Evolution of the Electronic Structure of Small Vanadium Clusters from Molecular to Bulklike

Hongbin Wu, Sunil R. Desai, and Lai-Sheng Wang*

Department of Physics, Washington State University, Richland, Washington 99352
and EMSL, Pacific Northwest National Laboratory, MS K2-14, P.O. Box 999, Richland, Washington 99352

The evolution of the electronic structure of V_n clusters is probed by photoelectron spectroscopy (PES) at 3.49, 4.66, and 6.42 eV photon energies. Three regions of spectral evolution are distinctly observed as a function of cluster size: molecularlike behavior for $n = 3-12$; transition from molecular to bulklike for $n = 13-17$; gradual convergence to bulk for $n > 17$, for which a surfacelike feature is observed to slowly merge into the bulk feature near $n = 60$. The PES spectra provide an atom-by-atom view of the evolution of the electronic structure of the V_n clusters from molecular to bulklike. [S0031-9007(96)01200-8]

Transition metal clusters have attracted considerable attention in cluster science because of their diverse and interesting physicochemical properties, which are of potential technological significance, e.g., in novel catalysts and magnetic materials. Vanadium clusters in particular are interesting and have been extensively studied for these reasons [1–7]. Bulk vanadium is paramagnetic with a body-centered cubic (bcc) crystal structure [8]. Many studies have been focused on the magnetic properties of the vanadium clusters to see if these clusters would exhibit novel magnetism and how it would evolve towards the bulk paramagnetism [1–6]. Central to these questions are the electronic structures of these clusters. However, the electronic structures of transition metal clusters have posted considerable challenges both theoretically and experimentally due to the open d shells. Many of the theoretical works on the vanadium clusters are model calculations and there are few fully optimized studies [1–5].

Experimentally, the chemical reactivity [7], ionization potentials [9], and dissociation energies [10] of small vanadium clusters have been measured. However, except the diatomic V_2 [11], very little is known about the electronic structures of the vanadium clusters. The main purpose of the current work is to systematically probe the electronic structures of small vanadium clusters and their evolution toward bulk using photoelectron spectroscopy (PES) of size-selected anions. The electronic structure information obtained can also be used to understand the magnetic properties of these clusters and provides a basis for further theoretical understanding.

The PES spectra of V_n^- clusters ($n = 3-65$) are studied for the first time at three detachment photon energies: 3.49, 4.66, and 6.42 eV. The low photon energy yields better resolved spectra while the high photon energy allows deeper valance states to be probed. A clear and gradual transition from molecular to bulklike behavior is observed. Extensive and discrete electronic features are resolved for clusters with $n < 17$, beyond which only two spectral features are observed at the 4.66 eV photon energy. The first feature near the threshold is sharper and its binding

energy (BE) increases with cluster size; the second feature is broader and its BE changes little with cluster size. The two features gradually merge, beyond about $n = 60$, into one broad band, which resembles the bulk photoemission feature. The current PES study provides an atom-by-atom picture of how the electronic structure of the V_n clusters evolves from molecular to bulklike.

The experimental apparatus [12] used for this study consists of a laser vaporization cluster source and a modified magnetic bottle time-of-flight (TOF) photoelectron analyzer [13]. A vanadium disk target is used and care is taken to minimize oxide contamination [12]. Negative clusters from the cluster beam are mass analyzed and decelerated before interacting with a detachment laser beam from the third (3.49 eV) or fourth (4.66 eV) harmonic of a Nd:YAG laser or an ArF excimer laser (6.42 eV). At 3.49 eV, photoelectron TOF spectra are measured for the selected clusters at a 10 Hz repetition rate. At 4.66 and 6.42 eV, spectra are taken at 20 Hz with the cluster beam on and off at an alternating laser shot for background subtraction. For relatively weak signals, the 4.66 and 6.42 eV spectra can still exhibit significant noise at low electron energies due to imperfect background subtraction. The TOF spectra are converted to kinetic energy distributions, calibrated with the spectrum of Cu^- anion, and smoothed with a 5 or 10 meV square window function. The binding energy spectra presented are obtained by subtracting the kinetic energy spectra from the photon energies. Our spectrometer has an energy resolution of better than 30 meV at 1 eV electron energy. Better resolved spectra are obtained at lower photon energies due to the dependence of resolution on electron energies while higher photon energies allow more valence states to be observed.

The PES spectra of V_n^- ($n = 3-65$) at 4.66 eV are shown in Fig. 1. The noise present at high BE for the small and large clusters is due to the effect mentioned above. These spectra represent transitions from the ground state of the anions to the ground and various excited states of the neutral clusters. In the single particle approximation, they
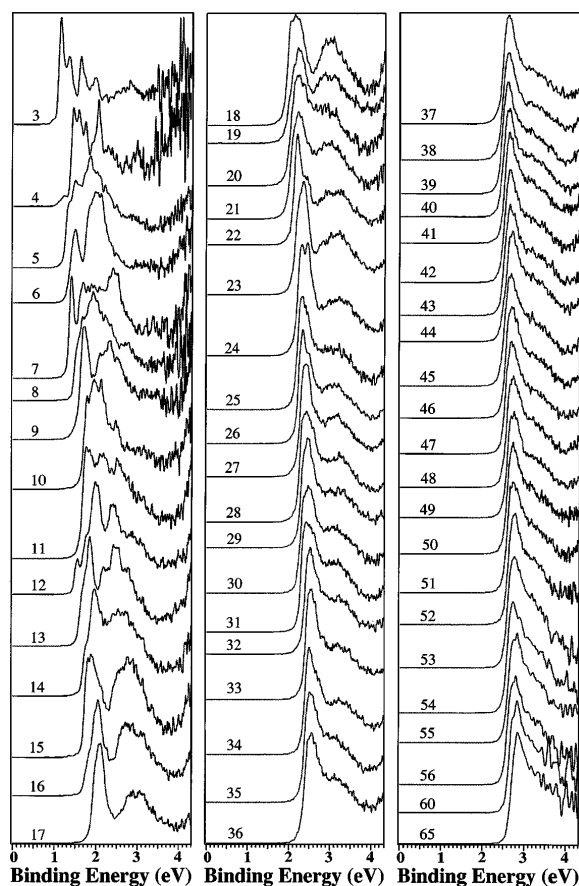

FIG. 1. Photoelectron spectra of V_n^- ($n = 3-65$) at 4.66 eV photon energy.

can be viewed as the electronic energy levels of the neutral clusters superimposed by the Franck-Condon factors of each discrete energy level [14]. The rather high density of electronic states is already revealed even for the very small clusters, indicating the complicated electronic structures of these systems. Nevertheless, discrete and sharp features are still resolved for clusters up to V_{16}. We have also taken the spectra at 3.49 eV for $n = 3-24$, where the spectra are slightly better resolved. In particular, the shoulders at the low BE side of V_{13}, V_{14}, and V_{16} are well resolved as distinct peaks and the first band of V_{15} is resolved into two features. However, above V_{16} such sharp features disappear abruptly and the spectra basically consist of two bands, a narrower band near the threshold, and a second broader band at a BE of about 3.2 eV, as seen in Fig. 1. Interestingly, the BE of the second band does not seem to change much with cluster size and the two bands eventually merge into one broader band near V_{60}.

The two-band pattern for the larger clusters between $n = 17-60$ can already be seen to emerge at V_{13} although each of the bands for V_{13} is still composed of several features, which are resolved better in the 3.49 eV spectrum. The clusters from V_{13} to V_{16} seem to represent the transition size range from the discrete spectra to the two-band spectra starting at V_{17}: The BE of the second band from V_{13} to V_{16} is systematically shifted to higher values until

V_{17} wherefrom the BE of the second feature changes very little with cluster size.

Therefore, the PES spectra shown in Fig. 1 can be roughly divided into four regions of evolution: (1) from $n = 3$ to 12, distinctly molecularlike with extensive discrete features; (2) from $n = 13$ to 16, transition region from discrete features to the two-band features at $n = 17$; (3) from $n = 17$ to about 60, convergence of the two-band feature to a single broad feature; (4) above $n = 60$, single broad spectral feature with little change as cluster size increases further.

To understand this spectral evolution, it is useful to compare the cluster spectra to bulk PES spectra of vanadium. Angle-resolved photoemission of the V(100) surface has been studied and shows two broad features at the normal emission angle [15], one near the Fermi level, and one about 2 eV below the Fermi level (Fig. 2). These have been compared to band structure calculations and they are understood to be due to the d bands of bulk vanadium [16]. The broad PES feature at larger cluster sizes shown in Fig. 1 already resembles the first bulk feature to a remarkable degree. To facilitate better comparisons with the bulk, we further measured the PES spectra at 6.42 eV, which allows more valence states to be revealed. A few such spectra are shown in Fig. 2 along with the bulk spectrum [17]. At 6.42 eV, a new feature emerges at V_{17} with a BE of about 5.2 eV that cannot be observed at the lower photon energies. Interestingly, this new feature apparently evolves into the second bulk feature. The spectrum of V_{65} almost exactly resembles the bulk spectrum. Clearly the main bulk PES features already appear from V_{17} and above. An obvious question arises: What is the nature of the first sharper peak that emerges from V_{13} and gradually merges with the second broad peak between V_{17} and V_{60}?

The most significant observation is the appearance of both bulklike features at V_{17} near 3.2 and 5.2 eV (Fig. 2). The BEs of these features are seen to change little except becoming broader with increasing cluster size. These bulklike features are attributed to be due to the interiors of the clusters, suggesting that the clusters may already possess structures similar to the bulk crystal lattice. Thus, one reasonable interpretation of the first sharp feature is that it is due to the cluster surfaces. This interpretation suggests that starting from V_{13} there is already a surface and an interior for the cluster and starting from V_{17} the interior of the clusters may already possess some similarity to the bulk. This is not surprising for V_{13} since any three-dimensional arrangements of a 13-atom cluster will produce an interior. There would be at least one interior atom for either an icosahedral (I_h) V_{13} or bcc V_{13} although the cluster structure is not exactly known. One recent tight-binding calculation suggests that V_{13} may have an I_h structure [5] while most calculations on V clusters have assumed bcc bulk structures [1–4].

The photon energy dependence of the relative intensities between the first sharp feature and the 3.2 eV feature provides another important clue regarding the nature of
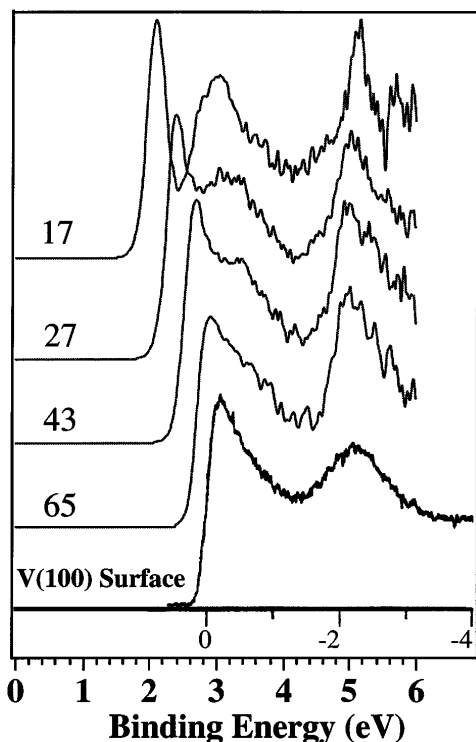
FIG. 2.   Photoelectron spectra of V_{17}^-, V_{27}^-, V_{43}^-, and V_{65}^- at 6.42 eV photon energy, compared to the bulk photoelectron spectrum of V(100) surface at 21.21 eV photon energy. It shows the appearance of bulk features at V_{17} and how the cluster spectral features evolve toward the bulk. The bulk spectrum (Fermi level at origin) is taken from Ref. [15] and plotted in the same energy scale as the cluster spectra.

these features. From Figs. 1 and 2, it is seen that the relative intensity of the 3.2 eV feature is increased at the higher photon energy. A similar trend is also observed by comparing the 4.66 to the 3.49 eV spectra. This suggests that the 3.2 eV feature is most likely due to d-like states and the first sharp feature is due to s-like states [18]. This is consistent with the assignment that the 3.2 eV feature corresponds to the first bulk band. It is then expected that the first sharp feature should merge to the d-like band as the clusters approach the bulk since in the bulk the density of states (DOS) near the Fermi level is mostly due to the d band [16].

Theoretical studies by Lee and Callaway, who calculated the DOS for a bcc V_{15} at the bulk lattice constant [3], lend more support to the surface-interior interpretation of the cluster PES spectra. They found two features for the DOS near the Fermi level. Their local DOS curves suggested that the first feature closer to the Fermi level was mainly due to the outer shell while the second feature was mainly due to the second shell. Even though these calculations were not for fully optimized clusters, this agreement is still informative. More systematic and optimized calculations might be needed to confirm our assignment and interpretation.

The electron affinity (EA) as a function of cluster size provides additional insight into the evolution of the V_n

clusters and these are shown in Fig. 3 [19]. The EAs for smaller clusters between V_3 and V_{16} exhibit significant size dependence with distinct local minima at V_5 and V_{12}, and maxima at V_4 and V_{10}. They abruptly become smoother starting from V_{17}. The metallic drop model, widely used to understand the behavior of metal cluster properties [20], predicts that for a metallic sphere the EA is linearly proportional to $1/R$: $EA = WF - \beta(e^2/R)$, where R is the effective radius of a cluster, WF is the bulk work function, and β is a constant. The inset of Fig. 3 shows such a plot for the cluster EAs vs $n^{-1/3}$ (proportional to $1/R$). Starting from V_{17}, the EAs are clearly seen to fall on a straight line that extrapolates to 4.2 eV at infinitive cluster size. This value agrees well with the bulk work function of vanadium (4.3 eV [21]).

It is expected that the PES spectra of the higher clusters will change little beyond V_{65} and the EAs will slowly approach the bulk work function according to the metallic drop model. The present PES spectra thus provide a rather complete view of the evolution of the electronic structure from molecular to bulklike as a function of cluster size.

Most of the previous theoretical studies have focused on the magnetic properties of the V_n clusters and suggested that the cluster magnetic properties depend on the atomic distances [1–4]. Assuming bulk bcc structures and bulk bond distances, several works have predicted that at V_{15} the cluster abruptly becomes paramagnetic similar to the bulk while smaller clusters show ferromagnetic and antiferromagnetic couplings [1–4]. The PES spectra shown in Figs. 1 and 2 are likely to have major implications for the theoretical understanding of the magnetic properties of these clusters. The electronic structures obtained from the PES spectra suggest the appearance of
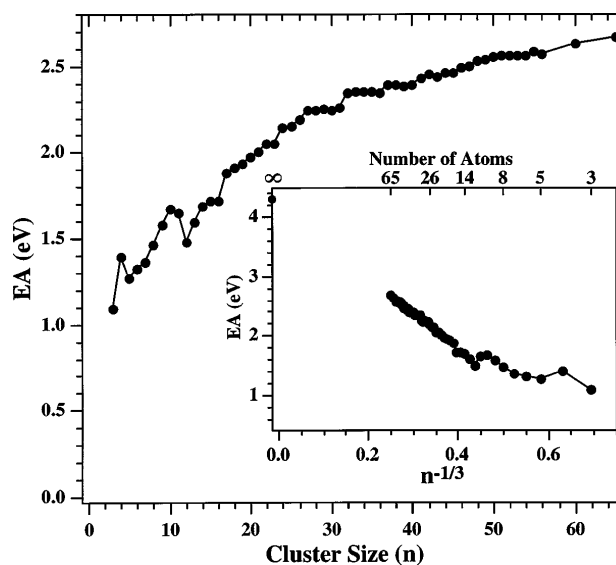

FIG. 3.   Electron affinity of the vanadium clusters as a function of cluster size n. Inset: electron affinity as a function of $n^{-1/3}$, showing that the EAs above V_{17} become approximately linear and extrapolate to the bulk work function at infinite cluster size (dot on the EA axis).

bulklike features between V_{13} and V_{17}. This seems to be consistent with the previous predictions that the bulk magnetic property turns on near V_{15}, although our results really should be compared to fully optimized calculations.

Finally, we comment on the geometrical structure implications of the observed results. The appearance of bulklike PES features in the clusters and their convergence to the bulk photoemission from a bcc crystal suggest that the clusters may grow according to the bcc structures or possess interiors similar to bcc structures. Alternatively, it may be that the electronic structure of the clusters as probed by PES is insensitive to the details of the cluster geometrical structures. The latter is quite unlikely and needs to be settled by accurate electronic structure calculations. bcc types of cluster structures have been suggested for clusters of other bulk bcc transition metals, e.g., Cr and Fe clusters [12,22,23]. Therefore, it is plausible for the V_n clusters to grow like bcc structures as well. This would considerably simplify future efforts to obtain fully optimized structures for these clusters.

In summary, the evolution of the electronic structure of V_n clusters is probed by photoelectron spectroscopy at various photon energies. Small clusters are molecularlike, showing dramatic size dependence. The transition from molecular to bulklike electronic structure is observed clearly between V_{13} to V_{17}. From V_{17} and above, both surfacelike and bulklike features are distinctly observed and the surfacelike feature is shown to gradually merge into the bulk feature. These results provide a complete and atom-by-atom picture of how the electronic structures of the vanadium clusters evolve toward that of the bulk and have important implications for the cluster structures and magnetic properties and should form the basis for further theoretical studies.

*To whom correspondence should be addressed.

[1] D. R. Salahub and R. P. Messmer, Surf. Sci. **106**, 415 (1981).

[2] F. Liu, N. Khanna, and P. Jena, Phys. Rev. B **43**, 8179 (1991).

[3] K. Lee and J. Callaway, Phys. Rev. B **48**, 15 358 (1993); **49**, 13 906 (1994).

[4] J. Dorantes-Davila and H. Dreysse, Phys. Rev. B **47**, 3857 (1993); P. Alvarado *et al., ibid.* **50**, 1039 (1994); H. Dreye *et al.,* J. Appl. Phys. **73**, 6207 (1993).

[5] J. Zhao *et al.,* Physica (Amsterdam) **215B**, 377 (1995).

[6] D. C. Douglass, J. P. Bucher, and L. A. Bloomfield, Phys. Rev. B **45**, 6341 (1992).

[7] Y. M. Hamrick and M. D. Morse, J. Phys. Chem. **93**, 6494 (1989); M. R. Zakin *et al., ibid.* **93**, 6823 (1989); D. M. Cox *et al.,* J. Chem. Phys. **88**, 111 (1988).

[8] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1986).

[9] M. R. Zakin *et al.,* Chem. Phys. Lett. **135**, 223 (1987).

[10] C. X. Su, D. A. Hales, and P. B. Armentrout, J. Chem. Phys. **99**, 6613 (1993).

[11] E. M. Spain, J. M. Behm, and M. D. Morse, J. Chem. Phys. **96**, 2511 (1992); E. M. Spain and M. D. Morse, J. Phys. Chem. **96**, 2479 (1992).

[12] L. S. Wang, H. S. Cheng, and J. Fan, J. Chem. Phys. **102**, 9480 (1995); H. Wu, S. R. Desai, and L. S. Wang, Phys. Rev. Lett. **76**, 212 (1996).

[13] P. Kruit and F. H. Read, J. Phys. E **16**, 313 (1983); O. Cheshnovsky *et al.,* Rev. Sci. Instrum. **58**, 2131 (1987); G. Gantefor, K. H. Meiwes-Broer, and H. O. Lutz, Phys. Rev. A **37**, 2716 (1988).

[14] Final state effects and anion relaxation effects have been shown to be important in theoretical simulations of photoelectron spectra of $Cu_n{}^-$ and $Si_n{}^-$ clusters, respectively [C. Massobrio, A. Pasquarello, and R. Car, Phys. Rev. Lett. **75**, 2104 (1995); N. Binggeli and J. R. Chelikowsky, *ibid.* **75**, 493 (1995)]. The major spectral features are reproduced at all three photon energies, suggesting they are primarily due to single particle transitions.

[15] P. Pervan, T. Valla, and M. Milum, Solid State Commun. **89**, 917 (1994).

[16] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[17] Photoelectron spectrum of polycrystalline vanadium should be used here. However, the available ones in the literature for the polycrystalline V films [J. Barth, F. Gerken, and C. Kunz, Phys. Rev. B **31**, 2022 (1985); L. Saisa, T. Kaurila, and J. Vayrynen, Solid State Commun. **83**, 407 (1992)] are rather poorly resolved and show two broad features quite similar to the one shown in Fig. 2 for the V(100) surface.

[18] Cross sections for higher momentum states increase with photon energies. See S. Hufner, *Photoelectron Spectroscopy* (Springer-Verlag, New York, 1995), p. 15.

[19] The electron affinity is systematically estimated by drawing a straight line along the leading edge of each spectrum. The intercept with the binding energy axis plus a constant of 0.06 to 0.10 eV (for compensation of finite resolution and thermal broadening) is taken as the adiabatic EA. The uncertainty for the EA values is ± 0.08 eV or better depending on the sharpness of the leading edge.

[20] D. M. Wood, Phys. Rev. Lett. **46**, 749 (1981); G. Makov, A. Nitzan, and L. E. Brus, J. Chem. Phys. **88**, 5076 (1988); M. Seidl *et al., ibid.* **95**, 1295 (1991).

[21] R. C. Weast *et al., CRC Handbook of Chemistry and Physics* (CRC, Boca Raton, 1986).

[22] H. S. Cheng and L. S. Wang, Phys. Rev. Lett. **77**, 51 (1996).

[23] G. M. Pastor, J. Dorantes-Davila, and K. H. Bennemann, Phys. Rev. B **40**, 7642 (1989).