The optical response of anionic alkali metal clusters

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Received 28 June 1993

Abstract. The dynamic response of atomic clusters made up of alkali atoms of sodium and potassium, negatively ionized, is studied microscopically and compared to the corresponding response in neutral and positively ionized species, making use of the FULL-SIC-TDLDA. An excellent agreement is found with recent experimental findings. Furthermore, a careful analysis of the line width is carried out, in order to disentangle the most important contributions to the lifetime of these systems.

PACS: 36.40.+d, 31.50.+w, 33.20.Kf

The first measurements of the photo-response of free metallic clusters [1] were performed on neutral species. More recently, it has been more feasible to study the response in ionized clusters, mostly of positively charged ones (cations). For all these systems, the surface plasmon is excited below the ionization threshold. This well known feature is used at profit experimentally to heat up clusters, since by irradiating them with laser light of a carefully tuned frequency, the surface plasmon is first excited, decaying then by transferring its energy to the normal modes of the vibrating ions. This decay mechanism, which we denote by *resistivity damping* [2], seems to be the preferred decay channel for a neutral or cationic alkali cluster, seemingly providing the most important contribution to the lifetime of the plasmon excitation. Under the assumptions of ref. [2], this mechanism will contribute to the photo-absorption cross section with a width which increases linearly with the vibrational temperature of the clusters.

In small, negatively charged clusters (anions), the plasmon is excited above the ionization threshold [3], and therefore it can decay via electron detachment. This decay channel, the branching ratio of which has been recently measured [4], is entirely analogous to the mechanism responsible for the so-called escape width of the Giant Dipole Resonance (GDR) excited in atomic nuclei, that is, it results from the coupling of the collective excitation (GDR or surface plasmon) to a continuum of unbound particle-hole ($p-h$) excitations with an energy which is degenerate with the excitation energy of the collective mode. In infinite systems, this coupling leads to the well known phenomenon of *Landau damping*, a name which is usually kept even in finite systems such as clusters and atomic nuclei. Because Landau damping implies a coupling to unbound excited states of the system, it works as to reduce the lifetime of the collective excitation, leading to enlarged line-shapes of the photo-absorption cross sections.

Similar to the Giant Dipole Resonance (GDR) in atomic nuclei, the surface plasmon excitation in metal clusters is well described, at a microscopic level, as a correlated superposition of $p-h$ excitations originating from transitions between occupied and unoccupied one-electron states moving in a single-particle, mean-field potential. In a more realistic, quasi-particle-like description [5], this mean-field potential is substituted by an orbital dependent potential. However, this refinement does not destroy the underlying physics of the optical response. In particular, the validity of the quasi-particle picture embodies the long lifetime of these one-electron states, as observed experimentally [6]. Therefore, linear response theory has proved an adequate tool to compute, at a fully microscopic level, the excitation of collective modes in both metal clusters [5] and atomic nuclei [7]. From the hole set of $p-h$ excitations out of which the collective mode is generated, one should distinguish those with energy below and those with energy above the ionization threshold for particle emission. Because the quasi-particle states are long lived, the coupling of that collective mode to $p-h$ transitions below the threshold will not contribute significantly to reduce the lifetime of the collective mode. However, and as is well known [8,9], this coupling leads to a *fragmentation* of the plasmon peak into a more complicated structure, every time such a bound $p-h$ transition occurs at an energy degenerate with that of the collective mode, therefore contributing to the linewidth of the photo-absorption line. Due to

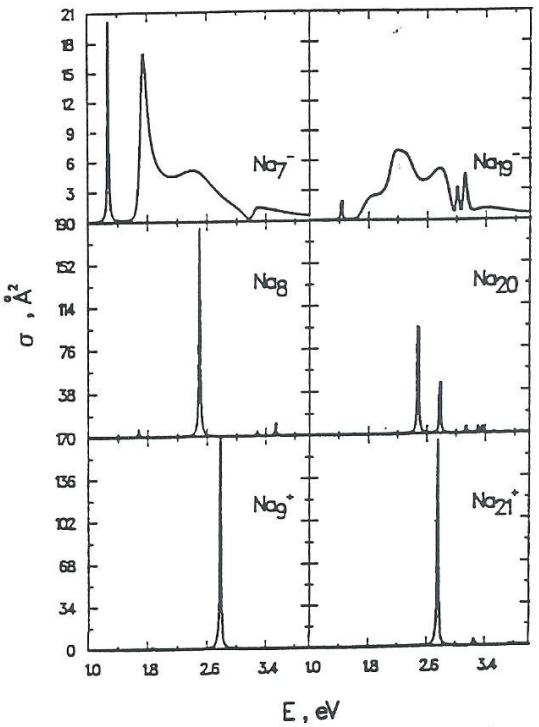

Fig. 1. Photoabsorption cross sections fot Na_7^-, Na_8 and Na_9^+ and for Na_{19}^-, Na_{20} and Na_{21}^+, in $Å^2$, calculated making use of the FULL-SIC-TDLDA. In all cases an intrinsic numerical width of 10 meV was used (for details cf. ref. [5]).

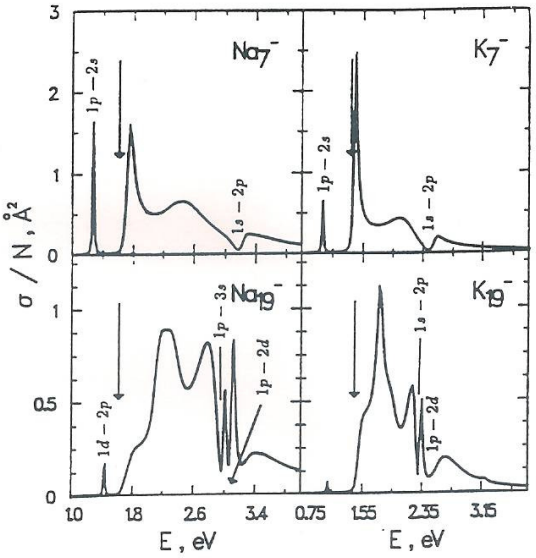

Fig. 2. Photoabsorption cross sections per valence electron of Na_7^-, K_7^-, Na_{19}^- and K_{19}^-, in $Å^2$, calculated making use of the FULL-SIC-TDLDA. The vertical lines indicate the (size-dependent) ionization threshold. Note that the ionization threshold is growing in energy faster than the corresponding blue shift of the overall plasmon response as a function of size, indicating that for larger clusters ($N > 100$), the plasmon resonance in anionic clusters will be excited below the ionization threshold. The bound $p-h$ transitions are indicated at the associated energies.

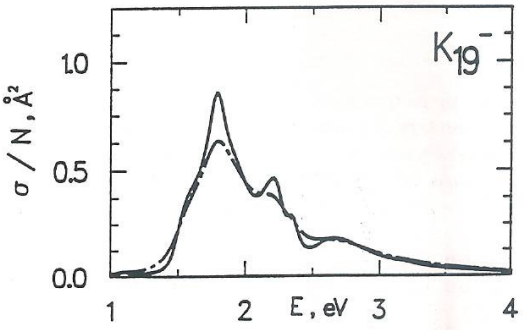

Fig. 3. Photoabsorption croos section per valence electron, in $Å^2$, for K_{19}^-. The FULL-SIC-TDLDA line shape from fig. 1 has been broadened by the 2 extra mechanisms discussed in main text (for details, cf. ref. [3]). The broadening mechanisms were included at two different temperatures, namely 100K (solid curve) and 500K (chain dashed curve), being very effective in smoothing the resulting line shape.

the analogy with Landau damping, this phenomenon is called *Landau fragmentation*. Both Landau damping and fragmentation take place via the same coupling that produces a plasmon out of a set of $p-h$ excitations, being therefore present at the level of linear response theory, such as the *FULL - SIC - TDLDA* [5]. This is in contrast with the *resistivity damping* as well as with the coupling of the collective mode to the quantal [2] (at $T = 0$) and thermal [11,12] (at $T \neq 0$) fluctuations of the surface, which are not accounted for in linear response.

Fig. 1 shows the photo-absorption cross section of sodium clusters as a function of size and ionization charge, for the magic configurations with 8 and 20 valence electrons and for ionization charges from -1 to $+1$ (for details of calculation, cf. refs. [5,3]). A sizeable difference in the plasmon lineshape is observed between the anions and their neutral and cationic partners, mostly due to the Landau damped peaks in the anionic cross sections. Multi-peaked structures are observed in all ionization states, corresponding to Landau fragmentation. The agreement between the calculated cross sections and the experimentally determined peak structures is, where available, metter than 0.01eV. In Fig. 2 the cross-sections for sodium and potassium anions are shown. All the peaks above the ionization threshold (indicated by the vertical arrows) are Landau damped, whereas the multipeaked structure resulting from Landau fragmentation is identified by indicating the bound $p-h$ transitions responsible for the observed fragmented multi-peak structure.

To compare the computed results with experimental results, one should include the other two mechanisms which are not accounted for in linear response: Resistivity damping and coupling to surface fluctuations. This is done in fig. 3 for two different temperatures, showing

that these temperature-dependent mechanisms can mask the multi-peak structure emerging from the linear response calculations, indicating that experimentally one should expect smooth line-shapes at temperatures of the order of room temperature, a feature which has been confirmed in recent experiments [4].

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12 In the adiabatic approximation, the coupling of the plasmon to thermal quadrupole surface fluctuations leads to a contribution to the line-width with a $\sqrt{T}$ dependence

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