The benefits of Cu Kβ radiation for the SC-XRD of crystalline sponges

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Motivation

Metal-organic frameworks inherit difficulties for X-ray structure determination such **disorder**, **diffuse solvent content** and **sample decay** upon elucidation. All of these problems limit the capabilities of the Crystalline Sponge (CS) method introduced by Fujita *et al.* in 2013.[1] As several improvements are made for the process of preparation, crystallisation and measurement,[2] we approached these problems employing the wavelength of Cu Kβ radiation (λ = 1.39222 Å).[3]

Cu Kβ radiation

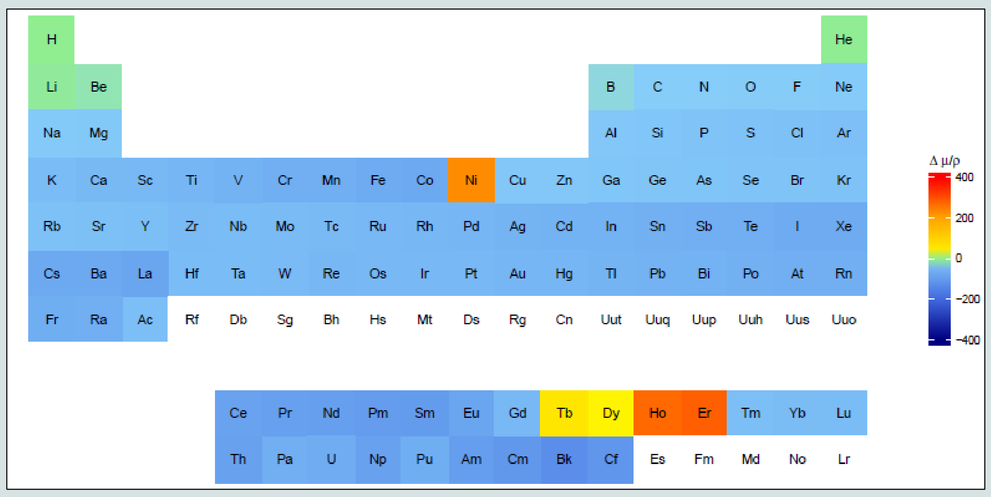

Fig. 1: Differences in elemental mass attenuation coefficients between Cu Kα and Cu Kβ radiation.[4]

Cu Kβ radiation is the second line in the copper emission spectrum and can be obtained at a standard Cu anode source by replacement of the mirror optics. Even though a lower intensity output of 1:8 compared to Cu Kα, the wavelength shows significant advantages regarding resolution, absorption (Fig. 1) and peak-splitting (Fig. 2). These are the key properties of a wavelength for good (MOF) structure elucidation.

Therefore, three comparison experiments were performed on two Fujita-type sponge crystals $[(ZnX_2)_3 \cdot tpt_2]_n$ (X = Cl, I) containing only solvent or an testing analyte.

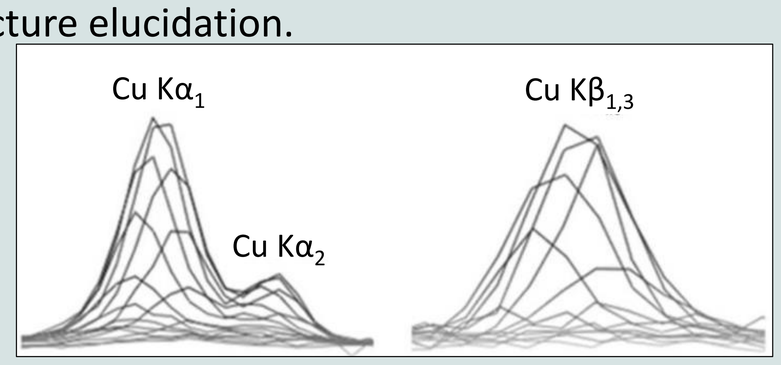

Fig. 2: Reflection profile from the same reflection at 0.81 Å resolution as collected with Cu Kα or Cu Kβ

Results

Cu Kα showed to be advantageous only when comparing measurement times (45h vs. 90h) and I/σ(I) (20.3 vs 14.4) are compared for the chloride species. For the highly absorbing iodine species, the experiments at identical experiment time (13.5h vs 13.5h) resulted in similar I/σ(I) (16.2 vs 13.6). The main reason for lower intensity is the reflection distribution towards high-resolution data, and more and for the iodide species even more strong unique reflections were obtained with Cu Kβ (Fig. 3).

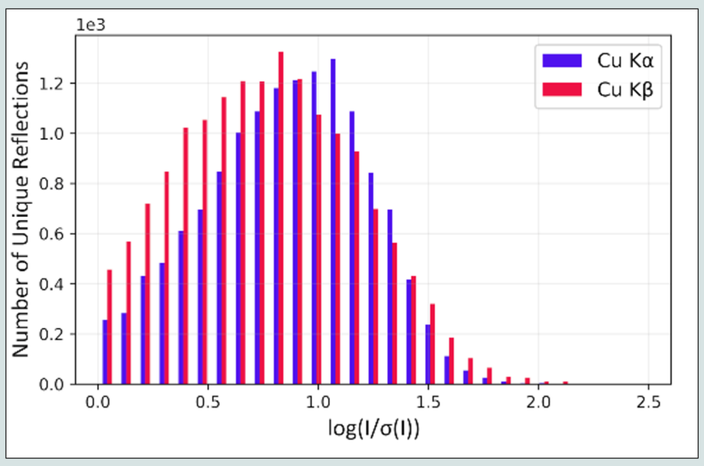

Fig. 3: Intensity distribution of unique reflections obtained

For all measurements, 25% lower absorption coefficient μ was observed with Cu Kβ radiation and up to 38% more unique data was collected due to a higher resolution available (0.80 Å vs 0.72 Å). This allowed for better crystallographic models for the Cu Kβ data sets: The lowest quality parameters R_1 and wR_2, a higher C-C bond precision and less electron density were observed in the models based on Cu Kβ radiation (Fig. 5). Less restraints and no constraints had to be employed for these models (Fig. 4), contrary to the ones based on Cu Kα even when the crystal for the comparison Cu Kβ measurement exhibited non-merohedral twinning.

More solvent positions could be subsequently determined from the residual density map in the Cu Kβ measurements.

All these results provide advantages in the complicated X-ray crystallography of sponge crystals. We hope to extend these insights to the absolute structure determination and to compare Cu Kβ also with Mo Kα radiation.

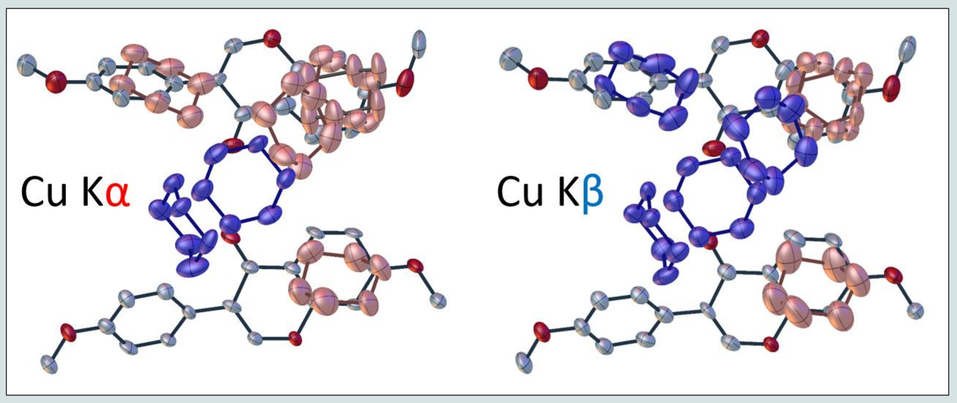

Fig. 4: Different solvent positions over the two 0.5 occupied analyte positions. Blue positions are modelled freely while bronze coloured positions were modelled with restraints or constraints on positional and occupational parameters.

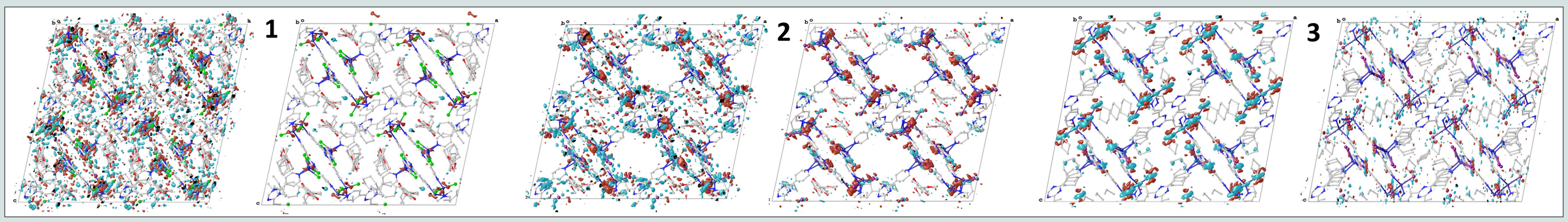

Fig. 5: Residual electron density maps for three measurements with data collected employing Cu Kα (left) or Cu Kβ (right) radiation. Iso-levels were at 0.4 e Å^{-3} (**1**), 1.0 e Å^{-3} (**2**) and 1.2 e Å^{-3} (**3**)

1 Hoshino, M., Khutia, A., Xing, H., Inokuma, Y. & Fujita, M. (**2016**). IUCrJ, 3, 139–151.
2 Zigon, N., Duplan, V., Wada, N. & Fujita, M. (**2021**). Angew. Chem. Int. Ed., 60, 25204–25222
3 Meurer, F., von Essen, C., Kühn, C., Puschmann, H. and Bodensteiner, M. (**2022**). IUCrJ 9, preprint.
4 Mayr, T., Dissertation (**2018**), University of Regensburg, Germany

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