Shape Phase Transitions in the Absorption Spectra of Atomic Clusters

J. M. Pacheco
Departamento de Física da Universidade, 3000 Coimbra, Portugal

W.-D. Schöne
Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee and Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6032

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A quantum-mechanical framework for calculating the photoabsorption cross section of atomic clusters, which explicitly includes the thermal motion of the ions, is proposed. We compute the photoabsorption cross section of Na_8 for ionic temperatures below and above melting. At equilibrium, the line shape of Na_8 is dominated by two peaks separated by 200 meV. This structure is found to survive up to $T = 100$ K. With increasing temperatures, the cross section undergoes a shape phase transition such that, at $T = 300$ K, the double-peak structure has changed into a broad and asymmetric line shape dominated by a single peak, providing an excellent fit to the available experimental data. [S0031-9007(97)04846-1]

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The study of the interaction of light with atomic clusters has constituted, during the last decade, an invaluable source of information towards a fundamental understanding of their structural and electronic properties. Features such as the size dependence and the material dependence of the photoabsorption process in small metallic particles have been known for centuries by craftsmen producing stained glasses. However, and in what concerns the size dependence of the absorption frequency in metallic particles, classical electrodynamics provides no answer to this problem, and only in the mid-1980s a fully microscopic and quantum mechanical theory has been successfully worked out [1]. The theoretical predictions of Ref. [1] relied on the spherical jellium background model (SJBM), which disregards any ionic structure effects. When compared with the first experimental data on free neutral clusters of sodium atoms at room temperature, obtained in Berkeley [2,3], the line shapes of magic clusters are well reproduced by the SJBM, typically within 10%. This apparent success has been attributed to the weak role played by the ionic structure [4,5], which can be treated perturbatively [6]. However, as we shall show below, although amenable to a perturbative treatment, the ionic skeleton leads to observable effects which change dramatically with the vibrational temperature of the cluster.

Ionic and temperature effects are intimately connected. The connection became noticeable when it has been realized [7] that the melting of a sodium cluster was size dependent. Indeed, the crossover between the so-called electronic shell numbers and the geometric shell numbers is temperature dependent, as witnessed in the changes of the abundance spectra as a function of the vibrational temperature of the clusters. More recently, the beautiful line shapes measured in Freiburg [8] clearly demonstrated that the photoabsorption process in small metal clusters is also strongly dependent on the vibrational temperature. Tremendous changes in the line shapes have been observed, typically evolving from narrow multipeak shapes at low temperatures into broader and smoother line shapes at higher temperatures which, often, bear no resemblance to their low temperature counterparts. While there is little doubt that such kind of phase transitions evidenced in the photoabsorption profiles must be directly related to the ionic background, neither the physical mechanisms responsible for this behavior have been fully identified, nor their temperature dependence has been clarified. This situation prompts a study of the photoabsorption process in metallic particles which not only incorporates, in a quantum mechanical fashion, the electronic degrees of freedom, but which treats explicitly the ionic degrees of freedom at different vibrational temperatures. This is the purpose of this Letter, in which we directly couple the electronic to the ionic degrees of freedom in an atomic cluster, and compute the photoabsorption cross section for the coupled system at different vibrational temperatures.

Although conceptually possible, a full time dependent local density approximation (TDLDA) calculation of the optical response of a metal cluster, spanning the phase space available to the cluster at a given temperature, constitutes a formidable task which exceeds the power of most computers. On the other hand, simpler approximations which either neglect the quantum-mechanical nature of the response [9], or which severely truncate the one-electron basis upon which the response is built up [10], lack essential ingredients in order to be able to provide physical insight into the nature of the coupling between the electronic and ionic degrees of freedom. Therefore, we adopt a different strategy, which takes advantage of some special features of metallic clusters, on which we elaborate in the following.

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First, we start by taking advantage of the different time and energy scales associated with the ionic and electronic degrees of freedom [11], and invoke the adiabatic approximation to establish the coupling between these physical variables. As a result, our simulation fully incorporates the thermal motion of the ions which will explore the available phase space, at a given temperature, via a canonical Monte Carlo sampling [12]. Of course, the tradeoff of this approximation is that quantal zero-point fluctuations are neglected, and therefore we should compute the optical response only at temperatures high enough so that the zero-point motion of the ions becomes unimportant. The criteria of validity have been studied in Ref. [11], from which we conclude that this does not constitute a stringent limitation of our formalism.

Second, we invoke the perturbative role played by the ionic skeleton and compute the total energy of an atomic cluster, for each set of ionic positions, in the LDA to density functional theory (DFT), using the second-order pseudopotential perturbation theory developed for metal clusters in Ref. [6]. This approximation retains the essential physics required, namely, the quantum-mechanical nature of the total energy of a cluster, and its sensitivity to the anisotropies introduced by the discrete ionic skeleton. It also results in a two orders of magnitude saving in the computation of the total energy of an atomic cluster, when compared to first-principles LDA. Finally, we compute the optical response, at each point in phase space, via the perturbative-χ TDLDA approach developed in Ref. [13], which has been shown to provide excellent results for the photoabsorption line shapes of simple metal clusters [13]. This approximation again leads to a very significant reduction of the overall computational burden. All together, these ansätze enable us to perform extensive Monte Carlo canonical samplings of phase space, at each temperature, without giving up on the physical contents of the theory. We discuss now the particular application of the method to a specific cluster, together with the results obtained.

We selected a small metallic cluster, Na_8, which has been the subject of much controversy in the literature. Indeed, its ground state (GS) equilibrium geometry has been associated with a D_{2d} structure [4,14], with a T_d [15], as well as with a D_{4d} structure [5]. In our case, since we make use of LDA to DFT, we obtain a D_{2d} structure for its GS. When we compute the photoabsorption cross section of this cluster for its equilibrium geometry, we obtain a line shape dominated by two main peaks, with an energy difference of 200 meV, as one would expect within the plasmon-pole approximation [16]. The line shape is displayed in Fig. 1(a) with a dotted line, corresponding to the $T = 0$ K calculation, in which *no* fluctuations are taken into account. This result contrasts with the available experimental evidence [2,3] (at $T \approx 300$ K), as well as with previous theoretical calculations [1,15,17], which lead to a line shape dominated by a single peak. However, as will become clear below, the discrepancy with experiment is only apparent, and hinges on the ubiquitous role played by the temperature in the photoabsorption process. Indeed, and before dwelling upon the detailed coupling between the electronic and ionic motion, a few remarks are in order.

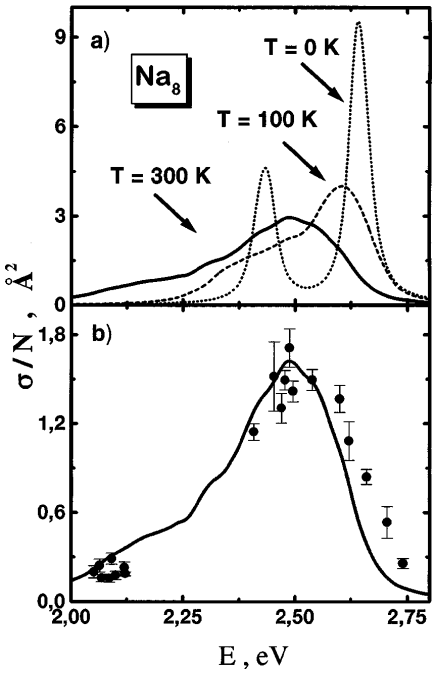

FIG. 1. (a)Line shape of the photoabsorption cross section of Na_8 at the three different vibrational temperatures indicated. In the TDLDA calculation, a numerical damping of 0.02 eV has been used, and determines the intrinsic width of the line shape at $T = 0$ K, which was obtained at the equilibrium configuration, therefore including no fluctuations. The other two curves include the coupling to the thermal motion of the ions at the temperatures specified. (b) Line shape of the photoabsorption cross section of Na_8 at $T = 300$ K, compared with the experimental data measured at similar temperatures [3]. The theoretical curve (solid line) has been renormalized in order to exhaust 55% of TRK sum rule, in accord with the experimental findings.

There are, at present, no experiments available for Na_8 as a function of temperature, since the recent techniques favor measurements on charged clusters. The available results go back to the pioneering work of Refs. [2,3], in which the absolute photoabsorption cross section of Na_8 has been measured at room temperature [9], for which the clusters have already melt [18], displaying one prominent peak at an excitation energy of 2.52 eV. Traditionally, such experimental data obtained at room temperatures have been used in order to assess the quality of different theories of the photoabsorption line shape, via direct comparison. In this sense, the experimental one-peak structure has been well reproduced by the SJBM, as well as by the configuration interaction (CI) calculation of Ref. [15], which corresponds to the response computed at the (highly symmetric) T_d ground-state geometry of Na_8, and also by the SAPS calculation of Ref. [19],

corresponding to the response computed at the (D_{4d}) SAPS-ground-state geometry of Na_8. Furthermore, the same direct comparison has been used [15] to assign the small amount of strength found experimentally at excitation energies around 2 eV to a specific transition between one-electron states of Na_8 in the T_d structure. As will be shown here, the role of thermal fluctuations of the ions is large enough to render inappropriate the direct comparison of theoretical line shapes obtained at equilibrium shapes with experimental data obtained in hot clusters. As a final remark, we would like to point out that all theoretical calculations carried out to date are able to reproduce at most the peak position measured at room temperature, whereas the width of the peak remains an open question. In this context, it is noteworthy that the surface plasmon excitation in small neutral metal clusters occurs below the ionization threshold, and therefore one expects that the lifetime of this excitation with respect to electron decay to be long. Furthermore, the coupling of the plasmon to multiple electron-hole configurations can be seen to be inhibited by the requirement of energy conservation [20]. In spite of this, the experimental peak has a large associated width which has only been accounted for, qualitatively, by superseeding the theoretical approaches with an extra width resulting from coupling the surface plasmon with thermal fluctuations of the cluster surface [9]. Finally, the strength carried out by this excitation can be estimated, from the experimental data, to exhaust between 50% and 60% of the Thomas-Reich-Kuhn (TRK) sum rule [3].

We proceed now to establish the adiabatic coupling between electrons and ions. We started by computing a canonical 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, we 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 [6]. We represented each sodium ion by a Heine-Abarenkov pseudopotential [21], which has been shown [6] to reproduce the structures obtained via first-principles LDA structural optimization [4]. For the LDA exchange-correlation functional, we used the Gunnarsson-Lundqvist parametrization [22]. We have chosen a step along the phase space leading to an acceptance ratio of 50% [12]. 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), we 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,

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

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

Yet, we still need to average the cross section with respect to the different orientations of the cluster, in order to be able to compare with the experimental data; that is, we must compute $\sigma_{\rm av}(\omega) = \frac{1}{3}\sum_{i=x,y,z}\langle\sigma_{ii}(\omega)\rangle$, 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 [23]. The results shown in Fig. 1(a) display $\sigma_{\rm av}(\omega)$ obtained in this way. With a dotted line the line shape associated with the equilibrium structure is shown (no fluctuations). With a dashed line the average cross section is shown for a vibrational temperature of 100 K. Finally, with a solid line the same quantity is shown at room temperature, that is 300 K. All theoretical curves exhaust the TRK sum rule to 100%.

From Fig. 1(a) one can observe the evolution of the photoabsorption line shape and linewidth as a function of temperature. At $T = 100$ K, 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 redshift of the response, directly related to the effective volume of the cluster which increases accordingly. This is an anharmonic effect not obtainable in a normal mode vibrational analysis. At $T = 300$ K, for which the cluster is already in a molten state, the line shape is now very different. Besides the sizeable overall redshift, a considerable amount of strength gets accumulated at low energies, a feature which was not present at lower temperatures. The overall line shape at 300 K reveals a major peak, strongly asymmetric, at an excitation energy which is in excellent agreement with the experimental findings. The accumulation of strength at low energies results from 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. Indeed, a gaussian fit to the radial distribution functions at $T = 100$ K and $T = 300$ K show a clear shift of the centroid to higher r-values as T increases, with an associated increase in the full width at half maximum (FWHM). This, in turn, translates well into the distribution of coordination numbers at each temperature, with extreme values of 2 and 7 only reached, in our simulations, at $T = 300$ K.

It is noteworthy that the line shape at room temperature is single peaked, in accord with the experimental findings. In Fig. 1(b) a comparison of our present results at $T = 300$ K with the experimental data from Ref. [3] is carried out. The theoretical curve has been renormalized in order to exhaust 55% of the TRK sum rule, as found experimentally. Apart from a (less than) 2% overall shift in excitation energy, the present results fit very well the experimental data, which shows that the coupling of the surface plasmon to the thermal motion of the ionic skeleton accounts for *both* the line shape and linewidth of the photoabsorption cross section of Na_8. Furthermore, the present calculation provides a novel interpretation to

the strength accumulated at low energies. It results from the contribution to the average cross section of the cluster coming from highly anisotropic structures which are now accessible at finite temperature. The present results point to the important role played by thermal fluctuations in the optical response of atomic clusters, and are to be contrasted with the traditional interpretation in which temperature effects are absent and only the optical profile at the equilibrium shape is taken into account.

As is well known [24], there is a close analogy between the absorption of visible light by an atomic cluster and that of gamma rays by an atomic nucleus, in spite of the profound differences in the fundamental interactions determining the physical behavior of these systems. In this respect, it is noteworthy that the coupling of the surface plasmon to the ionic motion accounts for the FWHM of the atomic cluster. This is to be contrasted with the damping of the giant dipole resonance (GDR) in nuclei, for which the corresponding mechanism, coined *large amplitude surface fluctuations*, accounts for just a fraction of the FWHM of the collective mode, and in which other mechanisms responsible for the linewidth of the GDR provide contributions of comparable magnitude. In small, neutral metal clusters, the decay width associated with electron detachment is strongly inhibited, since the surface plasmon is excited below the ionization threshold, and therefore the role of thermal ionic motion is predominant.

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 200 meV. We carried out extensive Monte Carlo simulations at different temperatures, making use of a perturbative model to compute both the total energy and the optical response of a cluster. We found that the photoabsorption cross section is strongly dependent on the vibrational temperature of the cluster. For Na_8, the double-peak structure survives up to $\approx$100 K. Above this temperature, the opening of phase space gradually increases until, already above the melting temperature, we found the cross section to be dominated by a single, broad peak, which reproduces with high accuracy the experimental measurements carried out at similar temperatures. The model proposed allows one to calculate the broadening associated with the thermal motion of the ions, as well as to incorporate, in a numerically exact way, the width associated with the lifetime against electron detachment, making it an excellent tool for establishing quantitative predictions concerning the optical properties of atomic clusters.

Finally, we would like to point out that, very recently, experimental evidence for the melting phase transition of a small sodium cluster has been obtained [18], at temperatures well below that of the melting transition in bulk sodium. In this sense, it would be very interesting to test whether the photoabsorption line shape is a convenient tool to study the melting of an atomic cluster. To this end, the method proposed here is directly applicable, requiring the repeated application of the Monte Carlo sampling at small temperature intervals within a temperature window which includes the transition temperature. Work along these lines is in progress.

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