ESRF	<b>Experiment title:</b> Photocleavage of Uranium-DNA complex	Experiment number: 20–01–749
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## **Report:**

Photoexcited uranyl(VI) is a mild oxidant and can decompose various biological substances including DNA. This reaction constitutes another environmental risk of uranium in addition to radiotoxicity and chemotoxicity. Although hydrogen abstraction from DNA sugar backbone by photoexcited uranyl(VI) is widely believed to be the key reaction in uranyl(VI)–

mediated photocleavage of DNA, our density functional theory (DFT) calculations have shown that direct charge transfer from DNA photoexcited uranyl(VI) can be an to alternative pathway that leads to DNA strand break. In the proposed experiments, we investigated uranium oxidation state and uranyl binding mode in uranyl-DNA complex with and without illumination. We initially assumed that uranyl(VI) binds to DNA through phosphate backbone of the DNA and upon illumination U(VI) will be reduced to U(V) and eventually to U(IV).

Samples are mixture of uranyl(VI) solution and genomic salmon testes DNA



**Fig.1** U– $L_{III}$  edge EXAFS spectra of illuminated (even numbers) and non-illuminated (odd numbers) samples of uranium–DNA mixture which show very similar feature to those of uranyl–sugar phosphate complexes.

(Calbiochem) in acetate buffer. Uranium  $L_{III}$  edge EXAFS spectra of the samples were measured in fluorescence mode. Fig.1 shows spectra of all 8 samples which have been measured. The samples with odd number are without illumination and the samples with even number are with illumination. Samples 1–4 are in shock–frozen states, samples 5–8 are aqueous samples. Uranium concentration were varied from 1 to 5 mM and DNA/U ratio was kept at 4 to 5. The pH of the samples are between 5.97 and 6.30 where maximum effect of photoillumination is expected, according to previous studies. We found that there is no oxidaition state change in illuminated and non–illuminated samples and uranium oxidation state remain as U(VI) after illumination. The uranium–DNA EXAFS spectra (both

illuminated and non-illuminated) are very similar to those of uranium-sugar phosphate complexes which have been measured previously. We can thereby conclude that uranium is bound to phosphate group of DNA.