Core level spectroscopy of free titanium clusters in supersonic beams

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Abstract. Synchrotron radiation x-ray absorption spectroscopy (XAS) is one of the most powerful techniques to interrogate the local electronic structure and chemical status of bulk and nanostructured systems. The application of this technique to the study of size effects in free clusters of transition metal atoms would advance substantially fundamental knowledge of nano-objects and the tailoring of their magnetic and catalytic properties. To date core level spectroscopy of free transition metal clusters has been out of reach due to the lack of a cluster source able to produce clusters in the gas phase with a density suitable for synchrotron radiation sources. Here we demonstrate the XAS characterization of free titanium clusters in a supersonic molecular beam. We use a high-intensity cluster beam source coupled to a synchrotron beamline to investigate the size dependence of core level excitation of Ti\textsubscript{n} clusters in the mass range

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$15 < n < 1000$. The x-ray absorption of Ti$_n$ evolves from a multi-peaked complex structure similar to that of Ti atoms towards spectra characterized by two main absorption features as in bulk titanium. The intensities and the fine structure of the spectra are size dependent showing regularities compatible with geometric shell closings and the presence of a structural transition at about 540 atoms/cluster.
a supersonic expansion [12], thus producing a particle density suitable for third generation synchrotron light sources [7, 13]. However despite widespread interest in free transition metal clusters, no results have been published to date on their core-level spectroscopy; this is due to the fact that available cluster sources cannot provide adequate cluster densities even for third generation synchrotron light sources.

Here we present the first synchrotron radiation XAS characterization of free titanium clusters in a seeded supersonic molecular beam. The experiment has been made possible by using a pulsed micro-plasma cluster source (PMCS) characterized by high intensity (i.e. high particle density in the cluster beam) coupled to a high flux third generation light source synchrotron beamline (the Gas Phase photoemission beam line at the Elettra synchrotron radiation facility, Trieste, Italy) [13, 14].

2. Experimental

In figure 1 we show a schematic representation of the experimental set-up. A PMCS produces a supersonic beam seeded with Tiₙ clusters (figure 1(a)). This type of cluster source coupled
with suitable aerodynamic focusing systems is able to produce extremely intense and collimated supersonic beams of refractory metal clusters under vacuum conditions compatible with those of synchrotron radiation facilities (peak cluster density is in the range of $10^{13}$ cm$^{-3}$ close to the nozzle exit) [15]–[17].

The core of the cluster beam apparatus is constituted by a PMCS connected to an expansion chamber. The PMCS operates outside the vacuum and it consists of a pulsed valve and a titanium electrode mounted on a ceramic body. The titanium target is sputtered by an aerodynamically confined He plasma [15, 18]. The ablated atoms condense to form clusters and the cluster–helium mixture is expanded through a nozzle into a vacuum to form a supersonic expansion. An aerodynamic lens system is used as a nozzle in order to concentrate the clusters on the beam axis and thus to increase the beam intensity. A skimmer in the expansion chamber allows only the central part of the jet into a second vacuum vessel (differential vacuum chamber). In the second chamber (base pressure $10^{-6}$ mbar) the cluster beam passes through a deflecting electric field and a gas cell filled with molecular hydrogen at $2.6 \times 10^{-2}$ mbar (supplied with a 5 sccm N$_2$ equivalent flux). Metastable helium species, which are produced in the source and are mixed with the clusters in the beam, are quenched by interaction with hydrogen molecules travelling through the gas cell; this device does not affect the cluster beam intensity. An electric field (500 V cm$^{-1}$) deflects the ions produced by the source and a neutral cluster beam is transmitted to the interaction chamber; here the cluster beam crosses the photon beam coming from the beamline. During the measurement the pressure is $10^{-8}$ mbar. The cluster beam and photon beam intensities are continuously monitored by a quartz microbalance and a photodiode respectively (not shown). The peak titanium cluster density at the interaction point was $10^{7}$–$10^{8}$ particles cm$^{-3}$.

The interaction point is placed in a time-of-flight mass-spectrometer oriented perpendicularly to the cluster beam, and measuring the mass/charge ratio of the x-ray-ionized clusters with a resolving power $\approx 20$ (m/Δm). The start signal is given by the detection of a photoelectron by a channel electron multiplier placed on the positive side of the accelerating field. A channel electron multiplier is used also as the ion detector. Taking into account a cluster beam velocity of about 1000 m s$^{-1}$, transverse to the spectrometer axis, the ion detector position is shifted downstream from the interaction position so that only clusters with mass ranging from about 15 to about 1000 atoms can be detected. This allows avoiding all the stop signals related to ionization of the background thus reducing false coincidences to a very low level.

The light source of the gas phase photoemission beamline is an undulator with a 12.5 cm period. For this experiment the undulator gap was automatically tuned synchronously with the monochromator setting of the photon energy in order to optimize the photon flux. Only a moderate resolving power ($h\nu/\Delta h\nu$) of about 1000 was used, in order to keep a flux of about $3 \times 10^{11}$ photon s$^{-1}$ in the range from 450 to 550 eV (titanium L-edge).

By varying the photon energy across the absorption edge, TOF mass spectra of the Ti$_n$ ions were collected around the L-edge; the data can also be displayed as partial ion yield (PIY) near edge x-ray absorption fine structure spectra (NEXAFS) with a cluster mass resolving power $m/\Delta m \approx 20$, determined by the geometrical configuration of the spectrometer (see figure 1).

3. Results and discussion

A typical mass spectrum measured at photon energy about the L-edge is reported in figure 2(a). Oscillation in the cluster abundance is observed, and clusters with 55 and 147 atoms are
Figure 2. (a) TOF mass spectrum of titanium clusters. The spectrum is obtained by averaging all the spectra taken at photon energies between 440 and 543 eV. (b) Trend of the average mass in the mass spectrum with varying photon energy. Particularly abundant. This is an indication of the presence of geometric shell closures [19] (see below).

Figure 2(b) shows the evolution of the average mass as computed from the core level ionized clusters as a function of photon energy. We observe several distinct features: a sharp rise to a value in the range of 150–160 Ti atoms per cluster when the photon energy exceeds \( \sim 455 \) eV, this behaviour is observed for photon energies up to about 470 eV. Below 455 eV the ion signal is negligible and the measured average mass has no physical meaning but simply reflects the distribution of the background signal. Above 470 eV the average size is lowered to about 140 Ti atoms/cluster but no significant trend in the evolution is observed if we exclude the last point in the energy range at \( \sim 543 \) eV; the energy of this last point exceeds the oxygen K-edge and the reduction in the average mass measured reflects an oxygen contamination of the smaller clusters in the mass distribution. The observation that no significant descending trend for the average size is present in the energy range 470–525 eV, i.e. extending over more than 50 eV in the continuum is an indication that the excess energy is not converted significantly into fragmentation channels. Any thermal process like loss of neutral atoms from the clusters would produce a definite trend towards smaller masses for the overall mass distribution with increasing the excess energy. On the other hand Coulomb fission of the particles can also be excluded due to the high cohesive energy of titanium and the observation (made on anions) that doubly charged titanium cluster ions are stable over a long period of time even in the case of small cluster sizes [20].

An important issue to be addressed is the charge state of the photo-ionized clusters. A change in the number of emitted electrons would be observed on the plot of figure 2(b) as a shift
Figure 3. Comparison between the cluster total ion yield NEXAFS spectrum (present work) and NEXAFS spectra obtained from bulk titanium (red curve; data from [26]) and titanium atoms (green curve; data from [25]). Cluster mass is in the range from 15 to 1000 atoms per cluster. The cluster spectrum is obtained by weighting the ion signal for different sizes by taking into account a cross section linearly proportional with the number of atoms per cluster.

of the average mass towards smaller masses, and namely as a reduction to one half of the size when moving from singly ionized clusters to doubly ionized ones. In the presence of multiple competing decay channels with different number of emitted electrons, the situation could be less clear and only a smaller reduction in cluster size could be produced, namely a reduction percentage of $1/z$ is expected for a changing in the charge state from $z$ to $z + 1$; therefore, the observed reduction of 10% when moving from the L$_{23}$ resonance to the continuum region in the case of present data is very unlikely to be due to a change in the charge state, and can be alternatively explained as an evolution with cluster size of the L$_{23}$ resonance strength (see below). We thus infer that the charge state of the particles does not significantly change across the photo-ionization threshold and a double positive charge is assumed for the clusters, as most generally expected in XAS processes [21].

The x-ray absorption spectra of transition metals show strong resonances for dipole transitions from 2p$_{1/2}$ and 2p$_{3/2}$ core levels to unoccupied d states; this produces characteristic L$_2$ and L$_3$ absorption edge peaks, often called ‘white lines’ (WL) [22]–[24]. In figure 3 we show the NEXAFS spectrum obtained from free titanium clusters (blue curve) at the L$_{23}$ edge. The absorption intensity is that of the total ion yield, as each point in the curve is the integral sum of an entire mass spectrum acquired at fixed photon energy. This spectrum can be compared with spectra recently published for Ti atomic vapour (green curve taken from [25]) and spectra of bulk Ti (red curve taken form [26]).

In order to extract information about how the absorption spectral features change depending on the selected mass of the partial ion yield (PIY) signal, we have analysed the L$_{2,3}$ features for different sizes of the free clusters. Figure 4(a) represents in a colour scale the PIY NEXAFS spectra for each cluster size. Each row in the map is a PIY NEXAFS spectrum acquired at a given ion mass; each column is a photoionization TOF mass spectrum at given photon energy. This analysis shows that the similarity of the total ion yield (TIY) to the bulk spectrum stems from averaging the PIY spectra, which are different from each other (see figure 4(b)) and from

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Figure 4. (a) Colour scale representation of the PIY NEXAFS spectra for the mass range of interest (each row is a PIY NEXAFS spectrum acquired at a given ion mass; each column is a mass spectrum recorded at a given photon energy). (b) PIY NEXAFS spectra for different cluster mass ranges. Black, 15–55; red, 80–150; blue, 300–500; green, 600–800. See also the movie.

The observation that, in the characterized mass range, the d-band features evolve and depend on the cluster size (number of atoms) suggests that the electronic structure of the clusters has not yet reached the configuration typical of the bulk.

We observe that very small Ti\textsubscript{n} clusters (15 < n < ∼55) have a complex absorption spectrum qualitatively similar to that of the atom, whereas for n > ∼55 the L\textsubscript{2,3} edge qualitatively resembles the bulk metal. The relative intensity of the two WL is size dependent and evolves up to the largest mass that we have investigated. Moreover we observe differences with respect to the bulk spectrum, such as the presence of fine structures on the high energy sides of the L\textsubscript{2} and L\textsubscript{3} peaks and, for small cluster sizes, the absence of a shoulder on the low energy side of the L\textsubscript{2,3} resonances at 455 eV (see below).

For bulk transition metals, the total WL intensity can be related to the d orbital occupancy and many studies have related the WL intensity to changes of the d band occupancy due to
oxidation, alloying and doping of transition metal samples [27, 28]. The normalized intensity of the WL has been found to decrease almost linearly with increasing d-state occupancy across the first row series, since the transition probability is related to the number of valence holes [24], [27]–[29]. The WL intensities and their relative strength are determined by a complex interplay of atomic and density of states (DOS) effects [22, 23]. The role of many-body effects can also be recognized in the WL spectrum by considering the L3/L2 intensity ratio [22, 23]. For the early transition metals and in particular for titanium, the observed ratio does not correspond to the expected 2 : 1 ratio expected in bulk systems from the multiplicity of the 2p2/3 and 2p2/1 core levels [30] due to the complex and not yet completely clarified interactions between core-hole and the d electrons and spin–orbit interactions in the valence band [31, 32].

For free clusters of finite size, it is reasonable to expect that, depending on the number of atoms forming the aggregate, both atomic and band structure features will influence the spectra; moreover the role of crystal field and surface effects are a further important ingredient in the generation of the spectral features. The variation in the balance between these factors is the origin of the changes of the WL shape, relative intensities and fine structure.

Before relating in a more quantitative way the evolution of the WL intensity to the structure of the d band, we assess the chemical state of the particles. The presence of contaminants can have a direct and important influence on the observed spectra and on the estimated d band occupancy. The formation of TM oxide phases is well known to produce a shift in the WL behaviour towards the elements at the left in the periodic table and this produces almost a d0 configuration for stoichiometric TiO2, due to the strong ionic character of the Ti–O bond [33]. Titanium is strongly reactive towards oxygen and this is the main reason why the available literature on surface properties of pure metallic titanium is so scarce. Even in UHV the preparation and handling of a clean Ti surface is a complicated technological problem. Clusters are even more reactive and this makes the investigation of pure metallic Ti particles supported on surfaces nearly impractical.

In order to check for the presence of oxygen in the clusters, we recorded the x-ray absorption from mass-resolved clusters also above the L absorption edge at 544 eV, in correspondence to the oxygen K-edge region [25]. Only a small increase in the total ion signal is observed when comparing the yield for this photon energy with the intensity derived from extrapolating the data taken in the continuum above the Ti L edge (data points up to 525 eV); this indicates that most of the clusters in the observed size distribution have low oxygen content.

As can be seen by considering the last point on the plot of figure 2(b), a slight shift towards smaller masses can be recognized for the spectrum collected above the oxygen K-edge. This is an indication that the observed oxygen is mostly bound to the smaller particles in the observed population. From a detailed analysis of the single NEXAFS spectra corresponding to different times of flight, the mean oxygen content of clusters with a given mass can be evaluated. As a first-order size-resolved analysis of the data, the simplifying assumption that each time of flight channel is dominated by a fixed level of oxygen content can be made; we can then attempt a calibration of the mass spectra in terms of the number n of Ti atoms assuming that the particles observed at given time of flight are mostly TiOm. After this analysis a reasonable fit is observed between the m versus n dispersion plot and an m = k/n2/3 curve, thus indicating that the oxygen content is proportional to the cluster surface area (with a proportionality constant leading to a density in the range of ∼20 nm−2 if the oxygen was assumed to be located on the surface of the particles). For particles larger than roughly 400 atoms per cluster NEXAFS spectra do not contain indications of the presence of oxygen. These observations and a high resolution mass
spectrometric characterization of small Ti clusters\(^9\) may suggest that the observed oxygen is probably adsorbed on the particle surface in the form of hydroxyl groups rather than forming TiO\(_x\) structures.

Ti clusters can also react with hydrogen present in the experimental apparatus. Titanium strongly interacts with molecular hydrogen giving rise to dissociative chemisorption and, via diffusion into the lattice, to titanium hydride TiH\(_x\) phases \([34, 35]\). A major possible source of contamination in our experimental set-up is the use of a hydrogen cell for the quenching of metastable helium by penning processes. This results in an exposure that can be quantified as being in the range of a few Langmuir (the H\(_2\) pressure is about 2.6 \(\times\) \(10^{-2}\) mbar resulting in an exposure in the range 1.5 L to 5 L depending on particle speed which changes with time during each cluster pulse).

Hydrogen chemisorption on Ti is strongly exothermic (\(-124 \text{ kJ mol}^{-1} \text{H}_2\) at 293 K to \(-33 \text{ kJ mol}^{-1} \text{H}_2\) at 723 K) \([36]\) and in a small isolated system (like free clusters in a molecular beam) this would readily raise the temperature above the decomposition temperature of the hydride phase after adsorption of a few atomic percent of hydrogen. At this temperature (about 620 K at 2.6 \(\times\) \(10^{-2}\) mbar) the hydride is at equilibrium with the hydrogen pressure in the gas cell, and no further hydrogen adsorption is thus expected.

After leaving the gas cell the clusters fly towards the interaction zone in a high vacuum with a H\(_2\) partial pressure of 2.6 \(\times\) \(10^{-7}\) mbar; despite this strong reduction in the hydrogen partial pressure, only a slight reduction in the hydrogen concentration inside the particles is to be expected as the particles are subject to fast cooling both by hydrogen desorption and by radiative cooling.

We estimate that Ti clusters have at most a few atomic per cent (\(x < 0.2\)) of adsorbed hydrogen; moreover the hydrogen bonding is known to involve mainly the 4s band leaving the neighbouring Ti in the d\(^3\) configuration \([34]–[38]\). According to Smithson \(et\ al\) \([38]\), the H has anionic character with an average of 1.1 electrons in a 1 Å surrounding sphere. This is however not reflected in a correspondingly large decrease of d band occupation as the enhancement of charge density around the hydrogen ions was found to be mainly due to a redistribution of interstitial charge. From these considerations we conclude that the effect of the presence of hydrogen on XAS spectra, in our case, is negligible.

We performed a semi-quantitative analysis on the partial yield spectra by observing the variation with cluster size of the normalized integral of the L\(_{23}\) features. We adopted a similar analysis to that of Graetz \(et\ al\) \([28]\) for the bulk, i.e. we removed a continuum component in the region of the WL by subtracting a linear background determined by the intensity immediately before the L\(_3\) resonance (i.e. at 453.5 eV) and just after the tail of L\(_2\) (i.e. at 474 eV); the intensity was then normalized to the integral in a region above the WL (the energy range 500–540 eV).

In figure 5 the WL intensity is plotted versus cluster dimension (number of atoms). The overall trend shows a general increase of the intensity in the investigated mass range. The absolute values obtained do not compare with those reported for the bulk \([22]\) and a much higher apparent d band occupation is observed. This large discrepancy suggests that core–hole interaction and, in general, many-body effects are strongly dependent on cluster dimensions.

\(^9\) High-resolution mass spectrometric characterization of laser-ionized Ti clusters has been performed by Piseri \(et\ al\) on a different apparatus equipped with a reflectron mass spectrometer. Mass spectra are characterized by complex structures due to the natural isotope distribution of Ti, the relative intensities of the isotope peaks can be explained by the presence of OH groups on small clusters (unpublished).
Figure 5. WL intensity plotted versus the number of Ti atoms per cluster, and versus cluster radius (inset). Green (red) vertical lines correspond to icosahedral/cuboctahedral geometric shell closures. The vertical scale of the plot is the same as used in [26] (see text).

Although the WL intensity cannot be considered as an accurate measure of the d band occupancy, its increasing trend is an indication that the density of unoccupied d states increases with the mass of the clusters. It should be noted that this evolution supports our observation on the presence of contaminants: we would expect an increase of the WL intensity for smaller masses if significant oxygen contamination were present in the form of an oxide phase.

The trend towards increasing density of d holes presents significantly larger oscillations than the statistical error (figure 5). The most prominent features correspond to cluster mass abundances in our mass spectra and they fit with the second and third geometric shell closings of icosahedral or cuboctahedral systems (at 55 and 147 atoms/cluster) [19], while a distinct change in the slope is observed around 540 atoms/cluster. A narrowing in the photoelectron spectra of Ti$_{13}$ and Ti$_{55}$ cluster anions has been observed by other authors who have suggested the presence of icosahedral geometrical shell closing [39, 40]. Numerical simulations have shown the icosahedral structure to be energetically favourable for small Ti$_n$ clusters with $n = 13, 19, 55$ [41, 42]. We do not observe significant features in the WL trend corresponding to the size of the fourth atomic shell closing (309 atoms/cluster) but a distinct change in the slope is observed above 540 atoms/cluster which corresponds (taking into account the low mass resolution of our data) to the region of the closing of the fifth atomic shell at 561 atoms/cluster.

The line-shape analysis of the mass resolved NEXAFS spectra can help to understand the abrupt change in the WL intensity trend after 540 atoms. All the NEXAFS spectra above this size show the appearance of a shoulder at 455 eV resembling a feature which is clearly evident in bulk Ti metal [23, 26, 32] (figure 4(b)), and similar to the t$_{2g}$ feature observed in TiO$_2$ spectra [26]. This structure is caused by crystal field splitting and in the pure metal it can be related to band symmetry breaking, even though, due to the Ti hcp structure, a corresponding symmetry projection of the density of states is not possible [23]. In our case, the appearance of this feature in the spectra might be interpreted as a signal of a transition between different crystalline structures.
A similar situation has been predicted by numerical simulations for another transition metal system (nickel clusters) showing a transition from icosahedral structure to decahedral motifs around 2300 atoms/cluster [43]. Compared to nickel, titanium has a lower surface tension, higher melting point and cohesive energy, from which we expect a shift towards smaller cluster sizes for a structural transition like that of nickel.

4. Conclusions

We have performed core-level spectroscopy on free titanium clusters carried in a supersonic expansion. XAS indicates that free titanium clusters, in mass range between 15 up to 1000 atoms per cluster, have a size-dependent core-level electronic structure where atomic-like and bulk-like features coexist. This makes inadequate the models used to describe d band occupancy in bulk titanium. The geometric structure of the clusters reflects on the electronic structure showing regularities compatible with icosahedral or cuboctahedral structure up to the fifth geometric shell closing, where a structural transition seems to occur.

Our experiment successfully demonstrates the applicability of XAS with synchrotron radiation to the study of free transition metal clusters.

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