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X-ray absorption spectroscopy of mass-selected transition metal clusters using a cyclotron ion trap: An experimental setup for measuring XMCD spectra of free clusters

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ABSTRACT

A Fourier-Transform-Ion-Cyclotron-Resonance mass spectrometer has been installed at the BESSY II storage ring. This unique setup enables to record soft X-ray absorption and magnetic circular dichroism spectra (XMCD) of mass-selected clusters in the photon energy range 200–1200 eV. The photoabsorption signal is obtained by recording the fragmentation pattern as produced after X-ray absorption and subsequent Auger decay of the core-excited parent cluster ion. The experimental setup and first X-ray absorption spectra on V_{13}^+ and Nb_{13}^+ are discussed. The feasibility of recording X-ray induced XMCD spectra is demonstrated for Co_{22}^+. Improvements that allow for quantitative determination of spin and orbital momenta in the future are briefly outlined.

1. Introduction

In recent years X-ray magnetic circular dichroism (XMCD) has developed into an important magnetometry tool for studying dilute samples such as sub-monolayers [1], quantum wires [2], nanoparticles [3], as well as supported monodispersed clusters [4,5]. In general XMCD allows for separation of spin and orbital magnetic moments, and it provides for a route to determine magnetic anisotropies of selected samples [6,7]. XMCD has the particular advantage of being sensitive to low sample concentrations and being element specific.

Various deposited metal clusters have been investigated by XMCD. The total moments of these clusters increase with respect to bulk values, and the relative contributions of spin- and orbital moments differ from those of corresponding bulk samples [4,5]. However, the deposition of the clusters inevitably alters intrinsic cluster properties through substrate induced electronic reorganization. It is a challenge to accurately model the electronic coupling within the cluster-surface system [8]. Even the modelling of individual clusters causes such challenge and requires highly correlated relativistic ab initio levels of computation [9,10]. These circumstances request for additional investigation, i.e. XMCD experiments on *free* mass-selected clusters as those do not interact with any environment. Our present setup is designed to serve this purpose, i.e. to analyse the spin and orbit magnetic moments of free mass-selected cluster ions by recording the X-ray induced dichroic difference signal using circularly polarised soft X-ray undulator radiation.

Total magnetic moments of mass-selected metal clusters have been recorded by Stern–Gerlach experiments [11–14]. It turns out that the total moments of free clusters are clearly enhanced with respect to the bulk. Moreover the Stern–Gerlach measurements show that mass-selection is mandatory for the exploration of small clusters as the magnetic moments vary in a non-scalable way as function of size. This is particularly true for clusters with less than 100 atoms. As the relative contribution of orbital and spin moments cannot be received by Stern–Gerlach experiments XMCD spectroscopy serves as complementary tool for the investigation of the magnetic properties of free clusters.

Ion trapping has successfully been applied for exploring mass-selected clusters with respect to e.g. photofragmentation [15],

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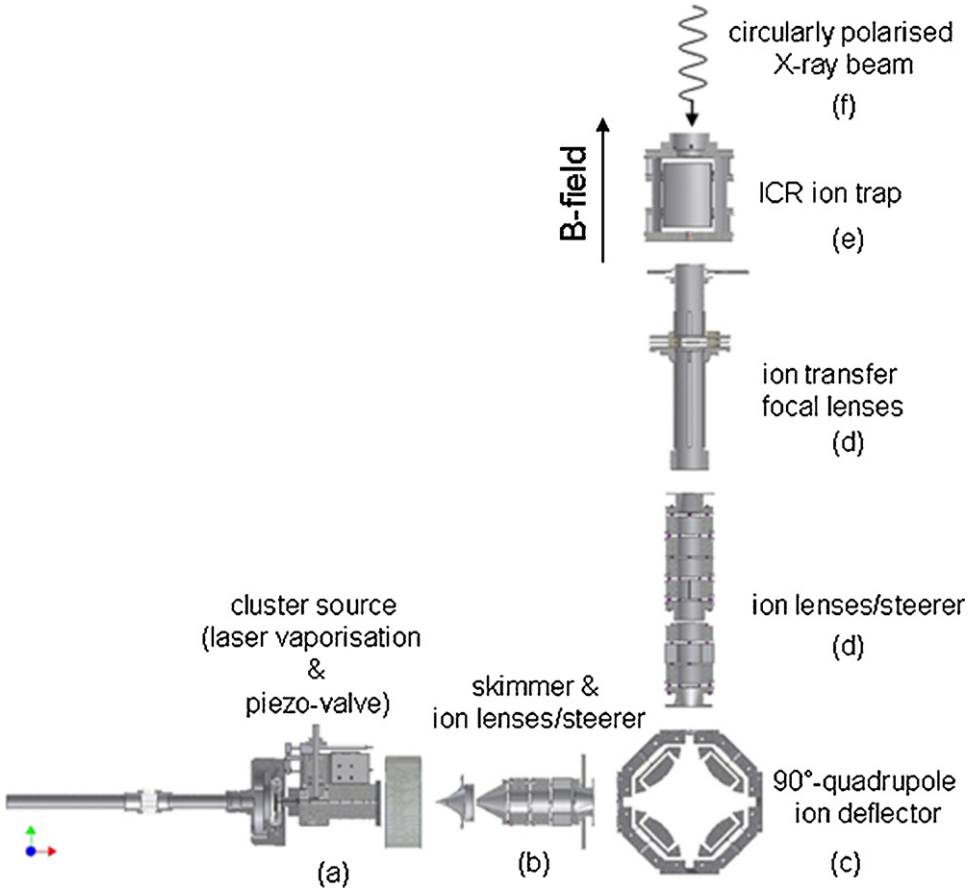

Fig. 1. Scheme of the experimental setup for XAS and XMCD measurements on free mass-selected clusters: (a) cluster source, (b) skimmer and extraction optics, (c) electrostatic quadrupole deflector, (d) focussing and transfer optics, (e) FT-ICR cell for trapping and analyzing the cluster ions, and (f) counter propagating X-ray photon beam. The FT-ICR cell is placed in the center of a superconducting magnet (7 T).

charge states [16], vibrational frequencies [17] and structure [18]. Moreover, ion trapping has recently been used to explore free nanoparticles and mass-selected clusters by soft X-ray absorption [19,20]. Ion trapping provides a spatially confined target density. Using an average photon flux of an undulator X-ray source of $\sim 10^{12}$ s^{-1} as well as a typical atomic photoionization cross sections in the soft X-ray region (σ = 1–10 Mb [21]) we estimate that a target density of $\geq 10^7$ clusters/cm^3 should provide a reasonable signal-to-noise ratio (>3) for doing soft X-ray photoabsorption spectroscopy. For this estimation we assumed a detection limit of >200 ions [22], 10 atoms/cluster and 100% photon and ion beam overlap. Photoabsorption of X-ray's and subsequent Auger decay creates multiply charged cluster ions. These final state ions are very likely to dissociate, in analogy to what has been observed in molecular X-ray spectroscopy [23]. The total fragment ion intensity is proportional to the X-ray absorption probability. Thus an absorption spectrum of the stored parent cluster is recorded by scanning the photon energy over an inner-shell absorption edge and detecting the fragment ion yield.

We built an experimental setup in order to perform XMCD spectroscopy on free clusters. This new setup, branded GAMBIT (General Abstraction of Magnetic Moments at BESSY by Ion Trapping), utilizes a cyclotron ion trap (combination of DC electric and static magnetic fields) which serves both as ion trap and mass detector (m/z). In contrast to dynamical RF traps which have recently been used for X-ray absorption spectroscopy of mass-selected ions and clusters [19,20] the Penning-like setup uses a strong homogeneous magnetic field for radial confinement of the cluster ions. This trapping field also defines the magnetization direction of the cluster ensemble for XMCD measurements.

We have taken first X-ray absorption spectra for V_{13}^+ and Nb_{13}^+ using linear polarisation. These clusters are supposed to have an icosahedral-like geometry. Circular polarisation has been used to record the absorption spectra of Co_{22}^+ which can be assumed to be superparamagnetic [13]. These cluster sizes have been chosen as these could be produced with highest intensity for the time being. Moreover, any higher harmonics (3rd, 5th, 7th) of the parent mass peak resulting from Fourier analysis of the recorded frequency spectra do not overlap with the fragment peaks.

2. Experimental setup

The setup is based on a commercial Fourier-Transform Ion-Cyclotron Resonance (FT-ICR) instrument (Bruker Apex III). The instrument was modified according to a similar instrument that serves to investigate transition metal cluster reactions [24]. The latter experiment is not combined with a synchrotron beamline, however. Metal clusters are formed by pulsed laser vaporisation (20 Hz, 532 nm, ~10 mJ/pulse) of a rotating thin foil into pulses of Helium carrier gas from a home-built piezo valve [17]. The valve opens shortly (60–120 μs) in order to allow for the admittance of high backing pressures (up to 15 bar). The cluster/gas mixture of the source region propagates along a channel (80 mm × 2 mm diameter), expands adiabatically into vacuum, and passes through a gas dynamic skimmer (opening 0.2 mm) for differential pumping. Subsequently, the cluster ion beam is bent by a home-built 90°