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Structure Determination of Anionic Metal Clusters via Infrared Resonance Enhanced Multiple Photon Electron Detachment Spectroscopy

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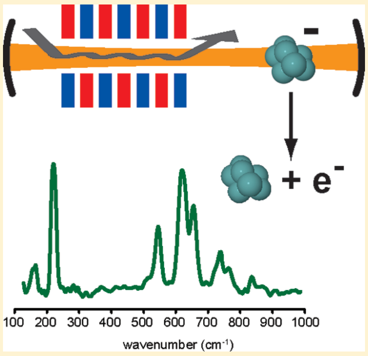
Supporting Information

ABSTRACT: We report vibrational spectra of anionic metal clusters, measured via electron detachment following resonant absorption of multiple infrared photons. To facilitate the sequential absorption of the required large number of photons, the cluster beam interacts with the infrared radiation inside the cavity of a free electron laser. Far-infrared spectra of the bare metal cluster anion Nb_{10}^- as well as of the Nb_6C^- anion are measured in the 130−1000 cm^{-1} range. The structures of these clusters can be unambiguously determined by comparison with calculated spectra of the putative global minima structures, identified by density functional theory calculations.

SECTION: Dynamics, Clusters, Excited States



The physical and chemical properties of nanosized metal particles, composed of only a few atoms, are often strongly size-dependent and can vary drastically from those of the bulk. The charge of the nanoparticles can also substantially influence their characteristics and is known to be crucial, for instance, for the catalytic activity of deposited gold nanoparticles.[1,2] It is of fundamental interest, therefore, to develop novel experimental methods that enable the geometric and electronic properties of metal nanoparticles of a given size and charge to be unraveled. In the gas phase, mass spectrometric detection schemes can be employed to selectively investigate clusters with a well-defined number of atoms. There, the effects of the charge can be studied by comparing the properties of neutral clusters to those of the (usually singly charged) cationic and anionic ones.

During the past decade, detailed information on the structure of charged metal clusters has been obtained from ion mobility measurements, from electron diffraction studies on trapped ions, and from photoelectron spectroscopy (PES), all in combination with quantum-chemical calculations. Gold cluster anions, in particular, have been intensively studied by these various methods.[3−8] Most other studies of cluster anions have, so far, been conducted using PES.[9,10] As PES probes transitions between electronic states of anionic and neutral clusters, in principle, a detailed theoretical description of both charge states is required, which can hamper a definite structural assignment. Vibrationally resolved PES can provide additional insight into the structure, but only very few studies of this type exist on metal clusters with more than three atoms.[11,12]

For the investigation of strongly bound neutral clusters in the gas phase, variants of infrared (IR) absorption spectroscopy have been developed. By measuring the line position and intensity of the vibrational modes of the cluster, the bonds between the atoms in the cluster are probed directly, and theoretically tractable information on the structure of the cluster is thus obtained. Due to the limited density of clusters that is achievable in the gas phase, the absorption of IR photons can only be probed via monitoring the response of the cluster to IR pumping, an approach generally referred to as "action" spectroscopy. The absorption of (multiple) IR photons on an allowed vibrational transition leads to a heating of the cluster and can be detected, for instance, via monitoring the resulting fragmentation or ionization of the neutral cluster.[13] Alternatively, the boiling off of a "messenger" atom, weakly bound to the cluster for this sole purpose, can be monitored; the latter approach has been used to record the IR absorption spectra of neutral gold clusters, for instance.[14]

IR spectroscopic techniques similar to those used for neutral clusters have also provided a wealth of structural information for cationic clusters. Recently, the messenger atom technique has been applied both in cooled ion traps and in supersonic beams.[15−17] For anionic metal clusters, on the other hand, no IR spectra have been recorded so far, in part because tagging of anionic metal clusters with rare gas atoms is prohibitively difficult. Moreover,

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the fundamental vibrations of bare metal clusters often have low IR intensities and are found in the far-IR region, typically below 500 cm^{-1}, where the photon energy is only a few tens of millielectron volts. Therefore, the absorption of many IR photons is required to induce fragmentation or ionization (electron detachment) of the anionic clusters.

Here we report the far-IR absorption spectra of two prototypical metal cluster anions Nb$_{10}^-$ and Nb$_6$C$^-$. Their spectra have been recorded by monitoring the depletion of the anion population in a molecular beam induced by IR resonance enhanced multiple photon electron detachment (IR-REMPED). This process has been observed in an experiment where the cluster beam is crossing the IR laser beam inside the optical cavity of a free electron laser (FEL). Besides gold, niobium clusters are particularly well studied by experiment[17−19] and theory.[20−22] Nb$_6$C$^-$ on the other hand shows bare metal cluster characteristics, but has absorptions over a wider wavelength range, thereby nicely demonstrating the capabilities of the spectroscopic technique.

The successful application of "action" spectroscopy in the far-IR has only become possible with the advent of IR-FELs, as these combine a wide tuning range with a sufficiently high intensity.[23] The temporal structure of the radiation emitted by IR-FELs based on normal conducting linear accelerators enables repeated cycling of the molecules or clusters through an absorption and subsequent internal energy redistribution process, thereby resonantly heating them on a microsecond time-scale.[24] For neutral fullerenes, for instance, the absorption of several hundred IR photons by a single cluster has been observed in IR resonance enhanced multiple photon ionization (IR-REMPI) experiments.[25] Recently, the mid-IR vibrational spectra of C$_{60}^-$,[26] SF$_5^-$,[27] and C$_{76}^{2-}$ (ref 28) have been recorded, using mass selected and trapped ions and probing the electron detachment by electron scavengers or, in the case of C$_{76}^{2-}$, by the appearance of the singly charged anion. By storing all ions in the ion trap, the signal intensity could be improved by extending the interaction time with the IR-FEL radiation over several macropulses. In the present experiments, the metal cluster anions are directly investigated in the molecular beam, which has the advantage that many cluster sizes can be studied at the same time. However, as the clusters are passing freely through the interaction region with the far-IR radiation, and as their IR intensities are at least an order of magnitude lower, the demands on the far-IR fluence (in J/cm^2, integrated over the interaction time) are significantly increased.

The required fluence for these experiments is obtained at a new beamline that is part of the Free Electron Laser for Infrared eXperiments (FELIX) user facility at the FOM Institute for Plasma Physics in Nieuwegein, The Netherlands, where the experiments have been performed. The Free Electron Laser for IntraCavity Experiments, FELICE, has an extended optical cavity that can host a user experiment, which allows the use of the full pulse energy available inside the optical cavity (for details, see ref 29). For the experiments, the molecular beam setup equipped with a laser ablation cluster source and a reflectron time-of-flight mass spectrometer has been used. In the extraction region of the mass spectrometer, the IR and the molecular beam cross under 35° to increase the interaction time. To ensure optimum overlap of both beams, the whole molecular beam setup can be moved horizontally and vertically with respect to the focus of the space-fixed IR beam, which also allows the laser fluence in the interaction region to be controlled.

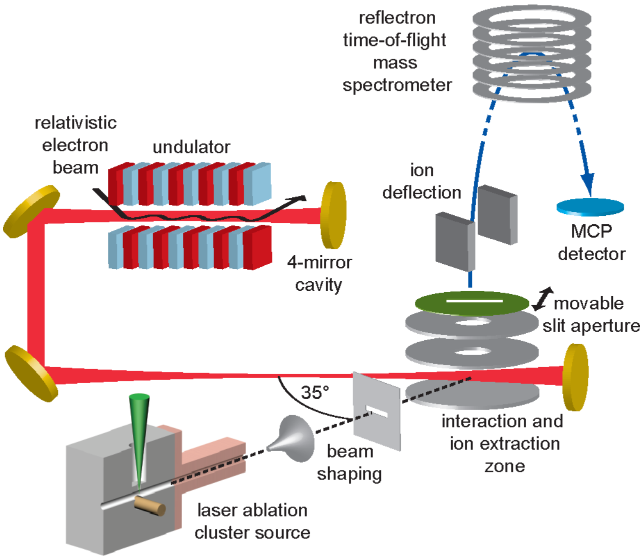

Figure 1. Schematic of the experimental setup. The clusters are made in a pulsed laser ablation cluster source. The molecular beam is shaped with a skimmer and a slit aperture and crosses the FELICE beam axis under 35°. To detect only the ions that have been irradiated by FELICE, a movable aperture is used to reduce the acceptance of the mass spectrometer.

In the case of a resonant absorption, ions in the molecular beam may be sufficiently heated to emit an electron, leading to a drop in their abundance. In order to detect this depletion, the cluster beam experiment runs with twice the repetition rate of FELICE, and mass spectra are taken on alternate shots with and without FELICE. Analysis of the IR wavelength-dependence of the mass spectra allows the construction of mass-specific depletion spectra. In a single run, the spectra for a large number of species can be recorded; however, we focus here only on the Nb$_{10}^-$ and Nb$_6$C$^-$ anions. The experimental settings have been optimized on Nb$_6$C$^-$, as this anion can be produced in high abundance under otherwise similar conditions as those for Nb$_{10}^-$. As a consequence of the crossed beam setup and the finite FELICE beam size, only a small fraction of the whole molecular beam is exposed to a sufficient IR fluence to induce REMPED. By inserting a slit aperture behind the extraction region of the mass spectrometer and by switching the extraction voltages on just after the end of the IR pulse, the packet that has been irradiated by the full pulse is selected.

In the focus, the IR beam waist only amounts to 0.4−1.1 mm in the covered wavelength range. The beam speed is ~1.6 mm/μs for the clusters made in the expansion of a helium gas pulse (seeded with 0.025% of methane for Nb$_6$C$^-$). To make use of the full macropulse duration of FELICE, which is typically 4−7 μs, the experiment has been performed out of the focus of the IR beam. By translating the whole molecular beam setup, the FELICE waist is adjusted to ~4 mm in each of the individual scan ranges necessary to cover the full considered wavelength range. The interaction time was thereby increased to more than 4 μs. The spatial extent in the vertical direction of the molecular beam was also shaped to ~4 mm for Nb$_{10}^-$ and ~2.5 mm for Nb$_6$C$^-$ by a combination of a skimmer and a slit aperture (see Figure 1).

Figure 2 shows the IR-REMPED spectra of Nb$_{10}^-$ and Nb$_6$C$^-$ in the 130−400 and 130−1000 cm^{-1} ranges, respectively. Both spectra show the direct depletion, not corrected for variations of the IR fluence over the scanning range. For both systems,

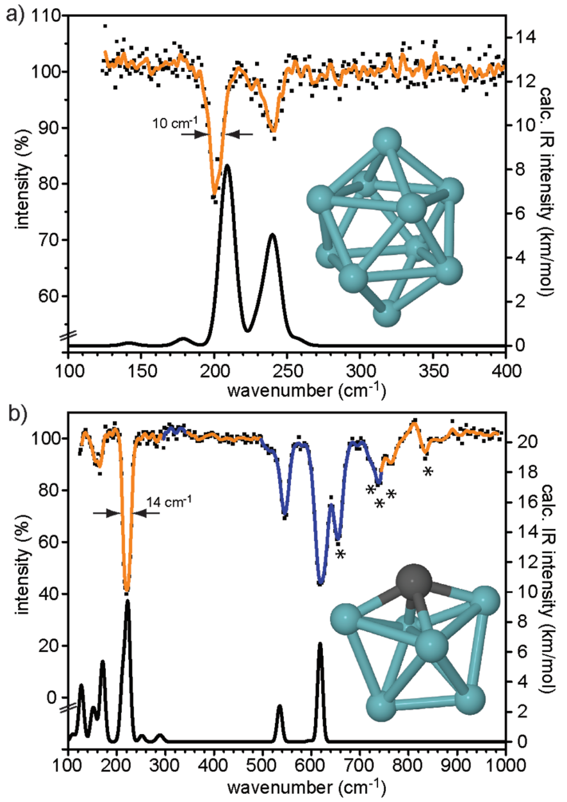

Figure 2. Comparison of the IR-REMPED spectra (left axis) of Nb_{10}^- (a) and Nb_6C^- (b) with the calculated linear IR absorption spectra (black lines, right axis) of their ground state structures. The experimental data (shown as dots) have been folded with a five point running average (solid red and blue lines). The asterisks indicate combination bands. For Nb_6C^- several different FELICE settings have been used to record the spectra, indicated by the different coloring. For Nb_{10}^- the IR fluence was up to 10 J/cm^2, while for Nb_6C^- it was up to a factor of 2 more. The bandwidth was 0.1−0.3% (full width at half-maximum) of the central frequency. The magnitudes of the depletion signals observed for different settings cannot be directly compared, due to differences in the overlap of the laser beam with the molecular beam.

well-resolved bands are observed with widths as low as 10 cm^{-1}. These widths are not limited by the bandwidth of the IR radiation, but rather by the multiple photon excitation process.[24] For Nb_{10}^-, a maximum depletion of only 20% is observed for the band around 200 cm^{-1}, whereas a maximum intensity drop of the Nb_6C^- signal of about 60% is seen.

To determine the ground state structures of Nb_{10}^- and Nb_6C^-, we compare the experimental spectra with the results of density functional theory (DFT) calculations using TURBOMOLE V6.2[30] (for details, see Supporting Information). A good agreement between the experimental depletion spectra and the calculated linear IR absorption spectra (see Figure 2) is obtained. This indicates that the absorption of the initial photon is rate limiting, and that shifts due to (cross-) anharmonicities are small as compared to the bandwidth of the IR laser.[31]

The Nb_{10} cluster has already been studied extensively by theory for all charge states and a bicapped square antiprism (BCSA) has been predicted as the ground state structure.[20−22] The calculated linear absorption spectrum for the anionic BCSA structure with D_4 symmetry in the $^2A_1$ electronic state agrees well with the measured IR-REMPED spectrum. This good agreement reinforces a previous hypothesis based on the sharp transitions observed in photoelectron spectra for the Nb_{10}^- cluster, typically indicative for electronic shell closing. The PES data,[18,19] which have not previously been compared to theory, shows a favorable agreement with the calculated electronic density of states for the BCSA structure (see Supporting Information). The calculated vertical detachment energy (VDE) is 1.49 eV and compares well with the experimental value of 1.46 eV.[18]

Little is known about Nb_6C. To the best of our knowledge, only the neutral cluster has been studied with photoionization efficiency spectroscopy,[32] and no structural assignment has been made. In order to locate low energy structures of Nb_6C^-, a basin-hopping algorithm was applied (described in the Supporting Information). A distorted pentagonal bipyramid (DPBP) in a ^2A state is predicted as the global minimum structure. The atoms in the five-membered ring are not in a plane. The structure has C_1 symmetry, but the distortion from C_2 is very small. The structure can be formed by adding a carbon atom to the structure of neutral Nb_6.[17] The carbon atom coordinates to four Nb atoms and appears to be incorporated in the cluster structure. The calculated VDE of this cluster is 0.98 eV.

Below 650 cm^{-1}, all features in the measured IR-REMPED spectrum of Nb_6C^- are reproduced by the calculated harmonic IR spectrum of the putative global minimum structure. The three highest energy bands between 530 and 620 cm^{-1} correspond to Nb−C stretch vibrations of the 4-fold bound carbon atom: ν_{14}, ν_{15} in the plane of the five-membered ring, and ν_{13} out of this plane. However, between 650 and 800 cm^{-1}, additional bands are observed in the experimental spectrum. Metal−carbon vibrations at such high frequencies are uncommon, which makes it unlikely that these bands are due to another isomer. Instead, we assign these bands as combination bands (see Supporting Information). Because of the C_1 symmetry of the structure, any combination band would be IR allowed. All combination modes are red-shifted with respect to the sum of the vibrational fundamentals by about 2−15 cm^{-1}. The feature at 655 cm^{-1} is particularly intense. Presumably, this $\nu_{13} + \nu_2$ combination borrows intensity from the mode at 621 cm^{-1} by a Fermi resonance. For this particular band, the presence of a second isomer could be an alternative explanation. However, the only structural isomer found with a single intense band at such a frequency, the third lowest one, lies 0.68 eV above the ground state, and the calculated band position is 24 cm^{-1} too low (see Supporting Information).

The number of photons necessary to detach the electron from the cluster can be estimated from the VDEs. For Nb_6C^-, the lowest frequency mode observed experimentally is close to the limit of the tuning range of FELICE at 124 cm^{-1}, which corresponds to a photon energy of only 15 meV. This means, more than 60 photons have to be absorbed to reach the detachment energy when starting from a cold cluster. A simple thermionic emission model following ref 33 gives a similar number of photons that need to be absorbed at 124 cm^{-1} to reach a rate constant of 2×10^4 s^{-1} for electron ejection, which corresponds to the lower limit to achieve detachment within the time window of the experiment. For the low frequency mode of Nb_{10}^-, the same number of photons is estimated. Although a multiple photon process was used to detect the absorption, the calculated linear IR intensities give, in these cases, a good indication for the expected relative intensities of the experimental depletion bands. The differences in the observed depletions between Nb_6C^- and Nb_{10}^- arise at least in part from varied experimental conditions, but may also reflect the 0.5 eV difference in the electron binding energies. The features observed for both systems have calculated IR intensities of 2−8 km mol^{-1}, which is comparable to other neutral and cationic metal clusters previously studied with rare-gas tagging.[16,17]

The results presented in this paper show that electron detachment by multiple photon excitation is possible even for the weak IR bands of transition metal clusters, and it opens up a new way to investigate metal cluster anions. IR-REMPED spectroscopy is expected to be applicable to a wide range of anionic metal clusters, as their electron affinity will generally be lower than the bond dissociation energy. Thus, IR spectroscopic methods are now available to determine the structure of isolated gas-phase metal clusters in their cationic, neutral, and anionic states.

ASSOCIATED CONTENT

Supporting Information. Details on the theoretical method, comparison to PES spectroscopy for Nb_{10}^-, and calculated data of higher energy isomers of Nb_6C^- as well as an assignment of the combination modes. This material is available free of charge via the Internet at http://pubs.acs.org.

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