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Infrared multiple photon dissociation spectroscopy of transition metal oxide cluster cations

Comparison of group Vb (V, Nb, Ta) metal oxide clusters

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Abstract. Infrared spectra in the range of 530–1400 cm^{-1} are presented for tantalum oxide cluster cations $\mathrm{Ta}_x\mathrm{O}_y^+$ ($x = 3$, 4 and 6). These spectra are obtained *via* multiple photon dissociation (MPD) spectroscopy of free cluster cations moving in a molecular beam. The IR spectra for $\mathrm{Ta}_x\mathrm{O}_y^+$ are compared to spectra of $\mathrm{Nb}_x\mathrm{O}_y^+$ as well as to the experimental data available for vanadium oxide cluster cations from IR-MPD spectroscopy. For $\mathrm{Ta}_x\mathrm{O}_y^+$ and $\mathrm{Nb}_x\mathrm{O}_y^+$ the IR spectra exhibit very strong similarities (including the band positions), whereas absorption bands in $\mathrm{V}_x\mathrm{O}_y^+$ are relatively blue-shifted by about 20–40 cm^{-1}.

PACS. 36.40.-c Atomic and molecular clusters – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 82.80.Gk Analytical methods involving vibrational spectroscopy

1 Introduction

Transition metal oxides are important ingredients in catalysts used for selective heterogeneous oxidation of hydrocarbons [1]. For this purpose, vanadium oxides are widely used already for a long time, *e.g.* in large-scale production of maleic anhydride and phthalic anhydride. Its homologue, niobium oxide, catalyzes hydrocarbon oxidation as well and converts NO_x for exhaust gas purification. Due to its acidic properties, it is found to effectively promote in vanadium phosphorus oxide (VPO) catalysts the activation and oxidation of butane towards maleic anhydride. Also the heaviest member of the group Vb, tantalum, is known to promote oxide catalysts, but does not yet possess an important role in technical catalysis [2,3].

For most catalytic oxidation reactions, the involved active sites and the elementary reaction steps are still under discussion. Gas phase clusters are suited as model systems for these studies, since they can be seen as isolated reaction sites. Experimental studies of reactions of the group Vb transition metal oxides with organic molecules have already been performed by several groups [4–9], but information about their geometric and electronic structures is scarcely available and has been obtained only by indirect methods, *e.g.* collision induced dissociation [4,5], or by theory [13–15].

In general, experimental vibrational spectra can provide a basis to uncover the geometric structure of clusters. Recently, vibrational spectra of metal oxide clusters in the gas phase have been obtained *via* IR resonance enhanced multiple photon ionization (IR-REMPI) spectroscopy [10,11] and *via* fragmentation of cluster cations in an ion trap [12]. Since IR-REMPI works only for clusters that have an ionization potential (IP) lower than their fragmentation energy, the application of this method is restricted. In particular, the spectra of transition metal oxide clusters containing the metal atoms in high oxidation states are inaccessible because of their rather high IP's.

Here we present infrared spectra for tantalum oxide cluster cations that are obtained by multiple photon dissociation spectroscopy. The frequency depended intensity growth of fragment cations reveals the dissociation behavior of parent clusters. Structural consequences for the tantalum oxide clusters are discussed and this is compared to the situation for niobium oxide clusters. A detailed discussion of the IR spectra of niobium oxide cluster cations and their structures will be reported elsewhere [16].

2 Experimental

IR multiple photon dissociation spectroscopy is performed in a two-stage molecular beam setup that is connected to the beamline of the Free Electron Laser for Infrared eXperiments (FELIX) [17]. The oxide clusters are produced

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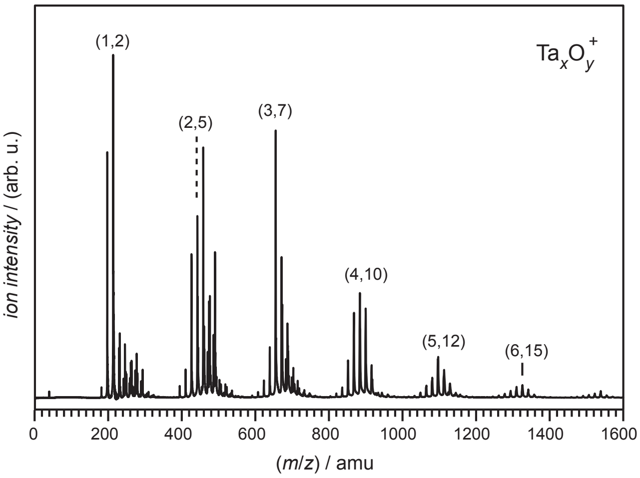

Fig. 1. Mass spectrum of tantalum oxide cluster cations. Dominant oxide cluster peaks are marked with their corresponding stoichiometry (x, y). The distribution shows additional signals that can be assigned to hydrates and carbon containing clusters.

in a pulsed laser vaporization source using a carrier gas containing 0.25% O_2 in He. The focused highly-intense IR laser beam counterpropagates with the beam of cationic clusters that is emitted directly from the source. If the IR laser is in resonance with a vibrational mode of a cluster, the clusters may absorb one or more IR photons. For those clusters, that fragment after excitation, the IR spectra can be obtained by recording the cluster intensity changes as a function of the IR wavelength. The mass distribution is analyzed using a perpendicularly extracting reflectron time-of-flight mass spectrometer (R.M. Jordan Company, Inc.).

The dissociation energies of transition metal oxide clusters are on the order of at least 1–2 eV implying that absorption of at least 8–16 photons at 10 μm is required. Therefore, to induce IR-MPD of oxide clusters and to obtain the IR spectra a tunable and intense IR source is needed, which is provided by FELIX. The IR light is emitted in 0.5–5 ps long micropulses spaced by 1 ns forming a macropulse of 5 μs duration. The total energy in a macropulse is typically 50 mJ, but due to the experimental geometry only about 20% of the focused IR beam passes through a 0.8 mm aperture in the molecular beam reducing the effective laser intensity.

3 Results and discussion

The distribution of tantalum oxide cluster cations that is produced directly in the source is shown in Figure 1. The source conditions are optimized for small clusters containing less than 10 tantalum atoms. Stoichiometric oxide cluster cations following the formulas $(Ta_2O_5)_n^+$ and $(Ta_2O_5)_nTaO_2^+$ are dominating the distribution and contain the tantalum atoms in a formal +5 oxidation state, which is commonly the most stable one in tantalum compounds. Additionally oxides with less and also with more oxygen content are observed. The lower limit of the composition is about $(TaO)_n^+$. Tantalum oxide clusters with an oxygen content much higher than in the stoichiometric +5 oxide have been observed earlier [6], but in our case the maximum number of additional O atoms is limited to about two atoms. Clusters that might at first sight appear to be even higher oxides are in fact hydrates or contain hydroxo groups; therefore, those clusters might be rather seen as tantalic acid than as oxide systems.

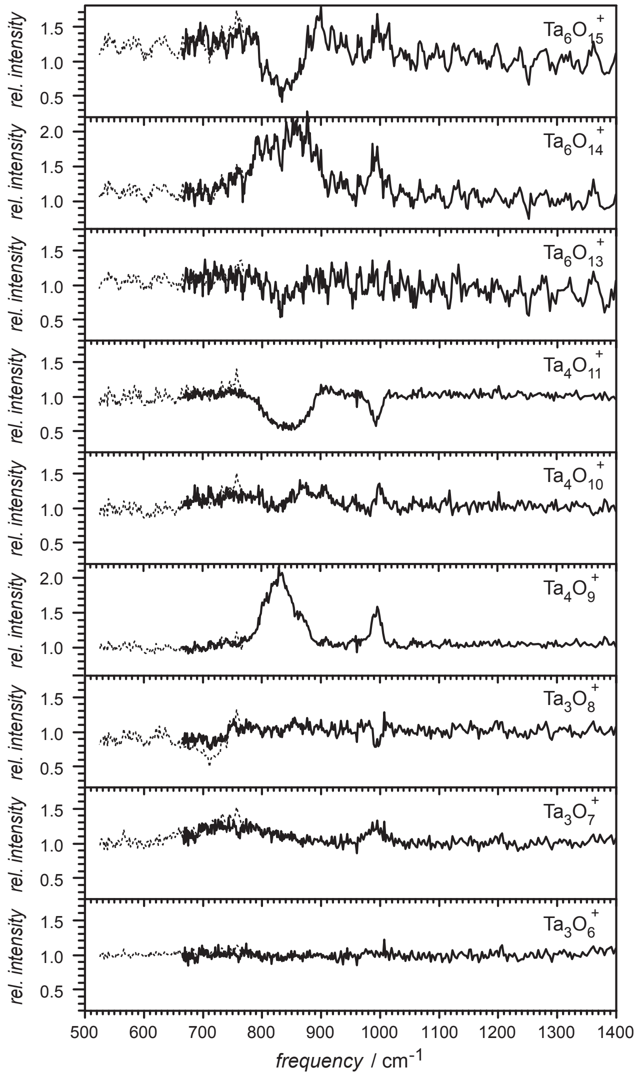

Fig. 2. Ion intensity of tantalum oxide cluster cations as function of IR frequency. The spectra are measured in two overlapping frequency scans that are plotted in different styles. Ion intensities are normalized to the signal in the 1100–1400 cm^{-1} range.

In Figure 2 the IR frequency dependence of the relative intensities of selected tantalum oxide clusters is shown. All ion intensities are normalized to the mass spectral intensities of the corresponding cluster ion in the region >1100 cm^{-1}, where no IR-induced changes are observed. Ion intensity decreases due to IR induced cluster dissociation and increases due to formation of the corresponding cluster ions by fragmentation of larger clusters.

The smallest tantalum oxide cluster cation for which infrared induced dissociation is observed is $Ta_3O_8^+$. Two absorption bands can be identified, one at about 995 cm^{-1} with a width of 15 cm^{-1} (FWHM) and a second much broader one (≈70 cm^{-1}) around 710 cm^{-1}. The next larger cluster, for which depletion is found is $Ta_4O_{11}^+$ and it also absorbs at 995 cm^{-1}. A second band is located around 845 cm^{-1} (FWHM 70 cm^{-1}). Both clusters contain additional oxygen with respect to the stoichiometric +5 oxide clusters, which could cause weaker binding. However, also the stoichiometric oxide cluster $Ta_6O_{15}^+$ ($(Ta_2O_5)_3^+$) depletes around 840 cm^{-1}, but instead of depletion at 995 cm^{-1} intensity growth is observed. This does not necessarily mean, that $Ta_6O_{15}^+$ does not absorb in this region; the depletion might be masked by the formation of this cluster ion as fragment.

The absorption band at 995 cm^{-1} can be assigned to a stretch of terminal doubly bonded oxo groups Ta=O. This assignment is supported by results of matrix isolation spectroscopy, where the stretch is found at 1014 cm^{-1} for TaO and at 993 cm^{-1} for TaO_2^+ [18]. In the later case, Ta has the same formal oxidation state as in our clusters. However, in the clusters the tantalum atoms may have a higher coordination number. The absorption frequencies in the 700–850 cm^{-1} range are typical for M–O–M stretches. In the matrix isolation spectra a 689 cm^{-1} band has been assigned to the vibration of a Ta–O–Ta bridge in a rhombic $(TaO)_2$ molecule. For Ta_3O the fundamental Ta–O–Ta stretch frequency has been found at 710±15 cm^{-1} *via* vibrationally resolved photoelectron spectroscopy [19].

Insights into the dissociation channels of cluster ions can be obtained *via* analysis of the frequency dependence of the ion intensity increase due to fragmentation. For example, the ion intensity of $Ta_3O_7^+$ increases at frequencies where $Ta_3O_8^+$ is depleted. Since larger clusters than $Ta_3O_8^+$ do not absorb around 700 cm^{-1} this indicates that loss of an O atom is a dominant fragmentation channel for this cluster. The loss of atomic oxygen has also been observed for the niobium oxide cluster with the same composition, although collisions with krypton did not lead to fragmentation for $Ta_3O_8^+$ in contrary to the niobium system [4,6]. The main dissociation channel of $Ta_4O_{11}^+$ can be identified as loss of O_2, since the intensity growth of $Ta_4O_9^+$ mirrors the depletion of $Ta_4O_{11}^+$ and no other fragments can be found with the same behavior. For $Ta_6O_{15}^+$ the fragmentation channel is possibly loss of atomic O and formation of $Ta_6O_{14}^+$.

Although the fragmentation patterns, *e.g.* for $Ta_4O_{11}^+$, indicate the presence of non-bridging dioxo species, no direct spectroscopic evidence for the presence of O–O containing species has been found. For instance, superoxo groups (formally O_2^-) are known to absorb around 1150 cm^{-1} and transition metal peroxides between 800–900 cm^{-1} [21]. It has to be concluded, therefore, that their absorption cross sections are either weak compared to the metal-oxygen stretches or that intramolecular vibrational redistribution is ineffective for the corresponding vibrational modes, which would restrict resonant multiple photon absorption.

Table 1. Experimentally observed absorption frequencies (in cm^{-1}) for oxide clusters of V, Nb, Ta in the M=O and M–O–M stretch regions. Only the center-frequencies of the experimental bands are given. It is expected that the measured bands are envelopes of several transitions. The data for V are taken from [12,20] and for Nb from [16] except all data for M_3O, which are from [19].

oxide cluster	M=O			M–O–M		
	V	Nb	Ta	V	Nb	Ta
$M_3O_8^+$	1036	995	995	740	710	710
$M_4O_{10}^+$	1032	990	-	842	818	825
$M_4O_{11}^+$	-	993	995	-	835	845
$M_6O_{15}^+$	-	993	-	-	830	838
M_3O	-	-	-	750 ±20	710 ±15	710 ±15

Table 1 summarizes the IR spectral features for oxide cluster cations of V, Nb, and Ta. The IR-MPD spectra of vanadium oxide clusters have been measured in an ion trap by Asmis *et al.* [12,20]. The smallest oxide clusters of Nb and Ta, $M_3O_8^+$ have absorption bands at the same position and also the overall shape of the dissociation spectra is comparable. The spectrum of $V_3O_8^+$ contains additional peaks of lower intensity that have been ignored in Table 1. A complete assignment of this spectrum has not been done yet. One of the weaker absorptions at around 850 cm^{-1} might in principle be caused by a peroxo group, but because the signal is quite broad it seems more probable that more than one isomer is present and that the bands are due to V–O–V stretches. For larger clusters, the $Ta_xO_y^+$ bands are slightly blue-shifted up to 10 cm^{-1} relative to those of $Nb_xO_y^+$ but still the spectra appear nearly identical. The absorptions of the corresponding vanadium oxide clusters are substantially blue-shifted by about 20–40 cm^{-1}. A similar behavior is also observed for the M–O–M stretching frequencies of the M_3O clusters. The increase of the metal-oxygen stretching force constant can be explained by the convergence of the *s* and *d* orbital radii when going from V to Nb to Ta and, as a consequence thereof, the increase of $s\ d\ \sigma$ hybridization [19]. The stretching force constants of M–O–M (in M_3O) and of the MO molecules are for V, Nb, Ta in the ratio of 0.9:1:1.1 [19]. For Nb and Ta this is nearly the ratio of the reduced masses. Since the IR spectra of Nb and Ta oxide clusters show the same metal-oxygen stretch absorption frequencies, this indicates identical cluster geometries.

It therefore seems reasonable to apply the structural information that we have obtained *via* DFT calculations on niobium oxide clusters [16] also to the tantalum system. Figure 3 shows the optimized structure and the calculated IR spectrum for $Ta_3O_8^+$ using the starting geometry of the energetically lowest $Nb_3O_8^+$ isomer. All atom distances in the optimized geometry of $Ta_3O_8^+$ are quite similar to

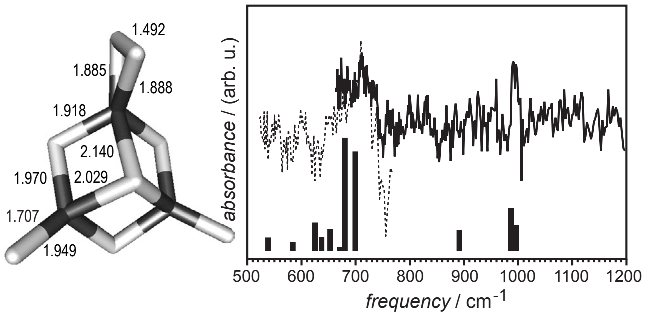

Fig. 3. Structure of $Ta_3O_8^+$ (C_s sym.) and comparison of experimental and calculated IR spectrum. The structure has been optimized with DFT (B3LYP, LACVP* basis set) using Jaguar 4.0 [22]. The wavenumber axis of the calculated IR spectrum has been linearly scaled to give overlap with the experimental Ta=O stretch frequency resulting in a scaling factor of 0.96.

those in $Nb_3O_8^+$, with some Ta–O distances being about 1 pm shorter. The O–O distance allows for classification of the dioxo unit as a peroxo ligand. Because of its low dissociation energy, the peroxo O–O bond can be easily broken, rather than that the complete dioxo ligand is removed from the cluster core. This could explain the observed fragmentation channel of atomic oxygen loss for $Ta_3O_8^+$. The calculated IR spectrum agrees with the experiment, except for the O–O stretch absorption at 892 cm^{-1} that has not been observed. By studying several isomers of $Nb_3O_8^+$ it has been found that absorptions around 700 cm^{-1} are typical for concerted M–O–M stretches, wherein also a threefold coordinated O-atom is involved. The M–O–M stretch absorptions are blue-shifted by about 50–100 cm^{-1} if the cluster contains only twofold coordinated bridging oxygen. Such a blue-shifted band is observed for $Ta_4O_{11}^+$, and, by comparison with the proposed structures of similar clusters such as $Nb_4O_{11}^+$ [16] or $V_4O_{10}^+$ [15], it can be assumed that this cluster consists of a tetrahedral core similar to the phosphorus oxide molecule (P_4O_{10}) with an additional O atom bound to it. Since the observed fragmentation channel is O_2 loss, it is most likely that $Ta_4O_{11}^+$ contains a relatively weakly bound dioxo group in a terminal (non-bridging) position.

4 Summary and conclusion

IR absorption spectra of transition metal oxide clusters in the gas phase are accessible *via* IR multiple photon dissociation spectroscopy. In the IR spectra for tantalum oxide cluster cations absorption bands are identified that correspond to stretches of Ta=O (995 cm^{-1}) and of Ta–O–Ta bridges (700–850 cm^{-1}). The nearly identical IR spectra of niobium and tantalum oxide clusters point to the existence of analogous geometric structures, in agreement with the condensed phase behavior of niobium and tantalum oxide.

Clusters with additional oxygen atoms relative to the stoichiometric compositions $(Ta_2O_5)_n^+$ and $(Ta_2O_5)_nTaO_2^+$ are found to contain dioxo units. Dependent on size they differ in their fragmentation behavior, exhibiting either loss of atomic O or of O_2. This behavior can be explained with different bonding of the dioxo units. A superoxo group would be released complete, whereas the weak peroxo bond can easily dissociate. For corresponding vanadium oxide clusters the IR spectra and the fragmentation behavior is less understood, requiring further experimental and theoretical investigations.

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