Infrared Spectroscopy of Extreme Coordination: The Carbonyls of U$^+$ and UO$_2$$^+$

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Abstract: Uranium and uranium dioxide carbonyl cations produced by laser vaporization are studied with mass-selected ion infrared spectroscopy in the C−O stretching region. Dissociation patterns, spectra, and quantum chemical calculations establish that the fully coordinated ions are U(CO)$_8$$^+$ and UO$_2$(CO)$_5$$^+$, with D_{4d} square antiprism and D_{5h} pentagonal bipyramid structures. Back-bonding in U(CO)$_8$$^+$ causes a red-shifted CO stretch, but back-donation is inefficient for UO$_2$(CO)$_5$$^+$, producing a blue-shifted CO stretch characteristic of nonclassical carbonyls.

The coordination of actinide metals has important implications for energy and the environment,[1−3] but the electronic structure and bonding in these systems present significant challenges for experiments and theory.[4] In aqueous solutions uranium exists as the uranyl cation, UO$_2$$^{2+}$, which has a closed shell $^1\Sigma_g^+$ electronic structure.[3] EXAFS measurements of aqueous UO$_2$$^{2+}$ cations reveal D_{5h} pentagonal bipyramidal UO$_2$(H$_2$O)$_5$$^{2+}$ structures;[3,5,6] reduction of the uranium generates eight-coordinate U(H$_2$O)$_8$$^{4+}$ ions.[3,5] Recent spectroscopy experiments have isolated uranium and its oxides in rare gas matrices or in the gas phase to probe the intrinsic structure and bonding in these systems,[7−11] and computational studies have complemented this work.[11−13] Selected complexes have been investigated to explore solvation and coordination.[14−18] However, the number of complexes studied is limited, particularly regarding those of the bare U$^+$ cation. Metal carbonyls provide classic examples of ligand bonding, and infrared spectroscopy is a sensitive indicator for the electronic structure and geometries of these systems.[3,19] In early work, U(CO)$_6$ was targeted for the Manhattan project but never successfully synthesized.[1] Small uranium carbonyls have been produced in matrix isolation experiments[20,21] and studied with theory,[8,22,23] but apparently no stable uranium carbonyl has been produced. Here we report the production of gas phase U$^+$ and UO$_2$$^+$ carbonyl *cations* and their study with infrared spectroscopy in the C−O stretching region.

The well-known 18-electron rule, describing the number of metal and ligand electrons that give the s^{2}p^{6}d^{10} noble gas configuration, provides qualitative predictions for the coordination and structures of many transition metal complexes.[3] Many isovalent variants of known complexes can be rationalized with electron counting, including ionized systems with either positive or negative charges. Our group has recently studied isolated carbonyl ions in the gas phase, where this rule continues to influence coordination even for seven-coordinate species.[24−28] For actinides and lanthanides with f electrons, the corresponding filled s^{2}p^{6}d^{10}f^{14} configuration requires 32 electrons, but steric effects preclude the high coordination
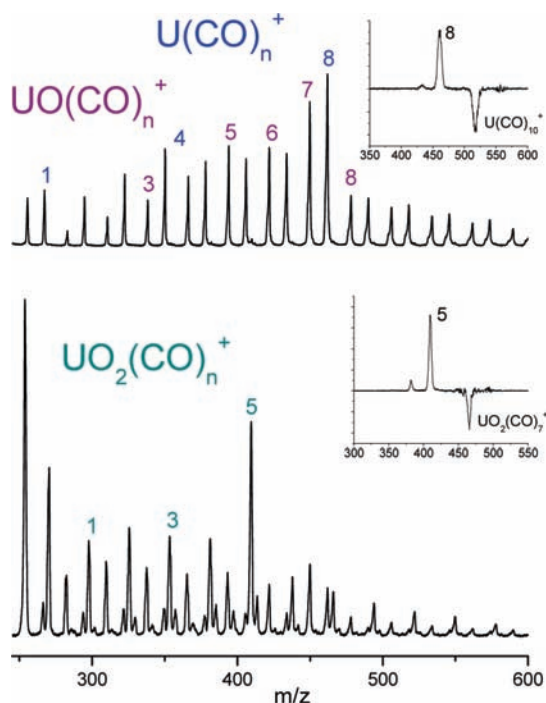

Figure 1. Mass spectra of U$^+$ and UO$_2$$^+$ carbonyl ions. The insets show representative fragmentation of clusters beyond the coordination.

numbers needed to achieve this.[3,29] However, the d orbitals in actinides are usually less important in bonding, and therefore stable actinide systems often have 22 electrons (e.g., U(C$_8$H$_8$)$_2$).[30] Because they have an odd number of electrons, U$^+$ and UO$_2$$^+$ cations cannot form 22-electron carbonyls, but they closely approach this electron count.

Uranium ions are generated by laser vaporization (Nd:YAG @ 355 nm; Spectra Physics INDI 30) of a depleted metal rod offset 2 cm from the flow of a pulsed gas valve (General Valve Series 9).[31] Coincident with vaporization, carbon monoxide gas or a mixture of 10% O$_2$ in CO is expanded through the pulsed valve; metal ion entrainment and subsequent cooling in a supersonic expansion produce cold complexes. These conditions produce primarily singly charged ions; we were not able to produce the UO$_2$$^{2+}$ carbonyls. The expansion is skimmed into a second chamber where cations are pulse-extracted into a reflectron time-of-flight mass spectrometer. Pulsed deflection plates select the ion of interest, which is then excited with an infrared laser in the turning region of the reflectron. A tunable optical parametric oscillator/amplifier (OPO/OPA, LaserVision) pumped with the fundamental output of a Nd:YAG laser (Spectra Physics Pro-230) provides infrared wavelengths in the 600−4500 cm^{-1} region. Because the ion density is too low for absorption spectroscopy, we use photodissociation
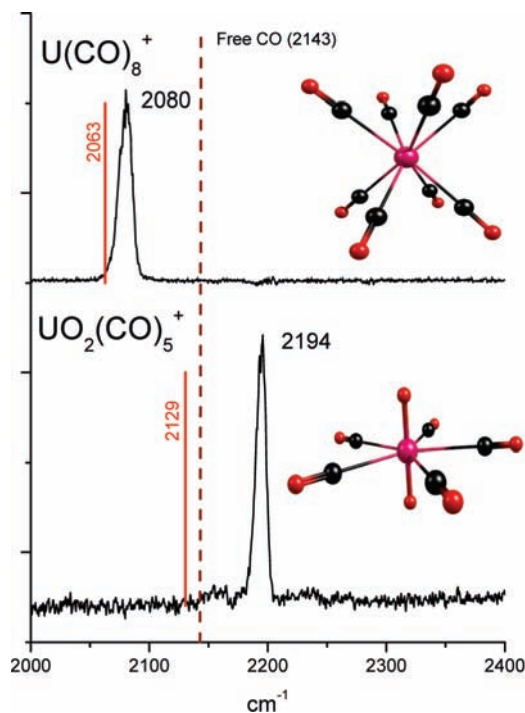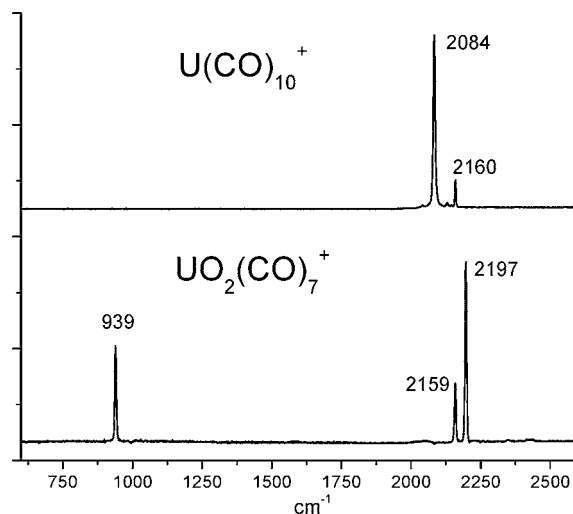
Figure 2. Infrared spectra of $U(CO)_8^+$ and $UO_2(CO)_5^+$ ions. The red vertical lines indicate the computed frequencies.[34]

to detect the vibrational spectra. Resonant absorption leads to fragmentation of the ion complex provided there is a bond weaker than the energy of the photon used for vibrational excitation. If IR absorption is strong, multiple photon fragmentation is also possible, even with the modest laser energies available (∼1 mJ/pulse). The fragment ion yield from a selected complex as a function of laser wavelength provides the spectrum. Density Functional Theory (DFT) computations were performed using the PBE functional[32] and the Turbomole program.[33] The VTZP basis set was used for carbon and oxygen, and the SDD small core (30 electron) pseudopotential was used for uranium.

Mass spectra of uranium and uranium oxide carbonyls (Figure 1) demonstrate the production of complexes containing up to $10-15$ CO's bound to U^+, UO^+, or UO_2^+ ions. These cluster ions contain both strongly bound ligands and weakly bound "excess" ligands which condense because of the cold supersonic beam conditions.[26-28] Enhanced abundances in mass spectra are found for $U(CO)_8^+$ (upper spectrum) and $UO_2^+(CO)_5$ (lower). The upper inset shows the fragmentation of $U(CO)_{10}^+$ obtained by subtracting a mass spectrum with the laser off from one with it on. Infrared excitation "burns" off excess ligands because of their weak binding, leaving the fully coordinated ion. In this and other experiments on larger $U(CO)_n^+$ ions, the abundant survivor is invariably $U(CO)_8^+$. Similar experiments on $UO_2(CO)_n^+$ ions (lower inset) produce $UO_2(CO)_5^+$ as the survivor. $U(CO)_8^+$ and $UO_2(CO)_5^+$ therefore represent the fully coordinated carbonyls of U^+ and UO_2^+. $U(CO)_8^+$ has 21 electrons, and $UO_2(CO)_5^+$ has 19.

The infrared spectra of $U(CO)_8^+$ and $UO_2(CO)_5^+$ ions obtained by monitoring the loss of CO from the parent ion are shown in Figure 2 along with predicted structures and spectra. The spectrum of each ion has a single peak, indicating a symmetric structure. Computations (see Supporting Information) on $U(CO)_8^+$ find an eight-coordinate complex with a D_{4d} square antiprism geometry; the ground electronic state is a sextet, but the quartet lies only 4.45 kcal/mol higher. Computations on $UO_2(CO)_5^+$ find a linear UO_2^+ core ion surrounded by five equivalent CO ligands around its waist,

Figure 3. Infrared spectra of $U(CO)_{10}^+$ and $UO_2(CO)_7^+$ ions, showing the "core ion" carbonyl bands, the "external" CO bands near 2160 cm^{-1}, and the oxide stretch at 939 cm^{-1}.

with a doublet ground electronic state. The isolated UO_2^+ ion also has a doublet ground state, $^2\Phi_{5/2,u}$.[7] The D_{5h} geometry is similar to that observed for aqueous $UO_2(H_2O)_5^{2+}$ ions[2-5] and predicted by theory for rare gas $UO_2^+(RG)_5$ complexes.[8] According to theory, the binding energies of CO to $U(CO)_8^+$ and $UO_2(CO)_5^+$ are 19.1 kcal/mol (6680 cm^{-1}) and 13.0 kcal/mol (4547 cm^{-1}) respectively (zero point included, but not counterpoise corrected). Photodissociation near 2200 cm^{-1} is therefore most likely a multiphoton process. However, the IR intensities computed are extremely high (∼1000 km/mol), making it understandable that multiphoton absorption could occur. The single CO stretch of $U(CO)_8^+$ at 2080 cm^{-1} is shifted 63 cm^{-1} to the red from the frequency of gas phase carbon monoxide (2143 cm^{-1}), while that of $UO_2(CO)_5^+$ at 2194 cm^{-1} is 51 cm^{-1} to the *blue* from the gas phase CO value and 114 cm^{-1} to the blue from the band of $U(CO)_8^+$. The single-band spectra and their frequencies are in reasonable agreement with the predictions of theory for the D_{4d} and D_{5h} structures, respectively.[34] However, $UO_2(CO)_5^+$ is predicted to have a small red shift compared to free-CO rather than a blue shift. In complexes having more ligands than these fully coordinated ones (Figure 3), an additional band assigned to external CO molecules[26-28] is detected near 2160 cm^{-1}, confirming the coordination numbers. Because of the weakly bound external ligands, photodissociation for these larger clusters is more efficient and can be measured at lower energy, allowing the asymmetric O−U−O stretch of $UO_2(CO)_n^+$ to be detected at 939 cm^{-1} (lower trace, Figure 3), in agreement with theory (computed at 931 cm^{-1}). For comparison to the latter, the asymmetric stretch of bare UO_2^+ was measured previously isolated in a neon matrix at 980 cm^{-1},[7] and in an argon matrix at 952 cm^{-1}.[8] The symmetric oxide stretch of gas phase UO_2^+ has been detected at 919 cm^{-1} in a ZEKE photoelectron spectrum.[10] The corresponding asymmetric stretch of the UO_2^{2+} uranyl dication has been detected near $930-950$ cm^{-1} in its complexes.[11-13] This oxide stretch apparently varies with charge state and ligand/solvent environment.

As noted before, the shift in the CO stretch in metal carbonyls is dominated by π-type back-donation from the metal orbitals into the antibonding orbitals of CO.[3,19,35] A red-shifted CO stretch implies significant back-bonding, as seen for many transition metal carbonyls with partially filled d orbitals.[3,16] Significantly smaller red shifts are seen for *cation* transition metal complexes,[26-28] which exhibit less back-donation because of their positive charge. A blue

shift is often observed for "nonclassical" carbonyls[36] with filled d shells such as Au^+ or Pt^+,[24,25] which have essentially no back-donation. The red-shifted C—O stretch of $U(CO)_8^+$ has a frequency comparable to those seen for *neutral* transition metal carbonyls with significant back-bonding.[19] In the unusual +1 oxidation state here, uranium has five unpaired electrons, which, according to CASSCF/CASPT2 calculations,[37] reside primarily in the 5f and 7s orbitals. Apparently, back-donation from f orbitals is also quite efficient, even though the spatial overlap is quite different from that of d orbitals. The blue shift for the C—O stretch of $UO_2^+(CO)_5$ is comparable to those seen before for nonclassical carbonyls.[24,25] Like these metals, the uranium in $UO_2(CO)_5^+$ has no open d shell and only a single f electron, and therefore back-bonding is not efficient. These conclusions are supported by a Mulliken charge analysis, as presented in the Supporting Information.

We have previously reported seven-coordinate carbonyls of niobium and tantalum cations,[27] but to our knowledge $U^+(CO)_8$ is the first example of an eight-coordinate homoleptic carbonyl. $UO_2(CO)_5^+$ is analogous to the uranyl hydrate $UO_2^{2+}(H_2O)_5$ believed to be present in aqueous uranium solutions[3,5,6] and to $UO_2^+(RG)_5$ complexes detected in rare gas matrices.[8] These new U^+ and UO_2^+ complexes therefore extend the range of coordination numbers known for metal carbonyls and provide new glimpses of ligand interactions and coordination for the actinide metals.

Supporting Information Available: Computational results and additional infrared spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Katz, J. J.; Rabinowitch, E. *The Chemistry of Uranium*; McGraw Hill: New York, 1951.
(2) Cotton, S. A. *Lanthanide and Actinide Chemistry*; John Wiley & Sons: Hoboken, NJ, 2006.
(3) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry Principles of Structure and Reactivity*, 4th ed.; Harper Collins: New York, 1993.
(4) Gagliardi, L.; Roos, B. O. *Chem. Soc. Rev.* **2007**, *36*, 893.
(5) Hennig, C.; Tutschku, J.; Rossberg, A.; Bernhard, G.; Scheinost, A. C. *Inorg. Chem.* **2005**, *44*, 6655.
(6) Hagberg, D.; Karlström, G.; Roos, B. O.; Gagliardi, L. *J. Am. Chem. Soc.* **2005**, *127*, 14250.
(7) Zhou, M.; Andrews, L.; Ismail, N.; Marsden, C. *J. Phys. Chem. A* **2000**, *104*, 5495.
(8) Wang, X.; Andrews, L.; Li, J.; Bursten, B. E. *Angew. Chem., Int. Ed.* **2004**, *43*, 2554.
(9) Goncharov, V.; Kaledin, L. A.; Heaven, M. C. *J. Chem. Phys.* **2006**, *125*, 133202.
(10) Merritt, J. M.; Han, J.; Heaven, M. C. *J. Chem. Phys.* **2008**, *128*, 084303.
(11) Gagliardi, L.; Heaven, M. C.; Krogh, J. W.; Roos, B. O. *J. Am. Chem. Soc.* **2005**, *127*, 86.
(12) Majumdar, D.; Balasubramanian, K.; Nitsche, H. *Chem. Phys. Lett.* **2002**, *361*, 143.
(13) Réal, F.; Gomes, A. S. P.; Visscher, L.; Vallet, V.; Eliav, E. *J. Phys. Chem. A* **2009**, *113*, 12504.
(14) Groenewold, G. S.; Oomens, J.; de Jong, W. A.; Gresham, G. L.; McIlwain, M. E.; Van Stipdonk, M. J. *Phys. Chem. Chem. Phys.* **2008**, *10*, 1192.
(15) Groenewold, G. S.; Van Stipdonk, M. J.; de Jong, W. A.; Oomens, J.; Gresham, G. L.; McIlwain, M. E.; Gao, D.; Siboulet, B.; Visscher, L.; Kullman, M.; Polfer, N. *Chem. Phys. Chem.* **2008**, *9*, 1278.
(16) Groenewold, G. S.; de Jong, W. A.; Oomens, J.; Van Stipdonk, M. J. *J. Am. Soc. Mass Spectrom.* **2010**, *21*, 719.
(17) Nichols, P.; Bylaska, E. J.; Schenter, G. K.; de Jong, W. A. *J. Chem. Phys.* **2008**, *128*, 124507.
(18) Bryanstev, V. S.; de Jong, W. A.; Cossel, K. C.; Dialo, M. S.; Goddard, W. A., III; Groenewold, G. S.; Chien, W.; Van Stipdonk, M. J. *J. Phys. Chem. A* **2008**, *112*, 5777.
(19) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley: New York, 1997.
(20) Slater, J. L.; Sheline, R. K.; Lin, K. C.; Weltner, W. *J. Chem. Phys.* **1971**, *55*, 5129.
(21) Zhou, M.; Andrews, L.; Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **1999**, *121*, 9712.
(22) Malli, G. L. *J. Chem. Phys.* **2006**, *124*, 021102.
(23) Sonnenberg, J. L.; Hay, P. J.; Martin, R. L.; Bursten, B. E. *Inorg. Chem.* **2005**, *44*, 2255.
(24) Velasquez, J., III; Njegic, B.; Gordon, M. S.; Duncan, M. A. *J. Phys. Chem. A* **2008**, *112*, 1907.
(25) Velasquez, J., III; Duncan, M. A. *Chem. Phys. Lett.* **2008**, *461*, 28.
(26) Ricks, A. M.; Bakker, J. M.; Douberly, G. E.; Duncan, M. A. *J. Phys. Chem. A* **2009**, *113*, 4701.
(27) Ricks, A. M.; Reed, Z. D.; Duncan, M. A. *J. Am. Chem. Soc.* **2009**, *131*, 9176.
(28) Reed, Z. D.; Duncan, M. A. *J. Am. Soc. Mass Spectrom.* **2010**, *21*, 739.
(29) (a) Dognon, J.-P.; Clavaguéra, C.; Pyykkö, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 1427. (b) Dognon, J.-P.; Clavaguéra, C.; Pyykkö, P. *J. Am. Chem. Soc.* **2009**, *131*, 238.
(30) Long, N. J. *Metallocenes: An Introduction to Sandwich Complexes*; Blackwell Sciences Ltd.: Oxford, U.K., 1998.
(31) Duncan, M. A. *Intl. Rev. Phys. Chem.* **2003**, *22*, 407.
(32) (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865. (b) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396.
(33) Ahlrichs, R.; Bar, M.; Haser, M.; Horn, H.; Kolmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.
(34) Computed vibrations are shifted by $+11$ cm^{-1} to bring the computed frequency for free-CO into agreement with experiment.
(35) Diefenbach, A.; Bickelhaupt, F. M.; Frenking, G. *J. Am. Chem. Soc.* **2000**, *122*, 6449.
(36) (a) Lupinetti, A. J.; Frenking, G.; Strauss, S. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 2113. (b) Lupinetti, A. J.; Strauss, S. J.; Frenking, G. *Prog. Inorg. Chem.* **2001**, *49*, 1.
(37) Andersson, K.; Malmquist, P.-A.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

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