Hydrogen bonding in natrochalcite $NaCu_2(SO_4)_2(OH)\ 2H_2O$ under high pressure

Kurz, Maditha (Institute of Mineralogy and Crystallography, University of Vienna, Wien, AUT);
Ende, Martin (Institute of Mineralogy and Crystallography, University of Vienna, Wien, AUT);
Giester, Gerald (Institute of Mineralogy and Crystallography, University of Vienna, Wien, AUT);
Miletich, Ronald (Institute of Mineralogy and Crystallography, University of Vienna, Wien, AUT)

Natrochalcite and its isotypic compounds have hydrogen bond lengths, which are among the shortest for known inorganic crystals structures (Krickl & Wildner, 2007). Especially for natrochalcite at ambient pressure neutron diffraction experiments have shown a very short "double-well low-barrier" hydrogen bond between O_4 and O_4', connected by a symmetry element, as well as a short asymmetric hydrogen bond between O_4 and O_2 (Chevrier et al., 1993). Low-temperature or high-pressure behaviour of these extremely strong hydrogen bridges are not yet known. The change in pressure or temperature can lead to the formation of an even shorter "single-well no-barrier" hydrogen bond, which is known e.g. for $K_3H(SO_4)_2$ below 100 K (Perrin & Nielson, 1997). Furthermore, such a single-well no-barrier hydrogen bond was not characterized with Raman spectroscopy so far.

With the help of a diamond anvil cell and several crystals (around 40x40x60 μm^3 in size), natrochalcite was investigated by in-situ pressure increase using a Horiba Jobin Yvon LabRAM-HR 800 Raman spectrometer, a Bruker Tensor 27 FTIR spectrometer as well as a Stoe StadiVari single-crystal X-ray diffractometer with micro source and PILATUS detector. The investigated pressure range is within 0.0001-10 GPa and the spectral region is between 40 cm-1 (400 cm-1 for FTIR) and 4000 cm-1.

In contrast to first X-ray diffraction results, which suggest continuously shrinking O_4-O_4 and O_4-O_2 distances, two discontinuities possibly due to phase transitions can be seen around 2 and 6 GPa. This is visible in the lattice vibrations, the vibrational bands of Na-O/Cu-O polyhedra, in the sulfate stretching and bending vibrations, as well as in the hydrogen stretching vibrations, producing shorter and longer hydrogen bonds.

References:

Chevrier, G., Giester, G., Zemann, J. (1992); Neutron refinements of NaCu2(H3O2)(SO4)2 and RbCu2(H3O2)(SeO4)2: Variation of the hydrogen bond system in the natrochalcite-type series, Zeitschrift für Kristallographie, 206, 7-14.

Krickl, R., Wildner, M. (2007): Crystal chemistry of synthetic Co- and Ni-analogues of natrochalcite - the shortest known hydrogen bonds among mineral-type compounds. Part I: Single-crystal X-ray structures. European Journal of Mineralogy, 19, 805-816.

Perrin, C.L., Nielson, J.B. (1997): Strong Hydrogen Bonds in Chemistry and Biology, Annual Review of Physical Chemistry, Vol. 48:511–44.