Cluster Compounds

Polyhedral Vanadium Oxide Cages: Infrared Spectra of Cluster Anions and Size-Induced d Electron Localization**

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The size-dependent properties of transition metal oxide clusters have been intensely studied not only because of interest in this peculiar state of matter, but also because of their relevance as building blocks for nanostructured materials. Vanadium oxides, in particular, are important in supported catalysts,[1] as cathode materials in lithium batteries,[2] in bolometric detectors,[3] and as ferromagnetic nanotubes.[4] While the structural characterization of vanadium oxide clusters deposited on surfaces[5] has reached atomic resolution, it remains a major experimental challenge in the gas

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phase.[6] Infrared photodissociation[7] paired with quantum chemistry is currently the most generally applicable approach for cluster ions even though it requires intense and tunable infrared radiation sources. Below 2000 cm^{-1}, in the fingerprint region of metal oxide clusters, only free-electron lasers meet these demands.[8]

Herein we report the first experimental infrared spectra of transition metal oxide cluster anions in the gas phase. We combine infrared multiple photon dissociation (IRMPD) spectroscopy with density functional theory (DFT) to characterize the geometric and electronic structures of a representative series of vanadium oxide cluster anions, $(V_2O_5)_n^-$ ($n = 2$, 3, or 4).[9] Compelling evidence is produced that these anions have the polyhedral cage structures that have been predicted before, but have eluded spectroscopic detection until now.[10, 11] Evidence is also found for a size-induced localization of the extra electron in this series of anions.

The IRMPD spectra of mass-selected $V_4O_{10}^-$, $V_6O_{15}^-$, and $V_8O_{20}^-$ are shown on the left in Figure 1. They were measured by irradiating vibrationally cold, mass-selected parent ions with intense, tunable IR radiation from the free-electron laser FELIX[12] and monitoring the mass-selected fragment ion yield as a function of laser wavelength. Only when the radiation is resonant with a fundamental vibrational transition can the cluster ions absorb photons, thereby initiating a sequential multiphoton absorption process[13] which leads to heating of the cluster ion and eventually to photodissociation. The simplicity of the $V_4O_{10}^-$ spectrum is striking and immediately suggests a structure of higher symmetry with degenerate transitions. The dominant feature is a single, rather narrow intense band at 990 cm^{-1}. Based on our previous measurements on vanadium oxide cluster cations it is assigned to a vanadyl stretching mode.[14] The weaker signal below 750 cm^{-1} is attributed to a V−O−V stretch. The IRMPD spectrum of $V_8O_{20}^-$ is markedly different. While the vanadyl band stays nearly unchanged, a new band, much broader and roughly four times stronger than the vanadyl band, is observed centered at 870 cm^{-1}. The appearance of the $V_6O_{15}^-$ spectrum is intermediate between the spectra described above. An intense vanadyl band, somewhat broader and red-shifted, is followed by a four times less intense band at 830 cm^{-1}. No signal is observed below 700 cm^{-1} for the two larger clusters.

To understand these vibrational spectra we performed DFT calculations (B3LYP functional[15, 16]) of cluster geometries and vibrational spectra (see Figure 1). All three anions are open-shell systems with a single unpaired electron. For $V_4O_{10}^-$ we find a tetragonal D_{2d} structure (**1**) which is minimally Jahn–Teller distorted from the T_d structure. Each vanadium atom is fourfold coordinated, forming one short V= O bond (159 pm) and three V−O bonds (181 pm). The four symmetry-equivalent vanadyl bond stretches combine to give three IR-active b_2 and e modes, which are quasi-degenerate and explain the single intense vanadyl band in the IRMPD spectrum. The six symmetric V−O−V bond stretches also give rise to three IR-active e and b_2 modes (629 and 609 cm^{-1}, respectively), and they have a cumulative oscillator strength that is about 1/3 that of the vanadyl bands, in good agreement with experiment. The modes resulting from the six antisym-
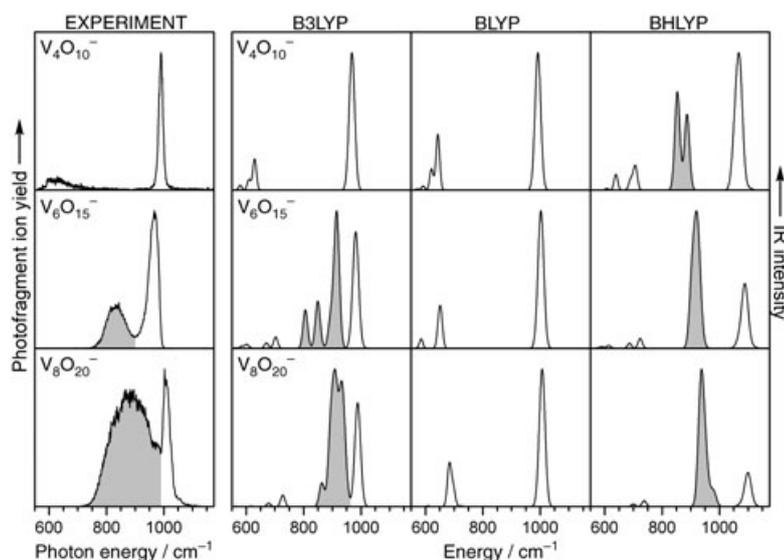
Figure 1. Experimental and simulated vibrational spectra of vanadium oxide cluster anions in the region of the V−O and V=O bond stretch modes. IRMPD spectra (left) of $V_4O_{10}^-$, $V_6O_{15}^-$, and $V_8O_{20}^-$ were measured from 550 to 1175 cm^{-1} by monitoring the dominant fragmentation channel, which leads to the formation of $V_3O_8^-$, $V_4O_{10}^-$, and $V_4O_{10}^-$, respectively. Simulated spectra (right) were obtained from scaled harmonic frequencies and oscillator strengths employing the B3LYP, BLYP, and BHLYP functionals. The calculated stick spectra were convoluted for better comparison with the experiment. Gray shaded peaks indicate localization of the unpaired d electron (see text).

metric V−O−V bond stretches are below 600 cm^{-1} and have vanishingly low intensities.
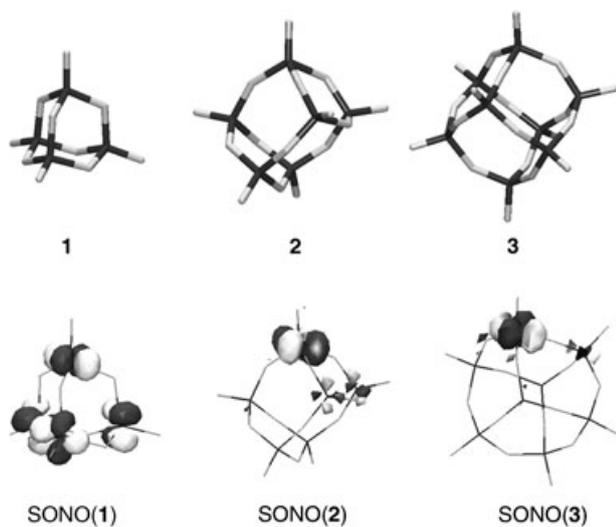
In $V_4O_{10}^-$ the unpaired electron is completely delocalized over d-states of all four vanadium sites, as illustrated by its singly-occupied natural orbital SONO(**1**). In contrast, in the larger anions the unpaired electron is localized at a single vanadium site, which lowers the symmetry of their structures to C_s. For $V_6O_{15}^-$ and $V_8O_{20}^-$ we find the distorted trigonal prism and cube structures **2** and **3**. Their singly occupied natural orbitals, SONO(**2**) and SONO(**3**), reflect the localization of the unpaired electron. Compared to $V_4O_{10}^-$, the

average V−O(−V) bond distances in $V_8O_{20}^-$ are longer at the electron localization site (189 pm), but shorter at the other sites (177–178 pm), while the V=O bond distances are similar and not affected by the localization. Unlike the closed-shell neutral parent compounds, the D_{3h} structure (trigonal prism) of $V_6O_{15}^-$ and the D_{2d} structure (cube) of $V_8O_{20}^-$ are higher-order saddle points that are 45 and 21 $kJ\,mol^{-1}$, respectively, above the ground state. For both $V_6O_{15}^-$ and $V_8O_{20}^-$ first-order saddle points with C_{2v} symmetry are found 9.8 and 8.7 $kJ\,mol^{-1}$, respectively, above the ground state. They represent transition structures for the interconversion of two equivalent C_s-minimum structures and have the additional electron delocalized over two sites.

The effects of symmetry breaking are directly observed in the vibrational spectra of these species (indicated by the gray-shaded area in Figure 1). Upon localization of the unpaired electron intense V−O−V stretch transitions appear at around 100–200 cm^{-1} below the strong vanadyl band, which replace the weak V−O−V feature more than 350 cm^{-1} below the vanadyl band in the spectrum of the delocalized case ($V_4O_{10}^-$). The calculated ratio of the cumulative oscillator strengths of the V−O−V modes and the V=O modes is 3.3 for $V_8O_{20}^-$ and 0.3 for $V_4O_{10}^-$; these values compare well to the experimental values of 4.4 and 0.4 respectively. The vanadyl modes are not affected by the electron localization and therefore their position and width remain nearly unchanged. Comparison with the experimental infrared spectra confirms the general predictions of the B3LYP model, in particular the pronounced, qualitative changes upon electron localization when the size of the cluster is increased.[17]

Figure 1 shows not only the B3LYP results discussed so far, but also the results of DFT calculations with the BLYP[16,18] and BHLYP[16,19] functionals. The increasing admixture of Fock exchange (0, 20, and 50% in BLYP, B3LYP, and BHLYP, respectively) leads to an increasing tendency for symmetry breaking.[20–22] BHLYP (right column in Figure 1) yields localization of the unpaired electron for all three cage-type anions, and also for $V_4O_{10}^-$. Consequently, the calculated BHLYP spectrum of $V_4O_{10}^-$ shows additional bands between 800 and 900 cm^{-1} that are absent from the experimental spectrum. In contrast, BLYP predicts delocalization of the unpaired electron for all three cage-type anions studied and C_{2v} and D_{2d} structures become the ground states of $V_6O_{15}^-$ and $V_8O_{20}^-$, respectively. All three BLYP spectra show no bands between 750 and 950 cm^{-1}, which is in clear contrast with the experimental spectra of $V_6O_{15}^-$ and $V_8O_{20}^-$. In summary, Figure 1 shows that only B3LYP reproduces correctly the transition from symmetric (delocalized) to broken-symmetry (localized) structures when passing from $V_4O_{10}^-$ to $V_6O_{15}^-$ in this series of $(V_2O_5)_n^-$ cluster anions.

Figure 2 compares the gas-phase IRMPD spectrum of $V_8O_{20}^-$ with the electron energy loss spectrum of a V_2O_5
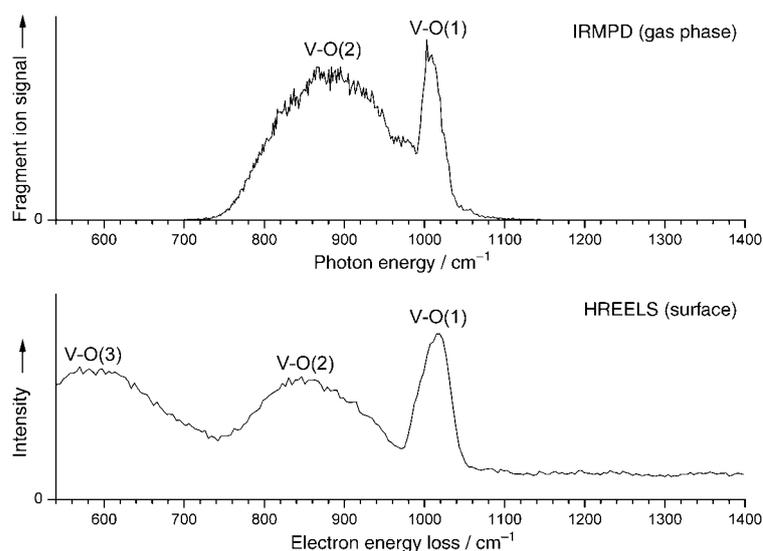
Figure 2. Vibrational spectra of different forms of vanadium oxide: The IRMPD spectrum of the gas-phase cluster anion $V_8O_{20}^-$ (top) and the spectrum of a freshly cleaved 001 surface of V_2O_5 (bottom), measured by high resolution electron energy loss spectroscopy (see text).

surface,[23] which also probes vibrational states. The spectra are surprisingly similar in the region above 740 cm^{-1}, with both displaying two bands of similar width and relative intensity. Their assignment is identical, that is, to vibrational modes of singly and doubly coordinated oxygen atoms. The third broad band of the surface spectrum is not observed in the gas phase. This can easily be rationalized because this band is assigned[11,24] to triply coordinated oxygen sites, which do not exist in the $V_8O_{20}^-$ cluster anion. Hence, the vibrational spectra reflect clearly the common (V=O and V–O–V bonds) and the discriminating (triply coordinated O) structural features of gas-phase clusters and solid surfaces.[25,26]

In this communication the polyhedral cage structures of $(V_2O_5)_n^-$ clusters ($n = 2, 3, 4$) have been identified spectroscopically for the first time by IRMPD spectroscopy. We have also found evidence for size-dependent charge localization in these clusters. Symmetry-breaking localization is observed in many other chemical systems for the reverse process—creation of an electron hole.[21] For example, the electron hole created in quartz when doped with Al is not delocalized over all four oxygen sites of the AlO_4 defect site, but localized at one oxygen only.[22] The proper description of electron (hole) localization phenomena by DFT depends on the functional used. In the present case we use the measured IRMPD spectra as the criteria for selecting the proper functional and find that only B3LYP has the right admixture of Fock exchange to reproduce the size-dependent change from delocalized to localized d electron states in vanadium oxide cages correctly. Even though the largest cluster anion studied here, $V_8O_{20}^-$, is still rather small, it reveals some striking similarities with the properties of a vanadium oxide single-crystal surface, making it an interesting gas-phase model for surface adsorption and reactivity studies.

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