Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for Disorder in the Hydrogen-atoms Uninvolved in Hydrogen Bonds in a Metal-Organic Framework

M. Viswanathan*

School of Physics and Astronomy, Queen Mary University of London, London E1 4NS, United Kingdom.

E-mail: viswanathan.mohandoss@outlook.com;viswanathan@qmul.ac.uk

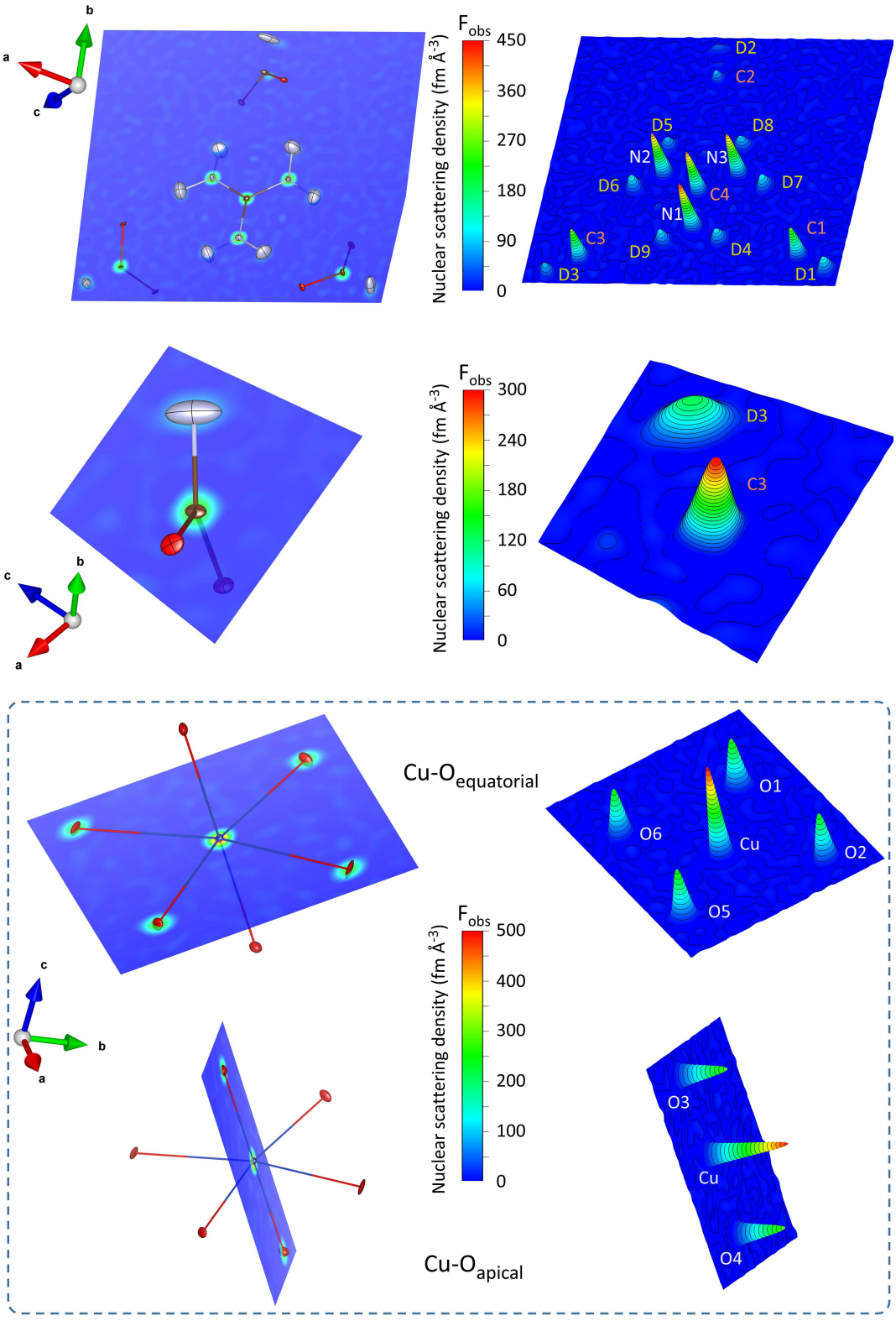

Figure 1: Fourier maps of CuGF, showing guanidinium, formate, and metal-oxygen octahedra, for the data collected at 30 K.

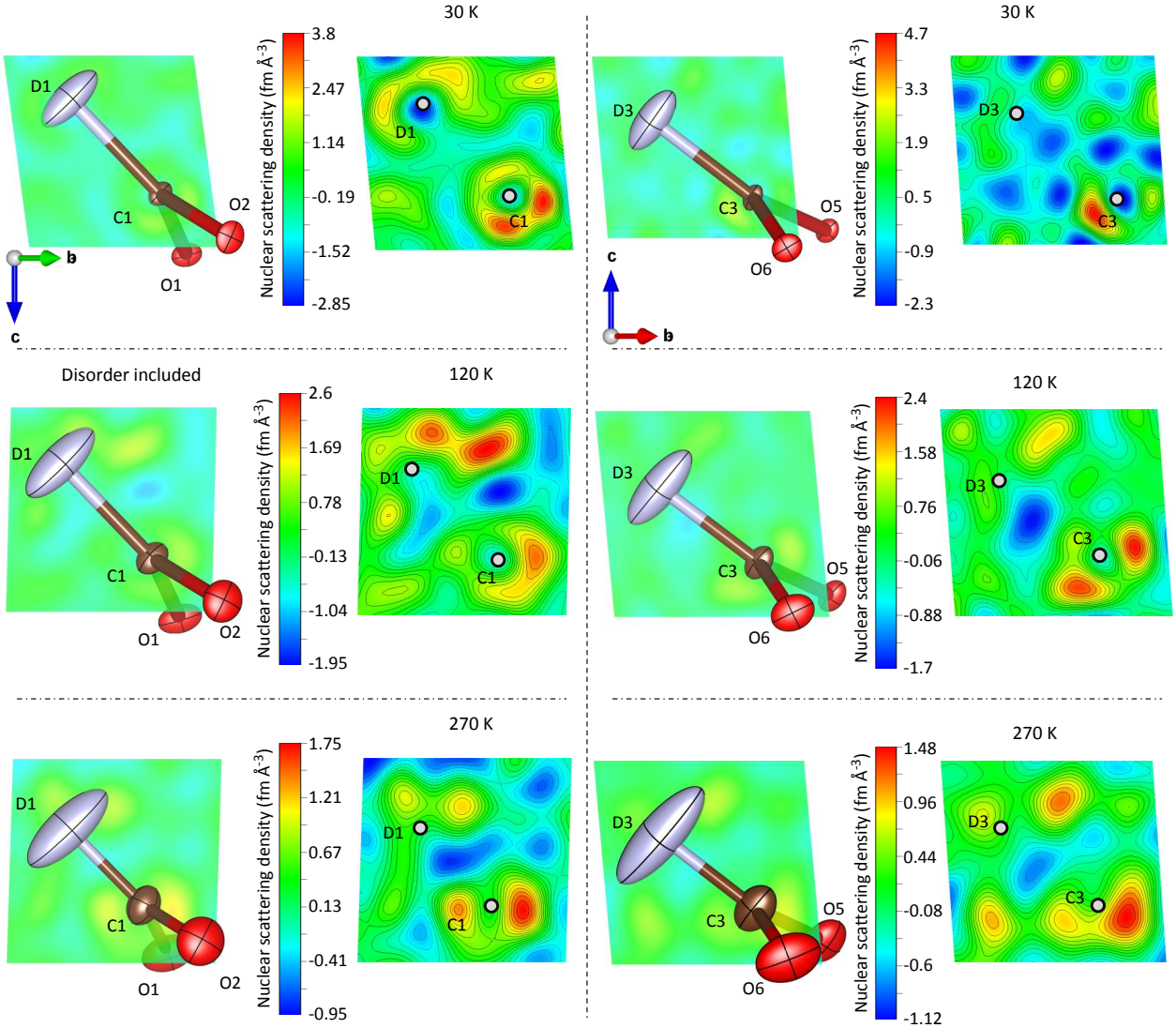

Figure 2: Difference Fourier maps showing C1-D1 (left) and C3-D3 (right) in CuGF at various temperatures, confirming no disorder.

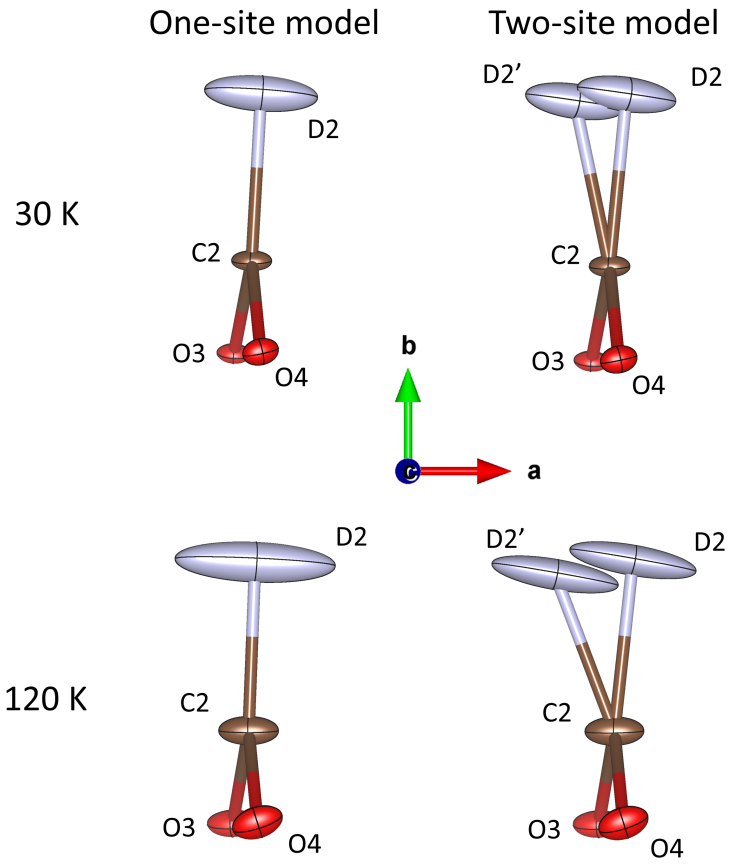

Figure 3: D2 refined as one-site and as two-site model with the thermal ellipsoids at 50% probability. At 30 K, $R_{\mathrm{all}} = 0.0814$ (one-site model), 0.0812 (two-site model); at 120 K, $R_{\mathrm{all}} = 0.0810$ (one-site model), 0.0806 (two-site model)

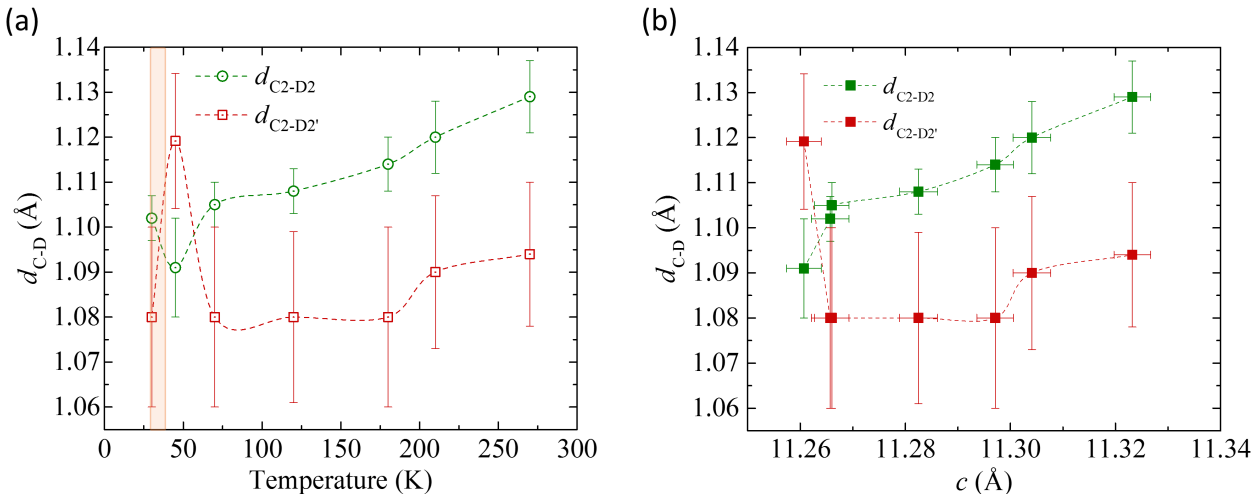

Figure 4: (a, b) shows the intra-formate proton distance, as a function of temperature and c-axis.

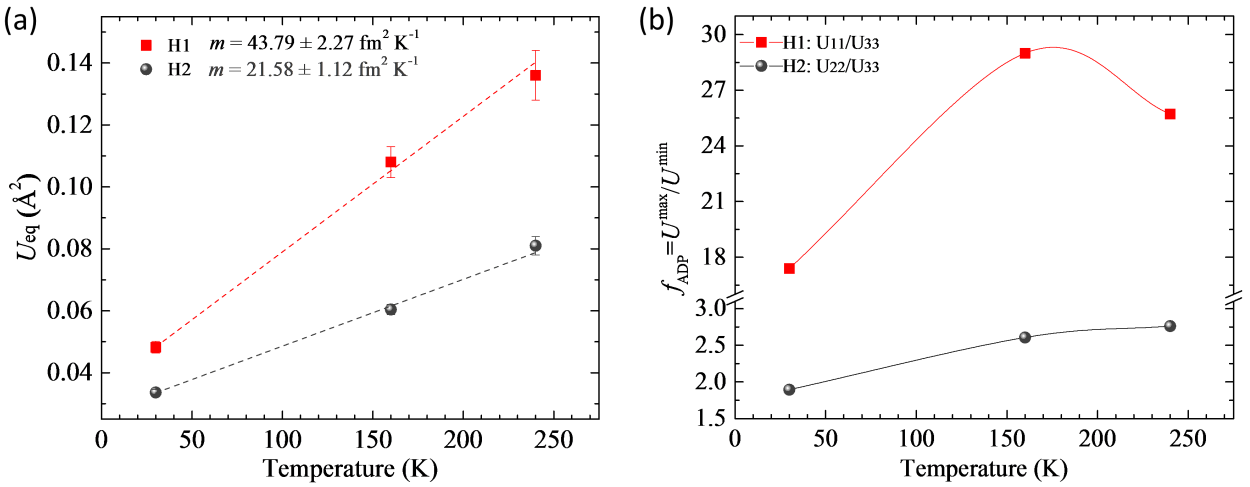

Figure 5: (a) Temperature dependence of average thermal displacements, with H1 featuring larger values than the other '*formato*-hydrogen': H2. (b) The larger anisotropic nature of D2 is revealed by the ratio of the maximum to minimum displacement, indicating a possible disorder in H1, whilst not in H2.

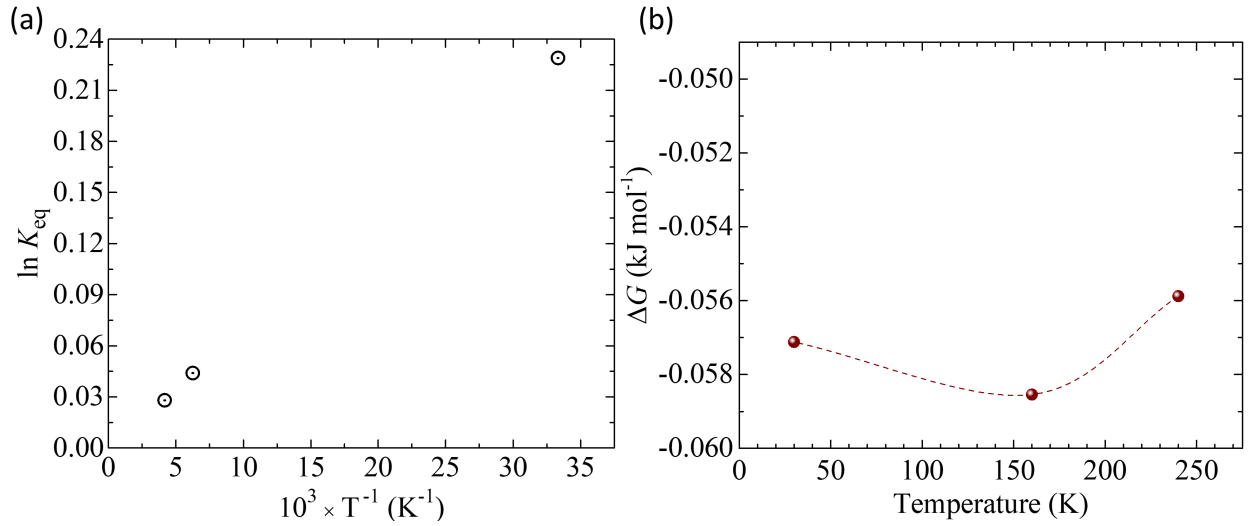

Figure 6: (a) van't Hoff plot for the site-occupancy factor of the disordered hydrogen; (b) corresponding change in Gibb's free energy.