

Appendix B

Vanadium Substitution in Aluminum Oxide Cluster Cations

The multiple photon IR-PD spectra of $\text{Al}_8\text{O}_{12}^+$, $\text{VAl}_7\text{O}_{12}^+$, and $\text{VAl}_7\text{O}_{13}^+$ are shown in Figure B.1. Ions are produced with the dual target laser vaporization source (see Section 2.1.1). The spectrum of $\text{Al}_8\text{O}_{12}^+$ is discussed in Chapter 4. All spectra are dominated by a strong band slightly below 1000 cm^{-1} : at 997 cm^{-1} in $\text{Al}_8\text{O}_{12}^+$, at 991 cm^{-1} in $\text{VAl}_7\text{O}_{12}^+$, and at 990 in $\text{VAl}_7\text{O}_{13}^+$. The absorption band at the highest energy is found in $\text{Al}_8\text{O}_{12}^+$ at 1024 cm^{-1} , while in the other two clusters it is present only as a shoulder with less intensity, at 1037 and 1020 cm^{-1} , for $\text{VAl}_7\text{O}_{12}^+$, and $\text{VAl}_7\text{O}_{13}^+$, respectively. The spectrum of $\text{VAl}_7\text{O}_{12}^+$ shows three bands between 850 and 950 cm^{-1} , with maxima at 937 , 913 , and 885 cm^{-1} , and two broad features around 800 and 630 cm^{-1} . The spectrum of $\text{VAl}_7\text{O}_{13}^+$ shows much weaker absorptions below 950 cm^{-1} , however a clear maximum can be identified at 865 cm^{-1} ; furthermore it presents two broad absorptions around 800 and 630 cm^{-1} . The only fragmentation channels are oxygen atom loss for $\text{Al}_8\text{O}_{12}^+$ and $\text{VAl}_7\text{O}_{13}^+$, and VO_2 loss for $\text{VAl}_7\text{O}_{12}^+$. Results are summarized in Table B.1.

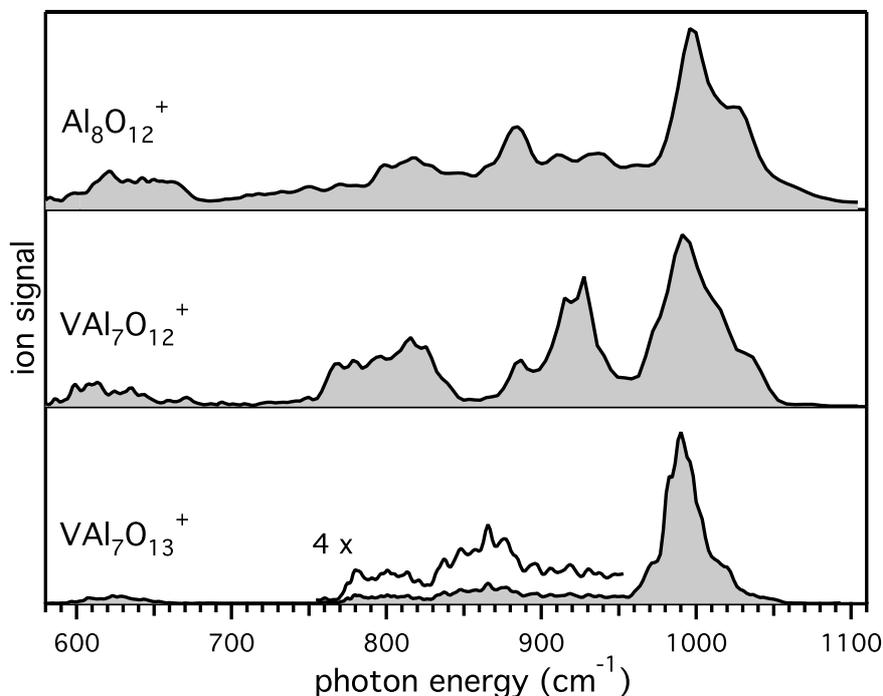


Figure B.1: IR-PD spectra of $\text{Al}_8\text{O}_{12}^+$, $\text{VAl}_7\text{O}_{12}^+$, and $\text{VAl}_7\text{O}_{13}^+$. They are obtained by monitoring the fragment ion yields mass-selectively in dependence of FELIX photon energy.

Parent Ion	Fragment	Position of Observed Bands (cm^{-1})
$\text{Al}_8\text{O}_{12}^+$	$\text{Al}_8\text{O}_{11}^+$	1024, 997, 937, 913, 885, 849(s), 817, 801(s) 771, 751, 662(s), 642, 622, 601, 584
$\text{VAl}_7\text{O}_{12}^+$	$\text{Al}_7\text{O}_{10}^+$	1037(s), 991, 919, 887, 816, 794, 778, 770(s), 671, 636, 613, 599(s)
$\text{VAl}_7\text{O}_{13}^+$	$\text{VAl}_7\text{O}_{12}^+$	1020(s), 990, 971(s), 865, 814, 780, 632, 607

Table B.1: Experimental vibrational frequencies (in cm^{-1}) of $\text{Al}_8\text{O}_{12}^+$, $\text{VAl}_7\text{O}_{12}^+$, and $\text{VAl}_7\text{O}_{13}^+$ clusters determined from the respective IR-PD spectra. Vibrational frequencies are determined from band maxima or estimated based on observable shoulders (s) formed by overlapping transitions.