

Model Systems for Probing Metal Cation Hydration

Central to understanding the bulk solvation of metal ions is the interaction of the individual ions and solvent molecules. Metal-cation/water complexes are of the most fundamental interest. However, the details of metal-solvation processes are difficult to determine experimentally, and gas-phase spectroscopic structures of water molecules in contact with a metal cation are rare in the literature.

Photodissociation spectroscopy has been used previously for many metal-ligand complexes to obtain vibrationally resolved spectra for electronic states, as well as rotationally resolved spectra that have provided some of the first direct structural determinations for these molecules. Beginning in the early and mid-1990s, several research groups investigated the electronic spectra of metal cation-water complexes,¹⁻¹¹ using size selection with various forms of mass spectrometry and laser photodissociation spectroscopy. In one of the first of these studies, Brucat and coworkers measured a vibrationally resolved electronic spectrum for $V^+(H_2O)$.¹ Electronic spectra of the alkaline earth cations Mg^+ and Ca^+ in complexes with water were studied by the Duncan group²⁻⁴ and that of Fuke.⁵⁻⁷ More recently, these studies have been extended to other metals⁸ and have included doubly charged ions.⁹⁻¹¹ Duncan and coworkers described the ZEKE photoelectron spectroscopy of $Al^+(H_2O)$ with partial rotational resolution.¹²

Lisy *et al.*¹³⁻¹⁶ were the first to apply *infrared* photodissociation spectroscopy (IRPD) to metal-ion/ligand systems, including alkali-cation/water complexes. Beginning in 2002, more extensive mass-selected IRPD studies were executed within the Duncan group on a variety of main group transition-metal/ligand complexes produced by laser vaporization sources.¹⁷⁻²⁷ In some of the most recent work, these IRPD studies were extended to various $M^+(H_2O)_n$ complexes ($M=V, Fe, Ni$).^{21,25-27} In 2004 Nishi and coworkers^{28,29} reported similar studies on $Mg^+(H_2O)$ and $Al^+(H_2O)$.

A stronger metal-ligand bond in complexes with a transition metal, as compared to alkali metals,³⁰⁻³⁷ makes these systems challenging candidates for spectroscopy. The bond energy of transition-metal-cation/water complexes is too high for single-photon infrared photodissociation; therefore, multiphoton dissociation or “argon tagging” is necessary. The principle behind “argon tagging” is that clusters with rare gas atoms loosely attached have dissociation channels that are accessible at lower photon energies, thus allowing mass spectrometric detection of infrared absorption across wider frequency ranges. It is generally assumed that the argon in such mixed complexes acts as a spectator and does not induce significant structural changes in the clusters or shift the vibrations by substantial amounts.

Recently, the Duncan group applied mass-selected IRPD spectroscopy to the vanadium-cation/water complex.²¹ This study provided the first gas-phase IR data on a transition-metal-cation/water system. Vanadium was chosen because it has a single isotope, thus simplifying the mass analysis. Additionally, the binding energies of V^+ to H_2O or to Ar have been measured previously.^{31,32,34,38,39} $V^+(H_2O)$, $V^+(H_2O)Ar_n$, $V^+(D_2O)$ and $V^+(D_2O)Ar_n$ were produced by laser vaporization of a metal target rod and entrainment in an Ar expansion gas. The observation of widely spaced rotational structure indicates that the argon atom attaches to the vanadium cation on the opposite side of the water molecule. After mass selecting the target species, the O-H and O-D stretches in the water moiety were vibrationally excited, and fragment-ion versus energy photodissociation spectra were recorded.

The IRPD spectrum of $ArV^+(H_2O)$ contains peaks at 3605 and 3690 cm^{-1} .²¹ These bands are $\sim 50\text{ cm}^{-1}$ and $\sim 70\text{ cm}^{-1}$ to the red of the symmetric (3657 cm^{-1}) and antisymmetric (3756 cm^{-1}) stretches in free water, respectively. Scaled vibrational frequencies of $ArV^+(H_2O)$ derived from the B3LYP/6-31G* level of theory (3642 and 3700 cm^{-1}) agree qualitatively with the measured red shifts. For the theoretically predicted 5B_1 ground state, the DFT computed H-O-H angle is 107.5°.

The rotational constants of $ArV^+(H_2O)$, corresponding to the Ar-V-O principal axis, surmised from the profile of the IRPD spectrum of the H_2O antisymmetric stretch were $A' = 7.96\text{ cm}^{-1}$ and $A'' = 12.52\text{ cm}^{-1}$, for the upper ($v_3 = 1$) and lower ($v_3 = 0$) vibrational levels, respectively.²¹ The A'' value would indicate an H-O-H angle (113.8°) much

more expanded upon complexation than predicted by B3LYP/6-31G* density functional theory. The large difference between A' and A'' would point to a prodigious vibrationally-averaged geometry distortion in the complex for the O-H antisymmetric stretching fundamental level.

Prior to the IRPD experiment performed by Duncan's group,²¹ the $V^+(H_2O)$ complex was probed by various experimental methods, including collision induced dissociation (CID),^{31,32,34} resonant one-photon dissociation spectroscopy,¹ and charge stripping mass spectrometry.³⁸ The vanadium-cation/water complex showed characteristics of an electrostatically bound species, with a dissociation energy $D_0 = 35 \pm 4$ kcal mol⁻¹ and a V-O stretching frequency $\omega_e'' = 420 \pm 75$ cm⁻¹. V^+Ar was studied with electronic spectroscopy by Brucat, which provided a binding energy for this system of 8.76 kcal mol⁻¹.³⁹

Various computational methods have been applied to $V^+(H_2O)$, including the modified coupled pair functional (MCPF) approach,^{40,41} Møller-Plesset perturbation theory,^{42,43} configuration interaction,⁴² density functional theory^{38,44-46} and limited coupled cluster methods.^{38,43-45} These theoretical studies focused on structures and dissociation energies for the ground state (5A_1) and the lowest-lying (5A_2 , 5B_1 , 5B_2) states. Also it was confirmed that the HV^+OH intermediate, hypothesized by experimentalists,³¹ is a well-defined minimum on the potential energy surface, lying 53.8 kcal mol⁻¹ above $V^+(H_2O)$.⁴⁴ To our knowledge, no theoretical data is available for the $ArV^+(H_2O)$ complex.

Motivated by the IRPD experiments, we thoroughly investigated $V^+(H_2O)$ and $ArV^+(H_2O)$ by high-level electronic structure theory as model systems for metal cation hydration.⁴⁷ Our best predictions were based on restricted open-shell CCSD(T) theory implemented with a massive $V[11s6p5d3f2g]$, $Ar[9s6p4d2f1g]$, $O[6s5p4d3f2g]$, and $H[5s4p3d2f]$ (QZVPP) basis set, and with the outer-core $V(3s,3p)$ electrons correlated. The microsolvation of V^+ with one water molecule gives an equilibrium V-O distance of 2.049 Å and a binding energy (D_0) of 36.2 kcal mol⁻¹. Monohydration of V^+ shifts the H_2O fundamentals (ν_1, ν_2, ν_3) by $(-43, +26, -72)$ cm⁻¹. Our computed red shifts for the O-H stretching modes (ν_1, ν_3) are in excellent agreement with the IRPD results ($\sim 50, \sim 70$) cm⁻¹ from the Duncan laboratory.²¹ When H_2O binds to V^+ , the H-O-H equilibrium bond angle widens by $+2.4^\circ$, with a concomitant increase in the O-H distance of $+0.004$ Å. The H_2O molecule splits the degenerate ground-state manifold of $V^+({}^5D)$, yielding electronic states in C_{2v} symmetry with the following relative energies: $T_e({}^5A_1, {}^5A_2, {}^5B_1, {}^5B_2) = (0, 0.15, 0.37, 5.09)$ kcal mol⁻¹. A second 5A_1 state of $V^+(H_2O)$ appears somewhat higher in energy, and the lowest-lying triplet state is more than 15 kcal mol⁻¹ above the ground 5A_1 state.

Argon tagging of $V^+(H_2O)$ places the Ar atom 2.538 Å from the V^+ center and 180° removed from the H_2O ligand, as sketched in Fig. 1. Theoretical argon dissociation curves for $ArV^+(H_2O)$ are shown in Fig. 2. The argon binding energy is $D_0 [Ar-V^+(H_2O)] = 9.4$ kcal mol⁻¹. Surprisingly, virtually none of this binding energy is obtained with Hartree-Fock theory, which yields only a 0.25 kcal mol⁻¹ stabilization even with the large QZVPP basis set. Argon tagging engenders only small perturbations in the $V^+(H_2O)$ structure: $\delta r_e(V-O) = -0.0105$ Å, $\delta r_e(O-H) = +0.0003$ Å, and $\delta \theta_e(H-O-H) = -0.14^\circ$. However, the Ar "spectator" is responsible for a number of subtle effects, such as switching the electronic ground state. For $ArV^+(H_2O)$ our best theory predicts a 5B_1 ground state and excitation energies $T_e({}^5A_1, {}^5A_2, {}^5B_2) = (0.49, 0.62, 4.17)$ kcal mol⁻¹. Argon tagging shifts the vibrational frequencies of $V^+(H_2O)$ by no more than 10 cm⁻¹, but the direction of the shift is in most cases dependent on whether the final electronic state in question is 5A_1 or 5B_1 .

An analysis of vibrational anharmonicity effects in $V^+(H_2O)$ and $ArV^+(H_2O)$ was executed by computing complete quartic force fields and then applying second-order vibrational perturbation theory (VPT2) to determine anharmonic constants and vibration-rotation interaction constants. This approach probes inherent anharmonic vibrational properties of single electronic states in these species. For free H_2O our quartic force fields reproduce the observed O-H stretching fundamentals to within 5 cm⁻¹, bolstering confidence in our analogous results for $V^+(H_2O)$ and $ArV^+(H_2O)$. Our vibration-rotation interaction constants allow quantification of the influence of zero-point vibrational (ZPV) averaging on the molecular structures of $V^+(H_2O)$ and $ArV^+(H_2O)$. A peculiar phenomenon is observed for the *effective* bond angle $\theta_0(H-O-H)$, specifically, a ZPV increase of 2° - 3° as a consequence of off-axis

motion of the heavy vanadium atom, as opposed to flattening and/or skewing of the water bending potential. Nonetheless, the total complexation effect on the water bond angle computed here (about $+4^\circ$) is substantially less than the 9° widening surmised from the IRPD experiments.²¹ Thermal averaging over excited vibrational states in the $V^+(H_2O)$ and $ArV^+(H_2O)$ complexes might increase the effective H-O-H angle more and further reduce the disparity between theory and experiment. However, it is clear that the interpretation of geometric parameters extracted from IRPD profiles is complicated by numerous effects, and thus care must be taken in equating effective bond angle widening with changes in electronic structure upon complexation.

A number of issues of theoretical interest were encountered in our study of $V^+(H_2O)$ and $ArV^+(H_2O)$: (1) The $V^+(H_2O)$ binding energy appears to be very sensitive to vanadium ($3s,3p$) core electron correlation. (2) There is large quartic anharmonicity in the H_2O wagging mode in $V^+(H_2O)$ and $ArV^+(H_2O)$. (3) Curve crossings within the lowest-lying quintet manifold of $ArV^+(H_2O)$ occur near the equilibrium geometry, giving rise to anomalous force constants in the local representations of the potential energy surfaces of some of the electronic states. These crossings arise along the Ar-V stretching mode, and thus are precipitated by the presence of the argon “spectator” atom. (4) Finally, the intricate vibronic coupling within the (${}^5A_1, {}^5A_2, {}^5B_1, {}^5B_2$) manifold of $V^+(H_2O)$ and $ArV^+(H_2O)$ remains unexplored. All of these issues would be worthy targets of future investigations.

Our investigation⁴⁷ of the $V^+(H_2O)$ and $ArV^+(H_2O)$ systems is the first in a series of high-level theoretical studies on metal cation hydration. The possibilities for investigating other transition-metal cations complexed with various numbers of water molecules and Ar atoms are virtually endless. Moreover, the alkali-metal systems $Ar_mM^+(H_2O)_n$ are prime candidates for theoretical/experimental collaborations because their spectroscopy is not complicated by the presence of numerous close-lying electronic states coupled vibronically. In addition to obtaining definitive theoretical structures and thermochemistry at or near the *ab initio* limit, the computation of anharmonic potential energy surfaces for hydrated metal cations promises to elucidate the vibrational dynamics that determine the IRPD signatures of these systems.

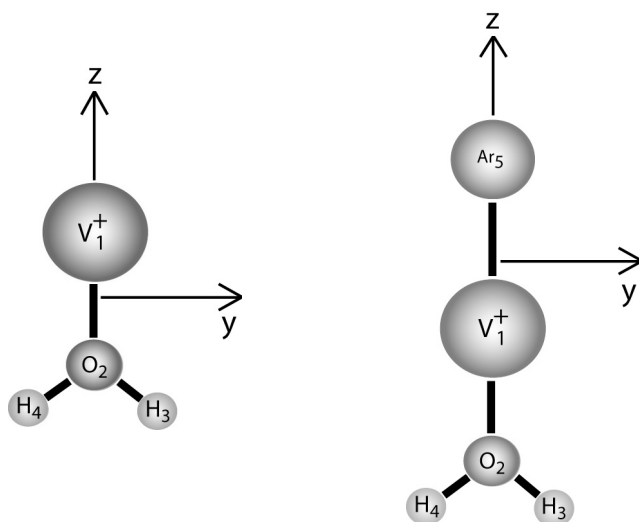


Figure 1. The C_{2v} structures of the (a) $V^+(H_2O)$ and (b) $ArV^+(H_2O)$ complexes.

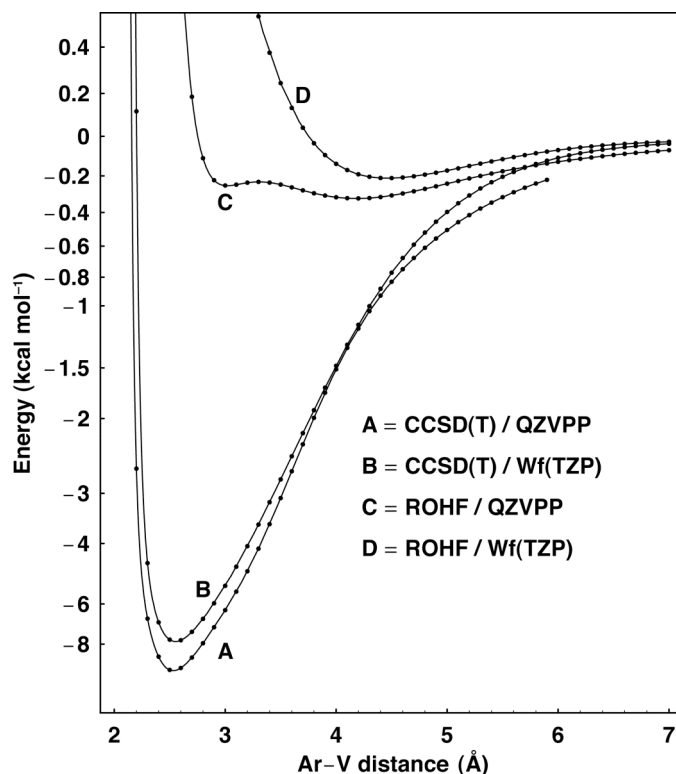


Figure 2. Theoretical argon dissociation curves for the 5A_1 state of $\text{ArV}^+(\text{H}_2\text{O})$. In this plot $\text{V}^+(\text{H}_2\text{O})$ is fixed at its optimum structure for the corresponding level of theory; only the Ar-V distance was changed. Note the nonuniform scale on the energy axis, which is necessary to reveal the shallow ROHF minima.

References

- (1) Lessen, D. E.; Asher, R. L.; Brucat, P. J. *J. Chem. Phys.* **1990**, *93*, 6102.
- (2) Willey, K. F.; Yeh, C. S.; Robbins, D. L.; Pilgrim, J. S.; Duncan, M. A. *J. Chem. Phys.* **1992**, *97*, 8886.
- (3) Scurlock, C. T.; Pullins, S. H.; Reddic, J. E.; Duncan, M. A. *J. Chem. Phys.* **1996**, *104*, 4591.
- (4) Duncan, M. A. *Annu. Rev. Phys. Chem.* **1997**, *48*, 69.
- (5) Sanekata, M.; Misaizu, F.; Fuke, K. *J. Chem. Phys.* **1996**, *104*, 9768.
- (6) Misaizu, F.; Sanekata, M.; Tsukamoto, K.; Fuke, K.; Iwata, S. *J. Phys. Chem.* **1992**, *96*, 8259.
- (7) Fuke, K.; Hashimoto, K.; Iwata, S. *Adv. Chem. Phys.* **1999**, *110*, 431.
- (8) Abate, Y.; Kleiber, P. D. *J. Chem. Phys.* **2005**, *122*, 084305.
- (9) Thompson, C. J.; Husband, J.; Aguirre, F.; Metz, R. B. *J. Phys. Chem. A* **2000**, *104*, 8155.
- (10) Faherty, K. P.; Thompson, C. J.; Aguirre, F.; Michne, J.; Metz, R. B. *J. Phys. Chem. A* **2001**, *105*, 10054.
- (11) Thompson, C. J.; Aguirre, F.; Husband, J.; Metz, R. B. *J. Phys. Chem. A* **2000**, *104*, 9901.
- (12) Agreiter, J. K.; Knight, A. M.; Duncan, M. A. *Chem. Phys. Lett.* **1999**, *313*, 162.
- (13) Lisy, J. M. *Int. Rev. Phys. Chem.* **1997**, *16*, 267.
- (14) Cabarcos, O. M.; Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1998**, *108*, 5151.
- (15) Cabarcos, O. M.; Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1999**, *110*, 8429.
- (16) Vaden, T. D.; Forinash, B.; Lisy, J. M. *J. Chem. Phys.* **2002**, *117*, 4628.
- (17) Gregoire, G.; Duncan, M. A. *J. Chem. Phys.* **2002**, *117*, 2120.

- (18) van Heijnsbergen, D.; von Helden, G.; Meijer, G.; Maitre, P.; Duncan, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 1562.
- (19) Walters, R. S.; Jaeger, T.; Duncan, M. A. *J. Phys. Chem. A* **2002**, *106*, 10482.
- (20) Duncan, M. A. *Int. Rev. Phys. Chem.* **2003**, *22*, 407.
- (21) Walker, N. R.; Walters, R. S.; Pillai, E. D.; Duncan, M. A. *J. Chem. Phys.* **2003**, *119*, 10471.
- (22) Jaeger, T.; Pillai, E. D.; Duncan, M. A. *J. Phys. Chem. A* **2004**, *108*, 6605.
- (23) Walker, N. R.; Walters, R. S.; Duncan, M. A. *J. Chem. Phys.* **2004**, *120*, 10037.
- (24) Walker, N. R.; Walters, R. S.; Grieves, G. A.; Duncan, M. A. *J. Chem. Phys.* **2004**, *121*, 10498.
- (25) Walters, R. S.; Duncan, M. A. *Aust. J. Chem.* **2003**, *57*, 1145.
- (26) Walker, N. R.; Walters, R. S.; Tsai, M.-K.; Jordan, K. D.; Duncan, M. A. *J. Phys. Chem. A* **2005**, *109*, 7057.
- (27) Walters, R. S.; Pillai, E. D.; Duncan, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 16599.
- (28) Inokuchi, Y.; Ohshimo, K.; Misaizu, F.; Nishi, N. *J. Phys. Chem.* **2004**, *108*, 5034.
- (29) Inokuchi, Y.; Ohshimo, K.; Misaizu, F.; Nishi, N. *Chem. Phys. Lett.* **2004**, *390*, 140.
- (30) *Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer: Dordrecht, 1996.
- (31) Magnera, T. F.; David, D. E.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 4100.
- (32) Marinelli, P. J.; Squires, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 4101.
- (33) Clemmer, D. E.; Chen, Y.-M.; Aristov, N.; Armentrout, P. B. *J. Phys. Chem.* **1994**, *98*, 7538.
- (34) Dalleska, N. F.; Honma, K.; Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 3519.
- (35) *Gas Phase Metal Ion Chemistry*, edited by J. A. Leary and P. B. Armentrout, special issue of *Int. J. Mass Spectrom.* **2001**, *204*, 1.
- (36) Duncan, M. A. *Adv. Met. Semicond. Clusters* **2002**, *5*.
- (37) Armentrout, P. B. *Int. J. Mass Spectrom.* **2003**, *227*, 289.
- (38) Schröder, D.; Engeser, M.; Schwarz, H.; Harvey, J. N. *ChemPhysChem* **2002**, *3*, 584.
- (39) Lessen, D.; Brucat, P. J. *J. Chem. Phys.* **1989**, *91*, 4522.
- (40) Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1989**, *90*, 7264.
- (41) Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1990**, *92*, 1876.
- (42) Magnusson, E.; Moriarty, N. W. *J. Comp. Chem.* **1993**, *14*, 961.
- (43) Trachtman, M.; Markham, G. D.; Glusker, J. P.; George, P.; Bock, C. W. *Inorg. Chem.* **1998**, *37*, 4421.
- (44) Irgoras, A.; Fowler, J. E.; Ugalde, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 574.
- (45) Klippenstein, S. J.; Yang, C.-N. *Int. J. Mass Spectrom.* **2000**, *201*, 253.
- (46) Dunbar, R. C. *J. Phys. Chem. A* **2002**, *106*, 7328.
- (47) Kasalová, V.; Allen, W. D.; Schaefer, H. F.; Pillai, E. D.; Duncan, M. A. *J. Phys. Chem. A* **2007**, *111*, 7599.