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Isomorphous Substitution in Bimetallic Oxide Clusters

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The geometric and electronic structure of bimetallic oxide clusters is studied as a function of their composition with gas phase vibrational spectroscopy. Infrared multiple photon dissociation spectra of titanium-vanadium oxide cluster anions are measured in the 500 to 1200 wave number range and assigned on the basis of harmonic frequencies calculated using density functional theory. Singly substituted $(V_2O_5)_{n-1}(VTiO_5)^-$ ($n = 2-4$) cluster anions are shown to form polyhedral caged structures similar to those predicted for their isoelectronic counterparts, the neutral $(V_2O_5)_n$ clusters. Upon systematic exchange of V by Ti atoms in $V_{4-n}Ti_nO_{10}^-$ ($n = 1-4$), the structure does not change. The stress induced by the isomorphous substitution results in an increased number of unpaired electrons ($n - 1$) for the Ti-rich systems, leading to a quartet ground state for $Ti_4O_{10}^-$.

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The size- and composition-dependent properties of gas phase transition metal oxide clusters are intensely studied, for example, to aid in the design of functional building blocks for nanostructured materials [1] and to gain a better understanding of the elementary steps in heterogeneous catalysis [2]. A long sought-after goal, in this regard, has been the tailoring of the electronic and geometric structure of clusters by carefully choosing the cluster composition. This approach has been limited up to now by both the availability of adequate cluster sources as well as structure-sensitive characterization techniques.

Recently, photodissociation spectroscopy [3–6] as well as resonance-enhanced multiple photon ionization [7–9] combined with radiation from a tunable infrared free electron laser have proven very useful in probing the structure of monometallic oxide clusters as a function of the cluster size. Here, we present the first systematic composition-dependent infrared study of bimetallic oxide clusters in the gas phase. The structures of titanium-vanadium oxide cluster anions are characterized by infrared multiple photon photodissociation (IRMPD) in combination with density functional theory (DFT) calculations. By sequentially exchanging V with Ti atoms we exploit the control over the clusters composition to investigate its influence on the electronic and geometric structure. Previously, IRMPD studies demonstrated that negatively charged $(V_2O_5)_n^-$ clusters ($n = 2-4$) form polyhedral cages made of $(-O)_3V=O$ units [4]. Opposite to the neutral $(V_2O_5)_n$ cages [10], the anionic clusters are open shell systems; they have one unpaired electron in vanadium d states. While the unpaired electron is fully delocalized over all V atoms in $n = 2$, it localizes on a single atom for the larger clusters [4]. Here we extend this study in two series of experiments. First, a single V atom is replaced by a Ti atom, yielding closed-shell $(V_2O_5)_{n-1}(VTiO_5)^-$ anions isoelectronic with the neutral $(V_2O_5)_n$ clusters. Second,

the number of atoms is kept constant, but each V atom in $V_4O_{10}^-$ is sequentially exchanged by a Ti atom, i.e., a stepwise removal of valence electrons. For both series the geometric and electronic structures are determined from the IRMPD spectra in combination with DFT calculations. It will be shown that the V by Ti substitution in the considered clusters results in a modified electronic structure while the cluster morphology remains unaltered.

The vanadium-titanium oxide cluster anions are produced in a 10 Hz dual laser vaporization source [11,12], coupled to a tandem mass spectrometer-ion trap system described in Ref. [5]. The helium gas contains 1% of O_2 , yielding oxygen saturated cluster growth conditions. The anion beam is collimated and mass-selected by a first quadrupole mass filter. Mass-selected cluster anions are accumulated in a linear radio-frequency 16-pole ion trap and collisionally cooled to the trap housing temperature (17 K) mediated by a helium buffer gas. IRMPD spectra of the trapped cold ions are obtained after multiple photon excitation and subsequent monitoring of the fragment ion yield with a second quadrupole mass filter and a channeltron detector.

The IR light source used is the Free Electron Laser for Infrared eXperiments (FELIX) [13] located in Nieuwegein, The Netherlands. In the present work FELIX is used at a repetition rate of 5 Hz in the 500 to 1200 cm^{-1} range. When FELIX is resonant with an IR allowed transition, multiple photon absorption can take place. The cluster is excited resonantly over discrete states into the quasicontinuum. It then continues to absorb photons, but this energy is quickly randomized among all vibrational degrees of freedom. Once the internal energy reaches the dissociation limit the molecule may fragment [14].

Mass spectra of $V_nO_p^-$, $Ti_mO_p^-$ and $V_nTi_mO_p^-$ cluster anions, produced under similar conditions, are shown in Fig. 1. The mass peaks of $Ti_mO_p^-$ are broadened due to the

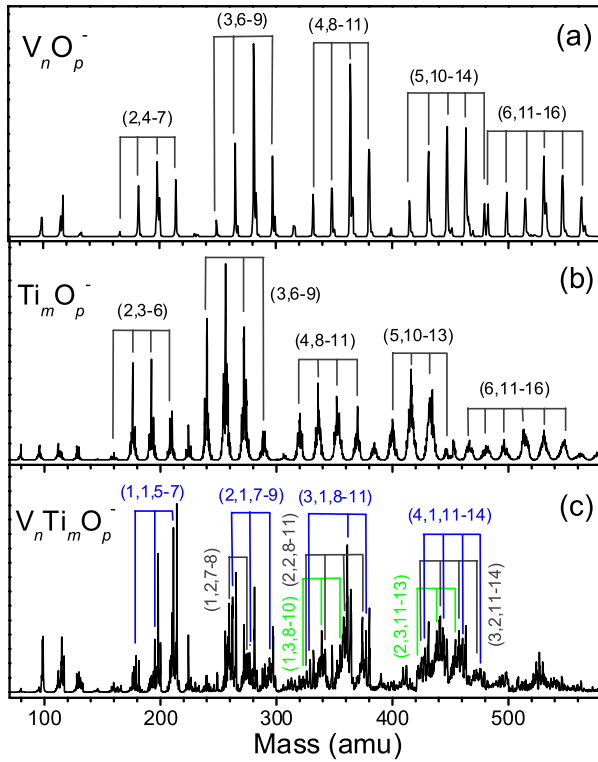


FIG. 1 (color online). Mass spectra of pure metal oxide (a) $V_n O_p^-$, (b) $Ti_m O_p^-$, and (c) bimetallic oxide $V_n Ti_m O_p^-$ clusters. In (c), for clarity only, a selection of peaks is labeled with (n, m, p) .

isotope distribution of Ti. Note that the masses of the most abundant isotope of Ti and O_3 are equal. A consistent assignment of the mass peaks starting from the small clusters and following the observed progression is possible and indicated by the labels in Fig. 1. The overall distributions of $V_n O_p^-$ and $Ti_m O_p^-$ are alike and similar to those observed before [4,15–17]. Investigations on neutral clusters using postionization, however, give a lower oxygen to metal ratio [9,18], most probably because of the higher ionization potential of highly oxidized clusters [17].

The mass spectrum of the bimetallic oxide clusters is considerably more complex, since many (n, m, p) combinations are possible. Source conditions were tuned to maximize the signal of the cluster composition under investigation. The IRMPD experiments are carried out on the corresponding ^{48}Ti containing isotopomers. A fit of a $V_{4-n}Ti_n O_{10}^-$ ($n = 1-4$) distribution, taking into account the natural isotope patterns, to the measured mass spectrum in the 348–366 amu region shows that the presence of other compositions in the selected mass channels is negligible except for the 355 amu mass peak ($VTi_3 O_{10}^-$), where there is a 10% contamination of $Ti_4 O_{10}^-$. An extended analysis of the mass spectra can be found in the supplementary information [19].

We performed IRMPD experiments on two cluster series. First, we studied the influence of substituting a single V atom by a Ti atom for $(V_2 O_5)_{n-1}(VTiO_5)^-$ ($n = 2-4$).

Then we examined the effect of the sequential replacement of V by Ti in $V_{4-n}Ti_n O_{10}^-$ ($n = 1-4$) anions. The observed fragmentation channels are listed in Table I. Note that different clusters can yield the same fragment, implying that double mass selection is imperative for these measurements. IRMPD spectra of bimetallic vanadium-titanium oxide anions are shown in the top panel of Fig. 2. The spectra are obtained by monitoring the fragment ion denoted with an asterisk in Table I.

The dissociation upon IR irradiation of $V_3 TiO_{10}^-$, $V_5 TiO_{15}^-$, and $V_7 TiO_{20}^-$ is governed by the formation of two closed-shell fragments. All three species form $V_3 O_8^-$, but the two larger anions prefer to dissociate into $V_3 TiO_{10}^-$. The IRMPD spectra of the $(V_2 O_5)_{n-1}(VTiO_5)^-$ ($n = 2-4$) series are characterized by three absorption regions: (i) a sharp peak around 1000 cm^{-1} , (ii) a broad and intense band in the $800-950\text{ cm}^{-1}$ region, and a weaker absorption band around 700 cm^{-1} .

To assist the structural assignment DFT geometry optimizations of $(V_2 O_5)_{n-1}(VTiO_5)^-$ ($n = 2-4$) and $V_{4-n}Ti_n O_{10}^-$ ($n = 1-4$) clusters were carried out with the TURBOMOLE program [20], employing the B3LYP hybrid functional [21] and the TZVP basis sets [22]. Harmonic vibrational frequencies are obtained from second analytic derivatives [23] and were scaled using a 0.9429 multiplication factor [6]. The calculated spectra are convoluted with a

TABLE I. Relative abundances of the IR fragmentation channels of $V_n Ti_m O_p^-$. Species with formal vanadium +V and titanium +IV oxidation states are marked with †. An * denotes the fragment monitored in the IRMPD study. Fragments with a relative abundance lower than 10% are not given.

Cluster	Fragment ion	Relative abundance (%)	Lost neutral
† $V_7 TiO_{20}^-$	*† $V_3 TiO_{10}^-$	100	† $V_4 O_{10}$
	† $V_3 O_8^-$	64	† $V_4 TiO_{12}$
† $V_5 TiO_{15}^-$	*† $V_3 TiO_{10}^-$	100	† $V_2 O_5$
	† $V_3 O_8^-$	64	† $V_2 TiO_7$
† $V_3 TiO_{10}^-$	$V_3 TiO_9^-$	26	O
	*† $V_3 O_8^-$	100	† TiO_2
	$V_3 O_7^-$	24	TiO_3
	$V_2 TiO_7^-$	33	VO_3
$V_2 Ti_2 O_{10}^-$	† VO_3^-	12	† $V_2 TiO_7$
	$V_2 Ti_2 O_9^-$	38	O
	*† $VTi_2 O_7^-$	100	VO_3
$VTi_3 O_{10}^-$	† $VTi_3 O_9^-$	100	O
	*† $VTi_2 O_7^-$	46	TiO_3
	$Ti_3 O_7^-$	12	VO_3
$Ti_4 O_{10}^-$	$Ti_4 O_9^-$	96	O
	$Ti_4 O_8^-$	100	O_2
	* $Ti_3 O_7^-$	54	TiO_3

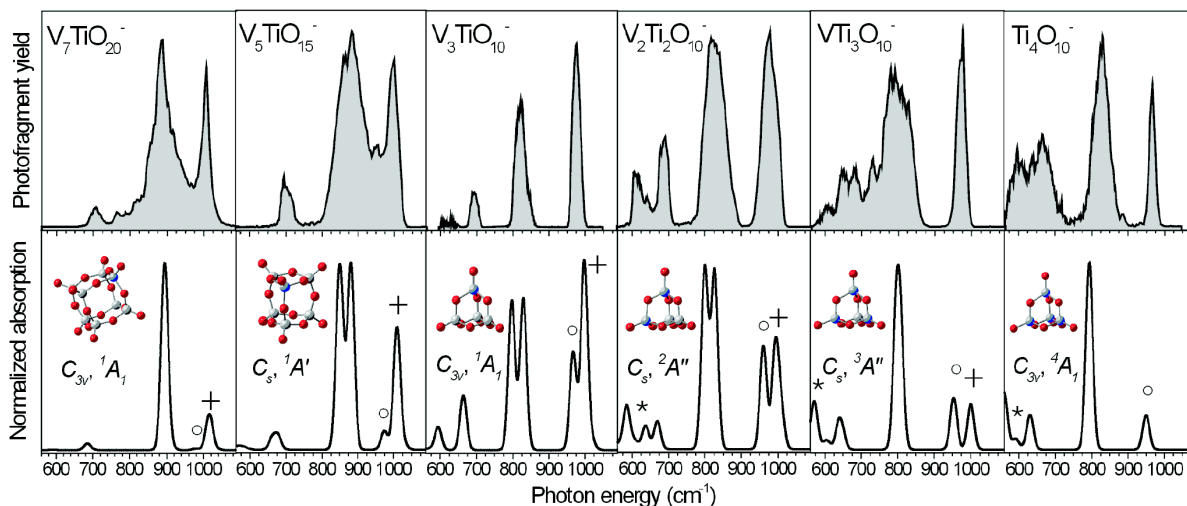


FIG. 2 (color online). Experimental IRMPD (top) and simulated IR spectra (bottom) of $V_7TiO_{20}^-$, $V_5TiO_{15}^-$, $V_3TiO_{10}^-$, $V_2Ti_2O_{10}^-$, $VTi_3O_{10}^-$, and $Ti_4O_{10}^-$ in the 560 to 1085 cm^{-1} range. The simulated spectra are based on scaled harmonic frequencies of the B3LYP/TZVP optimized geometries. Stretches of $V=O$, $Ti^{(-)}=O$, and $Ti-O^*$ bonds are labeled with +, O, and *, respectively.

Gaussian line shape of 20 cm^{-1} FWHM (bottom panel of Fig. 2).

Polyhedral cage structures, in which each metal atom M forms a single, terminal $M=O$ double bond and takes part in three $M-O-M$ single bond bridges, are found as lowest energy isomers for the closed-shell $(V_2O_5)_{n-1} \times (VTiO_5)^-$ ($n = 2-4$) clusters. Their simulated infrared absorption spectra agree satisfactorily with the experimental IRMPD spectra, yielding the following assignment of the three absorption regions. The narrow bands at 975, 1000, and 1005 cm^{-1} for $n = 2-4$ are formed by the $2n - 1$ $V=O$ and $Ti^{(-)}=O$ stretching modes, in good agreement with the 975 cm^{-1} stretching modes of compounds with titanyle groups in solution [24] and with stretches of vanadyl groups in anionic $(V_2O_5)_n^-$ [4] and neutral $(V_2O_5)_n$ (see below) clusters. The broad bands with maxima at 820 cm^{-1} ($V_3TiO_{10}^-$), 880 cm^{-1} ($V_5TiO_{15}^-$), and 885 cm^{-1} ($V_7TiO_{20}^-$) are due to the symmetric and anti-symmetric stretches of the $M-O-M$ bridges. The width of this band is considerably broader in the experimental spectra, similar to the IRMPD spectra of the larger vanadium oxide anions [4] and is tentatively attributed to pronounced intermode coupling, which is completely neglected within the harmonic approximation and therefore not well reproduced in the simulated spectra. Finally, the absorption below 800 cm^{-1} is due to vibration modes involving large parts of the cluster.

The singly substituted $(V_2O_5)_{n-1}(VTiO_5)^-$ ($n = 2-4$) cluster anions are isoelectronic with neutral $(V_2O_5)_n$ clusters. Because neutral clusters are experimentally difficult to mass select it is of interest to check if one can characterize the structure of neutral clusters by performing experiments on the corresponding mixed, isoelectronic cluster anions. The simulated IR spectra for $(V_2O_5)_n$ ($n = 2-4$) are shown in Fig. 3. The calculated geometries are similar but of higher symmetry than the corresponding Ti-doped

anions due to the presence of only one type of metal atoms. Indeed, the IR spectra are similar to the corresponding counterparts, supporting this indirect approach as an alternative method to probe the geometric structure of neutral clusters.

The IRMPD spectra of the more Ti-rich species $V_{4-n}Ti_nO_{10}^-$ ($n = 2-4$) are also shown in Fig. 2. The main fragmentation channel of $V_2Ti_2O_{10}^-$ is the formation of $VTi_2O_7^-$. $VTi_3O_{10}^-$ and $Ti_4O_{10}^-$ are oxygen richer and consequently the loss of molecular ($Ti_4O_{10}^-$) or atomic oxygen ($VTi_3O_{10}^-$ and $Ti_4O_{10}^-$) is prominent. These observations are in line with collision induced dissociation experiments on vanadium oxide clusters with a high oxygen to metal ratio for which loss of weakly bound O_2 and O species was reported [16].

Compared to the monotitanium species the spectra of more Ti-rich cluster anions $V_{4-n}Ti_nO_{10}^-$ ($n = 2-4$) are similar above 750 cm^{-1} . All give a sharp band slightly below 1000 cm^{-1} and a broad and intense band around 780–850 cm^{-1} . The vibrational structure below 750 cm^{-1} is richer than for the closed-shell systems.

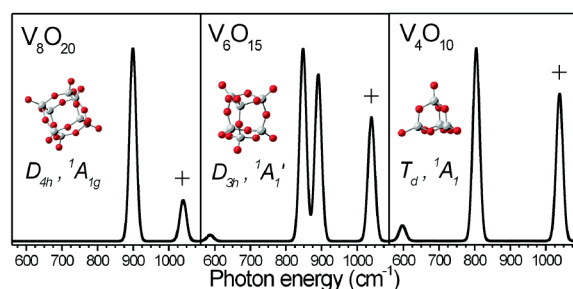


FIG. 3 (color online). Geometries and harmonic IR absorption of V_4O_{10} , V_6O_{15} , and V_8O_{20} obtained at the B3LYP/TZVP level. Stretches of the $V=O$ bonds are labeled with +.

The most stable structures found computationally for $V_{4-n}Ti_nO_{10}^-$ ($n = 1-4$) all have a tetrahedral shape similar to the geometry of V_4O_{10} . Electronically these clusters are in an open shell state; doublet, triplet, and quartet for $V_2Ti_2O_{10}^-$, $VTi_3O_{10}^-$, and $Ti_4O_{10}^-$, respectively. For each additional titanium atom there is a $(-O)_3Ti-O\cdot$ unit with a free radical localized on a singly titanium-bonded terminal oxygen atom, $O\cdot$ (i.e., three free radicals in $Ti_4O_{10}^-$). The length of the $Ti^{(-)}=O$ bond (163 pm) is comparable to the $V=O$ bond (159 pm) and significantly shorter than the weaker $Ti-O\cdot$ bond (188 pm). The presence of multiple $Ti-O\cdot$ radical sites in $Ti_4O_{10}^-$ is surprising because oxygen rich transition metal oxide species tend to form superoxo (O_2^-) or peroxo ($(O_2)^{2-}$) units as observed for $V_2O_6^+$ [6] and $V_2O_7^-$ [25,26]. Indeed, a $Ti_4O_{10}^-$ isomer with a superoxo ligand was found, but it is 0.52 eV higher in energy. To couple the two O radicals into a superoxo species, the tetrahedral cage opens to a bridged ring structure and two threefold coordinated $O=Ti(O^-)_2$ sites are created, while in the cage structure with the three radical sites, all four Ti are fourfold coordinated. The calculated IR spectrum (not shown) also is in less good agreement. The predicted band around 800 cm^{-1} shows a characteristic splitting that is not seen and the $Ti=O$ stretch bands are predicted to be more intense. Formation of two $W-O\cdot$ radical sites has also been shown for O-rich WO_n clusters [27].

Summarizing, the infrared spectroscopy of buffer gas cooled, mass-selected bimetallic oxide clusters has systematically been studied. By tuning the cluster composition we could change the number of valence electrons. Singly substituted $(V_2O_5)_{n-1}(VTiO_5)^-$ ($n = 2-4$) anions have structures similar to those of neutral, pure vanadium oxide clusters, and they are isoelectronic. $V_{n-4}Ti_nO_{10}^-$ ($n = 1-4$) cluster anions are shown to maintain a tetrahedral shape with increasing n , similar to V_4O_{10} , even though this leads to an increasing number of unpaired electrons. Our results show that IRMPD spectroscopy is also applicable to more complex clusters, which will prove useful for future investigations aimed at characterizing tailor-made model systems for adsorbate-support interactions in catalytic systems.

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