Photofragmentation of mass-selected titanium oxide cluster cations

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Photofragmentation of mass-selected titanium oxide cluster cations

M. Jadraque · B. Sierra · A. Sfounis · M. Velegrakis

Abstract In this paper we present the photofragmentation spectra of mass-selected positive titanium oxide cluster ions $Ti_xO_y^+$. The clusters are generated by the combination of laser ablation of a titanium target and the supersonic nozzle expansion of oxygen and are detected by time-of-flight mass spectrometry. Small clusters are mass-selected and photodissociated at a wavelength of 308 nm. The recorded photofragmentation spectra indicate that for all parent clusters the main fragment is TiO^+ and, in some cases, $Ti_2O_3^+$ is also observed. This is consistent with the assumption that small $Ti_xO_y^+$ clusters are built from a TiO^+ core with TiO_2 building blocks.

1 Introduction

After the recent discovery of new applications and improved properties [1, 2] of metal oxide nanoparticles there is an increased interest in forming and studying these species. Currently, there is extensive research activity in the direction of fundamental studies on gas-phase metal oxide clusters, to reveal the chemical and the physical properties of these systems, especially the issues of structure, bonding and reactivity at molecular level. In this context, a high number of studies [3–11] have been previously performed for the titanium oxide clusters Ti_xO_y and, even though these aggregates have found widespread use [12–16], many questions concerning their structures and properties as functions of the number of constituent atoms (e.g. cluster size) still remain open.

In a previous paper [17] we presented the mass spectra of the positive titanium oxide cluster ions $Ti_xO_y^+$ formed in a laser-ablation-oxygen-jet expansion source and we studied the interaction of UV photons with these aggregates. We found that the absorption of 308 nm photons strongly influences the mass distribution of $Ti_xO_y^+$ clusters leading to cluster fragmentation into smaller ones. In this contribution, we use the technique [18] of photofragmentation of mass-selected clusters to explore further the fragmentation processes and pathways of small $Ti_xO_y^+$ clusters in a more controlled manner. The results presented in this work are discussed and compared with other experimental and theoretical work.
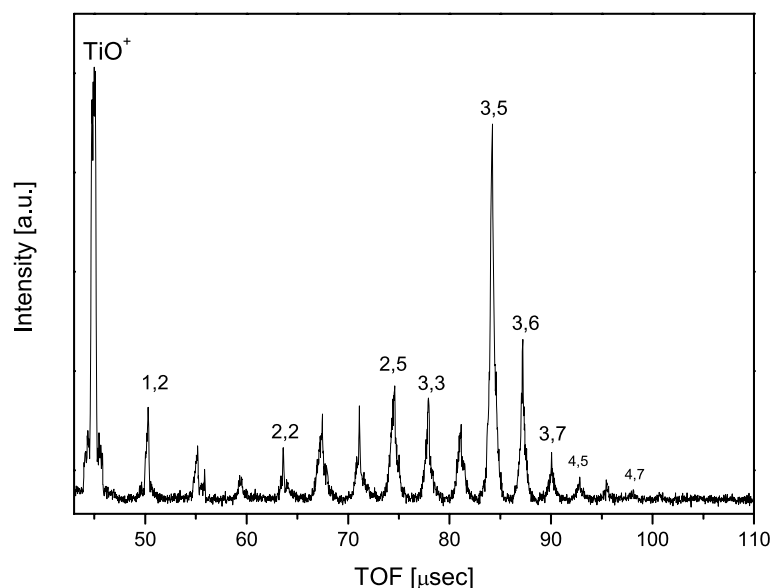
2 Experimental

The molecular beam apparatus used in these experiments has been described in detail previously [17, 19, 20]. Briefly, titanium oxide $Ti_xO_y^+$ clusters are formed by mixing the plasma plume, produced by laser ablation of a titanium metal rod with the supersonic expansion of molecular oxygen from a pulsed nozzle. The cationic complexes produced are accelerated by a pulsed double-field time-of-flight (TOF) device towards a reflectron assembly. The backwards-reflected ions are spatially focused onto a microchannel plate detector, and TOF mass spectra are recorded with a computer controlled digital storage oscilloscope. During their flight from the acceleration region to the reflectron assembly, specific cluster ions from the whole cluster size distribution are selected by a two-plates mass

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Fig. 1 TOF spectra of $Ti_xO_y^+$ clusters produced by the ablation of a Ti target with a XeCl excimer laser (308 nm, fluence of 1.4 J/cm^2) in the vicinity of the jet expansion of O_2 gas

gate. Closely behind the mass gate an unfocused laser beam from an excimer XeCl (308 nm, 15 ns) laser intersects the ion beam perpendicularly. The timing and the synchronization of the experiments are controlled by coupled delay generators. In the case of photodissociation the parent clusters and the fragments are separated by the aid of the reflectron and appear in the TOF spectrum as different peaks (the fragments first and the parent later).

3 Results and discussion

In Fig. 1 we display a typical TOF mass spectrum of $Ti_xO_y^+$ clusters obtained by the ablation of a Ti target with an excimer XeCl laser (308 nm, 15 ns pulse width, 10 Hz repetition rate) at a fluence of 1.4 J/cm^2 focused in a 0.5 mm diameter spot. The intensity peaks of $Ti_xO_y^+$ clusters in Fig. 1 are labeled as x, y ranging from 1, 1 to 4, 7. The intensity of $Ti_xO_y^+$ clusters with $x > 3$ is very low in the spectrum. As stated previously [17], the spectra are characterized mainly by the presence of the cluster ion series $(TiO)_n^+$, $(TiO_2)_n^+$, $TiO(TiO_2)_n^+$ and $TiO(TiO_2)_nO_2^+$.

To determine the composition of the $Ti_xO_y^+$ clusters we used the technique of photofragmentation of mass-selected clusters. Some of the clusters were mass-selected and photodissociated with a second 308 nm laser beam (10 mJ/cm^2). Under these conditions, the intensity for clusters larger than $Ti_3O_6^+$ is not high enough to be mass-selected for photofragmentation experiments. The data are accumulated by recording and averaging TOF spectra with and without the photofragmentation laser. The difference between these spectra results in the photofragmentation spectra shown in Fig. 2, which are due to the action of the dissociation laser. In this way, effects such as metastable fragmentation and/or

collision-induced dissociation with the background gas are excluded. Negative peaks indicate the depletion of the mass-selected parent, while positive ones correspond to charged fragments. For the laser fluence range (2–30 mJ/cm^2) employed in this experiment, the mass-selected TiO^+ and the small clusters TiO_2^+, $Ti_2O_3^+$ and $Ti_2O_4^+$ could not be significantly dissociated after the irradiation with 308 nm wavelength photons. All the other clusters investigated dissociate mainly into TiO^+ fragments and only $Ti_2O_5^+$ and $Ti_3O_4^+$ clusters dissociate also into $Ti_2O_3^+$. Obviously, the integrated intensity of the photofragmentation spectra shown in Fig. 2 should be zero, because of particle density conservation. In practice, for our arrangement this is not always the case, because of the different focusing conditions for each particular cluster and of the different flight paths of the clusters through the reflectron, which lead to particle losses etc. Furthermore, it should be mentioned that it is not clear enough if the observed photofragmentation is the result of single- or multi-photon processes. The signal of the fragments scales linearly with the laser intensity for the laser fluences range employed in this study, but also multi-photon processes are not unlikely.

These results can be compared with the observations made in our previous paper [17] on $Ti_xO_y^+$ decomposition where, in a two-laser experiment, $Ti_xO_y^+$ clusters were irradiated with an UV (308 nm) laser after their formation. The results clearly showed that $Ti_xO_y^+$ clusters with sizes x ≥ 4, y ≥ 7 absorb efficiently ultraviolet (4 eV) photons and break into smaller ones, such as $Ti_2O_3^+$, $Ti_2O_5^+$ and $Ti_3O_5^+$. In the present study, however, only $Ti_2O_3^+$ appears as another fragment besides the TiO^+ main fragment. Larger fragments such as $Ti_2O_5^+$ and $Ti_3O_5^+$ do not appear for mass-selected clusters up to size $x = 3$, $y = 6$ investigated in this work. This observation indicates that the fragments $Ti_2O_5^+$ and
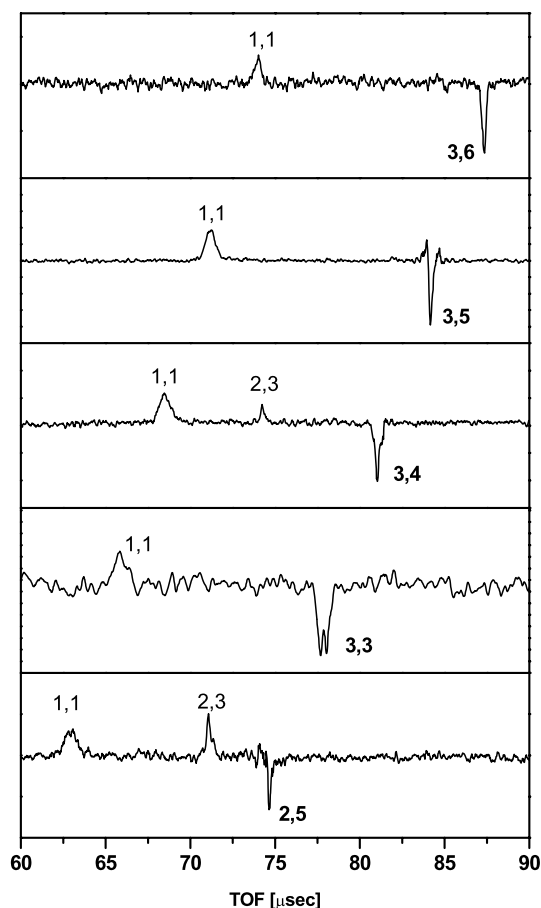
Fig. 2 The photodissociation spectra of mass-selected $Ti_xO_y^+$ clusters at 308 nm. Negative peaks correspond to the mass-selected parents, while the positive ones to the charged fragments. The labels denote the cluster size x, y

Table 1 The parent clusters, the charged photofragments and the proposed composition of some of titanium oxide clusters

Parent	Proposed composition	Charged fragments observed
$Ti_2O_5^+$	$TiO(TiO_2)O_2^+$	$TiO(TiO_2)^+$
		TiO^+
$Ti_3O_3^+$	$(TiO)_3^+$	TiO^+
$Ti_3O_4^+$	$(TiO)_2TiO_2^+$	$TiO(TiO_2)^+$
		TiO^+
$Ti_3O_5^+$	$TiO(TiO_2)_2^+$	TiO^+
$Ti_3O_6^+$	$(TiO_2)_3^+$	TiO^+

ent ion as an example, the following fragmentation channels are possible:

(a) $Ti_2O_5^+ \rightarrow Ti_2O_3^+ + O_2$
(b) $Ti_2O_5^+ \rightarrow Ti_2O_3 + O_2^+$
(c) $Ti_2O_5^+ \rightarrow TiO^+ + TiO_2 + O_2$
(d) $Ti_2O_5^+ \rightarrow TiO + TiO_2^+ + O_2$
(e) $Ti_2O_5^+ \rightarrow TiO + TiO_2 + O_2^+$

According to the above discussion for the ionization energies, several of these reactions may be excluded as unlikely. As mentioned before, O_2 exhibits the highest IP of all the species and therefore reactions (b) and (e) are not expected to occur. In a similar manner the channel (d) is less probable than the channels (a) or (c). Both (a) and (c) reaction channels lead to ionic fragments which, as neutrals, have low IP's and therefore are the most probable pathways. This is supported by our experimental results (Fig. 2).

Analogous arguments can be made for the other $Ti_xO_y^+$ clusters, although less information is available for the larger species. Generally, one can say that the $Ti_xO_y^+$ clusters are dissociated by losing mainly neutral O_2 and/or TiO_2 units, ending up as charged fragments which are characterized by the lowest ionization potential.

Similar experiments and observations have been reported for other transition metal oxide clusters by other research groups [18, 21]. Kooi and Castleman [18] have investigated the photofragmentation of mass-selected vanadium oxide cluster cations and Duncan's group [21] has measured the dissociation spectra of vanadium, niobium and tantalum oxide cluster cations $M_xO_y^+$ (M = V, Nb, Ta) with the same technique. Both groups came to the conclusion that by photodissociation the clusters eliminate O_2 units (in the case of V), atomic oxygen (for Nb and Ta) and also neutral MO_2 units, until some kind of "core" cluster is reached. These fragments can be considered as the starting unit for building larger clusters in a cluster growth process via e.g. association reactions.

All these considerations are taken into account in Table 1, which displays the studied parent $Ti_xO_y^+$ clusters, the charged photofragments obtained and the proposed cluster composition.

$Ti_3O_5^+$ observed earlier [17] are probably the end-products of the dissociation of clusters larger than $Ti_3O_6^+$.

The charged fragments observed here and in our previous [17] spectra can be explained if one assumes that in such photofragmentation processes the charge is localized at the species which exhibit the lowest ionization potential. Hence, in this type of processes, it is expected that fragments with a higher ionization potential (IP) will be lost as neutrals. For the neutral Ti_xO_y clusters Hagefeld et al. [9] calculated the ionization potentials as 4.8, 6.5, 3.8, 7.8, 3.9 and 7.7 eV for TiO, TiO_2, Ti_2O_3, Ti_2O_4, Ti_3O_5, and Ti_3O_6, respectively. O_2 has an IP of 12.07 eV, the highest one of the studied species, so it is expected to leave the clusters as a neutral molecule. These ionization energy considerations are consistent with our experimental studies, where the clusters TiO, Ti_2O_3 and Ti_3O_5 have the lowest ionization energies and they are the observed charged fragments in both our previous [17] and our present spectra.

By means of the ionization energies, different fragmentation channels can be also discussed. Taking the $Ti_2O_5^+$ par-

These experimental results support the scenario of an ionic TiO^+ core which attracts TiO_2 units as the building blocks of the clusters. This is also in agreement with the theoretical results of Qu and Kroes [8]; in the positively charged titanium oxide clusters, they find a "hole" localized on one terminal O-atom, belonging to an elongated Ti-O bond, which is surrounded by other units.

4 Conclusions

Most of the $Ti_xO_y^+$ cluster ions investigated in this work dissociate after the interaction with 308 nm photons mainly to TiO^+ ionic fragments. Other charged fragments recorded are the $Ti_2O_3^+$ clusters. The fact that only these charged fragments are observed suggests that they may possess the lowest ionization potential among all the possible fragments. This is in accordance with theoretical calculations for the neutral Ti_xO_y clusters. These results corroborate the assumption made earlier about the structure of these clusters, namely that they are formed from an ionic TiO^+ core which is the seed for building larger clusters with TiO_2 units.

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