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# Atomic and electronic structure of free niobium nanoclusters: Simulation of the $M_{4,5}$-XANES spectrum of $Nb_{13}^+$

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ABSTRACT

The atomic and electronic structure of free niobium nanoclusters has been studied on the basis of X-ray absorption near-edge structure (XANES) spectroscopy and density functional theory. $M_{4,5}$-XANES spectra have been calculated for several structural models of the 13-atomic niobium cluster. The calculations have been done on the basis of both full multiple scattering theory within the muffin-tin approximation for a potential and full-potential finite difference method. The comparison of the experimental $M_{4,5}$-edge XANES spectrum (Peredkov et al., J. Electron Spectros. Relat. Phenomena 184 (2011) 113–118) with the simulated X-ray absorption spectra of $Nb_{13}^+$ hints to a highly-symmetric icosahedral structure of the cluster. An internuclear distance of $2.2 \pm 0.1$ Å between neighboring "surface" atoms of the icosahedron and 2.09 Å between the central "bulk" atom and "surface" atoms, respectively, has been found upon comparison of the experimental and theoretical XANES spectra.



## 1. Introduction

Nanoclusters attract significant attention both from the fundamental point of view and from the standpoint of their possible applications in nanotechnologies. The properties of nanoclusters change significantly with size and atomic structure [1,2]. Thus, a deep insight into the nature of nanoclusters is impossible without the data on their atomic structure. Such data can most reliably be obtained by studying free clusters, because deposition on any kind of substrate might cause major changes in clusters geometry and electronic structure.

Among the wide variety of different types of clusters, nanoclusters of 4*d* transition metals are of particular interest because of their fundamental importance and potential applications as magnetic materials and nanocatalysts. Niobium nanoclusters are among the most extensively investigated transition-metal clusters due to the several features, such as the relatively large propensity for clusterization and the existence of ferroelectric state related to superconductivity [3]. Atomic and electronic structure of niobium nanoclusters has been previously studied by various experimental and theoretical methods. Niobium trimers $Nb_3$ in argon matrices have been investigated based on an analysis of absorption (scattering depletion) and Raman spectra [4]. Photoelectron spectra of mass-separated $Nb_n^-$ clusters ($n$ = 6-17) have been discussed by Kietzmann et al. [5], indicating a closed electronic shell of the neutral even-numbered clusters. Time-of-flight mass spectra of free niobium clusters $Nb_n$ produced by laser vaporization have been

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measured and magic numbers were observed at $n = 7, 13, 15, 22$ [6]. Theoretical methods of investigation have been applied to determine the most stable atomic geometries and electronic properties of niobium nanoclusters in the size range from 2 till 52 atoms [7–14]. Atomic structure and magnetic moment of 4*d* transition-metal clusters with 13 atoms (including $Nb_{13}$ cluster) have been discussed [15–18].

An effective modern technique for the analysis of nanoscale atomic structure (as well as the density of unoccupied electronic states near the bottom of the conduction band) is the X-ray Absorption Near-Edge Structure (XANES) spectroscopy [19,20]. XANES spectroscopy could give full information on the local atomic structure around the absorbing atom (coordination numbers, bond lengths and bond angles) with high precision, even for materials without long-range order in the atomic arrangement, such as nanoclusters. The bond length distances can be determined using XANES spectroscopy with the accuracy up to 0.02 Å, bond angles—with the accuracy of few degrees [21]. At the same time, the extraction of structural data from XANES spectra demands complicated theoretical analysis [22,23]. Recently, XANES spectroscopy has been successfully applied to investigate titanium and copper nanoclusters [24–26]. In the present work, the theoretical analysis of the $M_{4,5}$ XANES spectrum of free $Nb_{13}^+$ has been performed and compared with the recently measured experimental spectrum [27] in order to extract information on the geometry of the nanoclusters.

## 2. Experiment

The experimental setup used to measure $M_{4,5}$-XANES spectra of free mass-selected niobium clusters has been described in detail elsewhere [27,28]. In short, X-ray absorption spectra of free $Nb_{13}^+$ were measured at UE52-PGM beamline ($\sim 10^{12}$ photons/s, 1st undulator harmonics) of the synchrotron source BESSY II (Helmholtz-Zentrum Berlin, Germany). A cluster beam has been produced by pulsed laser vaporization (532 nm, 20 Hz) and supersonic expansion using a synchronized pulsed He buffer gas. Clusters have been mass-selected by using a Penning-like ion trap and FT-ICR mass spectrometer (7 T, Bruker). Fig. 1 shows the ICR-mass spectrum of mass-isolated $Nb_{13}^+$ clusters. Note the low degree of contamination after mass-selection and isolation. X-ray absorption spectra on $Nb_{13}^+$ have been recorded near the $M_{4,5}$-absorption edge of niobium using linearly polarized X-ray undulator radiation. As absorption signal, the number of ionic fragments has been recorded inside the ion trap (Fig. 2). The photon energy scans in Fig. 2 have been taken with the same mass-isolation parameters as were used to record Fig. 1. The two smallest fragment

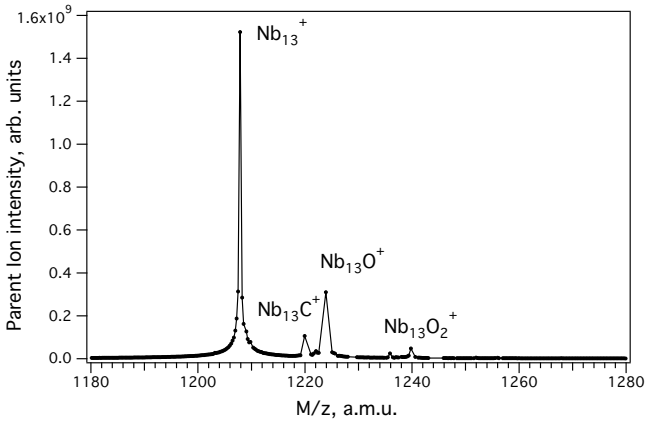


**Fig. 1.** ICR-mass spectrum of parent $Nb_{13}^+$ clusters after mass-isolation.

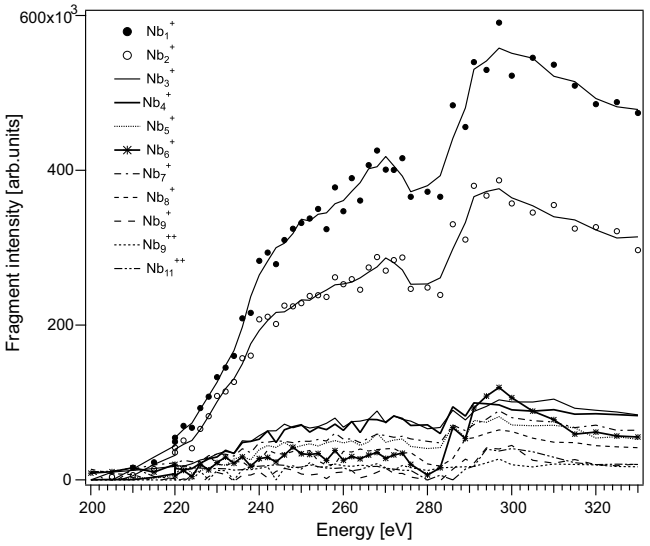


**Fig. 2.** Mass-resolved ion yield absorption spectra of $Nb_{13}^+$ recorded at the $M_{4,5}$-edge using soft X-ray undulator radiation (linear polarization).

ions ($Nb_1^+$, $Nb_2^+$) were the dominant ones and therefore they have been accumulated to represent the absorption spectrum of $Nb_{13}^+$ at best signal-to-noise ratio. The accumulated absorption spectra are shown as top curves in Figs. 4 and 6 (experimental spectrum). The fragmentation yield has been normalized to the photon flux of the beamline which was recorded by a GaAs-diode behind the monochromator exit slit. The second order light intensity (>500 eV) transmitted by the monochromator (plane grating) has been measured by us to be 2-3% of the first order intensity. Absorption by carbon and oxygen contaminated $Nb_{13}^+$-clusters can be ruled out by the tiny degree of contamination (Fig. 1) and the low degree of transmitted second order light. The ICR-cell has been quenched and refilled by new mother clusters after a few seconds of irradiation.

## 3. Computational details

Theoretical Nb $M_{4,5}$-XANES spectra for several structural models of 13-atomic niobium cluster have been calculated on the basis of two approaches.

First, the self-consistent real-space full multiple-scattering (FMS) theory has been used. The calculations are based on the formalism of the relativistic Green's function in the real space. The muffin-tin approximation [29] for the potential shape has been employed. This theory is implemented into the X-ray absorption spectra and electronic structure FEFF 8.4 code [30].

Secondly, the real-space full-potential finite difference method (FDM) realized in FDMNES2009 program code [31] has been applied. Its main advantage is the possibility to have a totally free potential shape, thus avoiding limitations associated with the classical muffin-tin approximation for a cluster potential.

Calculations of the Nb $M_{4,5}$-XANES spectra using both methods have been done within the Hedin–Lundquist model of the exchange-correlation potential taking into consideration a core hole effect.

Recently, FEFF code based on muffin-tin approximation has been applied to calculate the $M_{4,5}$-XANES spectrum of icosahedral $Nb_{13}$ in which the surface atoms have been considered as absorbing atom [28]. In the present study we use not only FEFF, but also FDMNES code, to exhibit the influence of non-muffin-tin effects. Such effects are particularly important to be considered in the simulations of nanoclusters due to the significant "surface" atoms contribution