Supporting Information to:

Interdisciplinary round-robin test on molecular spectroscopy of the U(VI) acetate system

Katharina Müller * (1), Harald Foerstendorf (1), Robin Steudtner (1), Satoru Tsushima (1, 2), Michael U. Kunke (3), Grégoire Lefèvre (4), Jörg Rothe (5), Harris Mason (6), Zoltán Szabó (7), Ping Yang (8), Christian K. R. Adam (5), Rémi André (9), Katlen Brennenstuhl (3), Ion Chiorescu (10), Herman M. Cho (11), Gaëlle Creff (12), Frédéric Coppin (13), Kathy Dardenne (5), Christophe Den Auwer (12), Björn Drobot (1, 14), Sascha Eidner (3), Nancy J. Hess (15), Peter Kaden (1, 5), Alena Kremleva (10), Jerome Kretzschmar (1), Sven Krüger (10), James A. Platts (16), Petra J. Panak (5, 17), Robert Polly (5), Brian A. Powell (18), Thomas Rabung (5), Roland Redon (19), Pascal E. Reiller (20), Notker Rösch (10, 21), André Rossberg (1, 22), Andreas C. Scheinost (1, 22), Bernd Schimmelpfennig (5), Georg Schreckenbach (23), Andrej Skerencak-Frech (5, 17), Vladimir Sladkov (24), Pier Lorenzo Solari (25), Zheming Wang (15), Nancy M. Washton (26), Xiaobin Zhang (23)

1 Helmholtz-Zentrum Dresden – Rossendorf, Institute of Resource Ecology, Bautzner Landstr. 400, D-01328 Dresden, Germany
2 Institute of Innovative Research, Tokyo Tech World Research Hub Initiative (WRHI), Tokyo Institute of Technology, Tokyo, 152–8550, Japan
3 Institute of Chemistry, University of Potsdam, 14476 Potsdam, Germany
4 Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), F-75005 Paris, France
5 Institute for Nuclear Waste Disposal (KIT-INE), Karlsruhe Institute of Technology, P.O. Box 3640, 76021 Karlsruhe, Germany
6 Physical and Life Science Directorate, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, U.S.A.
7 School of Chemistry, Organic Chemistry, Royal Institute of Technology, S-100 44, Stockholm, Sweden
8 Theoretical Division, Physics and Chemistry of Materials, Los Alamos National Laboratory, Los Alamos, NM 87545, U.S.A.
9 Laboratoire LIS-UMR CNRS 7020, Aix-Marseille Université, Université de Toulon, 83041 Toulon Cedex 9, France
10 Department of Chemistry, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany
11 Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, MS K2-57, Richland, WA 99352, U.S.A
12 Université Côte d’Azur, CNRS, Institut de Chimie de Nice, UMR7272, 06108 Nice, France
13 Institut de Radioprotection et de Sûreté Nucléaire (IRSN/PSE-ENV/SRTE/LR2T), CE Cadarache, BP3, 13115 Saint Paul lez Durance, France
14 Technische Universität Dresden, Central Radionuclide Laboratory, Zellescher Weg 19, 01069, Dresden, Germany
15 Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, 3335 Innovation Blvd, Richland, WA 99354, U.S.A.
16 School of Chemistry, Cardiff University, Park Place, Cardiff CF10 3AT, UK
17 Institute of Physical Chemistry, Heidelberg University, Im Neuenheimer Feld 253, D-69120 Heidelberg, Germany
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1 Organization of the RRT

Figure S1 1: General organization and aims of the RRT on molecular spectroscopy.
| CLUSTER | CONTRIBUTING INSTITUTION |
|---------|-------------------------|
| VIB     | Clemson University, U.S.A.  
Chimie ParisTech, PSL Research University, CNRS, France  
Helmholtz-Zentrum Dresden-Rossendorf, Germany  
Université Côte d'Azur, France  
Universität Potsdam, Germany |
| LUM     | Commissariat à l’énergie atomique et aux énergies alternatives, France  
Helmholtz-Zentrum Dresden-Rossendorf, Germany  
Institut de Radioprotection et de Sûreté Nucléaire, France  
Karlsruhe Institute of Technology, Germany  
Institut de Physique Nucléaire d’Orsay, France  
Pacific Northwest National Laboratory, U.S.A.  
Heidelberg University, Germany  
Universität Potsdam, Germany  
Université de Toulon, France |
| NMR     | Helmholtz-Zentrum Dresden-Rossendorf, Germany  
Karlsruhe Institute of Technology, Germany  
Lawrence Livermore National Laboratory, U.S.A.  
Pacific Northwest National Laboratory, U.S.A.  
Royal Institute of Technology, Sweden |
| XAS     | Helmholtz-Zentrum Dresden-Rossendorf, Germany @ ROBL-BL / ESRF  
Karlsruhe Institute of Technology, Germany @ INE-BL / KIT Synchrotron Light Source  
Université Côte d'Azur, France @ MARS-BL / SOLEIL |
| QCC     | Cardiff University, U.K.  
Helmholtz-Zentrum Dresden-Rossendorf, Germany  
Karlsruhe Institute of Technology, Germany  
Los Alamos National Laboratory, U.S.A.  
Technische Universität München, Germany  
University of Manitoba, Canada |
2 Calculated Speciation

A speciation calculation has been performed using the chemical equilibrium software MEDUSA with the corresponding thermodynamic database HYDRA, that includes NEA TDB\(^1\) and the database of Martell and Smith\(^2\) with the following log \(K_0\) data.

| Species    | (1,1) | (1,2) | (1,3) |
|------------|-------|-------|-------|
| \(\log K_0\) | 3.06  | 5.57  | 6.97  |

The HYDRA-MEDUSA code uses the following equation to calculate the activity coefficient of a species. This is a variation of the Extended Debye-Hückel equation based on an approximation to the model by Helgeson et al.\(^3\) and Oelkers and Helgeson\(^4\). \(Z_i\) is the charge of the ion, \(I\) the ionic strength (M), \(A\) is a constant equal to 0.5100 \(\text{mol}^{0.5} \cdot \text{kg}^{0.5}\) at 297.15 K, \(B\) is a parameter defined by temperature, pressure and the dielectric constant of water and \(b\) is a parameter dependent on temperature and pressure.

\[
\log(\gamma_i) = -Z_i^2 \left( \frac{A \sqrt{I}}{1 + B \sqrt{I}} \right) - \log(1 + 0.018I) + bI
\]

Figure SI 2: Speciation diagram of U(VI)–acetate complex system at the conditions used within the RRT (0.025 M U(VI), 0.95 M ac, \(I = 1\) M, \(T = 297.15\) K. The dotted lines represent the pH conditions of the RRT samples U1-U4.
According to the thermodynamic speciation calculations (Figure SI 2), four U(VI) species are expected in the U(VI) acetate system: the fully hydrated (1,0) species, i.e., the UO$_2$(H$_2$O)$_5^{2+}$ complex, under very acidic conditions and the (1,1), (1,2), and (1,3) species under less acidic conditions. Only the (1,0) and (1,3) species are present as predominant complexes at pH 1 and pH 4, respectively, whereas complex species mixtures exist in the intermediate pH range.
The RRT samples were prepared at HZDR and subsequently shipped to each participating institution in appropriate sample compartments. All sample preparation and analysis were conducted under ambient atmosphere and at room temperature (25 °C). All chemicals were of analytical grade. High purity double-deionized water with a resistivity of 18.2 MΩ/cm was used. Four samples containing U(VI), denoted U1 to U4, were prepared by dissolving uranyl acetate dihydrate (Merck) in 96% acetic acid (Merck) and then were diluted with water until the final concentration (0.025 M U(VI) and 0.95 M acetic acid) was reached. An excess of ligands was added to ensure that all uranium is complexed under the prevailing conditions. Subsequently, the samples were adjusted to pH 1.0, 2.0, 2.5, and 3.5 by adding appropriate amounts of acid (HCl for VIB and XAS; HClO₄ for LUM) or NaOH. Equivalent samples were prepared in one unique batch. An overview of the samples is given in Table SI 2.

Reference samples containing only acetic acid, denoted B1 to B4, were concordantly prepared. Samples for NMR spectroscopy were prepared in deuterated media using D₂O (>99.99%, Sigma Aldrich), DCl and NaOD (both Deutero, containing 0.01% internal NMR standard (4,4-dimethyl-4-silapentane-1-sulfonic acid, DSS, 97% Sigma Aldrich).

The spectroscopic properties of the samples were determined using vibrational, luminescence, X-ray absorption, and NMR spectroscopy. Furthermore, UV-vis absorption spectroscopy as easily accessible method was used for frequent quality control. In comparison to organic substances the molar extinction coefficient ($\varepsilon_{414\,\text{nm}}$) of U(VI) is extremely low with $\approx 8$ L·mol⁻¹·cm⁻¹. Based on the Lambert–Beer law ($E_{\lambda} = \varepsilon_{\lambda} \cdot c \cdot d$) the common working concentration is 1 mM for classical cuvette measurements, why UV-vis spectroscopy becomes nowadays less attractive for U(VI) speciation studies and was therefore not considered as single cluster in the RRT. Nevertheless, the long-term stability of the RRT samples were monitored using UV-vis absorption spectroscopy at various time steps (Figure SI 3, left), shaking rates,
temperatures (25 ± 10 °C) and in the presence and absence of light. For more information and reference spectra the reader is referred to recent UV-vis absorption spectroscopic studies of the U(VI) acetate complex system by Lucks and Kwiatek and respective co-workers.6-7

Aliquots were sealed in semi-micro plastic cuvettes (LUM, XAS) in sterile 10 mL injection glass bottles (VIB) or in NMR tubes (cf. Figure SI 3, right). For transport, the vessels were wrapped in aluminum foil. Prior to shipment and after reshipment, if applicable, the samples were analyzed using UV-vis absorption spectroscopy for reference and for further stability testing, respectively.

| Sample | c(UO$_2^{2+}$) / M | c(Ac) / M | I / M | pH |
|--------|------------------|-----------|-------|----|
| U1     | 0.025            | 0.95      | 1     | 1.0|
| B1     | 0.95             | 1         |       | 1.0|
| U2     | 0.025            | 0.95      | 1     | 2.0|
| B2     | 0.95             | 1         |       | 2.0|
| U3     | 0.025            | 0.95      | 1     | 2.5|
| B3     | 0.95             | 1         |       | 2.5|
| U4     | 0.025            | 0.95      | 1     | 3.5|
| B4     | -                | 0.95      | 1     | 3.5|
Figure SI 3: Left: Long-term stability of the RRT samples monitored using UV-vis absorption spectroscopy prior to shipment in 2013 (solid) and in 2019 (dashed). Right: Photograph of samples for luminescence and vibrational spectroscopy.
4 Clusters and Experimental Parameters of the Applied Methods

4.1 Vibrational Spectroscopy (VIB)

Five institutions participated in the VIB cluster (see Table SI 1), two of which provided both IR and Raman data. All spectra were recorded on commercially available instruments. For IR measurements, all participants used ATR accessories containing diamond as an internal reflection element. For Raman spectroscopy, various excitation wavelengths were chosen. All relevant setting parameters are given in Tables SI 3 and SI 4.

Table SI 3: Details of IR spectroscopic measurements.

| Participant | IR-1 | IR-2 | IR-3 | IR-4 |
|-------------|------|------|------|------|
| Model       | Bruker Vertex 70v | Thermo Nicolet 6700 | Thermo Nicolet 6700 | Bruker Tensor 27 |
| Software    | OPUS | Omnic | Omnic | OPUS |
| Detector    | MCT | DLaTGS | MCT | DLaTGS |
| No. of scans| 256 | 128 (64) | 256 | 100 |
| Resolution (cm\(^{-1}\)) | 4 | 4 (2) | 4 | 4 |
| Cell type   | ATR crystal covered with Teflon flow cell | Harrick ConcentratIR ATR (ATR, Smart iTR) | ATR crystal with flow cell | DuraSampIR II; Smiths detection |
| Cell details | DURA SampIR II (Smiths Inc.); horizontal diamond crystal (A = 12.57 mm\(^2\)) with nine internal reflections on the upper surface and an angle of incidence of 45° | multi-bounce diamond | Single bounce ZnSe/diamond (Smart MIRacle from PIKE) | Diamond ATR, 9 reflections - automatic correction of penetration depth in sample |
| Sample temperature | 23 °C | Room ~20 °C | RT | 19.3 °C |
| Background  | Difference spectra of single beam spectra U1-B1, U2-B2, U3-B3, U4-B4 | Diamond ATR crystal with no sample | Diamond ATR crystal with water | Air (diamond) |
Table SI 4: Details of Raman spectroscopic measurements.

|                  | Ra-1                                           | Ra-2                                           | Ra-3                                           |
|------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|
| **Model**        | Horiba Jobin Yvon LabRAM Aramis                | LabRam HR inverted microscope                  | Witec Raman Microscope Alpha300                 |
| **Software**     | LabSpec 5                                       | LabSpec                                        | Witec Control                                   |
| **Detector**     | Synapse CCD; 1024                               | air cooled CCD 1024 x 256                      | CCD                                            |
| **Laser type**   | HeNe 632.817 nm                                 | Diode 532 nm                                  | Nd:YAG 532 nm                                  |
| **Laser power**  | 100 mW at source                                | 23.5 mW                                       |                                                |
| **Microscope**   | Cuvette holder                                  | 40X                                            | Nikon E Plan 50x/0.75                           |
| **objective**    |                                                |                                                |                                                |
| **Calibration**  | automated calibration with Si                   |                                               |                                                |
| **method**       |                                                |                                                |                                                |
| **Cell**         | 5x5 mm glass cuvette                            |                                                |                                                |
| **No. of scans** | 3                                               | 10                                             |                                                |
| **Scan time**    | 60 seconds                                     | 10 pictures/10 s                              |                                                |
| **Sample**       | RT                                              | RT                                             | RT                                             |
| **temperature**  |                                                |                                                |                                                |
| **Other**        | Technical res.: 0.57 cm⁻¹/pixel                 | Gratings: 600 gv/mm                            | Confocal Hole: 150 µm                          |
4.2 Luminescence Spectroscopy (LUM)

Luminescence data from nine laboratories were submitted (see Table SI 1). All spectra and the respective luminescence decays were obtained at room temperature. Apart from one participant, who used a pulsed flash lamp, pulsed lasers emitting light of various wavelengths were applied for excitation. The majority of the participants applied the boxcar technique for the acquisition of the decay curves. In general, among the participants, the experimental setting parameters were found to vary widely, which hinders a direct comparison of the results obtained. A survey of these parameters is given in Table SI 5 and is explicitly considered in the section SI 5.2.

Table SI 5: Details of luminescence spectroscopy.

| Participant | $\lambda_{\text{exc.}}$ (nm) | Gate width (ns) | Initial delay (ns) | Gate steps (ns) |
|-------------|-------------------------------|-----------------|-------------------|----------------|
| LUM-1       | 266                           | 5,000           | 70                | 20             |
| LUM-2       | 266                           | 5,000           | 100               | 20             |
| LUM-3       | 266                           | 30              | 100               | 125            |
| LUM-4       | 280                           | 20,000          | 0                 | 1000           |
| LUM-4       | 280                           | 20,000          | 0                 | 1000           |
| LUM-5       | 355                           | 1,000           | 350               | 6              |
| LUM-6       | 400                           | 1,000           | 50                | 125            |
| LUM-7       | 400                           | 5,000           | 70                | 200            |
| LUM-8       | 415                           | n/s             | 0                 | 20             |
| LUM-9       | 430                           | n/s             | 150               | 12             |
4.3 X-Ray Absorption Spectroscopy (XAS)

Three laboratories located at three different European synchrotron sources contributed to the XAS cluster (see Table SI 1). The cluster members employed setups at different XAS end stations as adequate for data acquisition of a [U] = 25 mM aqueous solution with the flux given at the U L3-edge at the individual beamlines, including the usual double crystal monochromator set and harmonic reduction scheme and slit heights. Additionally, a typical number of scans averaged to obtain the data from an optimized k-range was selected. The collected data were initially provided as “raw data”, i.e., the energy calibrated average of all scans obtained for a given sample, allowing for comparison and statistical evaluation (e.g., point-to-point noise of data sets). Details are summarized in Table SI 6.

Higher level XAFS data treatment (normalization, background removal, extraction of EXAFS χ(k)-functions through spline fitting, etc.) based on well-established software packages for treating XAFS data was left to the individual preferences of the different laboratories. To extract metrical data of the uranium coordination spheres in the individual samples by EXAFS shell fitting, the cluster members agreed to use the crystal structure of uranyl acetate dihydrate (UO2(CH3COO)·2H2O) published in Howatson et al. as the basis for FEFF calculations of all required scattering and phase shift functions. EXAFS shell fitting was accomplished using the Athena/Artemis Demeter package based on Ifeffit (Participants XAS-1 and XAS-3) or the EXAFSPAK (Participant XAS-2).
Table SI 6: Beamline parameters and settings for XAS measurements and data analysis.

|                      | XAS-1                  | XAS-2                  | XAS-3                  |
|----------------------|------------------------|------------------------|------------------------|
| **Storage ring conditions** | 2.75 GeV, 430 mA       | 6 GeV, 200 mA          | 2.5 GeV, 180–120 mA    |
| **Flux ph/s (17.2 keV)** | 1.9 E+11               | 1.3 E+11               | 1.1 E+10               |
| **DCM**              | Si<111>                | Si<111>                | Ge<422>                |
| **Detection mode**   | transmission           | transmission           | transmission           |
| **Optimization energy** | 17.5 keV              | 18 keV                 | 17.6 keV               |
| **# Averaged scans** | 5                      | 3–5                    | 8                      |
| **Energy calibration** | Y metal*               | Y metal*               | Y metal*               |
| **Sample temperature** | ambient                | ambient                | ambient                |
| **K-range**          | 14 Å<sup>-1</sup>     | 20 Å<sup>-1</sup>     | 17 Å<sup>-1</sup>     |
| **Analysis package** | Athena/Artemis         | EXAFSPAK               | Athena/Artemis         |
|                      | Demeter package based on Ifeffit |                      | Demeter package based on Ifeffit |
| **Theory code**      | FEFF9                  | FEFF8.02               | FEFF8.4                |
| **Fit conditions**   | in R-range, k<sup>2</sup>-weighting | in R-range, k<sup>3</sup>-weighting | in R-range, k<sup>1,2,3</sup>-weighting U1 |
|                      |                        |                        |                        |
|                      |                        |                        |                        |
| **Structural model** | Uranyl acetate dihydrate** |                      |                        |
| **E<sub>0</sub> definition** | U L<sub>3</sub> WL peak max. | 17.185 keV | 17.187 keV |

* first Y K-XANES inflection point assigned to 17.038 keV
** structural data taken from 8
4.4 Nuclear Magnetic Resonance Spectroscopy (NMR)

Five institutions measured $^1$H and $^{13}$C NMR spectra (see Table SI 1). With the exception of one participant, who used special NMR tubes, all samples were measured in 5 mm diameter NMR tubes. All experiments were performed within a small temperature range around room temperature ($293–300$ K). An overview of the essential instrumental and experimental parameters applied, including the type of probes used and the method of referencing the $^1$H and $^{13}$C signals, is given in Table SI 7.
| Instrument          | NMR-1                      | NMR-2                      | NMR-3                      | NMR-4                      | NMR-5                      |
|---------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| Sample treatment    | Agilent DD2 400 as provided| Bruker Avance III 400 as provided | Bruker DRX 400 as provided | Bruker Avance III 600 as provided | Bruker Avance III 750 PTFE liners capped and inserted into 5 mm glass screw top NMR tubes (Wilmad) |
| Nucleus             | $^{13}$C $^{1}$H            | $^{13}$C $^{1}$H            | $^{13}$C $^{1}$H            | $^{13}$C $^{1}$H            | $^{13}$C $^{1}$H            |
| Carrier frequency (MHz) | 100.58 399.96 | 100.63 400.17 | 100.62 400.13 | 150.91 600.12 | 188.65 750.23 |
| Type of probe       | direct detection            | BBI (inverse) RT probe      | 5 mm inverse broadband probe head with gradient coil | BBFO                       | BBO                        |
| Pulse angle (°)     | 30                          | 30                          | 30                          | 30                          | 30                          | 45                          | 45                          | 30                          | 30                          | 90                          | 90                          |
| No. of scans        | 128–2048                    | 32                          | 256                         | 1                           | 128–1024                   | 16                          | 1024                        | 4                           | 128                         | 8                           |
| Relaxation delay / d1 (s) | 5                          | 5                           | 3                           | 3                           | 5                          | 2                           | 5                           | 90                          | 20                          |
| No. of acquisition points | 43k                        | 16k                         | 32k                         | 32k                         | 64k                        | 32k                         | 32k                         | 32k                         | 64k                         | 32k                         |
| Spectral width (kHz) | 21.55                      | 4                           | 29.76                       | 8                           | 21.18                      | 4                           | 50                          | 15                          |
| Reference           | $^{1}$H directly            | $^{1}$H directly            | $^{1}$H directly            | $^{1}$H directly            | $^{1}$H directly            | $^{1}$H directly            | $^{1}$H directly            | $^{1}$H directly            | $^{1}$H directly            | $^{1}$H directly            |
| Temperature (K)     | 298                         | 300                         | 296                         | 298                         | 298                         | 293                         |

* By applying the same correction to the carbon spectra as determined in the respective proton experiment

** According to 14
4.5 Theory/Quantum Chemical Calculations (QCC)

Electronic structure calculations focused on the two most relevant complexes, the (1,0) and the (1,3) species. The following properties were calculated: structures of the complexes, O=U=O symmetric and asymmetric stretching vibrational frequencies, NMR chemical shifts ($^1$C and $^1$H), and the reaction energy of complexation for (1,3). Six independent institutions (see Table SI 1) participated in this cluster and performed calculations using their own computational resources. Finally, 60 calculations were performed for both complexes by using various combinations of method, basis set, QC program, and solvation model. For the sake of testing reproducibility, a set of calculations was also carried out using identical method and basis set but different programs.

In the following, we describe some of the more important technical details of these calculations and collect pertinent references to programs and methods. We compare results of the programs Gaussian (Gaussian 09, Revision C.0) $^{15}$, TURBOMOLE $^{16-18}$, ParaGauss (Version 4.0) $^{19}$, which apply Gaussian type functions as basis functions, and ADF $^{20-22}$, which uses Slater type functions to represent electronic orbitals. The majority of the calculations was done using the segmented Stuttgart small core effective core potential for U $^{23-24}$ and a correlation consistent polarized triple zeta basis sets (cc-pVTZ, $^{25}$) for C, O, and H. This combination of effective core potential and basis sets is referred to as “common basis set” in Tables SI 13 and SI 14. Some calculations with Gaussian applied an alternative polarized triple zeta basis set (def2-TZVP $^{26}$). In the all-electron scalar relativistic calculations with ADF, the doubly polarized basis set ZORA-TZ2P $^{27}$ has been used. We compare electronic structure calculations with the wave function type Møller-Plesset perturbation theory second order (MP2, $^{28-29}$) method with density functional calculations applying exchange-correlation functionals of generalized gradient approximation (GGA, functionals BP86 $^{30-31}$, PBE $^{32}$, BLYP $^{30, 33}$, OLYP $^{33-34}$), meta-GGA (M06L $^{35}$), hybrid (B3LYP $^{33, 36}$, PBE0 $^{37}$, O3LYP $^{38}$), and meta-hybrid (M06 $^{39}$, TPSSH $^{40}$) type. Complexes in aqueous solution were modelled by
means of polarizable continuum models (PCM) to represent the solvent environment. The Gaussian calculations applied the integral equation formalism variant of PCM (IEFPCM)\(^\text{41}\), using UFF radii\(^\text{42}\) (U 1.698 Å, O 1.750 Å, C 1.926 Å, H 1.443 Å) for the construction of the solute cavity and a dielectric constant of 78.3553 for water. With ParaGauss the conductor-like screening model (COSMO) variant of PCM\(^\text{43-44}\) is used together with scaled Van der Waals radii\(^\text{45}\) (factor 1.125, except for H) and the FIXPVA algorithm\(^\text{46}\) for construction and tessellation of the solute cavity was used. The dielectric constant of water was set to 78.39. The COSMO variant of PCM is also used in TURBOMOLE and ADF calculations. In ADF calculations Van der Waals radii derived from the MM3 approach\(^\text{47}\) (scaled by 1/1.2; U 2.10 Å, O 1.52 Å, C 1.70 Å, H 1.35 Å) have been used. The parameters Ndiv and NFdiv, which control the tessellation quality of the cavity surface, were set to 4 and 2, which is one unit above the default. The dielectric constant of water was set to 78.39 and the effective radius of the solvent water to 1.93 Å. More details of the solvent implementation and parameters in ADF may be found at: https://www.scm.com/doc/ADF/Input/COSMO.html.

Other computational parameters, e.g., the grid quality for numerical integration of the exchange-correlation term in density functional calculations or the convergence parameters in the electronic self-consistent field and geometry optimization procedures, are expected to be chosen careful enough so that they have a negligible effect on the results compared to the more important features (basis sets, electronic structure method, solvation treatment) of the calculations. This claim is corroborated by the rather close agreement between results obtained with the same method and basis set with Gaussian and ParaGauss (Section SI 5.5).

Geometry optimization was done for complexes in gas phase and in aqueous solution. Vibrational frequencies in harmonic approximation were calculated by an analytic second derivative approach and NMR chemical shifts (C and H, relative to TMS) were determined. Also reaction energies of acetate complexation were calculated, including thermodynamic corrections based on the calculated normal modes of the species in the gas phase.
5 Results from the clusters: consistencies, discrepancies, and interpretative approaches

5.1 VIB

All vibrational spectra of the samples U1–U4 obtained by IR and Raman spectroscopy are shown in Figures SI 9 and SI 10, respectively. As an example, an overview of IR spectra of sample U2 is shown in Figure SI 4A. In Figure 1 (main text), the focus is set on the spectral region of the asymmetric (ν3(UO2)) and symmetric (ν1(UO2)) stretching modes for clarity. All other features observed in the spectra of the different samples mainly reflect the modes of the acetate molecule, which do not show a change in frequency but in intensity. The spectra provided by the single contributors are given in different colors.

![Figure SI 4: (A) IR spectra of samples U2. Different colors correspond to different participants. (B, C) Different procedures to obtain spectral information from Raman spectra of sample U2. For more details, the reader is referred to the text. Values are given in cm⁻¹.](image)

Generally, the agreement between all spectra throughout the mid-IR frequency range (1800–800 cm⁻¹) is extremely high. The slight deviations among the spectra that are sporadically observed can be attributed to small variations in the signal-to-noise ratios
provided by the different instruments used for the measurements or to different background correction methods. However, the main bands observed in all spectra are well resolved and are nearly superimposable for each sample (cf. Figure SI 9).

All significant modes of the uranyl ion and the acetate ligands can be clearly observed in the representative IR spectra of sample U2 shown in Figure SI 4A. The bands at 1710 and 1275 cm\(^{-1}\) as well as at 1468 and 1391 cm\(^{-1}\) can be assigned to the COOH and COO\(^-\) functional groups of uncoordinated and coordinated ligand molecules, respectively, whereas the band at 955 cm\(^{-1}\) represents the \(\nu_3(UO_2)\) mode.

The IR spectra show a successive lowering of the frequency of the \(\nu_3(UO_2)\) mode as the pH increases from U1 to U4 (Figure 1A, main text). As the spectral separation is quite good, four band maxima are observed at 961, 955, 940, and 925 cm\(^{-1}\). In the spectra of samples U3 and U4, shoulders, indicating overlapping bands, are observed. Notably, the intensities of these shoulders in the spectra slightly differ, leading to different interpretations after further evaluation of the data.

The interpretation of the IR data provided by the participants is also quite consistent and in accordance with recently published data. Considering the well-separated band maxima, four different dominant species are derived. The decrease in the frequency of the \(\nu_3(UO_2)\) mode with increasing pH is interpreted as an increasing number of ligand molecules coordinating to the uranyl moiety. Thus, the four maxima of the \(\nu_3(UO_2)\) mode found for samples U1 to U4 are assigned to the (1,0), (1,1), (1,2), and (1,3) species (Table SI 8).

In addition, after decomposition of the spectra using Gaussian functions, one participant revealed an additional species at approximately 909 cm\(^{-1}\), although its contribution is minor (~16%). Consequently, the presence of another species can be suggested, which might be identified as a (1,4) species because of the low frequency observed. However, this interpretation was ruled out for steric considerations. The decomposition of a noisy part of the spectra might contribute to this most likely artificial finding.
| Participant | IR-1 | IR-2 | IR-3 | IR-4 | Ref.          | Species assigned |
|------------|------|------|------|------|---------------|------------------|
| IR spectroscopy       |      |      |      |      |               |                  |
| IR-1        | 961  | 962  | 963–961 | 961 | 962<sup>50</sup>, 961<sup>7</sup> | (1,0)            |
| IR-2        | 955  | 957–953 | 952–951 | 955 | 954<sup>50</sup>, 949<sup>7</sup> | (1,1)            |
| IR-3        | 940  | 943–941 | 943–937 | 943 | 928<sup>50</sup>, 939<sup>7</sup> | (1,2)            |
| IR-4        | 924  | 926  | 925–924 | 924 | 924<sup>7</sup> | (1,3)            |
|             |      |      |      | 940, 909 |               |                  |

| Participant | Ra-1 | Ra-2 | Ra-3 | Ref. | Species assigned |
|------------|------|------|------|------|------------------|
| Ra-1       | 871  | 870  | 872  | 870<sup>50</sup> | (1,0)            |
| Ra-2       | 860  | 858  | 862  | 861<sup>50</sup> | (1,1)            |
| Ra-3       | ~852 | 849  | 849  | 841<sup>50</sup> | (1,2)            |
| Ra-4       | 845  | 848  | 823<sup>50</sup> | (1,3)            |

The Raman spectra provided by the participants are again in excellent agreement throughout all samples (Figure 1B in the main text and Figure SI 10). In the spectral range of the ν<sub>1</sub>(UO<sub>2</sub>) mode, all Raman spectra are dominated by a strong band at 892 cm<sup>−1</sup> which is assigned to a C–C mode of the acetate ligand.<sup>50</sup> As this band appears at a constant frequency with a fixed shape throughout all samples, interference of this band with those of the ν<sub>1</sub>(UO<sub>2</sub>) mode observed at lower frequencies only slightly hampers the evaluation of the spectra, but has to be considered in the evaluation process. As the pH increases, the ν<sub>1</sub>(UO<sub>2</sub>) mode in all spectra shifts from 871 cm<sup>−1</sup> at pH 1.0 (U1) to a lower frequency of 845 cm<sup>−1</sup> at pH 3.5 (U4). Hence, the maximal shift of the ν<sub>1</sub>(UO<sub>2</sub>) mode is only approximately 25 cm<sup>−1</sup>, whereas a more extended shift in the ν<sub>3</sub>(UO<sub>2</sub>) mode of approximately 35 cm<sup>−1</sup> was observed in the IR spectra (see above). Hence, the combination of the relatively low intensities of the ν<sub>1</sub>(UO<sub>2</sub>) mode and
the intense mode of the acetate ligand at 892 cm$^{-1}$, data evaluation of Raman spectra becomes quite ambiguous and thus, various approaches were applied by the participants.

As an example, the results of two approaches applied to sample U2 are shown in Figure SI 4B and C. One participant identified a species showing a peak maximum at 860 cm$^{-1}$ by subtracting the spectrum of U1, assumed to represent exclusively the (1,0) species with a maximum at 871 cm$^{-1}$, from that of U2 (Figure SI 4B). The subtracting factor was set to minimize the spectral intensity at 871 cm$^{-1}$. The resulting spectrum clearly shows a band at 860 cm$^{-1}$ indicating the presence of a second species significantly contributing to the spectrum of sample U2. The band at 892 cm$^{-1}$ can be attributed to residual intensity from incomplete subtraction. Another participant provided a very similar result from the best fit of the spectrum of this sample, revealing two predominant components obtained from the second derivative spectra, showing maxima at 860 and 870 cm$^{-1}$ (Figure SI 4C).

However, even though the bands of the $\nu_1$(UO$_2$) modes of the different species strongly interfere with each other, three species showing band maxima at approximately ~871, ~860, and ~847 cm$^{-1}$ were concurrently identified by the participants (Table SI 8). One participant identified an additional species with a maximum at approximately 852 cm$^{-1}$. In contrast to IR spectroscopy, an unequivocal assignment of the maxima to distinct species was not given by the participants except for the bands at 871 and 860 cm$^{-1}$ which were consistently assigned to the (1,0) and (1,1) species, respectively. The assignment of the (1,2) and (1,3) species was not consistent, as shown in Table SI 8.

For the latter species, a clear discrepancy with the only Raman data reported in the literature to date is observed. In that work, the authors did not present spectral data, and the assignments were presented only in a table. As all participants of this RRT independently detected the $\nu_1$(UO$_2$) mode at ~845 cm$^{-1}$ or above, the previous assignment of a band at 823 cm$^{-1}$ to the (1,3) species appears to be erroneous. In particular, all Raman spectra of this RRT do not indicate the presence of a spectral feature at this low frequency.
In summary, the vibrational spectroscopic data of this RRT provided by five independent participants are in excellent agreement for all samples. For IR spectroscopy, the interpretation of IR data by all participants is also consistent, and four different species could be spectrally identified. Generally, all species found in the IR spectra should be intrinsically observed in the Raman spectra as well. However, in contrast to intrinsic properties of Raman spectra showing more narrow band shapes than usually observed in IR spectra, the Raman spectra of the U(VI) acetate complexes are more difficult to interpret because of the strongly interfering bands of the symmetric stretching mode $v_1(UO_2)$ of the different species and a vibrational mode of the acetate ligand. Consequently, the results of this cluster demonstrate that IR and Raman spectroscopy are strongly complementary techniques for the aqueous speciation of actinyl complexes.
A survey of the time-resolved emission spectra revealed significantly different sets of acquisition parameters, resulting in a large time gate that ranged from a few nanoseconds to 100 ms (Figure 2A, main text). Beside the gate width, parameters such as the initial time delay and the number and size of the gate steps strongly varied between the data sets provided by the participants (cf. Table SI 5). However, general analysis of the time-resolved spectra from each participant suggested multi-exponential decay behavior, indicating the presence of at least two distinct species showing characteristic peak positions and luminescence lifetimes regardless of the variation in the spectral parameter applied (cf. Figures SI 11 – SI 19).

For a detailed analysis of the spectral peak positions, only spectra obtained after the same delay time after laser excitation from different participants can be considered. Analysis of the spectra recorded at various delay times is not accurate due to the individual luminescence characteristics of the U(VI) species under investigation, which are expected to show characteristic peak positions, luminescence lifetime and luminescence quantum yields. Consequently, for peak position analysis, spectra recorded 125 ns after laser excitation, which were obtained by four participants, were selected (Figure 2B in the main text). Generally, with increasing pH, samples U1 to U4 showed a changed spectroscopic signature of the uranyl moiety in the emission spectra, reflecting a variation in the speciation. Thus, a speciation analysis based on these two types of spectra is potentially feasible.

An overview of the selected spectra exhibited five peak maxima in the wavelength range from 460–580 nm (peaks I–V in Figure 2B in the main text). The spectral peak positions deviated slightly by up to 6 nm among the spectra which is most likely due to different calibration procedures of the respective spectrographs applied by the independent operators. The heterogeneity of the calibration routines performed in the various laboratories had already been found to be crucial in a luminescence RRT performed earlier. Thus, ensuring the reliable comparability of luminescence data required a further uniform correction routine,
which was applied after data submission. For this purpose, the local maximum at
approximately 490 nm (peak II) in each emission spectrum was set to the value
$\lambda_0 = 490.0$ nm, which served as an internal reference wavelength. The resulting emission
intensities were displayed as a function of the difference between the wavelengths measured
and $\lambda_0$, and denoted as $\Delta \lambda$ in Figure 2C in the main text. After this referencing procedure, the
average position of peak III was found to be 510.6 nm, whereas the variation of the spectral
positions significantly decreased to an average value of $\pm 0.6$ nm, reflecting the excellent
agreement of the spectra of sample U1 among all participants (see Table SI 9).

Table SI 9: Average and standard deviation values of the three major local luminescence peak maxima
after the correction routine was performed (see Fig. 2C in the main text).

| Sample | Maximum III (nm) | Maximum IV (nm) | Maximum V (nm) |
|--------|-----------------|----------------|---------------|
| U1     | 510.6 ± 0.6     | 534.0 ± 0.7    | 559.7 ± 0.8   |
| U2     | 513.7 ± 0.3     | 536.4 ± 0.4    | 560.6 ± 2.7   |
| U3     | 516.8 ± 1.6     | 537.4 ± 3.2    | 563.6 ± 3.2   |
| U4     | 514.5 ± 0.5     | 535.9 ± 0.8    | 563.1 ± 3.1   |

Similarly, the averaged peak positions of the main peaks (III–V) of all samples measured
by the four participants, as derived from a Gaussian fit analysis, are summarized in Table SI
9. Notably, the emission spectral data obtained were found to be independent of the excitation
wavelength applied. Table SI 9 clearly shows the high agreement of the peak positions in the
spectra displayed in Figure 2C (main text). Taking the standard deviation given in the table
as a quality measure, it revealed that sample U3 and peak V showed the largest uncertainties.
For peak V, the increased deviation can be rationalized by the overall low intensity of the
band and the reduced signal-to-noise ratio within this spectral range.

Only one participant of the cluster provided an interpretational approach on the molecular
level. Based on the relatively small number of samples providing only a small amount of
time-resolved luminescence spectral data, a parallel factor analysis (PARAFAC) was applied, which was expected to provide a result of restricted validity. Deconvolution of the data set resulted in three matrices, each of which contained intrinsic characteristics of the chemical species along with particular parameters, such as pH, emission wavelength, and time, which in turn provided direct access to species distribution, luminescence spectra and luminescence decays (Figure SI 5A).

For samples U1–U4, a three species model was consistently found to describe the investigated U(VI) acetate system. As PARAFAC yields no information on stoichiometry or molecular structures, the assignment of the postulated species to distinct complexes was accomplished based on the spectral properties of the isolated species (Figure SI 5B) and literature data. As species 1 is predominant at pH 1 and the luminescence spectrum corresponds exactly to the fully hydrated uranyl ion, this species was assigned to the (1,0) complex. According to the shortened lifetimes derived from the spectra of the samples U2–U4 and the bathochromically shifted peak positions, species 2 and 3 were assigned to the (1,2) and (1,3) species, respectively, suggesting an increasing extent of acetate complexation of the uranyl ion as the pH increased (Figure SI 5A). Importantly, the occurrence of a non-luminescent species, i.e., the (1,1) species, is expected to vary the contributions of all other
Thus, the derivation of a reliable speciation is hampered by the undetectability of a single species.

In summary, the strongly varying acquisition parameters applied by the participants of the LUM cluster required additional global data analysis prior to an adequate data evaluation. After an internal referencing of selected spectra, the relative peak positions show only marginal deviations, demonstrating the applicability of luminescence spectroscopy to the investigation of U(VI) speciation and the identification of single species. However, among the results of all participants, the obtained luminescence lifetimes displayed a broad distribution range. These discrepancies likely arose from the use of significantly differing experimental setups and algorithms for the spectral analysis. These aspects were already addressed during the first inter-laboratory RRT on aqueous solutions of U(VI) studied by luminescence spectroscopy.
5.3 XAS

The discussion of the XAS results will be focused on samples U1 (pH 1) and U4 (pH 3.5), which were analyzed by all groups (cf. Figure SI 20). As demonstrated in a recent comprehensive study, samples U2 (pH 2) and U3 (pH 2.5) are known to contain species mixtures that are impossible to be unequivocally resolved by XAFS analysis based on four data points, i.e., U(VI) acetate under four different pH conditions. 7

STATISTICAL CONSIDERATIONS. At the given uranium concentration of 25 mM in samples U1 and U4, all groups chose the direct sample transmission data for XAFS data analysis. These data exhibit superior signal-to-noise ratios in the higher k-range compared to the U Lα fluorescence detection mode. Due to the different photon fluxes near the U L3 absorption edge (~17.178 keV) and varying optical path lengths in the sample vials resulting in different absolute edge jumps, different numbers of scans were averaged to yield reasonable data quality within the limited beamtime. Up to 8 scans were averaged from participant XAS-3, whereas 3–5 scans were considered sufficient by participant XAS-2. A detailed comparison between these two participants indicates that the statistical point-to-point noise of the normalized EXAFS spectra levels out in the case of participant XAS-2 when averaging up to 3 scans, whereas this value has a slowly decreasing trend after averaging 4 scans for the data of participant XAS-3 – staying at twice the level of the data obtained from participant XAS-2. This finding reflects the higher flux available from the respective synchrotron source.

The standard deviations of the edge jumps obtained for repeated measurements of sample U1 in the E-4 range are up to five times higher for participant XAS-3 compared to the other contributors. Nevertheless, comparing the normalized spectra, extracted k^3-weighted $\chi(k)$ functions and corresponding Fourier transformations (while applying the same software package, background removal, $\mu_0$-spline fit and transformation parameters) clearly shows that the spectra obtained at all three beamlines are nearly congruent at this stage of data reduction.
This observation is most impressively shown by plotting the $k^3$-weighted EXAFS $\chi(k)$ functions and the corresponding FT magnitudes obtained by two beamlines for sample U4 (Figure SI 6A and B). All spectral features are identical up to $R-\Delta < 4.5 \text{ Å}$ (R-scale, not phase shift corrected). Data from participant XAS-1 are not shown here due to their limited $k$-range. Common EXAFS data treatment profits from the fact that photon flux induced statistical noise and — to some extend — noise related to overall stability of the beam delivery and data acquisition system is eliminated by Fourier-filtering, reducing effects on the error margins of fit parameters.

**EXAFS SHELL-FITTING RESULTS.**

The EXAFS curve fitting results for sample U1 obtained by the three cluster members are compared in Table 1 in the main text. Only the axial oxygen coordination number (CN) of 2 was fixed in the fit. The structure of the aquatic uranyl complex, in which the $\text{UO}_2^{2+}$ moiety is coordinated by 5 water molecules in the equatorial plane, is unambiguously reproduced by all groups. The metrical parameters coincide among the different groups and with the literature data. The deviations of the fit values are lower than the usual uncertainties (CN $\pm \sim 20\%$, R $\pm \sim 0.02 \text{ Å}$) given in the literature, i.e., less than 0.01 Å for the distances to the axial and equatorial oxygen neighbors and 0.5 for the equatorial coordination number. As
stated earlier, complex mixtures of fully or partially hydrated or different acetate species of the uranyl ion that potentially exist in samples U2 and U3 cannot be resolved using EXAFS without applying sophisticated statistical methods requiring more than four data points. Nevertheless, a clear spectral trend observed by two participants indicated the increase in the equatorial oxygen distance with increasing pH, i.e., increasing coordination by acetate ligands (fitted data not shown, original data cf. Figure SI 20).

The fit results for sample U4 are summarized in Table 1 in the main text. Metrical parameters (i.e., the equatorial oxygen bond distance and coordination number as well as the backscattering contributions from the carbon atoms in the carboxyl groups (C_carb) and the distal carbon atoms (C_meth) in the acetate ligands) indicate the predominance of the (1,3) species at pH 3.5, where each of three carboxyl groups are bound to U by two oxygen atoms in a bidentate fashion, as supported by earlier XAFS studies, other spectroscopy techniques and QCCs. However, the EXAFS analysis of sample U4 is not completely free from ambiguity. For measurements of two participants, the coordination number of the equatorial oxygen centers tends to be less than 6 (4.7 and 5.4, respectively) when this parameter is left free of additional fit constraints, which would be expected for the fully bidentately coordinated (1,3) species. The spectrum obtained by participant XAS-3 is equally well reproduced by assuming a mixed coordination of the ligands to the uranyl moiety, namely, two bidentate and one monodentate coordination, when the number of equatorial oxygen centers, Noeq is left free of refinement. When this value is fixed to 6, the data of participant XAS-2 and literature data are well reproduced.

To sum up these findings, we can conclude that

- The data sets for samples U1 and U4 obtained at different beamlines are consistent.
- U1: the presence of the (1,0) species was unambiguously confirmed by all three teams, and the structure reported in the literature was reproduced better than within typical EXAFS error margins.
• U2 and U3: complex mixtures of all the species considered cannot be differentiated using EXAFS through measurements of only 4 data points, but a clear spectral trend is discernible from the EXAFS measurements of participants XAS-2 and -3.

• U4: the dominant presence of the (1,3) species was confirmed by all the cluster’s participants. However, uncertainties in CN determination might cause different interpretations of the coordination schemes for the same data set.

The final point underpins the general importance of *a priori* speciation information that might be necessary for obtaining a conclusive picture from EXAFS curve fit analysis. Conversely, in most cases, EXAFS analysis will be biased by such *a priori* knowledge.
5.4 NMR

In the $^1$H spectra obtained by the participants, only small variations in the chemical shifts and the corresponding linewidths of the single peak representing the protons of the methyl group are observed. For samples U1-U4, the chemical shift varies slightly from 2.09 to 2.11 ppm (Figure SI 7 and cf. Table SI 11). In the spectra obtained in D$_2$O, the carboxylic acid proton cannot be observed due to H/D exchange with the solvent. The calibration of the spectra was accomplished using DSS as internal standard in the samples. For the B samples, almost no change in the chemical shifts and linewidths was observed irrespective of the pH (cf. Table SI 12). Hence, the observed significant increase of the linewidths reflects the increasing exchange rate for acetate molecules between the free and U(VI) bound states with increasing pH. However, the extent of line broadening can be attributed to different instrumentation and acquisition parameters applied by the participants.

![Figure SI 7: $^1$H NMR spectroscopic data. Representative data of the methyl spectral region of samples U1-U4 (left). Comparison of the chemical shifts (right, top) and linewidths (right, below) for samples U1–U4 obtained by different RRT participants. Note that for better comparison of the linewidths the same line broadening factor (lb) was applied to the raw data (see Tables SI 11 and SI 12).]
The $^{13}$C NMR spectra show two signals, each of which represents a carbon atom of the acetate molecule. The peak positions and the corresponding linewidths of the signals representing the methyl and carboxyl carbon atoms are depicted in Figure 3 in the main text. In general, both signals show a slight increase in chemical shift and linewidth with increasing pH, which is in accordance to the $^1$H spectra.

In contrast to the $^1$H spectra, the $^{13}$C spectra of the different participants are more divergent. In particular, the values of the chemical shifts differ significantly among the spectra of the participants. This result is due to the DSS reference signal, which was not directly observed in the $^{13}$C spectra by all participants. In these cases, the peak positions were derived from the corresponding $^1$H spectra employing the gyromagnetic ratio, leading to less consistent results among the participants. $^{57}$ Again, among the spectra of the participants, the range of linewidths observed varies significantly, especially for U4, which displays linewidths ranging from 5 to 25 Hz and from 20 to 200 Hz for the methyl and carboxyl carbon signals, respectively. The linewidths mainly depend on instrumental and acquisition parameters, such as magnetic field strengths and magnetic field homogeneity as well as carrier frequencies, $^1$H decoupling sequence applied, field amplitude, temperature, and cycle time, and these parameters were individually chosen by the participants; thus, the variability of the linewidths becomes obvious.

In summary, the NMR data are remarkably consistent and show little variation among the groups. Both, the use of an internal standard and the reliability of modern NMR spectrometers allow excellent and reproducible results. Based on the control samples, the impact of the pH on the acetate spectra was found to be negligible. Hence, the speciation of the acetate molecule does not significantly change in this pH range. Conversely, systematic changes are observed in the spectra of the U(VI) acetate samples with increasing pH. This effect is most dramatic in the $^{13}$C spectra, where the signal representing the carboxyl group broadens dramatically with pH. This line broadening is attributed to the exchange between free and
bound acetate groups, which is in the range of the relaxation time of the resonance signal. NMR spectroscopy can be used to examine exchange rates of such molecular complexes in solution and has successfully been applied to binary and ternary U(VI) complexes, which showed a high exchange rate. The observation of only one averaged peak per position in the $^1$H and $^{13}$C spectra of the U(VI) acetate complex system even at the higher field clearly indicates a fast exchange rate. The differences observed in the line widths of the signals measured at the same field (at 400 MHz) are mainly due to the variations in the homogeneity of the magnetic field, i.e., due to the differences in the shimming procedure. At higher fields the chemical shifts differ more (in Hz) between the exchanging sites (free acetate and complexes), and the exchange averaged signals are broader compared to those in the 400 MHz spectra.

As neither the chemical shifts of the individual exchanging species nor their relative population are known, simulation of the spectra via a matrix formalism cannot be applied to extract kinetic information. Adequate results can be achieved only by running experiments at lower temperatures, but these are far beyond the scope of this RRT. Nevertheless, the observations of increased linewidths and chemical shifts in the current data set are consistent with earlier findings, suggesting a correlation of the linewidths with the concentration of the U(VI) acetate species.
5.5 QCC

DFT is the most widely used method for calculations of uranyl(VI) complexes because U(VI) formally exhibits a $5f^0$ electronic configuration and thus a single-configurational approach is appropriate. The effect of the spin-orbit coupling is only marginal for most of the properties we considered and therefore was neglected. We tested various DFT functionals and a wave function method (MP2). The structural and spectroscopic properties of the two most relevant species, i.e., the complexes (1,0) and (1,3), and of the energy of ligand replacement, i.e., from (1,0) to (1,3), were calculated. In Figure SI 8, the structures of the complexes (1,0) and (1,3) optimized at the MP2 level in aqueous phase (first row in Table 2) is given. The results are listed in detail in Tables SI 13 and SI 14. We will focus the discussion on the results obtained with the same basis set for various methods (Programs Gaussian, TURBOMOLE, and ParaGauss), summarized in Table SI 10 and Table 2 in the main text, together with ADF results in solution for comparison.

Figure SI 8: The optimized structures of UO$_2$(H$_2$O)$_3^{2+}$ (left) and UO$_2$(CH$_3$COO)$_3^{-}$ (right) at the MP2 level using 6-311+G* basis sets on all elements except for U. For U, a small core ECP and corresponding basis set was used.
Table SI 10: Average gas phase U–O and U–C\text{carb} bond distances (Å) and O=U=O ν₁ and ν₃ stretching vibrational frequencies (cm⁻¹) of UO₂(H₂O)\text{5⁺} and UO₂(CH₃COO)\text{3⁻} using the same set of DFT functionals and basis sets but different QC programs. The last column gives the Gibbs energy of formation of UO₂(CH₃COO)\text{3⁻} in kcal mol⁻¹.

|                      | UO₂(H₂O)\text{5⁺} | UO₂(CH₃COO)\text{3⁻} |                     |                     | ν₁     | ν₃     | ν₁     | ν₃     | ΔG ²)   |
|----------------------|-------------------|-----------------------|---------------------|---------------------|--------|--------|--------|--------|---------|
|                      | U–Oₐx  | U–Oₐq  | ν₁     | U–Oₐx  | U–Oₐq  | U–C\text{carb} | ν₁     | ν₃     |         |
| MP2                  | T      | 1.761  | 2.462  | 887    | 995    | 1.803  | 2.472  | 2.828  | 826    | 928     | −386.3 |
| BP86                 | T      | 1.767  | 2.476  | 888    | 978    | 1.804  | 2.506  | 2.871  | 813    | 897     | −381.7 |
| G        | 1.765  | 2.487  | 901    | 993    | 1.802  | 2.513  | 2.878  | 821    | 906     | −394.7 |
| P        | 1.767  | 2.480  | 890    | 983    | 1.798  | 2.513  | 2.879  | 820    | 904     | −391.9 |
| PBE                  | T      | 1.765  | 2.476  | 893    | 983    | 1.801  | 2.513  | 2.868  | 819    | 903     | −378.7 |
| P        | 1.764  | 2.480  | 895    | 988    | 1.795  | 2.512  | 2.876  | 825    | 909     | −390.3 |
| PBE0                 | T      | 1.728  | 2.469  | 988    | 1068   | 1.760  | 2.484  | 2.846  | 904    | 982     | −377.9 |
| G        | 1.726  | 2.475  | 991    | 1075   | 1.758  | 2.491  | 2.853  | 912    | 993     | −388.1 |
| P        | 1.727  | 2.472  | 992    | 1075   | 1.756  | 2.493  | 2.854  | 913    | 992     | −391.2 |
| B3LYP                | T      | 1.745  | 2.493  | 947    | 1032   | 1.780  | 2.512  | 2.879  | 866    | 945     | −380.3 |
| G        | 1.744  | 2.498  | 952    | 1040   | 1.777  | 2.518  | 2.885  | 875    | 959     | −384.2 |
| M06L                  | G      | 1.738  | 2.503  | 954    | 1045   | 1.774  | 2.518  | 2.878  | 863    | 952     | −393.8 |
| P        | 1.739  | 2.497  | 945    | 1039   | 1.772  | 2.520  | 2.881  | 862    | 948     | −399.2 |
| M06                  | G      | 1.721  | 2.491  | 1003   | 1083   | 1.750  | 2.515  | 2.874  | 932    | 1010    | −386.7 |
| P        | 1.722  | 2.491  | 1017   | 1096   | 1.749  | 2.514  | 2.872  | 933    | 1010    | −387.1 |

1) T: TURBOMOLE, G: Gaussian 09, P: ParaGauss, utilizing segmented new small core effective core potential (SC-ECP) on U⁵₉ and an cc-pvtz basis set for other atoms.

2) For the reaction UO₂(H₂O)\text{5⁺} + 3 CH₃COO⁻ → UO₂(CH₃COO)\text{3⁻} + 5 H₂O

To compare directly the results of various approaches, we first discuss the major bond distances in the (1,3) species and the ν₁ and ν₃ stretching vibrational frequencies of the uranyl moiety in the gas phase. Among 11 different variants of theory, the variations in the U–Oₐx, U–Oₐq, and U–C\text{carb} (to carboxyl C) distances are 1.734–1.825, 2.407–2.550, and 2.763–2.917 Å, respectively (Table SI 13). The variations in the ν₁ and ν₃ frequencies are 787–933 and 871–1010 cm⁻¹, respectively (Table SI 13). For the complex (1,0) and for both complexes in solution comparable variations of bond lengths of up to 0.10 Å for U–Oₐx and 0.17 Å for U–Oₐq and for vibrational frequencies of up to 160 cm⁻¹ are found (Tables SI 13 and SI 14). The density functionals BLYP, OLYP, O3LYP, M06, M06L, and TPSSH, which are less
commonly used, tend to give either the shortest U–O or the longest U–C_{carb} distances and, in the case of the vibrational frequencies, the smallest or the largest wavenumbers. More commonly used methods (MP2, BP86, PBE, PBE0, and B3LYP) yield more similar U–O and U–C_{carb} distances with variations of less than 0.06 Å both in the gas phase and aqueous solution (Table SI 10 and Table 2 in the main text). Frequencies vary between 96 and 120 cm^{-1} between these functionals.

For the calculations with identical DFT functionals and basis sets but different QC programs, the deviations among the calculations became much smaller. In Table SI 10, U–O and U–C_{carb} distances and the frequencies of the ν_{1} and ν_{3} modes are given for the complexes UO_{2}(H_{2}O)_{5}^{2+} and UO_{2}(CH_{3}COO)_{3}^{-} optimized in the gas phase. The largest deviations among the programs are 0.011 Å for bond lengths and 15 cm^{-1} for frequencies. For aqueous phase calculations (Table 2 in the main text), these deviations are larger and were found to reach up to 0.036 Å for the bond distances and 33 cm^{-1} for vibrational frequencies. These deviations are more than twice as large as for the results for the complexes in the gas phase (Table SI 10). This latter outcome presumably is due to different solvation models used. Recall that the experimental error of bond distances, according to EXAFS measurements generally is about 0.02 Å. Therefore, deviations among QC programs for interatomic distances are commonly at the level of the experimental error.

Generally, gas phase calculations using Gaussian09 and ParaGauss are in very good agreement, and in many cases, the differences in bond distances and frequencies are within 0.002 Å and 2 cm^{-1}, respectively (Table SI 10). Some results for the (1,0) species exhibit slightly larger deviations and are found to increase up to 0.007 Å, and for vibrational frequencies up to 14 cm^{-1}. In the (1,3) species, acetate ligands, coordinated in bidentate fashion, are rigidly bound to the uranyl moiety, whereas in the aqua complex the orientation of the ligands is more flexible. Thus, small differences in the orientations of the aqua ligands as determined for the structures obtained with Gaussian09 and ParaGauss allow one to
rationalize the larger variation of parameters calculated for (1,0). For the systems in solution, the deviation between Gaussian 09 and ParaGauss increases up to about 0.02 Å for distances and up to about 30 cm\(^{-1}\) for frequencies (Table 2 in the main text). As stated above, this may be traced back mainly to different solvation models. The rather systematic and larger deviations for (1,0) compared to (1,3) (U-O\(_{ax}\) longer by 0.005 Å, U-O\(_{eq}\) shorter by 0.02 Å, almost all vibrational frequencies softer for ParaGauss) originate from different orientations of the aqua ligands. In the Gaussian calculations the molecular planes of two aqua ligands are essentially rotated into the equatorial plane of uranyl, while the ParaGauss results show all aqua ligands more or less with perpendicular orientation with respect to the equatorial plane, independent of the functional applied. This systematic deviation illustrates the flexibility of the aqua ligand orientation and the existence of various energetically close lying structures with similar bond distances can be obtained for (1,0), most probably depending on the starting structures in the optimizations. TURBOMOLE tends to give slightly longer U-O\(_{ax}\) distances and slightly shorter U-O\(_{eq}\) distances but only in a relative sense compared to Gaussian 09 and ParaGauss. The code ADF, despite of its use of Slater-type basis sets and a relativistic treatment of the core electrons in contrast to other programs, which all use Gaussian-type basis sets and effective core potentials, provides results that are very similar to those of Gaussian09 and ParaGauss when triple-zeta Gaussian type basis sets with two sets of polarization functions are used. For systems in the gas phase, U-O\(_{ax}\) distances in the (1,0) species obtained by ADF are only slightly longer (up to 0.009 Å for various functionals). For a basis set with only one set of polarization functions the results of ADF deviate somewhat more from the Gaussian 09/ParaGauss data (0.015 to 0.019 Å) (data not presented). Thus, for accurate results it is important to add a second set of polarization functions.

Depending on the computational method and the program applied, the gas phase Gibbs energy of formation for the reaction

\[
\text{UO}_2(\text{H}_2\text{O})_5^{2+} + 3 \text{CH}_3\text{COO}^- \rightarrow \text{UO}_2(\text{CH}_3\text{COO})_3^- + 5 \text{H}_2\text{O}
\]
varies by as much as 50 kcal/mol (Table SI 13). Gibbs energies are calculated differently amongst the programs. They all include electronic internal energy, zero point energy corrections, thermal corrections, and entropic contributions. This wide variation lowers to 20 kcal/mol for Gaussian based programs and applying the common basis set. Even when identical DFT functionals and basis sets are used, there is still a variation of up to 13 kcal/mol; however, Gaussian09 and ParaGauss again yield similar reaction energies within a few kcal/mol difference and TURBOMOLE results tend to be lower by about 3%. Comparing data obtained with Gaussian and another basis set (ADF/def2-TZVP, see Table SI 13) shows a systematic underestimation of Gibbs free energies, demonstrating the importance of a careful choice of basis set. Comparing results obtained with the same DFT functional clearly indicates that calculations yielding similar structures, lead also to similar reaction energies. The agreement of complexation energies between programs is somewhat worse in solution (Table 6). The differences between programs range from 6-13 kcal/mol for various density functionals, which is a larger relative error taking into account the absolute value of the complexation energy of about 90 kcal/mol. As noted for structure parameters and vibrational frequencies, these stronger variations in solution are mainly due to differences in solvation models and variations of the orientation of the aqua ligands in (1,0) (see above).

Calculations of the $^1$H NMR chemical shifts of the methyl group of complexes in the gas phase show a small dependence on the methods (Table SI 13): The shifts are between 1.5 and 2.2 ppm for spin free calculations and between 2.2 and 2.3 ppm when spin orbit (SO) interaction is taken into account. The absolute variation is larger in the case of $^{13}$C chemical shifts. For the methyl group carbon, C$_{\text{meth}}$, the chemical shift ranges from 21.3 to 25.4 ppm using spin free calculations and from 28.1 to 29.9 ppm using SO calculations. For the carboxylic carbon, C$_{\text{carb}}$, the chemical shift ranges from 177.5 to 199.2 ppm in calculations without SO interaction and from 191.2 to 199.9 ppm when using SO (Table SI 9). Similar but slightly larger shifts are calculated for the systems in solution (Table 2 in the main text and
Table SI 14). Differences in the calculated $^{13}$C chemical shifts, especially of the carboxylic carbon, might be primarily due to the difference in treatment of solvation. Marchenko et al. demonstrated the importance of explicit (micro)solvation for calculating NMR shifts of uranyl carbonate complexes. Additional errors are likely due to small unsaturated basis sets, as evidenced by the relatively large differences between STO (ADF) and GTO calculations. When compared to the corresponding spin free calculations at the same level, the use of SO calculations has a minimal effect of less than 1 ppm. This can be understood from the nature of the bonding in these uranyl complexes: It has been shown that chemical shifts from calculations with SO interactions are strong if $\sigma$ bonding character exists at both the heavy nucleus and the spinning nucleus. Indeed, calculated SO contributions to the $^1$H chemical shift are as large as 7.5 ppm in UF$_5$(OCH$_3$)$_3$, for a proton that is three bonds away from uranium. However, as already noted, the $\sigma$ bonding contributions on U are small in our complexes, and hence SO has only a minimal effect.

The above results suggest that the calculated spectroscopic parameters depend considerably on the optimized structures. Generally, all methods satisfactorily reproduce the U–O$_{ax}$ distances, whereas the U–O$_{eq}$ distances are generally overestimated compared to experimental data. To fully evaluate the calculated results, they must be compared with the experimental results, which is done in the main text subsection 3.2.
Presentation of all participants data

6.1 VIB

Figure SI 9: Infrared spectroscopic results of samples U1-U4 provided by 4 participants.
Figure SI 10: Raman spectroscopic results of samples U1-U4 provided by 3 participants.
Figure SI 11: Time-resolved luminescence spectra of samples U1-U4 provided by participant 1.

Figure SI 12: Time-resolved luminescence spectra of samples U1-U4 provided by participant 2.
Figure SI 13: Time-resolved luminescence spectra of samples U1-U4 provided by participant 3.

Figure SI 14: Time-resolved fluorescence spectra of samples U1-U4 provided by participant 4.
Figure SI 15: Time-resolved luminescence spectra of samples U1-U4 provided by participant 5.

Figure SI 16: Time-resolved luminescence spectra of samples U1-U4 provided by participant 6.
Figure SI 17: Time-resolved luminescence spectra of samples U1-U4 provided by participant 7.

Figure SI 18: Steady state luminescence spectra and decay time measurements of samples U1-U4 provided by participant 8.
Figure SI 19: Time-resolved luminescence spectra of samples U1-U4 provided by participant 9.
Figure SI 20: XAS spectroscopic results of samples U1-U4 provided by 3 participants.
### 6.4 NMR

Table SI 11: NMR data obtained from U1-U4. Note the two linewidth data sets for participants’ individual processing (red) and for same comparable processing (line broadening factor, lb) to all participants’ raw data (blue).

|        | U1 | U2 | U3 | U4 |
|--------|----|----|----|----|
| **1H** |    |    |    |    |
| meth   |    |    |    |    |
| shift  | ppm | (Hz) | lb | (Hz) | lb |
| NMR-1  | 2.090 | 1.0 | 0 | 1.4 | 0.5 |
| NMR-2  | 2.089 | 1.0 | n/a | 1.4 | 0.5 |
| NMR-3  | 2.100 | 1.6 | 0.3 | 1.8 | 0.5 |
| NMR-4  | 2.100 | 3.8 | 0.1 | 4.2 | 0.5 |
| NMR-5  | 2.090 | 5.5 | 2.3 | 3.2 | 0.5 |
| **13C** |    |    |    |    |
| carb   |    |    |    |    |
| shift  | ppm | (Hz) | lb | (Hz) | lb |
| NMR-1  | 23.11 | 0.5 | 0.3 | 1.1 | 1 |
| NMR-2  | 20.78 | 2.0 | n/a | 1.6 | 1 |
| NMR-3  | 20.20 | 1.6 | 1 | 1.6 | 1 |
| NMR-4  | 20.20 | 11.2 | 10 | 1.7 | 1 |
| NMR-5  | 23.10 | 4.3 | 2.5 | 3.1 | 1 |
| **13C** |    |    |    |    |
| carboxy |    |    |    |    |
| shift  | ppm | (Hz) | lb | (Hz) | lb |
| NMR-1  | 179.38 | 0.6 | 0.3 | 1.3 | 1 |
| NMR-2  | 177.05 | 2.0 | n/a | 1.7 | 1 |
| NMR-3  | 176.50 | 1.7 | 1 | 1.7 | 1 |
| NMR-4  | 176.60 | 11.4 | 10 | 2.2 | 1 |
| NMR-5  | 179.40 | 4.6 | 2.5 | 3.8 | 1 |
Table S12: NMR data obtained from B1-B4. Note the two linewidth data sets for participants’ individual processing (red) and for same comparable processing (line broadening factor, lb) to all participants’ raw data (blue).

|        | B1          | B2          | B3          | B4          |
|--------|-------------|-------------|-------------|-------------|
|        | shift       | FWHH        | FWHH        |             |
| ppm    | (Hz) lb     | (Hz) lb     | (Hz) lb     | (Hz) lb     |
| NMR-1  | Not measured|             |             |             |
| NMR-2  | 2.085       | 1.0 n/a     | 1.4 0.5    |             |
| NMR-3  | 2.08        | 1.2 0.3     | 1.4 0.5    |             |
| NMR-4  | 2.1         | 5.9 0.1     | 5.1 0.5    |             |
| NMR-5  | 2.08        | 4.2 2.3     | 2.7 0.5    |             |
| 13C     |             |             |             |             |
| meth   |             |             |             |             |
| ppm    | (Hz) lb     | (Hz) lb     | (Hz) lb     | (Hz) lb     |
| NMR-1  | Not measured|             |             |             |
| NMR-2  | 23.09       | 0.4 0.3     | 1.1 1      |             |
| NMR-3  | 20.66       | 1.9 n/a     | 1.6 1      |             |
| NMR-4  | 20.2        | 1.4 1       | 1.3 1      |             |
| NMR-5  | 23.1        | 4.2 2.5     | 3.1 1      |             |
| 13C     |             |             |             |             |
| carb   |             |             |             |             |
| ppm    | (Hz) lb     | (Hz) lb     | (Hz) lb     | (Hz) lb     |
| NMR-1  | Not measured|             |             |             |
| NMR-2  | 176.90      | 1.9 n/a     | 1.6 1      |             |
| NMR-3  | 176.5       | 1.3 1       | 1.3 1      |             |
| NMR-4  | 176.5       | 10.9 10     | 1.9 1      |             |
| NMR-5  | 179.4       | 4.2 2.5     | 3.4 1      |             |

Note: The data in red represents participants’ individual processing, while the blue data represents the same comparable processing applied to all participants’ raw data.
## 6.5 QCC

### Table SI 13: Calculations in gas phase

| theory | basis | program           | UO₂(H₂O)⁺⁺ Bond distances (Å) | Stretching vibrational frequencies ν₁ and ν₁(UO₂) (cm⁻¹) | NMR chemical shifts (ppm) | ν₁ H SO |
|--------|-------|-------------------|-------------------------------|---------------------------------------------------------|---------------------------|---------|
| MP2    | common| TURBOMOLE         | U-O₆₆ 1.761                    | 2.462                                                   | 887                       | 995     |
|        |       |                   | U-O₆₈ 1.761                    | 2.462                                                   | 887                       | 995     |
|        |       |                   | sym                           | 1.803                                                   | 2.472                     | 2.828   |
|        |       |                   | asym                          | 4.338                                                   | 826                       | 928     |
|        |       |                   | ν₁ H SO                       | 1.804                                                   | 2.506                     | 2.871   |
|        |       |                   |                               | 4.391                                                   | 813                       | 897     |
|        |       |                   |                               | 1.802                                                   | 2.513                     | 2.878   |
|        |       |                   |                               | 4.400                                                   | 821                       | 906     |
|        |       |                   |                               | 2.0                                                      | 187.6                     | 23.8    |
|        |       |                   |                               | 1.798                                                   | 2.513                     | 2.879   |
|        |       |                   |                               | 4.399                                                   | 820                       | 904     |
|        |       |                   |                               | 1.787                                                   | 2.530                     | 2.896   |
|        |       |                   |                               | 4.418                                                   | 810                       | 899     |
|        |       |                   |                               | 2.0                                                      | 189.1                     | 24.0    |
|        |       |                   |                               |                                                         |                           |         |
|        |       |                   |                               | 1.801                                                   | 2.513                     | 2.888   |
|        |       |                   |                               | 4.388                                                   | 819                       | 903     |
|        |       |                   |                               | 1.795                                                   | 2.512                     | 2.876   |
|        |       |                   |                               | 4.395                                                   | 825                       | 909     |
|        |       |                   |                               | 1.805                                                   | 2.514                     | 2.878   |
|        |       |                   |                               | 4.397                                                   | 817                       | 903     |
|        |       |                   |                               | 2.1                                                      | 195.6                     | 196.3   |
|        |       |                   |                               | 2.3                                                      | 24.2                      | 29.0    |
|        |       |                   |                               | 1.784                                                   | 2.528                     | 2.894   |
|        |       |                   |                               | 4.413                                                   | 816                       | 902     |
|        |       |                   |                               | 1.9                                                      | 188.9                     | 23.3    |
|        |       |                   |                               |                                                         |                           |         |
|        |       |                   |                               | 1.760                                                   | 2.484                     | 2.846   |
|        |       |                   |                               | 4.355                                                   | 904                       | 982     |
|        |       |                   |                               | 1.756                                                   | 2.493                     | 2.854   |
|        |       |                   |                               | 4.363                                                   | 913                       | 992     |
|        |       |                   |                               | 1.758                                                   | 2.491                     | 2.853   |
|        |       |                   |                               | 4.361                                                   | 912                       | 993     |
|        |       |                   |                               | 2.2                                                      | 189.5                     | 24.1    |
|        |       |                   |                               |                                                         |                           |         |
|        |       |                   |                               | 1.766                                                   | 2.492                     | 2.852   |
|        |       |                   |                               | 4.361                                                   | 898                       | 977     |
|        |       |                   |                               | 2.2                                                      | 194.8                     | 194.0   |
|        |       |                   |                               | 2.2                                                      | 25.1                      | 28.8    |
|        |       |                   |                               | 1.741                                                   | 2.504                     | 2.866   |
|        |       |                   |                               | 4.375                                                   | 918                       | 986     |
|        |       |                   |                               | 1.7                                                      | 188.4                     | 22.3    |
|        |       |                   |                               |                                                         |                           |         |
|        |       |                   |                               | 1.780                                                   | 2.512                     | 2.879   |
|        |       |                   |                               | 4.396                                                   | 866                       | 945     |
|        |       |                   |                               | 1.777                                                   | 2.518                     | 2.885   |
|        |       |                   |                               | 4.401                                                   | 875                       | 959     |
|        |       |                   |                               | 2.1                                                      | 191.9                     | 24.6    |
|        |       |                   |                               |                                                         |                           |         |
|        |       |                   |                               | 1.787                                                   | 2.519                     | 2.884   |
|        |       |                   |                               | 4.401                                                   | 860                       | 942     |
|        |       |                   |                               | 2.2                                                      | 197.8                     | 197.1   |
|        |       |                   |                               | 2.2                                                      | 25.4                      | 29.4    |
|        |       |                   |                               | 1.758                                                   | 2.531                     | 2.898   |
|        |       |                   |                               | 4.414                                                   | 875                       | 953     |
|        |       |                   |                               | 1.7                                                      | 190.5                     | 22.7    |

| UO₂(ACO)⁻⁻ Bond distances (Å) | Stretching vibrational frequencies ν₁ and ν₁(UO₂) (cm⁻¹) | NMR chemical shifts (ppm) | ν₁ H SO |
|-------------------------------|----------------------------------------------------------|---------------------------|---------|
| 1.803                         | 2.472                                                   | 2.828                     | 4.338   |
| 1.804                         | 2.506                                                   | 2.871                     | 4.391   |
| 1.802                         | 2.513                                                   | 2.878                     | 4.400   |
| 1.798                         | 2.513                                                   | 2.879                     | 4.399   |
| 1.787                         | 2.530                                                   | 2.896                     | 4.418   |
| 1.801                         | 2.513                                                   | 2.888                     | 4.388   |
| 1.795                         | 2.512                                                   | 2.876                     | 4.395   |
| 1.805                         | 2.514                                                   | 2.878                     | 4.397   |
| 1.784                         | 2.528                                                   | 2.894                     | 4.413   |
| 1.760                         | 2.484                                                   | 2.846                     | 4.355   |
| 1.756                         | 2.493                                                   | 2.854                     | 4.363   |
| 1.758                         | 2.491                                                   | 2.853                     | 4.361   |
| 1.766                         | 2.492                                                   | 2.852                     | 4.361   |
| 1.741                         | 2.504                                                   | 2.866                     | 4.375   |
| 1.780                         | 2.512                                                   | 2.879                     | 4.396   |
| 1.777                         | 2.518                                                   | 2.885                     | 4.401   |
| 1.787                         | 2.519                                                   | 2.884                     | 4.401   |
| 1.758                         | 2.531                                                   | 2.898                     | 4.414   |

| Reaction Energy | delta G (kcal mol⁻¹) | delta H (kcal mol⁻¹) | delta U (kcal mol⁻¹) | delta E (kcal mol⁻¹) |
|-----------------|----------------------|----------------------|----------------------|----------------------|
|                 | 386.27               | -383.10              | -378.25              | -394.73              |
|                 | 391.86               | -371.07              | -376.66              | -390.31              |
|                 | 390.31               | -410.57              | -383.10              | -384.28              |
|                 | 370.64               | -377.90              | -375.43              | -388.11              |
|                 | 391.23               | -410.27              | -382.80              | -383.99              |
|                 | 367.87               | -380.30              | -372.10              | -384.23              |
|                 | 365.15               | -407.45              | -379.98              | -381.17              |
| Method   | Basis Set | (geom, fr) | ADF       | 1.785 | 2.520 | 865 | 957 | 7.5 | 7.9 | 1.825 | 2.539 | 2.910 | 4.438 | 787 | 871 | 2.1 | 2.3 | 199.2 | 199.9 | 24.9 | 29.9 | -406.48 | -379.02 | -380.20 |
|----------|-----------|------------|-----------|--------|--------|-----|-----|-----|-----|--------|--------|--------|-----|-----|-----|-----|--------|--------|-----|-----|--------|--------|---------|
| BLYP     | TZ2P      |            | ADF       | 1.731 | 2.375 | 965 | 1052 | 7.9 | 8.4 | 1.760 | 2.407 | 2.763 | 4.239 | 895 | 976 | 2.2 | 2.3 | 196.0 | 195.9 | 23.6 | 28.1 | -406.89 | -379.42 | -380.61 |
| O3LYP    | TZ2P      |            | ADF       | 1.750 | 2.542 | 915 | 1010 | 7.1 | 7.5 | 1.787 | 2.550 | 2.917 | 4.440 | 832 | 923 | 2.1 | 2.3 | 190.3 | 191.2 | 24.1 | 28.7 | -412.28 | -384.81 | -386.00 |
| OLYP     | TZ2P      |            | ADF       | 1.750 | 2.542 | 915 | 1010 | 7.1 | 7.5 | 1.787 | 2.550 | 2.917 | 4.440 | 832 | 923 | 2.1 | 2.3 | 190.3 | 191.2 | 24.1 | 28.7 | -412.28 | -384.81 | -386.00 |
| TPSSH    | common    | TURBOMOLE |          | 1.746 | 2.469 | 940 | 1026 |     |     | 1.782 | 2.485 | 2.851 | 4.367 |     |     |     |     |        |        |     |     |        |        | -415.97 |
| M06L     | common    | ParaGauss |          | 1.740  | 2.507 | 948 | 1036 | 5.8 |     | 1.754 | 2.518 | 2.870 | 4.386 | 879 | 958 | 1.5 | 21.6 |        |        |     |     | -399.15 |        |         |
| M06L     | common    | Gaussian 09|         | 1.719  | 2.505 | 975 | 1048 | 5.8 |     | 1.754 | 2.518 | 2.870 | 4.386 | 879 | 958 | 1.5 | 21.6 |        |        |     |     | -399.15 |        |         |
| M06L     | TZ2P      | ADF       |          | 1.750  | 2.542 | 915 | 1010 | 7.1 | 7.5 | 1.787 | 2.550 | 2.917 | 4.440 | 832 | 923 | 2.1 | 2.3 | 190.3 | 191.2 | 24.1 | 28.7 | -412.28 | -384.81 | -386.00 |
| M06L     | def2-TZVP | Gaussian 09|         | 1.719  | 2.505 | 975 | 1048 | 5.8 |     | 1.754 | 2.518 | 2.870 | 4.386 | 879 | 958 | 1.5 | 21.6 |        |        |     |     | -399.15 |        |         |
| M06      | common    | ParaGauss |          | 1.722  | 2.491 | 1017 | 1096 |     |     | 1.749 | 2.514 | 2.872 | 4.372 | 933 | 1010 |     |     |        |        |     |     | -387.14 |        |         |
| M06      | common    | Gaussian 09|         | 1.721  | 2.491 | 1003 | 1083 | 7.0 |     | 1.750 | 2.515 | 2.874 | 4.379 | 932 | 1010 | 2.2 | 24.4 |        |        |     |     | -386.71 |        |         |
| M06      | TZ2P      | ADF       |          | 1.706  | 2.513 | 1015 | 1081 | 5.7 |     | 1.734 | 2.525 | 2.882 | 4.388 | 930 | 1001 | 1.7 | 21.3 |        |        |     |     | -364.98 |        |         |
| M06      | TZ2P      | ADF       |          | 1.727  | 2.492 | 998 | 1078 |     |     | 1.759 | 2.510 | 2.866 | 4.371 | 914 | 991 |     |     |        |        |     |     | -407.47 | -380.00 | -381.19 |
| minimum  |           |           |           | 1.706  | 2.375 | 865 | 957 | 5.5 | 7.2 | 1.734 | 2.407 | 2.763 | 4.239 | 877 | 871 | 1.5 | 2.2 | 177.5 | 191.2 | 21.3 | 28.1 | -414.04 | -386.58 | -387.76 |
| maximum  |           |           |           | 1.785  | 2.542 | 1017 | 1096 | 7.9 | 8.4 | 1.825 | 2.550 | 2.917 | 4.440 | 933 | 1010 | 2.2 | 2.3 | 199.2 | 199.9 | 25.4 | 29.9 | -364.98 | -379.02 | -380.20 |
| theory  | basis | program         | UO$_2$(H$_2$O)$_{2+}$ | UO$_2$(Ac)$_{3-}$ |
|---------|-------|-----------------|-----------------------|-------------------|
|         |       |                 | Bond distances (Å)    | Bond distances (Å) |
|         |       |                 | U-O$_\text{aq}$   | U-O$_\text{aq}$ |
|         |       |                 | Sym         | Asym         | Sym   | Asym   |
|         |       |                 | U-H SO      | U-H SO      | U-H SO | U-H SO |
| MP2     | common | TURBOMOL E     | 1.778       | 2.419     | 872   | 958     |
| MP2     | 6-31+G* | Gaussian 09 | 1.767       | 2.420     | 896   | 988     |
| BP86    | common | TURBOMOL E     | 1.781       | 2.431     | 856   | 918     |
| BP86    | common | Gaussian 09   | 1.774       | 2.467     | 880   | 951     |
| BP86    | common | ParaGauss      | 1.780       | 2.444     | 857   | 923     |
| BP86    | common | Gaussian 09   | 1.762       | 2.491     | 853   | 918     |
| PBE     | common | TURBOMOL E     | 1.777       | 2.432     | 862   | 924     |
| PBE     | common | ParaGauss      | 1.777       | 2.443     | 863   | 929     |
| PBE     | common | ADF            | 1.779       | 2.453     | 865   | 921     |
| PBE     | common | Gaussian 09   | 1.758       | 2.496     | 860   | 927     |
| PBE0    | common | TURBOMOL E     | 1.741       | 2.420     | 953   | 999     |
| PBE0    | common | Gaussian 09   | 1.734       | 2.454     | 967   | 1026    |
| PBE0    | common | ParaGauss      | 1.739       | 2.431     | 956   | 1004    |
| PBE0    | common | ADF            | 1.742       | 2.444     | 953   | 991     |
| PBE0    | common | Gaussian 09   | 1.719       | 2.468     | 975   | 1014    |
| B3LYP   | common | TURBOMOL E     | 1.759       | 2.441     | 910   | 963     |
| B3LYP   | common | Gaussian 09   | 1.752       | 2.474     | 930   | 994     |
| B3LYP   | common | ADF            | 1.762       | 2.460     | 912   | 954     |
| B3LYP   | common | Gaussian 09   | 1.733       | 2.492     | 934   | 984     |

**Stretching vibrational frequencies v$_1$ and v$_2$(UO$_2$) (cm$^{-1}$) and NMR chemical shifts ppm**

| U-O$_\text{aq}$ | U-C$_\text{car}$ | U-C$_\text{carb}$ | Sym | Asym | U-H SO | U-H SO | U-C$_\text{car}$ | U-C$_\text{carb}$ | U-C$_\text{car}$ | U-C$_\text{carb}$ | U-C$_\text{car}$ | U-C$_\text{carb}$ |
|-----------------|-----------------|-----------------|-----|-----|-------|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1.805           | 2.471           | 2.831           | 4.340 | 822 | 923   |       |     |     |     |     |     |     |     |
| 1.796           | 2.450           | 2.832           | 4.336 | 833 | 922   |       |     |     |     |     |     |     |     |
| 1.815           | 2.478           | 2.870           | 4.374 | 790 | 851   |       |     |     |     |     |     |     |     |
| 1.811           | 2.492           | 2.879           | 4.387 | 799 | 863   | 2.3   | 194.1 | 25.9 | 25.9 | 25.9 | 25.9 | 25.9 |
| 1.809           | 2.482           | 2.874           | 4.376 | 795 | 852   |       |     |     |     |     |     |     |     |
| 1.795           | 2.510           | 2.898           | 4.407 | 791 | 857   | 2.3   | 198.0 | 25.5 | 25.5 | 25.5 | 25.5 | 25.5 |
| 1.812           | 2.477           | 2.867           | 4.371 | 795 | 855   |       |     |     |     |     |     |     |     |
| 1.806           | 2.482           | 2.872           | 4.372 | 801 | 857   |       |     |     |     |     |     |     |     |
| 1.818           | 2.482           | 2.877           | 4.377 | 784 | 829   | 2.5   | 2.8  | 208.2 | 209.3 | 26.0 | 30.2 | 30.2 | 30.2 |
| 1.791           | 2.508           | 2.894           | 4.409 | 799 | 864   | 2.2   | 197.7 | 24.7 | 24.7 | 24.7 | 24.7 | 24.7 |
| 1.769           | 2.458           | 2.845           | 4.340 | 880 | 929   |       |     |     |     |     |     |     |     |
| 1.765           | 2.471           | 2.853           | 4.351 | 894 | 949   | 2.5   | 197.7 | 24.8 | 24.8 | 24.8 | 24.8 | 24.8 |
| 1.764           | 2.464           | 2.851           | 4.344 | 890 | 935   |       |     |     |     |     |     |     |     |
| 1.775           | 2.465           | 2.852           | 4.344 | 869 | 901   | 2.6   | 2.6  | 206.6 | 206.1 | 26.7 | 29.8 | 29.8 | 29.8 |
| 1.747           | 2.487           | 2.868           | 4.366 | 901 | 944   | 2.0   | 196.8 | 23.5 | -73.5 | -73.5 | -73.5 | -73.5 |
| 1.789           | 2.485           | 2.877           | 4.379 | 827 | 891   |       |     |     |     |     |     |     |     |
| 1.785           | 2.497           | 2.884           | 4.389 | 856 | 915   | 2.4   | 200.4 | 25.3 |     |     |     |     |
| 1.797           | 2.490           | 2.883           | 4.382 | 832 | 866   | 2.6   | 2.7  | 209.8 | 209.4 | 27.1 | 30.4 | 30.4 | 30.4 |
| 1.763           | 2.513           | 2.900           | 4.405 | 859 | 911   | 2.1   | 199.0 | 24.0 |     |     |     |     |
| 1.763           | 2.513           | 2.900           | 4.405 | 859 | 911   | 2.1   | 199.0 | 24.0 |     |     |     |     |

**Reaction Energy**

$\text{UO}_2$(H$_2$O)$_{2+}$ + 3 CH$_3$COO$^-$ → UO$_2$(CH$_3$COO)$_3^-$ + 5 H$_2$O

(kcal mol$^{-1}$)

| delta G | delta H | delta U | delta E |
|---------|---------|---------|---------|
| -98.95  | -85.65  | -78.11  |         |
| Method  | TZ2P (opt,fr) | ADF    | 1.768 | 2.490 | 891 | 952 | 7.7 | 8.2 | 1.838 | 2.510 | 2.909 | 4.418 | 758 | 801 | 2.5 | 2.9 | 212.1 | 213.3 | 26.7 | 31.1 | -93.86 | -66.39 | -67.58 |
|---------|---------------|--------|-------|-------|-----|-----|-----|-----|-------|-------|-------|-------|-----|-----|-----|-----|-------|-------|-----|-----|-------|-------|-------|
| O3LYP   | TZ2P (opt,fr) | ADF    | 1.741 | 2.345 | 938 | 982 | 8.0 | 8.5 | 1.772 | 2.381 | 2.766 | 4.224 | 862 | 901 | 2.6 | 2.8 | 208.5 | 208.7 | 25.2 | 29.0 | -82.91 | -55.45 | -56.63 |
| OLYP    | TZ2P (opt,fr) | ADF    | 1.759 | 2.496 | 887 | 946 | 7.3 | 7.5 | 1.797 | 2.520 | 2.915 | 4.421 | 802 | 854 | 2.4 | 2.8 | 201.5 | 202.7 | 25.9 | 29.9 | -93.63 | -66.16 | -67.34 |
| M06L    | common        | Gaussian 09 | 1.747 | 2.477 | 926 | 995 | 7.0 |     | 1.782 | 2.496 | 2.877 | 4.372 | 840 | 906 | 2.4 |     | 188.1 | 24.8 |     |     | -97.10 |     |     |
| M06L    | common        | ParaGauss | 1.752 | 2.458 | 902 | 962 |     |     | 1.781 | 2.490 | 2.875 | 4.365 | 836 | 891 |     |     |     |     |     | -90.74 |     |     |
| M06L    | TZ2P (opt,fr) | def2-TZVP | 1.750 | 2.464 | 916 | 958 |     |     | 1.790 | 2.486 | 2.871 | 4.361 | 816 | 855 |     |     |     |     |     | -92.11 | -64.64 | -65.82 |
| M06L    | TZ2P (opt,fr) | Gaussian 09 | 1.725 | 2.519 | 949 | 997 | 5.7 |     | 1.759 | 2.500 | 2.880 | 4.376 | 863 | 917 | 1.8 |     | 185.2 | 22.5 |     |     | -80.23 |     |     |
| M06     | common        | Gaussian 09 | 1.728 | 2.470 | 980 | 1034 | 6.9 |     | 1.756 | 2.497 | 2.876 | 4.370 | 916 | 968 | 2.4 |     | 198.7 | 23.8 |     |     | -86.64 |     |     |
| M06     | common        | ParaGauss | 1.733 | 2.451 | 983 | 1026 |     |     | 1.755 | 2.490 | 2.874 | 4.362 | 909 | 950 |     |     |     |     |     | -80.99 |     |     |
| M06     | def2-TZVP     | Gaussian 09 | 1.713 | 2.478 | 989 | 1028 | 5.8 |     | 1.738 | 2.509 | 2.885 | 4.381 | 916 | 961 | 1.9 |     | 195.8 | 22.1 |     |     | -71.47 |     |     |
| M06     | TZ2P (opt,fr) | ADF    | 1.736 | 2.454 | 971 | 1002 |     |     | 1.766 | 2.484 | 2.867 | 4.356 | 886 | 916 |     |     |     |     |     | -86.18 | -58.72 | -59.90 |

**minimum value**

| Method  | 1.713 | 2.345 | 853 | 918 | 5.5 | 5.5 | 5.5 | 5.5 | 1.738 | 2.381 | 2.766 | 4.224 | 758 | 801 | 1.8 | 2.6 | 205.2 | 205.2 | 25.2 | 29.2 | -98.95 | -66.39 | -67.58 | 0.00 |
|---------|-------|-------|-----|-----|-----|-----|-----|-----|-------|-------|-------|-------|-----|-----|-----|-----|-------|-------|-----|-----|-------|-------|-------|

**maximum value**

| Method  | 1.781 | 2.519 | 989 | 1034 | 8.0 | 8.0 | 8.0 | 8.0 | 1.838 | 2.520 | 2.915 | 4.421 | 916 | 968 | 2.6 | 2.9 | 212.1 | 213.3 | 27.1 | 31.1 | -70.77 | -55.45 | -56.63 | 0.00 |

ADF
7 Calibration Approach for LUM

Calibrating the wavelength scale of an array spectrometer typically involves measurements of lines at well-known wavelengths from a calibration lamp. Photo-diode array and charge-coupled device (CCD) spectrometers measure the spectrum of an optical signal by dispersing it across an array of light-sensitive detectors (pixels). A conventional Hg lamp (HG-1 Calibration Source, Ocean Optics) was used for the calibrations presented here.

Figure SI 21A shows the spectrum of the Hg lamp in the pixel space. First we estimated the pixel position for the main Hg lamp emission lines, at 404.66, 435.83 and 546.07 nm. Afterwards, a quadratic assumption was used to fit the pixel-wavelength curve to interpolate wavelength for every pixel in the array (Figure SI 21B). By this equation the wavelength range of measured spectra can be corrected (Figure SI 21C).
Figure SI 21: proposed calibration routine. Spectrum of the Hg lamp in the pixel space (A). Fit of the pixel-wavelength curve to interpolate wavelength for every pixel in the array (B). Correction of measured spectra (C). For further explanation the reader is referred to the text.
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