

# Infrared spectroscopy of water adsorption on vanadium cluster cations ( $V_x^+$ ; $x = 3-18$ )

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## Abstract

Vanadium cluster cations with one, two or three adsorbed water molecules are investigated with infrared photodissociation spectroscopy in the region of the bending mode of water. In all of these complexes, the bending mode of adsorbed water is measured near the corresponding frequency of the isolated molecule. Dissociation processes are efficient, indicating that these resonances are characteristic of a substantial fraction of all complexes present. This indicates that water is adsorbed without significant dissociation on these clusters. Clusters with two or three water molecules have similar resonances near the bending mode of free water, indicating independent absorption without hydrogen bonding.

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## 1. Introduction

Gas phase metal clusters are convenient models for surface science and catalysis [1,2]. In early experiments, chemisorption reactions were found to depend dramatically on cluster size [3–8]. These measurements were conducted on neutral and ionic clusters with various adsorbates, investigating the rates of reaction and the dependence on charge [6,7]. However, these studies were difficult to interpret because the structures of the clusters are not generally known. Cluster measurements have not yet been able to provide specific insights like those available from vibrational spectroscopy on metal surfaces [9,10]. There has been some success in vibrational spectroscopy of adsorbates on clusters using line-tunable CO<sub>2</sub> lasers [11–14]. However, a major goal continues to be vibrational spectroscopy on clusters and their adsorbates. In recent work using infrared free electron lasers, vibrational spectroscopy has been demonstrated for metal carbide and oxide clusters [15–17], and this work has been extended to pure metal clusters

[18]. Similar experiments have begun to probe the vibrational structure of ligands [19] or adsorbates [20,21] binding to metals.

In the present work, the adsorption of water on vanadium clusters is probed in its bending mode vibration. There are many previous studies of chemisorption rates on vanadium clusters [3–8]. Physical properties have been measured as a function of cluster size [22–24], and theory has investigated vanadium cluster structures [24,25]. The bending mode of water occurs at 1595 cm<sup>-1</sup> in the isolated molecule. On metal surfaces, this mode is a simple diagnostic for adsorption of intact water, as opposed to dissociative chemisorption [26,27].

Vibrational spectroscopy of size-selected metal ion-complexes via infrared photodissociation methods has been reviewed recently [28]. With excitation in the mid-IR, ligand elimination may occur via a one or two-photon process, using laboratory optical parametric oscillator (OPO) systems. Using these methods, we recently investigated  $V^+(H_2O)Ar_n$  complexes in the O–H stretching region [29], detected by the loss of argon. However, elimination of strongly bound ligands (e.g., water) requires the absorption of multiple IR photons. Previous vibrational spectroscopy of metal clusters has

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employed infrared resonance-enhanced multiple photon ionization (IR-REMPI) [15–17] or infrared resonance-enhanced multiple photon dissociation (IR-REMPD) [18] using a tunable infrared free electron laser. In recent work, metal clusters with adsorbates have been investigated, including studies of ammonia on silver clusters [20] and carbon monoxide on rhodium clusters [21]. In this report, we study vanadium cation clusters ( $V_x^+$ ) in the size range of  $x = 3$ –18 with 1–3 adsorbed water molecules. IR-REMPD spectroscopy of the bending mode resonance provides a probe of the metal–adsorbate interaction in these systems.

## 2. Experimental

Vanadium clusters and adsorbate complexes are produced by laser vaporization at 532 nm in a pulsed-nozzle cluster source. Clusters entrained in a helium expansion gas pick up water molecules injected via a second pulsed valve into a short reaction chamber [21]. Adjustment of the pressure of water makes it possible to produce  $V_x(H_2O)_y^+$  complexes for  $y = 1$ –3. The molecular beam passes through a skimmer into a differentially pumped chamber, where pulsed acceleration plates sample the clusters into a reflectron time-of-flight mass spectrometer (Jordan). The Free Electron Laser for Infrared eXperiments (FELIX) [30] provides tunable high intensity infrared radiation for photodissociation of these cation clusters. The pulse energy of FELIX and its temporal profile are favorable for multiple photon excitation of clusters [17]. In the present experiment, the infrared beam is aligned co-linear with the molecular beam and focused through an aperture placed before the extraction region of the mass spectrometer. The depletion of specific complexes caused by IR-REMPD as FELIX is scanned in wavelength provides the desired vibrational spectroscopy.

## 3. Results and discussion

Fig. 1 shows a portion of the mass spectrum of cation clusters produced from the laser vaporization source. As indicated, pure vanadium clusters are formed as well as oxides and  $V_x^+(H_2O)_y$  complexes. Weaker signals correspond to carbides and other impurities. As shown in the inset, the intensities of the desired vanadium clusters with adsorbed  $H_2O$  are relatively weak in the small cluster sizes ( $x = 1$ –5). The intensity of water adducts increases above  $x = 6$ , resulting in better dissociation signals, as shown below. The intensities of mono-water complexes are generally greater than those of multi-water complexes, and this ratio can be controlled by the amount of added water.

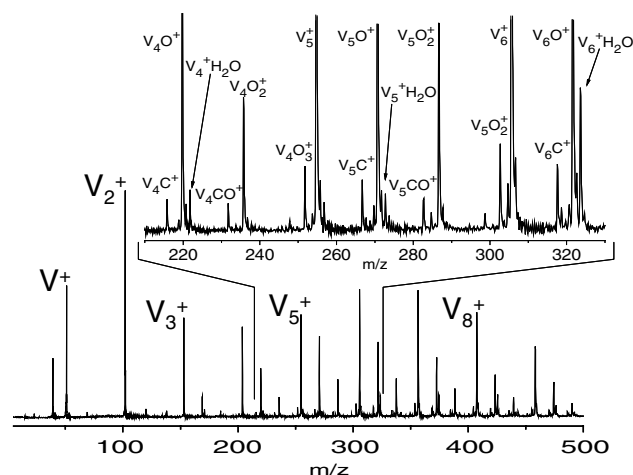


Fig. 1. The mass spectrum of  $V_x(H_2O)_y^+$  clusters produced in this experiment. The inset shows an expansion of the lower mass region, where  $x = 4, 5, 6$  clusters are found.

When the infrared laser is adjusted to coincide in time with the pulse of clusters, depletion of water complexes can be seen at certain wavelengths consistent with photodissociation. The binding energy of water to the atomic  $V^+$  cation is about 35 kcal/mol [31]. If water binding energies on clusters are similar, then dissociation with photons near  $1600\text{ cm}^{-1}$  (4.6 kcal/mol) requires at least eight photons. However, multiple photon processes requiring up to several hundred photons have been measured previously with FELIX [17]. The mechanism for dissociation is believed to involve on-resonance single-photon absorption followed by rapid intramolecular vibration energy redistribution (IVR) [17], which can occur repeatedly during the several microsecond duration of one laser macropulse. We thus denote the process as *multiple photon* to distinguish it from coherent multiphoton processes. The progressive heating of the cluster in this multiple photon process may broaden the absorption resonance and cause a slight red shift in band positions that can vary with cluster size.

Fig. 2 shows the spectra of selected  $V_x(H_2O)_y^+$  masses, with the intensity inverted to show depletion as a positive signal. As indicated, when the infrared laser scans near the bending mode of water, many of these complexes photodissociate. We cannot measure any signal for the  $V^+(H_2O)$ ,  $V_2^+(H_2O)$  and  $V_5^+(H_2O)$  complexes because their parent ions are too weak. We detect only weak depletion for  $V_3^+(H_2O)$  and  $V_4^+(H_2O)$ , consistent with their weak parent ions.  $V_6^+(H_2O)$  and larger clusters have stronger parent ions and better photodissociation signals. For these clusters, the depletion on resonance is 20–60%, indicating that these signals represent a significant fraction of the clusters present at each size. Similar signals are seen for larger clusters up to about  $x = 18$ . Linewidths in these spectra are about

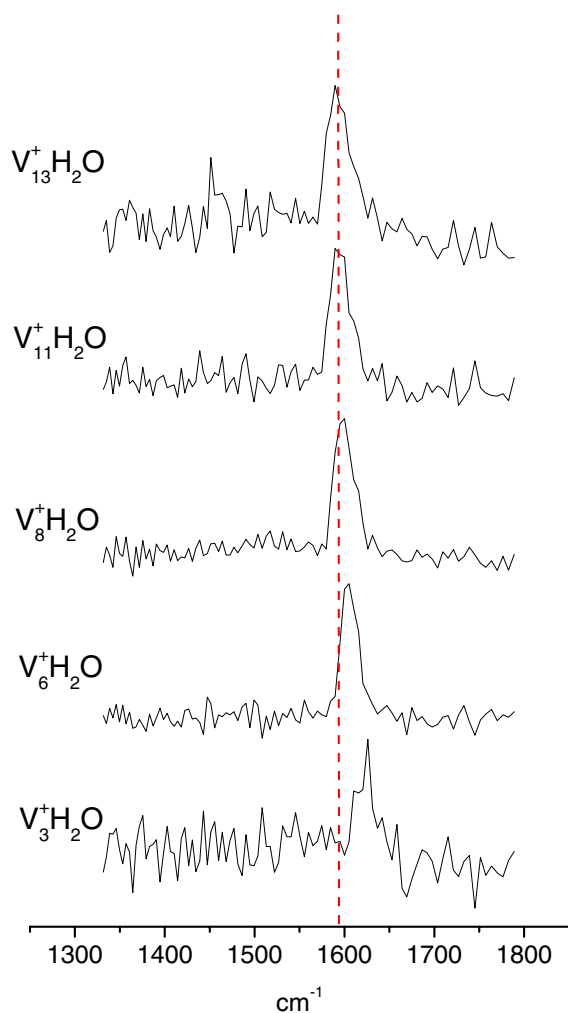


Fig. 2. The infrared photodissociation spectra measured in the water bending mode region for selected mono-water complexes. The position of the bending mode in free water is indicated with the vertical dashed line.

$30 \text{ cm}^{-1}$  FWHM, which is greater than the laser line-width of  $10 \text{ cm}^{-1}$ . However, this is consistent with linewidths seen in the past using this laser system in other multiple photon dissociation processes [19]. The line positions measured are shown in Table 1. As indicated, all of these bands occur within  $20 \text{ cm}^{-1}$  of the bending mode frequency for the isolated water molecule ( $1595 \text{ cm}^{-1}$ ).

Fig. 3 shows similar vibrational spectra for  $V_x(\text{H}_2\text{O})_2$  complexes, where  $x = 6, 8, 11$ . These spectra are noisier because of the smaller parent ion intensities. Table 1 also shows the line positions from these spectra. We could not measure spectra for the  $x = 1, 3, 4, 5$  species because their parent ions are too small. We also detect very weak spectra for three water molecules on the  $x = 6-9$  complexes (data not shown). These resonances occur at essentially the same frequency as that of the free water bend.

Table 1  
IR frequencies ( $\text{cm}^{-1}$ ) measured for the water bending mode in  $V_x^+(\text{H}_2\text{O})_y$  clusters

$x$	$y = 1$	$y = 2$	$y = 3$
2	–	1629	–
3	1622	–	–
4	1613	–	–
5	–	–	–
6	1606	1605	1595
7	1602	1599	1593
8	1600	1597	1594
9	1596	1596	1594
10	1594	1594	–
11	1594	1594	–
12	1594	1594	–
13	1594	1590	–
14	1594	1591	–
15	1591	1591	–
16	1593	1591	–
17	1593	1593	–
18	1593	1588	–

The bending mode in the free water molecule occurs at  $1595 \text{ cm}^{-1}$ .

We can compare these cluster measurements to similar studies on bulk metal surfaces [26,27]. Water adsorption has not been studied on vanadium to our

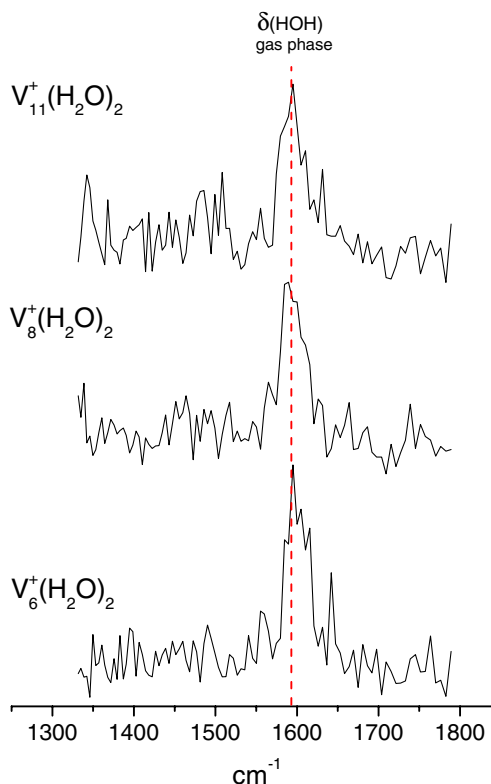


Fig. 3. The infrared photodissociation spectra measured in the water bending mode region for selected bis-water complexes. The position of the bending mode in free water is indicated with the vertical dashed line.

knowledge. In general, however, the bending mode is an indicator for the condition of adsorbed water. When this mode is observed, it indicates that intact water molecules are present on the surface, i.e., those that have not undergone dissociative chemisorption. Our data indicates that this is the case for at least some of the water on all of the clusters here. We cannot rule out the presence of some isomeric clusters in which dissociative chemisorption has occurred. These species would exhibit no bending mode resonance, and they would not be detected in this experiment. However, because the photodissociation signals here are strong, the resonances indicating non-dissociative adsorption must represent a significant fraction of all the clusters present.

On bulk metal surfaces, isolated water usually binds in an erect configuration, with the oxygen atom down and the hydrogens oriented nearly perpendicular to the surface [26,27]. In this configuration the bending mode occurs near the vibration in the free molecule ( $1595\text{ cm}^{-1}$ ). There is some evidence from recent experiments and theory for water adsorption in flat configurations, with O–H bonds parallel to the surface [32,33]. However, aggregation of water occurs readily on surfaces, making it difficult to detect isolated monomers [26,27]. Aggregation and hydrogen bonding lead to blue shifts of the bending mode by  $10\text{--}30\text{ cm}^{-1}$ . We investigate these concepts for our clusters by comparing their resonances to that of the free molecule. As shown in Fig. 4, all of the resonances are within about  $20\text{ cm}^{-1}$  of the free-water resonance. There is no great deviation from the

behavior of an isolated water molecule in any of these clusters. However, in the smaller clusters with both one and two waters the absorption is shifted systematically to the blue. This shift gradually decreases with increasing cluster size, and eventually becomes a slight red shift in the larger clusters. These shifts are similar to the linewidths of our peaks, and are therefore real, albeit small, effects. As noted above, IR-REMPD may induce a red shift into resonances, and this alone is probably enough to explain the slight red shift in the larger clusters. However, it is less plausible that a multiple photon process would induce a blue shift in a vibrational resonance, and therefore we consider other explanations for this behavior.

The electronic effect of binding to metal is well known to induce charge transfer in molecular systems, which may shift vibrational modes. However, the binding to metal is expected to weaken the bonding in the water moiety, which should lower vibrational frequencies. We have recently investigated this for the O–H (and O–D) stretch vibrations in the  $V^+(\text{H}_2\text{O})$  and  $V^+(\text{D}_2\text{O})$  complexes [29]. These complexes were concluded from both theory and experiment to have  $C_{2v}$  structures, consistent with a strong charge-dipole bonding interaction. In these systems, the O–H stretch vibrations shift  $30\text{--}80\text{ cm}^{-1}$  to the red from the free molecule frequencies. This shift arises from a polarization effect, as bonding electron density in the water orbitals is withdrawn toward the metal cation. The resulting weaker bonding in water leads to lower vibrational frequencies. The observed red shift was reproduced in density functional theory (DFT) calculations (B3LYP) [29]. However, the effect of charge transfer on the bending mode of water is more complex. While the overall bonding is weakened, charge transfer also induces expansion of the H–O–H bond angle in many metal ion complexes [29,34], which itself perturbs the bending vibration. Theory predicts a small blue shift in the bending mode for such complexes [34,35]. Unfortunately, we are not able to observe a spectrum for  $V^+(\text{H}_2\text{O})$  here. However, the small clusters studied do exhibit such a small blue shift in the bending mode. As cluster size increases, the blue shift decreases, consistent with a gradual reduction of the charge transfer interaction.

Blue shifts in the binding of water are also seen in the bulk surface science when water aggregates into clusters via hydrogen bonding [26,27]. This is of course not possible on the clusters with only one water molecule. However, the blue shift in hydrogen bonded water is associated with a steric hindrance for this vibration, which could also occur in other binding configurations. If water is bound parallel to the surface or in the depression of a bridged or threefold binding site, the bend could be hindered more than it would be in an ‘atop’ site. Recent experiments and calculations on transition metal surfaces indicate that water can bind in parallel

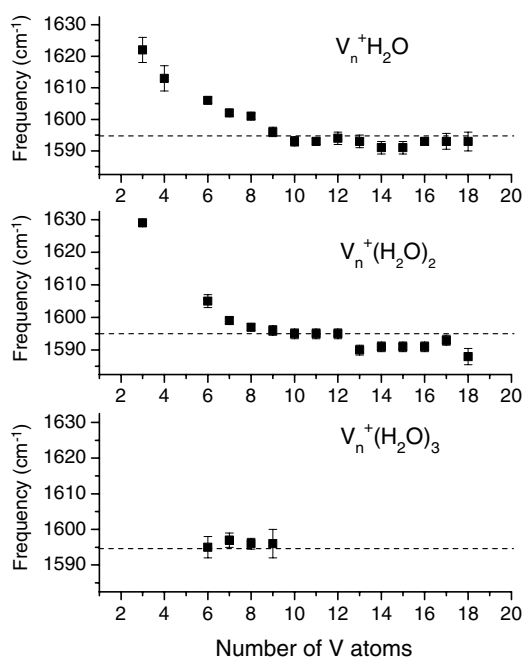


Fig. 4. The size dependence of the IR spectra in the water bending mode, indicated as band position compared to the free water infrared mode at  $1595\text{ cm}^{-1}$ .

configurations [32,33]. Unfortunately, we do not know the binding sites on these clusters, and indeed the structures of the pure metal species are not known. However, in charged clusters, the binding likely includes a significant electrostatic component, especially in the small clusters that exhibit the greatest blue shift. This interaction is favored more when the dipole of water is aligned directly at the charge center rather than parallel to it. It is therefore more likely that the blue shifts here come from a charge transfer interaction rather than because of parallel bonding configurations.

The complexes studied here with multiple water molecules also have their bending mode resonance close to that of the free molecule. The two-water complexes exhibit a very slight blue shift in the smaller cluster sizes that evolves to a red shift in the larger clusters, paralleling the trend seen for the mono-water complexes. The data on three-water complexes is more limited, but again there is essentially no shift compared to free-water. On bulk metal surfaces, hydrogen bonding induces a blue shift in the bending mode of  $10\text{--}30\text{ cm}^{-1}$ , which is larger than the shifts seen here. Additionally, there is no apparent difference in the trend here for clusters with one or two adsorbed water molecules. We therefore conclude that the water molecules on all of these clusters are adsorbed independently without any hydrogen bonding.

#### 4. Conclusions

Infrared photodissociation spectroscopy is employed to study the chemisorption of water on small vanadium cluster cations. The bending mode of water provides a convenient probe of the water on these clusters, in much the same way that it does on bulk metal surfaces. On all these clusters, the bending mode lies close to the frequency for the free water molecule. This suggests that water is adsorbed intact on these clusters. The dissociation signals are strong, indicating that these resonances represent a significant fraction of all the clusters. However, we cannot rule out the possibility of some dissociative chemisorption. A general trend is observed for the bending mode, with a small blue shift for the small clusters that gradually changes over to a small red shift for the large clusters. The blue shift can be explained by a charge transfer interaction that dominates in the small clusters, while the red shift is likely a result of the multiple photon excitation scheme. All clusters studied with multiple water molecules also have resonances near that of the free molecule, implying that these molecules are adsorbed independently on the cluster surfaces.

Together with other recent studies, these experiments establish the feasibility of IR spectroscopy on metal cluster surfaces and point to the fascinating chemistry that may be revealed. The combination of IR spectroscopy

and theory holds exciting promise for evaluating the relationship between cluster studies and bulk surface science.

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