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Chemical Communications

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Modelling Uranyl Chemistry in Liquid Ammonia from Density Functional Theory.

Received 00th January 20xx,
Accepted 00th January 20xxNicolas Sieffert,^a Amol Thakkar,^b and Michael Bühl^{b,*}

DOI: 10.1039/x0xx00000x

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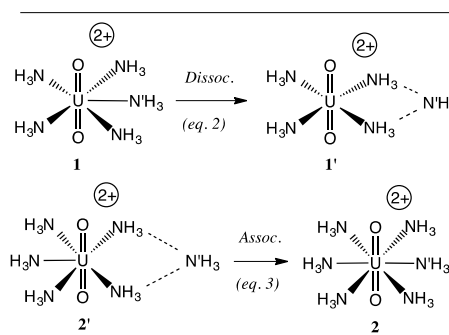
We developed a computationally-efficient protocol based on Density Functional Theory (DFT) and a continuum solvation model (CSM) to predict reaction free energies of complexation reactions of uranyl in liquid ammonia. Several functionals have been tested against CCSD(T) and different CSMs have been assessed relative to Car-Parrinello Molecular Dynamics (CPMD) simulations in explicit solvent.

Even though uranium is only mildly radioactive, its chemistry can be hazardous; therefore, reliable computational modelling is highly desirable in order to limit the number of experiments that have to be conducted in the laboratory. Much progress has been made in modelling the aqueous chemistry of uranyl, UO_2^{2+} , from first principles.^[1] A major challenge is the description of the solvent, because the strong and specific solvent-solute interactions make an explicit treatment of the solvent in a dynamic ensemble mandatory. Liquid ammonia is emerging as a promising solvent for uranium chemistry.^[2] Its polarity is between that of water and organic solvents, the use of which had helped to spark the renaissance of uranium chemistry in the last decade.^[3] Because solvent-solute interactions involving ammonia are weaker than those involving water, there is hope that simple implicit solvent models could be accurate enough for routine quantum-chemical applications. We now report the first steps toward developing a cost-effective computational protocol allowing for the modelling of the reactivity of uranyl complexes in liquid ammonia. In particular, we aim at computing accurate reaction free energies in solution (ΔG_{liq} , eq. 1), following the approach established in Reference^[4] for d-block chemistry:

$$\Delta G_{\text{liq}} = \Delta E_{\text{gas}} + \delta E_{\text{BSSE}} + \delta E_{\text{solv}} + \delta E_{\text{G}} \quad (\text{eq. 1})$$

ΔE_{gas} stands for reaction energies in the gas phase, whereas δE_{BSSE} , δE_{solv} and δE_{G} are correcting terms for the basis set superposition error (BSSE), solvation effects and thermochemistry, respectively.

In practice, routine applications will be based on DFT calculations. DFT can be a powerful and accurate tool, but the results can also depend a lot on the specific choice of exchange-correlation functional. Thus, careful validation is required prior to any applications. In the absence of reliable thermochemical data, benchmark energies for ΔE_{gas} can be obtained from accurate *ab initio* wave-function based methods. We have considered two reactions involving the prototypical pentammine complex $[\text{UO}_2(\text{NH}_3)_5]^{2+}$ (**1**) for this purpose, involving either NH_3 decoordination from **1** (referred to as the dissociative pathway) and the coordination of an additional NH_3 ligand (referred to as the associative pathway, see eq. 2 and 3, in Scheme 1). Complex **1** has been characterised in numerous solids by X-ray crystallography.^[5] Note that the dissociated NH_3 ligands remain in the second shell in the dissociated state in our model reactions.



Scheme 1: Reactions and labelling of the complexes considered for the development of the computational protocol.

We first focus on the calculation of the reaction energies, in the gas phase (ΔE_{gas}). To make our protocol computationally effective, we propose that the geometries of the complexes are computed with “medium-sized” basis sets (namely, SDD on

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Electronic Supplementary Information (ESI) available: Full computational details, including references to all density functionals, CSMs and software employed in this study. Atomic coordinates of the complexes. See DOI: 10.1039/x0xx00000x

U and 6-311+G** on other elements, see ESI for details), and that single point energies are computed on these geometries, using larger basis sets. We performed single-point calculations on B3LYP-D3(bj) optimised structures, because, in conjunction with continuum solvation models (CSMs), the B3LYP functional tends to afford U=O and U-N bond distances in **1** that fit quite well to the body of X-ray crystallographic data for this ion.^[5a]

We have assessed 17 density functionals in their capability to provide accurate binding energies of NH₃ to UO₂²⁺ against a coupled cluster singles doubles and connected triples level, CCSD(T), considering the two reactions described in eq. 2 and 3. BSSE corrections (δE_{BSSE}) have been applied for the two reactions under study (see ESI for details). The relative BSSE-corrected reaction energies (referred to as $\Delta\Delta E$ in the following) are gathered in Table 1.

Table 1 shows that wB97X and PBE0-D3(bj) provide the most accurate relative energies,^[6] with mean absolute errors (MAE) lower than 1 kcal/mol (namely 0.6 and 0.8 kcal/mol, respectively). Of the two, we prefer PBE0-D3(bj), despite its slightly larger MAE, because it contains a correction for dispersion interactions, which may become more important in the study of larger ligands. Next, PBE0, B3PW91-D3(bj), B3LYP-D3(bj), ω B97 and B3LYP also provide satisfying results, with a MAE below 2 kcal/mol. The other tested functionals (namely, B3PW91, M06, BLYP-D3(bj), BLYP, BP86-D3(bj), B97-D3(bj), BP86, M05-2X, M06-2X and M06-L) provide larger MAEs, and are thus less well suited. Interestingly, the -D3(bj)^[7] dispersion correction favours **1** over **1'** and **2** over **2'** (see also the absolute reaction energies in Table S1 in ESI), *i.e.* systematically making the higher coordinated complex more stable. On average (over the two reactions), the addition of the dispersion correction is beneficial to reproduce the CCSD(T) reference.

Next, we considered the correction for solvent effects (δE_{solv}). We investigated several implicit solvent models, allowing for a cost-effective calculation of solvation effects, and we estimated their accuracy by comparison with the results of CPMD calculations involving explicit solvent (which can be considered as reliable benchmarks, because all solvent-solute interactions are included explicitly). In a previous study, we performed CPMD/BLYP simulations in the gas phase and in explicit ammonia, in conjunction with the pointwise thermodynamic integration technique.^[5a] These simulations allowed us to compute the Helmholtz free energies corresponding to eq.2, both in the gas phase and in liquid NH₃ (hereafter noted, $\Delta A_{\text{gas}}(\text{eq.2}) = 5.3$ kcal/mol and $\Delta A_{\text{liq}}(\text{eq.2}) = 9.1$ kcal/mol, respectively; see Figure 1a). As a result, the influence of solvent effects on NH₃ binding, noted $\Delta\Delta A_{\text{solv}}(\text{eq.2})$, equals to 3.8 kcal/mol. We now have extended these calculations to the association of NH₃ to **1**, to afford **2** (*i.e.* corresponding to eq. 3). The resulting free energy profile (shown in Figure 1b) indicates that the pentaammine complex is more stable than its hexaammine analogue and that solvation slightly stabilizes the former ($\Delta A_{\text{gas}}(\text{eq.3}) = 7.2$ kcal/mol and $\Delta A_{\text{liq}}(\text{eq.3}) = 6.0$ kcal/mol), by $\delta A_{\text{solv}}(\text{eq.3}) = -1.1$ kcal/mol. We note in passing that the highest point on both profiles in solution is

lower for the associative pathway (7.7 kcal/mol, Figure 1b) than for the dissociative pathway (10.7 kcal/mol, Figure 1a).

Table 1: Influence of the density functional on the reaction energies corresponding to eq. 2 and 3. Deviation of the BSSE-corrected reaction energies (namely, $\Delta E_{\text{gas}} + \delta E_{\text{BSSE}}$, in kcal/mol) from the BSSE-corrected CCSD(T) reference (marked as zero).^a

	$\Delta\Delta E^b$ Eq. 2 <i>dissoc.</i>	$\Delta\Delta E^c$ Eq. 3 <i>assoc.</i>	MAE ^d	# ^e
CCSD(T)	0.0	0.0		
BLYP	5.5	0.0	2.8	11
BLYP-D3(bj)	2.1	3.2	2.7	10
B3LYP	2.6	-0.7	1.7	7
B3LYP-D3(bj)	-0.2	1.9	1.1	5
PBE0	1.7	-0.2	1.0	3
PBE0-D3(bj)	0.4	1.1	0.8	2
B3PW91	3.0	-0.9	2.0	8
B3PW91-D3(bj)	0.2	1.8	1.0	4
BP86	5.3	0.5	2.9	14
BP86-D3(bj)	2.6	3.0	2.8	12
M06	-2.1	2.9	2.5	9
M06-L	-1.5	6.2	3.9	17
M06-2X	-4.9	1.9	3.4	16
M05-2X	-4.6	1.8	3.2	15
B97-D3(bj)	3.1	2.6	2.9	13
ω B97	-2.0	0.4	1.2	6
ω B97X	-1.1	0.0	0.6	1

^aThe same SDD/cc-pVTZ basis set has been employed throughout. Reactions energies are given in Tables S6 in ESI. ^b $\Delta\delta E_{\text{BSSE}} = -1.0(\text{MP2}) + 0.3(\text{DFT}) = -0.7$ kcal/mol. ^c $\Delta\delta E_{\text{BSSE}} = 1.2(\text{MP2}) - 0.4(\text{DFT}) = 3.5$ kcal/mol. ^d Mean absolute error (MAE), in kcal/mol. ^e Ranking following increasing MAE.

As both profiles describe the same chemical process, namely exchange of a bound ammine ligand against one from the bulk solvent, these findings have important implications for the mechanism of ligand exchange reactions in liquid ammonia.^[8] For the purpose of the present paper (where we are interested in the thermodynamics rather than kinetics), it is noteworthy that solvation increases $\Delta\Delta A$ for dissociation, but lowers that of association (compare the ordering of Gas and Liq profiles in Figure 1), which may be a stringent test for CSMs.

According to the thermodynamic cycle shown in Scheme 2, and considering that Helmholtz free energies can be essentially equated to Gibbs free energies in a condensed phase, our computed values of $\Delta\Delta A_{\text{solv}}$ can therefore be used to estimate the free energy difference between the solvation energies of **1** and **1'** (namely $\Delta\Delta G_{\text{solv}}(\text{eq.2})$). Alternatively, this term can be modelled using CSMs, by taking the difference between reaction energies computed in the continuum and in the gas phase ($\delta E_{\text{solv}} = \Delta E(\text{CSM}) - \Delta E(\text{Gas}) \sim \Delta\Delta G_{\text{solv}}$).

For that purpose we have investigated five CSMs (namely, IEFPCM, CPCM, IPCM, COSMO as implemented in Turbomole, and SMD). These models require the creation of a molecule-shaped "cavity" in the continuum.^[9] Unfortunately, the results can be critically affected by the definition of the cavity.^[10]

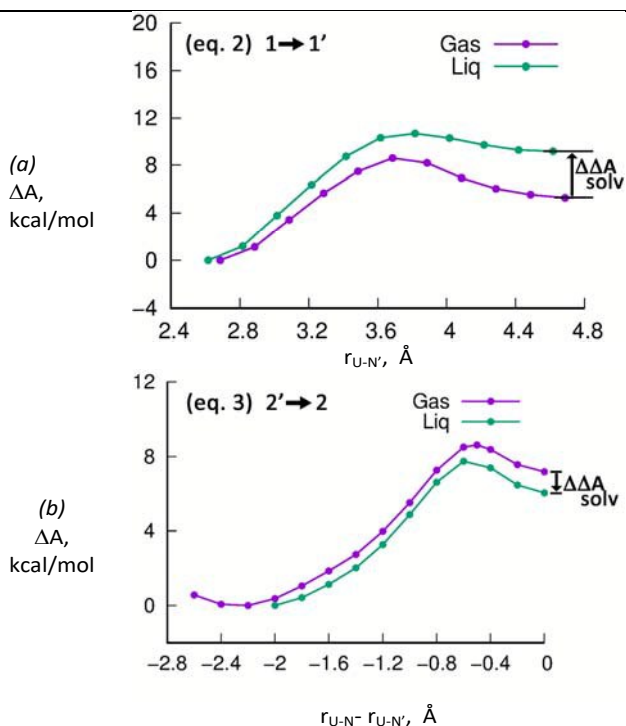
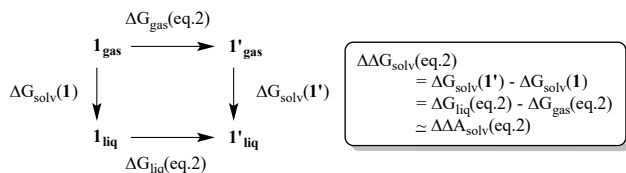


Figure 1: Free energy profiles for dissociation of NH₃ from **1** (eq. 2, top panel (a), adapted from reference^{[5a])} and for NH₃ association to **1**, to afford **2** (eq. 3, bottom panel (b), this work). The reaction coordinate is the U-N' distance in Figure 1a, and is the difference between U-N' and U-N (i.e. the ligand being in *cis* position relative to the associated ligand; see Scheme 1 for schematic representations of the complexes).



Scheme 2: Definition of $\Delta\Delta G_{\text{solv}}(\text{eq.2})$ and corresponding thermodynamic cycle. Note that $\Delta\Delta G_{\text{solv}}(\text{eq.3})$ is computed similarly, considering **2'** and **2**, in place of **1** and **1'**, respectively.

In all models, excepted IPCM, the latter is obtained from overlapping spheres of given radii, centred on atom nuclei. Herein, three different definitions of the cavity have been considered in conjunction with the IEFPCM and CPCM models: UFF (the hydrogens are explicitly represented, and the radii of all atoms are taken from the UFF force field), UA0 (the hydrogen are not explicitly represented, but are considered as united atoms with N, using UFF force field parameters), and UAKS (united atom model, using atomic radii optimized for the PBE0/6-31G(d) level). Standard atomic radii have been used with COSMO and SMD (see ESI). IPCM uses a different definition of the cavity, based on the isosurface of the total electron density.^[10] Note that ammonia is not included in the original SMD solvent database,^[11] however, the required solvent parameters are available in the literature and the SMD model for ammonia used herein has been made consistent to those of other models for amines (see ESI for details).

Table 2 confirms that the choice of cavity model greatly affects the results. In contrast, considering either IEFPCM or CPCM (using a given cavity definition) has negligible effect. The UFF cavity model systematically underestimates δE_{solv} by 3 - 4 kcal/mol, for both reactions. In contrast, UA0 overestimates δE_{solv} by 1.7 kcal/mol for eq. 2 and underestimates δE_{solv} by 4.5 kcal/mol for eq. 3. The UAKS model provides good description of solvation effects for eq. 2 (within 0.4 kcal/mol) but exhibits large deviations to our CPMD reference for eq. 3 (up to 6.7 kcal/mol). Also, IPCM exhibits significant errors for both reactions. Conversely, COSMO provides more accurate results, even if the model still tends to overestimate the solvation of **1** and **2** by 1.8 and 2.5 kcal/mol, respectively. COSMO results do not critically depend on the choice of basis set (6-311+G** vs cc-pVTZ) or density functional (B3LYP vs BLYP), and is the most accurate model tested herein. SMD also provides a satisfying description of solvation effects, as deviations from the CPMD references are *ca.* 1.5 and 3.0 kcal/mol for the dissociation and association reactions, respectively. The choice of basis set/density functional affects the results to a very small extent.

Table 2: Correcting term for solvation effects (δE_{solv} , in kcal/mol) computed using different implicit and explicit solvent models, and using different combination of basis set and density functionals.

Basis set	Functional ^a	δE_{solv}^b (eq. 2) dissoci.	δE_{solv}^b (eq. 3) assoc.	
CPMD (explicit solvent)		3.8	-1.1	
<i>B3LYP-D3(bj)/SDD/6-311+G** optimized structures in vacuo.^c</i>				
IEFPCM/UFF	SDD/6-311+G**	B3LYP	0.8	-3.9
CPCM/UFF	SDD/6-311+G**	B3LYP	0.1	-4.0
IEFPCM/UA0	SDD/6-311+G**	B3LYP	5.5	-5.1
CPCM/UA0	SDD/6-311+G**	B3LYP	5.6	-5.2
IEFPCM/UAKS	SDD/6-311+G**	B3LYP	3.6	-6.2
CPCM/UAKS	SDD/6-311+G**	B3LYP	3.4	-6.8
IPCM	SDD/6-311+G**	B3LYP	8.1	-5.2
COSMO	SDD/6-311+G**	B3LYP	5.7	-3.7
COSMO	SDD/cc-pVTZ	B3LYP	5.6	-3.6
COSMO	SDD/cc-pVTZ	BLYP	5.6	-3.9
SMD	SDD/6-311+G**	B3LYP	2.2	-5.1
SMD	SDD/cc-pVTZ	B3LYP	2.3	-5.1
SMD	SDD/cc-pVTZ	M06-2X	2.0	-4.7
SMD	SDD+/aug-cc-pVTZ	M06-2X	1.9	-4.6
<i>BLYP/SDD/6-311+G** optimized structures in the continuum.^d</i>				
COSMO	SDD/6-311+G**	BLYP	5.1	-4.5
COSMO	SDD+/aug-cc-pVTZ	BLYP	4.9	-4.3
SMD	SDD/6-311+G**	BLYP	2.1	-6.1

a. Functional employed in the single point energy calculations, both in the gas phase (to compute ΔE_{gas}) and in the continuum (to compute ΔE_{solv}). b. $\delta E_{\text{solv}} = \Delta E_{\text{solv}} - \Delta E_{\text{gas}}$. c. Single points on gas phase B3LYP-D3(bj)/SDD/6-311+G** optimized structures. d. Single points on BLYP/SDD/6-311+G** optimized structures, considering gas phase optimized structures for ΔE_{gas} and IEFPCM/UA0 optimized structures for ΔE_{solv} .

Also, the addition of diffuse functions has almost no influence on the results (compare SDD/cc-pVTZ with SDD+/aug-cc-pVTZ in Table 2). When considering structures optimized in the continuum (rather than gas phase optimized structures), COSMO remains the most accurate model, whereas SMD show larger deviations, especially as far as eq. 3 is concerned.^[12]

Finally, the correcting term for free energies (δE_G) can be computed from standard statistical thermodynamics expressions using the computed harmonic vibrational frequencies.^[13] The free energies are compared to CPMD results in sect. III in ESI.

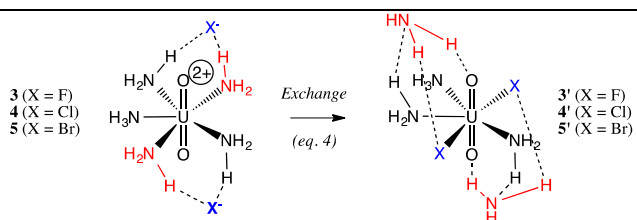
Taking all these results together, the reaction free energies corresponding to eq. 2 and 3 can be estimated from eq. 1 (see Table 3). We found $\Delta G_{\text{liq}}(\text{eq.2}) = 11.2$ and $\Delta G_{\text{liq}}(\text{eq.3}) = 6.1$. These results indicate that uranyl is thermodynamically more stable as a pentacoordinated complex in liquid ammonia, in keeping with recent experimental studies, where the $[\text{UO}_2(\text{NH}_3)_5]\text{X}_2$ complexes have been characterized by X-ray diffraction for $\text{X} = \text{Cl}^{[5b]}$ and $\text{Br}^{[5a]}$. In both cases, the pentammine complexes co-crystallize with solvent NH_3 molecules rather than forming hexammine complexes.

Table 3: Reaction free energies in solution (ΔG , computed according to eq. 1) and corresponding correcting terms.^a All values in kcal/mol.

	ΔE	δE_{BSSE}	δE_{solv}^a	δE_G^b	ΔG
1 \rightarrow 1'	9.9 ^b	0.3 ^b	5.6	-0.8	11.2
2' \rightarrow 2	5.8 ^b	0.4 ^b	-3.6	3.5	6.1
3 \rightarrow 3'	-40.3 ^c	-0.5 ^c	15.6	0.9	-24.3
4 \rightarrow 4'	-31.0 ^c	0.0 ^c	27.6	0.6	-2.9
5 \rightarrow 5'	-27.7 ^c	-0.1 ^c	29.7	0.8	2.7

a. B3LYP/SDD/cc-pVTZ level, using COSMO. b. B3LYP-D3(bj)/SDD/6-31G**, at $p = 1$ atm and $T = 298.15$ K. c. PBE0-D3(bj)/SDD/cc-pVTZ. d. PBE0-D3(bj)/SDD+aug-cc-pVTZ (basis set on U is SDD augmented with a g -function with exponent 0.5). Diffuse functions are included for anionic ligands.

To further examine the predictive power of our protocol, we considered the formation of pentacoordinated dihalide uranyl complexes $[\text{UO}_2\text{X}_2(\text{NH}_3)_3]$ ($\text{X} = \text{F}, \text{Cl}$ and Br) according to eq. 4 (see Scheme 3). Our results indicate that the two F^- displace NH_3 ligands with a substantial driving force (-24.3 kcal/mol). The dichloro complex is significantly less stable ($\Delta G = -2.9$ kcal/mol), whereas the dibromo complex should stay dissociated ($\Delta G = +2.7$ kcal/mol). Again, these results correlate well with experiment, where $[\text{UO}_2\text{F}_2(\text{NH}_3)_3]$ is observed both in solution and in the solid state below -40°C , $[\text{UO}_2\text{Cl}_2(\text{NH}_3)_3]$ only in solution, but not in the solid, and $[\text{UO}_2\text{Br}_2(\text{NH}_3)_5]$ not at all.^[2]



Scheme 3: Formation of dihalide complexes according to eq. 4.

To summarize, after careful benchmarking of several density functionals and solvation models, we propose herein a new computational protocol, based on eq. 1, to compute complexation free energies in liquid ammonia. The latter involve gas phase optimizations of the complexes and the calculation of thermochemistry corrections (δE_G) from frequency calculations. All these calculations are performed on B3LYP/SDD/6-311+G** gas phase optimized geometries, with

energies refined at the PBE0-D3(bj)/SDD/cc-pVTZ level (ΔE_{gas} and δE_{BSSE} terms) and evaluating solvation effects using the COSMO model (δE_{solv}). Using this protocol, we obtain that the pentaammine complex is more stable than the hexaammine, in keeping with experimental results. The experimental trends for the formation of dihalide complexes are also well reproduced. Our proposed protocol is computationally efficient and should be practical to investigate a broad range of complexation reactions conducted in liquid ammonia. Ultimately, it could complement experimental studies to obtain stability constants of uranyl complexes in this medium, which are still scarce in the literature.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

N.S. thanks the Univ. Grenoble Alpes, the CNRS, the ICMG FR 2607 and the PCECIC and Froggy platforms of the CIMENT infrastructure (project "liqsim"). The work has been performed under the Project HPC-EUROPA3 (INFRAIA-2016-1-730897), with the support of the EC Research Innovation Action under the H2020 Programme; The authors thank EaStCHEM and EPCC for computer resources and technical support.

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Graphical abstract:

