

Shape Resonance in $4d$ Inner-Shell Photoionization Spectra of Antimony Clusters

C. Bréchnignac, M. Broyer,^(a) Ph. Cahuzac, M. de Frutos, P. Labastie,^(b) and J.-Ph. Roux

Laboratoire Aimé Cotton, Bâtiment 505, 91405 Orsay CEDEX, France

and Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bâtiment 209, 91405 Orsay CEDEX, France

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The photoionization of antimony clusters has been studied in the energy range 20–120 eV, probing the inner-valence $4d$ - np transitions as well as the shape resonance $4d$ - ϵf . When the cluster size is varied the photoionization efficiency presents a quite surprising behavior: For all clusters, except the Sb_{4p} group with $p > 1$, the photoionization pattern is similar to that which is known for the bulk. On the other hand, the shape resonance collapses completely for Sb_{4p} . It is further shown that this dramatic change of the resonance intensity is itself dependent on the nucleation conditions, which could indicate the influence of the molecular architecture.

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The concept of shape or giant resonance in free atoms emerged in the late 1960s [1,2]. It involves resonant ionization of inner-shell electrons for which the escaping electron is temporally trapped by a potential barrier. The experimental feature which characterizes the giant resonance is that it takes up so much of the oscillator strength available that it dominates the absorption cross section. The systematic evolution of shape resonances as a function of atomic number is understood in terms of a one-electron effective potential in which the centrifugal radial contribution plays a critical role [3–5].

Most frequently inner-shell excitations in molecules, solids, and adsorbates exhibit giant resonances if the constituent atoms do so. The persistence of these resonances indicates that the effect originates inside the constituent atoms, where the initial- and final-state wave functions are only little perturbed by the environment. A different type of shape resonance can occur in molecules where the molecular field couples high- l components of ionization channels with a photoelectron ejected from valence or inner shells [6]. An interesting case is the $2p$ -subshell ionization of the sulfur atom which strongly depends on its environment. For the H_2S molecule, hydrogen atoms do not perturb appreciably the inner-shell spectra of sulfur. On the other hand, a radical reorganization of the oscillator strength occurs in the photoionization of SF_6 as a consequence of potential barriers caused by the molecular environment of the sulfur atom [7]. The various aspects of giant resonances are pedagogically presented in the proceedings of Ref. [8].

Nothing is known with regard to shape resonances in clusters. Even if the behavior of the shape resonance is identical for the atomic vapor and the corresponding bulk, it is not a trivial matter to extrapolate to the clusters in between. We expect this to be particularly true for semimetallic clusters like antimony, where the tetramer Sb_4 , favored by its saturated p bonds, can form molecular substructures. Sattler, Mühlbach, and Recknagel have shown that antimony clusters produced by the gas aggregation technique consist mainly of Sb_{4p} clusters [9]. Recent studies of the fragmentation of antimony cluster ions produced evidence that the evaporation of the

tetramer prevails [10]. On the other hand, neutral and singly charged anion or cation antimony clusters produced by laser vaporization present abundance patterns which are strikingly charge dependent [11]. They do not present the four-block period and are interpreted in the context of cluster growth dynamics in which the Wade electron counting rule predicts the stability pattern. An interesting question is whether antimony clusters present isomeric structures, like bulk allotropic structures, and whether this aspect may be revealed by the behavior of the shape resonance.

We have measured the photoionization of antimony clusters involving the inner-valence $4d$ - np transitions as well as the shape resonance $4d$ - ϵf . We have indeed found that the photoionization spectra depend strongly on the cluster size and on the nucleation conditions and that the Sb_{4p} clusters play an eminent role.

The basic elements of the experimental setup are as follows. The antimony clusters are formed by the gas aggregation technique, similar to those developed by Abe, Schulze, and Tesche [12] and Sattler, Mühlbach, and Recknagel [9]. The antimony is vaporized in 30 torr of helium cooled at liquid-nitrogen temperature. The differentially pumped quadrupole chamber is connected to a monochromatized-undulator-radiation exit of the Super Anneau de Collisions d'Orsay (SuperACO) storage ring. The synchrotron radiation provides more than 10^{14} photons $\text{\AA}^{-1} \text{s}^{-1}$ and is focused at right angles to the neutral cluster beam to ionize the clusters. The clusters are then mass selected by a commercial quadrupole mass spectrometer, modified to reach more than 8000 mass units [13]. Only clusters with $n \geq 4$ have been observed. The resulting photoionization spectrum of each Sb_n ($4 \leq n \leq 36$) is monitored by varying the photon energy in the energy range 25–120 eV. Photoelectric yield measurements from a gold mesh allowed a normalization of the cluster ion signal with respect to the incident photon flux.

Figure 1 shows examples of the photoionization cross sections obtained for Sb_n . The behavior of the photoionization spectra depends strongly on cluster size. There are basically two different kinds of spectra, namely, those for Sb_{4p} , with $p > 1$, and those of all other clusters.

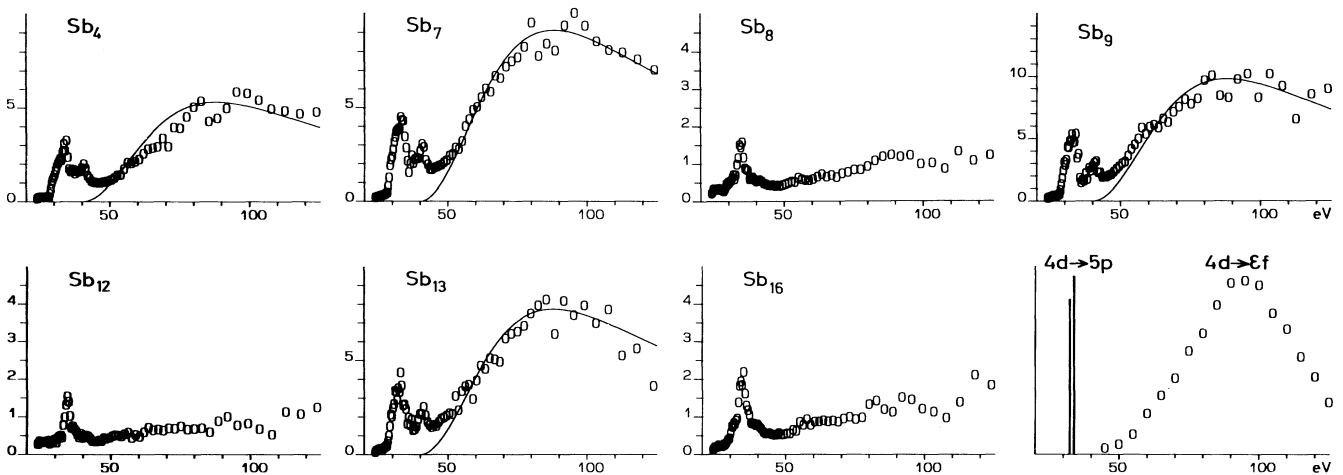


FIG. 1. Photoionization cross section normalized by Eq. (1) for Sb_n with $n=4,7,8,9,12,13,16$ in the 25–120 eV range. The absolute value is in arbitrary units. Solid line is the calculated profile from Ref. [15]; only its intensity is adjusted to fit the data. Also shown is the shape resonance of antimony in GaSb crystal from Ref. [16]. The $4d$ binding energies referred to the Fermi level are represented by vertical bars [15].

For all clusters except Sb_{4p} , the photoionization spectrum consists of two discrete structures of a few eV width centered, respectively, at 32 and 41 eV, and a broad huge resonance of 50-eV half-width centered at 88 eV. The peak at 32 eV corresponds to the $4d \rightarrow 5p$ excitation, followed by Auger ionization. Its energy is located near the energies of the corresponding atomic and bulk transitions. In fact, a recent experiment on inner $4d$ -subshell photoabsorption of neutral antimony atomic vapor [14], in the energy range 25–50 eV, has shown that the $4d^{10}5s^25p^3 \rightarrow 4d^95s^25p^4$ transition array is centered around 31.8 eV. It consists of 97 allowed transitions displayed in a region of less than 2 eV, and it is well reproduced by Hartree-Fock calculations. For the bulk the corresponding absorption is the $4d$ binding energies referred to the Fermi level. The measured values in a polycrystalline sample of Sb are 33.44 and 32.14 eV for $D_{5/2}$ and $D_{3/2}$, respectively [15], which are thus blueshifted from the atomic transition by at most 1 eV. The observed peak at 41 eV, which cannot be identified as belonging to the $4d \rightarrow np$ transition since it is located above the ionization limits SbII of both the atom (40.16 eV) and the bulk (37.3 eV), has not yet been assigned. The large resonance peaking at 88 eV is assigned to the $4d$ - ϵf shape resonance. Its position coincides with the position of the shape resonance of Sb in cleaved GaSb crystal, which has been measured by Johanson *et al.* [16]. In order to compare with our results on clusters, Fig. 1 shows the relative amplitude of the $4d$ photoemission as a function of photon energy in the energy range 50–125 eV taken from Ref. [16]. The shape resonances in solids are recognized to be of atomic origin [7]. *Ab initio* calculations of $d \rightarrow f$ giant resonances using an independent particle in an effective potential have been performed by Combet-Farnoux and Heno [4] for all free atoms from

Ag ($Z=47$) to La ($Z=57$). While the general trends are predicted correctly, the calculated profile for antimony is too narrow and the location of the maximum differs by about 15 eV from the experiment. Following Connerade [17], better agreement is obtained by using the “universal curve” connecting the breadth of the giant resonance to its energy above the “ d ” ionization threshold. The solid lines in Fig. 1 represent the deduced profile of the atomic $4f \rightarrow \epsilon f$ giant resonance, which perfectly fit the Sb_n cluster data for $n \neq 4p$.

For Sb_{4p} with $p > 1$ an extraordinary unexpected change occurs in the photoionization spectra. Their shape resonance as well as the discrete transitions mostly disappear. There emerges only a small unassigned narrow peak at 34.5 eV. This component which exists for all cluster sizes is hidden in the blue wing of the $4d \rightarrow 5p$ transitions for odd-numbered clusters. It has to be noted that for even-numbered clusters the $4d \rightarrow 5p$ transition not only disappears for $n=8,12,16, \dots, 36$ but also decreases for $n=4,6,10, \dots$, and thereby partially reveals the unassigned component as shown for $n=4$ and 10 (Fig. 2). In order to be more specific concerning the relative ionization efficiency of the different clusters, we consider, for each cluster, the fractional intensity ratio $I(h\nu)$ of the photoion signal at $h\nu$ divided by the cluster ion signal obtained in zeroth order of the grating. The grating at zero order reflects the photons from the undulator and behaves like a bandpass filter from the infrared up to 120 eV, but only those with $h\nu > 7$ eV lead to efficient ionization [10]. Therefore

$$I(h\nu) = \frac{N_i \sigma_i(h\nu) n_{ph}(h\nu)}{N_i \int_7^{120} \sigma_i(h\nu) n_{ph}^0(h\nu) d(h\nu)}, \quad (1)$$

where N_i is the number of neutral clusters i , $\sigma_i(h\nu)$ its photoionization cross section at $h\nu$, and $n_{ph}(h\nu)$ and

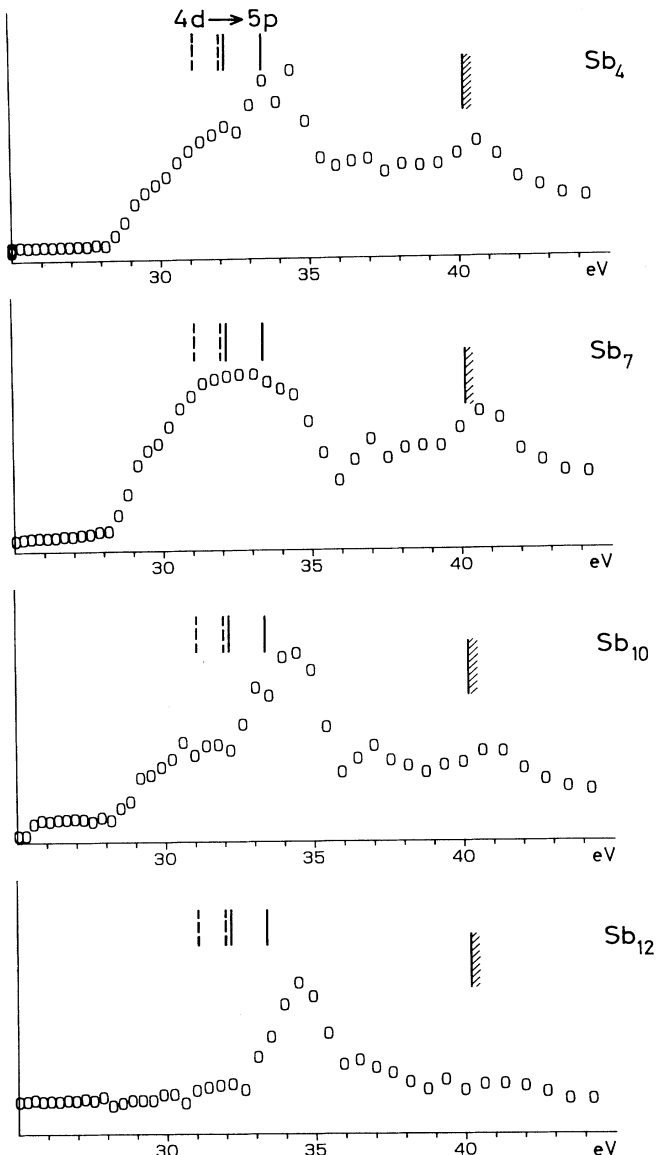


FIG. 2. Detailed photoionization spectra of Sb_n for $n=4, 7, 10, 12$ around the $4d \rightarrow 5p$ transition. Dashed vertical bars represent the two maxima of the atomic transition array and solid vertical bars represent the binding energies of the $4d$ levels referred to the Fermi level. The hatched lines indicate the atomic ionization potential of the "d" electron.

$n_{ph}^0(h\nu)$ the photon flux at $h\nu$ in the first and zeroth order, respectively. At the shape resonance energy this ratio is roughly constant for all odd-numbered clusters but decreases by 1 order of magnitude for Sb_{4p} . Even if fragmentation cannot be totally ruled out it is difficult to explain the vanishing of the resonances only by fragmentation process. However, if it were the case this would indicate that the relaxation of the electronic excitation into vibration would be much more efficient for Sb_{4p} clusters than for the other clusters. This would be very interest-

ing as regards cluster stability. Moreover, as an example, for Sb_8 excited at the shape resonance energy, the excess energy of the photoelectron is roughly twice the atomization energy and its relaxation into vibration would induce the total fragmentation of the cluster. This must lead to an increase of Sb^+ signal which is not even present in the mass spectra. So the decrease of $I(h\nu)$ for Sb_{4p} is more likely indicative of a transfer of the photoionization efficiency in the energy range lower than 25 eV.

There are several known cases whereby the shape resonance of a free atom becomes modified upon binding into a molecular system. This could be the case for antimony clusters in which the successive cluster sizes represent a sequence of different molecular environments. In most of the known cases the molecular field causes the inner well to become more attractive [18]. The shifted position of the resonance level with respect to the top of the barrier leads to a corresponding shift of the shape resonance below threshold where it resolves into discrete peaks. Such a reorganization is observed in the barium atom where a radical change occurs for the different charge states Ba , Ba^+ , Ba^{++} which shift the ionization thresholds [19]. In our case it is difficult to explain how only a modification of the centrifugal barrier can totally or even partially eliminate the shape resonance and shift the oscillator strength from 90 eV to lower than 25 eV. It is necessary to involve a huge molecular reorganization in which the atom totally loses its own individuality.

In order to analyze the influence of the molecular environment, we changed the nucleation conditions, i.e., oven and helium temperatures, which allowed us to shift from the commonly obtained Sb_{4p} mass spectrum [9] to the cluster distribution favoring odd-numbered clusters [11]. Figure 3 presents two mass spectra obtained at different helium temperatures and ionized with the broad photon energy distribution reflected by the grating at zeroth order. The same relative intensities are also obtained after electron impact ionization. Also shown are two sets of photoionization cross-section measurements of Sb_8 obtained under these different nucleation conditions. The shape resonance and the Auger transition, which do not clearly appear in the photoionization spectrum of Sb_8 from case *a*, where Sb_{4p} ($p > 1$) dominate the mass spectra, reappear in case *b*, showing the influence of the cluster formation on the $4d \rightarrow 5p$ and $4d \rightarrow f$ excitations. It has to be noted that all observable clusters of Sb_n , with $4 \leq n \leq 12$, formed at higher helium temperature (case *b*) present the same photoionization pattern where the shape resonance is present.

Since these excitations are atomiclike, their disappearance indicates that atomic levels involved in the excitation transition are considerably affected by the environment. Case *a* invokes the tetramer-building-block growth to form mostly Sb_{4p} species, whereas case *b* would correspond more likely to atomic growth. In case *a*, the tetramer-block Sb_{4p} present the same photoionization spectra. The additional atoms forming Sb_{4p+k} with

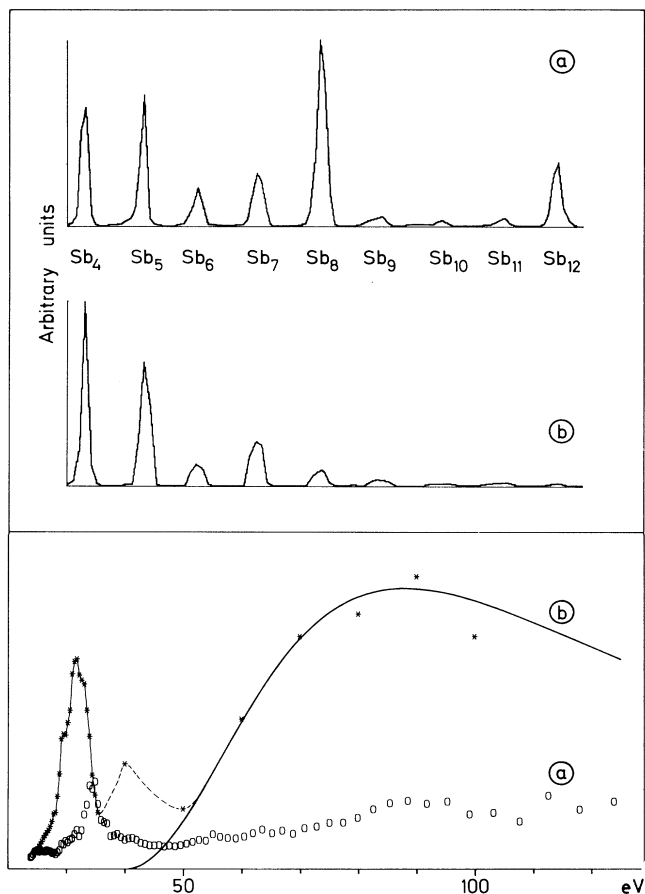


FIG. 3. Two different mass spectra of antimony clusters obtained under different nucleation conditions, but ionized with the same broad photon energy distribution (zero order of the grating). The two corresponding photoionization spectra of Sb_8 in the 25–120 eV energy range are quite different, showing that atomic electronic structure is clearly revealed in case *b* and disappears in case *a*.

$k=1,2,3$ show the atomic photoionization behavior. In case *b*, atomic structure is revealed for all clusters. The intermediate behavior of Sb_4 in case *a* may be attributed to two isomers. However, if it is well known that tetrahedral tetramers of group-V elements are molecularly bound and correspond to the s^2p^3 configuration [20], it is not clear why such a symmetry leads to a decrease or a huge transfer of the $4d \rightarrow 5p$ and $4d \rightarrow f$ oscillator strength.

To conclude, exploring the excitation spectra of clusters in the extreme UV range provides a new interesting tool for clusters studies. In particular, we have shown that the shape resonance $4d \rightarrow \epsilon f$ of antimony presents a spectacular dependence on cluster size as well as cluster

formation. This points to a strong modification of the potential inside the constituent atoms and may well constitute evidence for a molecular tetramer-block architecture. Clearly, *ab initio* calculations of antimony clusters would be very useful for deeply understanding the link between shape resonance and cluster symmetry.

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(a) Present address: Laboratoire de Spectroscopie Ionique et Moléculaire, Université Lyon 1, Campus de la Doua, Bâtiment 205, 69622 Villeurbanne CEDEX, France.

(b) Present address: Laboratoire de Physique Quantique, Université Paul Sabatier, 31062 Toulouse CEDEX, France.

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