Structure Determination of Small Metal Clusters by Density-Functional Theory and Comparison with Experimental Far-Infrared Spectra

C. Ratsch*, A. Fielicke**, J. Behler**, M. Scheffler**, G. von Helden**, and G. Meijer**

* UCLA, Department of Mathematics, Los Angeles, CA 90095
** Fritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

ABSTRACT

The far-infrared vibrational spectra for charged vanadium clusters as well as charged and neutral niobium clusters have been measured size specifically using far-infrared multiple photon dissociation. The ground state energy and vibrational spectra of a large number of stable and metastable structures for each of these sizes and systems have also been calculated using density-functional theory (DFT). A comparison of the calculated vibrational spectra with those obtained in the experiment allows us to deduce the cluster size specific atomic structures. Our results suggest that sometimes there is one unique atomic structure, while in other cases the experiment might observe several isomers. A comparison of the results for cationic vanadium and cationic niobium and the results for neutral niobium allows us to explore the differences between the different systems, and clusters with different charges.

Keywords: metal clusters, vibrational spectra, atomic structure, density-functional theory

1 INTRODUCTION

Small clusters or nano-particles exhibit properties that are often quite different from those in the bulk phase. For example, small metal clusters have been shown to exhibit unusual magnetic properties [1]. In particular vanadium clusters have been predicted to have large magnetic moments [2]–[6]. Small nanoparticles also play an increasingly important role in catalysis [7], [8]. With new approaches in synthesis, it may become feasible to control the size and possibly also the structure of the nanoparticles, and thus to control their properties. Therefore, it is paramount to gain a better understanding of the atomic structure and properties of small metal clusters.

In this paper we present the details of a combined theoretical and experimental study on the structure determination of metal clusters. We have recently shown that multiple photon dissociation spectroscopy on metal cluster rare gas complexes allows for the determination of cluster size specific far-infrared spectra, and that a comparison with vibrational spectra calculated by DFT can be used to determine the atomic structure [9], [10],
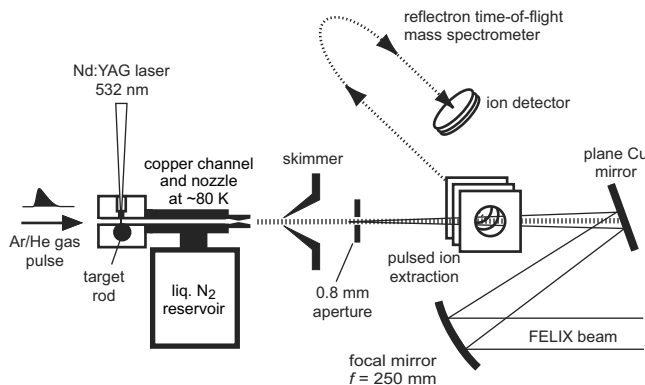

Figure 1: Scheme of the experimental set-up for the IR multiple photon dissociation spectroscopy of the argon complexes of metal cluster cations.

because these spectra are typically rather different for different atomic configurations. Moreover, we have shown that a detailed analysis and comparison does even allow for the determination of the atomic structure for different isomers for a certain size [11].

2 THE EXPERIMENT

The experiments are carried out in a molecular beam setup that is coupled to the beam-line of the Free Electron Laser for Infrared eXperiments (FELIX). This laser can produce intense, several μs long pulses of tunable IR radiation in the range of $\sim$40–2000 cm^{-1}. Each pulse consist of a train of $\sim$0.3–3 ps long micropulses of typically $\sim$10 μJ, spaced by 1 ns. The time and intensity profile of the radiation makes FELIX a suitable tool for studying multiple photon excitation processes in molecules or clusters [12]. Some details of the experimental set-up have already been given in Refs. [9], [10]. In short, cationic vanadium clusters V$_n^+$ are formed in a laser vaporization cluster source (see Fig. 1). Complexes with Ar atoms (V$_n^+$Ar) are formed after passing through a copper channel that is cooled to about 80 K. The molecular beam containing these complexes is overlapped with the far-IR output of FELIX. Resonant absorption of one or multiple IR photons by the complexes can be followed by evaporation of single or more

Ar atoms from the complex leading to decreases in their abundances.

After normalization for laser power variations and intensity fluctuations stemming from the cluster source, one obtains the absorption spectra of the corresponding $V_n^+ Ar_m$ cluster complexes. Although the thus obtained spectra correspond to the spectra of the Ar complexes, the vanadium clusters are the active chromophore and the influence of the Ar atoms is assumed and expected to be negligible. The spectra for cationic and neutral niobium clusters were obtained similarly.

3   DENSITY-FUNCTIONAL THEORY CALCULATIONS

The calculations presented below were obtained within the framework of density-functional theory (DFT). We used the DMol^3 code [13], which is an all-electron code that uses numerical atomic orbitals as a basis set. All results presented here were obtained using the generalized gradient approximation (GGA) in the parameterization of Perdew, Burke, and Ernzerhof (PBE) [14] for the exchange-correlation (XC) functional.

We employed the following computational procedure: First, we calculated the ground state energy for a large number of geometries for the clusters of each size. The atomic positions of the structures were always relaxed, and no symmetry constraints are applied. As initial geometries we started with all the structures that have been discussed previously in the literature [15]–[20]. In addition, we tried a large number of different geometries that were derived from previously calculated structures. For example, for many clusters one can describe the geometry as a superposition of smaller building blocks that typically are trigonal, tetragonal, pentagonal, or hexagonal pyramids. Thus, one can often simply add or subtract an atom from a cluster of size n to obtain a start geometry for a cluster of size $n+1$ or $n-1$. In this manner, we typically generated at least 10 or more different geometries for each size. It is important to emphasize that finding the correct initial geometry is a major challenge. As the cluster size increases, the number of possible atomic configurations increases dramatically. Therefore, it is possible that for certain cluster sizes (in particular the larger ones) we did not find the correct atomic structure.

We also tested the different possible spin states for all clusters. Once the structures and spin states that are energetically most favorable were detected, we calculated the vibrational spectrum of these systems. This was done by displacing each atom in each direction, in order to evaluate the $3n$ dimensional force-constant matrix. Then we diagonalized the resulting dynamical matrix. The IR intensities were obtained from the derivative of the dipole moment. For the purpose of an easy comparison to the experimental data, we folded for all
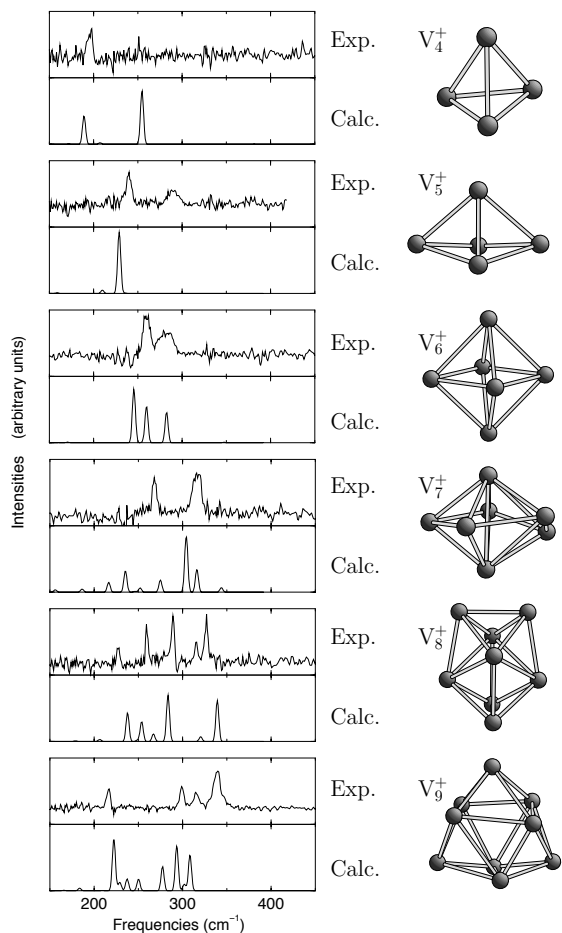

Figure 2: Comparison of the experimentally obtained spectra (Exp.) and calculated spectra (Calc.) for the six clusters V_4^+ to V_9^+. The corresponding atomic structures are shown to the right of each pair of experimental and calculated spectra.

results shown the calculated spectra with a Gaussian lineshape function of half width of 2 cm^{-1}. We apply a common scaling factor of 0.87 to all frequencies shown, which was obtained by comparison of the calculated vibrational frequency for V_2 with the experimental value.

All the calculations presented below are for V_n^+ clusters, while the experimental spectra are obtained from the dissociation of $V_n Ar^+ \longrightarrow V_n^+ + Ar$. Tests revealed that this is justified, because the rare gas atoms bind only very weakly to the V_n^+ cluster.

4   RESULTS FOR CATIONIC VANADIUM CLUSTERS

The main results of our calculations and comparisons to the experimental spectra are given in Fig. 2. In this figure we present the experimentally measured spectra for V_4^+ to V_9^+ that were obtained as described above. Underneath the experimental spectra we show

calculated spectra for these cluster sizes and on the right side the corresponding structures are shown. Based on similarities between experimental and calculated vibrational spectra and energetical arguments, these structures are suggested to be the structures of the clusters seen in the experiment. More details and further results for V_{10}^+ to V_{15}^+ are given in [10]. For almost all cluster sizes discussed here the lowest energy isomer leads also to the best agreement between calculated and measured spectra. The only exception is V_9^+; here we find two isomers that can be considered (within the accuracy of the calculations) as energetically degenerate, however, best agreement in the spectra is obtained for the isomer that is slightly higher in energy. Most structures are calculated to have the electronic state with the lowest possible multiplicity as the energetically lowest one, e.g. $S = 0$ for odd n and $S = 1/2$ for even n. For V_5^+ and V_9^+ the structures with $S = 0$ and $S = 1$ are close in energy, and the shown spectrum corresponds to the clusters with $S = 1$.

We will now briefly discuss the results presented here and compare them to previous work. For more details, we refer the reader to [10]. We find that a trigonal pyramid is the energetically preferred structure for V_4^+. This is in agreement with the calculations of Wu *et al.* [16]. We note that a planar structure (that has been predicted for neutral clusters) is rather unfavorable. We find that for V_5^+ a (slightly buckled) tetragonal pyramid is the energetically preferred structure, which is in agreement with previous results [16], [20]. We note that a buckled tetragonal pyramid is topologically similar to a distorted trigonal bi-pyramid, which has also been suggested, and that in fact the spectra of these 2 are very similar. For V_5^+ we find that the suggested structure has a spin of $S = 1$, but a spin state that is not the lowest possible spin state has also been reported in optical absorption spectroscopy experiments [21] for V_5^+ The most stable structure for V_6^+ is a tetragonal bi-pyramid. This is in agreement with previous results [15], [16], [18], [20] that all predict this structure. Our calculations for V_7^+ indicate that here a strongly distorted pentagonal bi-pyramid is the energetically most stable structure. The structure appears to be similar to the second lowest structure in Refs. [16], [17]. This result seems to be in contrast to previous DFT calculations [16] that suggested an almost symmetrical pentagonal bi-pyramid. The most stable structure for V_8^+ is the same that has been predicted previously for cationic vanadium [16], [17]. We have discussed the details for this isomer in Ref. [9]. A tricapped trigonal prism with approximate 3-fold symmetry is suggested to be the structure that is present in the experiment for V_9^+. We base this interpretation on the presence of 3 peaks in the frequency range 270 cm^{-1} to 340 cm^{-1}. An alternative structure that in fact might be even slightly lower in energy has

only 2 peaks in this region (cf. Ref. [10]).

As mentioned above, we have performed similar studies to determine the structure of larger clusters, e.g. for V_{10}^+ to V_{15}^+. However, for these slightly larger clusters an unambiguous structure determination is not always possible. There are several reasons for this: First, it is possible (and likely) that more than one isomer is present, and that in fact the experimentally observed spectra are a combination of several isomers. But due to space constraints we will not discuss multiple isomers for one size here, and refer the reader to Ref. [10]. An additional complication that arises when larger clusters are considered is the following: The number of possible atomic configuration increases dramatically, and it is very difficult to scan the entire parameter space for larger clusters. It is therefore possible that in particular for the larger clusters we have simply not considered the structure that is actually observed in the experiment. We believe that the development of efficient schemes to test a large number of atomic structure is a major challenge for this type of calculation, and we plan to address this issue in our future work.

5   COMPARISON WITH CATIONIC AND NEUTRAL NIOBIUM CLUSTERS

Following our initial studies on the vanadium cluster cations we measured recently the spectra of cationic as well as neutral niobium clusters using the same experimental technique [11], [22]. A comparison of both metals is interesting, since vanadium and niobium are often similar in their chemical and physical properties. However, the questions that may arise are the following: What are the differences and similarities between cationic vanadium and cationic niobium clusters? What are the differences and similarities between cationic and neutral niobium clusters? Experimentally it has been found that for certain sizes, the spectra for cationic vanadium and niobium clusters are very similar, while for other they are very different. This suggest that the atomic structure of vanadium and niobium clusters are sometimes similar, and very different in other cases. Similarly, for certain sizes the atomic structure for charged and neutral niobium clusters might be very similar, while they might differ more for other sizes. Our initial DFT results indicate that indeed a detailed comparison between calculated and experimentally measured spectra sheds new light on these questions. A detailed description of these results is beyond the scope of this article, and will be reported elsewhere [22].

6   CONCLUSIONS

We have shown that the atomic structure of small metal clusters can be identified by a comparison of ex-

perimental far-infrared spectra with vibrational spectra calculated with DFT. Results for V_4^+ to V_9^+ are presented here. Larger clusters are discussed in more details elsewhere [10]. For some cases, a unique atomic structure can be identified. However, for other cluster sizes an unambiguous identification of the atomic structure was not possible. The reason is that several isomers might be present, or that we simply have not found the correct atomic structure. We propose that more efficient computational schemes are required to scan the parameter space of atomic structures. Nevertheless, we believe that the methodology outlined here is useful to identify the atomic structure of small metal clusters, and in fact small nanoparticles in general.

REFERENCES

[1] I.M.L. Billas, J.A. Becker, A. Chatelain, and W.A. de Heer, Phys. Rev. Lett. **71**, 4067 (1993).

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

[3] K. Lee and J. Callaway, Phys. Rev. B **48**, 15358 (1993).

[4] P. Alvarado, J. Dorantes-Dávila, amd H. Dreyssé. Phys. Rev. B **50**, 1039 (1994).

[5] H. Wu, S.R. Desai, and L.-S. Wang, Phys. Rev. Lett. **77**, 2436 (1996).

[6] M. Iseda, T. Nishio, S.Y. Han, H. Yoshida, A. Terasaki, and T. Kondow, J. Chem. Phys. **106**, 2182 (1997).

[7] M. Valden, X. Lai, and D.W. Goodman, Science **281**, 1647 (1998).

[8] A.T. Bell, Science **299**, 1688 (2003).

[9] A. Fielicke, A. Kirilyuk, C. Ratsch, J. Behler, M. Scheffler, G. von Helden, and G. Meijer, Phys. Rev. Lett. **93**, 023401 (2004).

[10] C. Ratsch, A. Fielicke, A. Kirilyuk, J. Behler, M. Scheffler, G. von Helden, and G. Meijer, J. Chem. Phys., in press (2005).

[11] A. Fielicke, C. Ratsch, G. von Helden, and G. Meijer, J. Chem. Phys., in press (2005).

[12] G. von Helden, D. van Heijnsbergen, and G. Meijer, J. Chem. Phys. **107**, 1671 (2003).

[13] B. Delley, J. Chem. Phys. **92**, 508 (1990).

[14] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[15] H. Grönbeck and A. Rosén, J. Chem. Phys. **107**, 10620 (1997).

[16] X. Wu and A.K. Ray, J. Chem. Phys. **110**, 2437 (1998).

[17] S. Li, M.M.G. Alemany, and J.R. Chelikowsky, J. Chem. Phys. **121**, 5895 (2004).

[18] H. Sun, Y.-H. Luo, J. Zhao, and G. Wang, Phys. Stat. Sol. (b) **215**, 1127 (1999).

[19] J. Zhao, X. Chen, Q. Sun, F. Liu, G. Wang, and K.D. Lain, Physica B **215**, 377 (1995).

[20] A. Tanedo, T. Shimizu, and Y. Kawazoe, J. Phys. Cond. Matt. **13**, L305 (2001).

[21] S. Minemoto, A. Terasaki, and T. Kondow, J. Electron Spectroscopy **106**, 171 (2000).

[22] A. Fielicke, C. Ratsch, G. von Helden, and G. Meijer, in preparation.