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CESyRa: A versatile setup for core-level absorption experiments on free metallic clusters using synchrotron radiation

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ABSTRACT

The possibility to apply synchrotron radiation-based spectroscopic techniques, and in particular X-ray absorption spectroscopy (XAS), to isolated nanoparticles is expected to bring important insight into the electronic properties, the structural arrangement, and the chemical character of finite size systems. A precise knowledge of such properties has special relevance for a bottom-up approach to the description of nanostructured systems of technological interest. Element specificity, chemical sensitivity and local character are most significant qualities demanded from the characterization tools in this regards. The extremely low density of free particles samples is the main issue limiting the development of such techniques and only very recently first experimental results on systems of strong technological relevance like transition metal nanoparticles.

In this paper we describe an experimental setup for core-level absorption investigations on free metal clusters. The most critical issues for experiment feasibility are discussed and the adopted methodology is described in detail. Results from the application of this approach to core-shell photo-ionization studies on free Ti clusters are presented as a case study.

1. Introduction

The tuning of the electronic, optical and magnetic properties of nanoparticles by controlling their dimensions [1–3], as the first step towards the building of complex systems of many interacting nano-objects, is one of the most fascinating challenges of nanotechnology. Although this bottom-up approach is currently subject of an enormous attention in view of a wide range of applications, the investigation and the understanding of the fundamental properties of individual nano-systems free from perturbations is still in its infancy. Clusters are highly reactive and the interaction with solid or liquid matrices affects their properties [4,5]; moreover deposited clusters may suffer from fragmentation upon landing, or aggregation, coalescence, chemical contamination, or structure distortions, and from a large uncertainty in size determination [4,6].

Isolated clusters, i.e. aggregates consisting of up to tens of thousands of atoms, can be produced in the gas phase and, in particular, in molecular beams where their mass and thermodynamic state can be precisely defined [7,8]. The molecular beam approach allows real-time particle observation in at well defined time after formation or after induced transformations; it thus provides access to the mechanism of cluster growth, to the investigation of reactive and metastable species, to the fine-tuning of complex systems (e.g. particle-adsorbate systems) [9,10]. The characterization of clusters in the gas phase is nevertheless very difficult since the high degree of dilution makes the use of conventional spectroscopic techniques, and especially those based on electron or photon scattering and absorption, a formidable challenge [7]. The existing strong experimental difficulties and technical limitations cause the presence of a wide gap between applications of nanostructured materials and their fundamental understanding.

Recently different groups have demonstrated that the local electronic structure, electronic density of states, and correlation effects in isolated metal clusters produced in the gas phase can be studied by core-level spectroscopy [11,12] and, in particular, by X-ray absorption spectroscopy (XAS) using synchrotron radiation. This achievement has been possible by the coupling of high-brilliance, synchrotron radiation beamlines with high-intensity cluster sources.

Here we present and describe an experimental setup for the investigation of free metallic clusters by synchrotron radiation photo-ionization; the cluster experiment with synchrotron radiation (CESyRa) experimental design is based on the concept of coupling an apparatus for the production of intense supersonic metal cluster beams with a high flux third generation light source synchrotron beamline. The experimental work presented here was

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performed at the Gas Phase photoemission beam line at the Elettra synchrotron radiation facility, Trieste, Italy [13,14].

The paper is organized as follows: the experimental section gives an overview of the apparatus, with special focus on the concepts driving its design and on the enabling character of the implemented techniques. A separate section is dedicated to the possible data analysis approaches offered by the setup and to the discussion of their relevance within the characteristics and possibilities opened by the adopted nanoparticle synthesis route. The results section is included as an exemplification of the described techniques ad as an introduction to the results obtained applying the presented methodology to the study of free Ti clusters.

2. Experimental setup

2.1. Supersonic beam apparatus

The supersonic cluster beam apparatus is schematically outlined in Fig. 1: it consists of five differentially pumped vacuum chambers providing the required ultra high vacuum (UHV) conditions at the photon-cluster interaction point despite the high gas load typical of supersonic cluster source operation.

The first chamber is the expansion chamber of the molecular beam, it is evacuated by a 2000 l/s turbomolecular pump backed by a dry pumping stage boosted by a 120 l/min roots pump; the chamber is equipped with two sets of two-axis linear motion feed throughs allowing cluster beam alignment. The two sets act respectively on the molecular beam nozzle (for free-jet steering) and on the skimmer support (for nozzle-skimmer relative alignment). An electro-formed 2 mm diameter skimmer at 40 mm distance from the nozzle provides the selection of the central part of the free jet in order to guarantee stable high vacuum conditions in the following chamber, thus producing a suitably low background pressure for the molecular beam. The cluster source, whose design allows installation outside the vacuum vessel (see next section), is connected to the expansion chamber through an ISO100 port and evacuated through the source nozzle. A built-in system for differential pumping of the source body provides the preservation of high vacuum base-pressure conditions inside the cluster source.

The second chamber hosts a small cell, aligned with the molecular beam axis and connected to a mass flow control gas inlet. The cluster beam travels across the cell and possibly interacts with gas species at controlled pressure. Plates for electrostatic deflection of ionized species produced by the cluster source are also installed in the chamber in order to wipe them off the cluster beam. A narrow capillary aligned with the gas cell connects the second chamber to the next one, producing a two orders of magnitude pressure drop and ensuring the conditions for the operation of channel electron multipliers installed in the third differential vacuum chamber as beam diagnostics tools. The two detectors work in a pulse counting mode and can measure the cationic and anionic ion flux produced by the source. When performing this measurement the deflecting plates in the gas cell are grounded.

In the fourth chamber, photons from the synchrotron beam-line cross the cluster beam within the acceleration region of a single stage time of flight mass spectrometer (TOF/MS), oriented per-

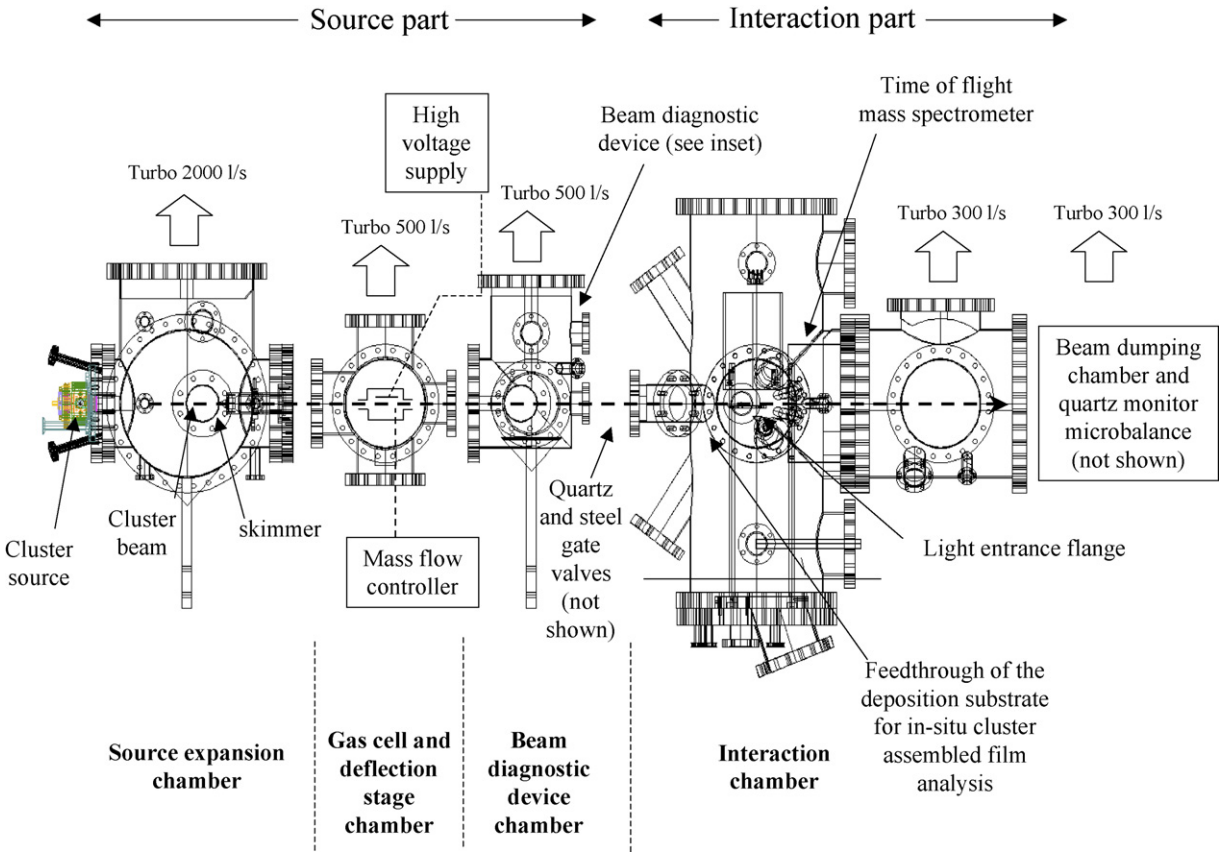

Fig. 1. Schematic representation of the experimental apparatus. From the left to the right, the sketch represents the cluster source faced on the expansion chamber, the gas cell chamber, the beam-diagnostic chamber, the interaction chamber and the beam-dumping chamber (see text). A gate valve separates the cluster beam generation section (first three chambers) from the interaction part where, at 1.5 m from their origin, the clusters cross the photon beam inside in the acceleration stage of a time of flight mass spectrometer. The cluster flux is measured by a quartz-crystal microbalance head on which clusters impact. The intensity of the photon beam from the synchrotron beam-line is monitored by a silicon photodiode.