Experimental Vibrational Spectra of Gas Phase Tantalum Cluster Cations

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We present gas-phase infrared spectra of tantalum cluster cations containing 6–20 atoms. Infrared multiple photon dissociation (IR-MPD) of their complexes with argon atoms is used to obtain vibrational spectra in the region between 90 cm^{-1} and 305 cm^{-1}. Many spectra have features in common with the vibrational spectra of the lighter homologues, vanadium and niobium, pointing to a common cluster growth mechanism.

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I. INTRODUCTION

The knowledge of the electronic and geometric structure of clusters is vital for the understanding of their physical and chemical properties. While photoelectron spectroscopy provides direct information on the electronic structure of clusters[1] the determination of the clusters' geometric structure is experimentally much more difficult. Investigations of the reactivity of metal clusters with small molecules, in particular their saturation behavior, have been used to draw conclusions about the clusters' structure.[2] Information on the shape of cluster ions can be obtained from ion mobility measurements[3–5] and, recently, electron diffraction of trapped charged clusters has shown to be promising for revealing their structure.[6–8] Information on the binding geometry of a given cluster is also contained in its vibrational spectrum, since the force constants are directly dependent on the structural arrangement of the atoms. In some cases, vibrational structure has been found in electronic excitation spectra.[9–13] Until recently, direct vibrational spectroscopy, however, could only be performed on clusters that were size-selectively deposited in rare-gas matrices.[14]

We have shown that infrared multiple photon dissociation (IR-MPD) of complexes of metal clusters with rare-gas atoms is a suitable experimental technique to obtain vibrational spectra for cationic,[15] as well as neutral clusters, in one case even isomer-selective.[16] These investigations have so far been limited to V_n^+ $(n = 3 - 23)$[15,17], $Nb_n^{0/+}$ $(n = 5 - 9)$[16,18,19] as well as to Ag_3 and Ag_4.[20]

Here we present the vibrational spectra of cationic tantalum clusters Ta_n^+, containing 6 to 20 atoms, and round off our investigations on clusters of the metals from group 5 of the periodic system, that in the bulk all have the same body centered cubic (bcc) structure. From this complete study one can learn about structural similarities and differences for a certain cluster size within one group.

Among the transition metals, clusters of tantalum are actually less studied. Magic numbers of tantalum clusters have been reported in time-of-flight (TOF) mass spectra,[21] even though intensities of transition-metal clusters in mass spectra normally show little size dependence. The reactivity of neutral Ta clusters with hydrocarbons and N_2 has been studied.[22–24] The ionization potentials of neutral Ta clusters are known from photoionization studies.[25] Raman spectra have been measured for Ta_{2-4} in an argon matrix. For the dimer a stretching frequency of $\omega_e = 300.2$ cm^{-1} has been measured.[26] Frequencies of 251.2 cm^{-1} and 501.9 cm^{-1} for Ta_3 are assigned to the symmetric stretch and its first overtone, in agreement with a supposed symmetric triangular structure.[27] Neutral Ta_4 shows three Raman resonances; a band at 270.2 cm^{-1} is assigned to the totally symmetric a_1 vibration, 185.1 cm^{-1} to a triply degenerate t vibration, and 130.6 cm^{-1} to a doubly degenerate e vibration of a tetrahedral Ta_4 cluster.[28] In bulk tantalum, there are two optically active phonon modes at ∼95 cm^{-1} and ∼145 cm^{-1}.[29,30] Recently, small Ta_n clusters have gained attention for their ferroelectrical properties[31] and for the spin-uncoupling from the cluster for small clusters with an odd number of atoms.[32] Both properties are thought to be connected to the clusters' structures. Theoretical investigations include high-level density functional theory (DFT) calculations for Ta_{2-3},[33] as well as pseudopotential DFT for Ta_{2-23}[34] and molecular dynamics simulations for large Ta_n clusters.[35]

II. EXPERIMENTAL SECTION

The experiments are carried out in a molecular-beam setup that is coupled to a beam line of the Free Electron Laser for Infrared eXperiments (FELIX) at the FOM-Institute for Plasma Physics in Nieuwegein, The Netherlands.[36] The molecular-beam machine has been presented previously[18,37,38] and only a brief description is given here. A scheme of the experiment is shown in Fig. 1. Metal clusters are produced by pulsed laser ablation of a tantalum rod using the 2nd harmonic output of a Nd:YAG laser and by subsequent condensation of the plasma in a mixture of 0.15 % Ar in He. Neutral, anionic, and cationic clusters are produced in this process and pass through a copper channel, which is temperature controlled at -95 °C by a flow of nitrogen. Only cationic clusters are investigated in this study. These form metal argon complexes efficiently at this temperature. The molecular beam expands into vacuum and

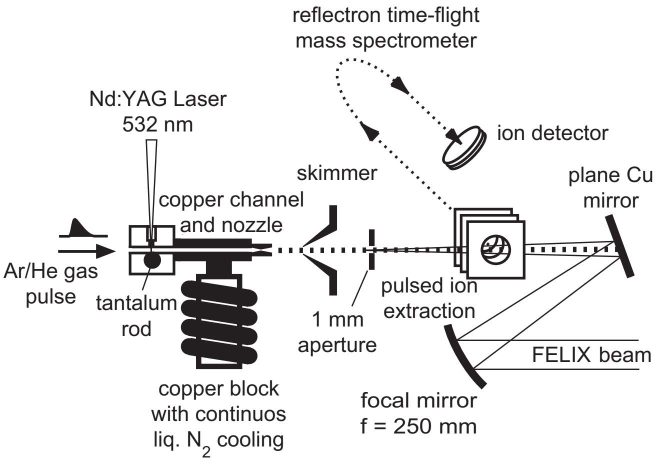

FIG. 1: Scheme of the experimental set-up used for IR multiple photon dissociation of metal-cluster rare-gas complexes.

passes through a skimmer and an aperture before entering the extraction region of a reflectron time-of-flight mass spectrometer. A counter-propagating pulsed far-IR laser beam delivered by FELIX is overlapped with the aperture to ensure that all species in the beam that are detected in the mass spectrometer have been exposed to the IR radiation.

The laser pulse consists of a 1 GHz train of ps-duration micropulses. The duration of such a macropulse is several μs while its energy ranges typically between 10 and 20 mJ, depending on the wavelength. When the IR radiation is resonant with an IR-allowed transition of the cluster complex, sequential absorption of single photons can take place.[39] The resulting heating of the cluster may induce evaporation of the argon atoms, which leads to depletion of the complexes in the beam. In order to correct for intensity fluctuations of the cluster source, the experiments are performed in a toggle mode with the cluster beam source running at 10 Hz and FELIX at 5 Hz. Using two different channels of a digital storage oscilloscope, mass spectra are recorded and averaged alternatingly with and without FELIX, and transferred to a computer. IR depletion spectra are constructed by recording the ion intensities of the metal argon complexes as a function of the FELIX frequency; from these, the far-infrared absorption spectra are obtained as described before.[18] As the detection is mass selective, the simultaneous measurement of far-IR spectra for different cluster sizes is possible.

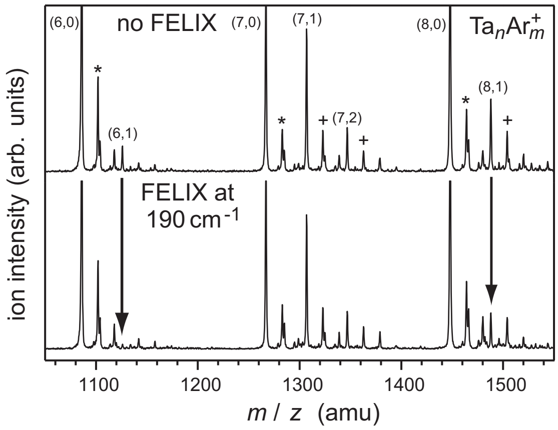

FIG. 2: Parts of the mass spectra of tantalum clusters and their argon adducts. The arrows in the lower spectrum show the depleted signals for $\mathrm{Ta_6Ar^+}$ and $\mathrm{Ta_8Ar^+}$, which have intense resonances around 190 cm^{-1}. The asterisks and the crosses mark oxide and water impurities $\mathrm{Ta}_n\mathrm{O}^+$ and $\mathrm{Ta}_n(\mathrm{H_2O})^+$ (*) and their argon complexes (+). The intensities of the bare Ta_n^+ peaks are slightly off-scale.

III. RESULTS AND DISCUSSION

Figure 2 shows parts of mass spectra of tantalum cluster cations between 1050 and 1550 amu with (lower trace) and without (upper trace) interaction with FELIX radiation. The strongest peaks in the mass spectra are due to the bare Ta_n^+ clusters. In addition, peaks resulting from $\mathrm{Ta}_n\mathrm{Ar}_m^+$ complexes (indicated as (n, m)) are observed as well. Tantalum clusters are highly reactive towards oxygen and water impurities. Although considerable attention is paid to maintain a clean gas manifold, oxide and water impurities, as well as their argon complexes cannot be avoided and are marked in the spectrum (*, +). The mass resolution of our mass spectrometer ($m/\Delta m$ = $\sim$1500) allows to unambiguously distinguish between the bare cluster-argon complexes and any impurities in the size range discussed in this work. As can be seen from Fig. 2, at a FELIX wavelength of $\sim$53.4 μm ($\sim$190 cm^{-1}), the clusters $\mathrm{Ta_6Ar^+}$ and $\mathrm{Ta_8Ar^+}$ absorb IR photons and are depleted, while the intensity of $\mathrm{Ta_7Ar^+}$ is unaffected.

Figure 3 shows the IR-MPD spectra of the argon complexes of tantalum cluster cations containing six to twenty metal atoms. In all cases, the IR-MPD spectra are measured using the cluster complexes containing a single argon atom, except for Ta_{11}^+ and Ta_{13}^+, where the complexes with two argon atoms are used (vide infra). The frequency range from 95 cm^{-1} to 305 cm^{-1} covers the least energetic bulk phonon mode (95 cm^{-1})[29,30] as well as the dimer vibrational frequency of 300.2 cm^{-1}.[26] The highest frequency mode is found at 285 cm^{-1} for Ta_{13}^+, a factor of two higher in energy than the highest frequency bulk mode of $\sim$145 cm^{-1}.[29,30] Obviously, every cluster is characterized by a unique vibrational pattern, i.e., the spectra provide a true structural fingerprint of each cluster size. The quality of the spectra is the best yet obtained by us for far-infrared gas-phase spectra of bare metal clusters. Many peaks have a full width at half maximum of less than 3 cm^{-1}. This is very close to the bandwidth of FELIX, which is about 2–3 cm^{-1}, nearly constant over the whole tuning range. Note that for bet-

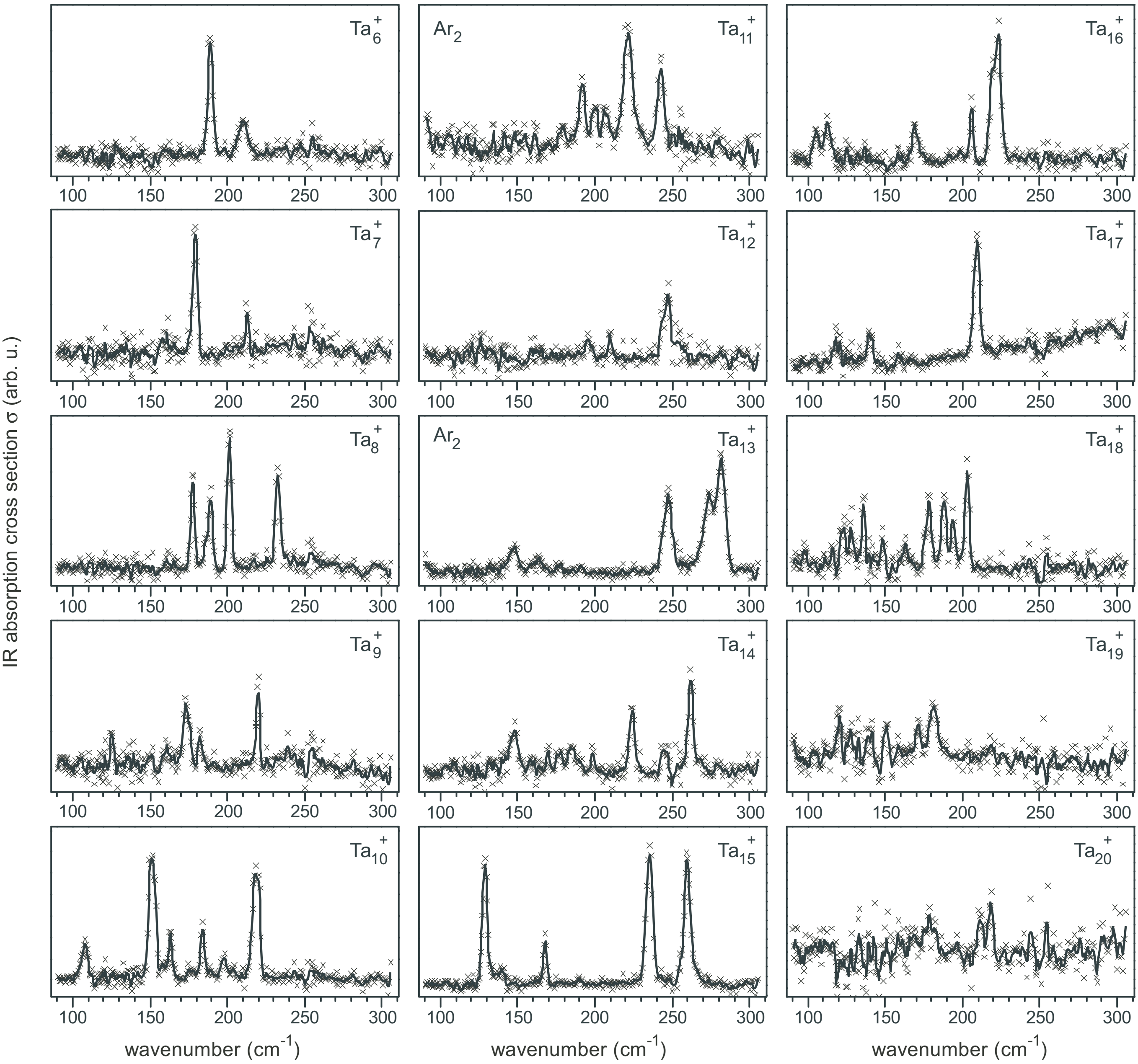

FIG. 3: Far-infrared multiple photon dissociation spectra of $\mathrm{Ta}_n\mathrm{Ar}^+$ ($n = 6 - 20$). The gray crosses represent the raw data while the black line interconnects the adjacent three point average of the raw data points. In case of Ta_{11}^+ and Ta_{13}^+ the spectra are obtained upon IR-MPD of their complexes with two argon atoms.

ter visibility of the peaks the IR absorption cross sections σ of the spectra of different cluster sizes are plotted on different scales. Usually, the laser power of FELIX is tuned in such a way that the most intense absorptions in the frequency range measured, lead to a nearly complete depletion of the ion signal of the metal rare-gas complex; care is taken to avoid saturation of the absorption peaks. The experimental cross section σ for IR-MPD of the Ar complex does not correspond directly to the transition probability of a linear absorption process and can thus not be compared easily for different cluster sizes.[39] It is difficult to specify exactly the effect of the rare-gas atom on the structure of the bare metal cluster.[18] The bond dissociation energy of argon on transition-metal clusters is estimated to be only around a tenth of an electron volt. The IR-MPD spectra of tantalum cluster complexes with one or two argon atoms have been checked for any changes that would point to a changing structure upon increasing argon coverage. No fundamental differences have been found (vide infra). For vanadium oxide clusters, it has been observed that the ordering of low lying isomers can be changed upon absorption of an argon ligand.[40] Similar findings have not been reported for bare metal clusters and our previous studies suggest that, in most cases, the IR-MPD spectrum of a given cluster complex resembles the linear IR absorption spectrum of the lowest energy structure of the bare metal cluster.

In our experiment there is no mass selection of the complexes prior to fragmentation and only the product distribution is analyzed. Therefore, in case of resonant IR absorption, the ion intensity of a certain metal argon complex in the mass spectrum contains two opposing contributions. First, there is a decrease in intensity due to the evaporation of the argon atom from the complex upon heating of the cluster. However, there is also an increase in intensity due to fragmentation of complexes containing more rare-gas atoms, complicating the interpretation of the observed depletion spectra. These complications can be avoided if, in the excitation of a complex with multiple rare-gas atoms, sufficient energy is provided to evaporate off all rare-gas atoms. In particular at the low frequency end of the spectrum this is often difficult to achieve and one thus has to be aware of possible spectral distortions. For the tantalum clusters, the only spectra in which a deviation has been noted upon addition of a second argon atom, are the ones of Ta_{11}^+ and Ta_{13}^+. For both of these, one additional small peak becomes visible for the complexes with two argon atoms, which is not present in the monoligated complexes.

For many sizes the spectra of cationic clusters of tantalum Ta_n^+ are very similar to the ones of its lighter homologues niobium[19] and especially vanadium.[15] This holds true for clusters with $n = 6, 7, 13, 15$, and 17 atoms. The cluster growth seems to follow a similar mechanism for all elements of group 5. Thus a distorted tetragonal bipyramid and a distorted pentagonal bipyramid seem to be the most probable structures for the two smallest investigated structures. Theory also finds such geometries for neutral tantalum clusters.[34] Ta_{13}^+ is interesting as a 13-atom cluster is the first magic size according to the geometric shell model and can form highly symmetric icosahedral or cuboctahedral structures. In fact, it has been reported to also be a magic peak in the mass spectra.[21] Recently, capped cubic structures have been proposed for 13-atom clusters of the later transition metals.[41–43] Supposing that only one isomer is present in the molecular beam, a strictly symmetric icosahedral structure can be ruled out for Ta_{13}^+, since it would only show two infrared-active(T_{1u}) bands.[44] A cuboctahedral structure would show three infrared (F_{1u}) bands and is thus also impossible. Of course, distorted variants of either structure are well possible. The similarity of the spectra of Ta_{13}^+ and V_{13}^+ is striking.[15] In both cases these sizes show the most energetic band of all clusters investigated. In a 13-atom cluster twelve atoms can fully surround a central atom. For V_{13}^+ it has been discussed before that the vibration of the central atom against the surrounding cage can be responsible for such a high energy mode;[17] with increasing cluster size the cage around the central atom becomes larger and the vibration decreases in energy due to increasing bond lengths. Theory predicts a distorted icosahedron for V_{13}^+, but the overall agreement with experiment is rather poor.[17] A DFT study with a global minimum search for neutral tantalum clusters predicts an unusual five-capped hexagonal bipyramid.[34]

Ta_{15}^+ is the smallest cluster that could adopt a structure similar to the bulk bcc. In fact, theory predicts this to be the most stable structure for neutral Ta_{15}.[34] A perfect bcc fragment of O_h symmetry has four IR active F_{1u} vibrations, which would be in line with the four intense peaks observed in the experimental spectrum. Again the spectrum is similar to that of the corresponding vanadium cluster, for which a structure like a bcc fragment is proposed.[17] Ta_{17}^+ is the largest cluster for which a relatively simple spectrum is obtained. A Frank-Kasper Z 16 polyhedron[45] could give rise to such a simple spectrum. A similar structure was recently proposed for doped gold clusters, i.e., a filled cage structure derived from taking away all apex atoms of a 20-atom tetrahedron.[46] Interestingly, Ta_{17}^+ is the only cluster that shows a rising slope towards higher frequencies, which is a truly unique phenomenon, since all spectra are recorded together. Neither for vanadium nor niobium clusters such a behavior has been observed before. A very low lying electronically excited state could be an explanation for this broad, unstructured absorption.

The spectra for Ta_n^+ clusters with n=8–12,14,16 and >17 are more complicated, showing all a variety of peaks. Also the vibrational patterns for vanadium and niobium clusters become more complex in these size ranges and a comparison of the spectra becomes speculative. Theory is indispensable for these clusters. For neutral Ta_{12} it has been suggested that two isomers are formed in a molecular beam.[24,25] That again would be a hint to the similarity of the structures of tantalum clusters with vanadium and niobium clusters. For both V_{12}^+ and $\mathrm{Nb}_{12}^{+/0}$, experiment and theory have found evidence for the presence of different isomers.[17,47,48] However, in case of Ta_{12}^+ it is impossible to either proof or disproof the existence of isomeric structures in the molecular beam, as the vibrational spectrum shows only few and very weak peaks.

The spectra of clusters containing more than 17 atoms become even more complicated. Most bigger clusters are less likely to have highly symmetric structures and the number of modes increases with increasing number of atoms. Furthermore it is possible that bigger clusters bear structural isomers. Also the decreasing signal to noise ratio makes an unambiguous assignment of the peaks and their positions difficult. However, it is clearly observed that the spectra of Ta_{18}^+, Ta_{19}^+ and Ta_{20}^+ are still fundamentally different and no common features can be found.

IV. CONCLUSION

We have presented far-infrared spectra for cationic tantalum clusters containing six to twenty atoms. The spectra are well resolved and true fingerprints of the clusters' geometrical structure. The stable elements of group 5 of the periodic table seem to have a common cluster growth mechanism. For the exact determination of the clusters' structures theoretical calculations are desirable. However, calculations on transition-metal clusters are an extremely demanding task. The number of possible structural isomers quickly gets very large for clusters with several atoms. Moreover, hardly any theoretical approach is originally designed to describe the electronic properties of transition-metal clusters. With this experimental work we hope to have provided benchmark experimental spectra that will stimulate further theoretical research on gas-phase transition-metal clusters.

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