IRMPD OF CATIONIC URANYL COMPLEXES IN THE GAS PHASE

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Introduction

Mass spectrometry is an attractive approach for investigating metal complexes because ions having a defined composition can be formed and isolated in the solvent-controlled atmosphere of a Fourier transform ion cyclotron resonance instrument. A drawback is that definitive structural information is not available, however this limitation is overcome by infrared multiphoton dissociation (IRMPD) using a free electron laser interfaced to an FTICR. Here, the IRMPD spectra of $[UO_2(acetone)_n]^{2+}$ complexes were measured and evaluated versus alterations to the ligand field.

Experimental

Experiments were conducted at the FOM Institute for Plasma Physics "Rijnhuizen" (Nieuwegein, The Netherlands), using the Free Electron Laser for Infrared eXperiments (FELIX)[1] which is continuously tunable over a practical range of 500 to 1800 cm^{-1}. FELIX is interfaced to a FTICR equipped with a 4.7 Tesla superconducting magnet (Cryomagnetics) and a homebuilt ICR cell and vacuum system.[2] Uranyl complex ions were generated by electrospray ionization (ESI) of a 1 mM solution of $UO_2(NO_3)_2$ in a 9:1 H_2O:acetone solvent. Ions of interest were isolated using a SWIFT pulse and irradiated with 1-2 FELIX pulses, and then the relative amounts of intact complexes and photofragments were determined from the mass spectrum. IRMPD spectra were generated by plotting the inverse log of the photofragment yield versus FELIX wavelength.

Results and Discussion

IRMPD spectra were acquired for $[UO_2(acetone)_n]^{2+}$ complexes (n = 2 – 4) formed in the ESI mass spectra of uranyl nitrate/acetone/ water solutions.[3] The U=O stretch at about 1000 cm^{-1} was progressively red shifted as the number of acetone ligands increased from 2 to 4 (Figure 1), consistent with increased e^- density at the metal center weakening the uranyl bond. Conversely the C=O stretch was blue shifted from ~ 1500 cm^{-1} to ~1630 cm^{-1}, which showed that the acetone ligands are pushed away from the U center as n increased from 2 to 4, resulting in a higher frequency. IRMPD of mixed complexes $[UO_2(acetone)_{4-m}(acetonitrile)_m]^{2+}$ revealed a regular systematic blue shift for the U=O stretch from to 987 cm^{-1} to 1007 cm^{-1} as m increased from 0 (all acetone) to 4 (all acetonitrile), consistent with decreased nucleophilicity of acetonitrile.

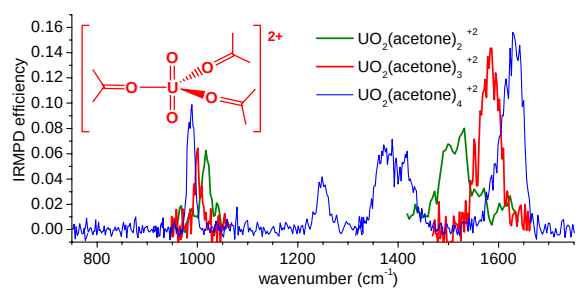

Figure 1. Superimposed IRMPD spectra of $[UO_2(acetone)_n]^{2+}$, n = 2, 3, 4. Peaks correspond to wavelength-dependent ligand elimination. Structure of the n = 3 complex is shown (red spectrum).

Conclusions

IRMPD of uranyl complex ions trapped in the gas-phase provided species-discrete vibrational data consistent with alterations in U=O bonding consistent with chemical modification of the equatorial ligand field.

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