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Gary S Groenewold, Anita K Gianotto, Michael E Mcilwain, Michael J van Stipdonk, Michael Kullman, et al.. Infrared Spectroscopy of Discrete Uranyl Anion Complexes. *Journal of Physical Chemistry A*, 2008, 112 (3), pp.508-521. 10.1021/jp077309q . cea-02353204

**HAL Id: cea-02353204**

**<https://cea.hal.science/cea-02353204>**

Submitted on 20 Nov 2019

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# Infrared Spectroscopy of Discrete Uranyl Anion Complexes

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**RECEIVED DATE (automatically inserted by publisher);**

TITLE RUNNING HEAD: Discrete Uranyl Anion Complexes

1 ABSTRACT: The Free-Electron Laser for Infrared Experiments (FELIX) was used to study the  
2 wavelength-resolved multiple photon dissociation of discrete, gas phase uranyl ( $\text{UO}_2^{2+}$ ) complexes  
3 containing a single anionic ligand (A), with or without ligated solvent molecules (S). The uranyl  
4 antisymmetric and symmetric stretching frequencies were measured for complexes with general formula  
5  $[\text{UO}_2\text{A}(\text{S})_n]^+$ , where A was either hydroxide, methoxide, or acetate; S was water, ammonia, acetone, or  
6 acetonitrile; and  $n = 0-3$ . The values for the antisymmetric stretching frequency for uranyl ligated with  
7 only an anion ( $[\text{UO}_2\text{A}]^+$ ) were as low or lower than measurements for  $[\text{UO}_2]^{2+}$  ligated with as many as  
8 five strong neutral donor ligands, and are comparable to solution phase values. This result was  
9 surprising because initial DFT calculations predicted values that were 30–40  $\text{cm}^{-1}$  higher, consistent  
10 with intuition but not with the data. Modification of the basis sets and use of alternative functionals  
11 improved computational accuracy for the methoxide and acetate complexes, but calculated values for  
12 the hydroxide were greater than the measurement regardless of the computational method used.  
13 Attachment of a neutral donor ligand S to  $[\text{UO}_2\text{A}]^+$  produced  $[\text{UO}_2\text{AS}]^+$ , which produced in only very  
14 modest changes to the uranyl antisymmetric stretch frequency, and did not universally shift the  
15 frequency to lower values. DFT calculations for  $[\text{UO}_2\text{AS}]^+$  were in accord with trends in the data, and  
16 showed that attachment of the solvent was accommodated by weakening of the U-anion bond as well as  
17 the uranyl. When uranyl frequencies were compared for  $[\text{UO}_2\text{AS}]^+$  species having different solvent  
18 neutrals, values decreased with increasing neutral nucleophilicity.

19 KEYWORDS: IRMPD, DFT, actinide, free electron laser, coordination complex, mass spectrometry

20

21

## 1 INTRODUCTION

2 The chemical behavior of uranium in general, and the linear uranyl dication  $[\text{UO}_2]^{2+}$  in particular, is  
3 diverse on account of the relative ease of redox processes,<sup>1</sup> and the availability of f and d orbitals<sup>2-4</sup> for  
4 complex formation. The latter has a profound affect on the solubility of the element.<sup>5,6</sup> In solution,  
5  $[\text{UO}_2]^{2+}$  is the dominant species,<sup>6-8</sup> where it plays an important role in heavy element separations<sup>9</sup> and in  
6 mobility of the element in the environment.<sup>10</sup> At low pH,  $[\text{UO}_2]^{2+}$  exists as the solvated dication in  
7 solution with weakly complexing anions.<sup>10</sup> Hydrolysis<sup>11,12</sup> at higher solution pH values, or the presence  
8 of more strongly coordinating anions, produces uranyl complexes coordinated by one or more anionic  
9 ligands.<sup>8,13</sup>

10 The chemical diversity of species has motivated research in vibrational spectroscopy and  
11 computational chemistry to understand the coordination and nature of bonding in uranyl complexes  
12 containing different ligands because these factors have reactivity and stability implications.<sup>14,15</sup> Infrared  
13 and Raman spectroscopy studies of  $[\text{UO}_2]^{2+}$  have shown that the respective antisymmetric ( $\nu_3$ ) and  
14 symmetric ( $\nu_1$ ) stretching frequencies<sup>16</sup> act as convenient “thermometers” for gauging the electron-  
15 donating capability of the equatorial ligand field, because the frequencies are strongly correlated with  
16 the coordination environment. Nucleophilic ligands in the coordination sphere donate electron density to  
17 the cationic metal center, and this spills over into the  $\pi^*$ -antibonding orbitals of the uranyl ion to cause a  
18 concomitant decrease in the associated  $\nu_1$  and  $\nu_3$  frequencies. Increased electron density at the uranium  
19 metal center can be effected by attachment of more donor ligands,<sup>17</sup> or by increasing the nucleophilicity  
20 of the ligands.<sup>18,19</sup> Generally for a modestly complexing solution environment,  $\nu_3$  values near  $960\text{ cm}^{-1}$   
21 are typical,<sup>18</sup> as originally reported by Jones and Penneman in 1953.<sup>20</sup> However, when more strongly  
22 basic ligands like hydroxide<sup>7,12,21,22</sup> are present, the resulting complexes exhibit much lower  $\nu_3$  values,  
23 which have been noted in both solutions<sup>23,24</sup> and solids.<sup>25-28</sup> Similar trends for the symmetric  $\nu_1$  stretch  
24 are seen in Raman spectra<sup>12,15,29</sup> and strong correlations between  $\nu_1$  and  $\nu_3$  frequencies have been

1 established.<sup>30</sup> Increasing the local electron density at the metal center in other ways, such as by formal  
2 reduction (to  $\text{UO}_2^+$ )<sup>24,31</sup> or substitution of a more electron-rich metal (i.e. Np, Pu, Am), produces a  
3 similar effect.<sup>29,32</sup>

4 Computational chemistry<sup>2,3</sup> helps provide a quantitative understanding of structure and bonding in  
5 uranyl complexes. Impressive progress has been made using density functional theory (DFT),<sup>33-36</sup> which  
6 is remarkable given the theoretical difficulty of accounting for the large number of electrons, spin-orbit  
7 coupling, and relativistic effects encountered in modeling uranyl molecules.<sup>33,35</sup> The computational  
8 results are strongly influenced by the choice of functional, basis set and effective core potential  
9 employed.<sup>37,38</sup> Vibrational frequencies generated using DFT<sup>37,39,40</sup> are invaluable because they provide a  
10 basis for the interpretation of spectroscopy experiments. However, comparisons between theory and, for  
11 example, solution-phase experimental studies are complicated because multiple species may be present  
12 in solution<sup>8,41</sup> as a result of rapid ligand exchange, ion pair formation, redox reactions, and solvent  
13 effects.<sup>1,7,11,12,17,42</sup> Because vibrational spectra collected from solution-phase experiments potentially  
14 contain contributions from multiple species, comparisons to results produced by DFT calculations  
15 (which are generated for discrete, well-defined species) are difficult. Longer-range interactions with the  
16 second solvation sphere also influence the spectroscopy of the complexes, and further complicate  
17 comparisons. An elegant way around this is to compare DFT results to structures determined using X-  
18 ray crystallography, however the effect of neighboring molecules in the crystal lattice is a complicating  
19 factor.<sup>43</sup>

20 An alternative approach for converging vibrational spectroscopy and computational chemistry is to  
21 measure the infrared spectra of discrete species isolated in the gas phase,<sup>44</sup> which can be accomplished  
22 using a trapped ion mass spectrometer (MS) (e.g., a Fourier transform ion cyclotron resonance [FT-ICR]  
23 or quadrupole ion trap instrument) interfaced to a high intensity, tunable infrared source that is provided  
24 by a free electron laser.<sup>41,44-47</sup> Using electrospray ionization (ESI),<sup>48-51</sup> a wide range of  $\text{UO}_2^{2+}$  species<sup>52-55</sup>  
25 can be formed and isolated in the FT-ICR-MS. Normally, ion concentrations in the gas phase are too

1 low to enable direct absorption measurements, but by rapid absorption of 10s to 100s of photons, the  
2 vibrational energy of a discrete species may be raised to the point where bond cleavage occurs.<sup>44,56</sup> In  
3 this case, photon absorption is signaled by a change in ion mass, and plotting ion intensities as a  
4 function of wavelength produces infrared multiple photon dissociation (IRMPD) spectra which bear  
5 strong similarity to those measured using conventional absorption approaches.<sup>57-59</sup>

6 In prior research campaigns, the IRMPD strategy was used to produce spectra of discrete uranyl-  
7 solvent complexes  $[\text{UO}_2\text{S}_{n=2-5}]^{2+}$  where S = acetone (ACO) and or acetonitrile (ACN).<sup>60</sup> The uranyl  $\nu_3$   
8 frequency underwent systematic red shifts with serial addition of donor ligands, and with substitution of  
9 a stronger nucleophilic ligand for a weaker one (e.g. ACO for ACN). Interestingly, the uranyl  $\nu_3$   
10 frequencies measured using IRMPD were never as low as the value for  $\text{UO}_2^{2+}$  in solution,<sup>20</sup> despite the  
11 fact that the ligands in the gas-phase experiments (ACO and ACN) were stronger nucleophiles than  $\text{H}_2\text{O}$   
12 (the dominant ligand in solution). This observation led to conjecture that additional interactions may be  
13 contributing to the observed uranyl shift in solution-phase experiments.

14 The subject of this report is the IRMPD spectroscopy of gas-phase  $[\text{UO}_2\text{A}]^+$  species (where anion A =  
15 OH,  $\text{OCH}_3$ , and acetate (OAc)), and complexes in which  $[\text{UO}_2\text{A}]^+$  is modified by the attachment of a  
16 single neutral donor solvent S, to form  $[\text{UO}_2\text{AS}_{1-2}]^+$  (where S =  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , ACN, or ACO). The  
17 hydroxide and acetate anions are representative of those commonly encountered in solution-phase  
18 studies of  $\text{UO}_2^{2+}$  speciation,<sup>61</sup> and acetate and methoxide are models for functional groups expected to  
19 interact with  $\text{UO}_2^{2+}$  in biological and geochemical environments. The primary focus of this work is to  
20 explore and understand the trends in the antisymmetric uranyl stretching frequency ( $\nu_3$ ), as a function of  
21 the number and binding strength of the various anionic and neutral ligands, by comparing the  
22 experimental IRMPD results with predictions from electronic structure calculations employing several  
23 different computational methods. In general, the measured  $\nu_3$  frequencies for the bare anion complexes  
24 were significantly lower than the predicted computational values, and approached those measured in  
25 solution for coordinatively saturated  $\text{UO}_2^{2+}$ . Addition of a neutral donor to form  $[\text{UO}_2\text{AS}]^+$  did not

1 substantially alter the  $\nu_3$  values compared to  $[\text{UO}_2\text{A}]^+$ , which was surprising because prior studies  
2 showed that the antisymmetric stretch is systematically red-shifted upon attachment of a donor neutral  
3 ligand. Comparison of the  $\nu_3$  values for different  $[\text{UO}_2\text{AS}]^+$  complexes showed a systematic decrease  
4 with increasing nucleophilicity of the neutral donor S. DFT calculations also suggested that when the  
5 neutral is added bonding is accommodated by weakening both the uranyl-anion bond, as well as the  
6 uranyl moiety.

## 7 EXPERIMENTAL

8 IRMPD spectra were collected at the Free Electron Laser for Infrared eXperiments (FELIX) facility,  
9 located at the FOM Instituut voor Plasmafysica 'Rijnhuizen' (Nieuwegein, The Netherlands).<sup>47</sup> The free  
10 electron laser is interfaced to a custom-built Fourier transform ion cyclotron resonance (FT-ICR) mass  
11 spectrometer.<sup>57,62</sup>

12 Generation of Uranyl Complexes by Electrospray Ionization (ESI). ESI was used to generate singly-  
13 and doubly-charged uranyl complexes.<sup>52,54</sup> A one millimolar solution of uranyl nitrate was generated by  
14 dissolving the hexahydrate salt (Fluka/Sigma-Aldrich, St. Louis, MO, USA) in water to produce uranyl  
15 complexes that were introduced into the hexapole ion accumulation chamber. The ESI source  
16 (Micromass, Manchester, U.K.) was operated at 3 kV with respect to ground. Ions were generated at  
17 atmospheric pressure and were extracted into vacuum using ion optics oriented orthogonally with  
18 respect to the spray axis, and then gated into a hexapole ion accumulation chamber where they were  
19 stored for 0.5–1.0 s prior to being transmitted into the FT-ICR-MS. The mass spectra observed were  
20 sensitive to various temperatures, voltages and carrier-gas and solution flow rates of the ESI source.  
21 Particularly important were the desolvation temperature<sup>54</sup> (which was controlled by a heater and  
22 thermocouple on the block through which the spray capillary passed) and the temperature of the  
23 desolvation gas, which were maintained at 29 and 52°C, respectively. The flow rate of the spray solution  
24 was 25  $\mu\text{l min}^{-1}$ , and the desolvation gas ( $\text{N}_2$ , which ensheathed the solution spray) flow rate was

1 maintained at 30 L min<sup>-1</sup>. Attempts to make hydrated [UO<sub>2</sub>NO<sub>3</sub>]<sup>+</sup> were not successful because traces of  
2 methanol, acetone, acetonitrile, acetic acid and ammonia in the spray chamber resulted in production of  
3 hydroxide, methoxide and acetate complexes. By increasing the radio frequency power on the ion  
4 accumulation hexapole, most of the ion population was converted to [UO<sub>2</sub>OH]<sup>+</sup>, [UO<sub>2</sub>OCH<sub>3</sub>]<sup>+</sup> and  
5 [UO<sub>2</sub>OAc]<sup>+</sup>; these species were also formed as complexes with a single solvent molecule (see below),  
6 which provided the ensemble of species for infrared spectroscopy.

7 Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS), and Infrared  
8 Multiphoton Dissociation (IRMPD).<sup>46,57,59</sup> Ions accumulated in the external hexapole were gated into  
9 the ICR cell, where complexes identified for IRMPD were isolated using a stored waveform inverse  
10 Fourier transform (SWIFT) pulse.<sup>63</sup> This ejected all species except those having the desired mass.  
11 Isolated ionic complexes were irradiated using two FELIX macropulses, which induced elimination of a  
12 solvent molecule, a radical or a rearrangement product (depending on the complex) when the incident  
13 wavelength matched an absorption band. The IRMPD mechanism has been described in detail  
14 elsewhere.<sup>45,62,64</sup> Briefly, it involves sequential, non-coherent absorption of many (tens to hundreds)  
15 infrared photons, with each photon being “relaxed” by intramolecular vibrational redistribution (IVR)  
16 before the next one is absorbed. In this way, the internal vibrational energy of the molecule can be  
17 resonantly increased above the dissociation threshold, resulting in fragmentation. It has been shown that  
18 the infrared spectra obtained are comparable to those obtained using linear absorption techniques.<sup>56,65</sup>  
19 FELIX (60 mJ per macropulse, 5 μs pulse duration, bandwidth 0.2 – 0.5 % of central λ) was scanned  
20 primarily through the spectral region of interest around 10 μm, in increments ≤ 0.04 μm, after which  
21 IRMPD product ions and un-dissociated precursor ions were measured using the excite/detect sequence  
22 of the FT-ICR-MS.<sup>66,67</sup> The IRMPD efficiency was then expressed as -log(1-[summed fragment ion  
23 yield]), corrected for the width of the acquisition channels and linearly normalized to correct for  
24 variations in FELIX power over the spectral range. Peak centers were chosen by fitting a Gaussian peak  
25 to the data using Origin plotting software(version 7.5, OriginLab, Northampton, MA). Precision was



1 not evaluated, on account of the time required for repetitive acquisition of the peak profiles, and the  
2 precious nature of beam time at FELIX. Nevertheless, the precision of measurement of peak position is  
3 probably on the order of a couple of  $\text{cm}^{-1}$ , based on earlier examination of the position(s) of the  
4 antisymmetric uranyl stretch and carbonyl C=O stretch in double charged complexes.<sup>60</sup>

5 Because some of the complexes were difficult to fragment, signal-to-noise was less than desired, and  
6 so the isolated complexes were subjected to multiple irradiation/acquisition sequences at each  
7 wavelength across the scanned region. This lengthened acquisition time, and this factor together with the  
8 need to strictly economize beam time at the FELIX FT-ICR-MS beamline constrained data acquisition  
9 for most complexes to the diagnostic O=U=O antisymmetric stretch ( $\nu_3$ ).

10 Density Functional Theory (DFT) Structure and Frequency Calculations. DFT calculations were  
11 performed using several different approaches, which varied in treatment of relativistic and core  
12 polarization effects, functional, basis set, and software package used. This was done to compare  
13 approaches that are commonly available and executable by non-specialists with more advanced methodologies  
14 that require access to substantial computational power.

15 (1) Calculations using local density approximation (LDA) with the Vosko, Wilk and Nusair (VWN)  
16 parameterization<sup>68,69</sup> were performed using the Accelrys Inc. DMol<sup>3</sup> suite.<sup>70,71</sup> This approach was  
17 employed because these calculations could be readily executed and provided an instant theoretical  
18 feedback on the recorded spectra. This efficiency is in large part due to use of a semi-core  
19 pseudopotential<sup>72</sup> was applied to describe the core electrons, combined with the use of polarized  
20 numerical basis sets (DNP) for the active electrons. A fine ( $10^{-8}$ ) energy convergence criterion was  
21 employed to ensure optimal geometries and representative vibrational frequencies. With this approach it  
22 was possible to calculate most structures in only a few hours using eight processors. No scaling of the  
23 calculated frequencies was performed.

24 (2) DFT calculations of structures and harmonic frequencies with the more accurate hybrid B3LYP  
25 functional<sup>73,74</sup> were performed with the NWChem<sup>75,76</sup> and Gaussian<sup>77</sup> suite of programs. Different

1 combinations of functionals and basis sets were employed in efforts to derive a consistent view of the  
2 IRMPD phenomena measured in the context of complex structure and dissociation behavior. Uranium  
3 was described by an effective core potential and its associated basis set: either the LANL2dz ECP and  
4 orbital basis set<sup>78</sup> or the MWB60 ECP and basis set (SDD),<sup>83-86</sup> which features Stuttgart/Dresden  
5 effective core potentials were used for uranium. Other atoms in the complexes (O, C, H, and N) were  
6 described using the aug-cc-pVDZ orbital basis sets,<sup>79</sup> the D95V basis set,<sup>83-86</sup> the all-electron 3-21g\*  
7 basis sets, or the 6-31+g(d) basis set. The relatively small 3-21g basis (which include single first  
8 polarization functions on row 2 atoms) set is generally considered to be too small for use in modeling  
9 actinide molecules, but one goal of this study was to evaluate the use of the SDD/3-21g\* general basis  
10 set approach for interpretation of gas-phase IRMPD experiments.

11 (3) In addition NWChem was used to perform correlation corrected vibrational self consistent field  
12 (cc-VSCF) calculations<sup>80-82</sup> that provide an estimate of the effect of anharmonicity and mode-coupling  
13 for the fundamental vibrational states. Starting with the vibrational self-consistent field (VSCF)  
14 method, degenerate perturbation theory is used to correct for effects of correlation between different  
15 vibrational modes, enabling calculation of anharmonic vibrational states for polyatomic molecules.

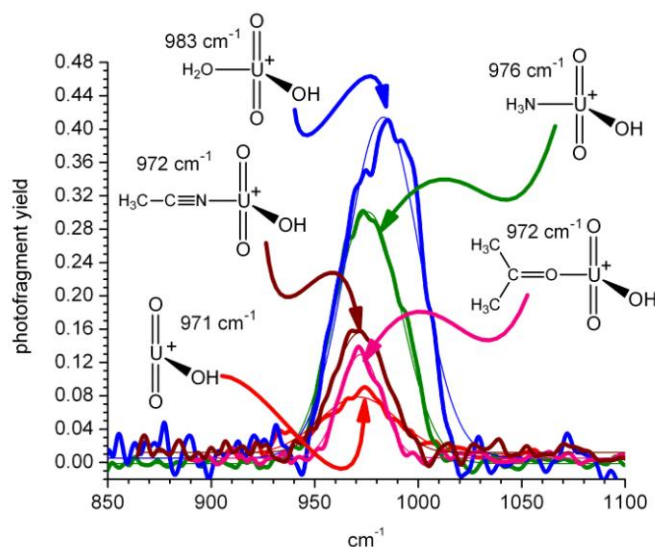
16 (4) Finally we also employed the ADF2006.01<sup>87</sup> package to quantitatively assess the donation of the  
17 ligands to the uranyl moiety and to compute the energetic requirements for different dissociation  
18 channels. Prior experience indicated reliable thermodynamic accuracy and thus motivated this approach.  
19 Geometric parameters (structures and frequencies) were thereby determined at the scalar relativistic  
20 ZORA<sup>88</sup>-PW91<sup>89</sup>-TZ2P level of theory using a restricted DFT and a small frozen core, while  
21 fragmentation energies were computed including spin-orbit coupling terms. The charge transfer between  
22 ligands and the uranyl was analyzed using both Hirshfeld charge analysis and Voronoi Deformation  
23 Density (VDD) methods. The energy differences reported do not reflect energies to transition states  
24 (which may be relevant for the loss of H<sub>2</sub>O from [UO<sub>2</sub>OH(ACO)]<sup>+</sup> and photo-fragmentation of  
25 [UO<sub>2</sub>OCH<sub>3</sub>]<sup>+</sup>).

## 1 RESULTS AND DISCUSSION

2 IRMPD of Uranyl-Hydroxide Complexes [UO<sub>2</sub>OH]<sup>+</sup>. Electrospray ionization mass spectrometry of  
3 aqueous uranyl nitrate solutions modified with organic solvents had previously been shown to produce  
4 dications ligated with neutral donors, provided the capillary temperature was kept close to ambient.<sup>54,60</sup>  
5 However, by modestly increasing the capillary temperature and the RF power of the ion accumulation  
6 hexapole, uranyl ion pairs were formed that enabled examination of their IRMPD spectra, as a  
7 complement to prior measurements made for the uranyl dication bound with neutral ligands.<sup>60</sup> A  
8 prominent [UO<sub>2</sub>OH]<sup>+</sup> ion was produced at *m/z* 287, and lower abundance complexes were observed at  
9 *m/z* 345, 328, 305 and 304 that correspond to [UO<sub>2</sub>OH(ACO)]<sup>+</sup>, [UO<sub>2</sub>OH(ACN)]<sup>+</sup>, [UO<sub>2</sub>OH(H<sub>2</sub>O)]<sup>+</sup> and  
10 [UO<sub>2</sub>OH(NH<sub>3</sub>)]<sup>+</sup>, respectively. The ammonia, acetone, and acetonitrile were present in the hexapole  
11 accumulation region of the ESI/FT-ICR instrument from prior experiments that involved the use of the  
12 solvents and ammonium acetate buffer solutions. The five different hydroxide complexes that were  
13 furnished by manipulation of the electrospray conditions were isolated using a SWIFT sequence,<sup>67</sup> and  
14 then photo-fragmented by scanning the free electron laser over the spectral region corresponding to the  
15 uranyl antisymmetric stretching frequency (~ 1000 cm<sup>-1</sup>); the resulting IRMPD spectra are shown in  
16 Figure 1.

17 Photo-fragmentation of [UO<sub>2</sub>OH]<sup>+</sup> resulted in reductive elimination of a hydroxyl radical, and the  
18 antisymmetric uranyl  $\nu_3$  stretch for this species appeared as a broadened absorption centered at 971 cm<sup>-1</sup>  
19 (Figure 1). The low abundance and profile of the peak reflected inefficient photo-fragmentation and high  
20 energetic requirements:<sup>44</sup> Calculations using ZORA-PW91-TZ2P (*vide infra*) indicated that the energy  
21 to dissociate the complex to [UO<sub>2</sub>]<sup>+</sup> and a hydroxyl radical was 96.4 kcal mol<sup>-1</sup>. The  $\nu_3$  value for  
22 [UO<sub>2</sub>OH]<sup>+</sup> was lower than the most red-shifted dication complexes [UO<sub>2</sub>(ACO)<sub>4</sub>]<sup>2+</sup> (988 cm<sup>-1</sup>) and  
23 [UO<sub>2</sub>(ACN)<sub>5</sub>]<sup>2+</sup> (995cm<sup>-1</sup>), which suggested at first glance that a single hydroxide transfers as much or  
24 more electron density to the uranium center as does four or five strong donors in a fully coordinated  
25 uranyl complex. This conclusion was surprising, and in fact opposed the results of VDD analyses, that

1 indicated a charge transfer of 0.52 e from the hydroxide to the uranyl, while the charge transfer from  
2 four acetones accounted for 0.62 e.  
3



4

5 **Figure 1.** Infrared multiple photon dissociation spectra of the antisymmetric O=U=O stretching region  
6 for  $[\text{UO}_2\text{OH}]^+$  and ligand complexes containing (clockwise) a single ACN,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and ACO. The  
7 yield values for the ACN complex were multiplied by a factor of two, to visually distinguished it from  
8 the unmodified hydroxide complex.

9 The value for the  $[\text{UO}_2\text{OH}]^+$  uranyl antisymmetric stretching frequency was lower than anticipated  
10 based on prior DFT calculations using B3LYP. A red shift of  $183\text{ cm}^{-1}$  was calculated for  $[\text{UO}_2(\text{OH})_2]$   
11 by Marsden and coworkers;<sup>40</sup> subtraction of this value from  $1140\text{ cm}^{-1}$  (the value calculated for  
12 unligated  $[\text{UO}_2]^{2+}$ )<sup>38</sup> produces a frequency of  $957\text{ cm}^{-1}$  for the bis-hydroxy complex. The measured  
13 value of  $971\text{ cm}^{-1}$  for the monohydroxy cannot be compared directly, because the modeled and measured  
14 complexes are different. But the values are reasonably close to each other, which suggests that most of  
15 the red shift results from attachment of the first  $\text{OH}^-$  ligand, and that attachment of the second ligand

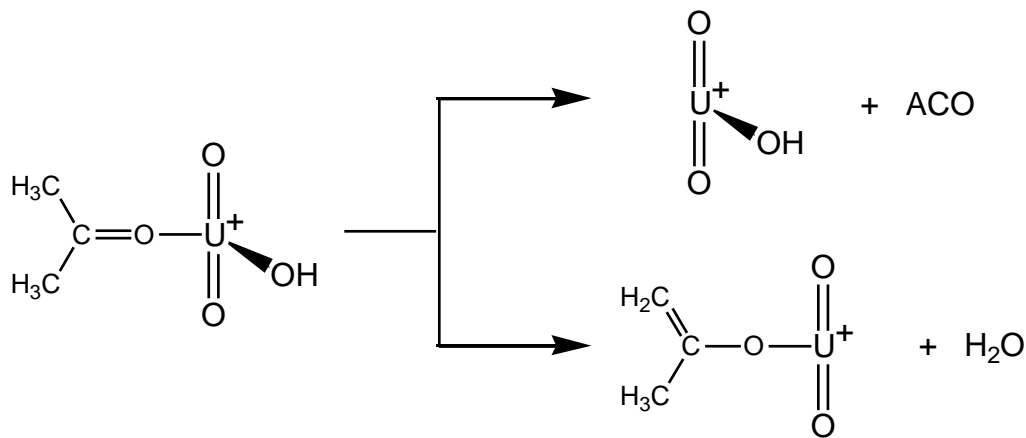
1 produces a much more modest change in frequency. This trend is in qualitative agreement with very  
2 small shifts produced by attachment of neutral donors to  $[\text{UO}_2\text{A}]^+$  complexes (*vide infra*).

3 The  $[\text{UO}_2\text{OH}]^+$   $\nu_3$  value measured in the gas phase is very close to that measured in aqueous solution  
4 for  $[\text{UO}_2]^{2+}$  (960 to 965  $\text{cm}^{-1}$ ), which is considered to have five inner sphere aquo ligands.<sup>17,18,20,90,91</sup>  
5 Lower values have been measured for hydroxide complexes in solution, but these have been attributed  
6 to species having multiple uranyl moieties, e.g. a  $\nu_3$  measurement at  $\sim 940 \text{ cm}^{-1}$  has been assigned to  
7  $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$ ,<sup>17,21,92</sup> and an even lower  $\nu_3$  value of 923  $\text{cm}^{-1}$  to  $[(\text{UO}_2)_3(\text{OH})_5]^+$ .<sup>17,92</sup> These  $\nu_3$   
8 measurements indicate that the frequency is decreased by the presence of more than one U atom in the  
9 complexes, but are also certainly influenced by coordinated solvent molecules.

10 The appearance of  $[\text{UO}_2\text{OH}]^+$  complexed with one or more solvent molecules enabled the effect of  
11 neutral donor ligands on the antisymmetric stretching frequency to be examined. The prior study of  
12  $[\text{UO}_2]^{2+}$  complexes with neutral ligands<sup>60</sup> showed that the antisymmetric stretching frequency was  
13 sequentially red-shifted by the serial attachment of additional neutral donor ligands, for example in the  
14 acetone (ACO) complexes  $[\text{UO}_2(\text{ACO})_n]^{2+}$ , the frequency decreased from 1017 to 1000 to 988  $\text{cm}^{-1}$  as n  
15 went from 2 to 3 to 4 (respectively).<sup>60</sup> The trend measured for a series of acetonitrile (ACN) complexes  
16 was similar, as was the magnitude of the red shift caused by an additional donor neutral. These  
17 observations led to the expectation that attachment of a neutral donor to  $[\text{UO}_2\text{OH}]^+$  would result in a  
18 similar red shift.

19 Isolation and photo-fragmentation of  $[\text{UO}_2\text{OH}(\text{ACO})]^+$  resulted in parallel elimination reactions: loss  
20 of intact ACO, and loss of  $\text{H}_2\text{O}$  (Scheme 1, Table 1). Computationally, the two pathways were found to  
21 have very similar reaction energies: using ZORA-PW91-TZ2P both channels were endothermic by 41.4  
22 kcal/mol, and a similar conclusion was derived using B3LYP/LANL2dz/aug-cc-pVDZ, which predicted  
23 values of 46.5 and 42.6 kcal/mol for loss of ACO and  $\text{H}_2\text{O}$  respectively. The loss of  $\text{H}_2\text{O}$  involves  
24 transfer of a proton from a methyl carbon on ACO to the hydroxide, leaving behind the acetone enolate  
25 which calculations show remains coordinated through the oxygen atom. No difference in frequencies

1 was observed in the two photo-fragment channels, which had maxima at  $972\text{ cm}^{-1}$ . This value was  
2 effectively equal to the measurement for the unmodified  $[\text{UO}_2\text{OH}]^+$ , which initially would seem to  
3 indicate that addition of the strong ACO donor had no further effect on the uranyl moiety. However, this  
4 conclusion is inconsistent with the fairly strong binding predicted by the PW91 and B3LYP calculations.  
5 Furthermore, the carbonyl stretching region for the  $[\text{UO}_2\text{OH}(\text{ACO})]^+$  complex was scanned and an  
6 absorption with a value of  $1633\text{ cm}^{-1}$  was found. In our previous study of  $[\text{UO}_2(\text{ACO})_n]^{2+}$  complexes, we  
7 observed that the ligand CO stretch was strongly red-shifted to  $1515\text{ cm}^{-1}$  in the  $n=2$  complex, and that  
8 this shift decreased with increasing cluster size, to  $1583$  for  $n=3$  and  $1630$  for  $n=4$ , as the binding energy  
9 per ligand was reduced.<sup>60,93</sup> Thus based on this comparison of carbonyl stretching data, one would  
10 expect the binding of the ACO ligand in the  $[\text{UO}_2\text{OH}(\text{ACO})]^+$  complex to be comparable to binding in  
11 the  $[\text{UO}_2(\text{ACO})_4]^{2+}$  complex. Interestingly, addition of a second and third ACO ligand to  
12  $[\text{UO}_2\text{OH}(\text{ACO})]^+$  produced red-shifts consistent with the prior experiments. Photo-fragmentation of  
13  $[\text{UO}_2\text{OH}(\text{ACO})_2]^+$  and  $[\text{UO}_2\text{OH}(\text{ACO})_3]^+$  both resulted in the loss of an ACO, with a  $\nu_3$  of  $961$  and  $948$   
14  $\text{cm}^{-1}$  respectively. Therefore, a red-shift of  $11$  and  $13\text{ cm}^{-1}$  were observed on going from  
15  $[\text{UO}_2\text{OH}(\text{ACO})]^+$   $[\text{UO}_2\text{OH}(\text{ACO})_2]^+$  to  $[\text{UO}_2\text{OH}(\text{ACO})]^+$ , which agrees well with the magnitude of the  
16 red-shifts resulting from ACO addition to the  $[\text{UO}_2(\text{ACO})_n]^{2+}$  complexes.<sup>60</sup> Taken together, these results  
17 suggest that it may be the uranyl antisymmetric stretching frequency in the bare  $[\text{UO}_2\text{OH}]^+$  complex that  
18 is anomalously shifted, which is certainly possible given the particular susceptibility of this very small  
19 system to anharmonicity effects arising from the IRMPD mechanism. These anharmonicity effects are  
20 examined in more detail below.



1

2 **Scheme 1.** Parallel elimination reactions of isolation and photo-fragmentation of  $[\text{UO}_2\text{OH}(\text{ACO})]^+$ .

3 Table 1. Dissoication energies for IRMPD reactions of  $[\text{UO}_2\text{OH}(\text{ACO})]^+$  calculated using different  
4 basis sets.

Reaction / binding energy (kcal/mol)	B3LYP SVWN Stuttgart RSC TZVP NWChem	B3LYP PW91 ZORA TZ2P (ADF)
$[\text{UO}_2\text{OH}(\text{ACO})]^+ \rightarrow [\text{UO}_2\text{OH}]^+ + \text{ACO}$	48.3	41.4
$[\text{UO}_2\text{OH}(\text{ACO})]^+ \rightarrow [\text{UO}_2(\text{OC}_3\text{H}_5)]^+ + \text{H}_2\text{O}$	52.8	41.4

5

6 Isolation of the  $[\text{UO}_2\text{OH}(\text{ACN})]^+$  complex followed by photo-fragmentation produced elimination of  
7 ACN. The antisymmetric  $\text{UO}_2$  stretch was measured at  $972 \text{ cm}^{-1}$ , nearly identical to that for  
8  $[\text{UO}_2\text{OH}(\text{ACO})]^+$  and to  $[\text{UO}_2\text{OH}]^+$ . The hydroxide complex with ammonia  $[\text{UO}_2\text{OH}(\text{NH}_3)]^+$  underwent  
9 photo-fragmentation solely by loss of  $\text{NH}_3$ , with a  $\nu_3$  value at  $976 \text{ cm}^{-1}$ , which is slightly *blue* shifted  
10 compared to the unmodified uranyl hydroxide. The final hydroxide complex examined was  
11  $[\text{UO}_2\text{OH}(\text{H}_2\text{O})]^+$ , which eliminated  $\text{H}_2\text{O}$  upon irradiation that maximized at  $983 \text{ cm}^{-1}$ , which was  
12  $12 \text{ cm}^{-1}$  higher than the  $[\text{UO}_2\text{OH}]^+$  value.

1 The trend for the uranyl  $\nu_3$  frequencies for the  $[\text{UO}_2\text{OH}(\text{S})]^+$  complexes were internally self-  
2 consistent, i.e., they decreased in the order  $\text{H}_2\text{O} > \text{NH}_3 > \text{ACN} \sim \text{ACO} > (\text{ACO})_2$ . These frequency  
3 values are inversely correlated with the calculated coordination energies of different S molecules,<sup>40</sup> and  
4 are in accord with comparisons of ACO and ACN uranyl complexes.<sup>60</sup> The observed ordering again  
5 highlights the remarkably low value measured for unmodified  $[\text{UO}_2\text{OH}]^+$ , which would be expected to  
6 be higher than  $983 \text{ cm}^{-1}$  (i.e., the value for the complex with the most weakly bound neutral,  
7  $[\text{UO}_2\text{OH}(\text{H}_2\text{O})]^+$ ). Because it does not seem reasonable to expect that the addition of weakly donating  
8 species actually strengthens the uranyl U=O bonds, we must seek other explanations for the blue shifted  
9 bands for the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  complexes.

10 One likely contributing factor is vibrational anharmonicity derived from the multiple photon  
11 absorption process. Red-shifts in the spectra of the *para*-aminobenzoic acid<sup>58</sup> and  $[\text{CeOH}(\text{ACO})_3]^{2+}$   
12 cations<sup>93</sup> have been attributed to IRMPD anharmonicity, and the same phenomenon may contribute to  
13 the low frequency measured for  $[\text{UO}_2\text{OH}]^+$ . These studies demonstrate that when molecules or  
14 complexes attain very high internal energies via the IRMPD process, their vibrational bands exhibit non-  
15 negligible red-shifts. This can be particularly dramatic for systems with low densities of states,<sup>44</sup> such as  
16 the  $[\text{UO}_2\text{OH}]^+$  complex studied here, which only has 9 vibrational modes. The energy required to  
17 dissociate  $[\text{UO}_2\text{OH}]^+$  to  $[\text{UO}_2]^+$  and a hydroxyl radical was evaluated computationally, and both the  
18 Stuttgart RSC ECP and the ADF TZ2P basis sets, which have some similarity, produced high values  
19 (Table 2). However, a lower value was generated using the LANL/aug-cc-pvdz basis set, which may  
20 reflect that difficulty is encountered in dealing with  $[\text{UO}_2]^+$  species using the LANL/aug-cc-pvdz basis  
21 set, which is fairly small, without any diffuse functions. This could conceivably create an unbalanced  
22 description of uranium, leading to a low calculated dissociation energies. Therefore, we conclude that  
23 the calculations in general predict high dissociation energies, which is consistent with the fact that  
24 hydroxide had the highest coordination energy of any ligand in the extensive compilation calculated by  
25 Marsden and coworkers.<sup>40</sup> These considerations support the attribution of the anomalously low



1  $[\text{UO}_2\text{OH}]^+$   $\nu_3$  value to anharmonicity effects. The B3LYP calculations using the Stuttgart RSC/TZVP  
 2 basis was also performed starting from a triplet excited state, and it was found to require 43.8 kcal mol<sup>-1</sup>.  
 3 This value, when added to the promotion energy (see below) yields a value of nearly 90 kcal mol<sup>-1</sup>.  
 4 Table 2. Dissociation energies calculated for IRMPD of  $[\text{UO}_2\text{OH}]^+$ .

Reaction / binding energy (kcal/mol)	B3LYP SVWN Stuttgart RSC TZVP (NWChem)	B3LYP PW91 ZORA TZ2P (ADF)
$[\text{UO}_2\text{OH}]^+ \rightarrow [\text{UO}_2^+] + \text{OH}$ dissociation via a singlet ground state	74.5	96.0
$[\text{UO}_2\text{OH}]^+ \rightarrow [\text{UO}_2^+] + \text{OH}$ dissociation via a triplet excited state	43.8	--

5  
 6 In contrast to the small  $[\text{UO}_2\text{OH}]^+$  molecule, more complex systems containing a neutral ligand tend  
 7 to have reduced dissociation energies and a significantly higher vibrational density of states. For  
 8 example, water binds to the  $[\text{UO}_2\text{OH}]^+$  complex by only 30 kcal/mol, while doubling the number of  
 9 vibrational modes, three of which are low-frequency intermolecular modes, that may contribute  
 10 disproportionately to the vibrational density of states. This may explain why the  $\nu_3$  frequencies of the  
 11  $[\text{UO}_2\text{OH}(\text{S})]^+$  complexes are not apparently affected by anharmonicity, compared to the bare  $[\text{UO}_2\text{OH}]^+$   
 12 which is strongly shifted by anharmonicity induced by the IRMPD process. A  $\nu_3$  value unshifted by  
 13 anharmonicity would be expected to be ~990 cm<sup>-1</sup> for  $[\text{UO}_2\text{OH}]^+$  to be consistent with the trend in the  $\nu_3$   
 14 bands of the  $[\text{UO}_2\text{OH}(\text{S})]^+$  complexes measured here.

15 Correlation corrected vibrational SCF (cc-VSCF) calculations can provide an estimate of whether or  
 16 not differential red-shifting would be expected in comparing  $[\text{UO}_2\text{OH}]^+$  and  $[\text{UO}_2\text{OH}(\text{S})]^+$  complexes.

1 cc-VSCF estimates the effect of anharmonicity by including coupling between the lower vibrational  
2 modes calculated in the harmonic approximation. Factoring in an influence by anharmonicity the  
3 calculated  $\nu_3$  value for  $[\text{UO}_2\text{OH}]^+$  decreased by  $10\text{ cm}^{-1}$ , which would account for part of the expected  
4 red shift for the hydroxide based on the IRMPD data. However, the shift calculated for  $[\text{UO}_2\text{OH}(\text{H}_2\text{O})]^+$   
5 was very nearly the same at  $8\text{ cm}^{-1}$ , since there are other factors that are expected to mitigate the effects  
6 of anharmonicity in the latter system, the differential anharmonic shift calculated for  $[\text{UO}_2\text{OH}]^+$  and  
7  $[\text{UO}_2\text{OH}(\text{H}_2\text{O})]^+$ . It should be noted that the cc-VSCF calculations only consider coupling of the lowest  
8  $\sim 10$  vibrational levels, whereas coupling and population of the higher excitation levels would certainly  
9 be expected to contribute at the high excitation energies achieved in the IRMPD experiments.

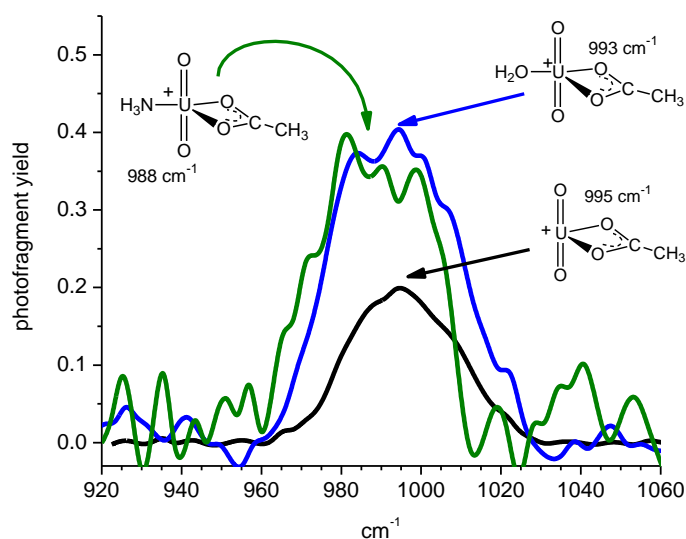
10 Participation of an electronically excited state  $[\text{UO}_2\text{OH}]^+$  may also contribute to the apparently low  $\nu_3$   
11 frequency. The energy calculated for promotion of an electron into the lowest excited triplet state  
12 calculated using both B3LYP/LANL2dz-aug-cc-pVDZ and PW91/unrestricted/scalar was  $\sim 45\text{ kcal/mol}$ ,  
13 which was less than that calculated to dissociate  $[\text{UO}_2\text{OH}]^+$  (except for the LANL basis set). If  
14 vibrational-to-electronic transitions are occurring in the multiple photon experiments, then a lowered  
15 frequency would be expected for the electronically excited molecule.<sup>94</sup> The  $\nu_3$  value calculated for  
16  $[\text{UO}_2\text{OH}]^+$  in its lowest excited state was quite a bit lower, at  $908\text{ cm}^{-1}$ , however the hydroxide profile is  
17 broadened, which may be the result of overlap of absorptions of ground state and excited state  
18 molecules. It should also be noted that this triplet state may be directly related to the observed  
19 dissociation pathway, suggesting that the molecule can be considered to be a complex of reduced uranyl  
20  $[\text{UO}_2]^+$  and neutral hydroxyl radical.

21 IRMPD of Uranyl-Acetate Complexes  $[\text{UO}_2\text{OAc}]^+$ . ESI produced a relatively abundant ion at  $m/z\ 329$   
22 which was attributed to uranyl acetate  $[\text{UO}_2\text{OAc}]^+$ , that was formed from residual acetic acid that had  
23 been used to enhance the protonated ion formation from peptide and protein solutions in previous  
24 experiments at FELIX. Because acetate is a stronger conjugate base, it replaces nitrate in the ion  
25 accumulation chamber prior to injection into the FT-ICR-MS. The composition was confirmed by

1 accurate mass measurement and the photo-fragmentation pathway observed in the IRMPD experiment,  
2 in which a neutral loss of 42 mass units (presumably as ketene) furnished  $[\text{UO}_2\text{OH}]^+$  as the product ion.  
3 For IRMPD of  $[\text{UO}_2\text{OAc}]^+$  the maximum for the antisymmetric uranyl stretch was  $995\text{ cm}^{-1}$  (Figure 2),  
4 higher than any of the hydroxide complexes measured. This is consistent with the fact that acetate is a  
5 weaker gas-phase base<sup>95</sup> than either hydroxide or methoxide (vide infra), and consequently is also likely  
6 to be a weaker uranophile. Despite the presumed lower basicity, the antisymmetric uranyl stretching  
7 frequency for  $[\text{UO}_2\text{OAc}]^+$  appeared at a lower value than nearly all of the uranyl dication complexes  
8 ligated with multiple neutral donor ligands reported earlier.<sup>60</sup> In solution, acetate complexes have been  
9 the subject of several infrared studies, and the most appropriate value for the antisymmetric stretch to  
10 use in a comparison is  $954\text{ cm}^{-1}$ , which was measured by Quiles<sup>17</sup> for  $[\text{UO}_2\text{OAc}]^+$ . This value is  
11 significantly lower than the IRMPD measurement, which reflects the attachment of additional solvent  
12 ligands to the  $[\text{UO}_2\text{OAc}]^+$  metal center. Other studies have produced values that ranged as low as  $919$   
13  $\text{cm}^{-1}$ ,<sup>18,23</sup> but these measurements probably contain contributions from species that contain more than  
14 one acetate ligand, and the possibility of variable acetate coordination.<sup>17</sup> Recently, LDA was used by de  
15 Jong and coworkers to calculate uranyl  $\nu_3$  value for  $[\text{UO}_2\text{OAc}]^+$  at  $1025\text{ cm}^{-1}$ .<sup>96</sup> A careful examination  
16 of the carbonyl stretching frequencies could provide insight into this, and will be investigated in further  
17 experimental campaigns.

18 Also observed in the ESI spectrum were low abundance ions at  $m/z$  346 and 347 that corresponded to  
19 ammonia and water complexes (respectively), having compositions  $[\text{UO}_2\text{OAc}(\text{NH}_3)]^+$  and  
20  $[\text{UO}_2\text{OAc}(\text{H}_2\text{O})]^+$ . Photo-fragmentation of these complexes involved elimination of either  $\text{NH}_3$  or  $\text{H}_2\text{O}$ ,  
21 producing  $[\text{UO}_2\text{OAc}]^+$  in each case. Consistent with prior studies of donors, the antisymmetric  $\text{UO}_2$   
22 stretching frequency was red-shifted for both  $\text{H}_2\text{O}$  and  $\text{NH}_3$  complexes relative to  $[\text{UO}_2\text{OAc}]^+$ , although  
23 the magnitude of the shifts were small: the value for the  $\text{H}_2\text{O}$  complex at  $993\text{ cm}^{-1}$  was lower by  $2\text{ cm}^{-1}$ ,  
24 while a shift  $7\text{ cm}^{-1}$  to  $988\text{ cm}^{-1}$  was observed for the  $\text{NH}_3$  complex. The trend in the measured  
25 frequencies indicate that both  $\text{H}_2\text{O}$  and  $\text{NH}_3$  are donating electron density, and that  $\text{NH}_3$  is a stronger

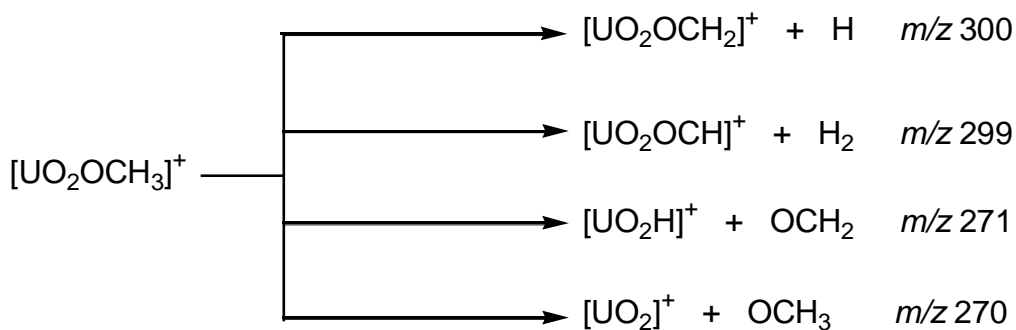
1 uranophile than is H<sub>2</sub>O, consistent with Marsden's prior DFT results,<sup>40</sup> the relative order of proton  
 2 affinities,<sup>95</sup> and bonding to other metal cations.<sup>97</sup> The fact that the frequency of the unmodified acetate is  
 3 very close to that of both ligand complexes suggests that the frequency for the [UO<sub>2</sub>OAc]<sup>+</sup> complex may  
 4 also be red-shifted as a result of anharmonicity or perhaps other factors. However the effect is less  
 5 pronounced than in the case of the hydroxide complex, as indicated by the fact that the  $\nu_3$  of the  
 6 unmodified [UO<sub>2</sub>OAc]<sup>+</sup> complex is not lower than the values of the H<sub>2</sub>O and NH<sub>3</sub> adducts. Compared to  
 7 the hydroxide complex, a smaller anharmonic red shift for OAc is consistent with a higher density of  
 8 states,<sup>44</sup> and with a lower energy requirement for fragmentation of the acetate complex, which involves  
 9 rearrangement rather than direct bond-cleavage and elimination of a radical.



10

11 **Figure 2.** Infrared multiple photon dissociation spectra of the antisymmetric O=U=O stretching region  
 12 for [UO<sub>2</sub>OAc]<sup>+</sup> and ligand complexes containing a single NH<sub>3</sub> and H<sub>2</sub>O.

13 IRMPD of Uranyl-Methoxide Complexes [UO<sub>2</sub>OCH<sub>3</sub>]<sup>+</sup>. The accurate mass measurement of the ion at  
 14 *m/z* 301 confirmed the composition of uranyl methoxide, which was formed by reaction of uranyl  
 15 species with methanol that was present in the ESI solution. Photo-fragmentation of [UO<sub>2</sub>OCH<sub>3</sub>]<sup>+</sup>  
 16 produced four different product ions corresponding to the elimination of the OCH<sub>3</sub> and H radicals, H<sub>2</sub>,  
 17 and H<sub>2</sub>CO (Scheme 2).

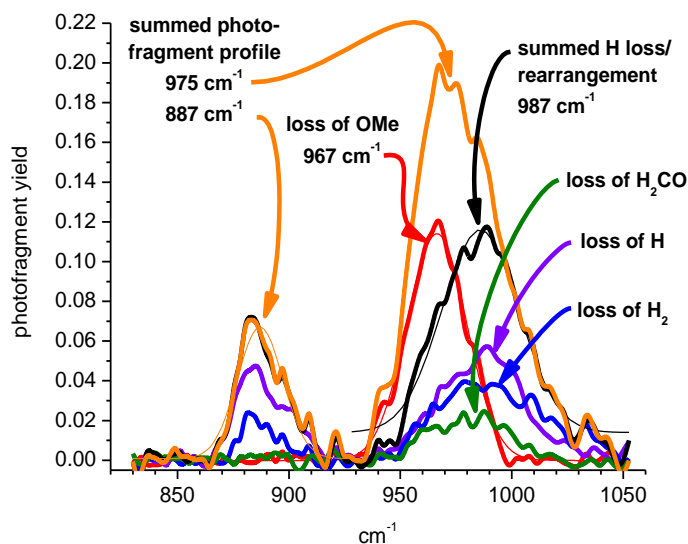


1

2 **Scheme 2:** Photo-fragmentation of  $[UO_2OCH_3]^+$  produced four different product ions corresponding to  
 3 the elimination of the  $OCH_3$  and H radicals,  $H_2$ , and  $H_2CO$ .

4 The IRMPD spectrum of the methoxide complex contained two bands, with maxima at  $975\text{ cm}^{-1}$  and  
 5  $887\text{ cm}^{-1}$  (Figure 3, black trace). DFT calculations (B3LYP/SDD-3-21G\*) indicated that the higher  
 6 frequency corresponded to overlapped antisymmetric uranyl  $\nu_3$  and C-O stretching bands, and the lower  
 7 frequency to the symmetric uranyl  $\nu_1$  band normally observed in the Raman spectrum.<sup>7,12,15,22,29</sup> The  
 8 appearance of the symmetric stretch indicates a lowered symmetry in the complex, resulting from strong  
 9 binding of the methoxide that perturbs the linearity of the uranyl functional group. This was supported  
 10 by the lowest energy structures and bond angles produced by B3LYP calculations (vide infra).

11 Striking differences were observed when the IR spectra produced using the different photo-  
 12 dissociation channels were compared. The spectrum generated by monitoring the loss of the  $OCH_3$   
 13 radical contained a single sharply defined peak with a maximum at  $967\text{ cm}^{-1}$ , a frequency slightly lower  
 14 than that measured for the uranyl antisymmetric stretch for the unmodified hydroxide complex, and  
 15 consistent with the fact that methoxide is a stronger base than is hydroxide. The peak centered at  $967$   
 16  $\text{cm}^{-1}$  was not observed in the spectra generated by the other three fragmentation channels, either because  
 17 it is not occurring in these channels, or because it was overlapped with the O-C stretch (see below). If  
 18 the latter is true, then it suggests that the  $\nu_3$  frequency in the spectrum of the  $OCH_3$  loss channel is red  
 19 shifted by about  $20\text{ cm}^{-1}$  due to the higher energetic requirements for that channel; shifts of this  
 20 magnitude have been observed previously.<sup>58</sup>



1

2 **Figure 3.** Infrared multiple photon dissociation spectra of the symmetric and antisymmetric O=U=O  $v_3$   
 3 stretching region for  $[\text{UO}_2\text{OCH}_3]^+$ . The black trace represents the spectrum generated by the summed  
 4 photofragment abundance; red the  $\text{OCH}_3$  radical elimination, violet the H radical elimination; blue the  
 5  $\text{H}_2$  elimination; green the  $\text{H}_2\text{CO}$  elimination, and orange the sum of the H loss/rearrangement related  
 6 channels.

7 The IR spectra generated from the photo-dissociation channels corresponding to either the loss of H or  
 8  $\text{H}_2$  bore strong similarities to one another in that they contained a peak with a maximum at  $987\text{ cm}^{-1}$  and  
 9 second peak at about  $887\text{ cm}^{-1}$ . The higher frequency peak probably contains components from  
 10 unresolved uranyl asymmetric stretch and C-O stretching, while the lower frequency peak corresponds  
 11 to the symmetric  $\text{UO}_2$  stretch. The IR spectrum generated by the  $\text{H}_2\text{CO}$  elimination was similar to the H-  
 12 loss spectra, but lacked the band for the symmetric stretch. The appearance of very dissimilar IR spectra  
 13 in the different photo-dissociation channels was remarkable, because IRMPD spectra generated from  
 14 competing mass channels are normally identical or are very similar, with the fragmentation channels  
 15 having the higher energetic requirements being modestly red-shifted as a result of anharmonicity that  
 16 results from population of higher vibrational levels when multiple photons are serially absorbed.<sup>58,93</sup>  
 17 Fast intramolecular vibrational redistribution randomizes the deposited energy regardless of the

1 frequency of initial deposition, and thus the competing fragmentation channels display similar if not  
2 identical IR spectra.<sup>56</sup>

3 A hypothetical interpretation of these observations is that the order of reaction endothermicities for the  
4 four reactions is  $-H_2 \sim -H < -OCH_2 < -OCH_3$ . In the spectra generated by losses of H and H<sub>2</sub> peaks are  
5 seen in all three absorption modes, symmetric uranyl, asymmetric uranyl and C-O (assuming that the  
6 asymmetric uranyl and C-O are overlapping). The symmetric uranyl and C-O are weakly absorbing  
7 modes and hence are only seen in those eliminations having low energy requirements. The spectrum  
8 generated by loss of OCH<sub>2</sub> contains the asymmetric uranyl and perhaps the C-O, but energetic  
9 requirement for this channel is too high to enable observation of the symmetric uranyl stretch. The  
10 higher energetic requirements are probably related to the fact that the  $[UO_2H]^+$  product ion has to be  
11 reduced, forming either a U(IV) species or a uranyl hydride. Finally, the spectrum generated by loss of  
12 OCH<sub>3</sub> contains only the antisymmetric uranyl peak, because the energetics for this reaction are higher,  
13 which means that it can only be accessed via the high intensity  $\nu_3$  uranyl absorption. This peak is  
14 substantially red-shifted as a consequence of the large number of photons that must be deposited in  
15 order for the reaction to occur. Further, the fast kinetics of the OCH<sub>3</sub> radical loss reduces observation of  
16 the slower, lower energy losses.

17 Enthalpy changes for the calculated for the different fragmentation channels display modest agreement  
18 with this hypothesis. B3LYP calculations using different parameterization and basis sets (Table 3)  
19 showed that elimination of H<sub>2</sub> was the lowest, followed by loss of H radical. Enthalpy requirements for  
20 the loss of H<sub>2</sub>CO and reductive elimination of the methoxy radical were higher, and the order of these  
21 two varied depending on the basis sets employed. The B3LYP calculations identified two possible  
22 outcomes for the elimination of H<sub>2</sub>CO: formation of a U(IV) oxyhydroxide  $[UOOH]^+$ , and a U(VI)  
23 uranyl hydride  $[UO_2H]^+$ , with the U(IV) species appearing to be somewhat disfavored energetically.  
24 However the significant energetic variations seen in comparisons of the different approaches do not  
25 allow us to state the energetic order of the elimination reactions, and thus computational support is

1 somewhat equivocal for the hypothetical explanation for the differences seen in the spectra from the four  
2 elimination channels.

3 Table 3. Calculated enthalpies for the dissociation reactions of  $[\text{UO}_2\text{OCH}_3]^+$  (Scheme 2). Values are in  
4  $\text{kcal mol}^{-1}$ .

Reaction \ binding energy (kcal/mol)	?????? SVWN DNP DNP (DMOL)	B3LYP B3LYP SDD SDD (Gaussian)	B3LYP SVWN Stuttgart RSC TZVP (NWChem)	B3LYP PW91 ZORA TZ2P (ADF)*
$[\text{UO}_2\text{OCH}_3]^+ \rightarrow \text{H}_2 + [\text{UO}_2(\text{OCH})]^+$		52.8	52.7	52.3
$[\text{UO}_2\text{OCH}_3]^+ \rightarrow \text{H} + [\text{UO}_2(\text{OCH}_2)]^+$		67.3	73.7	78.3
$[\text{UO}_2\text{OCH}_3]^+ \rightarrow \text{OCH}_3 + [\text{UO}_2]^+$		68.4	69.8	100.1
$[\text{UO}_2\text{OCH}_3]^+ \rightarrow \text{OCH}_2 + [\text{UO}_2(\text{H})]^+$ (H equatorial)		59.0	80.7	--
$[\text{UO}_2\text{-OCH}_3]^+ \rightarrow \text{OCH}_2 + [\text{UOOH}]^+$ (H linear)		79.9	85.2	85.6

5 \* ZORA numbers include spin-orbit interaction.

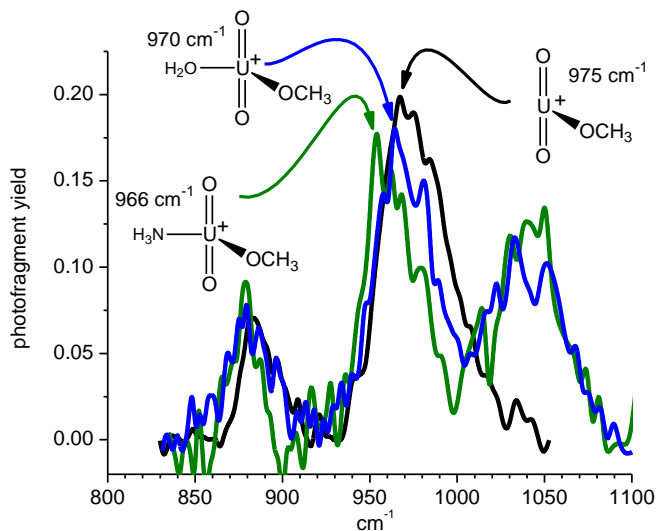
6 An alternative explanation would be the existence of two or more isomers of  $[\text{UO}_2\text{OCH}_3]^+$ , however  
7 DFT calculations did not support the existence of energetically competitive isomers, although  
8 rearrangement may be occurring during the IRMPD process. An alternative structure that was  
9 considered contained an H atom bound to uranium, with formaldehyde equatorially coordinated: for  
10 such a structure an absorption corresponding to carbonyl group should be observed, but a survey of the  
11  $1500\text{--}1700 \text{ cm}^{-1}$  wavelength region did not show an additional peak. Thus a structure involving a bound  
12 formaldehyde ligand is unlikely, as our prior studies<sup>60,93</sup> showed that the C=O stretch can be readily  
13 detected in complexes with carbonyl-containing ligands.

14 Involvement of an excited state for the uranyl methoxide can also be argued, which would be expected  
15 to have energetic requirements similar to the 45 kcal/mol required for the hydroxide complex.  
16 Intuitively, this is an attractive explanation because a higher spin species would be expected to have a  
17 higher propensity for rearrangement and elimination of H and  $\text{OCH}_3$  radicals. When the energetic



1 requirement for conversion to a triplet excited state was calculated, it was found to be  $45 \text{ kcal mol}^{-1}$ , in a  
2 range that would be accessible during the IRMPD photofragmentation. However, as in the two  
3 previously offered rationalizations, this too remains speculative at the present time, and hence an  
4 unequivocal identification of the origin of the differences in the spectra of the different mass channels is  
5 still elusive.

6 The assignment of the higher frequency to a C-O stretch drew support from the spectra acquired for  
7 the  $[\text{UO}_2\text{OCH}_3(\text{H}_2\text{O})]^+$  and  $[\text{UO}_2\text{OCH}_3(\text{NH}_3)]^+$  adducts (Figure 4). The three peaks in the spectra of  
8 these complexes had frequencies consistent with the spectra of unmodified  $[\text{UO}_2\text{OCH}_3]^+$ . In the adduct  
9 ions, photo-fragmentation of the methoxide ligand did not occur; instead, only the energetically favored  
10 losses of  $\text{H}_2\text{O}$  or  $\text{NH}_3$  were observed.



11

12 **Figure 4.** Infrared multiple photon dissociation spectra of the antisymmetric  $\text{O}=\text{U}=\text{O}$  stretching region  
13 for  $[\text{UO}_2\text{OCH}_3]^+$  (black trace, sum of all photo-fragment channels),  $[\text{UO}_2\text{OCH}_3(\text{H}_2\text{O})]^+$  (blue trace,  
14 scaled by 0.55) and  $[\text{UO}_2\text{OCH}_3(\text{NH}_3)]^+$  (green trace scaled by 0.6). The photofragment yield for the  $\text{H}_2\text{O}$   
15 and  $\text{NH}_3$  complexes was higher than for the unmodified methoxide complex, and scaling was performed  
16 to facilitate comparison.

1 The frequencies measured for the antisymmetric  $\text{UO}_2$  stretch for the  $\text{H}_2\text{O}$  and  $\text{NH}_3$  complexes were  
2 modestly red-shifted compared to the maximum value for the summed photo-fragment channels of the  
3 unmodified  $[\text{UO}_2\text{OCH}_3]^+$ , and the trend observed is consistent with what would be expected for addition  
4 of a second weak donor ligand ( $\text{H}_2\text{O}$ ), and then substitution of a slightly more basic ligand  $\text{NH}_3$  for  $\text{H}_2\text{O}$ .  
5 Similarly, the frequencies measured for the symmetric stretch were very similar for all three complexes:  
6 the  $\nu_1$  value for the unmodified  $[\text{UO}_2\text{OCH}_3]^+$  was measured at  $887\text{ cm}^{-1}$ , and the peak position is only  
7 very modestly shifted to  $880\text{ cm}^{-1}$  when  $\text{H}_2\text{O}$  is attached, and to  $879\text{ cm}^{-1}$  for  $\text{NH}_3$ . These values are  
8 about  $20\text{ cm}^{-1}$  higher than that measured for solvated  $[\text{UO}_2\text{OAc}]^+$  using Raman spectroscopy.<sup>12</sup> As in the  
9 case of the hydroxide complexes, the uranyl stretching frequencies of the methoxide complexes were not  
10 significantly red shifted by addition of a neutral donor ligand. This suggests that in the unmodified  
11 methoxide complex  $[\text{UO}_2\text{OCH}_3]^+$ , the uranyl frequency may be shifted to a lower value as a result of  
12 anharmonicity, in a fashion similar to that suspected to be occurring in the hydroxide complexes. As  
13 noted, this would be facilitated by high energetic requirements for the elimination reaction in the  
14 unmodified  $[\text{UO}_2\text{OCH}_3]^+$  which was indicated by calculations, and was comparable to the value  
15 calculated for the hydroxide. The high value is consistent with the idea that elimination of the  $\text{OCH}_3$   
16 radical would be most susceptible to red-shifting resulting from absorption of multiple photons during  
17 the IRMPD process.

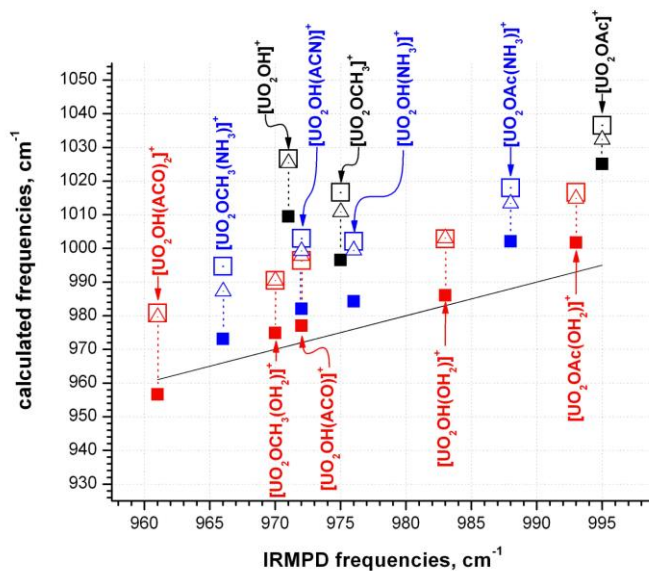
18 While addition of a second donor ligand does not cause large changes in the uranyl stretching  
19 frequencies,<sup>43,96</sup> it appears to strengthen the C-O bond in the methoxide ligand. This would be expected  
20 if the methoxide were modestly repelled by attachment of  $\text{H}_2\text{O}$  or  $\text{NH}_3$  to the uranium center. In the  
21 spectra for both  $[\text{UO}_2\text{OCH}_3(\text{H}_2\text{O})]^+$  and  $[\text{UO}_2\text{OCH}_3(\text{NH}_3)]^+$ , the C-O stretch was observed at ca. 1038  
22 and  $1040\text{ cm}^{-1}$ , shifted to higher frequency by  $\sim 50\text{ cm}^{-1}$  compared to unmodified  $[\text{UO}_2\text{OCH}_3]^+$ . This  
23 trend is directly analogous to what was observed in the IR spectra of discrete uranyl acetone dication  
24 complexes: when an additional donor ligand was added, the binding of all equatorial ligands was  
25 weakened, and the C=O stretching frequency increased, approaching that of free acetone,<sup>60</sup> in the

1 present case, it is the C-O stretch of methoxide that is increased. Calculations also suggested loosening  
2 of the U-OCH<sub>3</sub> bond upon ligation with a neutral donor.

### 3 Comparisons of Calculated Frequencies

4 The changes in vibrational frequencies can be understood in part by comparison with frequencies,  
5 bond lengths and angles calculated using density functional theory. Because calculations of complexes  
6 containing actinide elements are challenging, different combinations of functionals and basis sets were  
7 used. These results provided multiple opportunities for comparison with measurements, in particular  
8 using the antisymmetric uranyl stretch, which was the salient figure of merit in this study. A comparison  
9 of the unscaled uranyl frequencies calculated using B3LYP with different basis sets versus the IRMPD  
10 measurements (Figure 5, Table 4) showed that more accurate values were obtained using the SDD basis  
11 set for all elements. Calculated values using 3-21g\* and 6-31+g(d) for C, H, N and O were 20 – 30 cm<sup>-1</sup>  
12 higher than measurements for the solvent complexes, depending on the donor. Values calculated using  
13 6-31+g(d) were slightly better than those generated using 3-21g\*, but differences between the two  
14 calculations were small. The data in Figure 5 may be grouped into three categories: anion complexes  
15 with no donor, an O-donor (H<sub>2</sub>O or acetone), or an N-donor (NH<sub>3</sub> or acetonitrile). Calculations for the  
16 O-donor anion complexes were in best agreement with experiments, being within a few cm<sup>-1</sup> for the all-  
17 SDD basis sets, and on the order of 20 cm<sup>-1</sup> high for the SDD/3-21g\* and SDD/6-31+g(d) basis sets.  
18 Calculations for the complexes containing a neutral that coordinates via a N atom were slightly less  
19 accurate, with differences ranging from 5 – 10 cm<sup>-1</sup> for the all-SDD calculation to ~ 30 cm<sup>-1</sup> using the  
20 gen basis sets. This suggests that N-donation is slightly more aggressive in the gas phase experiment  
21 than predicted by theory. Calculations for the [UO<sub>2</sub>(anion)]<sup>+</sup> complexes containing no neutral donor  
22 displayed the poorest agreement with experiment, being 20 to nearly 60 cm<sup>-1</sup> higher than the  
23 measurements, depending on the basis set used. The poorer agreement likely reflects the high energetic  
24 requirements for photo-fragmentation pathways for these complexes, which is reasonable since they  
25 involve elimination of an oxy radical with concomitant reduction of the uranium center. The need to

1 vibrationally excite the uranyl-anion complexes to a higher level increases the opportunity for the  
2 measured  $\nu_3$  value to be shifted lower as a result of vibrational anharmonicity, or perhaps by  
3 participation of an excited state, as suggested above.



4  
5 **Figure 5.** Uranyl  $\nu_3$  frequencies calculated using B3LYP plotted versus IRMPD measurements. The line  
6 represents the experimental data. Filled square data points were generated using the SDD basis set for all  
7 elements, values unscaled. Values represented by open squares were generated using SDD for uranium  
8 and 3-21g\* for C, H, N and O, while values represented by open triangles utilized 6-31g(d) for C, H, N  
9 and O. Black points represent  $[\text{UO}_2(\text{anion})]^+$  complexes with no neutral donor, red represent those with  
10 O-donating neutrals, and blue represent those with N-donating neutrals.

11

1 Table 4a. Uranyl antisymmetric stretching frequencies ( $\nu_3$ ) for complexes  $[\text{UO}_2\text{AS}_{0,1,2}]^+$ . IRMPD values  
 2 were generated experimentally, and calculated using the B3LYP functional with various basis sets. All  
 3 values reported are unscaled.

A (anion)	S (neutral solvent)	IRMPD measure- ments	B3LYP/ SDD/ 3-21g*	B3LYP/ Stuttgart RSC/RLC (SDD)	B3LYP/ Stuttgart RSC/RLC (SDD)/ 6-31+g(d)	B3LYP/ Stuttgart RSC/RLC/ TZVP	B3LYP/ LANL2dz/ aug-cc- pvdz
OH	-	971	1027	1009	1025	1035	988
OH	H <sub>2</sub> O	983	1003	986	1003	1015	971
OH	NH <sub>3</sub>	976	1002	984	999	1011	964
OH	ACN	972	1003	982	999	--	966
OH	ACO	972	996	977	998	--	961
OH	2 ACO	961	981	957	980	--	945
OAc	-	995	1037	1025	1032	--	993
OAc	H <sub>2</sub> O	993	1017	1002	1015	--	985
OAc	NH <sub>3</sub>	988	1018	1002	1013	--	976
OCH <sub>3</sub>	-	975	1017	997	1011	1018	976
OCH <sub>3</sub>	H <sub>2</sub> O	970	990	975	990	994	961
OCH <sub>3</sub>	NH <sub>3</sub>	966	995	973	987	994	959

4

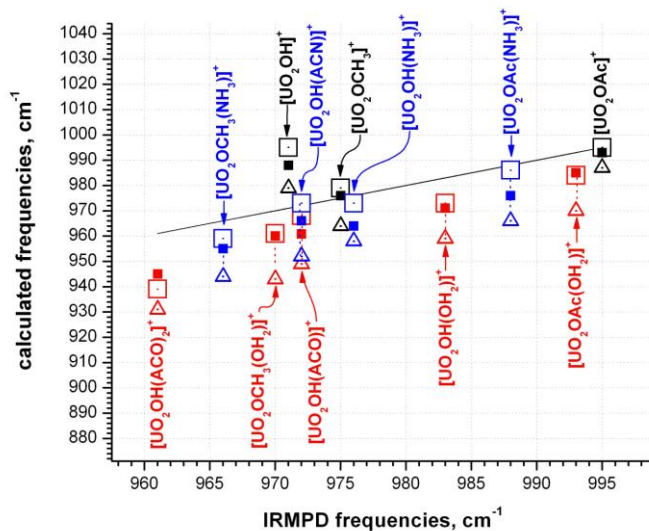
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1 Table 4b. Uranyl antisymmetric stretching frequencies ( $\nu_3$ ) for complexes  $[\text{UO}_2\text{AS}_{0,1,2}]^+$ . IRMPD values  
 2 were generated experimentally, and calculated using LDA and PW91 functionals with various basis sets.  
 3 All values reported are unscaled.

A (anion)	S (neutral solvent)	IRMPD measure- ments	LDA/ SVWN/ DNP	LDA/ LANL/ aug-cc- pvdz	LDA/ Stuttgart RSC / TZVP	PW91/ LANL / aug-cc-pvdz	PW91/ Stuttgart RSC / TZVP	ZORA/ PW91/ TZ2P
OH	-	971	995	958	1017	928	987	979
OH	H <sub>2</sub> O	983	973	939	1001	910	969	959
OH	NH <sub>3</sub>	976	973	937	990	910	962	958
OH	ACN	972	973	--	--	--	--	952
OH	ACO	972	968	--	--	--	--	949
OH	2 ACO	961	939	--	--	--	--	931
OAc	-	995	995	--	--	--	--	987
OAc	H <sub>2</sub> O	993	984	--	--	--	--	970
OAc	NH <sub>3</sub>	988	986	--	--	--	--	966
OCH <sub>3</sub>	-	975	979	949	1003	920	973	964
OCH <sub>3</sub>	H <sub>2</sub> O	970	961	933	997	904	954	943
OCH <sub>3</sub>	NH <sub>3</sub>	966	959	932	980	905	950	944

4  
 5 In contrast, calculations using LDA, PW91, and B3LYP/LANL2dz/aug-cc-pVDZ produced unscaled  
 6 uranyl  $\nu_3$  frequencies that were slightly lower than measurements (Figure 6). . The LDA (calculated  
 7 using DMol<sup>3</sup>) values (Figure 6, open squares) for the  $[\text{UO}_2\text{A}]^+$  complexes and those with a N-donating  
 8 neutral were in good agreement with measurement, with the salient exception of  $[\text{UO}_2\text{OH}]^+$ . Compared  
 9 to experiments, the LDA values for anion complexes with O-donating ligands were systematically lower

1 than values for complexes with N-donors, by about  $10\text{ cm}^{-1}$ . The value calculated for the  
2  $[\text{UO}_2\text{OH}(\text{ACO})_2]^+$  was ca.  $20\text{ cm}^{-1}$  lower than the measured value.



3  
4 **Figure 6.** Unscaled uranyl  $\nu_3$  frequencies calculated using B3LYP/LANL2dz/aug-cc-pVDZ, LDA/VWN  
5 and ZORA/PW91/TZ2P, plotted versus IRMPD measurements. The line represents the experimental data.  
6 The open squares were generated using LDA/VWN, the filled squares B3LYP/LANL2dz/aug-cc-pVDZ,  
7 and the triangles ZORA/PW91/TZ2P. The black points represent  $[\text{UO}_2\text{A}]^+$  complexes with no neutral  
8 donor, red correspond to complexes with O-coordinating neutrals, and blue to those with N-coordinating  
9 neutrals.

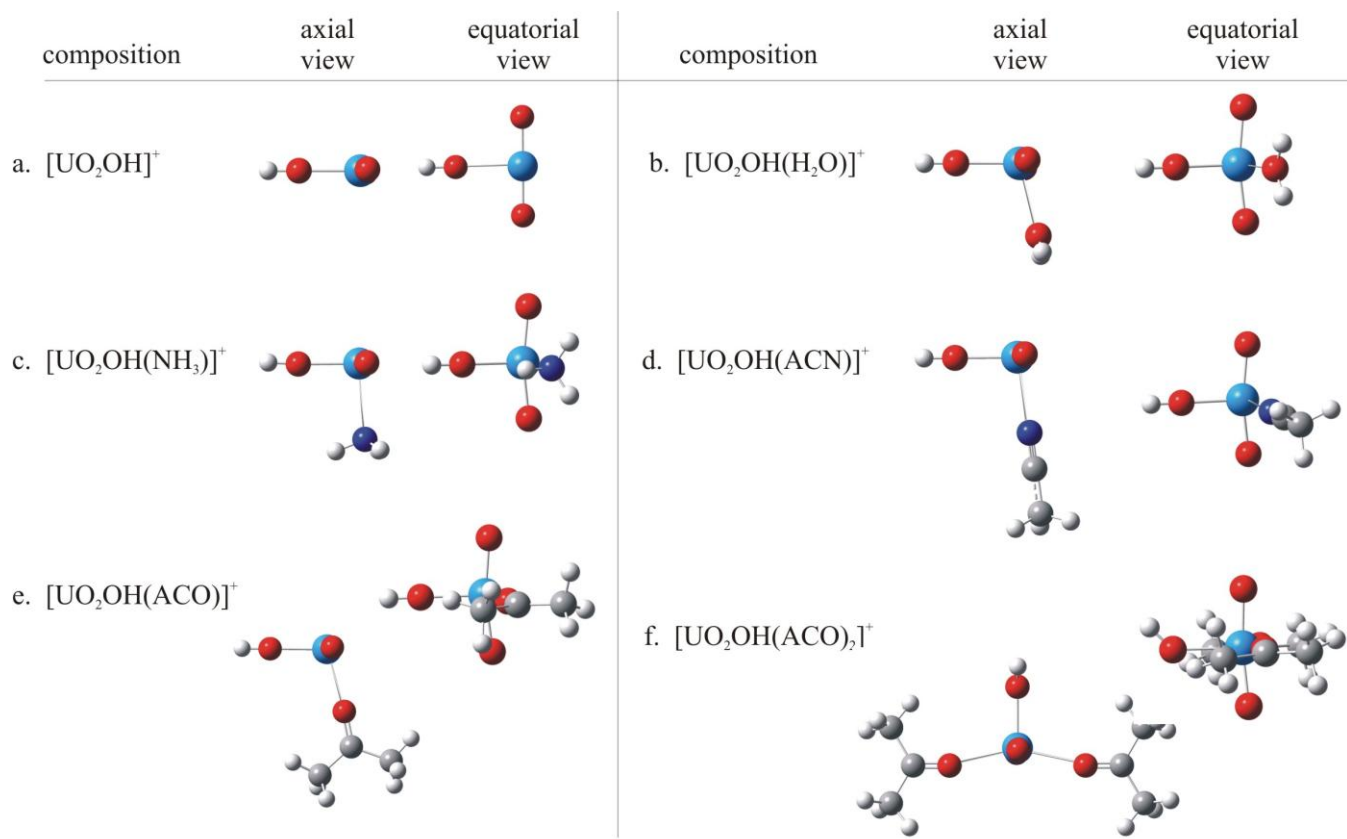
10 The values calculated using B3LYP in Figure 6 (filled squares) differed from those in Figure 5 in that  
11 they were generated using the LANL2dz/aug-cc-pVDZ basis sets. Values calculated for the uranyl  
12 methoxide and acetate complexes without neutrals agreed well with the measured values; the hydroxide  
13 species was on the order of  $18\text{ cm}^{-1}$  higher. The  $[\text{UO}_2\text{AS}]^+$  complexes were all on the order of  $7\text{--}15\text{ cm}^{-1}$   
14 lower than the measurements, and there was no apparent systematic difference between the complexes  
15 containing O-donors and those with N-donors, which indicated that B3LYP/LANL2dz/aug-cc-pVDZ  
16 predicted shifts resulting from both types of ligands consistently.

1 The frequencies were also computed with ZORA/PW91/TZ2P. The results are consistently lower than  
2 the pseudopotential LDA/VWN or B3LYP/LANL2dz/aug-cc-pVDZ values, a feature that was also observed  
3 in our earlier work on the neutral donor ligands.<sup>60</sup> The ligand induced shifts are very similar to the  
4 results obtained with the other approaches, however, and systematic differences between O- and N-  
5 donors were not calculated.

6 Additional insight into the potential interactions from anion binding can be gained by examining the  
7 changes in the calculated bond lengths and angles, which would also check the internal consistency of  
8 the predicted stretching frequencies. We selected the calculations performed using B3LYP/SDD/6-  
9 31+g\*\* for discussing relationships between calculated bond lengths and frequencies, which are listed in  
10 Table 3, and trends in bond lengths with varying ligation are depicted graphically in Figure 7 (detailed  
11 structural parameters generated using B3LYP with three different basis sets are contained in  
12 Supplementary Tables S1 – S12, and visual representations are provided in Figures 7 - 9). As ligands  
13 are added, calculations show that all distances within the uranyl coordination sphere increase. The  
14 magnitude of the increase depends not only on the nucleophilic strength of the different ligands but also  
15 on their volumes, and the calculations provide a means to develop a more quantitative assessment of the  
16 effect of ligand addition to uranyl. The O=U=O bond length is represented by the lower three traces,  
17 and the effect of the anion A, and subsequent addition of a neutral solvent S is very similar for the  
18 acetate, the hydroxy and the methoxide complexes. The uranyl bond elongates by 0.042 Å, 0.044, and  
19 0.048 Å for OAc<sup>-</sup>, OH<sup>-</sup> and OCH<sub>3</sub><sup>-</sup>, respectively. This is also the order of increasing anion basicity,  
20 resulting in donation of more electron density to the uranium atom, and attendant repulsion of the axial  
21 oxygen atoms. The amount of donation was quantified by performing charge analysis calculations with  
22 ZORA/PW91/TZ2P. The Hirshfeld method shows donation to uranyl of 0.56e (OAc), 0.53e (OH), and  
23 0.65e (OCH<sub>3</sub>) while the VDD method gives very similar values of 0.53, 0.52 and 0.63e, respectively.

24





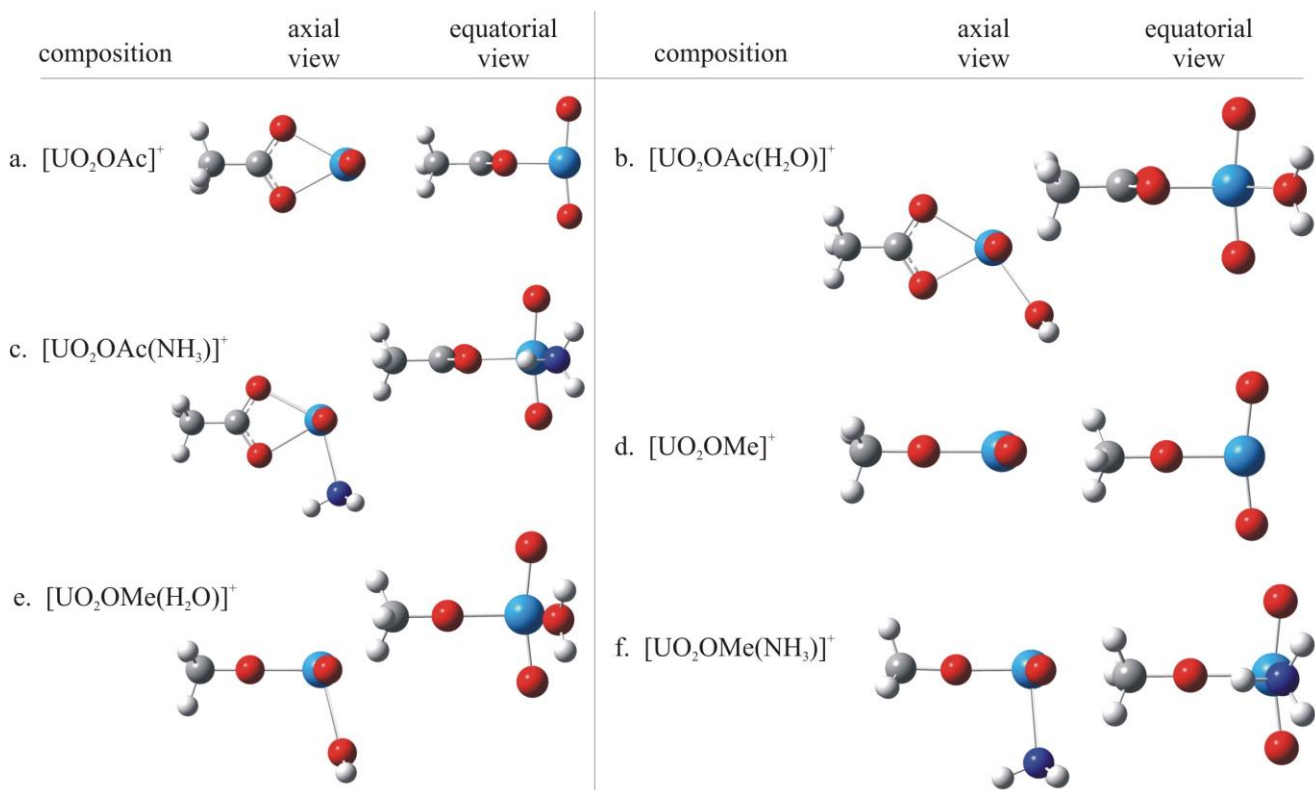
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2 **Figure 7.** Lowest energy conformations of calculated for  $[\text{UO}_2\text{OH}]^+$  and its solvated complexes.

3 Calculations were performed using hybrid B3LYP functional with the SDD basis set on U and 3-21g\*

4 on C, H, N and O.

5



1

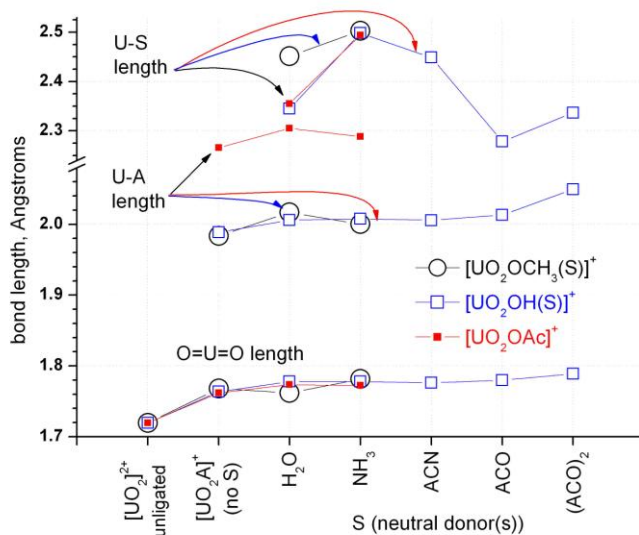
2 **Figure 8.** Lowest energy conformations of  $[\text{UO}_2\text{OAc}]^+$ ,  $[\text{UO}_2\text{OMe}]^+$  and their solvent complexes with  
 3 water and ammonia. Calculations were performed using hybrid B3LYP functional with the SDD basis  
 4 set on U and 3-21g\* on C, H, N and O.

5

1 Table 3. Bond lengths (Angstroms) and O=U=O bond angles for [UO<sub>2</sub>AS]<sup>+</sup> complexes, calculated using  
 2 Gaussian 03, at the B3LYP level of theory. The MWB60 (SDD) basis set was used for U, and 3-21g\*  
 3 for C, H, N and O.

A (anion)	S (neutral solvent)	U=O length, Å	U-anion length, Å	U-neutral length, Å	O=U=O angle
[UO <sub>2</sub> ] <sup>2+</sup> , unligated	n/a	1.7002	n/a	n/a	179.578
OAc	n/a	1.7444	2.2687	n/a	170.346
OAc	H <sub>2</sub> O	1.7735	2.2968	2.4616	171.024
OAc	NH <sub>3</sub>	1.7540	2.3015	2.5566	171.716
OH	n/a	1.7450	2.0104	n/a	167.409
OH	H <sub>2</sub> O	1.7546	2.0277	2.4416	167.606
OH	NH <sub>3</sub>	1.7581	2.0332	2.5437	167.245
OH	ACN	1.7571	2.0318	2.4771	166.983
OH	ACO	1.7592	2.0052	2.3252	169.898
OH	(ACO) <sub>2</sub>	1.7682	2.0828	2.3931	172.640
OCH <sub>3</sub>	n/a	1.7510	1.9986	n/a	167.237
OCH <sub>3</sub>	H <sub>2</sub> O	1.7618	2.0167	2.4514	167.559
OCH <sub>3</sub>	NH <sub>3</sub>	1.7633	2.0211	2.5561	167.187

4



1

2 **Figure 9.** Bond lengths plotted versus neutral for  $[\text{UO}_2\text{AS}]^+$  complexes. Values for unligated  $[\text{UO}_2]^{2+}$   
 3 and  $[\text{UO}_2\text{A}]^+$  complexes are also included. Values were calculated using B3LYP (Gaussian) with the  
 4 SDD/3-21g\* basis set. (Note break in Y axis at 2.08 Å.)

5 The addition of a neutral donor to the uranyl anion complexes induces a further lengthening of the  
 6 uranyl bonds (Figure 9), by 0.011 to 0.016 Å, with the largest shifts occurring for the more basic  
 7 neutrals: in this study addition of ACO caused the largest O=U=O elongation, consistent with the low  
 8 uranyl frequency measured in the IRMPD spectrum. The magnitude of the elongation on addition of a  
 9 neutral is much less than that calculated for the initial attachment of the anion. Hirshfeld analysis  
 10 showed that the strongest donating neutral species, acetone, donates 0.17 e (for one acetone) or 0.25e  
 11 (for two acetones) to an uranylhydroxide unit in the  $[\text{UO}_2\text{OH}(\text{ACO})_{1,2}]^+$  complexes (which have the  
 12 greatest O=U=O elongation); these values are significantly lower than those calculated for the anions.

13 The calculations also predict that the uranium-anion distance will be lengthened by addition of a  
 14 neutral ligand, which is shown by the middle three traces in Figure 9. Increases ranging from 0.017 to  
 15 0.024 Å occurred in the U-OH length for the hydroxide complexes, with the magnitude depending on  
 16 the basicity of the neutral, and the largest elongation being for addition of ACO. When a second ACO is

1 added, the U-OH distance elongates by another 0.036 Å. The U-OCH<sub>3</sub> bond distance experiences very  
2 nearly identical increases upon addition of H<sub>2</sub>O and NH<sub>3</sub> to [UO<sub>2</sub>OCH<sub>3</sub>]<sup>+</sup>. The U-anion distance  
3 calculated for the acetate complex is substantially longer than that for either the hydroxide or the  
4 methoxide, and the B3LYP calculations indicated a bidentate-bound acetate, although LDA/VWN  
5 suggested a monodentate structure. Using either approach, the U-acetate length is nearly 0.27 Å longer  
6 than for the hydroxide or methoxide. Addition of H<sub>2</sub>O or NH<sub>3</sub> to the complex causes elongation of the  
7 U-acetate bonds by ~ 0.04 and 0.02 Å, respectively. The fact that H<sub>2</sub>O produced a longer U-anion  
8 elongation than NH<sub>3</sub> is contrary to what would be expected based on calculated coordination energies  
9 (NH<sub>3</sub> ~9 kcal/mole greater than H<sub>2</sub>O),<sup>40</sup> but may be consistent with the fact that uranyl behaves as a hard  
10 acid,<sup>6,40</sup> interacting more strongly with the oxygen donors.

11 The U-S bond length in [UO<sub>2</sub>AS]<sup>+</sup> increased when NH<sub>3</sub> was substituted for H<sub>2</sub>O, for all three anions  
12 studied. Further U-neutral bond length comparisons involved only the hydroxide, and decreased in the  
13 order NH<sub>3</sub> > ACN > ACO, minimizing at 2.27 Å. The trend correlates inversely with increasing ligand  
14 nucleophilicity. Addition of a second ACO as the third equatorial ligand in [UO<sub>2</sub>OH(ACO)<sub>2</sub>]<sup>+</sup> loosens  
15 the overall complex: the U-neutral bond is lengthened by nearly 0.06 Å, and this is accompanied by a  
16 lengthening of the U-OH bond by 0.036 Å, and the O=U=O bond by nearly 0.01 Å. As the coordination  
17 sphere is completed, distortions of the O=U=O angle from linearity are lessened, and the value  
18 approaches 180°.

## 19 CONCLUSIONS

20 The structure of uranium complexes has been a persistent topic of research in the chemical community  
21 because the participation of 5f, 6d and 7s orbitals offers a broad array of possible structures and reaction  
22 pathways. The desire to understand and then manipulate uranium chemistry has motivated determined  
23 investigations of structure and bonding using spectroscopy and computational chemistry. In principle  
24 these approaches should be highly complementary, but in practice results from each cannot be correlated  
25 with each other because spectroscopy measurements on condensed phase systems almost always

1 measure an ensemble of species, while calculations produce data for single discrete species, and do not  
2 always include specific and/or long-range interactions with solvent. Consequently it is difficult to use  
3 condensed-phase spectroscopic measurements to evaluate computational accuracy, which is badly  
4 needed for molecules containing  $f$  elements. Infrared spectra of gas phase complexes generated using  
5 IRMPD provide data for discrete species that are of great value for evaluating ligand binding trends and  
6 computational chemistry results.

7 Much emphasis has been placed on the study of uranyl dication complexes, and prior IRMPD studies  
8 of ACO complexes by our groups enabled comparison of antisymmetric O=U=O and C=O frequencies  
9 with solution phase measurements and computational results.<sup>60</sup> However at mid-pH ranges, uranyl-anion  
10 pairs are more prevalent and hence in the present study, IRMPD of ion pairs involving hydroxide,  
11 acetate and methoxide were examined. The uranyl antisymmetric frequency values were red-shifted  
12 equal to or greater than  $\text{UO}_2^{2+}$  coordinated with four or five neutral donor ligands. While vibrational  
13 anharmonicity no doubt contributes to these low frequency values, the intrinsic frequencies of the ion  
14 pair complexes are lower than expected when compared with solution phase measurements and with  
15 past and present DFT results. The addition of a solvent neutral S to the ion pairs did not result in  
16 systematic decreases in the  $\nu_3$  values. But when frequencies for the  $[\text{UO}_2\text{AS}]^+$  species were compared  
17 for differing neutrals, the  $\nu_3$  value decreased with increasing S nucleophilicity, consistent with theory,  
18 intuition and previous IRMPD results.<sup>60</sup>

19 The  $[\text{UO}_2\text{OCH}_3]^+$  molecule underwent wavelength-specific fragmentation reactions, eliminating the  
20  $\text{OCH}_3$  radical at a frequency  $20\text{ cm}^{-1}$  lower than fragmentations involving rearrangement and or loss of  
21 H atom(s). DFT modeling suggested that the  $\text{OCH}_3$  radical loss was activated by absorption at the uranyl  
22 stretching frequency, while the H atom loss/rearrangement eliminations were activated by absorption at  
23 the C-O stretching frequency. Identifying the cause of this phenomenon remains an outstanding task:  
24 IRMPD anharmonicity together with absorption non-linearities (as observed in the spectra of the *para*-  
25 aminobenzoic acid cation<sup>58</sup> and  $[\text{CeOH}(\text{ACO})_{n=3,4}]^{2+}$  cation<sup>93</sup>) may contribute to the phenomenon,

1 however the very large differences in the different photo-fragmentation channels suggests that there may  
2 be another factor at work, such as promotion to an excited state electronic configuration, which would  
3 be energetically feasible.

#### 4 ACKNOWLEDGMENTS

5 Work by G. S. Groenewold and A. K. Gianotto was supported by the U.S. Department of Energy,  
6 Assistant Secretary for Environmental Management, and the INL Laboratory Directed Research &  
7 Development Program under DOE Idaho Operations Office Contract DE-AC07-05ID14517. M. J. Van  
8 Stipdonk was supported in part through a grant from the U. S. National Science Foundation (CAREER-  
9 0239800). Gaussian 03 calculations were performed at the Wichita State University High-performance  
10 Computing Center (HIPECC), a facility supported by the U. S. National Science Foundation under  
11 Grant No. EIA-0216178 and Grant No. EPS-0236913, with matching support from the State of Kansas  
12 and HIPECC. W. A. de Jong's research was performed, in part, using the Molecular Science Computing  
13 Facility in the William R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility  
14 sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research located at the  
15 Pacific Northwest National Laboratory, which is operated for the Department of Energy by Battelle. The FOM  
16 authors, Ivan Infante and Lucas Visscher were supported by the Nederlandse Organisatie voor  
17 Wetenschappelijk Onderzoek (Dutch National Science Foundation). The skillful assistance by the  
18 FELIX staff, in particular Dr. B. Redlich, is gratefully acknowledged. Construction and shipping of the  
19 FTMS instrument was made possible through funding from the National High Field FT-ICR Facility  
20 (grant CHE-9909502) at the National High Magnetic Field Laboratory, Tallahassee, FL, as was travel  
21 support for one of the INL authors; John Eyler's assistance was particularly invaluable.

22

1 SUPPORTING INFORMATION AVAILABLE:

2 Complete listings of structural data calculated using B3LYP with the SDD, and SDD / 3-21g\* basis  
3 sets are provided in tables S1–S7 in the supplementary information. Visual representations are also  
4 provided, in Figures S1–S4. Complete citations for references 73 and 80 are also included. The material  
5 is available free of charge on the Internet at <http://pubs.acs.org>.

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- 20

## 1 SUPPLEMENTARY INFORMATION

2 **Infrared Spectroscopy Discrete Uranyl Anion Complexes**

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4 Kullman, Travis J. Cooper, David T. Moore, Nick Polfer, Jos Oomens, Ivan Infante, Lucas Visscher,  
5 Bertrand Siboulet, and Wibe A. de Jong

6  
7  
8 **Table S1.** Unscaled frequencies for  $[\text{UO}_2]^{2+}$  and  $[\text{UO}_2\text{A}]^+$  complexes, calculated using B3LYP and the  
9 SDD (MWB60) basis set for all atoms.

A (anion)	Antisymmetric O=U=O Stretch ( $\nu_3$ ), $\text{cm}^{-1}$	Symmetric O=U=O Stretch ( $\nu_1$ ), $\text{cm}^{-1}$	Other
$[\text{UO}_2]^{2+}$	1120.30	-	157.42
OAc	1025.08	936.23	-
OH	1009.46	926.75	701.70 (U-O)
OCH <sub>3</sub>	996.53	905.71	1029.72 (O-CH <sub>3</sub> )

10

11

1 **Table S2.** Unscaled frequencies for  $[\text{UO}_2\text{AS}]^+$  complexes. calculated using calculated using B3LYP  
 2 and the SDD (MWB60) basis set for all atoms.

A (anion)	S (neutral)	Antisymmetric O=U=O Stretch ( $\nu_3$ ), $\text{cm}^{-1}$	Symmetric O=U=O Stretch ( $\nu_1$ ), $\text{cm}^{-1}$	Other
OH	H <sub>2</sub> O	986.06	905.13	683.38 (U-OH)
	NH <sub>3</sub>	984.23	903.71	685.28 (U-OH)
	ACN			
	ACO	977.01	896.07	666.76 (U-OH)
	(ACO) <sub>2</sub>	956.65	-	638.17 (U-OH)
OCH <sub>3</sub>	H <sub>2</sub> O	974.85	886.98	1054.48
	NH <sub>3</sub>	973.09	885.89	1056.86
OAc	H <sub>2</sub> O	1001.69	914.06	-
	NH <sub>3</sub>	1002.08	914.76	-

3

4 **Table S3.** Bond lengths (Angstroms) and O=U=O bond angles for  $[\text{UO}_2]^{2+}$  and  $[\text{UO}_2\text{A}]^+$  complexes.  
 5 calculated using B3LYP and the SDD (MWB60) basis set for all atoms.

A (anion)	U=O length, Å	U-O length (U to anion), Å	O=U=O angle
$[\text{UO}_2]^{2+}$ unligated	1.7167	-	180.0
OAc	1.7609	2.2705	169.656
OH	1.7630	2.0008	166.912
OCH <sub>3</sub>	1.7685	1.9915	166.611

6

7



- 1 **Table S4.** Bond lengths (Angstroms) and O=U=O bond angles for [UO<sub>2</sub>AS]<sup>+</sup> complexes. calculated  
 2 using B3LYP and the SDD (MWB60) basis set for all atoms.

A (anion)	S (neutral)	U=O length, Å	U-anion length, Å	U-ligand length, Å	O=U=O angle
OH	H <sub>2</sub> O	1.7763	2.0197	2.3869	166.982
	NH <sub>3</sub>	1.7773	2.0237	2.5085	166.566
	ACN				
	ACO	1.7795	2.0303	2.2863	167.059
	(ACO) <sub>2</sub>	1.7899	2.0556	2.3510	169.423
OCH <sub>3</sub>	H <sub>2</sub> O	1.7814	2.0099	2.3954	166.803
	NH <sub>3</sub>	1.7822	2.0134	2.5183	166.374
OAc	H <sub>2</sub> O	1.7718	2.3185	2.3978	170.367
	NH <sub>3</sub>	1.7713	2.3027	2.5104	170.651

3

4

1 **Table S5.** Unscaled frequencies for  $[\text{UO}_2]^{2+}$  and  $[\text{UO}_2\text{A}]^+$  complexes, calculated using B3LYP with the  
 2 SDD (MWB60) basis set for U, and 3-21g\* for C, H, N and O.

A (anion)	Antisymmetric O=U=O stretch ( $\nu_3$ ), $\text{cm}^{-1}$	Symmetric O=U=O stretch ( $\nu_1$ ), $\text{cm}^{-1}$	Other
$[\text{UO}_2]^{2+}$	1124.69	-	183.27 (U-O)
OAc	1036.514	945.49	-
OH	1026.58	941.42	734.61 (U-O)
$\text{OCH}_3$	1016.62	922.96	1041.61 (O-CH <sub>3</sub> )

3

4 **Table S6.** Unscaled frequencies for  $[\text{UO}_2\text{AS}]^+$  complexes, calculated using B3LYP with the SDD  
 5 (MWB60) basis set for U, and 3-21g\* for C, H, N and O.

A (anion)	S (neutral)	Antisymmetric O=U=O stretch ( $\nu_3$ ), $\text{cm}^{-1}$	Symmetric O=U=O stretch ( $\nu_1$ ), $\text{cm}^{-1}$	Other
OH	$\text{H}_2\text{O}$	1002.78	919.82	715.99 (U-OH)
	$\text{NH}_3$	1002.03	919.38	717.72 (U-OH)
	ACN	1002.93	919.29	714.40 (U-OH)
	ACO	996.34	913.06	705.59 (U-OH)
	$(\text{ACO})_2$	980.77	897.11	666.29 (U-OH)
$\text{OCH}_3$	$\text{H}_2\text{O}$	990.49	905.25	1079.62 (U-OCH <sub>3</sub> )
	$\text{NH}_3$	994.66	904.73	1067.07 (U-OCH <sub>3</sub> )
OAc	$\text{H}_2\text{O}$	1016.66	927.48	-
	$\text{NH}_3$	1017.97	928.55	-

6

7

1 **Table S7.** Bond lengths (Angstroms) and O=U=O bond angles for  $[\text{UO}_2]^{2+}$  and  $[\text{UO}_2\text{A}]^+$  complexes,  
 2 calculated using B3LYP with the SDD (MWB60) basis set for U, and 3-21g\* for C, H, N and O.

A (anion)	U=O length, Å	U-O length (U to ligand), Å	O=U=O angle
$[\text{UO}_2]^{2+}$ unligated	1.7193	-	180.000
OAc	1.7617	2.2658	170.628
OH	1.7636	1.9887	167.618
OCH <sub>3</sub>	1.7681	1.9835	167.555

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4 **Table S8.** Bond lengths (Angstroms) and O=U=O bond angles for  $[\text{UO}_2\text{AS}]^+$  complexes, calculated  
 5 using B3LYP with the SDD (MWB60) basis set for U, and 3-21g\* for C, H, N and O.

A (anion)	S (neutral)	U=O length, Å	U-anion length, Å	U-ligand length, Å	O=U=O angle
OH	H <sub>2</sub> O	1.7778	2.0060	2.3450	168.121
	NH <sub>3</sub>	1.7780	2.0078	2.4979	167.681
	ACN	1.7762	2.0056	2.4486	167.422
	ACO	1.7797	2.0133	2.2784	168.146
	(ACO) <sub>2</sub>	1.7890	2.0493	2.3368	172.843
OCH <sub>3</sub>	H <sub>2</sub> O	1.7618	2.0167	2.4514	167.559
	NH <sub>3</sub>	1.7814	2.0004	2.5031	167.652
OAc	H <sub>2</sub> O	1.7735	2.3050	2.3552	171.450
	NH <sub>3</sub>	1.7723	2.2884	2.4942	171.715

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1 **Table S9.** Unscaled frequencies for  $[\text{UO}_2]^{2+}$  and  $[\text{UO}_2\text{A}]^+$  complexes, calculated using B3LYP with the  
 2 SDD (MWB60) basis set for U, and 6-31+g\*\* for C, H, N and O.

A (anion)	Antisymmetric O=U=O stretch ( $\nu_3$ ), $\text{cm}^{-1}$	Symmetric O=U=O stretch ( $\nu_1$ ), $\text{cm}^{-1}$	Other
$[\text{UO}_2]^{2+}$	1140.17	-	183.41 (U-O)
OAc	1032.31	949.82	-
OH	1025.38	945.98	678.71 (U-O)
$\text{OCH}_3$	1010.81	923.05	1054.43 (O- $\text{CH}_3$ )

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4 **Table S10.** Unscaled frequencies for  $[\text{UO}_2\text{AS}]^+$  complexes, calculated using B3LYP with the SDD  
 5 (MWB60) basis set for U, and 6-31+g\*\* for C, H, N and O.

A (anion)	S (neutral)	Antisymmetric O=U=O stretch ( $\nu_3$ ), $\text{cm}^{-1}$	Symmetric O=U=O stretch ( $\nu_1$ ), $\text{cm}^{-1}$	Other
OH	$\text{H}_2\text{O}$	1003.05	925.22	658.56 (U-OH)
	$\text{NH}_3$	999.39	922.3	656.09 (U-OH)
	ACN	999.23	921.31	652.34 (U-OH)
	ACO	997.79	917.85	626.43 (U-OH)
	$(\text{ACO})_2$	979.63	900.29	592.51 (U-OH)
$\text{OCH}_3$	$\text{H}_2\text{O}$	990.49	905.25	1079.62 (U- $\text{OCH}_3$ )
	$\text{NH}_3$	987.23	902.94	1080.10 (U- $\text{OCH}_3$ )
OAc	$\text{H}_2\text{O}$	1014.81	925.96	-
	$\text{NH}_3$	1013.37	926.16	-

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1 **Table S11.** Bond lengths (Angstroms) and O=U=O bond angles for  $[\text{UO}_2]^{2+}$  and  $[\text{UO}_2\text{A}]^+$  complexes,  
 2 calculated using B3LYP with the SDD (MWB60) basis set for U, and 6-31+g\*\* for C, H, N and O.

A (anion)	U=O length, Å	U-O length (U to ligand), Å	O=U=O angle
$[\text{UO}_2]^{2+}$ unligated	1.7002	-	179.578
OAc	1.7450	2.0104	167.409
OH	1.7510	1.9986	167.237
OCH <sub>3</sub>	1.7681	1.9835	167.555

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4 **Table S12.** Bond lengths (Angstroms) and O=U=O bond angles for  $[\text{UO}_2\text{AS}]^+$  complexes, calculated  
 5 using B3LYP with the SDD (MWB60) basis set for U, and 6-31+g\*\* for C, H, N and O.

A (anion)	S (neutral)	U=O length, Å	U-anion length, Å	U-ligand length, Å	O=U=O angle
OH	H <sub>2</sub> O	1.7546	2.0277	2.4416	167.606
	NH <sub>3</sub>	1.7581	2.0332	2.5437	167.245
	ACN	1.7571	2.0318	2.4771	166.983
	ACO	1.7592	2.0052	2.3252	169.898
	(ACO) <sub>2</sub>	1.7682	2.0828	2.3931	172.640
OCH <sub>3</sub>	H <sub>2</sub> O	1.7618	2.0167	2.4514	167.559
	NH <sub>3</sub>	1.7633	2.0211	2.5561	167.187
OAc	H <sub>2</sub> O	1.7735	2.2968	2.4616	171.024
	NH <sub>3</sub>	1.7540	2.3015	2.5566	171.716

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