Niobium oxide cluster ions grow to have more compact structures than vanadium oxides

Compositions and geometrical structures of niobium oxide cluster ions, $Nb_mO_n^{\pm}$ ($m \leq 12$), were studied comparing with the lighter Group 5 counterpart vanadium oxide cluster ions by ion mobility mass spectrometry (IM-MS). As a result of collision induced dissociation occurred at the inlet of the ion drift cell at increasing injection energy in IM-MS, compositions were found to depend on odd and even number of niobium atoms, which was similar to vanadium oxide cluster ions: The ions with $(NbO_2)(Nb_2O_5)_{(m-1)/2}^+$ and $(NbO_3)(Nb_2O_5)_{(m-1)/2}^-$ were identified as stable compositions for odd number of Nb atoms, and $(Nb_2O_5)_{m/2}^{\pm}$ and $(Nb_2O_6)(Nb_2O_5)_{(m-2)/2}^-$ for even number of Nb atom clusters. These compositions can be applied up to mass number of 3000, which approximately corresponds to m = 22. Furthermore, we deduced experimental collision cross sections (CCSs) of cluster ions with these stable compositions from the measurement of arrival time distributions. As a result, structure transitions were observed between m = 8-9 for cluster cations and m = 7-8 for cluster anions for experimental CCSs. On the other hand, quantum chemical calculations were conducted on several structure candidates of these compositions for m = 2-12. Theoretical CCSs of these optimized structural candidates, which were based on past studies and structures of vanadium oxide cluster ions, were also calculated.

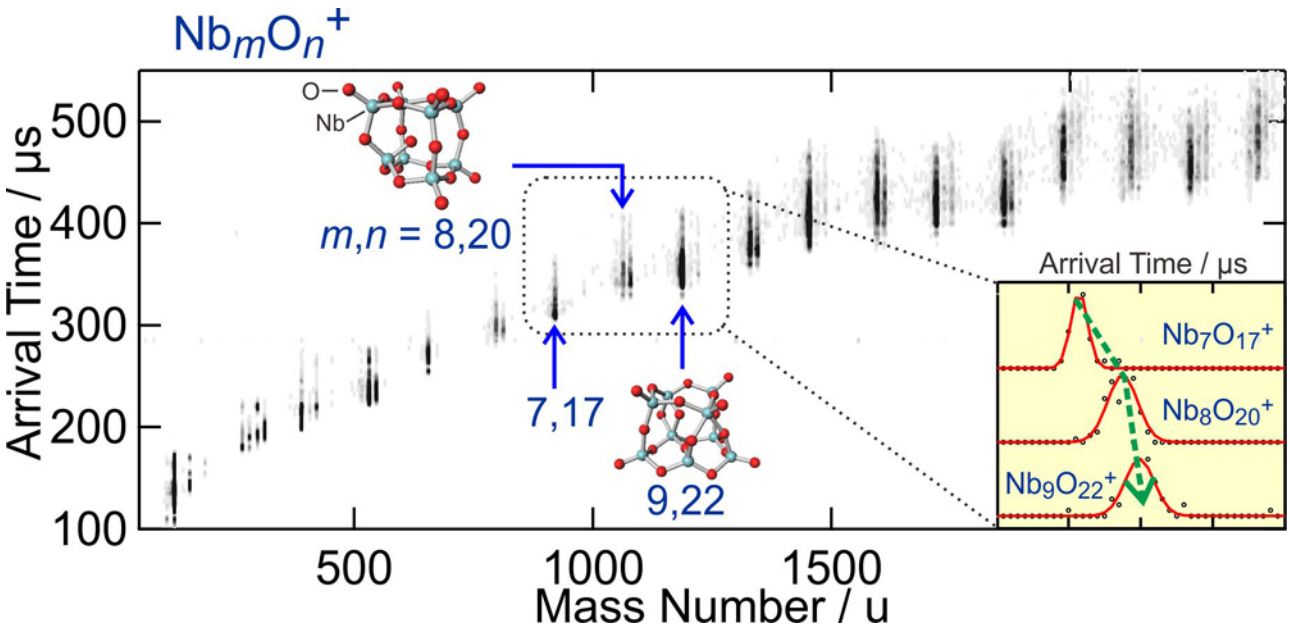

Fig. 1. 2D plot of mass number and arrival time (proportional to cross section) for NbmOn+.

As a result, for cluster cations with sizes between m = 2-8 and cluster anions with m = 2-7, structures were assigned to those similar to vanadium oxide cluster ions by comparing the

experimental CCSs to theoretical CCSs of optimized structures. In these ions, bridge or pyramid-type framework structures were assigned for odd sized clusters. The even sized cluster cations were mainly composed of prism or polyhedron framework structures. For larger cluster size with *m* = 9-12, structural transition to more compact structures was observed, and thus the structures with some niobium atoms bonded to more than 4 oxygen atoms were favored to satisfy the decrease in experimental CCSs. Similarly, a structural transition was found between *m* = 7 and 8 for cluster anions, and therefore, more compact structures were proposed for *m* = 8-12. These compact structures also contain niobium atoms with multiple coordination.

Our work suggests that niobium oxide cluster ions had similar structural growing trend as the vanadium oxide cluster ions of the same compositions with small cluster size, whereas the structures become more compact as cluster size increases. The niobium oxide cluster cations of *m* ≥ 9 and anions of *m* ≥ 8 consist of structures where some niobium atoms have at least five oxygen atoms coordination, in order to achieve the formation of compact structures, whereas all of the vanadium atoms coordinate with four oxygen atoms in this size region.

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