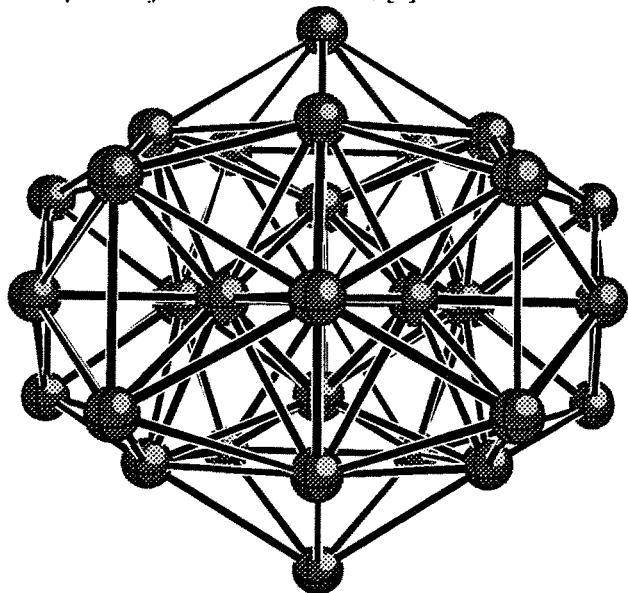


Fig. 1. Lowest structure of Na_{34} found with the MCGM algorithm.

An interesting example of the temperature dependence of the sampling is illustrated in fig. 2 for the Na_7 case where it is seen that at low temperature (100K), the actual minimum found is very seldomly obtained, the most frequent occurrence corresponding to high energy isomers.

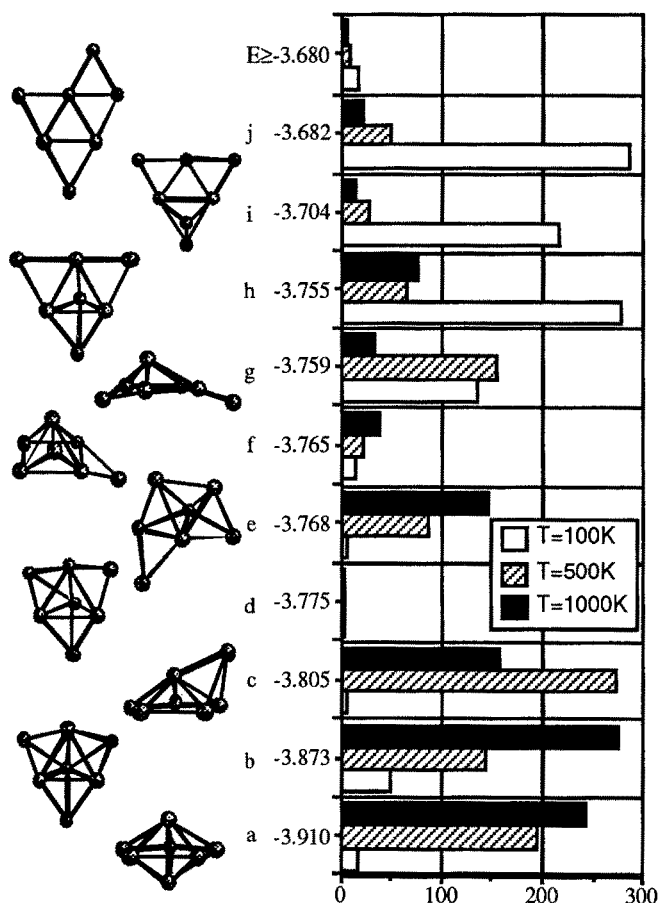


Fig. 2. Histogram of the stable isomers of Na_7 obtained at different temperatures with the MCGM algorithm. The energies are given in eV.

This trend is reversed when the temperature is raised ($T \geq 500\text{K}$). The same behaviour is observed in the case of Na_{10} , for which the abundance of the lowest structure is almost vanishing at $T=100\text{K}$. Another interesting case concerns Na_8 , for which the frequency of the lowest isomer (T_d) is only 10-15% at any temperature between $T=100\text{K}$ and 1000K. The temperature dependence is further discussed in section 3, in relation with absorption spectra.

2. Dynamical description of the optical spectrum of Na_4

The studies of the optical spectra of alkali clusters may provide a good way to probe the geometrical configurations of these clusters. A direct comparison with static *ab initio* calculations of electronic levels and oscillator strengths (vertical lines) has been successful in assigning the structures of ground state minima. In some cases however, the correlation is ambiguous (Na_6 [8], Na_8 [9]). Until now, there has been no *ab initio* attempt to reproduce the spectra themselves, and in particular the width correlated with the interaction between electronic excitation and vibrational motion. We suggest here to take into account this coupling by allowing nuclear motion on the ground state PES through

Monte-Carlo sampling. The energy of the ground state and the 25 first excited singlet of Na_4 are calculated from second order perturbation on wavefunctions built from all single and double excited configurations from the reference [10] (providing results very close to the exact valence energy).

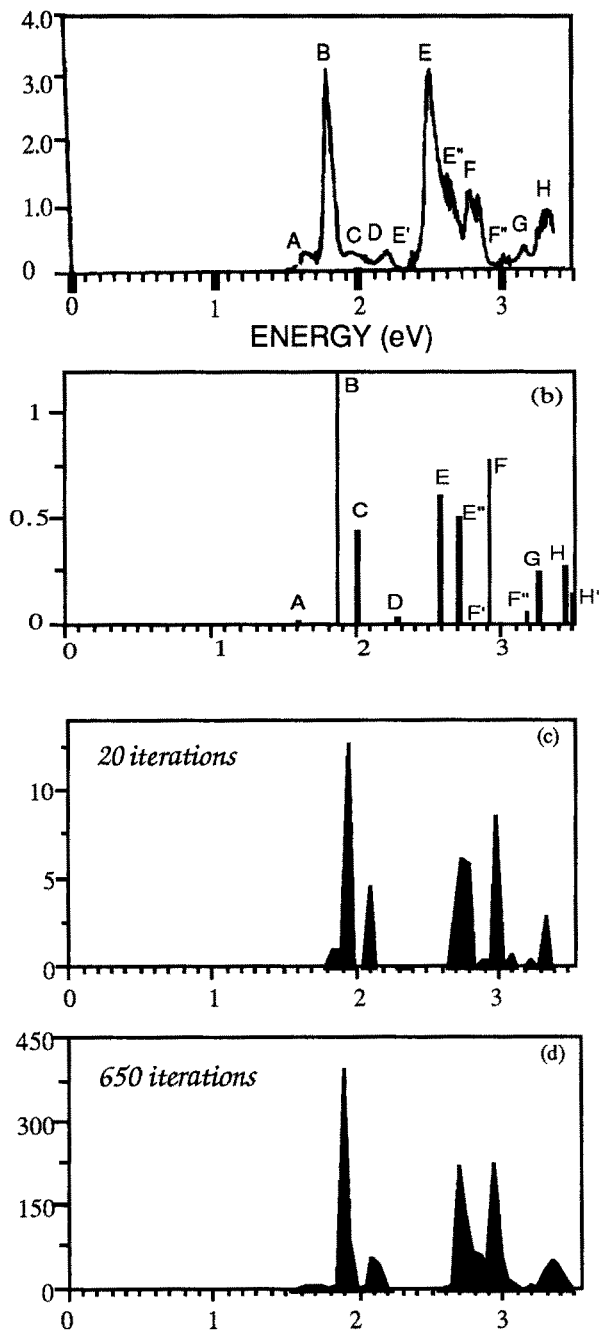


Fig. 3. Spectra of Na_4 . (a) experimental spectrum ; (b) static spectrum corresponding to the equilibrium geometry ; (c) dynamical spectrum ($T=150\text{K}$) after 20 iterations ; (d) dynamical spectrum ($T=150\text{K}$) at convergence after 650 iterations.

The excitation energy thus lies in range from $\Delta=1.5\text{-}3.5$ eV. The gaussian basis set is composed of 2s orbitals on each atom augmented by a 4s4p4d basis at the center of mass (CM). The quality of the calculations has been checked by comparing the results to those issued from a larger calculation (6s6p6d3f at CM) and to the results reported by

Bonacic-Koutecky *et al.* [11]. The general shape of the vertical transitions lines for the equilibrium geometry (in the static calculation) was the same in the three calculations (detailed comparison will be published elsewhere). Starting the simulation at the equilibrium geometry D_{2h} of Na_4 (the long diagonal of the rhombus is $R=12.4$, the short diagonal is $r=6.0$), a small displacement at a given temperature T is accepted or rejected according to the Metropolis criterion. For each accepted geometry, standard excitation levels T_e and oscillator strengths f_e are determined for the 25 singlets. The total energy range Δ is divided into small interval $\Delta_i=[T_i, T_i+\delta]$ and if one of the calculated transition T_e belongs to Δ_i , the corresponding oscillator strength f_e is added in the corresponding interval. This provides a temperature dependent simulation of the actual spectrum. Preliminary results corresponding to $T=150\text{K}$ are reported in fig. 3 b-c-d along with the experimental spectrum by Wang *et al.* [12] at different steps of the simulation.

A tentative assignment for the vertical spectrum (fig. 3a) is provided, following partially the one proposed by Bonacic-Koutecky *et al.* A noticeable difference is the assignment of the $(2)^1B_{2u}$ and $(3)^1B_{2u}$ states. In our work, they seem to correspond to structures E and E'', whereas in the work of Bonacic-Koutecky *et al.*, they were assigned as E' and E respectively. Starting from the vertical static description (fig. 3b), one can see the broadening and the modifications in the spectrum when the geometry of the cluster is allowed to change. The most noticeable feature is the drastic reduction of the intensity of peak C and the transformation of the structures between E and F lines. It is interesting to underline the agreement between experiment and calculation as concerns the widths, in particular for peaks B, E, and F. The intensity of structure D in the final simulation is vanishing. E'' finally appears as a shoulder, in consistency with experiment. The final structure at ≈ 3.3 eV can be assigned as H, while the intensity initially corresponding to line G has significantly decreased.

Some discrepancies do remain. In particular, the intensity of the E-band is underestimated in the calculation and the F-band does not exhibit any splitting. It should be stressed that the accuracy of the oscillator strengths is more tedious to obtain, depending on the basis set and the quality of CI.

However, this work opens the route to a systematic *ab initio* study of the influence on spectra of coupling between electronic and nuclear motions on small clusters. Simulations for other temperatures and larger systems are underway.

3. Discussion

Both calculated spectra and statistical abundancies are important quantities to explain the spectroscopy of cold clusters obtained in beams. For instance, Wang *et al.* [13] have obtained spectra in particular for Na_5 , Na_6 , and Na_7 for which they tentatively established a correspondance between spectra and geometries with the help of the vertical spectra determined by Koutecky *et al.* [14]. However, the direct correlation of the presently determined abundancies (which correspond to a pure growth mechanism) with the conclusions of Wang *et al.* is hazardous. Nevertheless, for

some clusters the present abundancies are consistent with their results. This is the case of Na_4 for which the obtention frequency of the rhombus is approximately 70% at any temperature (30% for the T-shape), and also of Na_5 which is found the most frequently ($\geq 90\%$) in its planar C_{2v} geometry at any temperature (fig. 4).

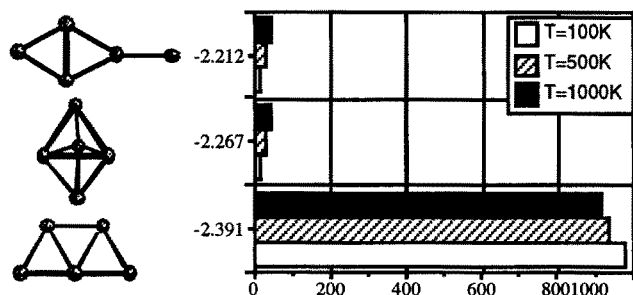


Fig. 4. Histogram of the stable isomers of Na_5 obtained at different temperatures with the MCGM algorithm.

The situation is different for Na_6 and Na_7 . For Na_6 , indeed, the experimental spectrum [13] is slightly closer from the vertical calculated one [14] for the D_{3h} configuration. However, the calculated vertical spectrum [14] for the C_{5v} pyramid was not so much different, and definitive conclusion is still difficult in our opinion. In our sampling, the D_{3h} and C_{5v} configurations appear with respective rates $\approx 40\%$ and $\approx 45\%$ respectively (fig. 5) whatever the temperature is. For Na_7 , the situation is apparently clearer since the calculated vertical spectrum corresponding to the lowest isomer (D_{5h} bipyramid) seemed in unambiguous agreement with the experimental data [13]. In the growth sampling the situation is strongly dependent upon the temperature (fig. 2). At 100K indeed, the lowest isomers (and in particular the D_{5h} structure) are obtained with small frequencies, the most important ones being those resulting from the addition of an extra atom to Na_6 - D_{3h} (isomers h, i, j - see fig. 2). At higher temperature, the situation is reversed and the most frequently obtained structures are the lowest ones. Thus, the present work seems to confirm that clusters in beams do not result from direct growing processes, but rather from more complex mechanisms such as multiple fragmentation processes. It is not obvious that the use of a reverse Monte-Carlo simulation (corresponding to evaporation) would yield the same frequencies. For a given cluster, nevertheless, the MCGM algorithm is certainly an efficient tool for the determination of the lowest isomers as well as the estimation of the catching areas. As a final conclusion, we may state that combination of theoretical investigations concerning both the genesis of clusters and the dynamical effects on absorption spectra should be useful to provide a global understanding of the optical properties of metal clusters.

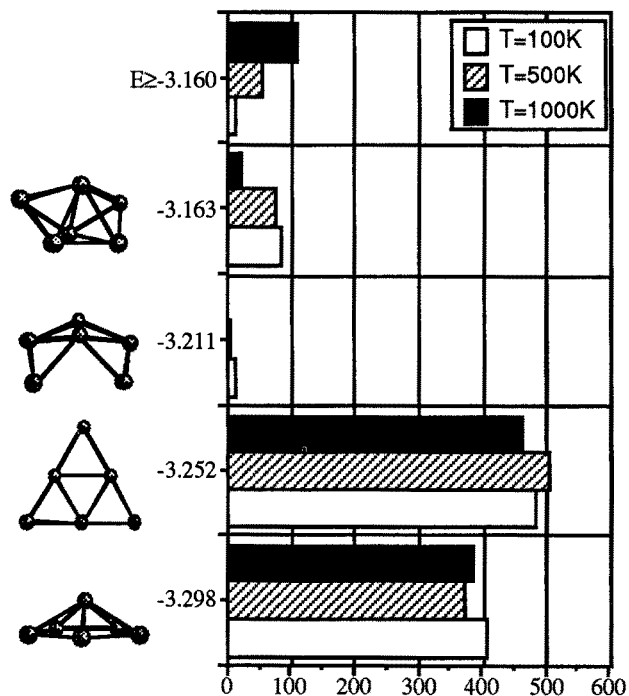


Fig. 5. Histogram of the stable isomers of Na_6 obtained at different temperatures with the MCGM algorithm.

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