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Radiation-induced debromination monitored by polarized X-ray absorption spectroscopy

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The application of radiosensitizing halogenated nucleotides for therapeutic cancer treatments using synchrotron X-rays is currently under investigation. It is believed that the primary radiation-induced reaction is a dehalogenation, leading to highly reactive radical species. In a different light, halogenated nucleic acids have also been used in macromolecular crystallography to solve the structure of nucleic acids by anomalous scattering techniques. However, for brominated compounds, a relative moderate X-ray dose can induce sufficient debromination to prevent structure determination.

In the present study, we show that polarized absorption spectra on single crystals can yield useful information about radiation-induced reactions. Polarization effects in X-ray absorption spectra recorded on oriented single crystals enable an enhanced detection of features occurring in certain crystal and/or molecular directions. We present here time-resolved polarized X-ray absorption measurements taken on a single crystal of a brominated 23-nucleotide RNA fragment corresponding to the dimerization-initiation site (DIS) of HIV-1(Lai) genomic RNA. The radiation-induced dissociation of the bromine atom from the nucleotide is concomitant with a change in symmetry of the immediate chemical environment of the Br atoms (from highly anisotropic to spherically symmetric). This symmetry change manifests itself as a change of linear X-ray dichroism near the Br *K*-edge.

These measurements show that the nature and the progress of the radiation-induced debromination reaction can be followed easily by absorption or fluorescence measurements, especially if the polarization direction is nearly parallel to the C-Br bonds. Since this type of spectra can be easily and quickly recorded, polarized X-ray absorption emerges as a useful tool for studying radiation-induced reactions in the solid state and for monitoring radiation damage in macromolecular crystallography.

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A comparative UV-Vis and EXAFS investigation of the coordination of the uranyl ion UO_2^{2+} in solution

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The identification of uranyl complexes in solution is not always straightforward. Unlike crystal structures, which can be revealed by X-ray diffraction, the structure of solution species could only be indicated in the past by means of spectroscopic techniques (UV-Vis absorption spectroscopy, luminescence, magnetic circular dichroism). This kind of methods demonstrated the existence of a uranyl tetrachloro complex $[\text{UO}_2\text{Cl}_4]^{2-}$ with D_{4h} coordination symmetry and a uranyl trinitrato complex $[\text{UO}_2(\text{NO}_3)_3]^-$ with D_{3h} symmetry in solution, based on their characteristic absorption spectra. Nowadays, limited structural parameters of solution species can be determined using Extended X-ray Absorption Fine Structure (EXAFS). The complex formation of the uranyl ion UO_2^{2+} with small inorganic ligands like Cl^- and NO_3^- in non-aqueous solution is investigated using U L_{III} EXAFS spectroscopy and UV-Vis absorption spectroscopy. Both techniques confirm the existence of a $[\text{UO}_2\text{Cl}_4]^{2-}$ limiting species with D_{4h} symmetry as well as a $[\text{UO}_2(\text{NO}_3)_3]^-$ limiting species with D_{3h} symmetry in solution. The distances in the U(VI) coordination sphere of $[\text{UO}_2\text{Cl}_4]^{2-}$ are $\text{U-O}_{\text{ax}} = 1.77 \pm 0.01 \text{ \AA}$ and $\text{U-Cl} = 2.68 \pm 0.01 \text{ \AA}$ [1]. For $[\text{UO}_2(\text{NO}_3)_3]^-$ the distances in the U(VI) coordination sphere are $\text{U-O}_{\text{ax}} = 1.77 \pm 0.01 \text{ \AA}$ and $\text{U-O}_{\text{eq}} = 2.49 \pm 0.01 \text{ \AA}$. The U-N distance of $2.94 \pm 0.01 \text{ \AA}$ points at a bidentate coordination of the nitrate group [2].

[1] Servaes, K.; Hennig, C.; Van Deun, R.; Görrler-Walrand, C. *Inorg. Chem.* 2005, 44, 7705.

[2] Servaes, K.; Hennig, C.; Van Deun, R.; Görrler-Walrand, C. submitted to *J. Am. Chem. Soc.*