IONIC AND TEMPERATURE ASPECTS OF THE PHOTORESPONSE OF METALLIC CLUSTERS *)

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A calculation of the electronic response of alkali metal clusters is carried out in the Adiabatic Time-Dependent Local Density Approximation. The role played by the ionic structure is investigated in the framework of second-order pseudopotential perturbation theory. The calculations are carried out at different temperatures, and the effect of temperature in the decay of the collective excitations is analyzed. It is found that the coupling of the electrons to the thermal vibrations of the ions accounts for the width of the plasmon resonances.

The Adiabatic Time-Dependent Local Density Approximation (ATDLDA) has been shown to provide an accurate description of the collective charge density waves which are excited in metallic clusters under the influence of a photon field (cf. e.g. Ref. 1 and references therein). Therefore, we use this formulation to study the role played by the ionic structure, at different temperatures of the clusters, in the characterization of their photoresponse. In order to study ionic effects we shall make use of second order pseudopotential perturbation theory, as developed in Refs. 2 and 3, which has been shown to account for the anisotropic effects induced by the discrete ionic structure.

Recently, it has been shown [4] that, contrary to the general case, a local pseudopotential can account for most of the Ground State (GS) and Optical Properties (OP) of sodium clusters. Therefore, we shall adopt a local pseudopotential parametrization [5] for each sodium ion and study the influence of the vibrational temperature of a cluster in its OP. We shall take as an example Na_8, for which there exist available theoretical and experimental data. As usual, whereas all theoretical calculations so far have been carried out at zero temperature, the experimental data available has been obtained in clusters at room temperature. Most calculations of the OP of Na_8 carried out to date have been performed using ATDLDA in the jellium model, or within the *ab-initio* quantum-chemical approach of Ref. 6 (and references therein). All theoretical results lead to a single peak structure located at $\approx 2.5\,\mathrm{eV}$, accounting very well for the experimental findings of de Heer et al. [7] who measured the photoabsorption cross-section for Na_8 at room temperature, and found it is dominated by a single peak at $2.53\,\mathrm{eV}$, exhausting $\approx 55\%$ of the f-sum rule.

In spite of this apparent agreement, it is also well-known [8] that the equilibrium structure of Na_8 in LDA corresponds to a $D_{2\mathrm{d}}$ structure, with 2 degenerate principal moments of inertia which are different from the third one. This, in turn,

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leads classically to a split of the surface plasmon peak into 2 peaks, in sharp contrast with the predictions from quantum chemistry which assign a T_d structure to Na_8 with all principal moments of inertia degenerate leading naturally to a single peak. While at first thought the results from quantum chemistry seem to be more consistent, in particular in view of the available experimental data, the recent measurements of the Freiburg group [9] in sodium clusters as a function of temperature, besides providing a spectacular evidence for what can be considered as shape phase transitions in the OP of small metallic clusters, do not rule out the possibility that the equilibrium geometry of Na_8 is actually a $D_{2\mathrm{d}}$ structure. Indeed, tremendous changes in the lineshapes have been observed, typically evolving from narrow multi-peak structures at low temperatures into broader and smoother lineshapes at higher temperatures which, often, bear no resemblance with their low temperature counterparts.

With this scenario in mind, I will carry out an investigation of the OP of Na_8 as a function of the vibrational temperature of the cluster. To this end, I shall consider the adiabatic coupling between electrons and ions, and start by computing a canonical Monte Carlo path along the Potential Energy Surface (PES) $E[\{\vec{R}_i\}]$, where $\{\vec{R}_i\}$ represents the set of all coordinates of the constituent ions in the cluster. Since a good sampling is mandatory I took 10^4 points along the Monte Carlo path in $E[\{\vec{R}_i\}]$, for each temperature, which is easily accomplished using second-order pseudopotential perturbation theory [2]. At each of these 10^4 configurations, weighted with the Monte-Carlo probability $\exp(-\beta E[\{\vec{R}_i\}])$ (with β the inverse vibrational temperature of the cluster), I computed the instantaneous photoabsorption cross-section of the cluster $\sigma(\omega;\{\vec{R}_i\})$, which becomes a parametric function of the ionic coordinates. The thermally averaged cross-section at a given temperature reads,

$$\langle\sigma(\omega)\rangle = \frac{1}{Z}\sum_i \sigma(\omega;\{\vec{R}_i\})\exp(-\beta E[\{\vec{R}_i\}])\,, \tag{1}$$

where the partition function is $Z=\sum_i \exp(-\beta E[\{\vec{R}_i\}])$.

In order to be able to compare with the experimental data one still has to rotationally average the cross-section, that is, one must compute

$$\sigma_\mathrm{av}(\omega) = \tfrac{1}{3}\sum_{i=x,y,z}\langle\sigma_{ii}(\omega)\rangle\,, \tag{2}$$

in which $\langle\sigma_{ii}(\omega)\rangle$ is the thermally averaged cross-section along each of the principal axes of the cluster, at each point in phase space.

In Fig. 1 we display the results of the Monte-Carlo runs at 2 different temperatures, 100 K and 300 K, in direct comparison with those at the equilibrium GS configuration. In Fig. 1a we show the temperature evolution of the average coordination number of Na_8, whereas in Fig. 1b the results for the averaged photoabsorption line-shape have been plotted at all temperatures and compared with the experimental data from Ref. 7. As can be seen from Fig. 1a, the range of coordination numbers increases significantly with increasing temperature, which reflects the

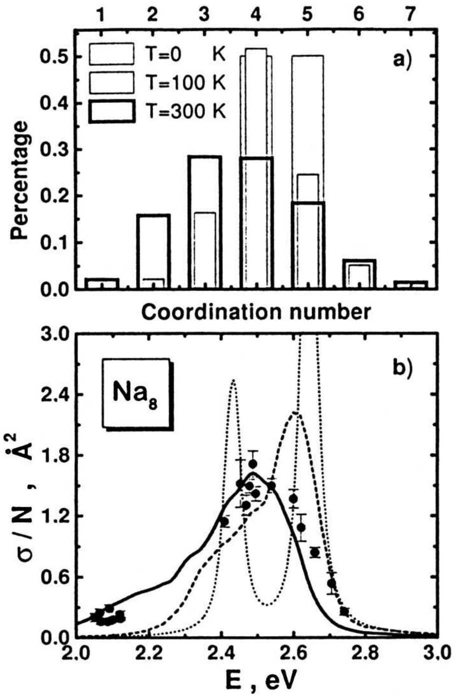

Fig. 1. a) Average coordination number of Na_8 as a function of the cluster vibrational temperature. The coordination number has been determined as the number of neighbours of each atom within a distance which is 1.5 times the nearest-neighbour bond-length of sodium in the bulk. b) Lineshape of the photoabsorption cross-section of Na_8 in its GS configuration (dotted line), at $T = 100\,\mathrm{K}$ (dashed line), and at $T = 300\,\mathrm{K}$ (solid line), compared with the experimental data measured at similar temperatures [7]. The theoretical curves have been renormalized in order to exhaust 55% of f-sum-rule, in accord with the experimental findings.

many different ionic configurations available for the small cluster at finite T. Still, at $T = 100\,\mathrm{K}$ the coordination number 4 clearly dominates, whereas at $T = 300\,\mathrm{K}$ the situation has changed completely. The exploration of the available phase-space at a given temperature becomes clear when the average photoabsorption cross-section is explicitly computed, as is plotted in Fig. 1b. At $T = 100\,\mathrm{K}$ (dashed line), thermal fluctuations are already sizeable, leading to an increase of the linewidth associated with each of the original GS peaks. Yet, the double peak structure can still be identified. Also, one can witness an overall red-shift of the response, directly related to the effective volume of the cluster which increases accordingly, an anharmonic effect not obtainable in a normal mode vibrational analysis. At $T = 300\,\mathrm{K}$ (solid line), at which the cluster has already melted, the lineshape becomes sizeably affected. Besides the overall red-shift, a considerable amount of strength gets accumulated at low energies, a feature which was not present at lower temperatures and which can be attributed to the high mobility of the ions (and electrons) when the cluster has melted, a feature which indicates that rather exotic shapes are already reachable for molten clusters at room temperature. The overall lineshape at 300 K reveals a major peak, strongly asymmetric, at an excitation energy which is in excellent agreement with the experimental findings.

In summary, the equilibrium structure of Na_8 is found to display a D_{2d} point group symmetry. The photoabsorption cross-section for this geometry is dominated by two main peaks separated in energy by 20 meV. Extensive Monte Carlo simulations carried out at different temperatures, making use of a perturbative model to compute both the total energy and the optical response of a cluster show that the photoabsorption cross-section is strongly dependent on the vibrational temperature of the cluster. For Na_8, the double-peak structure is found to survive up to $\approx$ 100 K above which the opening of phase space gradually increases until, at room temperature, the cross-section is already dominated by a single, broad peak, which reproduces very well the experimental measurements carried out at similar temperatures.

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