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1 Temperature-dependent luminescence spectroscopic investigations of  
2 U(VI) complexation with the halides F<sup>-</sup> and Cl<sup>-</sup>

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18 **keywords:** uranyl, luminescence, complexation, halides, quenching

19

20 **Abstract**

21 In the present study we have investigated the complexation of uranyl(VI) with chloride and  
22 fluoride using luminescence spectroscopy (TRLFS, time-resolved laser-induced fluorescence  
23 spectroscopy). At 25 °C, in the presence of 0 – 0.175 M fluoride, the first single-component  
24 emission spectra for all four U(VI)-fluoride complexes, i.e.  $\text{UO}_2\text{F}^+$ ,  $\text{UO}_2\text{F}_2$ ,  $\text{UO}_2\text{F}_3^-$ , and  
25  $\text{UO}_2\text{F}_4^{2-}$  could be extracted. Based on the aqueous speciation derived from the TRLFS data,  
26  $\log K^*$  values at  $I = 1$  M were calculated for all these complexes and extrapolated to infinite  
27 dilution using the SIT approach. In the case of chloride, however, quenching of the U(VI)-  
28 luminescence hampered the experiments. Thus, U(VI)-complexation was studied with TRLFS  
29 at liquid nitrogen temperatures. Samples were prepared at 25 °C with chloride concentrations  
30 ranging from 0 to 1.0 M followed by instantaneous freezing and subsequent luminescence  
31 spectroscopic measurements at  $-120$  °C. This allowed for the determination of the first  
32 luminescence spectra for the  $\text{UO}_2\text{Cl}^+$  complex with the TRLFS method. The chloride quench  
33 reaction was further studied in the temperature range 1 – 45 °C using Stern-Volmer analysis.  
34 By applying the Arrhenius and the Eyring equations we obtained the first thermodynamic  
35 parameters for the dynamic quench process, i.e. the activation energy ( $E_a = 55.0 \pm 12.9$  kJ/mol),  
36 enthalpy ( $\Delta H^\ddagger = 52.5 \pm 13.0$  kJ/mol), and entropy ( $\Delta S^\ddagger = 103.9 \pm 42.8$  J/mol·K).

37

## 38 1 Introduction

39 Uranyl(VI) complexation in aqueous solution with inorganic and organic ligands have an  
40 influence on the retention behavior and therefore, on the mobility and (bio)availability of U(VI)  
41 in the environment. The halides are an important group of elements to be considered in such  
42 U(VI)-complexation reactions. Chloride is the most abundant inorganic ligand in our water  
43 reservoirs and in natural salt deposits<sup>1</sup>. It is also one of the most important constituents in the  
44 pore waters of crystalline rock<sup>2</sup> and clay<sup>3</sup> in subsurface formations. In addition, the strong halide  
45 ligand fluoride, is present in several minerals such as fluoroapatite and fluorite, which are  
46 frequently encountered in crystalline rock formations such as granite.<sup>4,5</sup> Complexed uranyl(VI)  
47 with fluoride is further a trace indicator for the uranium enrichment process, as the produced  
48  $UF_6$  in contact with moist air will form uranyl(VI) fluoride under oxic conditions.<sup>6,7</sup>

49 Several studies dedicated to uranyl(VI) complexation reactions with the above-mentioned  
50 halide ligands and the extraction of complexation constants for the formed U(VI)-halide  
51 complexes, have been conducted at ambient conditions.<sup>8-14</sup> In addition, few studies report on  
52 complexation investigation at elevated temperatures<sup>15, 16</sup>, which are of relevance in deep  
53 subsurface environments<sup>17</sup> related to e.g. geothermal energy production or in the vicinity of  
54 heat-generating spent nuclear fuel repositories.<sup>18</sup> Published complexation constants at various  
55 temperatures were compiled in Table S1 and Table S2 in the supporting information (SI) for  
56 U(VI)-fluoride and U(VI)-chloride complexes, respectively. These constants were derived with  
57 various indirect methods using ion selective electrodes<sup>9, 19, 20</sup> or cation exchange<sup>10</sup>, and direct  
58 spectroscopic methods including spectrophotometry<sup>11-13, 16</sup> and NMR.<sup>21</sup> The use of time-  
59 resolved laser-induced luminescence spectroscopy (TRLFS) has only been used in a few  
60 studies<sup>15</sup> for the derivation of U(VI)-halide complexation constants despite its low detection  
61 limits and the excellent luminescent properties of U(VI) allowing for the direct *in situ*  
62 monitoring of complexation reactions in aqueous environments. For the fluoride ligand,  
63 luminescence studies are limited to the early U(VI)-fluoride complexes,  $UO_2F^+$  and  $UO_2F_2$ ,  
64 prevailing at low total fluoride concentrations. In the presence of chloride, no luminescence  
65 spectra have been published for U(VI)-chloride complexes and consequently TRLFS has not  
66 been used for the derivation of any U(VI)-chloride complexation constants. The lack of  
67 luminescence data for chloride-containing solutions can be traced back to the severe quenching  
68 of the luminescence emission in the presence of this halide. The quenching has been proposed  
69 to occur through electron transfer from chloride to uranyl(VI), resulting in the formation of a  
70 non-luminescent U(V)-like transition state.<sup>22-25</sup> The quenching has been shown to occur already  
71 at very low total chloride concentrations, where no  $UO_2Cl^+$  complexes are present in solution,

72 implying that dynamic quenching plays a crucial role in the quench-reaction. At higher total  
73 chloride concentrations additional static quenching by the formed  $\text{UO}_2\text{Cl}^+$  complex can be  
74 assumed to occur. Temperatures below the freezing point have been shown to decrease dynamic  
75 quenching effects. Samples can easily be cooled down to temperatures of  $-196\text{ }^\circ\text{C}$  and  $-269\text{ }^\circ\text{C}$   
76 by use of liquid nitrogen and liquid helium, respectively. When rapid cooling is undertaken, *i.e.*  
77 when a sample prepared at room temperature is directly immersed in liquid nitrogen, the  
78 chemistry prevailing at ambient conditions should be preserved due to the very low reaction  
79 rates at these low temperatures.<sup>26, 27</sup> This allows for luminescence spectroscopic investigations  
80 of systems containing quenching ligands, such as chloride.

81 In the present study we have investigated the complexation of uranyl(VI) with chloride and  
82 fluoride using TRLFS. The fluoride concentration range has been chosen so, that also higher  
83 U(VI)-fluoride complexes ( $\text{UO}_2\text{F}_3^-$  and  $\text{UO}_2\text{F}_4^{2-}$ ) are present in solution in addition to the  
84 already reported  $\text{UO}_2\text{F}^+$  and  $\text{UO}_2\text{F}_2$  ones, allowing the extraction of spectroscopically derived  
85 complexation constants for all above-mentioned complexes at  $25\text{ }^\circ\text{C}$ . As the chloride quenching  
86 phenomenon can be overcome by cooling down the samples to liquid nitrogen temperatures,  
87 U(VI)-chloride samples initially prepared at  $25\text{ }^\circ\text{C}$  have been frozen and measured at  $-120\text{ }^\circ\text{C}$   
88 using a liquid nitrogen jet stream for the derivation of the first  $\text{UO}_2\text{Cl}^+$  luminescence spectra  
89 with the TRLFS method. The spectra of the  $\text{UO}_2\text{F}^+$  and  $\text{UO}_2\text{Cl}^+$  were compared to draw  
90 analogies. Finally, due to the role of temperature in the quench process chloride and fluoride  
91 complexation in the temperature-range from  $1\text{ }^\circ\text{C}$  to  $45\text{ }^\circ\text{C}$  have been studied. From the  
92 observed chloride-induced quench reaction, constants for the dynamic and static quench  
93 processes using the Stern-Volmer equations<sup>28</sup> could be derived in addition to thermodynamic  
94 data, *i.e.* the activation energy, enthalpy, and entropy.

95

96

## 97 2 Materials and methods

### 98 2.1 Sample preparation

99 Uranyl(VI) stock solutions were prepared by converting  $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  (Merck KGaA) to  
100 uranyl peroxide using  $\text{H}_2\text{O}_2$  solution, which was heated in contact with air at  $350 \text{ }^\circ\text{C}$  to obtain  
101  $\text{UO}_3 \cdot 2 \text{H}_2\text{O}$ . The uranium oxide was dissolved in concentrated  $\text{HClO}_4$  and thereafter diluted  
102 with deionized water to a final concentration of  $0.1 \text{ M UO}_2^{2+}$  in  $0.5 \text{ M HClO}_4$ . All other high  
103 purity reagent grade materials were used without any further treatment.  $\text{NaCl}$  ( $> 99.5 \%$ ; Merck  
104 KGaA) and  $\text{HF}$  ( $48 \%$ ; Carl Roth GmbH + Co. KG) were used in the preparation of solutions  
105 containing chloride and fluoride, respectively.  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  ( $> 99 \%$ ; Merck KGaA) served as  
106 a background electrolyte. Milli-Q water was used in the dilution of all samples.

107 For the correct adjustment of the sample pH to the desired total proton concentration  $[\text{H}]$  in the  
108 rather high background electrolyte concentrations used in the present work, a correction of the  
109 experimental  $\text{pH}_{\text{exp}}$  by an empirical coefficient  $A_c$  according to equation (1) is required.

$$-\log[\text{H}^+] = \text{pH}_{\text{exp}} + A_c \quad (1)$$

110  $A_c$  was determined by an empirical equation published by Jordan et al (2018).<sup>29</sup> To avoid  $\text{KClO}_4$   
111 precipitation and unwanted chloride contamination a double junction electrode from Metrohm  
112 was prepared, using  $3 \text{ M KCl}$  in the inner chamber and  $3 \text{ M NaClO}_4$  in the outer chamber. pH  
113 electrode calibration was performed using standard WTW buffer solutions.

114 To study the temperature-dependent complexation between uranyl(VI) and fluoride, solutions  
115 containing a constant U(VI) concentration of  $0.1 \text{ mM}$  and fluoride concentrations between  
116  $0$  and  $0.175 \text{ M}$  were prepared at a constant pH of  $2$  ( $[\text{H}] = 0.01$ ) and an ionic strength of  $1 \text{ M}$   
117 was adjusted with  $\text{NaClO}_4$ . The samples were equilibrated at the desired temperatures ( $1$  to  
118  $45 \text{ }^\circ\text{C}$ ) using thermoelements from Quantum Northwest.

119 For luminescence spectroscopic studies of U(VI)-chloride complexation at liquid nitrogen  
120 temperatures ( $-120 \text{ }^\circ\text{C}$ ,  $153 \text{ K}$ ) uranyl(VI) chloride samples with  $[\text{U}] = 0.04 \text{ mM}$  and  
121  $[\text{Cl}] = 0 - 1.0 \text{ M}$  were prepared at a constant pH of  $1.4$  ( $[\text{H}] = 0.040$ ). The overall ionic strength  
122 was kept constant at  $1.1 \text{ M}$  using  $\text{NaClO}_4$ . At a temperature of  $1 \text{ }^\circ\text{C}$ , the uranyl(VI) chloride  
123 speciation was investigated in solutions containing  $[\text{U}] = 5 \text{ mM}$  with  $[\text{Cl}]$  ranging from  
124  $0$  to  $0.5 \text{ M}$ ,  $I = 0.5 \text{ M}$  and  $-\log[\text{H}] = 0.5$  and  $2.5$ . The quenching of U(VI) luminescence in the  
125 presence of chloride for the derivation of thermodynamic data of the quench process was  
126 investigated in solutions containing  $[\text{U}] = 0.1 \text{ mM}$  with  $[\text{Cl}] = 0 - 0.01 \text{ M}$  at  $-\log[\text{H}] = 1$  and  
127  $I = 0.11 \text{ M}$  at temperatures ranging from  $1$  to  $45 \text{ }^\circ\text{C}$ . Similarly to the fluoride samples,

128 thermocouples from Quantum Northwest were used to equilibrate the samples at the desired  
129 temperatures.

## 130 **2.2 Time-resolved laser-induced luminescence spectroscopy**

131 The speciation of uranyl(VI) can be monitored via the detection of the uranyl(VI) luminescence.  
132 The change of the coordination environment of uranyl(VI) will result in the spectral shift and  
133 change of intensity of its characteristic luminescence emission signals. The luminescence  
134 spectroscopic investigations in the temperature-range 1 – 45 °C were conducted by transferring  
135 3 ml of the sample volume into a quartz glass cuvette. For the uranyl(VI) chloride series at  
136 –120 °C a 1 ml aliquot was frozen instantly in plastic cuvettes using liquid nitrogen. The sample  
137 was kept at –120 °C during the measurements using a jet stream of liquid nitrogen. Laser  
138 spectroscopic measurements were performed using nanosecond Nd:YAG lasers (Continuum  
139 Minilite I and Continuum Minilite II; Continuum Electro-Optics Inc.) as an excitation source  
140 in the 1 – 45 °C experiments, while Continuum Inlite; Continuum Electro-Optics Inc. was used  
141 in the liquid nitrogen experiments. Luminescence spectra were recorded at 425 – 625 nm at a  
142 delay of 40 to 135 ns after the excitation impulse, depending on the experiment, with a constant  
143 excitation wavelength of 266 nm. For time-resolved measurements luminescence spectra were  
144 recorded step-wise every 5 to 50 ns after the excitation pulse depending on the measured  
145 sample.

## 146 **2.3 Determination of complexation constants**

147 Conditional constants  $\log K^*$  can be determined from the spectroscopically derived U(VI)-  
148 fluoride and U(VI)-chloride species distributions using slope analysis. Hereby the logarithmic  
149 concentration of the ligand [L] is plotted against the logarithmic ratio of the reaction product  
150 [RL] and the reactant molecule [R] according to formula (3) derived from formula (2). The  
151 slope  $a$  corresponds to the number of reacting ligands, while the intercept with the y-axis yields  
152 the logarithmic conditional complexation constant  $\log K^*$ .

153



$$\log \left( \frac{[RL]}{[R]} \right) = a \cdot \log([L]) + \log(K^*) \quad (3)$$

154

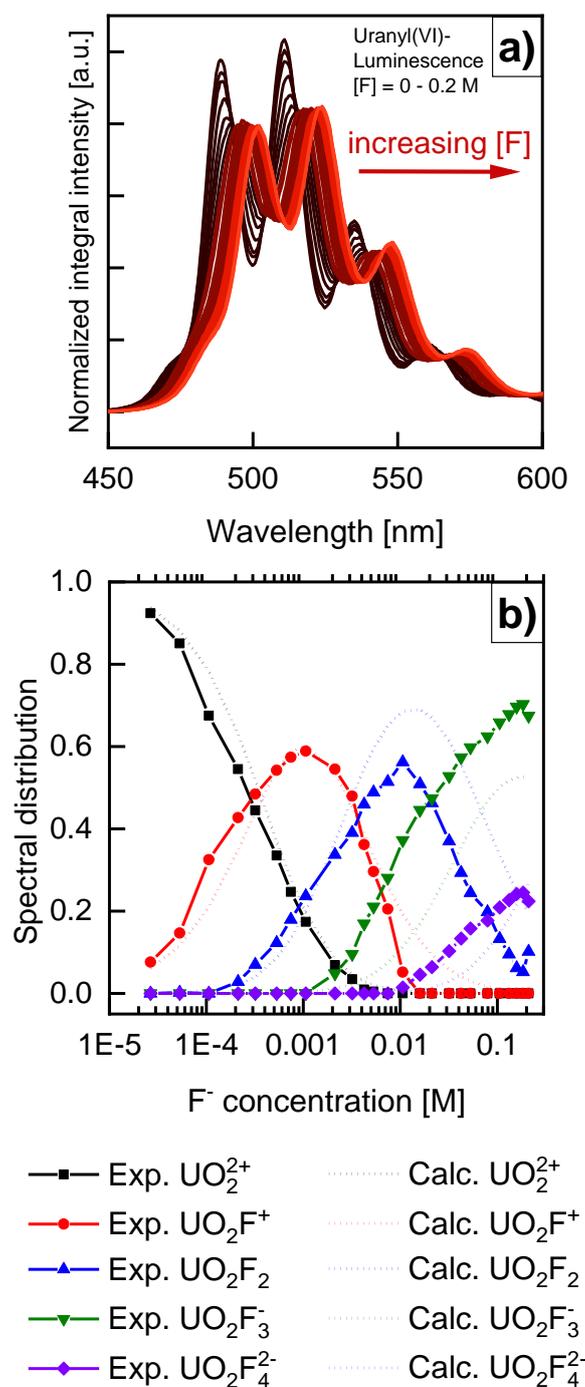
155 The ligand concentration [L], i.e. the concentration of free  $F^-$  and  $Cl^-$  in solution was calculated  
156 using the PHREEQC program Version 3.4.0.<sup>30</sup> The calculations were based on the  
157 Thermochemie V9.0 SIT database from ANDRA.<sup>31, 32</sup> Further needed SIT parameters were  
158 taken from literature (see Table S3 and S4).<sup>33, 34</sup> For the calculations a temperature of 25 °C and  
159 an ionic strength of 1 M ( $F^-$  samples) or 1.1 M ( $Cl^-$  samples)  $NaClO_4$  were used. Molar values  
160 were converted to the molal scale using density values listed in the Thermochemie V9.0 SIT  
161 database. The reaction product [RL] and the remaining uranium concentration in solution [R]  
162 were derived from the species distribution obtained from TRLFS data. The spectroscopically  
163 derived species distribution for the U(VI)-fluoride and chloride systems were compared with  
164 calculated distributions, based on average values of reported complexation constants for the  
165 various U(VI)-fluoride/chloride complexes. The distribution was determined using a uranium  
166 concentration of 0.1 mM (in  $F^-$  media) or 0.04 mM (in  $Cl^-$  media).

167

168 **3 Results**

169 **3.1 Uranium(VI) complexation with fluoride at 25 °C**

170 The luminescence emission spectra of U(VI) in the presence of fluoride at 25 °C are presented  
 171 in Figure 1 a). A constant red shift of the uranyl(VI) signal with increasing fluoride  
 172 concentration can be seen as a result of progressing complexation in solution.



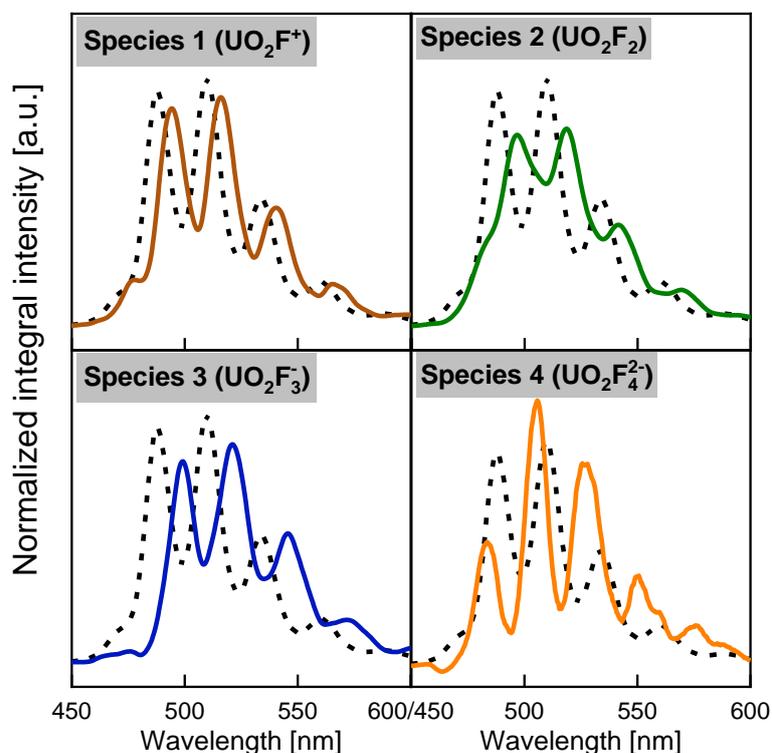
173

174 Figure 1: **a)** Luminescence spectra of uranyl(VI) with increasing fluoride concentration [F] = 0 – 0.175 M;  $-\log[\text{H}] = 2$ ;  
 175  $I = 1 \text{ M}$ ;  $T = 25 \text{ }^\circ\text{C}$  and **b)** Calculated and spectroscopically derived speciation of uranyl(VI) in the aqueous system in  
 176 dependence of the fluoride concentration at  $-\log[\text{H}] = 2$ ,  $I = 1 \text{ M}$  at  $25 \text{ }^\circ\text{C}$ .

177

178 Using spectral deconvolution, the collected composite spectra could be described by four  
179 U(VI)-fluoride species (species 1 – species 4) in addition to the free uranyl(VI) aquo ion  
180 ( $\text{UO}_2^{2+}$ ), see Figure 2 and Figure S2 in the supplementary information (SI). A comprehensive  
181 discussion of the deconvolution process can be found in Huittinen et al.<sup>35</sup> The single component  
182 spectra of the complexes were then smoothed using a 5 to 6 point FFT (Fast Fourier Transform)  
183 due to a poor signal-to-noise ratio of the extracted components.

184 Based on the peak positions of the extracted components, the emission spectra of the two first  
185 fluoride species compare very well with already existing data for  $\text{UO}_2\text{F}^+$  and  $\text{UO}_2\text{F}_2$ , see  
186 Table 1.<sup>15</sup> Thus, species 1 and species 2 can tentatively be assigned to these two above-  
187 mentioned fluoride complexes.



188

189 Figure 2: Single component spectra of  $\text{UO}_2^{2+}$  (black dashed line), species 1, species 2, species 3 and species 4 extracted from  
190 fluoride-containing solutions  $[\text{F}] = 0 - 0.175 \text{ M}$ ;  $-\log[\text{H}] = 2$ ;  $I = 1 \text{ M}$ ;  $T = 25 \text{ }^\circ\text{C}$ .

191 To gain further insight into the U(VI)-fluoride speciation in solution, a relative species  
192 distribution was calculated based on the extracted pure component spectra.

193

194

Table 1: Main emission peaks of the single component spectra of the uranyl(VI) fluoride complexes.

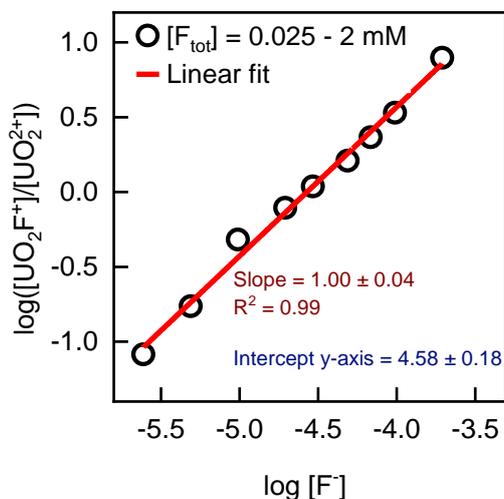
Component	Peak I [nm]	Peak II [nm]	Peak III [nm]	Literature
UO <sub>2</sub> <sup>2+</sup>	488.1 ± 0.1	509.9 ± 0.1	533.7 ± 0.1	
Species 1 (UO <sub>2</sub> F <sup>+</sup> )	494.5 ± 0.1	516.3 ± 0.1	540.3 ± 0.1	This work
Species 2 (UO <sub>2</sub> F <sub>2</sub> )	496.8 ± 0.1	518.7 ± 0.1	542.3 ± 0.1	
Species 3 (UO <sub>2</sub> F <sub>3</sub> <sup>-</sup> )	499.0 ± 0.1	521.0 ± 0.1	545.8 ± 0.1	
Species 4 (UO <sub>2</sub> F <sub>4</sub> <sup>2-</sup> )	505.3 ± 0.1	527.4 ± 0.1	550.6 ± 0.2	
UO <sub>2</sub> <sup>2+</sup>	488	510	533	Kirishima et al. <sup>15</sup>
UO <sub>2</sub> F <sup>+</sup>	495	517	541	
UO <sub>2</sub> F <sub>2</sub>	498	520	544	

196 For this, relative luminescence intensity (LI) factors for the present species had to be calculated  
 197 (see Table S6). They take into account the differences in luminescence quantum yields of the  
 198 various species relative to the non-complexed uranyl(VI) aquo ion. A detailed description of  
 199 the LI factor calculation can be found in literature.<sup>35</sup>

200 Using the obtained LI factors and the single component spectra it was possible to calculate the  
 201 speciation of uranyl(VI) in dependence of the fluoride concentration ( $-\log[H] = 2$ ,  $I = 1$  M) at  
 202 room temperature applying the least squares fitting method. The obtained results in Figure 1 b)  
 203 were compared to calculations determined by PHREEQC using existing complexation  
 204 constants for U(VI)-fluoride complexes. Figure 1 b) shows that the calculated and  
 205 experimentally derived species distributions in dependence of the fluoride concentrations are  
 206 in general agreement with each other. Thus, we can primarily assign the four U(VI)-fluoride  
 207 species to the four progressing UO<sub>2</sub>F<sub>n</sub><sup>2-n</sup> complexes, with  $n$  being the number of fluoride ligands  
 208 ranging from 1 to 4. Each new fluoride complexing the uranyl(VI) induces an additional red  
 209 shift of the luminescence emission. Starting with UO<sub>2</sub>F<sub>2</sub> the spectroscopically derived species  
 210 distribution seems to differ slightly from the calculated species distribution. To verify the  
 211 proposed stoichiometry of the complexes as well as to determine the conditional complexation  
 212 constants we performed a slope analysis using the calculated F<sup>-</sup> concentrations.

213 Slope analysis was applied to all species using equation (3). The slope obtained for species 1,  
 214 assuming the reaction  $UO_2^{2+} + F^- \rightleftharpoons UO_2F^+$ , is  $1.00 \pm 0.04$  as shown in Figure 3 and it indicates  
 215 a one step reaction between the uranyl(VI) cation and one fluoride ligand resulting in the  
 216 formation of the proposed UO<sub>2</sub>F<sup>+</sup> complex. The intercept with the y-axis yields the conditional  
 217 complexation constant  $\log K^*$  at  $I = 1$  M, which is in very good agreement with published data  
 218 for this complex, see Table 2. Further slope analyses were performed for the other species,  
 219 confirming the existence of the proposed UO<sub>2</sub>F<sub>n</sub><sup>2-n</sup> complexes to the different species

220 respectively. The corresponding slope analyses based on the equations in Table 2 can be found  
 221 in the SI (Figure S5).



222  
 223 Figure 3: Slope analysis for the UO<sub>2</sub>F<sup>+</sup> complex according to equation (3) assuming the reaction UO<sub>2</sub><sup>2+</sup> + F<sup>-</sup> ⇌ UO<sub>2</sub>F<sup>+</sup>.  
 224 The obtained results and a comparison to known literature values are shown in Table 2. The  
 225 literature values are average values of complexation constants for the respective U(VI)-fluoride  
 226 complexes recommended by the NEA-TDB (for more details, see the SI). For the  
 227 experimentally determined slope and logK\* values, the error range was determined using two  
 228 times the standard deviation of the data sets. LogK<sup>0</sup> values were determined using SIT equations  
 229 suggested by NEA using values listed in Table S4.<sup>34</sup>

230 Table 2: Used reactions for the slope analysis, the obtained slope and a comparison of experimentally determined logK\* values  
 231 (this study) with literature values for uranyl(VI) fluoride complexes at I = 1 M and T = 25 °C.

Reaction scheme	Slope	Exp. logK* (logK <sup>0</sup> )	Lit. logK*
UO <sub>2</sub> <sup>2+</sup> + F <sup>-</sup> ⇌ UO <sub>2</sub> F <sup>+</sup>	1.00 ± 0.04	4.58 ± 0.18 (5.19)	4.54 ± 0.03 <sup>9, 19, 20, 36</sup>
UO <sub>2</sub> F <sup>+</sup> + F <sup>-</sup> ⇌ UO <sub>2</sub> F <sub>2</sub>	1.02 ± 0.20	3.59 ± 0.67 (3.69)	3.40 ± 0.09 <sup>9, 19, 20, 36</sup>
UO <sub>2</sub> F <sub>2</sub> + F <sup>-</sup> ⇌ UO <sub>2</sub> F <sub>3</sub> <sup>-</sup>	1.02 ± 0.07	2.77 ± 0.17 (2.60)	2.39 ± 0.39 <sup>8, 9, 19, 20, 36</sup>
UO <sub>2</sub> F <sub>2</sub> + 2 F <sup>-</sup> ⇌ UO <sub>2</sub> F <sub>4</sub> <sup>2-</sup>	2.05 ± 0.34	4.41 ± 0.65 (4.05)	3.68 ± 0.79 <sup>8, 9, 19, 36</sup>
UO <sub>2</sub> F <sub>3</sub> <sup>-</sup> + F <sup>-</sup> ⇌ UO <sub>2</sub> F <sub>4</sub> <sup>2-</sup>	---	1.64 ± 0.67 (1.45) <sup>1</sup>	

232 <sup>1</sup>Calculated from the logK\* values of the UO<sub>2</sub>F<sub>2</sub> + 2 F<sup>-</sup> ⇌ UO<sub>2</sub>F<sub>4</sub><sup>2-</sup> and UO<sub>2</sub>F<sub>2</sub> + F<sup>-</sup> ⇌ UO<sub>2</sub>F<sub>3</sub><sup>-</sup> reactions.

233 Table 2 shows that the slope corresponds to the number of fluoride ligands taking part in the  
 234 proposed reaction. The logK\* values obtained in this work are slightly higher in comparison to  
 235 literature values. It is not unreasonably to assume the difference might be due to the use of a  
 236 sensitive spectroscopic method. Tian et al. (2009) determined logK\* values for the UO<sub>2</sub>F<sub>n</sub><sup>2-n</sup>  
 237 (n = 1 – 4) complexes at I = 1 M and T = 25 °C using spectrophotometry. Their complexation  
 238 constants were moderately higher than the values suggested by NEA (1992), see Table S1.  
 239 Their values (logK\* (I = 1 M) UO<sub>2</sub>F<sup>+</sup>/UO<sub>2</sub>F<sub>2</sub>/UO<sub>2</sub>F<sub>3</sub><sup>-</sup>/UO<sub>2</sub>F<sub>4</sub><sup>2-</sup> = 4.60 / 8.07 / 10.78 / 11.92) are

240 very similar to ours ( $\log K^* (I = 1 \text{ M}) = 4.58 / 8.17 / 10.94 / 12.58$ ), suggesting a slightly  
241 enhanced fluoride complexation behavior than previously reported.

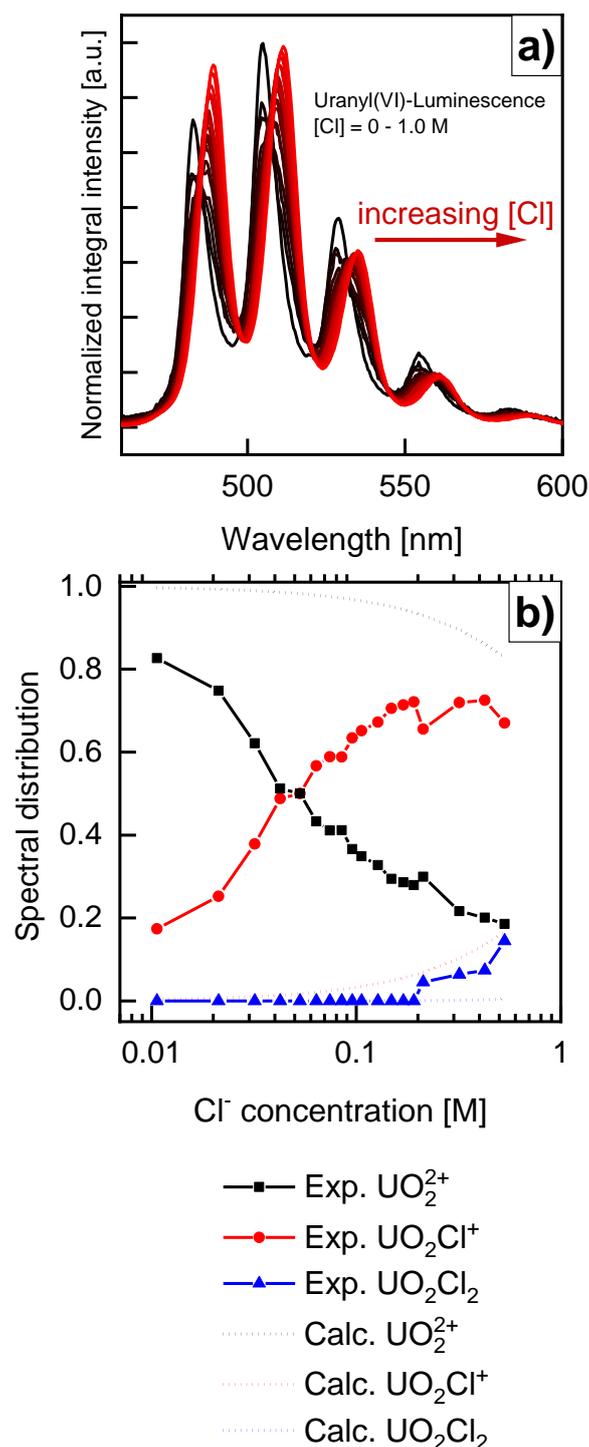
242 Finally, having extracted pure component spectra for all four U(VI)-fluoride complexes (Figure  
243 2), changes in the total symmetric stretch vibration frequency ( $\nu_s$ ), of the uranyl moiety as a  
244 function of the number of fluoride ligands could be calculated. The stretch vibration frequency  
245 can be obtained from the spacing between the electronic transition line E, and the higher  
246 vibronic level  $S_1$  of the electronic ground state. Therefore, the peak positions of the first and  
247 second peak emission peaks of the extracted pure component spectra were recalculated to obtain  
248 their respective wavenumbers (see Table S5). The wavenumber and the stretch vibration  
249 frequency show a linear decrease with increasing fluoride ligand number in Figure S3 and  
250 Figure S4, respectively, which is an indication of a systematic weakening of the U=O bond by  
251 the coordination of the strongly donating fluoride ligands in the equatorial plane. The linear fit  
252 of the stretch vibration frequency as a function of fluoride complexation resulted in the  
253 following expression (4):

$$\nu_s(\text{cm}^{-1}) = -11 \text{ cm}^{-1} \cdot n(\text{F}^-) + 870 \text{ cm}^{-1} \quad (4)$$

254 A similar electron donating effect resulting in a linear relation between  $\nu_s$  and the number of  
255 coordinating ligands was previously reported for U(VI)-hydroxyl  
256 species ( $\nu_s(\text{cm}^{-1}) = -22 \text{ cm}^{-1} \cdot n(\text{OH}^-) + 870 \text{ cm}^{-1}$ ).<sup>37</sup>

### 257 **3.2 Complexation of uranyl(VI) with chloride**

258 Chloride complexation with uranyl(VI) was investigated using liquid nitrogen at  $-120 \text{ }^\circ\text{C}$  to  
259 overcome the quenching of the uranyl(VI) luminescence through chloride. Similar to the  
260 complexation with fluoride, chloride induces a continuous red shift of the uranyl(VI)  
261 luminescence (see Figure 4 a). The red shift indicates progressing complexation of the  
262 uranyl(VI) with chloride as the ligand concentration increases.

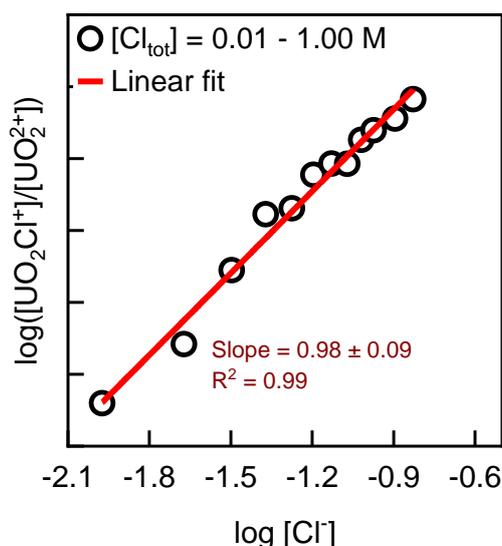


263

264 Figure 4: **a)** Luminescence spectra of uranyl(VI) with increasing chloride concentration [Cl] = 0 – 1.0 M;  $-\log[\text{H}] = 1.5$ ;  
 265  $I = 1.1 \text{ M}$ ;  $T = -120 \text{ }^\circ\text{C}$  and **b)** calculated and uncorrected spectroscopically derived speciation of uranyl(VI) in the aqueous  
 266 system in dependence of the chloride concentration at  $-\log[\text{H}] = 1.4$ ,  $I = 1.1 \text{ M}$  at  $25 \text{ }^\circ\text{C}$ .

267 To determine the species in solution peak deconvolution was performed. From the individual  
 268 spectra three single component spectra could be determined (see Figure S6 in the SI). The first  
 269 component is the free uranyl(VI) aquo ion, however, at  $-120 \text{ }^\circ\text{C}$  it is blue shifted in comparison  
 270 to the aquo ion at  $25 \text{ }^\circ\text{C}$  (see Table 3). The blue shift is slightly more pronounced for peak I  
 271 ( $4.7 \text{ nm}$ ,  $174 \text{ cm}^{-1}$ ) than peak III ( $4.1 \text{ nm}$ ,  $166 \text{ cm}^{-1}$ ). This blue shift has been observed to

272 increase with decreasing temperature, but the underlying reasons for it are not well  
273 understood.<sup>38</sup> The two other pure components extracted from the composite spectra measured  
274 in the chloride containing solutions must belong to U(VI)-chloride complexes, i.e. the  $\text{UO}_2\text{Cl}^+$   
275 complex (species 1) and  $\text{UO}_2\text{Cl}_2$  (species 2) (see Figure S6). Species 1 is present already at  
276 rather low chloride concentrations of 10 mM, while species 2 appears at chloride concentrations  
277 exceeding 0.2 M. The resulting, uncorrected species distribution is presented in Figure 4 b),  
278 right, together with a calculated species distribution based on published complexation constants  
279 from the NEA-TDB.<sup>33</sup> The uncorrected experimental and calculated species distributions differ  
280 very strongly from one another. A correction of the species distribution, however, could not be  
281 done, as the LI factor determination was unsuccessful. Generally the luminescence intensity  
282 increases with increasing chloride concentration (Figure S7), but light scattering from the  
283 frozen samples is very incongruent. This results in very different luminescence intensities  
284 between the samples which subsequently hampers an accurate determination of the LIs, which  
285 is unfortunate as the speciation depends strongly on these LI factors.



286  
287 Figure 5: Slope analysis for the  $\text{UO}_2\text{Cl}^+$  complex according to equation (3) assuming the reaction  $\text{UO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}^+$ .  
288 Nevertheless, the stoichiometry of the formed complexes can be extracted from the uncorrected  
289 species distribution by slope analysis. Due to the low amount of samples (only 5) for which the  
290 second species is present, slope analysis was successful only for the first chloride complex. The  
291 results of the slope analysis is presented in Figure 5.

292

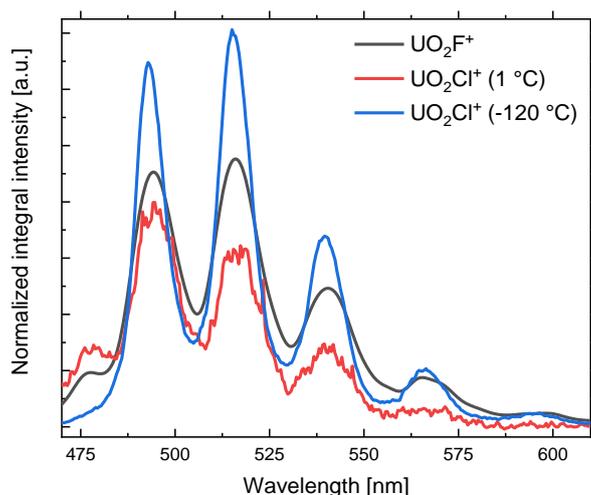
293

294 Table 3: Main emission peaks of the single component spectra of the uranyl(VI) halide complexes.

Component	Peak I [nm]	Peak II [nm]	Peak III [nm]	Literature
UO <sub>2</sub> <sup>2+</sup> (-120 °C)	484.0 ± 0.1	505.6 ± 0.1	529.0 ± 0.1	
Species 1 (UO <sub>2</sub> Cl <sup>+</sup> ) (-120 °C)	488.6 ± 0.1	510.6 ± 0.1	534.5 ± 0.1	
Species 2 (UO <sub>2</sub> Cl <sub>2</sub> ) (-120 °C)	490.1 ± 0.1	512.1 ± 0.1	536.0 ± 0.1	This work
UO <sub>2</sub> <sup>2+</sup> (25 °C)	488.1 ± 0.1	509.9 ± 0.1	533.7 ± 0.1	
UO <sub>2</sub> F <sup>+</sup> (25 °C)	494.5 ± 0.1	516.3 ± 0.1	540.3 ± 0.1	

295 The slope analysis results in a slope of  $0.98 \pm 0.09$ , indicating a one-step reaction between the  
 296 uranyl(VI) cation and the chloride ligand, which confirms that species 1 is the UO<sub>2</sub>Cl<sup>+</sup> complex.  
 297 This is the first pure component spectrum for a U(VI)-chloride complex obtained with the  
 298 TRLFS method. Having seen complex formation in a frozen state at -120 °C, it is of interest to  
 299 investigate complex formation in the aqueous state. While no complex formation of uranyl(VI)  
 300 ([U] = 0.1 mM) in a solution containing chloride [Cl] = 0 – 0.05 M at room temperature could  
 301 be observed due to severe quenching, it was possible to measure a uranyl(VI) luminescence at  
 302 1 °C in solution. With increasing chloride concentration a red shift of the luminescence signal  
 303 was obvious (Figure S8) and a peak deconvolution, similar to the procedure for the uranyl(VI)  
 304 fluoride complexes, was possible. Hereby we obtained the first single component spectrum for  
 305 the UO<sub>2</sub>Cl<sup>+</sup> complex in the aqueous state using TRLFS (see Figure 6). A rather similar redshift  
 306 of the UO<sub>2</sub>Cl<sup>+</sup> complex at 1 °C in comparison to -120 °C as seen for the aquo ion at 25 °C and  
 307 -120 °C can be observed (see Table 4). Therefore, the UO<sub>2</sub>Cl<sup>+</sup> spectrum at -120 °C has been  
 308 shifted by the amount the aquo ion shifts between -120 °C and 25 °C in Figure 6 to allow direct  
 309 comparison of the halide spectra measured at different temperatures. For the non-shifted  
 310 spectrum of UO<sub>2</sub>Cl<sup>+</sup> at -120 °C see Figure S6 in the SI.

311



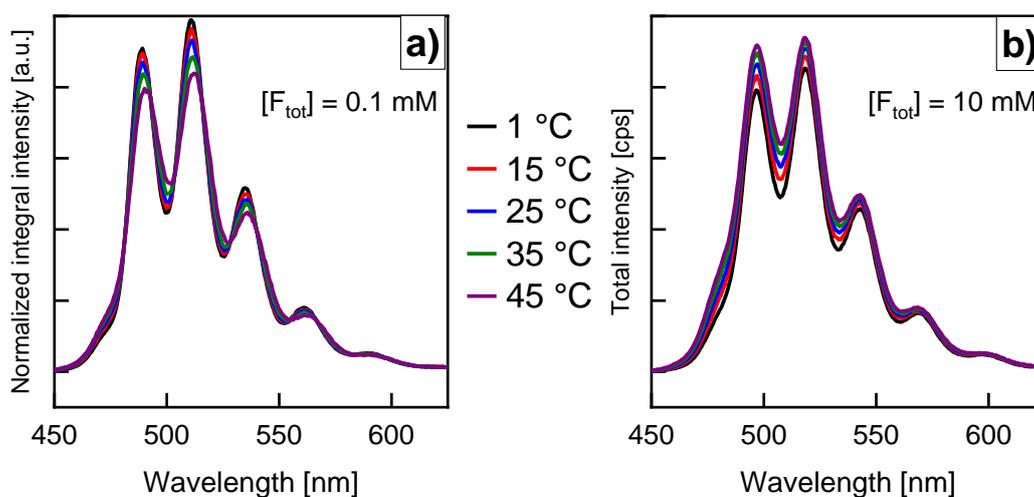
312  
 313 Figure 6: Comparison of the single component spectra of the  $\text{UO}_2\text{F}^+$  complex at 25 °C,  $\text{UO}_2\text{Cl}^+$  complex at 1 °C and – 120 °C.  
 314 Despite some discrepancies regarding the relative intensities of the emission peaks, it is clear  
 315 that the  $\text{UO}_2\text{Cl}^+$  spectra measured at the two different temperatures and the  $\text{UO}_2\text{F}^+$  spectrum are  
 316 very similar. The peak positions are almost identical in all cases speaking for the formation of  
 317 a very similar 1:1 halide complex both in the presence of chloride and fluoride.

318 Table 4: Main emission peaks of the single component spectra of the uranyl(VI) halide complexes.

Component	Peak I [nm]	Peak II [nm]	Peak III [nm]	Literature
$\text{UO}_2\text{Cl}^+$ (1 °C)	$495.1 \pm 0.1$	$516.7 \pm 0.1$	$540.4 \pm 0.1$	This work
$\text{UO}_2\text{Cl}^+$ (–120 °C)	$489.5 \pm 0.1$	$511.5 \pm 0.1$	$535.3 \pm 0.1$	
$\text{UO}_2\text{F}^+$ (25 °C)	$494.5 \pm 0.1$	$516.3 \pm 0.1$	$540.3 \pm 0.1$	

319  
 320 **3.3 Influence of temperature and halides on uranyl(VI) luminescence behavior**  
 321 At ambient conditions, no quenching of the uranyl(VI) luminescence signal in the presence of  
 322 fluoride has been observed.<sup>22-24</sup> It has been suggested, however, that the strong oxidizing  
 323 potential of  $\text{UO}_2\text{F}_4^{2-}$  is accompanied by luminescence quenching effects in the presence of  
 324 redox-sensitive ligands.<sup>39</sup> Thus, the luminescence behavior of U(VI) in fluoride-containing  
 325 solutions was studied at selected fluoride concentrations in the temperature range between 1 °C  
 326 and 45 °C. As shown in Figure 7, at lower fluoride concentrations of  $[\text{F}] = 0.1$  mM, increasing  
 327 the temperature from 1 to 25 °C results in a drop of the luminescence intensity. At this low  
 328 fluoride concentration, the majority of the luminescence signal stems from the U(VI) aquo ion.  
 329 The loss of intensity can thus be traced back to a stronger thermal quenching effect of the water  
 330 molecules coordinating to  $\text{UO}_2^{2+}$  due to their thermal vibrations.<sup>40</sup> Beyond 25 °C, the relative  
 331 luminescence intensity in comparison to the aquo ion is greater, even in the presence of this

332 very low amount of fluoride (0.1 mM). This implies that the thermal quenching by coordinating  
 333 water molecules has decreased as a result of an enhanced formation of the  $\text{UO}_2\text{F}^+$  and  $\text{UO}_2\text{F}_2$   
 334 complexes with increasing temperature. The higher intensity of the complexes is due to the  
 335 replacement of water molecules in the coordination sphere by the fluoride ligand, decreasing  
 336 the quenching effect by water. The enhanced complexation at this fluoride concentration can  
 337 also be seen in Figure 7 a), as a systematic red-shift of the luminescence signal with increasing  
 338 temperature. The red-shift is much more pronounced than observed for the U(VI) aquo ion (see  
 339 SI, Figure S9). This points toward an endothermic reaction enthalpy of the formed  $\text{UO}_2\text{F}^+$  and  
 340  $\text{UO}_2\text{F}_2$  complexes, in agreement with literature.<sup>41</sup> Further, no indications of luminescence  
 341 quenching at any of the investigated temperatures can be established. Increasing the  
 342 temperature in the same range at higher fluoride concentrations of  $[\text{F}] = 10 \text{ mM}$  (Figure 7 b)  
 343 can be seen to further increase the relative luminescence intensity in comparison to the aquo  
 344 ion. The increase is a result of the formation of the  $\text{UO}_2\text{F}_3^-$  and  $\text{UO}_2\text{F}_4^{2-}$  complexes and further  
 345 replacement of coordinating  $\text{H}_2\text{O}$  by  $\text{F}^-$ .<sup>41</sup> Corresponding data for 1 mM and 100 mM fluoride  
 346 concentrations can be found in the SI, Figure S9.



347  
 348 Figure 7: Luminescence spectra of uranyl(VI) ( $[\text{U}] = 0.1 \text{ mM}$ ) with fluoride at **a)**  $[\text{F}] = 0.1 \text{ mM}$  and at **b)**  $[\text{F}] = 10 \text{ mM}$  at  
 349  $1 - 45 \text{ }^\circ\text{C}$ ;  $I = 1 \text{ M}$ ;  $-\log[\text{H}] = 2$ .

350 The apparent increasing fluoride complexation with increasing temperature observed in the  
 351 present work are in contrast with published results by Kirishima et al. (2004), who indicated  
 352 that an increasing temperature would decrease U(VI)-fluoride complexation<sup>15</sup>. In a more recent  
 353 study by Tian et al. (2009), the opposite was observed for all four investigated  $\text{UO}_2\text{F}_n^{2-n}$   
 354 complexes, in agreement with the results obtained in the present study.<sup>16</sup> From our results we  
 355 can conclude that fluoride does not quench the luminescence of uranyl(VI) even at elevated  
 356 temperatures. The luminescence lifetimes of the uranyl(VI) fluoride complexes are longer than

357 the uranyl(VI) aquo ion lifetime, which indicate a lack of quenching caused by the fluoride  
358 anion.

359 The situation is very different for chloride. At the same low halide concentration of 10 mM, the  
360 U(VI) luminescence signal is reduced by almost 97 % in the presence of chloride in comparison  
361 to the aquo ion (Figure S1). Thus, dynamic quench processes play a large role in the quench  
362 reaction. In addition, the  $\text{UO}_2\text{Cl}^+$  is likely to contribute to static quench effects. As dynamic  
363 quenching is temperature dependent and the formation of the  $\text{UO}_2\text{Cl}^+$  complex is  
364 endothermically driven<sup>11</sup> and will be favored with increasing temperature, the quench process  
365 has been investigated in the 1 – 45 °C temperature range using Stern-Volmer analysis.<sup>28</sup> The  
366 Stern-Volmer equation (5) describes the ratio of unquenched luminescence  $I_0$  to quenched  
367 luminescence  $I$  in relation to the quencher concentration  $[Q]$ . Those parameters are connected  
368 by the Stern-Volmer constant  $K_{SV}$ , which is a measure of the amount of quenching.

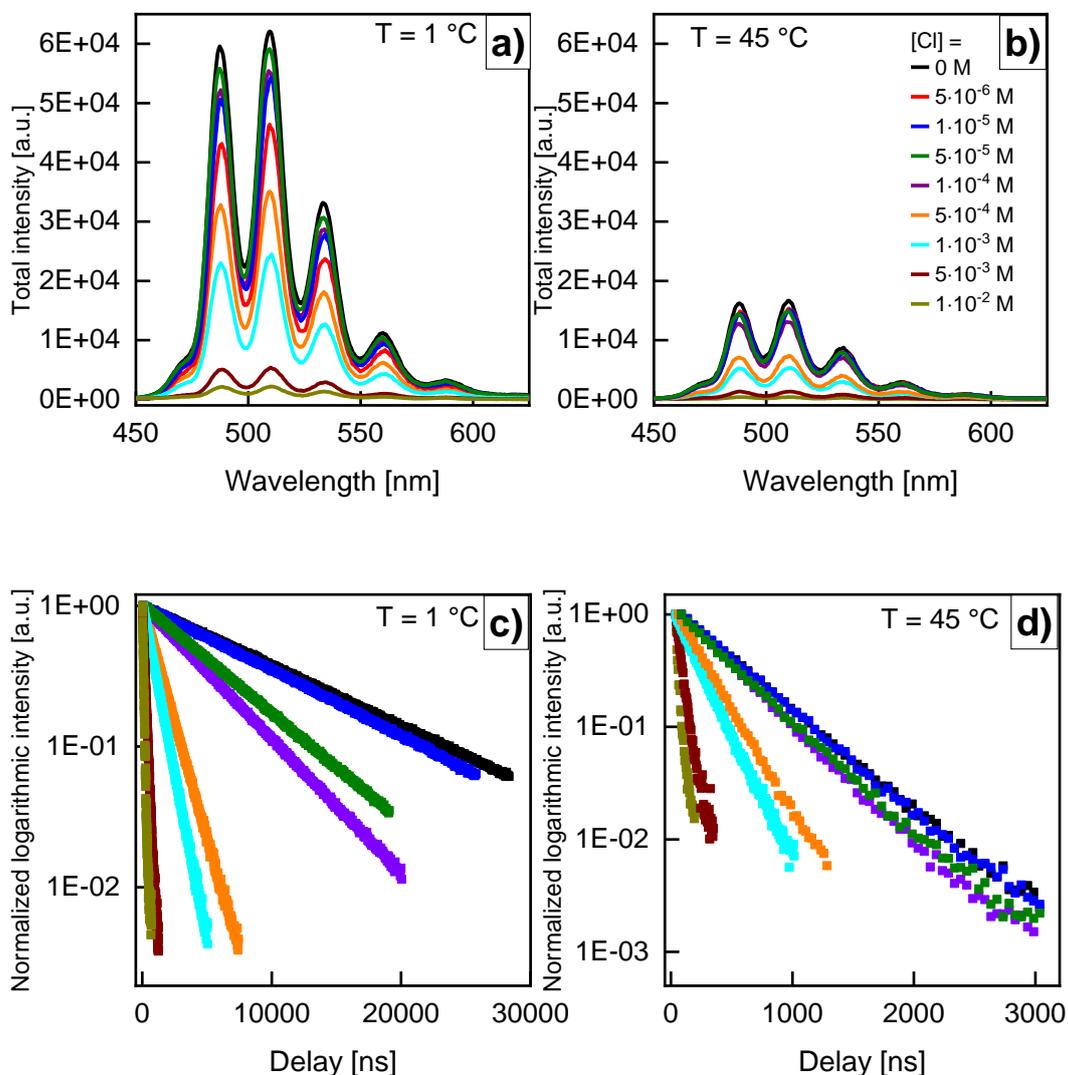
$$\frac{I_0}{I} - 1 = K_{SV} \cdot [Q] \quad (5)$$

369 As already mentioned, two quenching processes can be distinguished: dynamic and static  
370 quenching. During dynamic quenching a bimolecular collision between an excited fluorophore  
371 and a quenching molecule takes place, which results in an energy loss of the fluorophore  
372 without emission of luminescence. Static quenching describes a process, in which a fluorophore  
373 forms a complex with the quencher, thereby creating a non-luminescent complex.

374 To determine which quenching process occurs in solution the chloride concentration is plotted  
375 against  $I_0/I$  and  $\tau_0/\tau$ , where  $\tau_0$  describes the lifetime of the fluorophore without quencher and  $\tau$   
376 with a quencher present. In the case of purely dynamic quenching  $I_0/I$  equals  $\tau_0/\tau$ , whereas in a  
377 purely static quenching process  $\tau_0/\tau$  is always one. To investigate the quenching process  
378 solutions containing uranyl(VI) ( $[U] = 0.1 \text{ mM}$ ) and chloride ( $[Cl] = 0 - 0.1 \text{ M}$ ) were prepared  
379 at a  $-\log[H]$  of 1 with an ionic strength of 0.11 M. To obtain  $I_0/I$  and  $\tau_0/\tau$  the static luminescence  
380 spectra and the luminescence lifetimes of the uranyl(VI) at varying chloride concentration are  
381 required.

382 From the static luminescence spectra in Figure 8 a) at 1 °C and b) at 45 °C it becomes evident,  
383 that the luminescence intensity of the uranyl(VI) decreases with increasing chloride  
384 concentration and increasing temperature. Similarly, the luminescence lifetime in Figure 8,  
385 measured at c) 1 °C and d) 45 °C, decreases with increasing chloride concentration and  
386 increasing temperature. Lifetimes with chloride concentrations greater than 5 mM show a  
387 biexponential decay, indicating the presence of two uranyl(VI) species in solution: the

388 uranyl(VI) aquo ion and the former observed  $\text{UO}_2\text{Cl}^+$  complex. This observation agrees with  
 389 our speciation data obtained at  $-120^\circ\text{C}$ . The complex shows a luminescence lifetime, which is  
 390 at  $25^\circ\text{C}$  much shorter ( $8 \pm 3\text{ ns}$ ) than the lifetime of its fluoride analogue ( $41 \pm 15\ \mu\text{s}$ ).



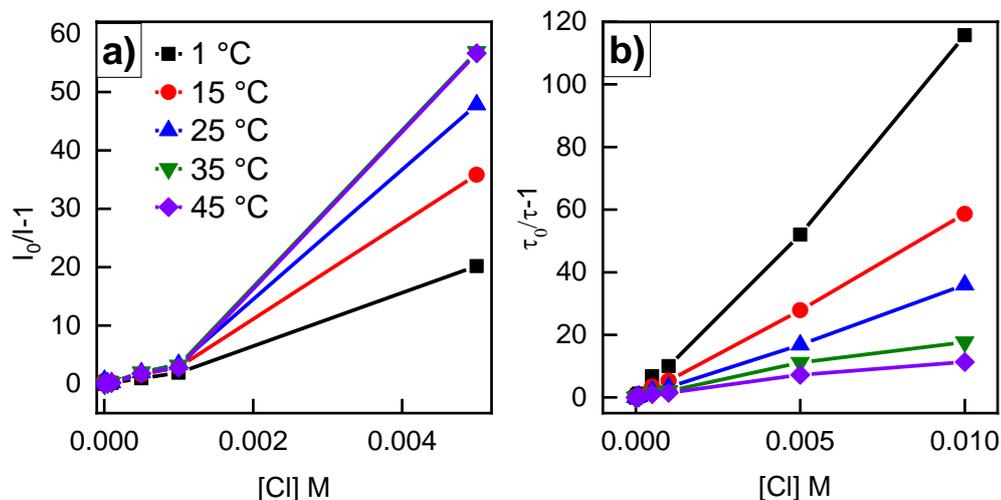
391

392

393 Figure 8: Luminescence spectra of the uranyl(VI) luminescence ( $[\text{U}] = 0.1\text{ mM}$ ) with chloride ( $[\text{Cl}] = 0 - 0.01\text{ M}$ ) at **a)**  $1^\circ\text{C}$   
 394 and **b)**  $45^\circ\text{C}$ . Recorded lifetimes of the uranyl(VI) luminescence intensity of the same samples at **c)**  $1^\circ\text{C}$  and **d)**  $45^\circ\text{C}$  at  
 395  $-\log[\text{H}] = 1$  and  $I = 0.11\text{ M}$ .

396 Generally two trends can be observed from plotting  $I_0/I$  and  $\tau_0/\tau$  against the chloride  
 397 concentration at different temperatures: with increasing temperature a less linear behavior for  
 398  $I_0/I$  against  $[\text{Cl}]$  is observed in Figure 9 a), indicating the existence of primarily dynamic  
 399 quenching at lower temperatures and additionally static quenching at elevated temperatures.  
 400 This is further supported by Figure 9 b), which shows that  $\tau_0/\tau$  against  $[\text{Cl}]$  is getting smaller  
 401 with increasing temperature and the linearity decreases, indicating the presence of static  
 402 quenching besides dynamic quenching at higher temperatures. This is not surprising, since

403 Awasthi et al. have determined the formation of  $\text{UO}_2\text{Cl}^+$  to be an endothermic reaction  
 404 ( $\Delta_r H_m^\circ = 8 \pm 2 \text{ kJ mol}^{-1}$ ), meaning complex formation is favored at higher temperatures.<sup>11</sup>



405  
 406 Figure 9: **a)** Ratios of the static luminescence intensity  $I_0/I$  and **b)** ratios of the luminescence lifetimes  $\tau_0/\tau$  against the chloride  
 407 concentration at 1 to 45 °C.

408 To differentiate between the observed static and dynamic quench processes,  $K_{SV}$  is divided into  
 409 a Stern-Volmer constant for dynamic quenching  $K_d$  and static quenching  $K_s$  according to  
 410 equation (S1). By rewriting the equation as presented in equation (S2), a linear regression  
 411 obtained by plotting the known values for  $\left(\frac{I_0}{I} - 1\right) \cdot \frac{1}{[\text{Q}]}$  against  $[\text{Q}]$  will yield  $K_d K_s$  as the slope  
 412 and  $K_d + K_s$  as the intercept with the y-axis, from which  $K_d$  and  $K_s$  can be derived. The results  
 413 of the linear regression for all investigated temperatures can be found in the SI, Figure S10. The  
 414 obtained values for the dynamic and static quenching are presented in Table S7. By comparing  
 415  $K_d$  with  $K_s$  it becomes obvious, that dynamic quenching is approximately two to five times  
 416 higher than static quenching, meaning that dynamic quenching has a bigger impact on the  
 417 overall quenching process. From the  $K_d$  it is possible to determine the bimolecular quenching  
 418 constant  $k_q$  using equation (6), which describes the possibility of collisional quenching in  
 419 solution to occur.

$$K_d = \tau_0 \cdot k_q \quad (6)$$

420  
 421  $k_q$  was determined for temperatures from 1 – 45 °C as presented in Table S8, which shows that  
 422 the event of a collisional quenching increases exponentially with increasing temperature. At  
 423 25 °C in 0.11 M  $\text{NaClO}_4$ ,  $-\log[\text{H}] = 1.0$ , a  $k_q$  value of  $1.16 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  was found. This value is  
 424 in very good agreement with published values for the  $k_q$  in chloride containing media.  
 425 Yokoyama et al. (1976) found a  $k_q$  value of  $1.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  in 1 M  $\text{HClO}_4$ .<sup>22</sup> A value of

426  $1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was reported in 3 M  $\text{NaClO}_4$  at  $\text{pH} = 3.4$  by Park et al. (1990).<sup>42</sup> As our  
427 investigations were conducted at a significantly lower ionic strength (0.11 M), a lower  $k_q$  value  
428 is expected for the quench process.<sup>43-46</sup> The  $k_q$  value obtained in this work is comparable to  
429 quench constants found for 10 mM U(VI) solutions in 1 M  $\text{HClO}_4$  in the presence of metal ions  
430 in their reduced oxidation states (e.g.  $1.0 \times 10^9$  for  $\text{Fe}^{2+}$ ,  $4.5 \times 10^9$  for  $\text{Tl}^+$ ) and several orders of  
431 magnitude larger than corresponding values for metal ions in their oxidized oxidation states  
432 ( $2.2 \times 10^6$  for  $\text{Fe}^{3+}$ ,  $8.7 \times 10^7$  for  $\text{Tl}^{3+}$ ).<sup>47</sup> This implies that the redox-reactions resulting in U(VI)  
433 reduction to U(V) and/or U(IV) and subsequent oxidation of Fe or Tl are comparable to the  
434 photoinduced “reduction” of U(VI) by the chloride ligand resulting in non-luminescent U(V)-  
435 like excited state.

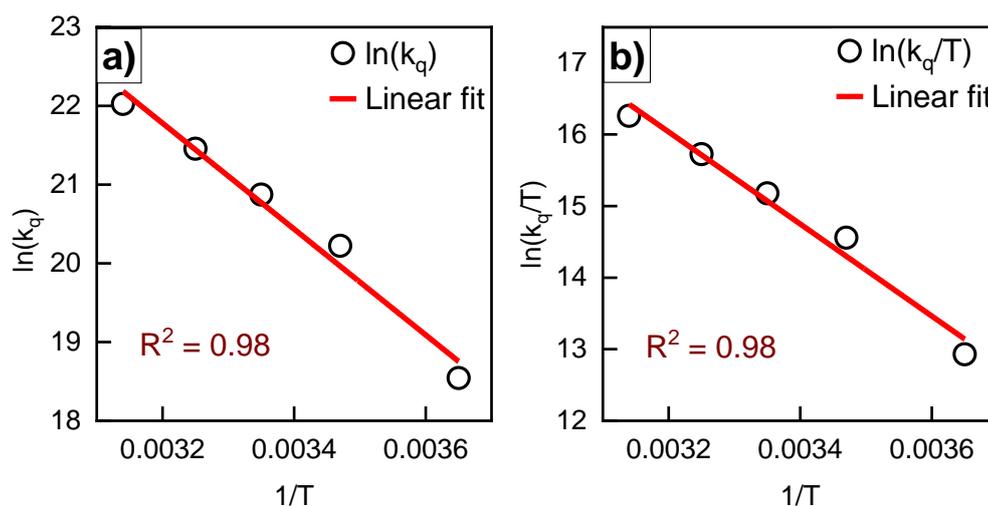
436 Finally, the temperature dependence of  $k_q$  can be used to calculate the activation energy of the  
437 quenching process using the logarithm of the Arrhenius equation (S3).<sup>48</sup> Using a linear fit, the  
438 activation energy  $E_a$  and the pre-exponential factor  $A$  can be obtained from the slope and the  
439 intercept with the y-axis, respectively. The resulting plot is shown in Figure 10 a and results in  
440  $E_a = 55.0 \pm 12.9 \text{ kJ mol}^{-1}$  or  $0.592 \pm 0.134 \text{ eV}$  and  $A = (1.47 \pm 0.09) \times 10^{19} \text{ s}^{-1}$  (Table 5).  $E_a$   
441 describes the amount of energy that is required to form the transition state, called the collisional  
442 complex, between the excited uranyl(VI) and the chloride. The activation energy determined  
443 experimentally in this work is of the same order of magnitude as an estimated value of 0.11 eV  
444 from Yokoyama et al.<sup>22</sup> It is slightly larger than activation energies reported for  $\text{UO}_2^{2+}$  in  
445 aqueous solution containing various concentrations of  $\text{HClO}_4/\text{NaClO}_4$  (see summary in Allsopp  
446 et al. (1979)) which range from 23.9 to 51.9  $\text{kJ mol}^{-1}$ .<sup>49</sup> However, the pre-exponential factor is  
447 almost 6 to 8 magnitudes larger in chloride solution in comparison to other common media  
448 containing e.g. fluoride or perchlorate, which explains the much higher influence of chloride  
449 on the quenching of uranium(VI) luminescence in comparison to aqueous solutions containing  
450 non-quenching ligands such as perchlorate. Further information of the quench process can be  
451 obtained by applying the Eyring equation (S4).<sup>50</sup> Using equation (S4) as a linear fit, the  
452 activation enthalpy  $\Delta H^\ddagger$  can be obtained by the slope and the activation entropy  $\Delta S^\ddagger$  by the  
453 intercept with the y-axis (see Figure 10 b).  $\Delta H^\ddagger$  was calculated to be  $52.5 \pm 13.0 \text{ kJ mol}^{-1}$  or  
454  $0.567 \pm 0.135 \text{ eV}$ , while  $\Delta S^\ddagger$  is  $103.9 \pm 42.8 \text{ J mol}^{-1} \text{ K}^{-1}$  or  $1.1 \cdot 10^{-3} \pm 0.4 \cdot 10^{-3} \text{ eV K}^{-1}$ . Because  
455 the enthalpy and entropy terms are both positive, the energy barrier between the reactants and  
456 the transition state is lowered with increasing temperature. Since the transition state formation  
457 is favored, this directly increases the dynamic quenching of the uranyl(VI) luminescence  
458 through chloride in the system. In two different studies Marcantonatos and Deschaux reported  
459 activation enthalpy and entropy values for the quenching process of uranyl(VI) with  $\text{Ag}^+$  and

460  $\text{TI}^+$ .<sup>46, 51</sup> The activation enthalpy  $\Delta H^\ddagger(\text{Ag}^+)$  was decreasing with increasing ionic strength  
 461 ( $I = 0.019 - 0.1 \text{ M}$ ) from 36.9 to 36.5  $\text{kJ mol}^{-1}$ , while the activation entropy  $\Delta S^\ddagger(\text{Ag}^+)$  increased  
 462 from 2.3 to 4.6  $\text{J mol}^{-1} \text{ K}^{-1}$ . For  $\text{TI}^+$  at  $I = 0.034 \text{ M}$  an activation enthalpy of 13.89  $\text{kJ mol}^{-1}$  and  
 463 entropy of 23.4  $\text{J mol}^{-1} \text{ K}^{-1}$  was determined. The resulting  $k_q$  for both metals were in the same  
 464 order of magnitude as the value obtained for chloride in this work being  $k_q(\text{Ag}^+; I = 0.019 - 0.1 \text{ M}) = (1.96 - 2.51) \times 10^9$  and  $k_q(\text{TI}^+) = 1.6 \times 10^9$ . This shows that while the energy  
 465 barrier  $\Delta H^\ddagger$  for the quenching process with  $\text{Ag}^+$  and  $\text{TI}^+$  might be lower, the entropic term  $\Delta S^\ddagger$   
 466 in systems with chloride is much larger, therefore resulting in similar  $k_q$  values.  
 467

468 Table 5: Determined thermodynamic parameters by applying Arrhenius and Eyring equations.

Arrhenius equation	Pre-exponential factor A [ $\text{s}^{-1}$ ] $(1.47 \pm 0.09) \times 10^{19}$	Activation energy $E_a$ [ $\text{kJ mol}^{-1} \mid \text{eV}$ ] $55.0 \pm 12.9 \mid 0.592 \pm 0.134$
Eyring equation	Activation enthalpy $\Delta H^\ddagger$ [ $\text{kJ mol}^{-1} \mid \text{eV}$ ] $52.5 \pm 13.0 \mid 0.567 \pm 0.135$	Activation entropy $\Delta S^\ddagger$ [ $\text{J mol}^{-1} \text{ K}^{-1} \mid \text{eV K}^{-1}$ ] $103.9 \pm 42.8 \mid 1.1 \cdot 10^{-3} \pm 0.4 \cdot 10^{-3}$

469



470

471 Figure 10: Linear fits of the **a**) logarithmic Arrhenius equation (S3) and **b**) logarithmic Eyring (S4).

472

#### 473 4 Conclusions

474 Using TRLFS we were able to present pure component luminescence spectra for the  $\text{UO}_2\text{F}^+$ ,  
475  $\text{UO}_2\text{F}_2$ ,  $\text{UO}_2\text{F}_3^-$  and  $\text{UO}_2\text{F}_4^{2-}$  complexes at 25 °C in the aqueous uranyl(VI) fluoride system.  
476 From the pure component spectra it was possible to obtain the species distribution, from which  
477 we determined the  $\log K^*$  values at 25 °C and  $I = 1 \text{ M}$  for the above mentioned complexes for  
478 the first time using TRLFS as an analytical method and performed an extrapolation to obtain  
479 the  $\log K^0$  values at infinite dilution. The obtained results were comparable to the latest existing  
480 literature values determined by other analytical methods, which investigated the same  
481 uranyl(VI) fluoride ( $\text{UO}_2\text{F}_n^{2-n}$ ;  $n = 4$ ) complexes. A spectrum of a uranyl(VI) complex with  
482 five coordinating fluoride has yet to be obtained using TRLFS and is of interest for future  
483 investigations. In the uranyl(VI) chloride system spectral deconvolution of luminescence  
484 spectra yielded the very first pure component luminescence spectra of  $\text{UO}_2\text{Cl}^+$  at  $-120 \text{ °C}$  and  
485 at  $1 \text{ °C}$ . The uranyl(VI) chloride complex shows luminescence bands in the same region as the  
486  $\text{UO}_2\text{F}^+$  complex, indicating a similar complex structure between uranyl(VI) and the two halides,  
487 although the  $\log K$  values show that  $\text{UO}_2\text{F}^+$  is more stable than the  $\text{UO}_2\text{Cl}^+$  complex. Knowledge  
488 of the pure component spectrum of  $\text{UO}_2\text{Cl}^+$  will provide valuable information for future  
489 investigations of the uranyl(VI) luminescence in chloride bearing systems. The slope analysis  
490 of the uncorrected U(VI)-chloride species distribution showed that the stoichiometry of the  
491 formed complex corresponds to the  $\text{UO}_2\text{Cl}^+$  complex. This is the first time information of a  
492 complex stoichiometry has been derived at liquid nitrogen temperatures. This shows that the  
493 challenge of chloride quenching of uranyl(VI) can be overcome by freezing the sample,  
494 allowing investigations of uranyl(VI) luminescence in (natural) media containing chloride.  
495 More work, however, is required to be able to obtain reliable relative luminescence quantum  
496 yields (LI factors) of frozen samples to be used in the correction of the species distribution and  
497 the subsequent calculation of the complexation constant using slope analysis.

498 Temperature dependent studies in the uranyl(VI) fluoride system showed, that at higher  
499 temperatures uranyl(VI) fluoride complex formation is favored. This generally leads to an  
500 increase in luminescence intensity due to replacement of quenching water molecules with  
501 fluoride. Hence, no indications for temperature-dependent quenching for uranyl-fluoride  
502 complexes could be established. Further, the uranyl(VI) chloride system was investigated at  
503 different temperatures using Stern-Volmer analysis. The chloride induces an overall strong  
504 quenching of the uranyl(VI) luminescence, caused by static and dynamic quenching effects.  
505 Static quenching increases at higher temperatures due to enhanced complexation taking place  
506 in solution. The contribution of the dynamic quenching to the overall quenching effect is two

507 to five times larger than the contribution of the static quenching. From the  $K_d$  values we  
508 calculated the bimolecular quenching constants  $k_q$  at 1 to 45 °C, which show an exponential  
509 increase with increasing temperature. Applying the Arrhenius and the Eyring equations we  
510 obtained the activation energy, activation entropy, and activation enthalpy of the dynamic  
511 quench process. The results show that with increasing temperature the energetic barrier between  
512 the transition state of the excited uranyl(VI) and chloride is lowered, therefore increasing the  
513 quenching effect.

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