Investigation of the luminescence of $[\text{UO}_2\text{X}_4]^{2-}$ (X=Cl, Br) complexes in organic phase using time-resolved laser-induced fluorescence spectroscopy and quantum chemical simulations

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The luminescence properties of the $[\text{UO}_2\text{Cl}_4]^{2-}$ complex in an organic phase, especially the influence of large organic counter cations, have been studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS) and ab initio modeling. The experimental spectrum was assigned by vibronic Franck-Condon calculations on quantum chemical models based on relativistic density functional approaches. The shape of the luminescence spectrum of the uranyl tetrachloride complex is determined by symmetrical vibrations and geometrical change upon emission. The possible change of the luminescence properties depending on the first and second uranyl coordination sphere was predicted theoretically for $[\text{UO}_2\text{Br}_4]^{2-}$ and $[\text{R}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ ($[\text{R}_4\text{N}] = [\text{Bu}_4\text{N}], [\text{A}336]$) model systems. The computations reveal that for $\text{U(VI)}$, the second coordination sphere has little influence on the spectrum shape, making speciation of uranyl complexes with identical first coordination-sphere ligands tedious to discriminate. The computed structural changes agreed well with experimental trends; theoretical spectra and peaks attribution are in a good accordance with TRLFS and MCD data respectively.

I. INTRODUCTION

The knowledge of the stoichiometries and stabilities of the chemical species of uranium is of key importance for the understanding of the chemical reactivity of uranium in environmental or industrial situations. The speciation of uranium in solution has then been a major topic of investigations by both experimental and theoretical methods. Among the powerful spectroscopic techniques, time-resolved laser-induced luminescence spectroscopy (TRLFS) has been widely used for the characterization of uranyl species in solutions and in solid phases, because of its high sensitivity to changes of the inner-sphere coordination of $\text{UO}_2^{2+}$. The luminescence spectra of uranyl complexes in solution show in general a narrow energetic range about $6000 \text{ cm}^{-1}$. In this region just a single electronic transition between the initial and final states can be identified and it is vibrationally resolved with bands to different vibrational quantum numbers [1]. In the case of mixtures of uranyl species, the interpretation of TRLFS data can be difficult because of low resolution and overlapping of the emission spectra in similar time frame. Then spectroscopic considerations are often insufficient to unambiguously determine the nature of the complexes. This is why a theoretical support based on quantum chemical modeling appears as a way to better validate TRLFS data interpretations by decomposing the different effects that might induce changes in the emission spectra of uranyl complexes.

Several research teams have tried to simulate emission spectra of uranyl complexes with quantum chemical methods [2–4], based on either wave-function theory (WFT), or density functional theory (DFT). While WFT methods are efficient for accurate calculations, the high computing cost limits the simulation to small clusters of heavy elements like uranium. DFT approaches are more appropriate for cost-effective calculations applied to actinides, but can be challenged regarding the accuracy of the description of the electronic ground state and excited states, and its ability to reproduce low-lying electronic transitions and their vibronic resolution. Relativistic effects, electron correlation, and spin-orbit coupling must be correctly taken into account for those heavy elements. Tecmec et al. [5] have evaluated the accuracy of pure and hybrid exchange-correlation functionals for the bare uranyl cation isoelectronic uranium triatomics, arguing that hybrid functionals can be used for quantitative prediction of the low-lying excited states of uranyl. Uranyl tetrachloride complexes have been thoroughly studied as a reference cluster because direct comparison with luminescence data from crystals is possible [6]. Moreover, this complex can also be stabilized in non-aqueous solvents [7–9], and is of interest in some solvent extraction protocols [10, 11]. The structure of the uranyl tetra-chloride is well-established with four chloride ions in the equatorial plane of the $\text{UO}_2^{2+}$ moiety, resulting in a $D_{4h}$ symmetry. The effects of second-sphere counter cations, solvent molecules or solvating agents have also to be considered, as to quantify their influence on the structures, the electronic states energies, and the vibronic progressions.

In this work we will compare the results of ab initio calculations to experimental data obtained from a n-dodecane solution in which the uranyl tetrachloride complex was extracted by a tetra-alkyl ammonium molecule.
(Aliquate® 336). The methodology is a step-by-step approach in order to validate hypotheses and approximations that we made. The computations of the ground and the excited state structural and vibrational parameters are necessary for the understanding of theoretical and experimental spectra. Because the main effect on the luminescence data is commonly accepted to originate from the inner-sphere coordination, the first hydration sphere chloride ligands were substituted by bromides to discuss the trends, validate our method, and evaluate its applicability to other types of uranyl complexes. We will also quantify the effects of outer-sphere counter ions and long-range solvation on the computed spectra.

II. EXPERIMENTAL DETAILS

A. Sample preparation

\( [A336]_2[UO_2Cl_4] \) in \( n \)-dodecane The sample preparation method has been adapted from Hellé et al. [11, 12]. Aliquate® 336 (98%) was purchased from Alfa Aesar. HCl (32%), 1-decanol (99%) and \( n \)-dodecane were purchased from Sigma-Aldrich. HClO\(_4\) was purchased from Merck. All reagents were used as received without further purification. A stock solution of uranium(VI) was prepared by dissolution of \( U_2O_8 \) in a hot perchloric acid solution. The U(VI) concentration was checked by inductively coupled plasma mass spectrometry (ICP-MS). The aqueous solution was prepared by dilution of this stock solution into a 5\( \times \)10\(^{-5}\) M. Deionized water (Alpha-Q, Millipore, 18.2 MΩcm) was used for the preparation of all aqueous solutions.

The organic solution was prepared by dissolving weighed amounts of Aliquate® 336 and 1-decanol in sufficient amount of \( n \)-dodecane to get a concentration of 10\(^{-2}\) M. Deionized water (Alpha-Q, Millipore, 18.2 MΩcm) was used for the preparation of all aqueous solutions.

For uranium extraction, 2mL of the aqueous solution was contacted with an equal volume of the pre-equilibrated organic solution. The mixture was shaken in a thermomixer at 20°C during 1h, and about 2mL of the organic phase was sampled after 2h of decantation for the spectroscopic measurements.

B. Time-Resolved Laser-Induced Fluorescence Spectroscopy

The sample was put in a 1cm-long quartz cuvette that was placed in a TRLFS set-up as described afterwards. The excitation wavelength was provided by a tunable OPO system (PantherEx OPO, Excel Technology) pumped by a Nd:YAG laser at 355 nm (Surelite-I, Excel Technology). The excitation was tuned to \( \lambda_{ex} = 427\text{ nm} \) which corresponds to a maximum of absorption by uranium(VI) in our samples. The 5ns laser pulses were generated at 10 Hz for an energy of about 3.15 mJ. The detection set-up has already been described elsewhere [13]. The luminescence signal was collected during a gate width of 200 ps, at a gate delay of 100 ns after the excitation by the laser pulse. The luminescence spectrum of the sample was recorded at room temperature ((22 ± 1°C). The luminescence spectrum in this work was obtained after 1000 accumulations. The background noise was subtracted from recorded spectrum.

C. Computational details

Since our aim is to use quantum chemical methods to elucidate the luminescence band shapes of the complexes, several data are required. The ground-state and first excited state geometries, their associated harmonic frequency spectra and Hessian matrices have to be computed in order to obtain the overlap integrals between the vibrational wave-functions associated to the ground and excited states - Frank-Condon factors (FCFs). The FCFs were computed using ezSpectrum 3.0 [14] program by taking all necessary data generated by the \textit{ab initio} packages described below. The Duschinsky rotations were used as implemented in the program. The numbers of vibrational quanta in excited and ground state were selected to be one and five, respectively. All the spectra were computed at 300 K.

a. Model systems The interactions of uranyl with the first and second coordination spheres affect the electronic structure of uranium. As the influence of the chloride ligands in UO\(_2\)Cl\(_4^2\) complex was excellently reviewed by variety of experimental [7, 8, 15–17] and theoretical methods [18–22], this system was selected as a benchmark to quantify the effect of ligands in the first coordination sphere by substituting chlorides by bromides, and the effect of the counter-ions in the second coordination sphere, i.e. the quaternary ammonium cations. Furthermore, to discuss the importance of long-range solvent effects, the model systems were computed in gas phase and with inclusion of solvent effect (n-dodecane and acetone). The structures are represented in Fig. 4

b. Structures of the ground and excited states, and harmonic frequencies In the sake of keeping the computational costs within week scale and of simplifying the data analysis, the structures of the uranyl tetrahalides complexes were enforced to \( D_{4h} \) symmetry, whereas no symmetry constrains were applied to the complexes with a second coordination sphere. All the ground-state molecular geometries were optimized including the relativistic effects at the spin-free level in the gas phase and with solvent effect using Density functional Theory (DFT). The Kohn-Sham equation was solved using the hybrid PBE0 functional [23]. The structure of the first low-lying excited state was optimized using the time-
FIG. 1. [UO₂X₄]²⁻

FIG.2.
[B₄N]₂[UO₂X₄]

FIG. 3. [A₃36]₂[UO₂X₄]

FIG. 4. The complexes structures of [R₂N]₂[UO₂X₄] ([R₂N] = [B₄N], [A₃36] and X=Cl, Br) in gas phase optimized at the DFT/PBE0 level of theory.

dependent (TD)-DFT/PBE0 method as implemented in Turbomole V7.3 2018 [24] and Gaussian 16 [25] codes. The vibrational harmonic frequencies were computed using either an analytic Hessian matrix or numerical finite differences of the gradient. All geometries considered for the vibronic spectra calculations represent true minima as they have no imaginary frequencies. The optimized structures are available in ESI.

In these calculations, def2-TZVP (second generation of triple-ζ polarization quality) Karlsruhe basis sets [26, 27] have been used for all light elements (H, C, N, O, Cl). For the heaviest atoms, small-core Relativistic Effective Core Pseudopotentials (RECP) were used, namely the 60-core electron one for uranium [28, 29] along with the def-TZVP (first generation of triple-ζ polarization quality) basis set [30], and the 28-core electrons ECP for bromine with the associated aug-cc-pVTZ-PP basis set [31]. To speed up the calculations, the resolution of the identity approximation to compute the Coulomb Integrals (RI-J) [32, 33] with appropriate auxiliary basis sets [30, 34] was employed.

c. Vertical absorption and emission energies Based on the benchmark calculations carried out by Tecmer et al. [5, 35, 36] on a series of uranium(VI)-based compounds, the CAM-B3LYP [37] exchange-correlation functional was found to be more accurate than PBE0 for uranyl valence transition energies. Thus, to accurately position the “hot bands”, the vertical excitation and emission energies with and without accounting for solvent effect were obtained from the ground and excited-state structures, respectively, with TD-DFT single-point calculations with the latter functional and the Amsterdam Density Functional package (ADF2018.01) [38]. All atoms were described by TZ2P Slater-type basis sets [39] (triple-ζ with two polarization functions quality). The scalar relativistic (SR) and spin-orbit coupling (SOC) effects were accounted for by the ZORA Hamiltonian [40].

d. Continuum solvent models Long-range solvent effects were modeled by polarized continuum medium models, with two similar flavors, the Continuum Polarizable Conductor Model (CPCM) [41, 42] one implemented in Gaussian 16 program, and the conductor-like screening model (COSMO) model [43–45] implemented in the ADF package.

III. RESULTS AND DISCUSSIONS

A. Experimental luminescence spectra

The time-resolved luminescence spectrum of the uranyl sample in the presence of chloride ions and Aliquate® 336 in n-dodecane with 1% of 1-decanol is shown on Figure 5 (black line). It is superimposed with the spectrum (red line) acquired by Görller-Walrand et al. in similar conditions and in acetone [7]. The spectrum also compares well to those obtained earlier in chloroaluminate [17], tetraalkylammonium [9] and pyrrolidinium [8] ionic liquids. The spectrum of [A₃36]₂[UO₂Cl₄] in n-dodecane in Figure 5 show an electronic transition maximum (”hot band”) at low energy about 21 000 cm⁻¹ followed by a series of vibronic peaks in the 20 300 cm⁻¹ to 16 000 cm⁻¹ range, which is typical of the [UO₂Cl₄]²⁻ species with a D₁h coordination symmetry [46]. A mono-exponential decay with a fluorescence lifetime of 0.3 μs was measured for the uranium(VI) sample in a presence of chloride ions, Aliquate® 336 and n-dodecane. It confirms the formation of a unique complex, which was assumed to be [A₃36]₂[UO₂Cl₄] with four chloride ions coordinated to uranyl in its equatorial plane, consistently with the extracted complex stoichiometry [10].

The decomposition of the [A₃36]₂[UO₂Cl₄] luminescence spectra has been performed by Reiller et al. [10]. The poor resolution of the presently used apparatus did not allow to resolve well some of the transitions, and revealed only the wide components. Moreover, a difference of the relative intensities is observed around 20 295 cm⁻¹ in n-dodecane due to the long gate width selected for our measurements and small deviations, as the spectrum was predicted by a Lorentzian fit (Table S1 in ESI). The spectrum in n-dodecane is shifted to the blue side by 3 cm⁻¹ to 4 cm⁻¹, compared to the one in acetone, and only by 5 cm⁻¹ with respect to the one in [Bu₃MeN][Tf₂N] ionic liquid [9]. Thus, from the measurements, one can conclude that neither the counter-ion nor the type of solvent have any significant influence on the position of maxima of the luminescence bands. The change in the relative intensities of the transitions along the vibronic progression has been attributed by Sornein et al. [9] to the formation
FIG. 5. Recorded luminescence spectra of [Bu$_4$N]$_2$[UO$_2$Cl$_4$] in acetone (the maxima taken from Ref. [7], the Lorentzian shape computed) and [A336]$_2$[UO$_2$Cl$_4$] in $n$-dodecane. Vertical dashed red line shows the “hot band” position and $R_n$, (n = 1 − 5) corresponds to vibronic progression region. Details on the spectral data are available in Table S1 of the ESI.

of C–H···Cl hydrogen bonding between the chloride of the [UO$_2$Cl$_4$]$^{2−}$ moiety and a hydrogen atom of a cation present in the ionic liquid. As we are using an aprotic solvent ($n$-dodecane), this effect may also be present in our uranyl tetrachloride sample.

The spacing between the vibronic progressions of the luminescence spectrum corresponds to the ground state uranyl stretching frequency value $ν_s$. The bands are not equally spaced, as the oscillator strength of the electronic transition from the excited state to the highest vibrational level of the ground state is very small. As a result, large uncertainty exist on the determination of the “hot band” maximum. One can extract $ν_s$ value by only taking into account the spacing between the vibronic maxima of the same nature for [A336]$_2$[UO$_2$Cl$_4$] in $n$-dodecane. The resulting $ν_s$ value amounts to (836 ± 18) cm$^{-1}$. It is in good agreement with the values, (823 ± 14) cm$^{-1}$, 825 cm$^{-1}$, and (850 ± 25) cm$^{-1}$ observed in acetone [7], [C$_4$Et$_4$][H$_2$N][F$_2$N] [8], and in [Bu$_3$MeN][H$_2$N][F$_2$N] [9], respectively. This vibration corresponds to a Raman active vibration of the uranyl unit and can be correlated to the $ν_{1'}$–$ν_{0}$ bond length. Using the empiric relation of Bartlett and Cooney [47]:

$$R_{U−O} (/Å) = 106.5 \times ν_s^{-2/3} + 0.575$$

we calculated the U–O bond length to be equal to (1.77 ± 0.01) Å (using $ν_s = (836 ± 18) \text{ cm}^{-1}$) for our uranyl sample. This value is in a good agreement with all experimental data listed in Table I, and can therefore serve as reference data to assess the accuracy of the ab initio calculations we will now discuss.

B. Ground and excited state structures of the uranyl tetrahalide complexes

a. Uranyl tetrahalide dianions The structure of uranyl tetrachloride dianion has been well-studied by the variety of theoretical and experimental techniques [6, 15, 20, 35, 48–51]. Insofar as the inclusion of all effects like in experimental conditions is challenging for ab initio calculations because of the difficulties in building chemically relevant models and the fast growing of the computational costs as the model expands, the present quantum chemical study was performed on models with increasing chemical complexity, to approach the solution sample.

The spin-free optimized ground and the first excited state distances between uranium and the coordinated atoms of the [UO$_2$Cl$_4$]$^{2−}$ and [UO$_2$Br$_4$]$^{2−}$ together with experimental data are shown in Table I.

In the [UO$_2$Cl$_4$]$^{2−}$ gas-phase PBE0 calculations, the ground state $R_{U−O} = 1.758$ Å value is in a good agreement with 1.766 Å obtained with the CCSD(T) wave-function method, while $R_{U−Cl} = 2.714$ Å comes out shorter than 2.735 Å. Moreover, the PBE0 geometries are in good accordance with the all-electron CAM-B3LYP results reported by Tecner et al. [35]. This gives us confidence in the ability of PBE0 to provide fairly accurate geometries of the uranium containing complexes. The inclusion of solvent effects on [UO$_2$Cl$_4$]$^{2−}$ does not significantly change the $R_{U−O}$ distance as compared to the gas-phase calculations, but it shortens $R_{U−Cl}$ as the solvent polarity increases. Keeping in mind that we do not have strictly the same conditions as in the experiment, it is worth examining trends in both theoretical and experimental data. The comparison of the experimental crystal structure of Cs$_2$UO$_2$Cl$_4$ [6] with the structure of uranyl tetrachloride dianion in acetonitrile [49]) shows that the $R_{U−O}$ bond length is almost the same in both conditions, while $R_{U−Cl}$ values are found to be longer in solution by about 0.01 Å.

To quantify the influence of the ligand nature in the first equatorial coordination sphere, the chloride ligands were replaced by bromide ligands which have the same type of bonding with uranium, but larger ionic radii. The uranyl ion coordinated by four bromide ligands has been prepared in crystal form [50], while it is hardly stabilized in solution. The experimental structure of Cs$_2$UO$_2$Br$_4$ crystal shows that $R_{U−O}$ distance (1.777 Å) is almost equal to the one found in the chloride homologue, Cs$_2$UO$_2$Cl$_4$ ($R_{U−O} = 1.774$ Å), whereas the $R_{U−Br}$ distance is longer by 0.149 Å than $R_{U−Cl}$. The gas-phase geometries of [UO$_2$Cl$_4$]$^{2−}$ and [UO$_2$Br$_4$]$^{2−}$ follow this trend; the substitution of chloride by bromide ligands leads to the insignificant stabilization of $R_{U−O}$, and the U–Br distance is longer by 0.169 Å than the U–Cl one because of a weaker uranium–bromide ionic interaction. The latter lengthening is larger by 0.063 Å than in the crystals, simply because our quantum model does not account for crystal packing effects.

The lowest triplet excited state in [UO$_2$X$_4$]$^{2−}$ com-
TABLE I. Ground and excited state geometries of the $[\text{UO}_2\text{X}_4]^{2-}$, $\text{X} = \text{Cl}, \text{Br}$ compared to selected previous results.

| Ground state                    | RU–O, Å   | RU–X, Å   | Compound/media | Method                  | Ref.          |
|--------------------------------|-----------|-----------|----------------|-------------------------|--------------|
| $[\text{UO}_2\text{Cl}_4]^{2-}$| 1.798     | 2.714     | gas-phase      | R-ECP/PBE0              | this work    |
|                                | 1.766     | 2.735     | gas-phase      | CCSD(T)                | [48]         |
|                                | 1.764     | 2.712     | gas-phase      | all-electron/CAM-B3LYP  | [35]         |
|                                | 1.774     | 2.671     | CPCM n-dodecane| X-ray                   | [6]          |
|                                | 1.759     | 2.699     | CPCM acetone   | R-ECP/PBE0              | this work    |
|                                | 1.761     | 2.683     | CPCM acetone   | R-ECP/PBE0              | this work    |
|                                | 1.770     | 2.680     | acetonitrile   | EXAFS                   | [40]         |
| $[\text{UO}_2\text{Br}_4]^{2-}$| 1.750     | 2.883     | gas-phase      | R-ECP/PBE0              | this work    |
|                                | 1.749     | 2.905     | gas-phase      | R-ECP/CAM-B3LYP         | this work    |
|                                | 1.777     | 2.820     | C$_2$UO$_2$Br$_4$| X-ray                   | [50]         |

Excited state

| $[\text{UO}_2\text{Cl}_4]^{2-}$| 1.789     | 2.721     | gas-phase      | R-ECP/PBE0              | this work    |
|                                | 1.844     | 2.685     | C$_2$UO$_2$Cl$_4$| Two-photon absorption  | [15]         |
|                                | 1.790     | 2.706     | CPCM n-dodecane| R-ECP/PBE0              | this work    |
|                                | 1.791     | 2.692     | CPCM acetone   | R-ECP/PBE0              | this work    |
| $[\text{UO}_2\text{Br}_4]^{2-}$| 1.778     | 2.895     | gas-phase      | R-ECP/PBE0              | this work    |
|                                | 1.780     | 2.918     | gas-phase      | R-ECP/CAM-B3LYP         | this work    |

The analysis of vibrational frequencies is very important for the characterization of the theoretical luminescence spectra, as specific vibrations appear in the vibronic progression. Some of the ground-state vibrational frequencies are responsible for the band spacing in the experimental luminescence spectrum, while the atomic displacement between the ground and excited-state geometries is responsible for the intensities ratio. The uranium - halide ($\nu_{\text{U-X}}$), uranium - oxygen($\nu_a$) symmetrical stretching modes and uranium - oxygen bending mode ($\nu_s$) contribute to the luminescence spectra shape to a large extent, and their values for the $[\text{UO}_2\text{Cl}_4]^{2-}$ and $[\text{UO}_2\text{Br}_4]^{2-}$ complexes are listed in Table II. The uranium - oxygen asymmetrical stretching mode ($\nu_b$), which is vibronically silent, is also shown to discuss trends. Using the vibrational perturbation theory [52, 53] as implemented in Gaussian 16 [25], we have computed the anharmonic corrections, which turned out to be small, of the order of 5 and 3 cm$^{-1}$ for the ground and excited states respectively (See Table S2 in the ESI).

For the gas-phase $[\text{UO}_2\text{Cl}_4]^{2-}$ model, the computed $\nu_{\text{U-Cl}}$, $\nu_b$, $\nu_a$ and $\nu_s$ frequencies are smaller in the excited state than in the ground state by 4, 4, 80 and 115 cm$^{-1}$, respectively. The PBE0 calculations reproduce with an impressive accuracy the measured red shift of the stretching mode, $\nu_s$, 82 cm$^{-1}$, in C$_2$UO$_2$Cl$_4$, and underestimates that for the bending mode, 20 cm$^{-1}$. The latter discrepancy has negligible impact as the symmetric stretching $\nu_s$ dominates the vibronic progresses in the luminescence spectra.

Turning now to the vibrational frequencies obtained with solvent effects, we observed opposite behavior of the U – Cl and U – O frequencies. With increasing of polarity the $\nu_{\text{U-Cl}}$ stretching frequencies insignificantly increase (4 and 7 cm$^{-1}$) for the ground and excited states, respectively, while the uranyl $\nu_b$, $\nu_s$ and $\nu_a$ decrease by 5 up to 25 cm$^{-1}$ in both states. This shift of the ground-state frequencies should be observable in the computed luminescence spectra, namely in the spacing between the vi-
TABLE II. Ground and excited state vibrational frequencies (in cm$^{-1}$) of the [R$_4$N]$_2$[UO$_2$X$_4$], ([R$_4$N] = [Bu$_4$N], [A336]) compounds.

| System                  | $\nu_{U-X}$ | $\nu_b$ | $\nu_s$ | $\nu_a$ | Method             | Ref.           |
|-------------------------|-------------|---------|---------|---------|--------------------|----------------|
| Ground state            |             |         |         |         |                    |                |
| [UO$_2$Cl$_4$]$^{2-}$   | 237         | 275     | 894     | 974     | R-ECP/PBE0 gas-phase | this work      |
|                         | 235         | 269     | 889     | 960     | R-ECP/PBE0 n-dodecane | this work      |
|                         | 241         | 265     | 889     | 949     | R-ECP/PBE0 acetone   | this work      |
| Cs$_2$UO$_2$Cl$_4$      | 264 [15]    | 250     | 832     | 915     | Raman and IR in solid | [46]           |
| [Me$_4$N]$_2$[UO$_2$Cl$_4$] | 831   | 909     |         |         | Raman and IR in solid | [54]           |
| [Et$_4$N]$_2$[UO$_2$Cl$_4$] | 240   | 263     | 869     | 954     | Raman in solid       | [55]           |
| [Bu$_4$N]$_2$[UO$_2$Cl$_4$] | 270   | 286     | 869     | 945     | R-ECP/PBE0 gas-phase | this work      |
|                         | 258         | 262     | 833     | 919     | Raman and IR in CH$_2$Cl$_2$ solution | [56]           |
| [A336]$_2$[UO$_2$Cl$_4$] | 266         | 288     | 876     | 957     | R-ECP/PBE0 gas-phase | this work      |
| [UO$_2$Br$_4$]$^{2-}$   | 144         | 262     | 907     | 988     | R-ECP/PBE0 gas-phase | this work      |
| [C$_7$H$_{16}$NO$_2$][UO$_2$Br$_4$] | 173 | 252     | 826     | 904     | Raman and IR in solid | [57]           |
| Excited state           |             |         |         |         |                    |                |
| [UO$_2$Cl$_4$]$^{2-}$   | 233         | 271     | 814     | 859     | R-ECP/PBE0 gas-phase | this work      |
|                         | 236         | 268     | 811     | 854     | R-ECP/PBE0 n-dodecane | this work      |
|                         | 240         | 263     | 808     | 848     | R-ECP/PBE0 acetone   | this work      |
| Cs$_2$UO$_2$Cl$_4$      | 230         | 750     | 830     |         | N.A.               | [7]            |
| [Bu$_4$N]$_2$[UO$_2$Cl$_4$] | 266   | 281     | 799     | 845     | R-ECP/PBE0 gas-phase | this work      |
| [A336]$_2$[UO$_2$Cl$_4$] | 261         | 284     | 802     | 854     | R-ECP/PBE0 gas-phase | this work      |
| [UO$_2$Br$_4$]$^{2-}$   | 151         | 264     | 876     | 935     | R-ECP/PBE0 gas-phase | this work      |

b. Organic cation - uranyl tetrachloride: [A336]$_2$[UO$_2$Cl$_4$] The [UO$_2$Cl$_4$]$^{2-}$ dianion in interaction with the organic ligand has been prepared in the conditions described in the experimental section. The sample was prepared based on the general ion-exchange mechanism [58, 59], where in our scheme the extracting substance was Aliquate ™ 336. Then the final compound is predicted to be the uranyl tetrachloride associated with two extractant cations of methyltrioclylammonium [A336]$_2$[UO$_2$Cl$_4$] as a result of an ion-exchange mechanism [10]. Interestingly, Görller-Walrand et al. [7] stabilized the [UO$_2$Cl$_4$]$^{2-}$ dianion in solution with tetrabutylammonium chloride (Bu$_4$NCl), a ligand belonging to the group of tetraalkylammonium salts as the Aliquate ™ 336. For our purpose, the geometries of ground and luminescent states of complexes were optimized with the two tetraalkylammonium cations placed in the second sphere in a trans position. The bond distances are shown in Table III, while the vibrational frequencies are shown in Table II.

If one compares the computed geometrical parameters to that of the models without an explicit second-coordination sphere (Table I), the counter-cations induce a weakening of uranyl bond and the loss of the D$_{4h}$ symmetry. These changes are due to the presence of a weak hydrogen bond between the hydrogen atoms of the alkyl chains of cation with the oxygen and chloride atoms of uranyl tetrachloride unit [9] (see ESI Figure S1, Table S3). The ground-state geometries of uranyl tetrachloride in [Bu$_4$N]$_2$[UO$_2$Cl$_4$] and [A336]$_2$[UO$_2$Cl$_4$] have been found to be nearly the same; the R$_{U-O}$ bond lengths are longer by about 0.010 Å than in the bare [UO$_2$Cl$_4$]$^{2-}$ complex. Moreover, because of the symmetry distortion and interaction of chloride ligands with the counter ion, the R$_{U-Cl}$ distances differ by 0.026 up to 0.118 Å.
as compared to the bare $[\text{UO}_2\text{Cl}_4]^{2-}$. Despite our theoretical model does not account for the crystal-field influence, these gas-phase structures are in a good accordance with the experimental crystal structures measured for parent compounds with a shorter alkyl chain, such as $[\text{Me}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ and $[\text{Et}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$) [54]. This observation makes us conclude that the chain length of a tetraalkilammonium cation has merely no influence on the $R_{\text{U}−\text{O}}$ and $R_{\text{U}−\text{Cl}}$ values and that both organic counter-cations ($R_4\text{N}$) interact with the uranyl tetrachloride dianion in a similar way. Since the influence of long-range solvent effects on the $[\text{UO}_2\text{Cl}_4]^{2-}$ bare complex is negligible, we rely in the following on the gas-phase structures for the $[R_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ complexes.

The addition of two counter-cations in our chemical model does not change the nature of the first excited state, which still is the excitation out of the $\sigma_u$ orbital to a $\delta_u$ non-bonding orbital. As a result, the luminescent-state geometry is impacted by the counter-cations as the ground-state one: as compared to the bare $[\text{UO}_2\text{Cl}_4]^{2-}$ complexes, the $R_{\text{U}−\text{O}}$ stretches by 0.028 Å for $[\text{R}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ and the $R_{\text{U}−\text{Cl}}$ distances are increased by 0.003 Å for both types of complexes. From these computed differences of the $R_{\text{U}−\text{Cl}}$, we may expect different ratios of relative intensities in the vibronic progressions of the uranyl chloride and uranyl bromide complexes.

The calculated frequencies have been compared with data from experimental Raman and IR measurements of different crystals or liquid samples of $[R_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ [54–56]. The computed symmetrical stretching frequency $\nu_s$ ($[\text{Bu}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$) matches the value measured for the $[\text{Et}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ crystal [55]. For $[\text{Bu}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$, the gas-phase computed frequencies $\nu_{\text{U}−\text{Cl}}$, $\nu_\text{y}$, $\nu_\text{u}$ and $\nu_\text{a}$ are overestimated by 12, 24, 36 and 26 cm$^{-1}$, respectively, with respect to the values measured in dichloromethane solution [56]. From emission spectroscopy measurements, symmetric-stretching vibrational frequency ($\nu_s$) for $[\text{Bu}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ in acetone and for $[\text{A}_3\text{A}_3\text{S}_6]_2[\text{UO}_2\text{Cl}_4]$ in n-dodecane, were estimated at 823 [7] and 836 cm$^{-1}$, respectively. Our gas-phase calculations for these exact complexes yield slightly blue-shifted values, 869 and 876 cm$^{-1}$. We conclude that, our theoretical models and methods are appropriate to capture structural and spectroscopic trends.

The difference in computed harmonic frequencies of $[\text{UO}_2\text{Cl}_4]^{2-}$ in the two $[R_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ complexes is found to be small, the maximum variation from one counter ion to another is 12 cm$^{-1}$, for the asymmetric uranyl stretching mode. The counter-ions in the second-coordination sphere only slightly affect the calculated frequencies with respect to the $[\text{UO}_2\text{Cl}_4]^{2-}$ bare ion; the uranium-chloride stretching mode is 29 cm$^{-1}$ higher, the uranyl bending mode has increased by 13 cm$^{-1}$, while the uranyl symmetrical and asymmetrical stretching modes were found to be lower by 18 and 14 cm$^{-1}$, respectively. This is a result of the loss of symmetry together with the interplay of some motions of hydrogen and carbon atoms in alkyl chain in the vibrational motions. Based on the Franck-Condon principle, one can note that it should improve the band spacing between the vibronic progressions of theoretical luminescence spectrum that will be discussed further.

The shifts of theoretical frequencies between the ground and excited state of $[\text{A}_3\text{A}_3\text{S}_6]_2[\text{UO}_2\text{Cl}_4]$ are found to be similar to what was experimentally obtained for $\text{Cs}_2\text{UO}_2\text{Cl}_4$. The computed uranyl symmetrical stretching mode shifted by 74 cm$^{-1}$, very close to the experimental value of 82 cm$^{-1}$. However, the $\nu_{\text{U}−\text{Cl}}$ and $\nu_\text{u}$ do not vary during the excitation. We will later discuss the impact of this on the computed vibronic spectra.

C. Theoretical absorption and emission energies

As the luminescence spectrum of uranium (VI) complexes arises from the electronic transition from the lowest excited state to the ground state, coupled to progressions of vibronic bands, the examination of the whole electronic spectrum is useless. In this step, we aim at foreseeing the sensitivity of the quantum chemical method on the first triplet excited state absorption and emission energies of the uranyl tetrachloride complex, and on the spectral features of uranium (VI) complexes.

The $[\text{UO}_2\text{Cl}_4]^{2-}$ dianion electronic spectrum have been computed previously at the different levels of theory and detailed discussions of the electronic structure can be found in the literature [19–21, 35]. From the previous studies it is known that for uranyl dication coordinated by ligands the lowest excited state arises from the $\sigma_u$ highest molecular orbital (HOMO) to the $\delta_u$ lowest unoccupied orbital (LUMO). The HOMO corresponds to the bonding combination of uranium 5f and 6p and oxygen 2p atomic orbitals, and 3p orbital of first-shell ligands, while the LUMO is a nonbonding uranium 5f orbital (Figure 8). The detailed analysis of the atomic orbitals contributions performed with multi-reference CASSCF (complete active space self-consistent field) calculations by Pierloot and van Beisen [20] suggests that the lowest-lying excitation corresponds to a metal-centered transition from the bonding to nonbonding orbital of uranium, with a marginal ligand-to-metal charge transfer character. Hence, we can use in our discussion the $\text{UO}_2^{2+}$ spin-free notations ($D_{\text{soch}}$), thus labelling the ground state as $^1\Sigma_g^+$ and the luminescent state as $^3\Delta_g$.

The vertical absorption $E_{\text{VA}}$ and emission $E_{\text{VE}}$ energies, were obtained at all-electron SOC CAM-B3LYP level of theory and are reported here together with experimental values (Table IV). They were computed with the summation of the fully relativistic electronic vertical energies associated with the spin-free zero-point energies correction. It should be noted that the experimental data correspond to the band-origin values obtained from polarized absorption or luminescence spectra and emission energies taken from UV-Visible spectroscopic measurements. Thus the direct comparison with theoretical re-
TABLE III. Ground and excited state geometries of the \([R_4N]_2[UO_2Cl_4]\) compounds compared to selected experimental results.

| Ground state | Compounds | Method | Ref. |
|--------------|-----------|--------|------|
| RU–O, Å      | RU–Cl, Å  |        |      |
| 1.766(6)     | 2.648(1)-2.677(1) | Me₄N₂[UO₂Cl₄] | X-ray | [54] |
| 1.76(2)-1.77(3) | 2.65(1)-2.68(1) | Et₄N₂[UO₂Cl₄] | X-ray | [54] |
| 1.769        | 2.596-2.753  | Bu₄N₂[UO₂Cl₄] | R-ECP/PBE0 this work |
| 1.767        | 2.609-2.740  | [A336]₂[UO₂Cl₄] | R-ECP/PBE0 this work |
| Excited state | Compounds | Method | Ref. |
| 1.796        | 2.599-2.780  | Bu₄N₂[UO₂Cl₄] | R-ECP/PBE0 this work |
| 1.795        | 2.614-2.761  | [A336]₂[UO₂Cl₄] | R-ECP/PBE0 this work |

results is not relevant, but we rather discuss whether the theoretical data reproduce the experimental trends.

As seen in Table IV, the vertical absorption energy of \([UO₂Cl₄]^{2–}\) increases by 85 cm⁻¹ with the addition of acetone due to its small polarity. A blue shift of 117 cm⁻¹ is observed when chlorides are replaced by bromides ligands. On the contrary, the band origins seem red shifted by 128 cm⁻¹, from chloride to bromide complexes according to experimental data [46, 60]. The presence of multiple non-equivalent uranyl sites in \([UO₂Br₄]^{2–}\) crystal studied by Flint et al. [60] may cause a reverse shift of the whole spectrum and hampers a direct comparison between theoretical and experimental results.

The luminescent state is known to be more sensitive to the solvent polarity [61]. We indeed observed a larger shift of about 192 cm⁻¹ with the inclusion of acetone solvent than for absorption energies. With addition of Bu₄N in the second coordination sphere, the E_{VE} increased by 85 cm⁻¹, as expected since the displacements between the ground and excited state \([UO₂Cl₄]^{2–}\) energies are larger with than without counter cations. Both theoretical E_{VE} and experimental emission energies of \([UO₂Cl₄]^{2–}\) are blue shifted by 32 or 25 cm⁻¹ when immersed in n-dodecane or acetone, respectively.

It is worth noting that in the experimental spectra, the band-origin value of \([UO₂Cl₄]^{2–}\) is the same within 1 cm⁻¹ in the C₆₁₂UO₂Cl₄ crystal and in [Bu₄N]₂[UO₂Cl₄] in acetone. This is fully consistent with the fact that the excitation molecular orbitals (See Figure 8) of the luminescent state do not show any contribution from the second-sphere counter-ions.

D. Theoretical luminescence spectra

To simplify the comparison within all spectra, let them be obtained from our quantum chemical calculations or from experiment, they are all normalized so that the first peak matches the experimental amplitude. Neither homogeneous and heterogeneous line broadening effects are included because of their complicated prediction [2]. We will thus only discuss the stick spectra.

The most relevant parameters influencing the spectral intensity distribution are the vibrational wavefunctions of both initial and excited states. The spectral shape is significantly linked to the bond-length changes between the two electronic states, as identified by Su et al. [4] thanks to a semi-classical vibronic approach. Especially, they concluded that the computed bond-length of the excited state is estimated without a sufficient accuracy to properly simulate the intensities. In our study, the theoretical luminescence spectra of \([UO₂Cl₄]^{2–}\) and \([UO₂Br₄]^{2–}\) in gas phase are displayed on Figure 9. In all uranium-based compounds at room temperature (300 K), luminescence arises from a low oscillator strength electron transition followed by the vibrational progression in the νₘ mode of the electronic ground state, as the νₘ is totally symmetric and preserves the symmetry of the vibronic (electronic+vibrational) wave function. The first observed band corresponds to the 0-0 vibrational transition. In the \([UO₂Cl₄]^{2–}\), the totally symmetric ν₁−C₁ mode is also excited vibronically, contributing to a line in the vibronic progression which is distant from the 0-0 line by 235 cm⁻¹. However, as we already commented upon the fact that the U-X lengthening from the ground and excited states is underestimated by our quantum approach, we cannot expect the computed relative intensities to match the experimental ones. Still, our predicted spectra place the peaks distribution and band spacing in great agreement with the experimental results. The complete assignment of the observed peaks is provided in ESI.

Setting the \([UO₂Cl₄]^{2–}\) spectrum computed in gas phase with those computed in n-dodecane and acetone solvents (See Fig. S2 of the ESI) reveals that long-range solvent interactions have no influence on the spectral profile. However, \([UO₂Br₄]^{2–}\) luminescence spectrum displays some more intense contributions and longer vibronic pro-

FIG. 6. HOMO
FIG. 7. LUMO

FIG. 8. The highest occupied and lowest unoccupied molecular orbitals of [Bu₄N]₂[UO₂Cl₄] in gas phase obtained at RECP DFT/PBE0 level of theory.
TABLE IV. Experimental and computed electronic transition energies of uranyl tetrahalide complexes (in cm\(^{-1}\)). All-electron SOC CAM-B3LYP level of theory, the fully relativistic electronic vertical energies associated with the spin-free ZPE correction.

| Complex | Theor. \(E_{VA}\) | Exp. \(E_{VE}\) | Band-origin Emission |
|---------|-----------------|-------------|------------------|
| \([\text{UO}_2\text{Cl}_4]^{2-}\) gas-phase | 20737 | 19924 | 20096 \(^a\) |
| \([\text{UO}_2\text{Cl}_4]^{2-}\) acetone | 20822 | 20116 | |
| \([\text{UO}_2\text{Br}_4]^{2-}\) gas-phase | 20746 | 20041 | 19968 \(^b\) |
| \([\text{Bu}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]\) acetone | 20009 | 20097 \(^c\) | 21000 \(^c\) |
| \([\text{A336}]_2[\text{UO}_2\text{Cl}_4]\) n-dodecane | 20041 | 21025 | |

\(^a\) Ref. [46], \(^b\) Ref. [60], \(^c\) Ref. [7]

FIG. 9. Theoretical luminescence spectra of \([\text{UO}_2\text{Cl}_4]^{2-}\) and \([\text{UO}_2\text{Br}_4]^{2-}\) in gas phase computed at 300 K.

IV. CONCLUSIONS

Probing and quantifying the long-range effects of large organic counter-cations on \([\text{UO}_2\text{Cl}_4]^{2-}\) complex luminescence spectra was realized by two approaches, one experimental using TRLFS, and the second using \textit{ab initio}-based approaches. For the latter, relativistic DFT quantum chemical methods were found to be quantitative and effective tools to rationalize and predict uranium-based complex luminescence properties. Thanks to a benchmark with respect to previous studies on \([\text{UO}_2\text{Cl}_4]^{2-}\) in crystal and solvent phases, we have been able to assess the degree of reliability of such an approach by comparison of ground and luminescence states structures and frequencies. However, this theoretical protocol reaches some limitations, since we were not able to compute the exact geometrical displacements of the complexes upon excitation from the ground to first excited state. As a result, the computed intensities of the vibronic bands do not coincide with the experimental ones. Conversely, the peak positions of the luminescence spectra are correctly reproduced, and the band spacings and theoretical assignments are in a good accordance with our experimental data.

In this work, we have used step-wise growing chemical models to quantify the influence of i) the first coordination sphere by substituting chloride anions by bromides; ii) the influence of second-sphere counter cations; iii) and long-range solvent effects with a polarizable continuum model, with the aim of approaching the experimental conditions. We have found that both long-range solvent effect and outer-sphere counter ion have a little influence on vibronic intensities, while their effect is more significant for the prediction of other spectroscopic parameters.
such as emission energies and vibronic band spacings of the [UO$_2$Cl$_4$]$^{2-}$ complex. This also confirms that the TRLFS spectroscopy may not be sensitive enough to discriminate long-range interactions induced by the counterions present in the vicinity of the luminescent center.

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ASSOCIATED CONTENT

The following file supplemental-uo2x4-Oher.pdf is available free of charge. It contains:

- Figures of theoretical spectra of the [UO$_2$Cl$_4$]$^{2-}$ obtained with the long-range counter-ion and solvent effects.

- Tables of assignments for theoretical and experimental spectra.

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Supporting information for:

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S2 Influence of solvent effects on theoretical [UO_2Cl_4]^{2-} complex shape at 0K (upper panel) and 300K (lower panel). The spectral shapes were obtained by a Lorentzian convolution; the assignments are provided in Tables S4, S5 and S6 for the [UO_2Cl_4]^{2-} in gas-phase, n-dodecane and acetone, respectively. . . . . . . . . . . . S14

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S4 Comparison of theoretical spectra of [Bu_4N]_2[UO_2Cl_4] and [A_{336}]_2[UO_2Cl_4] complexes in a gas-phase at 300K. The spectral shapes were obtained by a Lorentzian convolution; the assignments are provided in Tables S8 and S9 for the [Bu_4N]_2[UO_2Cl_4] and [A_{336}]_2[UO_2Cl_4], respectively. . . . . . . . . . . . . S15
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S1  Experimental luminescence data of the $[R_4N]_2[UO_2Cl_4]$ complexes at room temperature. The $\nu$ corresponds to the position of the band, the $\Delta\nu$ is a difference between the bands position in a region, the $\Delta\nu_n$ is a difference between the peaks of the same nature located in different regions. All data are in cm$^{-1}$. The luminescence spectra are shown on Figure 2 in the main text.  

S2  Ground and excited state harmonic and anharmonic frequencies (in cm$^{-1}$) of the $[UO_2Cl_4]^{2-}$ complex in a gas phase computed by G16 at R-ECP DFT/PBE0 and TD-DFT/PBE0 level of theory for the ground and first excited states respectively.  

S3  The chloride-hydrogen bond lengths (in Å) in $[R_4N]_2[UO_2Cl_4]$ complexes computed at the R-ECP DFT/PBE0 and TD-DFT/PBE0 levels of theory for the ground and first excited states, respectively. Atom labeling corresponds to the one shown on Figure S1.  

S4  Assignment of the $[UO_2Cl_4]^{2-}$ (gas-phase) theoretical luminescence spectrum. The energy of the spectrum was adjusted to experimental band-origin value of $[UO_2Cl_4]^{2-}$ in acetone. The nature of bands is explained in Table S2.  

S5  Assignment of the $[UO_2Cl_4]^{2-}$ (dodecane) theoretical luminescence spectrum. The energy of the spectrum was adjusted to experimental band-origin value of $[UO_2Cl_4]^{2-}$ in acetone. The nature of bands is explained in Table S2.  

S6  Assignment of the $[UO_2Cl_4]^{2-}$ (acetone) theoretical luminescence spectrum. The energy of the spectrum was adjusted to experimental band-origin value of $[UO_2Cl_4]^{2-}$ in acetone. The nature of bands is explained in Table S2.  

S7  Assignment of the $[UO_2Br_4]^{2-}$ theoretical luminescence spectrum. The energy of the spectrum was adjusted to experimental band-origin value of $[UO_2Cl_4]^{2-}$ in acetone. The bands representation is taken from the $[UO_2Cl_4]^{2-}$ frequencies, the nature of bands is explained in Table S2.
Assignment of the $[\text{Bu}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ (gas-phase) theoretical luminescence spectrum. The energy of the spectrum was adjusted to experimental band-origin value of $[\text{UO}_2\text{Cl}_4]^{2-}$ in acetone. The nature of bands is shown in Table S2.

Assignment of the $[\text{A}_{336}]_2[\text{UO}_2\text{Cl}_4]$ gas-phase theoretical luminescence spectrum. The energy of the spectrum was adjusted to experimental band-origin value of $[\text{A}_{336}]_2[\text{UO}_2\text{Cl}_4]$ in $n$-dodecane. The bands representation is taken from the $[\text{UO}_2\text{Cl}_4]^{2-}$ frequencies, with details found in Table S2.

Theoretical displacements of geometries $\Delta R$, and absolute frequency shifts $\Delta \nu$ from the ground to the first excited state.

Cartesian coordinates (in Å) of the $[\text{UO}_2\text{X}_4]^{2-}$ complexes in different media at their ground and first excited state minima obtained by R-ECP DFT/PBE0 and TD-DFT/PBE0 methods, respectively.

Cartesian coordinates (in Å) of the $[\text{Bu}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ in gas phase at its ground and first excited state minima obtained in Turbomole 7.3.1 by R-ECP DFT/PBE0 and TD-DFT/PBE0 methods respectively.

Cartesian coordinates (in Å) of the $[\text{A}_{336}]_2[\text{UO}_2\text{Cl}_4]$ in gas phase at its ground and first excited state minima obtained in Turbomole 7.3.1 by R-ECP DFT/PBE0 and TD-DFT/PBE0 methods respectively.
Table S1: Experimental luminescence data of the $[\text{R}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ complexes at room temperature. The $\nu$ corresponds to the position of the band, the $\Delta\nu$ is a difference between the bands position in a region, the $\Delta\nu_n$ is a difference between the peaks of the same nature located in different regions. All data are in cm$^{-1}$. The luminescence spectra are shown on Figure 2 in the main text.

| Region | $[\text{A}_{336}]_2[\text{UO}_2\text{Cl}_4]$ in n-dodecane | $[\text{Bu}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ in acetone |
|--------|-----------------|-----------------|
|        | $\nu$/cm$^{-1}$ | $\Delta\nu$ | $\Delta\nu_n$ | Intensity | $\nu$/cm$^{-1}$ | $\Delta\nu$ | $\Delta\nu_n$ | Intensity |
| 1 $I_1$ | 20295 | 730 | 0.84 | | 20325 | - | 0.74 |
|        | 20015 | 280 | 1.00 | | 20032 | 293 | 0.95 |
|        | 19944 | 88 | 0.91 | | 19763 | 181 | 0.40 |
| 2 $I_2$ | 19488 | 527 | 807 | 0.70 | | 19501 | 262 | 824 | 0.84 |
|        | 19155 | 333 | 860 | 0.81 | | 19238 | 263 | 794 | 0.83 |
|        | 19113 | 125 | 831 | 1.00 | | 18925 | 188 | 838 | 0.34 |
| 3 $I_3$ | 18651 | 504 | 837 | 0.28 | | 18664 | 261 | 837 | 0.39 |
|        | 18305 | 346 | 850 | 0.30 | | 18403 | 261 | 836 | 0.36 |
|        | 18282 | 121 | 832 | 0.51 | | 18103 | 179 | 822 | 0.16 |
| 4 $I_4$ | 17839 | 466 | 812 | 0.08 | | 17825 | 278 | 838 | 0.11 |
|        | 17454 | 385 | 851 | 0.08 | | 17593 | 232 | 810 | 0.09 |
|        | 17452 | 141 | 830 | 0.16 | | 17289 | 163 | 814 | 0.05 |
| 5 $I_5$ | 16996 | 458 | 843 | 0.02 | | 17013 | 277 | 813 | 0.03 |
|        | 16625 | 371 | 829 | 0.02 | | 16795 | 217 | 798 | 0.02 |
|        | 16628 | 168 | 824 | 0.03 | | 16442 | 186 | 847 | 0.01 |
Table S2: Ground and excited state harmonic and anharmonic frequencies (in cm\(^{-1}\)) of the \([\text{UO}_2\text{Cl}_4]^{2-}\) complex in a gas phase computed by G16 at R-ECP DFT/PBE0 and TD-DFT/PBE0 level of theory for the ground and first excited states respectively.

| \(\nu\) | \(\nu_{\text{harm}}\) | \(\nu_{\text{anharm}}\) | \(\nu_{\text{harm}}\) | \(\nu_{\text{anharm}}\) | Nature of the band                      |
|-------|-----------------|-----------------|-----------------|-----------------|---------------------------------------|
| 1     | 75.7            | 76.4            | 71.3            | 72.4            | out-of-plane asymmetrical Cl-U-Cl bending |
| 2     | 76.6            | 76.6            | 77.2            | 77.2            | in plane Cl-U-Cl bending               |
| 3     | 76.6            | 76.6            | 77.2            | 77.2            |                                       |
| 4     | 97.3            | 98.0            | 98.7            | 99.8            | U-Cl scissoring                        |
| 5     | 110.0           | 110.3           | 104.1           | 105.0           | out-of-plane symmetrical Cl-U-Cl bending |
| 6     | 197.2           | 193.7           | 170.5           | 166.7           | O-U-O rocking                          |
| 7     | 197.2           | 193.7           | 170.5           | 166.7           |                                       |
| 8     | 202.3           | 202.5           | 199.2           | 199.0           | asymmetrical Cl-U-Cl stretching        |
| 9     | 219.1           | 219.2           | 214.5           | 214.6           | asymmetrical Cl-U-Cl stretching        |
| 10    | 219.1           | 219.2           | 214.5           | 214.6           | asymmetrical Cl-U-Cl stretching        |
| 11    | 237.3           | 237.0           | 232.6           | 231.6           | symmetrical Cl-U-Cl stretching         |
| 12    | 274.5           | 271.4           | 271.8           | 268.5           | O-U-O bending                          |
| 13    | 274.5           | 271.4           | 271.8           | 268.5           | O-U-O bending                          |
| 14    | 894.5           | 889.4           | 813.7           | 810.9           | symmetrical O-U-O stretching           |
| 15    | 974.2           | 966.9           | 858.9           | 854.3           | asymmetrical O-U-O stretching          |
Figure S1: Illustrations of hydrogen bondings between the first and second coordination spheres of uranyl in \([R_4N]_2[UO_2Cl_4]\) complexes. Left panel is representing interactions in \([Bu_4N]_2[UO_2Cl_4]\) and right in \([A_{336}]_2[UO_2Cl_4]\).

Table S3: The chloride-hydrogen bond lengths (in Å) in \([R_4N]_2[UO_2Cl_4]\) complexes computed at the R-ECP DFT/PBE0 and TD-DFT/PBE0 levels of theory for the ground and first excited states, respectively. Atom labeling corresponds to the one shown on Figure S1.

| Bond                  | GS (Å) | ES (Å) | Bond                  | GS (Å) | ES (Å) |
|-----------------------|--------|--------|-----------------------|--------|--------|
| Cl33-H83              | 2.534  | 2.524  | Cl25-H57              | 2.427  | 2.411  |
| Cl36-H53              | 2.642  | 2.606  | Cl28-H48              | 2.557  | 2.535  |
| Cl33-H97              | 2.646  | 2.632  | Cl28-H37              | 2.656  | 2.626  |
| Cl36-H71              | 2.789  | 2.744  | Cl28-H151             | 2.672  | 2.685  |
| Cl36-H66              | 2.893  | 2.885  | Cl27-H71              | 2.851  | 2.901  |
Table S4: Assignment of the \([\text{UO}_2\text{Cl}_4]^{2-}\) (gas-phase) theoretical luminescence spectrum. The energy of the spectrum was adjusted to experimental band-origin value of \([\text{UO}_2\text{Cl}_4]^{2-}\) in acetone. The nature of bands is explained in Table S2.

| Region | E, cm\(^{-1}\) | Δν, cm\(^{-1}\) | I, a.u. | Identification |
|--------|----------------|----------------|--------|----------------|
| 0      | 20325.0        | —              | 6.50E-01 | 0(0)->1(0)     |
|        | 20087.9        | 237.1          | 1.43E-02 | 0(0)->1(ν\(_{11}\)) |
|        | 19930.6        | 394.4          | 1.72E-03 | 0(0)->1(2ν\(_{7}\)) |
|        | 19850.8        | 474.2          | 3.29E-04 | 0(0)->1(2ν\(_{11}\)) |
| 1      | 19430.6        | 894.4          | 2.46E-01 | 0(0)->1(ν\(_{14}\)) |
|        | 19193.5        | 237.1          | 7.21E-03 | 0(0)->1(ν\(_{11}\), ν\(_{14}\)) |
|        | 19036.2        | 394.4          | 6.52E-04 | 0(0)->1(2ν\(_{7}\), ν\(_{14}\)) |
|        | 18955.6        | 475.0          | 1.84E-04 | 0(0)->1(2ν\(_{11}\), ν\(_{14}\)) |
| 2      | 18536.2        | 894.4          | 5.91E-02 | 0(0)->1(2ν\(_{14}\)) |
|        | 18299.1        | 237.1          | 2.11E-03 | 0(0)->1(ν\(_{11}\), 2ν\(_{14}\)) |
|        | 18141.8        | 394.4          | 1.56E-04 | 0(0)->1(2ν\(_{7}\), 2ν\(_{14}\)) |
|        | 18061.2        | 475.0          | 5.94E-05 | 0(0)->1(2ν\(_{11}\), 2ν\(_{14}\)) |
| 3      | 17641.8        | 894.4          | 1.11E-02 | 0(0)->1(3ν\(_{14}\)) |
|        | 17404.7        | 237.1          | 4.66E-04 | 0(0)->1(ν\(_{11}\), 3ν\(_{14}\)) |
|        | 17247.4        | 394.4          | 2.95E-05 | 0(0)->1(2ν\(_{7}\), 3ν\(_{14}\)) |
|        | 17166.7        | 475.0          | 1.44E-05 | 0(0)->1(2ν\(_{11}\), 3ν\(_{14}\)) |
| 4      | 16747.4        | 894.4          | 1.80E-03 | 0(0)->1(4ν\(_{14}\)) |
|        | 16510.3        | 237.1          | 8.61E-05 | 0(0)->1(ν\(_{11}\), 4ν\(_{14}\)) |
| 5      | 15853.0        | 894.4          | 2.62E-04 | 0(0)->1(5ν\(_{14}\)) |
Table S5: Assignment of the $[\text{UO}_2\text{Cl}_4]^{2-}$ (dodecane) theoretical luminescence spectrum. The energy of the spectrum was adjusted to experimental band-origin value of $[\text{UO}_2\text{Cl}_4]^{2-}$ in acetone. The nature of bands is explained in Table S2.

| Region | E, cm$^{-1}$ | $\Delta$\nu, cm$^{-1}$ | I, a.u. | Identification |
|--------|-------------|--------------------------|--------|----------------|
| 0      | 20325.0     | 6.59E-01                 | 0(0)->1(0) |
|        | 20116.9     | 1.48E-04                 | 0(0)->1(2\nu_5) |
|        | 20085.5     | 2.42E-02                 | 0(0)->1(\nu_{11}) |
|        | 19926.6     | 1.79E-03                 | 0(0)->1(2\nu_7) |
|        | 19845.9     | 6.63E-04                 | 0(0)->1(2\nu_{11}) |
| 1      | 19435.4     | 2.34E-01                 | 0(0)->1(\nu_{14}) |
|        | 19227.4     | 5.26E-05                 | 0(0)->1(2\nu_5, \nu_{14}) |
|        | 19195.9     | 8.19E-03                 | 0(0)->1(\nu_{11}, \nu_{14}) |
|        | 19037.0     | 6.34E-04                 | 0(0)->1(2\nu_7, \nu_{11}) |
|        | 18956.4     | 2.17E-04                 | 0(0)->1(\nu_{11}, \nu_{14}) |
| 2      | 18545.9     | 889.6                    | 5.30E-02 | 0(0)->1(2\nu_{14}) |
|        | 18337.8     | 208.1                    | 1.19E-05 | 0(0)->1(2\nu_5, 2\nu_{14}) |
|        | 18306.3     | 239.5                    | 1.79E-03 | 0(0)->1(\nu_{11}, 2\nu_{14}) |
|        | 18147.5     | 398.4                    | 1.44E-04 | 0(0)->1(2\nu_7, 2\nu_{14}) |
|        | 18066.8     | 479.1                    | 4.62E-05 | 0(0)->1(\nu_{11}, 2\nu_{14}) |
| 3      | 17656.3     | 889.6                    | 9.47E-03 | 0(0)->1(3\nu_{14}) |
|        | 17416.8     | 239.5                    | 3.09E-04 | 0(0)->1(\nu_{11}, 3\nu_{14}) |
|        | 17257.9     | 398.4                    | 2.57E-05 | 0(0)->1(2\nu_7, 3\nu_{14}) |
| 4      | 16766.7     | 889.6                    | 1.46E-03 | 0(0)->1(4\nu_{14}) |
|        | 16527.2     | 239.5                    | 4.60E-05 | 0(0)->1(\nu_{11}, 4\nu_{14}) |
| 5      | 15877.2     | 889.6                    | 2.01E-04 | 0(0)->1(5\nu_{14}) |
Table S6: Assignment of the $[\text{UO}_2\text{Cl}_4]^{2-}$ (acetone) theoretical luminescence spectrum. The energy of the spectrum was adjusted to experimental band-origin value of $[\text{UO}_2\text{Cl}_4]^{2-}$ in acetone. The nature of bands is explained in Table S2.

| Region | E, cm$^{-1}$ | $\Delta \nu$, cm$^{-1}$ | I, a.u. | Identification |
|--------|-------------|----------------|--------|----------------|
| 0      | 20325.0     | 5.30E-01       |        | 0(0)$\rightarrow$1(0) |
|        | 20081.4     | 1.45E-01       |        | 0(0)$\rightarrow$1($\nu_{11}$) |
|        | 19929.0     | 1.56E-03       |        | 0(0)$\rightarrow$1($2\nu_7$) |
|        | 19838.7     | 2.08E-02       |        | 0(0)$\rightarrow$1($2\nu_{11}$) |
|        | 19595.1     | 2.10E-03       |        | 0(0)$\rightarrow$1($3\nu_{11}$) |
| 1      | 19441.9     | 1.79E-01       |        | 0(0)$\rightarrow$1($\nu_{14}$) |
|        | 19198.3     | 4.82E-02       |        | 0(0)$\rightarrow$1($\nu_{11}, \nu_{14}$) |
|        | 19045.9     | 5.28E-04       |        | 0(0)$\rightarrow$1($2\nu_7, \nu_{14}$) |
|        | 18955.6     | 6.82E-03       |        | 0(0)$\rightarrow$1($2\nu_{11}, \nu_{14}$) |
| 2      | 18558.8     | 3.89E-02       |        | 0(0)$\rightarrow$1($\nu_{14}$) |
|        | 18316.0     | 1.03E-02       |        | 0(0)$\rightarrow$1($\nu_{11}, \nu_{14}$) |
|        | 18162.8     | 1.14E-04       |        | 0(0)$\rightarrow$1($2\nu_7, \nu_{14}$) |
|        | 18072.4     | 1.44E-03       |        | 0(0)$\rightarrow$1($2\nu_{11}, \nu_{14}$) |
| 3      | 17675.6     | 6.66E-03       |        | 0(0)$\rightarrow$1($3\nu_{14}$) |
|        | 17432.9     | 1.74E-03       |        | 0(0)$\rightarrow$1($\nu_{11}, 3\nu_{14}$) |
|        | 17280.5     | 1.96E-05       |        | 0(0)$\rightarrow$1($2\nu_7, 3\nu_{14}$) |
|        | 17189.3     | 2.40E-04       |        | 0(0)$\rightarrow$1($2\nu_{11}, 3\nu_{14}$) |
| 4      | 16793.3     | 9.80E-04       |        | 0(0)$\rightarrow$1($4\nu_{14}$) |
|        | 16549.8     | 2.54E-04       |        | 0(0)$\rightarrow$1($\nu_{11}, 4\nu_{14}$) |
| 5      | 15910.2     | 1.30E-04       |        | 0(0)$\rightarrow$1($5\nu_{14}$) |
Table S7: Assignment of the $\left[\text{UO}_2\text{Br}_4\right]^{2-}$ theoretical luminescence spectrum. The energy of the spectrum was adjusted to experimental band-origin value of $\left[\text{UO}_2\text{Cl}_4\right]^{2-}$ in acetone. The bands representation is taken from the $\left[\text{UO}_2\text{Cl}_4\right]^{2-}$ frequencies, the nature of bands is explained in Table S2.

| Region | E, cm$^{-1}$ | $\Delta\nu$, cm$^{-1}$ | I, a.u. | Identification |
|--------|-------------|----------------|--------|----------------|
| 0      | 20325.0     | 4.70E-01      | 0(0)$\rightarrow$1(0) |
|        | 20229.0     | 96.0          | 1.63E-02 | 0(0)$\rightarrow$1(2$\nu_3$) |
|        | 20181.4     | 143.6         | 4.06E-02 | 0(0)$\rightarrow$1(1$\nu_{11}$) |
|        | 20081.4     | 243.6         | 7.03E-03 | 0(0)$\rightarrow$1(2$\nu_8$) |
|        | 19971.8     | 353.2         | 2.07E-03 | 0(0)$\rightarrow$1(2$\nu_7$) |
| 1      | 19418.5     | 906.5         | 1.53E-01 | 0(0)$\rightarrow$1(1$\nu_{14}$) |
|        | 19274.1     | 144.4         | 1.54E-02 | 0(0)$\rightarrow$1(1$\nu_{11}$, 1$\nu_{14}$) |
|        | 19174.9     | 243.6         | 2.29E-03 | 0(0)$\rightarrow$1(2$\nu_8$,1$\nu_{14}$) |
| 2      | 18511.2     | 907.3         | 2.76E-02 | 0(0)$\rightarrow$1(2$\nu_{14}$) |
|        | 18367.6     | 143.6         | 3.16E-03 | 0(0)$\rightarrow$1(1$\nu_{11}$, 2$\nu_{14}$) |
|        | 18268.4     | 242.8         | 4.13E-04 | 0(0)$\rightarrow$1(2$\nu_8$,2$\nu_{14}$) |
| 3      | 17604.7     | 906.5         | 3.63E-03 | 0(0)$\rightarrow$1(3$\nu_{14}$) |
|        | 17461.1     | 143.6         | 4.66E-04 | 0(0)$\rightarrow$1(1$\nu_{11}$, 3$\nu_{14}$) |
| 4      | 16697.4     | 907.3         | 3.88E-04 | 0(0)$\rightarrow$1(4$\nu_{14}$) |
|        | 16553.8     | 143.6         | 5.49E-05 | 0(0)$\rightarrow$1(1$\nu_{11}$, 4$\nu_{14}$) |
| 5      | 15790.9     | 906.5         | 3.56E-05 | 0(0)$\rightarrow$1(5$\nu_{14}$) |
Table S8: Assignment of the $[\text{Bu}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ (gas-phase) theoretical luminescence spectrum. The energy of the spectrum was adjusted to experimental band-origin value of $[\text{UO}_2\text{Cl}_4]^{2-}$ in acetone. The nature of bands is shown in Table S2.

| Region | E, cm$^{-1}$ | $\Delta\nu$, cm$^{-1}$ | I, a.u. | Identification |
|--------|-------------|-----------------|------|---------------|
| 0      | 20325       | 1.73E-01        |      | 0(0)->1(0)   |
|        | 20114       | 1.24E-04        |      | 0(0)->1(1$\nu_7$) |
|        | 20092       | 2.29E-03        |      | 0(0)->1(1$\nu_8$) |
|        | 20056       | 1.32E-03        |      | 0(0)->1(1$\nu_{11}$) |
|        | 19902       | 4.00E-04        |      | 0(0)->1(2$\nu_7$) |
| 1      | 19456       | 5.26E-02        |      | 0(0)->1(1$\nu_{14}$) |
|        | 19245       | 1.47E-05        |      | 0(0)->1(1$\nu_7,1\nu_{14}$) |
|        | 19223       | 7.05E-04        |      | 0(0)->1(1$\nu_8,1\nu_{14}$) |
|        | 19187       | 3.53E-04        |      | 0(0)->1(1$\nu_{11},1\nu_{14}$) |
|        | 19034       | 1.19E-04        |      | 0(0)->1(2$\nu_7,1\nu_{14}$) |
| 2      | 18588       | 1.03E-02        |      | 0(0)->1(2$\nu_{14}$) |
|        | 18356       | 1.40E-04        |      | 0(0)->1(1$\nu_8,2\nu_{14}$) |
|        | 18318       | 6.24E-05        |      | 0(0)->1(1$\nu_{11},2\nu_{14}$) |
|        | 18165       | 2.32E-05        |      | 0(0)->1(2$\nu_7,2\nu_{14}$) |
| 3      | 17719       | 1.60E-03        |      | 0(0)->1(3$\nu_{14}$) |
|        | 17487       | 2.19E-05        |      | 0(0)->1(1$\nu_8,3\nu_{14}$) |
| 4      | 16851       | 2.14E-04        |      | 0(0)->1(4$\nu_{14}$) |
| 5      | 15982       | 2.57E-05        |      | 0(0)->1(5$\nu_{14}$) |
Table S9: Assignment of the $[A336]_2[UO_2Cl_4]$ gas-phase theoretical luminescence spectrum. The energy of the spectrum was adjusted to experimental band-origin value of $[A336]_2[UO_2Cl_4]$ in $n$-dodecane. The bands representation is taken from the $[UO_2Cl_4]^{2-}$ frequencies, with details found in Table S2.

| Region | E, cm$^{-1}$ | $\Delta \nu$, cm$^{-1}$ | I, a.u. | Identification |
|--------|-------------|----------------|--------|----------------|
| 0      | 21025.0     | 7.55E-01       |        | 0(0)->1(0)     |
|        | 20786.3     | 238.7          | 2.59E-03 | 0(0)->1(1$\nu_8$, 1$\nu_{12}$) |
|        | 20758.9     | 266.1          | 1.25E-02 | 0(0)->1(1$\nu_{11}$) |
|        | 20492.7     | 532.3          | 2.54E-04 | 0(0)->1(2$\nu_{11}$) |
| 1      | 20149.1     | 875.9          | 8.88E-02 | 0(0)->1(1$\nu_{14}$) |
|        | 19910.4     | 238.7          | 2.93E-04 | 0(0)->1(1$\nu_8$, 1$\nu_{12}$, 1$\nu_{14}$) |
|        | 19883.0     | 266.1          | 1.32E-03 | 0(0)->1(1$\nu_{11}$, 1$\nu_{14}$) |
| 2      | 19274.1     | 875.1          | 6.75E-03 | 0(0)->1(2$\nu_{14}$) |
|        | 19032.9     | 241.1          | 3.44E-05 | 0(0)->1(1$\nu_9$, 1$\nu_{12}$, 2$\nu_{14}$) |
|        | 19007.1     | 267.0          | 9.21E-05 | 0(0)->1(1$\nu_{11}$, 2$\nu_{14}$) |
| 3      | 18398.2     | 875.9          | 4.07E-04 | 0(0)->1(3$\nu_{14}$) |
|        | 18159.5     | 238.7          | 1.26E-06 | 0(0)->1(1$\nu_8$, 1$\nu_{12}$, 3$\nu_{14}$) |
|        | 18132.1     | 266.1          | 5.13E-06 | 0(0)->1(1$\nu_{11}$, 3$\nu_{14}$) |
| 4      | 17522.4     | 875.9          | 2.11E-05 | 0(0)->1(4$\nu_{14}$) |
|        | 17256.2     | 266.1          | 2.48E-07 | 0(0)->1(1$\nu_{11}$, 4$\nu_{14}$) |
Figure S2: Influence of solvent effects on theoretical [UO$_2$Cl$_4$]$^{2-}$ complex shape at 0K (upper panel) and 300K (lower panel). The spectral shapes were obtained by a Lorentzian convolution; the assignments are provided in Tables S4, S5 and S6 for the [UO$_2$Cl$_4$]$^{2-}$ in gas-phase, $n$-dodecane and acetone, respectively.

Figure S3: The effect of a $[A336]^+$ counter ion on the theoretical [UO$_2$Cl$_4$]$^{2-}$ complex shape in gas-phase at 300K. The spectral shapes were obtained by a Lorentzian convolution; the assignments are provided in Tables S4 and S9 for the [UO$_2$Cl$_4$]$^{2-}$ and $[A336]_2[UO_2Cl_4]$, respectively.
Figure S4: Comparison of theoretical spectra of $[\text{Bu}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ and $[\text{A336}]_2[\text{UO}_2\text{Cl}_4]$ complexes in a gas-phase at 300K. The spectral shapes were obtained by a Lorentzian convolution; the assignments are provided in Tables S8 and S9 for the $[\text{Bu}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ and $[\text{A336}]_2[\text{UO}_2\text{Cl}_4]$, respectively.

Table S10: Theoretical displacements of geometries $\Delta R$, and absolute frequency shifts $\Delta \nu$ from the ground to the first excited state.

|             | $\Delta R$, Å | $\Delta \nu$, cm$^{-1}$ |
|-------------|----------------|-------------------------|
|             | $R_{\text{U-O}}$ | $R_{\text{U-X}}$ | $\nu_{\text{U-X}}$ | $\nu_b$ | $\nu_s$ | $\nu_a$ |
| $[\text{UO}_2\text{Cl}_4]^{2-}$ | gas phase | 0.031 | 0.007 | -4 | -4 | -80 | -115 |
|             | dodecane | 0.031 | 0.007 | 1 | -1 | -78 | -106 |
|             | acetone | 0.03 | 0.009 | -1 | -2 | -81 | -101 |
| $[\text{UO}_2\text{Br}_4]^{2-}$ | gas phase | 0.028 | 0.012 | 7 | 2 | -31 | -53 |
| $[\text{Bu}_4\text{N}]_2[\text{UO}_2\text{Cl}_4]$ | gas phase | 0.026 | 0.003-0.027 | -4 | -5 | -70 | -100 |
| $[\text{A336}]_2[\text{UO}_2\text{Cl}_4]$ | gas phase | 0.029 | 0.005-0.021 | -5 | -4 | -74 | -103 |
Table S11: Cartesian coordinates (in Å) of the [UO$_2$X$_4$]$^{2-}$ complexes in different media at their ground and first excited state minima obtained by R-ECP DFT/PBE0 and TD-DFT/PBE0 methods, respectively.

| Complex | Media | Ground state | Excited state |
|---------|-------|--------------|---------------|
| [UO$_2$Cl$_4$]$^{2-}$ | gas phase, Turbomole 7.3.1 | 1.919262 1.919262 0 | 1.9246369 1.9246369 0 |
| | | Cl -1.919262 -1.919262 0 | -1.9246369 -1.9246369 0 |
| | | Cl 1.919262 -1.919262 0 | 1.9246369 -1.9246369 0 |
| | | Cl -1.919262 1.919262 0 | -1.9246369 1.9246369 0 |
| | | O 0 0 -1.7581059 | 0 0 -1.7888649 |
| | | O 0 0 1.7581059 | 0 0 1.7888649 |
| | | U 0 0 0 | 0 0 0 |
| [UO$_2$Cl$_4$]$^{2-}$ | n-dodecane, G16 | Cl 0 2.698696 0 | 0 2.706546 0 |
| | | Cl 0 -2.698696 0 | 0 -2.706546 0 |
| | | Cl -2.698696 0 0 | -2.706546 0 0 |
| | | Cl 2.698696 0 0 | 2.706546 0 0 |
| | | O 0 0 1.759301 | 0 0 1.789492 |
| | | O 0 0 -1.759301 | 0 0 -1.789492 |
| | | U 0 0 0 | 0 0 0 |
| [UO$_2$Cl$_4$]$^{2-}$ | acetone, G16 | Cl 0 2.683942 0 | 0 2.691882 0 |
| | | Cl 0 -2.683942 0 | 0 -2.691882 0 |
| | | Cl -2.683942 0 0 | -2.691882 0 0 |
| | | Cl 2.683942 0 0 | 2.691882 0 0 |
| | | O 0 0 1.760965 | 0 0 1.790628 |
| | | O 0 0 -1.760965 | 0 0 -1.790628 |
| | | U 0 0 0 | 0 0 0 |
| [UO$_2$Br$_4$]$^{2-}$ | gas phase, Turbomole 7.3.1 | Br -2.03856600 -2.0385665 0.0000001 | -2.0466917 -2.0466919 -0.0001551 |
| | | Br 2.03856650 2.0385659 0.0000001 | 2.0466764 2.0466945 -0.0001593 |
| | | Br -2.03856600 2.0385658 0 | -2.0467227 2.0466596 0.0001346 |
| | | Br 2.03856600 -2.0385662 0.0000001 | 2.0466703 -2.0467211 0.0001357 |
| | | O -0.00000030 0.0000005 -1.7503044 | 0.0000395 0.0000376 -1.7775715 |
| | | O -0.00000030 0.0000005 1.7503042 | 0.0000372 0.0000294 1.7776021 |
| | | U 0.00000010 -0.0000001 -0.0000001 | -0.000091 -0.0000081 0.0000135 |
Table S12: Cartesian coordinates (in Å) of the [Bu₄N][UO₂Cl₄] in gas phase at its ground and first excited state minima obtained in Turbomole 7.3.1 by R-ECP DFT/PBE0 and TD-DFT/PBE0 methods respectively.

|        | Ground state          | Excited state          |
|--------|-----------------------|------------------------|
| C      | -1.7231178 2.6706283  | -1.6793731 2.6734267   |
|        | -2.0317492 1.2075078  | -1.9941509 1.2097959   |
|        | -3.3758543 1.0920197  | -3.3303708 1.0965456   |
|        | -4.4133376 0.4600839  | -4.3783182 0.4748322   |
|        | -0.3096963 4.4588521  | -0.2615627 4.4594906   |
|        | -0.1792549 2.2495675  | -0.1678411 2.265401    |
|        | 0.7403436 2.4820091   | 0.7867802 2.4586391    |
| N      | -0.3714943 2.9649229  | -0.3341219 2.9638944   |
|        | 8.2198311 0.6994753   | 8.1677943 0.7167897    |
|        | 7.1078312 -0.2278135  | 7.0503487 -0.2071862   |
|        | 6.9992163 -0.8016964  | 6.925001 -0.7710549    |
|        | 8.9381358 4.0843228   | 8.84534 4.1199889     |
|        | 10.0010406 4.3693995  | 9.8818182 4.4204104    |
|        | 0.7639403 3.0479043   | 0.8343909 3.0027856    |
|        | 1.8951095 2.3959104   | 1.9678381 2.3254385    |
|        | 2.0237276 2.9657649   | 2.1229064 2.8737564    |
|        | 0.9646197 5.0129435   | 1.0009632 5.0091596    |
|        | 0.8803024 6.5064323   | 0.939701 6.5038335    |
|        | 0.9391448 7.2434357   | 0.9678758 7.2674491   |
|        | -1.173654 2.5638109   | -1.1765075 2.6033288   |
|        | -0.8081203 1.7683579  | -0.8394835 1.822709    |
|        | -1.7407864 2.0567479  | -1.7907905 2.1336595   |

Continued on next page
|       | Ground state | Excited state |
|-------|--------------|---------------|
| C     | 7.7399134    | 4.2181381     | -1.6440369 | 7.7130724 | 4.2168068 | -1.6083406 |
| C     | 8.4885346    | 5.4138149     | -1.0823067 | 8.4722942 | 5.4061695 | -1.0476814 |
| C     | 7.5036746    | 6.4986065     | -0.7691173 | 7.4928854 | 6.4846622 | -0.6976385 |
| C     | 7.5741331    | 7.7276482     | -1.2582746 | 7.551544  | 7.7209691 | -1.1697449 |
| C     | 7.6175083    | 2.0055634     | -2.570823  | 7.5738296 | 2.0153299 | -2.5661762 |
| C     | 9.5478961    | 3.458312      | -3.1755071 | 9.486048  | 3.4809697 | -3.1912622 |
| C     | 9.4345973    | 2.524316      | -0.9564187 | 9.4275313 | 2.518378 | -0.9822147 |
| C     | 8.6866428    | 1.9672626     | 0.2325169 | 8.7091061 | 1.9397153 | 0.2146703 |
| C     | 9.65996      | 1.6011049     | 1.3469478 | 9.7073695 | 1.5752569 | 1.3073019 |
| C     | 8.9400933    | 1.0211657     | 2.5532241 | 9.0182853 | 0.9690792 | 2.5186037 |
| Cl    | 5.6570547    | 3.8447947     | 1.2252483 | 5.7037915 | 3.7874771 | 1.2948984 |
| Cl    | 2.6093874    | 0.1291399     | -1.1318178 | 2.5725988 | 0.1000307 | -1.0465703 |
| Cl    | 3.9992506    | 0.5892005     | 2.413443  | 3.9935588 | 0.5548479 | 2.4965168 |
| Cl    | 4.2352165    | 3.317432      | -2.1815109 | 4.2385258 | 3.2897317 | -2.1284497 |
| N     | 8.5911181    | 3.0516001     | -2.0914457 | 8.5562295 | 3.0576174 | -2.0899549 |
| O     | 2.6579787    | 2.8136216     | 0.6054672 | 2.6563163 | 2.8170192 | 0.6914103 |
| O     | 5.5781868    | 1.0410046     | -0.3099148 | 5.5865699 | 0.970901  | -0.2560554 |
| U     | 4.1153844    | 1.9065225     | 0.1791804 | 4.1164657 | 1.8664524 | 0.2561967 |
| C     | 11.0137114   | 5.434966      | -5.0831033 | 10.9007723 | 5.4842478 | -5.1095114 |
| H     | -2.4559006   | 3.0785152     | -1.9256472 | -2.419443 | 3.0935144 | -1.9657071 |
| H     | -1.7982081   | 3.2485531     | -3.5434355 | -1.7366446 | 3.2425793 | -3.5750709 |
| H     | -1.2748837   | 0.7780204     | -3.5571044 | -1.2315038 | 0.7691541 | -3.5577871 |
| H     | -2.0215924   | 0.6273467     | -1.968997 | -1.9995663 | 0.6384053 | -1.9782886 |
| H     | -3.4833213   | 1.5690257     | -4.5143349 | -3.4222629 | 1.5658076 | -4.5509215 |

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|          | Ground state     | Excited state   |
|----------|------------------|-----------------|
| H        | -4.3470267       | -0.033883       |
|          | -2.0491824       | -0.0114333      |
|          | -2.0841513       |                 |
| H        | -5.3636916       | 0.4031782       |
|          | -3.5307445       | 0.418791        |
|          | -3.5826978       |                 |
| H        | -1.1694865       | 4.7270943       |
|          | -1.2442715       | 4.7457184       |
|          | -1.3001097       |                 |
| H        | -0.4747673       | 4.889107        |
|          | -2.8484588       | 4.877186        |
|          | -2.8859806       |                 |
| H        | 0.8313591        | 2.485545        |
|          | -0.3933224       | 0.840782        |
|          |                 | 2.4954168       |
|          |                 | -0.3797986      |
| H        | -0.1703213       | 1.1851182       |
|          | -0.9538556       | -0.163531       |
|          | -0.9348487       |                 |
| H        | 1.6781943        | 2.7042229       |
|          | -2.4331307       | 1.7199389       |
|          |                 | 2.6815295       |
|          |                 | -2.409592       |
| H        | 0.6705955        | 1.3951138       |
|          | -2.9564868       | 0.7084254       |
|          |                 | 1.3722497       |
|          |                 | -2.9260715      |
| H        | 8.8870508        | 0.8395134       |
|          | -3.9189523       | 8.8181177       |
|          |                 | 0.8698745       |
|          |                 | -3.9472294      |
| H        | 8.8005869        | 0.2315785       |
|          | -2.2604406       | 8.7652978       |
|          |                 | 0.2387174       |
|          |                 | -2.2964379      |
| H        | 6.3554238        | -0.4110288      |
|          | -2.6867537       | 6.3082732       |
|          |                 | -0.3975701      |
|          |                 | -2.6882462      |
| H        | 7.7295906        | -0.6321114      |
|          | -5.4257046       | 7.6439182       |
|          |                 | -0.5943258      |
|          |                 | -5.4475929      |
| H        | 6.1758188        | -1.4679127      |
|          | -4.8672707       | 6.0987361       |
|          |                 | -1.4358077      |
|          |                 | -4.8740409      |
| H        | 8.1861272        | 3.4175562       |
|          | -4.8417619       | 8.0844216       |
|          |                 | 3.4567764       |
|          |                 | -4.8243736      |
| H        | 8.4286978        | 5.0183785       |
|          | -4.1607759       | 8.3401671       |
|          |                 | 5.0496251       |
|          |                 | -4.130119       |
| H        | 10.5203372       | 3.4386731       |
|          | -5.7291638       | 10.3972858      |
|          |                 | 3.4942487       |
|          |                 | -5.7671456      |
| H        | 9.4852783        | 4.6841782       |
|          | -6.3848823       | 9.3435881       |
|          |                 | 4.7443912       |
|          |                 | -6.3831726      |
| H        | -0.1819632       | 2.8781471       |
|          | -4.8734487       | -0.1066389      |
|          |                 | 2.8364979       |
|          |                 | -4.8766122      |
| H        | 0.9321954        | 4.1295991       |
|          | -4.3262175       | 1.0160613       |
|          |                 | 4.0824947       |
|          |                 | -4.3337166      |
| H        | 2.8304257        | 2.5281695       |
|          | -4.5847193       | 2.8966736       |
|          |                 | 2.4542972       |
|          |                 | -4.5414708      |
| H        | 1.7209957        | 1.3158409       |
|          | -5.1880289       | 1.7806363       |
|          |                 | 1.2470119       |
|          |                 | -5.1436291      |
| H        | 2.2450226        | 4.0363524       |
|          | -6.5097535       | 2.3576975       |
|          |                 | 3.9417306       |
|          |                 | -6.4957196      |
| H        | 1.1029825        | 2.8320793       |
|          | -7.1138735       | 1.2084956       |
|          |                 | 2.7438894       |
|          |                 | -7.0990188      |
| H        | 2.8306813        | 2.4769339       |
|          | -7.0874904       | 2.9308802       |
|          |                 | 2.3669528       |
|          |                 | -7.0437125      |

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|     | Ground state |             |     | Excited state |             |
|-----|--------------|-------------|-----|--------------|-------------|
| H   | 1.8452075    | 4.7093883   | -1.8236081 | 1.896008 | 4.677173 | -1.7843465 |
| H   | 1.1193957    | 4.6333552   | -0.2350723 | 1.1145126 | 4.6539952 | -0.2202624 |
| H   | 0.7760567    | 7.0020013   | -2.1843963 | 0.8806151 | 6.9763318 | -2.2382199 |
| H   | 1.0627443    | 6.7908448   | 0.8582337  | 1.0462638 | 6.838126  | 0.8175987  |
| H   | 0.8916486    | 8.3253259   | -0.1622608 | 0.9394954 | 8.3485261 | -0.2462526 |
| H   | -2.1998613   | 2.3154108   | 0.0783695  | -2.1995984 | 2.3587715 | 0.0481891  |
| H   | -1.1602673   | 3.6301845   | 0.6214414  | -1.1592043 | 3.6731832 | 0.5893362  |
| H   | 0.2246834    | 1.9950809   | 1.9040768  | 0.1897737 | 2.0454302 | 1.9203767  |
| H   | -0.8252225   | 0.6989652   | 1.3896435  | -0.8598857 | 0.7504031 | 1.4042654  |
| H   | -1.7098422   | 3.1134609   | 3.066007   | -1.7570608 | 3.1937903 | 3.0324141  |
| H   | -1.4578685   | 1.4754306   | 3.6661139  | -1.5285628 | 1.5620758 | 3.6581993  |
| H   | -2.7777888   | 1.8077791   | 2.54197    | -2.824966  | 1.8890225 | 2.505678   |
| H   | 7.0416344    | 3.8371666   | -0.8966282 | 7.0314797 | 3.8249679 | -0.8510347 |
| H   | 7.1386468    | 4.5036323   | -2.5057393 | 7.0918112 | 4.5117038 | -2.4524489 |
| H   | 9.2412281    | 5.799676    | -1.7765467 | 9.2087551 | 5.8030053 | -1.7531317 |
| H   | 8.9983067    | 5.1322407   | -0.1544231 | 9.0029946 | 5.1135421 | -0.1350372 |
| H   | 6.6948592    | 6.215431    | -0.0989246 | 6.6991158 | 6.1899392 | -0.014572  |
| H   | 8.3714955    | 8.0315552   | -1.9308543 | 8.3339235 | 8.0359822 | -1.8547064 |
| H   | 6.8389032    | 8.4794786   | -0.9972636 | 6.8212509 | 8.4677866 | -0.8818384 |
| H   | 6.9340373    | 1.8155002   | -1.7513022 | 6.9086759 | 1.8163625 | -1.7267325 |
| H   | 7.0229452    | 2.4744519   | -3.3603095 | 6.9587697 | 2.4920396 | -3.3274802 |
| H   | 10.2577446   | 4.1412972   | -2.7092372 | 10.2048478 | 4.1596966 | -2.7332091 |
| H   | 10.1018386   | 2.5586908   | -3.4467517 | 10.035903 | 2.5860505 | -3.4868352 |
| H   | 10.0744558   | 3.3546276   | -0.6526366 | 10.069342 | 3.3476496 | -0.679945  |

*Continued on next page*
|          | Ground state | Excited state |
|----------|--------------|---------------|
| H        | 10.0864893   | 10.0737623    |
|          | 8.1107541    | 8.1407886     |
|          | 7.9567762    | 7.9761006     |
|          | 10.226809    | 10.2603168    |
| H        | 10.4011149   | 10.453713     |
|          | 8.2046395    | 8.2763823     |
| H        | 9.6434408    | 9.7389617     |
| H        | 8.3999497    | 8.4916385     |
| H        | 11.634522    | 11.5420253    |
| H        | 10.515462    | 10.4066819    |
| H        | 11.6894051   | 11.5562527    |

Table S13: Cartesian coordinates (in Å) of the \([A336]_2[\text{UO}_2\text{Cl}_4]\) in gas phase at its ground and first excited state minima obtained in Turbomole 7.3.1. by R-ECP DFT/PBE0 and TD-DFT/PBE0 methods respectively.
Table S13 – Continued from previous page

|     | Ground state |          | Excited state |          |
|-----|--------------|----------|---------------|----------|
| C   | 1.9286199    | 1.7585894|-6.9158336     | 1.9844609| 1.814585 | -6.8823089 |
| C   | 0.6900871    | 4.0531035|-1.797232      | 0.654431 | 4.0591905|-1.7525596  |
| C   | 0.495246     | 5.5655171|-1.8656286     | 0.4762728| 5.5670984|-1.9064005  |
| C   | -0.9271163   | 1.5988199| 0.1906763     | -0.979795| 1.5620885| 0.1731472   |
| C   | -0.4031856   | 0.9528474| 1.474797      | -0.4617339| 0.9389285| 1.4703199   |
| C   | -1.223735    | 1.3168107| 2.7064365     | -1.3267301| 1.269012 | 2.6805805   |
| C   | 8.2115209    | 5.2420106|-1.590463      | 8.217084 | 5.2184853|-1.6148665  |
| C   | 9.0401054    | 6.2481231|-0.8140585     | 9.063911 | 6.2190133|-0.851928   |
| C   | 8.1481801    | 7.4186072|-0.3968068     | 8.1873978| 7.3976505|-0.4271156  |
| C   | 7.8496605    | 3.1628947|-2.7690856     | 7.8235677| 3.1374964|-2.7781333  |
| C   | 9.9606169    | 4.360842 |-3.0775044     | 9.9325979| 4.3263012|-3.1325281  |
| C   | 9.5942091    | 3.2511344|-0.9563462     | 9.6041048| 3.2244248|-1.0023766  |
| C   | 8.7007022    | 2.869779 | 0.204574      | 8.7341427| 2.841309 | 0.176905    |
| C   | 9.4294255    | 1.9580388| 1.1899717     | 9.4918775| 1.956401 | 1.1600231   |
| C   | 8.5778865    | 1.6647567| 2.4210161     | 8.6678887| 1.666431 | 2.4100975   |
| Cl  | 5.3884893    | 4.2984281| 0.3064566     | 5.4510299| 4.2706622| 0.3366167   |
| Cl  | 3.2420551    | -0.2944559|-1.3911706     | 3.1912206| -0.3097982|-1.3195414  |
| Cl  | 4.7608904    | 0.8807181| 1.9952177     | 4.8012604| 0.854579 | 2.0403593   |
| Cl  | 3.985672     | 3.0256857|-2.8432433     | 3.9528578| 3.024947 | -2.802491   |
| N   | 8.9204324    | 3.9995534|-2.0835293     | 8.9107053| 3.9715808|-2.1176084  |
| O   | 2.7388955    | 2.4540567| 0.1199908     | 2.7296024| 2.4763278| 0.1993843   |
| O   | 5.9502491    | 1.3823912|-0.8952207     | 5.9526931| 1.3344897|-0.8900281  |
| U   | 4.3485499    | 1.9091212|-0.3673548     | 4.3466912| 1.8905967|-0.316197    |
| H   | -1.4046432   | 3.4946698|-1.6658059     | -1.4383236| 3.4841597|-1.6985912  

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Table S13 – Continued from previous page

|         | Ground state | Excited state |
|---------|--------------|---------------|
| H       | -0.7817986   | -0.7564003    |
|         | 3.5928913    | 3.5894676     |
|         | -3.3225549   | -3.3313615    |
| H       | 1.012849     | 0.9855016     |
|         | 1.5669308    | 1.605448      |
|         | -0.7437302   | -0.7147684    |
| H       | 0.0389693    | 0.0756246     |
|         | 0.1413441    | 0.1487302     |
|         | -1.096228    | -1.0937655    |
| H       | 1.7025041    | 1.713517      |
|         | 1.6699581    | 1.6572178     |
|         | -2.784895    | -2.75183      |
| H       | 0.7455572    | 0.7482958     |
|         | 0.2633428    | 0.269755      |
|         | -3.2364128   | -3.2454746    |
| H       | 9.1608184    | 9.1184122     |
|         | 1.6398624    | 1.6155065     |
|         | -3.6540545   | -3.6882649    |
| H       | 8.276449     | 8.2617595     |
|         | 1.1382993    | 1.1112358     |
|         | -2.1884052   | -2.2091603    |
| H       | -0.2528237   | -0.2157256    |
|         | 1.6494442    | 1.737552      |
|         | -5.1786956   | -5.1651685    |
| H       | 0.8310311    | 0.9167018     |
|         | 2.9785813    | 3.0116095     |
|         | -4.6943621   | -4.6424521    |
| H       | 2.8019028    | 2.8268654     |
|         | 1.4814217    | 1.4427365     |
|         | -4.957075    | -4.9265565    |
| H       | 1.7477237    | 1.7242635     |
|         | 0.1563279    | 0.1769694     |
|         | -5.4765198   | -5.4952025    |
| H       | 2.0461717    | 2.1495802     |
|         | 2.8595914    | 2.9087937     |
|         | -6.9120747   | -6.8417109    |
| H       | 0.9709829    | 1.0227516     |
|         | 1.5539303    | 1.6691845     |
|         | -7.4348059   | -7.4141519    |
| C       | 3.0737849    | 3.1073145     |
|         | 1.1344469    | 1.1669667     |
|         | -7.7059526   | -7.6842936    |
| H       | 1.588215     | 1.5883639     |
|         | 3.7853979    | 3.7600546     |
|         | -2.3811357   | -2.2613403    |
| H       | 0.9247961    | 0.8126561     |
|         | 3.769382     | 3.822178      |
|         | -0.7589082   | -0.68769      |
| H       | -1.9691455   | -2.001234     |
|         | 1.2705236    | 1.1874134     |
|         | 0.0164803    | -0.0269822    |
| H       | -0.9495403   | -1.056413     |
|         | 2.6933871    | 2.6548985     |
|         | 0.3356569    | 0.3161883     |
| H       | 0.6484942    | 0.5735104     |
|         | 1.2578452    | 1.2844171     |
|         | 1.624974     | 1.6462799     |
| H       | -0.3878051   | -0.3978414    |
|         | -0.1466636   | -0.1589915    |
|         | 1.3526675    | 1.349348      |
| H       | -1.2285351   | -1.3800557    |
|         | 2.4174772    | 2.368776      |
|         | 2.8286919    | 2.801683      |
| C       | -0.7000726   | -0.8100195    |
|         | 0.6728983    | 0.64662       |
|         | 3.9854928    | 3.972517      |
| H       | -2.2806273   | -2.3666843    |
|         | 1.0212465    | 0.9309914     |
|         | 2.5518233    | 2.4992819     |
| H       | 7.3602861    | 7.3722848     |
|         | 4.8929891    | 4.8753488     |
|         | -0.9772772   | -0.9888143    |

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|      | Ground state |                       | Excited state |                       |
|------|--------------|------------------------|---------------|------------------------|
| H    | 7.784598     | 5.7082526             | -2.4937803    | 7.7798279             | 5.687144 | -2.5121589 |
| H    | 9.8914018    | 6.6306152             | -1.4077287    | 9.9115202             | 6.5925165 | -1.4568101 |
| H    | 9.458978     | 5.7836087             | 0.0958255     | 9.4896742             | 5.7532647 | 0.0543027  |
| H    | 6.9730742    | 3.1678889             | -2.1054602    | 6.9617209             | 3.1426009 | -2.0946294 |
| H    | 7.5773403    | 3.7324783             | -3.6724679    | 7.5304103             | 3.7079881 | -3.6745387 |
| H    | 10.4257158   | 3.8925993             | -0.622177     | 10.4426746            | 3.8655498 | -0.6849707 |
| H    | 10.0391224   | 2.3562154             | -1.4185107    | 10.039784             | 2.32803   | -1.4709907 |
| H    | 7.7968588    | 2.3505228             | -0.1526226    | 7.8287635             | 2.3145072 | -0.1580092 |
| H    | 8.3423506    | 3.7693938             | 0.7321074     | 8.371927             | 3.7470585 | 0.6998276  |
| H    | 10.3930872   | 2.412322              | 1.4982492     | 10.454286             | 2.4282738 | 1.4455823  |
| H    | 9.6845888    | 1.0062478             | 0.6840358     | 9.7530335             | 1.0018581 | 0.6619645  |
| H    | 8.4108146    | 2.6074578             | 2.9765874     | 8.4883168             | 2.6149005 | 2.9518627  |
| C    | 9.1797033    | 0.6234488             | 3.3562885     | 9.3095754             | 0.6560275 | 3.3521519  |
| H    | 7.5745105    | 1.3288947             | 2.1009016     | 7.6666959             | 1.3038002 | 2.1127397  |
| H    | -1.8902656   | 1.5901533             | -3.7883501    | -1.8540593            | 1.5597719 | -3.8167565 |
| H    | -2.447729    | 1.4721236             | -2.088683     | -2.4516826            | 1.4706455 | -2.128819  |
| H    | -1.5395344   | 0.1093463             | -2.8303285    | -1.5236557            | 0.0966638 | -2.8244662 |
| H    | 9.4976102    | 4.9488504             | -3.883417     | 9.4549004             | 4.9093163 | -3.9337219 |
| H    | 10.3964441   | 3.4420853             | -3.4938705    | 10.3615574            | 3.4052695 | -3.551459  |
| H    | 10.7487221   | 4.9522443             | -2.5917938    | 10.7293881            | 4.9208247 | -2.6647543 |
| H    | -0.7042952   | -0.4280191            | 3.8675313     | -0.7662474            | -0.453641 | 3.8553753  |
| C    | -1.4954405   | 1.0499705             | 5.2301499     | -1.6511198            | 0.9910132 | 5.1959948  |
| H    | 0.3602227    | 0.9565859             | 4.1253519     | 0.2342693             | 0.9728038 | 4.1390915  |
| H    | -2.558063    | 0.7696984             | 5.0870388     | -2.6976975            | 0.6680509 | 5.0261044  

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|         | Ground state                  | Excited state                  |
|---------|------------------------------|--------------------------------|
| H       | -1.4865368                   | -1.6903862                     |
| C       | 0.0877397                    | 0.0909875                      |
| H       | -2.8284367                   | -3.0220271                     |
| H       | -1.7460945                   | -2.004576                      |
| H       | -1.3642061                   | -1.5775278                     |
| C       | 3.17242                      | 3.2392894                      |
| H       | 2.95861                      | 2.9443251                      |
| H       | 4.0265774                    | 4.063717                       |
| H       | 2.2179737                    | 2.281857                       |
| C       | 4.3196435                    | 4.3666896                      |
| H       | 3.2885062                    | 3.4000453                      |
| H       | 4.2030578                    | 4.2064682                      |
| H       | 5.271899                     | 5.3222122                      |
| C       | 4.4147551                    | 4.4930493                      |
| H       | 3.4900981                    | 3.564844                       |
| H       | 5.2543813                    | 5.3177593                      |
| H       | 4.5686073                    | 4.6899982                      |
| H       | 0.2481085                    | 0.3638107                      |
| C       | 1.7498638                    | 1.6633694                      |
| H       | -0.3685886                   | -0.4592259                     |
| H       | 2.5997055                    | 2.5925927                      |

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Table S13 – Continued from previous page

|          | Ground state |          | Excited state |
|----------|--------------|----------|---------------|
| H        | 2.0156819    | 5.9683076 | 1.7598216     |
| C        | 1.621893     | 7.821337  | 1.5733997     |
| H        | 1.3468209    | 8.1576321 | 1.5007624     |
| C        | 2.8977845    | 8.5332185 | 2.7591406     |
| H        | 0.7860105    | 8.132416  | 0.635684      |
| H        | 3.7282081    | 8.2282757 | 3.6961867     |
| H        | 3.1832192    | 8.1797494 | 2.821807      |
| C        | 2.7878661    | 10.0541333| 2.7025212     |
| H        | 2.4966596    | 10.4043774| 2.6465683     |
| C        | 4.0723714    | 10.7513034| 3.8878001     |
| H        | 1.9628702    | 10.3561385| 1.7627083     |
| H        | 4.9088156    | 10.4991218| 4.8424853     |
| H        | 4.3726872    | 10.4469288| 3.9464154     |
| H        | 3.9598992    | 11.8496994| 3.8194902     |
| H        | 9.3290653    | -0.3217476| 2.7981355     |
| C        | 8.3064351    | 0.3489486 | 4.5760302     |
| H        | 10.1879736   | 0.9461786 | 3.6862418     |
| H        | 7.2905845    | 0.0738511 | 4.234217      |
| H        | 8.1846111    | 1.2856827 | 5.1546271     |
| C        | 8.8526336    | -0.7404977| 5.4923957     |
| H        | 8.9661239    | -1.677251 | 4.9137407     |
| C        | 7.9757058    | -1.000942 | 6.7099023     |
| H        | 9.8727278    | -0.4642193| 5.82345       |
| H        | 6.9588529    | -1.3095158| 6.4082246     |

Continued on next page
|     | Ground state          |         | Ground state          |         | Ground state          |         |
|-----|----------------------|---------|----------------------|---------|----------------------|---------|
| H   | 7.8734476            | -0.092412 | 7.3306414            |         | 8.0935955            | -0.015587 | 7.3620768 |
| H   | 8.3934291            | -1.7983681 | 7.3494375            |         | 8.6568835            | -1.7074323 | 7.4031953 |
| H   | 7.7335395            | 7.9032666 | -1.3015992           |         | 7.7675358            | 7.8846953 | -1.3284139 |
| C   | 8.871702             | 8.4612572 | 0.447091             |         | 8.9290822            | 8.4349345 | 0.4068213 |
| H   | 7.2800284            | 7.0229137 | 0.1620042            |         | 7.3218095            | 7.010128  | 0.1416234 |
| H   | 9.7429557            | 8.8539358 | -0.1133702           |         | 9.7990888            | 8.8172189 | -0.1630025 |
| H   | 9.2841725            | 7.9759179 | 1.3527107            |         | 9.3456572            | 7.9478288 | 1.3098248 |
| C   | 7.9730432            | 9.6206695 | 0.8631596            |         | 8.0459906            | 9.6036712 | 0.8282279 |
| H   | 7.5573021            | 10.1043126 | -0.0422156          |         | 7.6278218            | 10.0903772 | -0.074816 |
| C   | 8.6770028            | 10.669575 | 1.7162676            |         | 8.7688776            | 10.6455829 | 1.6734333 |
| H   | 7.1017052            | 9.2219058 | 1.4171583            |         | 7.1750414            | 9.2147353 | 1.3899872 |
| H   | 9.5487179            | 11.0696472 | 1.1616067          |         | 9.6415656            | 11.033952 | 1.1114653 |
| H   | 9.0912218            | 10.1860095 | 2.6226454          |         | 9.1843053            | 10.1582954 | 2.5774414 |
| C   | 7.7732165            | 11.8254896 | 2.1328072          |         | 7.8833334            | 11.8133195 | 2.0951097 |
| H   | 7.3575154            | 12.3058829 | 1.2265388           |         | 7.4678153            | 12.2987855 | 1.191301 |
| C   | 8.4796916            | 12.8705764 | 2.9854278          |         | 8.6095237            | 12.8492746 | 2.9419921 |
| H   | 6.9031796            | 11.4233346 | 2.6858029          |         | 7.0116265            | 11.4230405 | 2.6541581 |
| H   | 9.3334811            | 13.3182153 | 2.4452879          |         | 9.4660716            | 13.2847477 | 2.3959385 |
| H   | 8.87366              | 12.4270729 | 3.9175801           |         | 9.0036359            | 12.4012573 | 3.8721348 |
| H   | 7.7970997            | 13.6904076 | 3.2687092           |         | 7.9404078            | 13.6789762 | 3.2292191 |
| H   | 7.2044857            | 1.4401424 | -5.025524           |         | 7.1337586            | 1.4263597 | -5.0247294 |
| H   | 6.1087275            | 1.6176728 | -3.647695           |         | 6.0659397            | 1.5853394 | -3.6227615 |
| C   | 6.8959417            | -0.3599666 | -3.8483681         |         | 6.8613929            | -0.3860122 | -3.8574717 |
| H   | 7.7901407            | -0.8818376 | -4.2444778         |         | 7.7466163            | -0.898922  | -4.2848566 |

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|    | Ground state          | Excited state       |
|----|-----------------------|---------------------|
| C  | 5.6364194            | 5.5839534           |
| H  | -0.8599012           | -0.8858729          |
| C  | -4.5475215           | -4.52193            |
| H  | 6.8233575            | 6.8226859           |
| H  | -0.616522            | -0.654516           |
| H  | -2.7755191           | -2.7855294          |
| H  | 5.6968024            | 5.6058445           |
| H  | -0.6421862           | -0.6500665          |
| H  | -5.6330947           | -5.6052756          |
| H  | 4.7775496            | 4.734378            |
| H  | -0.2849136           | -0.3240671          |
| H  | -4.154714            | -4.0911763          |
| C  | 5.3616749            | 5.3280228           |
| H  | -2.3433383           | -2.3745386          |
| C  | -4.33576             | -4.3262149          |
| H  | 6.1998702            | 6.1530055           |
| H  | -2.9447878           | -2.962998           |
| C  | -4.7414065           | -4.776036           |
| C  | 4.0510556            | 3.9958091           |
| H  | -2.8086398           | -2.8367164          |
| H  | -4.9614694           | -4.9065779          |
| H  | 5.3274603            | 5.3398204           |
| H  | -2.5440842           | -2.5962546          |
| H  | -3.2482779           | -3.2420462          |
| H  | 4.0557129            | 3.9554334           |
| H  | -2.5728676           | -2.5808401          |
| H  | -6.0439645           | -5.9838837          |
| H  | 3.2256478            | 3.1860449           |
| H  | -2.2185758           | -2.2595093          |
| C  | -4.5197877           | -4.4209165          |
| C  | 3.7770649            | 3.7381282           |
| H  | -4.2933944           | -4.3263087          |
| H  | -4.76372             | -4.7258403          |
| H  | 4.5722748            | 4.5177204           |
| H  | -4.9122823           | -4.9322957          |
| H  | -5.2179134           | -5.22297            |
| H  | 2.8177685            | 2.762759            |
| H  | -4.5957644           | -4.6261617          |
| H  | -5.220045            | -5.1488016          |
| H  | 3.7320634            | 3.7374553           |
| H  | -4.5482681           | -4.6016267          |
| H  | -3.6897659           | -3.6558008          |