

Dynamically disordered hydrogen bonds in the hureaulite-type phosphatic oxyhydroxide $\text{Mn}_5[(\text{PO}_4)_2(\text{PO}_3(\text{OH}))_2](\text{HOH})_4$

A. Hartl,^{1,2} F. Jurányi,³ M. Krack,⁴ P. Lunkenheimer,⁵ A. Schulz,⁵ D. Sheptyakov,³ C. Paulmann,⁶ M. Appel,⁷ and S.-H. Park^{1, a)}

¹⁾Department of Geo- and Environmental Sciences, Section of Crystallography, Ludwig Maximilian University (LMU) Munich, Theresienstraße 41 C, 80333 Munich, Germany

²⁾Paul Scherrer Institute (PSI), Forschungsstrasse 111, 5232 Villigen, Switzerland

³⁾Laboratory for Neutron Scattering and Imaging, PSI, CH-5232 Villigen PSI, Switzerland

⁴⁾Laboratory for Materials Simulations, PSI, Forschungsstrasse 111, CH-5232 Villigen PSI, Switzerland

⁵⁾Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, Universitätsstraße 1, 86159 Augsburg, Germany

⁶⁾Institute of Mineralogy and Petrography, University of Hamburg, Grindelallee 48, 20146 Hamburg, Germany

⁷⁾Institut Laue-Langevin (ILL), 71 Avenue des Martyrs, 38000 Grenoble, France

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We report the temperature evolution of hydrogen bond (HB) chains and rings in $\text{Mn}_5[(\text{PO}_4)_2(\text{PO}_3(\text{OH}))_2](\text{HOH})_4$ to reveal conduction pathways based on difference Fourier maps with neutron- and synchrotron X-ray diffraction data. Localized proton dynamics for the five distinct hydrogen sites were observed and identified in this study. Their temperature evaluation over ten orders of magnitude in time were followed by means of quasielastic neutron scattering, dielectric spectroscopy and *ab initio* molecular dynamics. Two out of the five hydrogen sites are geometrically isolated and not suitable for long-range proton conduction. Nevertheless, the detected dc conductivity points to long-range charge transport at elevated temperatures, which occurs most likely 1) over H4-H4 sites between semihelical HB chains (interchain exchanges); 2) by rotations of O1-H1 and site-exchanging H4-O10-O5 groups along each semihelical HB chain (intrachain exchanges). The latter dynamics freeze into a proton-glass state at low temperatures. Rotational and site-exchanging motions of HOH and OH ligands seem to be facilitated by collective motions of framework polyhedra, which we detected by inelastic neutron scattering.

I. INTRODUCTION

Exploring efficient and sustainable compounds for energy storage and conversion in batteries and fuel cells, there is an ecologically- and economically-friendly approach to use the lightest element hydrogen as the mobile species in electrochemical systems.¹ Several proton conductors exhibiting high ionic conductivity under ambient conditions have been proposed in recent studies.^{2,3} Particularly, solid acids have been considered as promising proton conductors^{4–7} because they can enter a super-protonic state with an ionic conductivity value of 10^{-2} S·cm⁻¹ at room temperature.⁸ Among them, by considering high thermal stability and chemical flexibility,^{4,9} phosphatic oxyhydroxide minerals can serve as prototype matrices for conducting protons according to the concept of dynamically disordered hydrogen bonds (DDHBs), where charge transport proceeds via conducting protons of hydrogen bonds (HBs), e.g., CsH_2PO_4 ^{10,11} and KH_2PO_4 .^{12,13} It is, however, rare to find related research that goes beyond time-averaged data in order to ex-

plain the underlying proton conduction mechanisms concretely. Furthermore, the concerted behavior of protons and its "host lattice" needs to be explained under several conditions in order to understand and apply the complex mechanisms for charge transport via protons. The current study is dedicated to quantitatively elucidate time and length scales of various proton motions over HB-chains and -rings in a manganese phosphatic oxyhydroxide, $\text{Mn}_5[(\text{PO}_4)_2(\text{PO}_3\text{OH})_2](\text{HOH})_4$ (space group: C2/c; Z = 4) (denoted as Mn-hureaulite hereafter), based on the successful synthesis and characterization of pure Mn-hureaulite samples.¹⁴

Our recent neutron powder diffraction study of deuterated Mn-hureaulite ($\text{Mn}_5[(\text{PO}_4)_2(\text{PO}_3\text{OD})_2](\text{DOD})_4$) showed that pentamers of edge-sharing $(\text{Mn}(\text{O},\text{DOD})_6)$ octahedra comprise complex cross spin-canting configurations.¹⁵ Those Mn-pentamers are connected to each other via $\text{P}(\text{O},\text{OD})_4$ tetrahedra. As a result, this octahedral-tetrahedral framework features a one-dimensional 8-membered ring (8MR) channel system running along the crystallographic c axis and cage-like pores with a small 4MR-opening, as highlighted in Fig. 1. In the hureaulite-type compounds, protons are structurally bonded to the framework polyhedra as HOH or OH ligand groups. When describing HBs in its deuterated form, there are two facing D2-O9-D3

^{a)}Author to whom correspondence should be addressed; sohyun.park@lmu.de

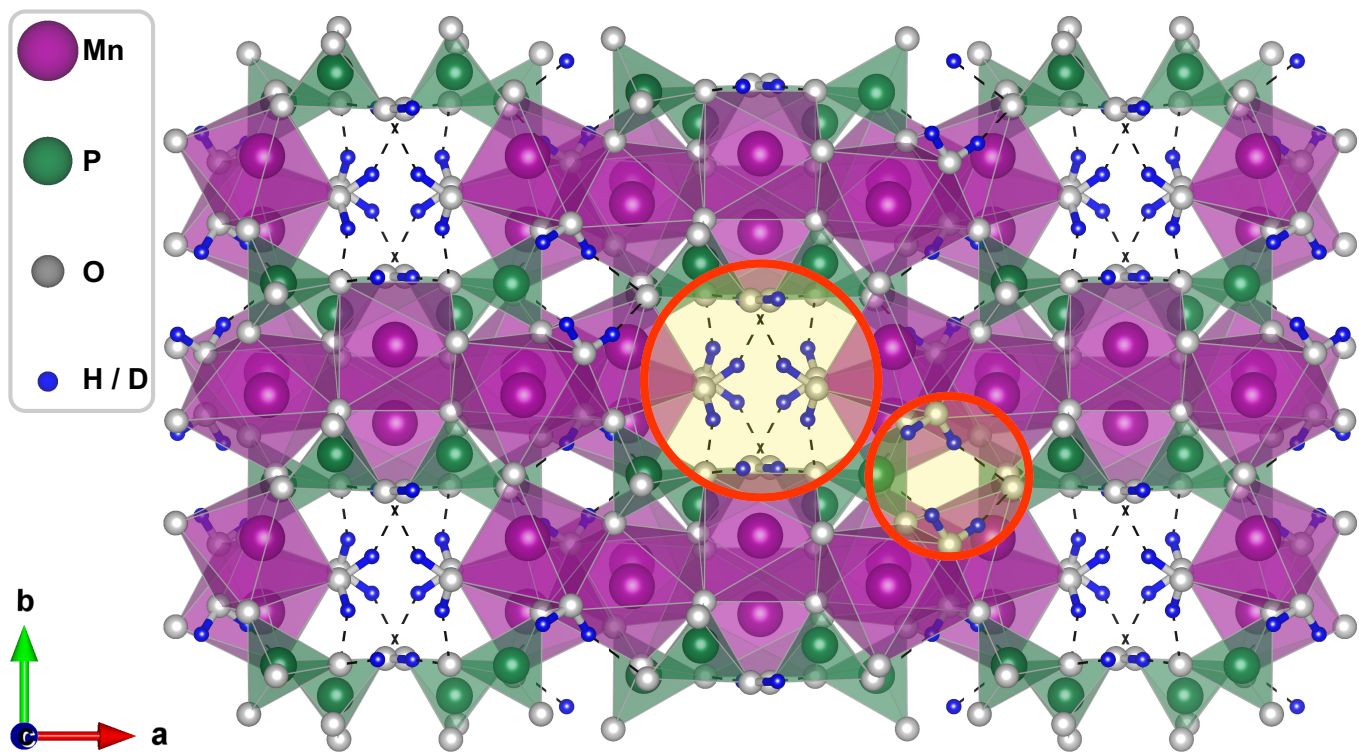


FIG. 1. Structure of deuterated Mn-hureaulite at 12 K¹⁴ with emphasis on the HB system. The octahedral-tetrahedral framework, built out of $\text{Mn}(\text{DO},\text{DOD})_6$ (pink) and $\text{P}(\text{O},\text{OD})_4$ (green), features one-dimensional 8MR-channels running along the c axis. Each channel contains an enantiomorphic pair of semihelical HB chains (large red circle). Besides, there are small HB rings in cage-like pores (small red circle). Mn, P, O and D atoms are illustrated in pink, green, pale grey, and blue, respectively, along with HBs highlighted by broken lines in black.

groups to make a small HB ring in the confined cage while D1-O1 and D4-O10-D5 groups form one pair of semihelical HB chains in each 8MR-channel. Their configurations give rise to several possible pathways for site-exchanging protons, as shown in Fig. 2: rotations and site-exchanges at O1-D1, D4-O10-O5 and D2-O9-D3 [Figs. 2(a) and (d)]; intrachain-exchanges between O1-D1 and D4-O10-O5 groups [Fig. 2(a)]; interchain-exchanges via D4-D4, D5-D5, and D4-D5 between two semihelical chains [Fig. 2(a-c)]. The dynamic disorder of protons over such sites and routes represents an interesting object for both experimental and

theoretical studies of complex proton behaviors.^{3,16–23} Furthermore, according to Baranov,⁸ hureaulite shows a high theoretical intrinsic charge carrier concentration of $N_p = 2.629 \times 10^{22}$ protons per cm^3 , exceeding the boundary value $N_{p,\text{limit}} = 10^{18}$ protons cm^{-3} between high and low proton mobility.²⁴ This motivated us to resolve a consistent picture of charge transport via protons over the DDHBs in this complex system by diffraction and spectroscopy tools in combination with density functional theory (DFT) based *ab initio* molecular dynamics (AIMD) simulations performed with the CP2K code, as described below.

II. METHODS

A. X-ray single crystal diffraction (XSD)

XSD was applied to monitor the response of the framework of Mn-hureaulite to temperature changes. For this purpose, single crystals of the title compound were obtained via hydrothermal synthesis, as described in the previous study.¹⁴ Each crystal sample with a size of $10 \times 20 \times 100 \mu\text{m}^3$ was selected and attached to silica glass

wires using a double-component adhesive and alumina paste for low-temperature (LT) and high-temperature (HT) XSD, respectively.

A series of LT-XSD was performed between 100 and 295 K on a four-circle κ single crystal diffractometer (Gemini A Ultra) equipped with a 2D charge-coupled detector (135 mm active area diameter, Atlas) from Rigaku-Oxford Diffraction. LT-XSD data collection was carried out with ($\text{MoK}_{\alpha 1}$) radiation [graphite(002) monochromator] in a crystal-to-detector distance of 60 mm with

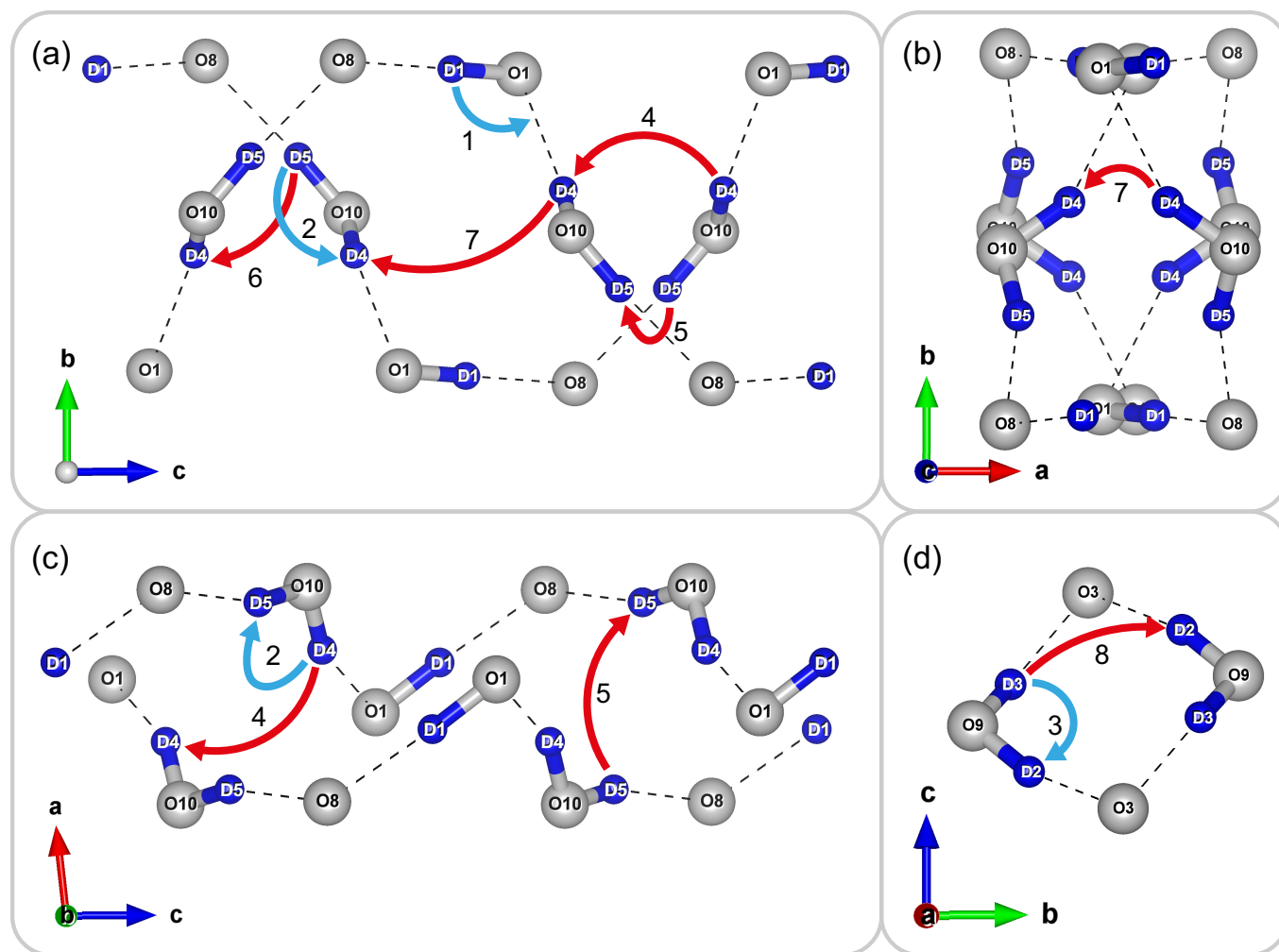


FIG. 2. Representative sections of HBs in Mn-hureaulite (deuterated): (a) a pair of two HB chains projected on the (b-c) plane; (b) through the 8MR-channel opening; (c) projected on the (a-c) plane; (d) a HB-ring of two D2-O9-D3 groups located within small 4MR cages. There are several possible routes for locally limited, rotational site-exchange (in blue), as well as inter- and intrachain exchanging motions (in red): 1. rotating O1-D1 group along the HB chain; 2. local rotation of D4 and D5 in a D4-O10-D5 group; 3. rotation of D2 and D3 in a D2-O9-D3 group; 4. interchain exchange of D4 and D4 between semihelical HB chains; 5. interchain exchange of D5 and D5 between two semihelical HB chains; 6. interchain motion cross over D4 and D5; 7. long-range proton dynamics over D4-D4 pairs; 8. hopping motions between two D2-O9-D3 groups.

a step size of $\Delta(\phi) = 1^\circ$. The temperatures was controlled using an open nitrogen cryostat (Cryojet 02, Oxford Instruments) ($\Delta T < \pm 0.1$ K). Data collection and reduction were performed using the software package CrysAlisPro.²⁵ Absorption corrections were done using the SCALE3 ASPACK scaling algorithm implemented in CrysAlisPro.

HT-XSD was conducted at the experimental station P24 at the synchrotron radiation source PETRA III at Deutsches Elektronen-Synchrotron (DESY). HT-XSD data sets were collected between 300 and 500 K every 50 K in sequence at elevated temperatures on a four-circle κ single crystal diffractometer using a wavelength of $\lambda = 0.49594$ Å [Si(111) monochromator]. The temperatures were set via a nitrogen gas stream heater. All HT-XSD data were acquired on a 2D Pilatus detector

(CdTe 1M) with a crystal-detector distance of 60 mm in ω/ϕ scans having a scan width of 1.0° . Raw HT-XSD data were converted to the CCD format of Atlas for integration and reduction processes using CrysAlisPro. Further experimental parameters and details on refinements of LT- and HT-XSD conducted in this study are given with agreement factors in Supplementary A and B.

Structure refinements with XSD data were carried out by the least-squares method against the squared structure factor (F^2) with an option of difference Fourier (ΔF) synthesis, implemented in the Jana2006 program.²⁶ An initial starting model delivered by Rietveld analyses using high-resolution neutron powder diffraction (HRNPD) data at room temperature in our previous study¹⁴ was used for structure refinements with LT- and HT-XSD data sets collected at room temperature. The refined

models were used as the successive starting models for further analyses with LT- and HT-XSD data. For each structure refinements, all atomic sites were fixed to be fully occupied because of high correlations between occupancy and atomic displacement parameters in addition to the low X-ray scattering power of light elements. All atomic parameters including anisotropic atomic displacement parameters (ADPs) at Mn, P and O sites, as well as isotropic ADPs at five independent H sites could be refined simultaneously without high correlations (<0.9). The refined atomic parameters are given in Supplementary C along with the obtained interatomic distances and angles in HBs.

B. High-resolution neutron powder diffraction (HRNPD)

We used HRNPD to determine the positions and ADPs of light elements accurately. These experiments have been performed on deuterated Mn-hureaulite because of the pronounced coherent neutron scattering cross section of deuterium (D) in contrast to the huge incoherent neutron scattering cross section of hydrogen (H). Variable-temperature HRNPD data sets allowed us to differentiate between dynamic- and static disorder. Furthermore, the pathways possible for the protonic conductivity can be estimated by inspecting the residual densities of coherent neutron scattering length distribution of D in ΔF maps.

For HRNPD, 1.8 g of deuterated Mn-hureaulite powder was air-tightly closed in a vanadium can ($\varnothing=12$ mm). HRNPD data sets were collected on the instrument HRPT at SINQ, PSI, Switzerland using $\lambda = 1.494$ Å with the medium resolution setup at 150, 250, 350 and 400 K, subsequently.

Rietveld calculations were executed using the program package Jana2006. The background was fitted with a Legendre polynomial of 36 terms. Profile parameters were described by Pseudo-Voigt function, including a preferred orientation of the 110 reflection via the March-Dollase approach.

Large ADPs can result from the depletion of atoms away from their equilibrium sites due to dynamic disorder, but also due to partial occupation. Hence, to prevent high correlations between occupancy and APD parameters, all atomic parameters were refined with full occupations at all atomic sites. Under this condition, all five unique D sites could be refined simultaneously with their anisotropic ADPs at all measuring temperatures. ADPs of O, P and Mn atoms at 150 and 250 K were refined direction-independently only while those of O and P at 350 K could be refined anisotropically. At 400 K, ADPs of the entire atoms including Mn sites could be determined anisotropically without high correlations with good agreement factors (Table I; Fig. 3). All atomic parameters refined with HRNPD data sets are found in Supplementary D.1. The resulting interatomic distances and angles of HBs are given in Table II.

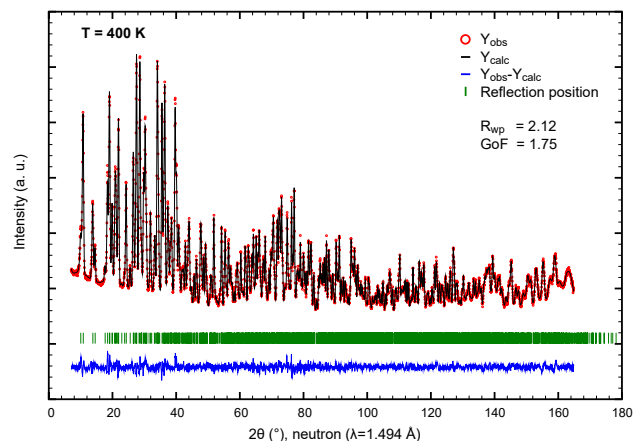


FIG. 3. Representative Rietveld refinement of HRNPD data of deuterated Mn-hureaulite at 400 K with agreement factors. The calculated profile (black line) is well matched to the observed one (red circles), as shown by their low difference profile (blue line). Short bars indicate Bragg reflection positions expected for the atomic structure of Mn-hureaulite in the space group C2/c.

Refinement parameters	150 K	250 K	350 K	400 K
a (Å)	17.58270(19)	17.60582(16)	17.6417(2)	17.6569(2)
b (Å)	9.12138(12)	9.12956(9)	9.14943(13)	9.15958(14)
c (Å)	9.49271(11)	9.49508(9)	9.50268(11)	9.50595(11)
β (°)	96.4215(7)	96.4491(4)	96.4807(8)	96.4912(9)
V (Å ³)	1512.88(3)	1516.52(3)	1524.04(3)	1527.54(3)
Number of model atoms	20	20	20	20
Number of refined parameters	150	156	156	229
R factors (%)				
R (reflections with $I > 3\sigma(I)$)	1.59	1.42	1.47	1.26
wR2 (reflections with $I > 3\sigma(I)$)	2.00	1.72	1.86	1.58
Profile R factors (%)				
GoF	1.69	1.57	1.66	1.72
Rp	2.34	2.05	1.91	1.64
wRp	2.97	2.57	2.41	2.07

TABLE I. Experimental and refinement parameters of HRNPD probed on deuterated Mn-hureaulite. The applied R factors are mathematically expressed in Supplementary B.

C. Neutron spectroscopy

Quasielastic neutron scattering (QENS) was performed to measure the characteristic time and length scales of both local and diffusional motions. Inelastic neutron scattering (INS) was used to obtain the lattice dynamics. QENS and INS data acquisitions were carried out on the time-of-flight spectrometer, FOCUS at SINQ (PSI) with a sample of 0.802(1) g powdered Mn-hureaulite, enclosed in a hollow cylindrical Al sample can. The sample was protonated in order to emphasize the mobile hydrogen atoms of OH and HOH groups via the large incoherent neutron scattering length. For measurements up to 510 K, $\lambda = 6$ Å was used with an energy resolution of 45 μ eV.

Data treatment and analysis was done with the DAVE software.²⁷ In the paramagnetic state of Mn-hureaulite above 6.17 K,¹⁵ the magnetic QENS signal showed no

significant temperature-dependence. Additional QENS signal with comparable intensity appeared above 250 K. Therefore, the 250 K measurement was used as background. The observed QENS signals are given in the supplementary Fig. E.1, where the paramagnetic contribution (and the background) is subtracted using the 250 K data.

A fixed window scan (FWS) between 2 and 483 K was performed on the high-resolution backscattering spectrometer IN16B at ILL, France, using $\lambda = 6.271 \text{ \AA}$ with an energy resolution of $0.75 \text{ } \mu\text{eV}$. Simultaneously, inelastic fixed window scan (IFWS) was recorded with the offset energy of $3 \text{ } \mu\text{eV}$, where the contribution from elastic scattering was small enough. FWS and IFWS data were alternately collected during heating with a rate of 1 K/min (Supplementary F). The data treatment was performed according to the instrument standard software Mantid.

D. Dielectric spectroscopy (DS)

Dielectric spectroscopy allows to probe time scales for changing orientations and dislocations of charge carriers. The measured real part of the capacitance and the conductance allow to evaluate dielectric properties, such as the respective real part of the dielectric constant ϵ' and conductivity σ' .

For DS studies, powder samples of both protonated and deuterated Mn-hureaulite were pressed into compact pellets, and then their top and bottom sides were coated with conductive silver paste. "Low frequency" (LF) dielectric spectra were acquired between 1 Hz and up to several MHz using a frequency response analyzer (Novocontrol Alpha analyzer). Additional data acquisitions in the "high frequency" (HF) range between 1 MHz and 3 GHz were performed employing an impedance analyzer (Keysight E4991B). For this reflectometric technique,²⁸ the sample was placed at the end of a coaxial line so that it bridged the inner and outer conductor. The temperature in the sample cell was controlled using a continuous flow N_2 -gas cryostat (Novocontrol Quatro).

For the correction of $\epsilon'(T)$, an additive factor was applied in the low-temperature (LT) region ($T < 200 \text{ K}$) of the HF data collected with the coaxial technique. The LF spectra were scaled with respect to the HF data due to stray capacitance effects and parasitic capacitance from the geometry of the setup in the frequency response analysis.

E. Ab initio molecular dynamics (AIMD) simulations

The complex, distorted framework polyhedral units and the particular proton sites in Mn-hureaulite made it insufficient to apply molecular dynamics (MD) calculations based on predefined interatomic potentials (force

fields). In addition, the impact of the antiferromagnetic sublattice formed by the Mn atoms cannot be captured by a force field approach. Thus AIMD calculations were executed for this system, where the forces acting on the atoms were calculated based on first principles.²⁹ We took advantage of the efficient implementation of Born-Oppenheimer AIMD within the program package CP2K.³⁰ Its DFT module QUICKSTEP³¹ employs a mixed Gaussian and plane waves basis set. The scalar-relativistic, norm-conserving pseudopotentials of Goedecker-Teter-Hutter (GTH)³²⁻³⁴ for Mn ($3s^2 3p^6 3d^5 4s^2$), P ($3s^2 3p^6$), and O ($2s^2 2p^6$) were used to avoid an explicit consideration of the core electrons. Unless otherwise stated, we employed the short-range double-zeta Gaussian (MOLOPT) basis sets with one set of polarization functions (DZVP-SR)³⁵ which were optimized for the GTH pseudopotentials. All calculations were performed with the spin-polarized implementation of the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional.³⁶ The empirical dispersion correction DFT-D3 of Grimme *et al.*³⁷ for PBE was applied for an improved description of the van der Waals interactions. An electronic density cutoff of 600 Ry and the orbital transformation (OT) method for self-consistent field (SCF) calculations with a convergence threshold of 3×10^{-7} for the wave function gradient was used in all calculations.

In sum, these computational parameters usually showed good agreement with experiment. Indeed, the optimized structure corresponded well to those refined with HRNPD data ($\pm 0.3\%$). Structural relaxations and band gap calculations at 0 K for a single ($1 \times 1 \times 1$) Mn-hureaulite unit cell (156 atoms) with a Γ -centred $4 \times 8 \times 8$ k -point mesh using the VASP code version 5.4.4^{38,39} agreed well with the corresponding CP2K results for a $1 \times 2 \times 2$ supercell (624 atoms). Further technical details about the Mn-hureaulite simulations can be found in Supplementary G.

A $1 \times 2 \times 2$ supercell of the Mn-hureaulite system was initially equilibrated for at least 10 ps within the isobaric-isothermal NpT ensemble at the pressure 1 bar and at the three temperatures 300, 350, and 400 K. The average cell parameters of the last 8 ps from the NpT MD trajectories were then used for the thermalization runs within the canonical ensemble (NVT). Finally, MD runs within the microcanonical ensemble (NVE) were performed which are free of any bias or frequency coupling from a barostat or thermostat. The energy drift along the NVE trajectories was fairly small ($\ll 1 \text{ K/atom}$) indicating a very good quality of these MD runs. The corresponding average temperatures of these NVE MD runs were 301 K, 379 K, and 511 K. The MD runs at 300 K were sampled with a time step of 0.5 fs, whereas the MD runs at the higher temperatures required a shorter time step of 0.4 fs. The program TRAVIS^{40,41} was used for the post-processing of the MD trajectories. The VMD Molecular Graphics Viewer helped for visualization purposes.⁴²

The density of states (DOS) for each characteristic pro-

ton site could be derived by the Fourier transform of the time dependent velocity-velocity autocorrelation function of the corresponding AIMD trajectories.^{43,44} In comparison to simulated Raman modes, this approach took anharmonic effects into account and helped to explain proton-site-dependent contributions to generalized density of states (GVDOS) delivered from INS techniques.

III. RESULTS AND DISCUSSION

A. Structural response to temperature, observed in diffraction studies

1. Thermal responses of the framework

The temperature dependence of the unit cell parameters reveals strongly anisotropic thermal expansion which is along the crystallographic *c* axis distinctively smaller than in the *a* and *b* direction [Supplementary Fig. D.2(a-c)]. This means that the one-dimensional channels running parallel to the *c* axis are widened in the (*a*-*b*) plane, i.e. perpendicular to the semihelical HB chains [Fig. D.2(e) in Supplementary D.3]. As a result, at elevated temperatures, the framework of Mn-hureaulite favors its OH and HOH ligand groups readily mobile towards the channel system. This promotes a distortion of the HB geometry, which can directly impact the long-range and local proton dynamics, e.g. the site-exchanging processes over O1-H1 and H4-O10-OH5 ligands within the 8MR-channel.

Eigenvalues U_i of anisotropic ADPs refined with XSD data (Supplementary C.1) show large values at the oxygen sites particularly for those of H4-O10-H5, O1-H1 and H2-O9-H3 groups. More interestingly, at elevated temperatures, U_3 values of all framework atoms distinctly enlarge in contrast to U_1 and U_2 values (Fig. D.1 in Supplementary). For instances, the "double" acceptor site O10 of the H4-O10-H5 group within the semihelical HB chain shows U_3 being 2.8 times larger than U_1 at 500 K. In contrast, another "double" acceptor site O9 of the H2-O9-H3 HB within the small cage shows much smaller ADP eigenvalues in comparison to O10. These observations indicate dynamic disorder profoundly occurring over the semihelical HB chains.

The thermal response of the entire Mn-hureaulite framework can be discussed with ΔF maps evaluated with XSD data: Once ΔF maps are generated with all atomic sites refined but without H atoms, positive electron density peaks are accumulated at the expected H atom sites below 250 K but smeared out around the semihelical HB-chains at 300 K (Fig. C.1 in Supplementary). They become more diffuse at elevated temperatures, reflecting the DDHB chains for proton dynamic disorder. At the same time, diffuse and positive ΔF densities are observed around the framework polyhedra, as well. This can be explained by superimposed anharmonic ADP terms of Mn, P and O atoms, which

may be a sign for their collective motions remarkably enhanced at $T \geq 300$ K (Fig. C.1). This reminds us of a redistribution of electron density residuals for fast rotating polyhedra in the superionic conductor γ -Na₃PS₄,⁴⁵ where strong electron density residuals were attributed to several possible oxygen positions around the tetrahedrally coordinated phosphorous cations. At $T \geq 300$ K, the electron density residual around the HB-ring within small cages in Mn-hureaulite increasingly redistributes, i.e. from O9 of H2-O9-H3 [related to Type 3 in Fig. 2(d)] towards the opposite oxygen site O3 [related to Type 8 in Fig. 2(d)].

In the following, we trace motions of deuterium atoms (D) occupying five independent sites in the deuterated Mn-hureaulite structure by means of their temperature-dependent ADP eigenvalues accurately determined by Rietveld analyses of the HRNPD data. When comparing these values between 150 and 400 K (Fig. 4), several site- and direction-dependent changes of ADPs are obvious, such as:

1) $U_3 \gg U_2 > U_1$ is valid for all D sites. The commonly strong increase of their U_3 at elevated temperatures points a strong dynamic disorder of HBs along the *c* direction;

2) at 250 K, $U_3(\text{D}_4)$ and $U_3(\text{D}_5)$ are larger than U_3 at the rest D sites, pointing re-orientations within a D4-O10-D5 group (see Type 2 in Fig. 2(a));

3) at 350 K, $U_3(\text{D}_4)$ is dramatically enlarged, accompanied by an increasing $U_3(\text{D}_5)$, as well as $U_2(\text{D}_5)$ and $U_3(\text{D}_1)$. This is an important sign for the onset of intrachain-exchanges over D1 and D4, and maybe also for the onset of interchain-exchanges over D4 and D5 [Type 1, 4 and 5, respectively in Fig. 2(a)];

4) also $U_3(\text{D}_2)$ increases obviously from 350 K to 400 K along with $U_3(\text{D}_3)$, indicating re-orientations within a D2-O9-D3 group confined in a 4MR-cage, and/or the onset of interring-exchanges of a pair of D2-O9-D3 groups. Their motions are connected with Type 3 and Type 8 in Fig. 2(d), respectively;

5) $U_3(\text{D}_4)$ solely keeps profoundly increasing up to 400 K. This corresponds to the site-exchange in Type 4, but also is a hint for high dynamic disorder over D4 sites in an extended path, e.g. Type 7 in Fig. 2(a-b).

2. DDHBs in Mn-hureaulite

XSD probes the electron density of the polarized hydrogen bond and not the nuclear position. Thus, the resulting interatomic distances in HBs are underestimated (Supplementary C.2). For this reason, the role of DDHBs for charge transport properties in the title compound is discussed based on results from HRNPD data analyses. These showed that from 150 K to 400 K the distance $d(\text{D}-\text{O}_A)$ between deuterium (D) and the oxygen acceptor (O_A) increases (Table II). At the same

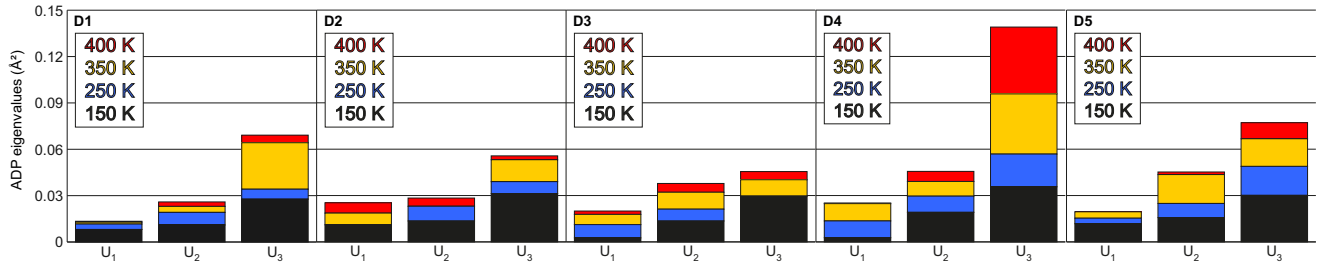


FIG. 4. Comparisons of temperature-dependent eigenvalues of anisotropic APDs at five independent deuterium sites, obtained from HRNPD data of deuterated Mn-hureaulite.

time, the HB angles $\angle(O_D - D \cdots O_A)$ slightly decrease with temperature at $D5 < D4 < D3 < D2 < D1$. Overall, according to T -dependent HB-lengths and -angles, the HBs in Mn-hureaulite correspond to moderate HB strengths and remain stable up to the first dehydration at 538 K.¹⁴

ΔF maps evaluated with HRNPD data revealed diffuse elastic neutron scattering length densities at 350 and 400 K (Fig. 5; Supplementary Fig. D.3 and Fig. D.4). Their maximal intensities are found at seven sites (labeled as X1,...,X7), as shown in Fig. 5(e). These new sites are suitable for deuterium atoms. On the other hand, negative contours at the five independent D sites in ΔF maps are indicative for a depletion of deuterium atoms. Indeed, as their site occupancy parameters were refined without constraints, we obtained 0.96 at D4 and 0.98 at the other D sites. These observations are regarded as a result from dynamic disorder rather than static disorder because at elevated temperatures diffuse streaks became more obviously between those new sites (X1,...,X7) and the equilibrium D sites [Fig. 5(c)]. Hence, these seven X sites could be connected with the possible types of DDHBs (Fig. 2), as follows:

1) X1 at (0.5, 0, 0) is located in the middle of the 8MR-channel between two D4 sites in an equal distance of $d(X1-D4) = 1.54$ Å. X1 is a cross-over point between each HB-chain pair and hence can be associated to the motion Type 7 [Fig. 2(a-b)];

2) X2 at (0.5, 0.5205, 0.0779) is distanced about 1.368 Å and 1.384 Å from D1 and D4, respectively. X4 at (0.4637, 0.1562, 0) is located 1.584 Å away from D1 and 1.849 Å from D4. Hence, X2 and X4 can be connected to dynamic disorder between D1 and D4. X3 at (0.5470, 0.1562, 0) is 0.770 Å close to D1 and 1.359 Å to D4. X3 reflects librations or rotations at D1 (Type 1). The largest angle change $\angle(O1 - D1 \cdots O8) = 3.6^\circ$ agrees with the geometrically flexible O1-D1 group against those containing double acceptor D4-O10-D5 and D1-O9-D3 groups, facilitating intrachain-exchanging processes over D1 [Fig. 2(a)]. Diffuse intensities centered at X2, X3 and X4 indicate intrachain DDHBs over D1 and D4 sites;

3) X5 at (0.5, 0.0182, 0.3802) may reflect the site-exchanging process between D4 and D5 within a D4-

O10-D5 group with the respective distance 0.847 Å to D4, 1.420 Å to O10 and 1.712 Å to D5. This can be assigned to motion Type 2 in Fig. 2;

4) X6 at (0.5, 0.792, 0.25) is centered between two D4 of the semihelical HB pair [Figs. D.3(a) and (c)]. Similarly, X7 at (0.5, 0.850, 0.75) lies between two D5 sites of the semihelical HB pair [Figs. D.3(b) and (d)]. X6 and X7 correspond to the respective interchain-exchanging process via D4-D4 (Type 4) and via D5-D5 (Type 5). X6 and X7 are connected by diffuse streaks of which center is located at (0.5, 0.0380, 0.25) in a distance of 1.346 Å to all D4 and D5 sites. This is a strong hint of an interchain-exchanging process via DDHBs involving D4 and D5 (Type 6 Fig. 2);

In addition, ΔF maps show three maxima found within 4MR-ring cages: Z1 at (0.25, 0.7116, 0.5381) is located between two D2-O9-D3 groups [Fig. 5(f)], and its peak intensity clearly increases from 350 K [Fig. 5(b)] to 400 K [Fig. 5(d)]. Interestingly, the related interring-exchanging process seems to occur via another site Z3 at (0.25, 0.7658, 0.6052) near D2 and O3, forming the dynamic route D3-Z1-Z3-D2. This is related to high electron density residuals near O3 in ΔF maps evaluated with XSD above 300 K. Hence, Z1 and Z3 can be related to interring-exchanges (Type 8). Z2 at (0.25, 0.6646, 0.4779) [Fig. 5(f)] originates from dynamic disorder between D2 and D3 of a D2-O9-D3 group (Type 3 in Fig. 2) and is associated to high electron density residuals around O9 in ΔF maps evaluated with XSD data (Fig. C.1).

The current neutron diffraction studies could resolve several new HBs of $(X \cdots O \cdots X)$ in Fig. 5(e) and $(Z \cdots O \cdots Z)$ in Fig. 5(f), allowing to trace its DDHB-chains and -rings. These are significantly distorted with respect to the original HBs of Mn-hureaulite, as demonstrated by blue lines in Fig. 6(a). The new HBs feature no distinct sides of acceptor and donor oxygens for the presence of vivid DDHBs. The consequent distortion of DDHBs in this phosphatic oxyhydroxide framework is associated to a lowering in HB strengths and, more importantly, to the shortened distances for charge carriers (D), particularly between the semihelical HB chains, as highlighted by a red line in Fig. 6(a). This cor-

HRNPD	Donor O _D	D site	Acceptor O _A	d(D-O _D) (Å)	d(D···O _A) (Å)	d(O _D -O _A) (Å)	∠(O _D -D···O _A) (°)
150 K	O1	D1	O8	1.001(4)	1.581(4)	2.581(4)	176.7(4)
	O9	D2	O3	0.963(5)	1.871(5)	2.771(5)	154.4(4)
	O9	D3	O3	0.989(5)	1.684(5)	2.653(5)	165.5(4)
	O10	D4	O1	0.965(5)	1.838(5)	2.723(5)	151.2(4)
	O10	D5	O8	0.985(5)	1.749(5)	2.707(5)	163.1(4)
250 K	O1	D1	O8	1.007(4)	1.602(4)	2.608(4)	175.9(4)
	O9	D2	O3	0.956(5)	1.893(5)	2.781(5)	153.4(3)
	O9	D3	O3	0.980(5)	1.694(5)	2.656(5)	166.1(4)
	O10	D4	O1	0.970(6)	1.848(5)	2.739(5)	151.3(4)
	O10	D5	O8	0.981(6)	1.761(5)	2.714(5)	163.0(4)
350 K	O1	D1	O8	1.006(5)	1.618(4)	2.621(4)	174.4(4)
	O9	D2	O3	0.970(5)	1.907(5)	2.806(5)	153.0(4)
	O9	D3	O3	0.976(5)	1.707(5)	2.664(5)	165.9(4)
	O10	D4	O1	0.965(6)	1.871(6)	2.754(6)	151.0(5)
	O10	D5	O8	0.988(6)	1.762(6)	2.721(6)	162.7(4)
400 K	O1	D1	O8	0.987(5)	1.632(5)	2.615(5)	173.1(5)
	O9	D2	O3	0.965(6)	1.923(6)	2.814(6)	152.4(4)
	O9	D3	O3	0.958(6)	1.722(6)	2.662(6)	166.5(4)
	O10	D4	O1	0.973(7)	1.863(8)	2.750(7)	150.1(6)
	O10	D5	O8	0.976(8)	1.790(7)	2.740(6)	163.6(5)

TABLE II. Interatomic distances and angles of hydrogen bonds analyzed by HRNPD of deuterated Mn-hureaulite from 150 K to 400 K.

responds to the longest charge transport path across the semihelical HB-chain pair via D4-X1-D4 (Type 7), clearly seen through the 8MR pore opening [Supplementary Fig. D.4(c)]. The neutron scattering density distribution around X1 is hardly recognizable at 350 K [Fig. D.4(a)], but quite obvious at 400 K [Fig. D.4(b)].

B. Fast proton motions seen in neutron spectroscopy

We observe quasielastic neutron scattering at FOCUS ($\Delta E=45 \mu\text{eV}$) down to the lowest measurement temperature. The QENS signal barely changes below 250 K, and can be assigned to paramagnetic scattering. Additional QENS intensity is observed at 300 and at 510 K, but surprisingly not in between (the data at 350 and 400 K are practically the same as at 250 K). The supplementary Fig. E.1 shows the difference spectra for the different temperatures. Based on these observations, we propose to eliminate the paramagnetic QENS signal by using the 250 K data as background. Detailed analysis reveals that at 300 K the QENS signal comes from water diffusion, presumably from adsorbed surface water (Supplementary F). At 350 K, the water diffusion is so fast that the broad QENS signal was not detected anymore. In the following, we focus on the QENS signal at 510 K, which can be associated with structural protons in Mn-hureaulite. The QENS spectrum at 510 K could be fitted with one Lorentzian function (Fig. 7):

$$I(Q, \omega) = \{A_{\text{elastic}}(Q) \delta(\hbar\omega) + A_{\text{QENS}}(Q) L(Q, \omega)\} \otimes R(Q, \omega) . \quad (1)$$

Hence, long-range charge transport may be realized once interchain-exchanging processes over the path D4-X1-D4 are thermally activated near 400 K.

The time scales of complex proton motions in Mn-hureaulite could be differentiated by QENS and DS, as described in the sections below.

The elastic line, $A_{\text{elastic}}(Q) \delta(\hbar\omega)$ has negative intensity, because the more static state at 250 K resulted in an over-subtraction. The amplitude $A_{\text{QENS}}(Q)$ incorporates both the structure factor of the mobile species and the intensity reduction at elevated temperatures due to thermal vibrations (Debye-Waller factor). The model function was convoluted with the resolution function measured by a Vanadium standard, $R(Q, \omega)$.

The line width is Q-independent ($\Gamma \approx 0.08 \text{ meV}$) and therefore the QENS signal can be assigned to localized proton motions. Unfortunately, the Bragg peaks, the paramagnetic QENS contribution and the small spectral weight of the localized motion hindered reliable evaluation of the elastic incoherent structure factor (EISF), which is commonly used to find the geometry of the motion. Therefore, we have performed a measurement at the IN16 backscattering spectrometer, which has significantly better energy resolution ($\Delta E=1 \mu\text{eV}$).

The inelastic fixed window scan (IFWS) integrated with respect to Q (Fig. 8) exhibits one weak peak at $T_{\text{max}}=261 \text{ K}$, which was assigned to the surface-adsorbed water. In addition, the IFWS shows a strong peak at $T_{\text{max}}=399 \text{ K}$, which is Q-independent apart of the intensity (Supplementary F), reinforcing that this relaxation stems from intrinsic local motions. The onset temperature for the local dynamics is close to 300 K, but still

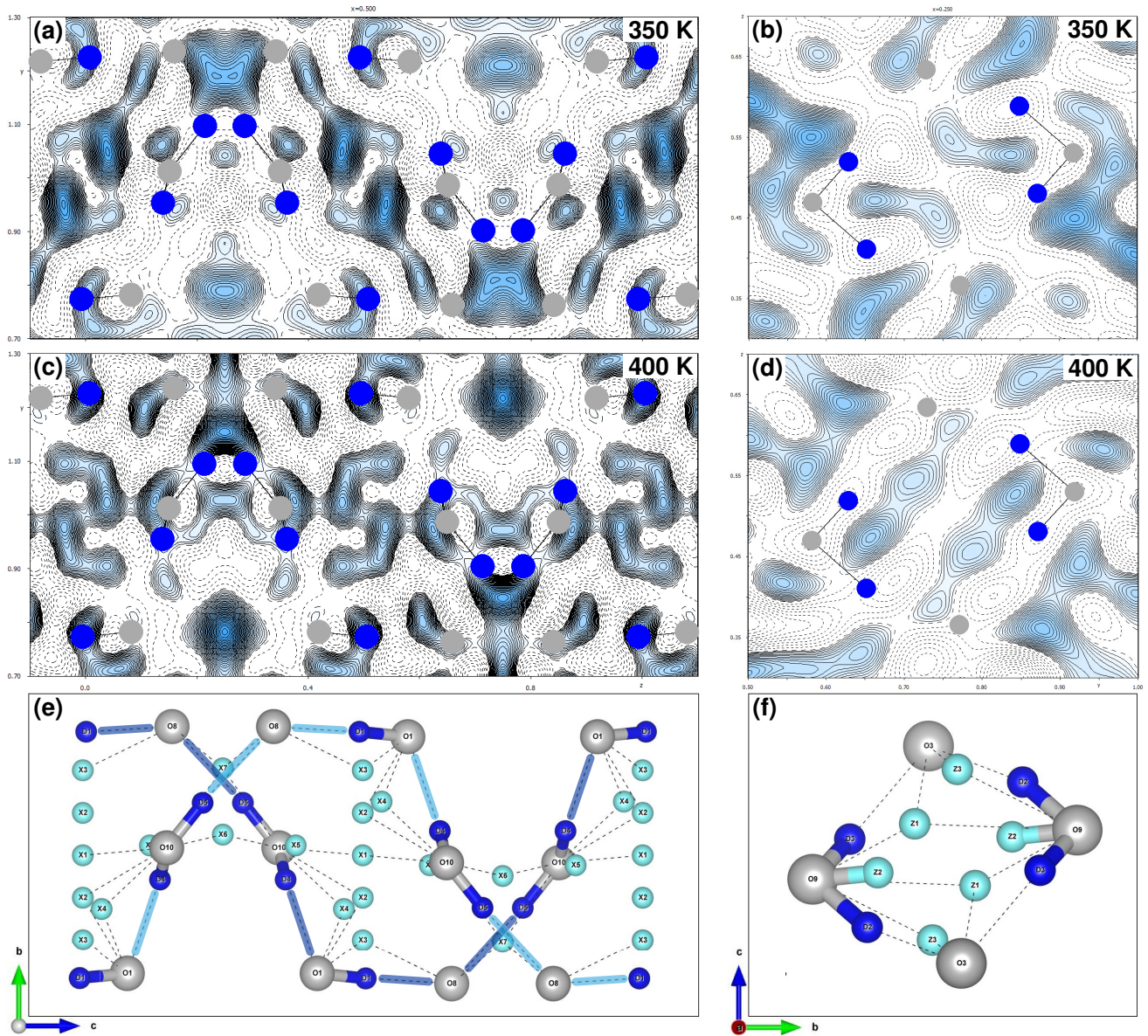


FIG. 5. ΔF maps of the Mn-hureaulite unit cell evaluated with HRNPD data at 350 K (a,b) and 400 K (c,d). ΔF slices are drawn for $x = 0.5$ from the section ($0 \leq x \leq 1.0$; $0.7 \leq y \leq 1.3$; $-0.1 \leq z \leq 1.1$) (a,c,e) and for $x = 0.25$ from the section ($0.1 \leq x \leq 0.4$; $0.5 \leq y \leq 1.0$; $0.3 \leq z \leq 0.7$) (b,d,f). Positive densities are contoured by black lines and highlighted in blue while negative densities are indicated by dotted lines. To guide the eyes, oxygen (light grey) and deuterium (blue) atoms in O1-D1, D2-O9-D3, and D4-O10-D5 groups are indicated. Diffuse elastic neutron scattering length densities are centered at seven possible deuterium sites (labeled as X1,...,X7). As a result, several new HBs (broken lines) are rendered along the original semihelical HB chains highlighted in light and dark blue lines in (e) and (f).

present at the highest measuring temperature of 483 K. Accordingly, this local dynamic process is the same as the one measured at 510 K at FOCUS (Fig. 7).

The Q-integrated IFWS spectra were fitted to obtain the relaxation time as a function of temperature according to Frick et al.⁴⁶:

$$I_{IFWS}(T) = C + A_{bw}L_{bw}(T, \Gamma_{bw}(T)) + A_{loc}L_{loc}(T, \Gamma_{loc}(T)) , \quad (2)$$

where $\Gamma(T)$ is the width of the Lorentzian function (see

e.g. Eq. 1), and C is a constant background. The peak intensity is related to the number of protons participating in the motion. We note that this model is only a crude approximation for the water diffusion with Q-dependent $\Gamma_{bw}(T)$, but it can satisfactorily reproduce the bump caused by the surface water. Using a simple Arrhenius-type model, we obtain $\Gamma_{loc}(T=510 \text{ K})=0.070(2) \text{ meV}$, which is in reasonably good agreement with the value from FOCUS ($\sim 0.08 \text{ meV}$). The corresponding relaxation time is 110(17) ps at 399K. The activation energy

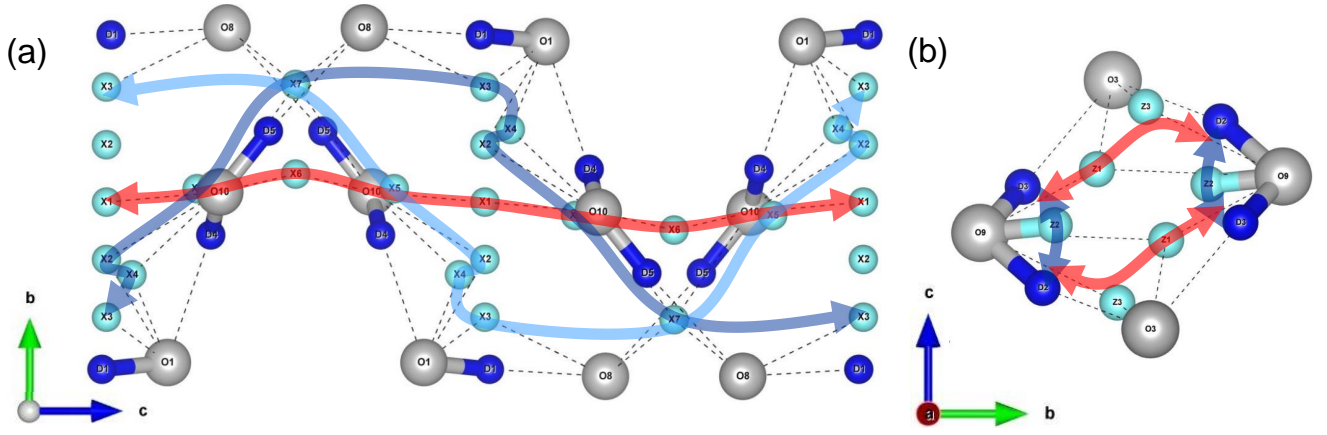


FIG. 6. Representative sections of semihelical HBs in deuterated Mn-hureaulite. The distortion of semihelical HB chain pairs highlighted by pale and dark blue lines can be realized in the presence of the new sites X1-X7 (a) and that of HB rings with Z1-Z3 (b). These rearrangements of HBs are due to DDHBs, by which new HBs connect to each other across the semihelical chain pair, as well as across the HB ring, indicated by thick red lines.

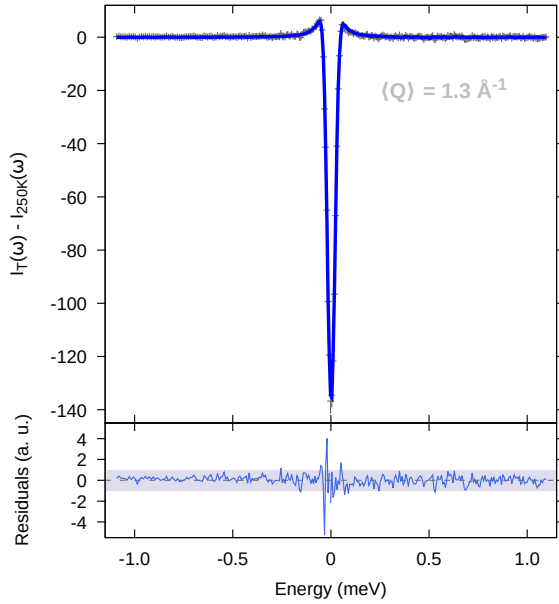


FIG. 7. Observed (+) and fitted (blue line) QENS spectra at 510 K for one representative Q-group. Their difference is shown at the bottom. Localized motions were described using one Lorentzian function (blue line).

was found to be $E_a = 0.390(4)$ eV for the local dynamics.

Fixing $\Gamma_{loc}(T)$ to the above obtained Arrhenius function, the measurement statistics of the IFWS allowed a Q-dependent fit with the simplified expression (Eq. 3.), where the surface water contribution was hidden by the statistical fluctuations, and so it could be neglected.

$$I_{IFWS}(Q, T) \propto \frac{\pi}{B} A_1(Q) \frac{\tau(T)}{1 + \omega_{off}^2 \tau(T)^2}, \quad (3)$$

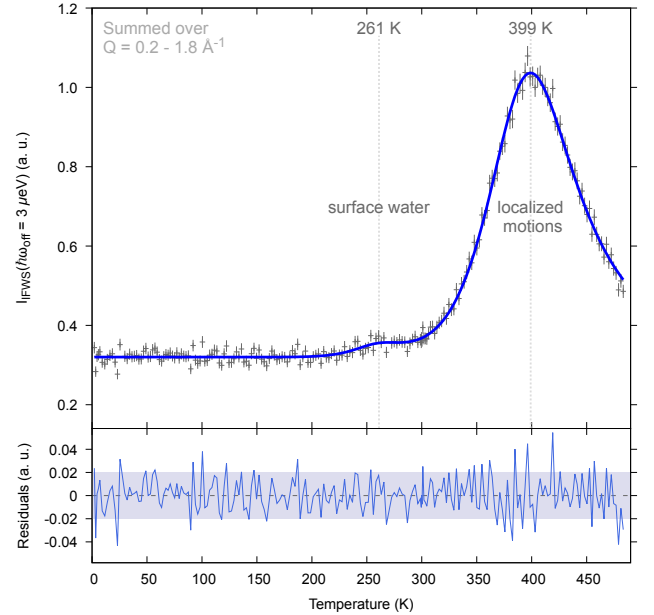


FIG. 8. IFWS data fit using a linear background and the Arrhenius relation for both observed relaxations. Their peak temperatures are highlighted by the gray dashed lines. I_{IFWS} data was summed over the measured Q-range.

where $A_1(Q)$ is the temperature-independent inelastic incoherent structure factor (IISF)⁴⁷ and $\omega_{off} = 3\mu\text{eV}$ is the energy offset of the IFWS. The Debye-Waller factor B did not change significantly in the limited temperature range of the IFWS peak. The simplest model for the local diffusion process, which complies with the previous structural observations, is the two-site jump model:⁴⁸

$$A_1(Q) = \frac{1}{2} (1 - j_0(Qd)), \quad (4)$$

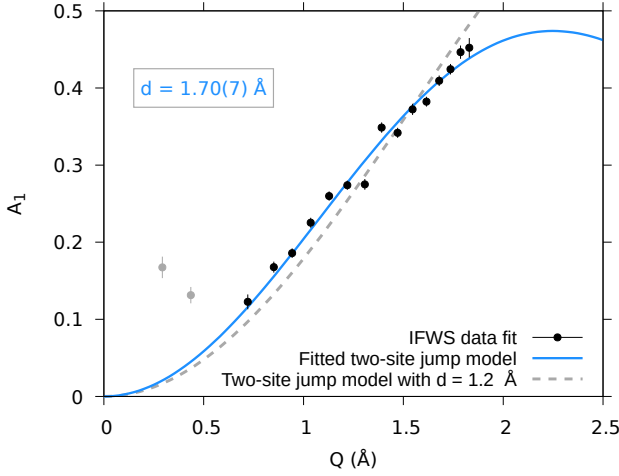


FIG. 9. Fitted quasielastic incoherent structure factor A_1 obtained from IFWS Arrhenius fits of the local relaxation peak. Black dots represent the A_1 values taken into consideration in the two-site model fit which resulted in a jump distance of $1.70(7)$ Å. The corresponding fit ($A_1 = 0.337(15) \times [1 - j_0(Q \times 1.7)]$) is drawn in blue. For comparison, the gray, dashed line gives the two-site model function with $d = 1.2$ Å, a typical proton-to-proton-donor distance (see Table II).

where we have approximated the first order Bessel function with $j_0(Qd) = \sin(Qd)/(Qd)$. $A_1(Q)$ was fitted well (Fig. 9) for a particle motion between two positions separated by the jump distance $d = 1.70(7)$ Å (Fig. 9).

These local hydrogen motions can be assigned to specific proton sites in Mn-hureaulite. We elaborate first the number of participating H atoms based on the IISF:

$$\frac{I_{\text{mobile}}}{I_{\text{mobile}} + I_{\text{static}}} = \frac{I_{QENS}}{A_1(I_{QENS} + I_{\text{elastic}})} \quad (5)$$

The mean value for A_1 was calculated by integration of Eq. 4 over $0.55 \leq Q \leq 1.45$ Å⁻¹. We find $I_{\text{mobile}}/(I_{\text{mobile}} + I_{\text{static}}) \approx 0.4$, which means that two out of the five different protons are participating in this localized motion. Most obviously, a site exchange could happen within an H-O-H group. Nevertheless, we have examined all possible jump distances, including interstitial positions. The direct distance $1.633(8)$ Å between D4 and D5 in a D4-O10-D5 group and $1.577(6)$ Å between D2 and D3 in D2-O9-D3 at 400 K (Table II) are comparable to the jump distance of $1.70(7)$ Å (Fig. 9). Considering that the APDs at D4 and D5 sites are much larger than those at D2 and D3 in the relevant temperature range (Fig. 4 and insights from simulations, section IIID), the site-exchanging proton pair within H4-O10-H5 is regarded as the main contributor to the localized jump dynamics.

C. Dielectric behavior of protonated and deuterated Mn-hureaulite

Figure 10 shows the temperature dependence of the dielectric constant, ϵ' , and the real part of the conductivity, σ' , plotted for various frequencies. Frames (a) and (c) present the results for the protonated and frames (b) and (d) for the deuterated hureaulite. The protonated system was measured in an extended frequency and temperature range. It should be noted that σ' and the dielectric loss ϵ'' are related via $\sigma' \propto \epsilon''\nu$. Therefore, the $\sigma'(T)$ curves in Figs. 10(c) and (d) exhibit the same temperature dependence as ϵ'' (irrespective of different absolute values).

ϵ' of both systems [Figs. 10(a) and (b)] significantly increases with increasing temperature above about 300 K (H-form) or 275 K (D-form). The shoulders seen in both cases and their shift to higher temperatures for higher measurement frequencies indicate a relaxational origin of this behavior.^{49,50} At elevated temperatures and low frequencies, $\epsilon'(T)$ approaches high values, even becoming "colossal"⁵¹ (> 1000) for the protonated sample. This indicates that this part of the dielectric response is of non-intrinsic nature and probably due to electrode polarization. Such effects, sometimes termed "blocking electrodes", are often found for ionic conductors and arise when the conducting ions are blocked at the electrodes to form space-charge regions acting as large capacitors.⁵²

The temperature-dependent conductivity σ' , shown in Figs. 10(c) and (d), reveals several peaks or shoulders, whose positions are indicated by the filled symbols. They shift to higher temperatures with increasing frequency, again pointing to a relaxational origin.^{49,50} For both materials, three intrinsic relaxation processes show up:

1) The protonated material [Fig. 10(c)] reveals a well-defined low-temperature (LT) relaxation mode at temperatures between about 180 and 300 K. A corresponding, but less pronounced LT mode is also found for the deuterated sample [Fig. 10(d)] at temperatures about 30 K higher for identical frequencies. The estimated peak positions of these relaxations are indicated by the filled circles in Figs. 10(c) and (d).

2) A middle-temperature (MT) relaxation mode at around 300 K is clearly resolved in the D-form but barely visible in the H-form [filled triangles in Figs. 10(c) and (d); a weak shoulder seen, e.g., around 400 K for the 1.9 MHz curve of the H-form may also be due to this relaxation]. The temperature of the MT-mode peak is only weakly frequency-dependent.

3) A strongly frequency-dependent HT-relaxation above 300 K is found in both systems [filled squares in Figs. 10(c) and (d)]. It only shows up as a shoulder because it is strongly superimposed by an additional increase of $\sigma'(T)$ at higher temperatures, which is due to dc conductivity (see discussion at the end of this section). For 1 Hz, the HT-mode appears at approximately 360 K in the D-form while it shows up at about 320 K in the H-form.

In principle, each of these relaxation features in $\sigma'(T)$ should be accompanied by a step-like increase (with increasing T) in $\varepsilon'(T)$. This indeed is the case for the HT relaxation in the protonated sample and for the MT and HT relaxations in the deuterated one [Figs. 10(a) and (b)]. The relaxation steps of the other processes are too small to be detected. For the protonated sample, it should be noted that the indicated peaks or shoulders in Fig. 10(c) show up at temperatures and frequencies that are far off the region where colossal ε' values are observed in Fig. 10(a). This is in accord with an intrinsic nature of the corresponding relaxation processes.^{51,52}

As discussed in section H of the supplementary material, the three detected relaxation processes are difficult to deconvolute in frequency-dependent plots of the dielectric quantities. Therefore, we rely on the temperature-dependent graphs of Figs. 10(c) and (d) to determine the corresponding relaxation times. In general, for a fixed measurement frequency ν , a peak in $\sigma'(T)$ [or in $\varepsilon''(T)$] occurs when the temperature-dependent relaxation time $\tau(T)$ matches the condition $\tau(T) = 1/(2\pi\nu) = 1/\omega$. Thus, from the peak temperatures in the $\sigma'(T)$ plots of Figs. 10(c) and (d), we can deduce temperature-dependent relaxation times. Figure 11 presents the obtained $\tau(T)$ results for all relaxation modes and both materials using an Arrhenius representation. The τ values determined for the HT modes (squares) can be reasonably well fitted by an Arrhenius law, $\tau = \tau_0 \exp[E/(k_B T)]$ (dash-dotted lines), with some deviations for the two highest temperatures of the H-form. We obtain energy barriers E of 0.84 and 1.5 eV for the H- and D-forms, respectively. The pre-exponential factor τ_0 can be assumed to be related to the inverse of the attempt frequency of the corresponding thermally-activated motion via $\nu_0 = 1/(2\pi\tau_0)$, which, usually, is in the phonon-frequency range for canonical relaxations. We find $\tau_0 \approx 6 \times 10^{-15}$ s and 4×10^{-22} s for the protonated and deuterated sample, respectively. Especially for the latter, τ_0 seems unreasonably low. Such discrepancies may indicate deviations from Arrhenius behavior, which are not resolved here due to the limited frequency and temperature region where the HT relaxation could be observed.

However, for the LT modes (circles in Fig. 11) such non-Arrhenius behavior of $\tau(T)$ could be clearly detected, especially for the H-form, which was measured in an extended frequency region up to several hundred MHz. Its $\tau(1/T)$ curve (blue circles) exhibits clear bending, characteristic for the glassy freezing of relaxational dynamics.^{49,53,54} Such behavior is usually described by the empirical Vogel-Fulcher-Tammann (VFT) equation:^{53,55,56}

$$\tau = \tau_0 \exp \left(\frac{DT_{VF}}{T - T_{VF}} \right) \quad (6)$$

Here, D is the so-called strength parameter, providing a measure of the deviations from the Arrhenius behavior.^{55,56} T_{VF} is the Vogel-Fulcher temperature, at

which the relaxation time would diverge. Indeed, a good fit of the experimental LT data for the H-form is achieved in this way (dashed blue line in Fig. 11). A close look at the $\tau(1/T)$ data of the LT relaxation of the D-form (red circles) reveals a curved behavior for this sample, too, and these data also could be well fitted by Eq. 6 (dashed red line).

For the protonated Mn-hureaulite, $\tau(T)$ of the dielectric LT-relaxation seems to be rather well consistent with τ of the localized relaxation, detected by QENS using the FOCUS spectrometer (pentagon in Fig. 11). The black solid line in Fig. 11 shows a VFT fit of the combined FOCUS and DS relaxation-time data. While some deviations of fit and experimental data show up at high temperatures, the agreement is satisfactory, having in mind that two completely different experimental methods were used. In this context, it also should be noted that inelastic neutron scattering essentially detects density fluctuations while dielectric spectroscopy is sensitive to dipolar fluctuations only. Thus, the small mismatch between the relaxation times from the two methods, suggested by the VFT fit in Fig. 11, in principle could indicate a weak decoupling of both dynamics. In general, such decoupling effects, leading to the detection of different relaxation times by DS, neutron scattering and other spectroscopic methods, are rather well known, especially in glass physics,^{54,57,58} and some theoretical explanations were provided.^{59,60}

The VFT parameters as obtained from the fits of the LT relaxation times are listed in Table III. In all cases, the VFT fits gave rise to reasonable inverse attempt frequencies τ_0 . The strength parameters between 6.8 and 13.0 classify these materials as fragile to intermediate within the strong/fragile classification scheme proposed by Angell.^{55,56} The obtained T_{VF} values point to an isotope effect of the relaxation dynamics: The Vogel-Fulcher temperature for the D-form is significantly higher than for the H-form sample (for both evaluations of the latter). Obviously, the deuterium dynamics slows down more strongly upon cooling, leading to much higher τ values in the investigated temperature range as directly revealed in Fig. 11. Based on the reasonable match of the DS and QENS relaxation-time data, the LT-mode can be assigned to site exchanging H4 and H5 (or D4, D5) in the H4-O10-H5 (or D4-O10-D5) groups [Type 2 in Fig. 2(a)]. This local proton-hopping process obviously exhibits glassy freezing and, similar to the findings in our previous work on a rockbridgeite-type compound,⁶¹ Mn-hureaulite approaches a "proton glass" state^{62,63} at low temperatures. The corresponding glass-transition temperature T_g can be deduced by applying the usual criterion $\tau(T_g) = 100$ s.⁵⁴ This leads to $T_g = 187$ and 212 K for the H- and D-form, respectively, implying that the deuterium dynamics freezes at higher temperature.

The MT mode (triangles in Fig. 11), for which significant $\tau(T)$ data are only available for the D-form, can, in principle, be also described by an Arrhenius law. However, due to the very weak temperature dependence of its

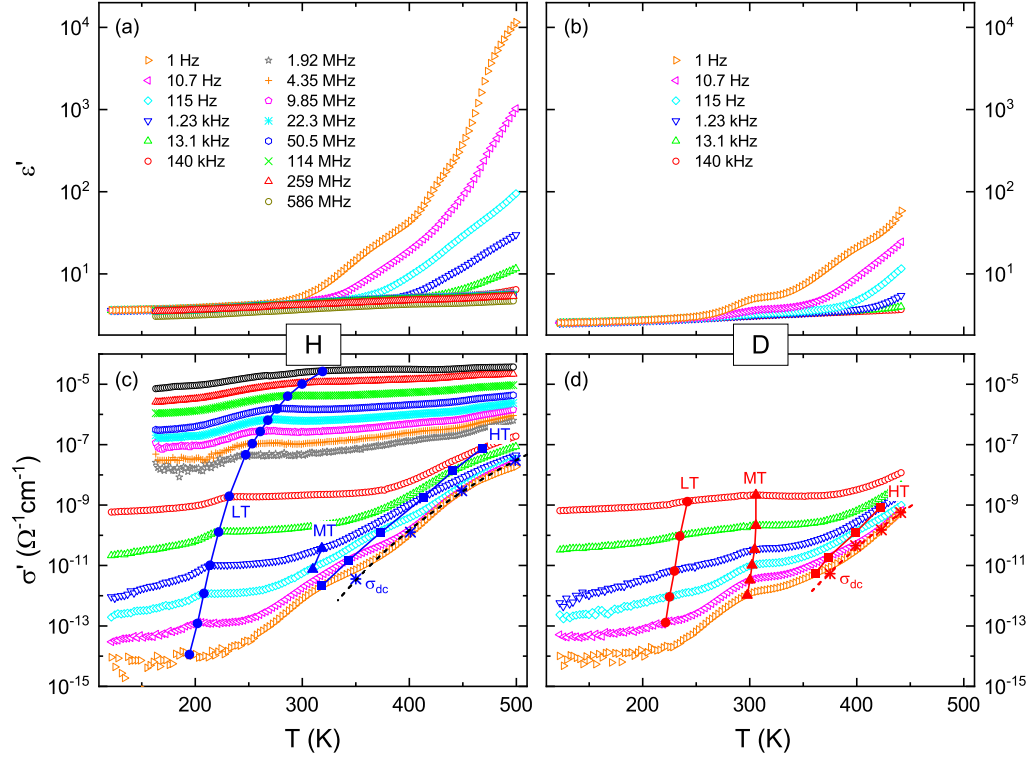


FIG. 10. $\epsilon'(T)$ and $\sigma'(T)$ of protonated (H) (a and c) and deuterated (D) (b and d) Mn-hureaulite, shown for various frequencies. The filled circle, triangle, and square symbols mark the respective LT-, MT-, and HT-relaxation modes. The solid lines are guides for the eye. The stars indicate the dc conductivity as obtained from fits of the dielectric spectra, shown in Fig. H.1. The dashed lines are Arrhenius fits of $\sigma_{dc}(T)$. Note that the imaginary part of the permittivity $\epsilon''(T)$ is not shown here since it is simply proportional to the real part of the conductivity via $\sigma' = 2\pi\nu\epsilon''\epsilon_0$. Degradation of the thin deuterated sample pellet limited the data acquisitions to a maximum of 450 K.

	D	T_{VF}	τ_0 (s)
H-form, DS	13.0	137	9.7×10^{-15}
H-form, DS + QENS	9.5	147	9.2×10^{-14}
D-form, DS	6.8	179	3.2×10^{-15}

TABLE III. Parameters obtained by fitting $\tau(T)$ of the LT relaxation (Fig. 11) using the VFT law (Eq. 6).

relaxation time, the inverse attempt frequency τ_0 (the y-axis intercept in the Arrhenius plot in Fig. 11) would be unreasonably low, rendering such a fit meaningless. More likely, strong deviations from Arrhenius behavior exist for this relaxation at higher temperatures that are not resolved due to the limited temperature range where this mode could be detected. Considering the similar ADP values at all D sites up to 300 K (Fig. 4), one may tentatively assign the MT-relaxational motions, resolved in the DS data near 300 K, to superimposed fast librations of dangling OH and HOH groups. The HT-mode, treated above, may be assigned to interchain and intrachain-exchanges involving H4 (or D4) sites. This is in agreement with the increased ADP eigenvalue $U_3(D4)$, which is significantly higher than $U_3(D1)$ in the same temperature interval from 350 to 400 K (Fig. 4).

Finally, the present dielectric data also provide information on the dc conductivity of Mn-hureaulite. As discussed in section H of the supplementary material, it shows up as a plateau in the $\sigma'(\nu)$ plots and can be derived from fits of the dielectric spectra. Here it is essential to account for the electrode contributions at low frequencies by an equivalent-circuit approach as discussed in detail, e.g., in Refs. 51 and 52. The resulting dc conductivities for four temperatures are shown by the stars in Figs. 10(c) and (d). They are well consistent with the $\sigma'(T)$ results at the lowest frequencies. The moderate absolute values of $\sigma_{dc}(T)$ indicate that Mn-hureaulite is not a superprotonic conductor. As shown by the dashed lines, these data can be reasonably well-fitted by an Arrhenius law, $\sigma_{dc}(T) \propto \exp[-E/(k_B T)]$. We obtain practically identical energy barriers for both systems, namely $E = 0.92$ eV for the H-form and $E = 0.97$ eV for the D-form.

D. DDHBs associated to the lattice dynamics

Polyhedral rotations of structural building units readily occur from a certain degree of distortion in releasing

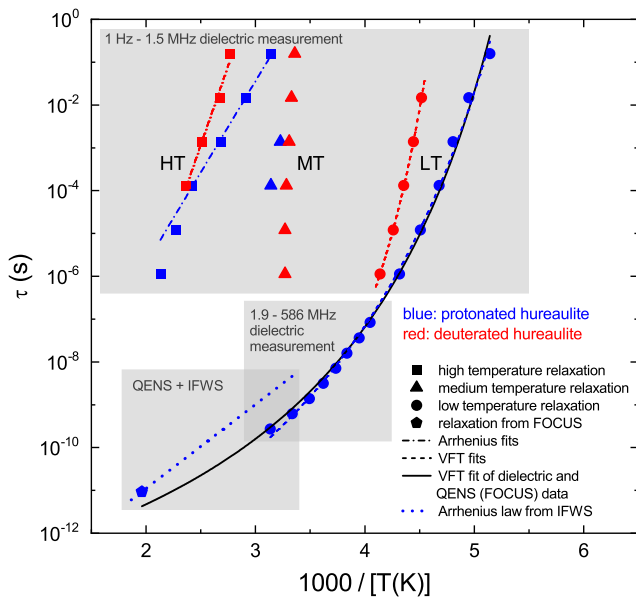


FIG. 11. Arrhenius representation of the relaxation times of the LT, MT, and HT relaxations as deduced from temperature-dependent σ' plots (Fig. 10) for the protonated (blue) and deuterated (red) Mn-hureaulite. In addition, results from neutron scattering are shown (pentagon: QENS using FOCUS; blue dotted line: IFWS using IN16B). The dash-dotted lines are Arrhenius fits of the HT data (parameters: see text). The dashed lines are fits of the LT relaxation times from DS with the VFT equation [Eq. (6)]. The solid line shows a VFT fit of the combined DS (blue circles) and FOCUS data (pentagon) of the H-form with Eq. (6). The parameters of the VFT fits are given in Table III. The gray boxes highlight from which type of measurements the data points originate.

intra-polyhedral and inter-polyhedral strains.⁶⁴ In Mn-hureaulite, three unique manganese octahedra Mn1O_6 , $\text{Mn2O}_4(\text{HOH})_2$ and $\text{Mn3O}_5(\text{HOH})$ are edge-sharing to build the highly-distorted pentamer unit established by the Mn2–Mn3–Mn1–Mn3–Mn2 atomic sites.^{14,15} Thus, all hydrogen motions might be coupled to bending motions of Mn1O_6 , $\text{Mn2O}_4(\text{HOH})_2$ and $\text{Mn3O}_5(\text{HOH})$. We expect an immediate impact of these motions both on the local re-orientations and on the long-range proton diffusion through the temporal alteration of the potential energy landscape.

Now let us consider the INS part of our neutron scattering spectra (Fig. 12). INS spectra are dominated by hydrogen vibrations due to their dominant neutron scattering length. We obtain a very good agreement of the density of states (DOS) between calculation and measurement even though only the subset of hydrogen atoms are evaluated (Fig. 13). Unfortunately, the non-linear transformation of measured intensity from the flight time to the energy scale made some spectral features less visible. Therefore, we plot the temperature dependence of the spectrum as time-of-flight data, corrected by the

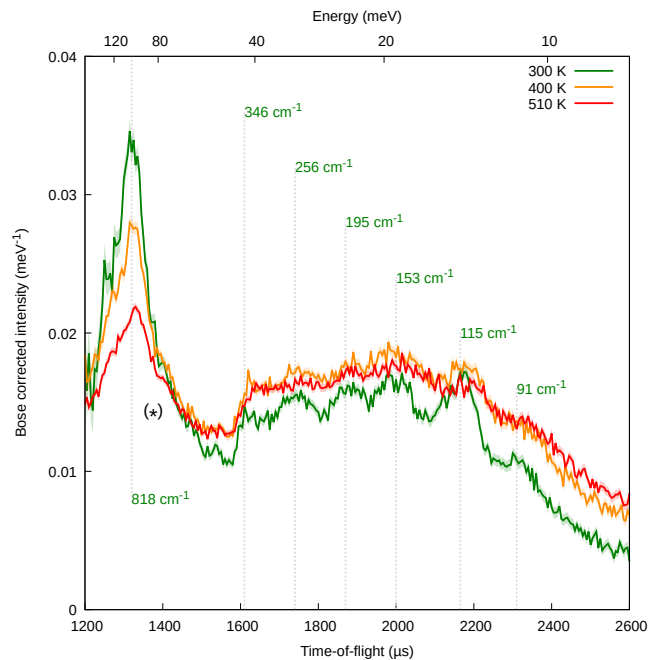


FIG. 12. Bose-corrected INS intensity summed over all detectors for each measuring temperature is shown within the flight time range. The black asterisk (*) marks a higher order spurion. Transparent bands represent the error of a measurement.

Bose-Einstein occupation factor (Fig. 12).

The most dominant peak in the INS spectrum at 300 K is located near 818 cm^{-1} (or 101 meV), as seen in Fig. 12 and Fig. 13. From simulated Raman spectra,⁶⁵ the wavenumber region near 818 cm^{-1} refers to the HOH libration modes of $\text{Mn2O}_4(\text{HOH})_2$ octahedra [i.e., a rocking (in-plane) mode, $\rho(\text{H4-O10-H5})$; a twisting (out-of-plane) mode, $\omega(\text{H4-O10-H5})$]. In addition, these modes are superimposed by the librations of HOH ligand groups of $\text{Mn3O}_5(\text{HOH})$ octahedra and $\text{P1O}_3(\text{OH})$ tetrahedra [i.e., $\omega(\text{H2-O9-H3})$; a wagging (out-of-plane) mode, $\tau(\text{H2-O9-H3})$; a out-of-plane-bending mode, $\gamma(\text{P1-O1-H1})$]. On the other hand, the low energy range below 400 cm^{-1} is assigned to bending motions of Mn1O_6 , $\text{Mn2O}_4(\text{HOH})_2$ and $\text{Mn3O}_5(\text{HOH})$ octahedra.

The main reason for the decreasing peak intensity near 818 cm^{-1} in INS spectra at elevated temperatures could be addressed to redistribution of motions of HOH and OH group. Above 300 K, the enhanced collective motions of framework polyhedra are supported by strongly smeared INS peaks below 400 cm^{-1} (Fig. 12). Considering the light-weighted H species, their motions can be enhanced by collective motions of the framework polyhedra, rather than the other way around.

Finally, we support the interpretation of previous experimental data by simulations. Based on the AIMD trajectories, the mean square displacement (MSD) and

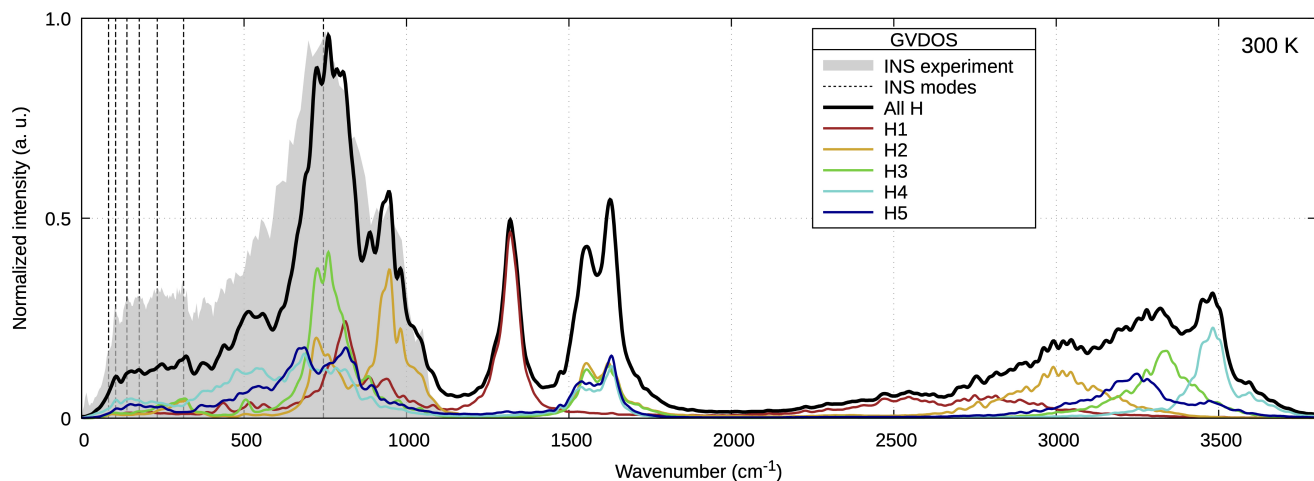


FIG. 13. GVDOS from observed INS spectra (gray) and simulated partial DOS for five sites for the five hydrogen sites in Mn-hureaulite at 300 K. The frequency of the experimental GVDOS was multiplied by a scaling factor of 0.95. The dashed lines highlight the vibrational modes found with INS (Fig. 12). The simulated DOS is calculated from CP2K NVE trajectories.

the spatial density distribution function (sdf) for each characteristic proton site were analyzed at different temperatures (Fig. 14). In accordance with ADP values determined by Rietveld analyses with HRNPD data, the increasing MSD of H4 with temperature clearly exceeds the MSD of other protons. The overlapping sdf of H4 with that at H5 having the second largest MSD [Fig. 14(a)] could unambiguously confirm the assignment of QENS signal and the LT-relaxation mode resolved in σ' spectra near 300 K to fast reorientational motions within H4-O10-H5. We would like to note here that the duration of the simulation is short in comparison to the experimental relaxation times. Therefore, it is not surprising that

we do not directly observe the diffusional motions in the simulations.

In the sdf plots from 300 K up to 500 K, the interchain site-exchanges over H4 along with H5 are strongly enhanced at 500 K [Fig. 14(g)]. However, the interring site-exchanges of (H2-O9-H3) pairs [Fig. 14(h)] are less promoted even at 500 K than the interchain-exchanging case. Hence, the HT-relaxation mode in Fig. 10 is related to interchain-exchanges. Furthermore, in Fig. 14(g), it is easy to recognize a strong overlapping of the spatial density distribution in H4-X1-H4, the pathway suggested for the protonic conductivity in Mn-hureaulite, as described in the section III A.

IV. CONCLUSION

Detailed inspection of difference Fourier maps from HRNPD data indicates the following dynamics for the five unique deuterium sites in Mn-hureaulite:

- 1) Deuterium at D1 in O1-D1 is fast rotating along a semihelical HB chain above 350 K. This motion can contribute to intrachain-exchanging processes;
- 2) D2 and D3 in D2-O9-D3 are confined by a 4MR-opening. Deuterium atoms at both sites show fast reorientations up to 350 K. At 400 K, interring-exchanging processes start across each HB ring;
- 3) Deuterium atoms at D4 and D5 in D4-O10-D5 show largest dynamic disorder along the 8MR-channel system, which is relevant for both intra- and interchain exchanges.

The most interesting finding in the HRNPD data analyses is the pathway D4-X1-D4, highlighted in red in

Fig. 6(a). This interchain-exchange enables thermally activated long-range charge transport by DDHB-chains along the *c* axis. The efficiency of proton transport between semihelical chains is limited by relatively large proton-to-proton-donor distances. This reflects a magnitude of 10^{-7} S/cm for the dc conductivity in the H-form at 500 K [Fig. 10(c)].

Besides, fast site-exchanges of the two protons in H4-O10-H5 (along with fast reorientation of H1) is a relevant prerequisite for intrachain charge transport. QENS evinced local dynamics corresponding to a two-site jump model characterized by an activation energy of 0.390(4) eV and relaxation time of 110(17) ps at 399 K with a jump distance of 1.70(7) Å. AIMD results agreed with the jump model for site-exchanging H4 and H5 in a H4-O10-H5 group even if the simulation time was too short to observe an explicit site-exchange. This local site-exchanging process showing non-Arrhenius behavior could be assigned to the LT-relaxational mode detected

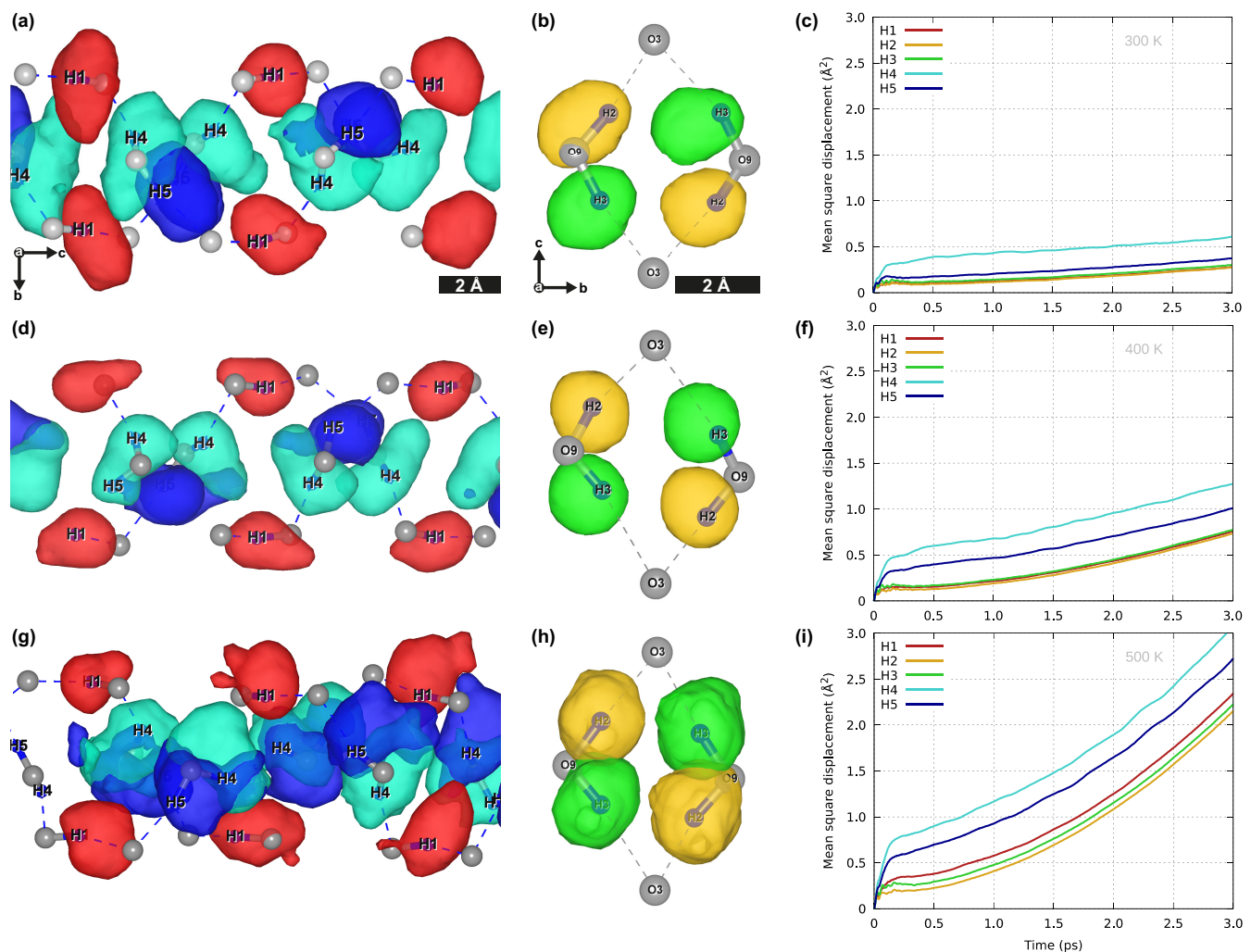


FIG. 14. Temperature evolution of spatial density distribution functions (left and middle column) and mean square displacements (right column) of the characteristic proton sites. Small sections of HB chains (a,d,g) and rings (b,e,h) plotted here. Both sections include the spatial density distributions around the proton sites. T -dependent mean square displacements at all five proton sites from NVE trajectories are drawn on the right (c,f,i).

in dielectric spectroscopy. This dynamics exhibits clear signatures of glassy freezing and, finally, a proton-glass state is approached at 187 K.

In conclusion, the long-range charge transport in Mn-hureaulite is realized by DDHB-chains. The thermal response of the framework structure insures the anisotropically widened channel opening at elevated temperatures for the ease of DDHBs with dangling HOH and OH groups. This requires in turn collective motions of the octahedral-tetrahedral framework, particularly of $\text{Mn}_2\text{O}_4(\text{HOH})_2$ octahedra and $\text{P}(\text{OH})_3$ tetrahedra with the respective H4-O10-H5 and O1-H1 dangling groups. Besides, both framework polyhedral moieties frame the pore opening of the 8MR-channel system. The low energy bending modes of $\text{Mn}_2\text{O}_4(\text{HOH})_2$ octahedra below 400 cm^{-1} are strongly smeared out from 300 K to 400 K. These are directly related to a strong intensity decrease of the dominant INS peak near 818 cm^{-1} asso-

ciated with $\rho(\text{H4-O10-H5})$ and $\omega(\text{H4-O10-H5})$ modes. This points to a narrow interplay between phonons and proton dynamic disorder in the title compound. Temperature evaluation of sdf calculations could confirm a significant contribution of interchain-exchanging protons over the longest pathway H4-H4 (Type 7) to the protonic conductivity. From 300 K up to 500 K, the most profound increase of mean square displacements was found at H4 by AIMD calculations in accord with results from neutron powder diffraction.

Despite the absence of superprotonic conductivity in Mn-hureaulite, the current study could comprehend subtle motions at five independent H/D sites by providing their length and time scales in the highly complex, dynamically disordered HB network. Upon this success, further investigation on various types of DDHBs are continued to achieve superprotonic conductivity under mild external fields.

ABBREVIATIONS

8MR: 8-membered ring; ADP: atomic displacement parameter; AIMD: *ab initio* molecular dynamics; bw: bulk water; CP2K: name of used DFT program; D: deuterium; DDHB: dynamically disordered hydrogen bond; ΔF : difference Fourier; DFT: density functional theory; DOS: density of states; DS: dielectric spectroscopy; EISF: elastic incoherent structure factor; FOCUS: neutron time-of-flight spectrometer at SINQ; PSI; FWS: fixed window scan; GoF: goodness of fit; GVDOS: generalized vibrational density of states; H: hydrogen; HB: hydrogen bond; HF: high frequency; HRNPD: high-resolution neutron powder diffraction; HT: high-temperature; IFWS: inelastic fixed window scan; IISF: inelastic incoherent structure factor; IN16B: neutron backscattering spectrometer at ILL; INS: inelastic neutron scattering; LF: low frequency; loc: localized; LT: low-temperature; MD: molecular dynamics; Mn-hureaulite: $\text{Mn}_5[(\text{PO}_4)_2(\text{PO}_3(\text{OH}))_2](\text{HOH})_4$; MSD: mean square displacement; MT: middle-temperature; NVE: microcanonical ensemble; NVT: canonical ensemble; QENS: quasielastic neutron scattering; sdf: density distribution function; VFT: Vogel-Fulcher-Tammann; XSD: X-ray single crystal diffraction.

SUPPLEMENTARY MATERIAL

See supplementary material for more details on structure refinements, QENS measurements, DFT computations and frequency-dependent dielectric data. A supplementary movie visualizes proton motions at elevated temperatures. The mp4 file was created from the NpT AIMD trajectories at 500 K.

AUTHOR'S CONTRIBUTIONS

S.H.P. designed the current study and was responsible for beamtime applications for synchrotron X-ray diffraction and neutron scattering. All authors contributed equally to investigations done in this study with their disciplines. The manuscript was written by S.H.P., A.H., P.L., F.J. and M.K. and edited by all authors. Supplementary was prepared mainly by A.H..

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DATA AVAILABILITY STATEMENT

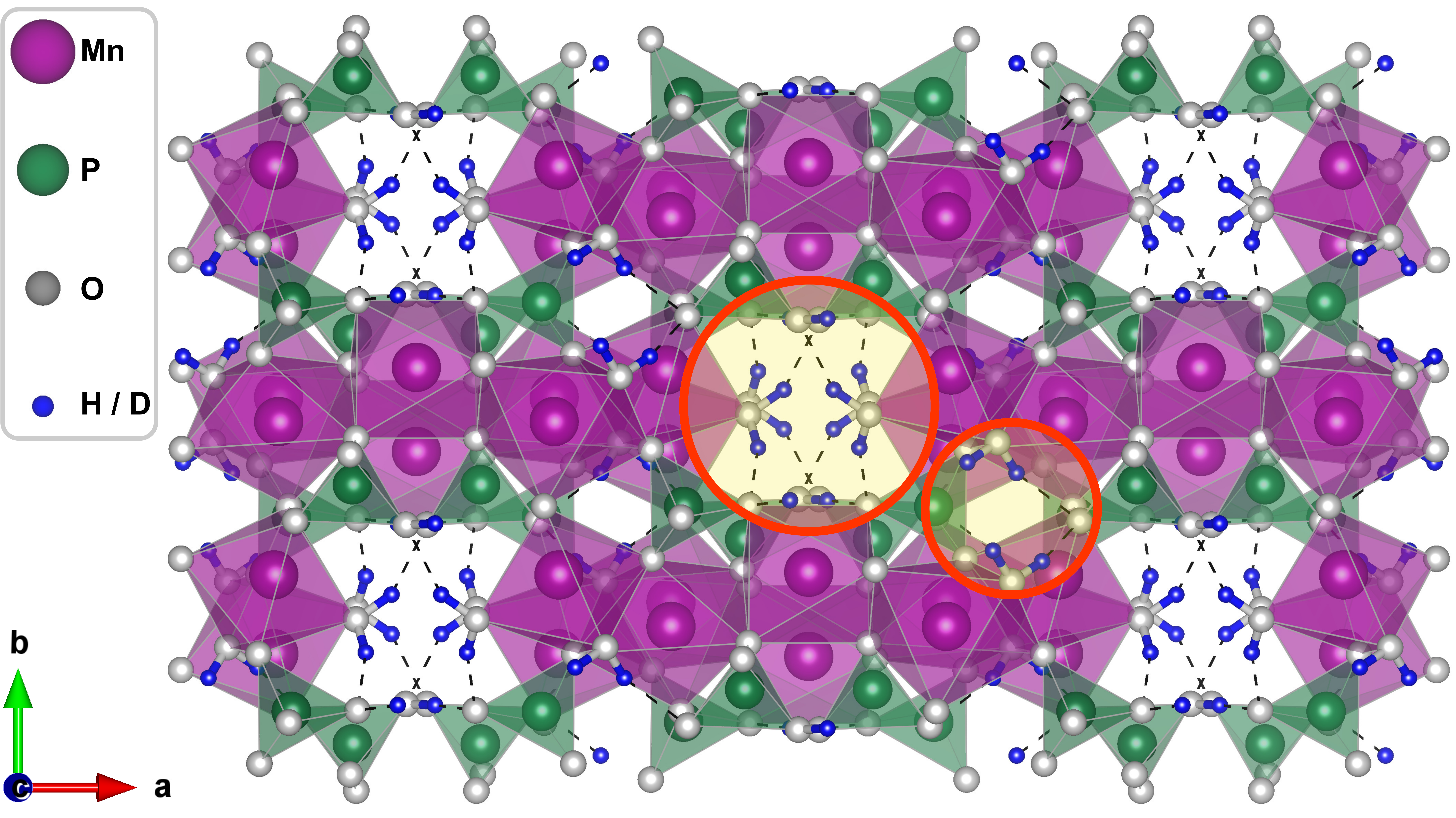
The data that supports the findings of this study are available within the article and its supplementary material. Raw data were generated at the DESY, PSI and ILL large scale facilities. Derived data supporting the findings of this study are available from the corresponding author (S.H.P.) upon reasonable request.

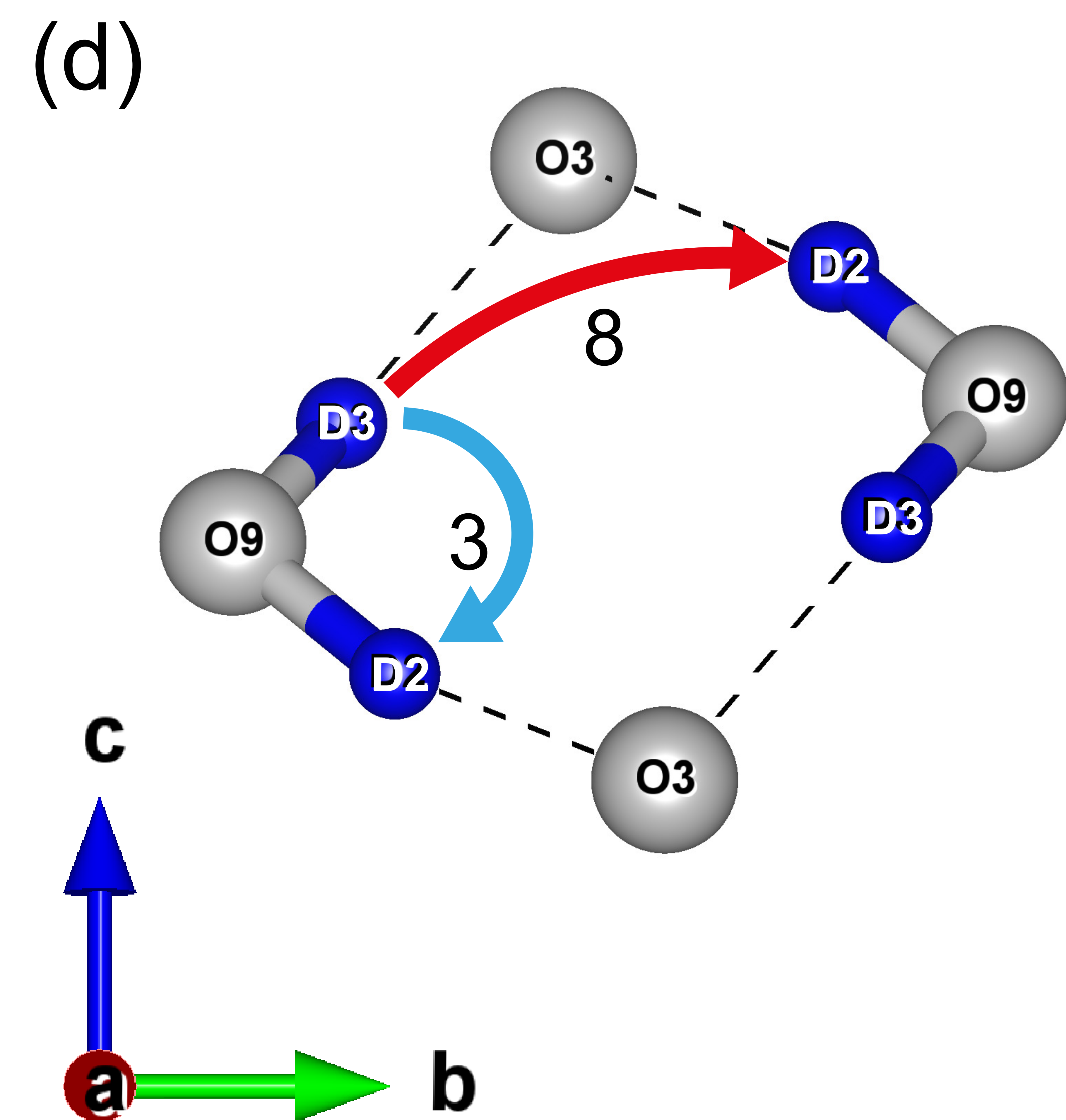
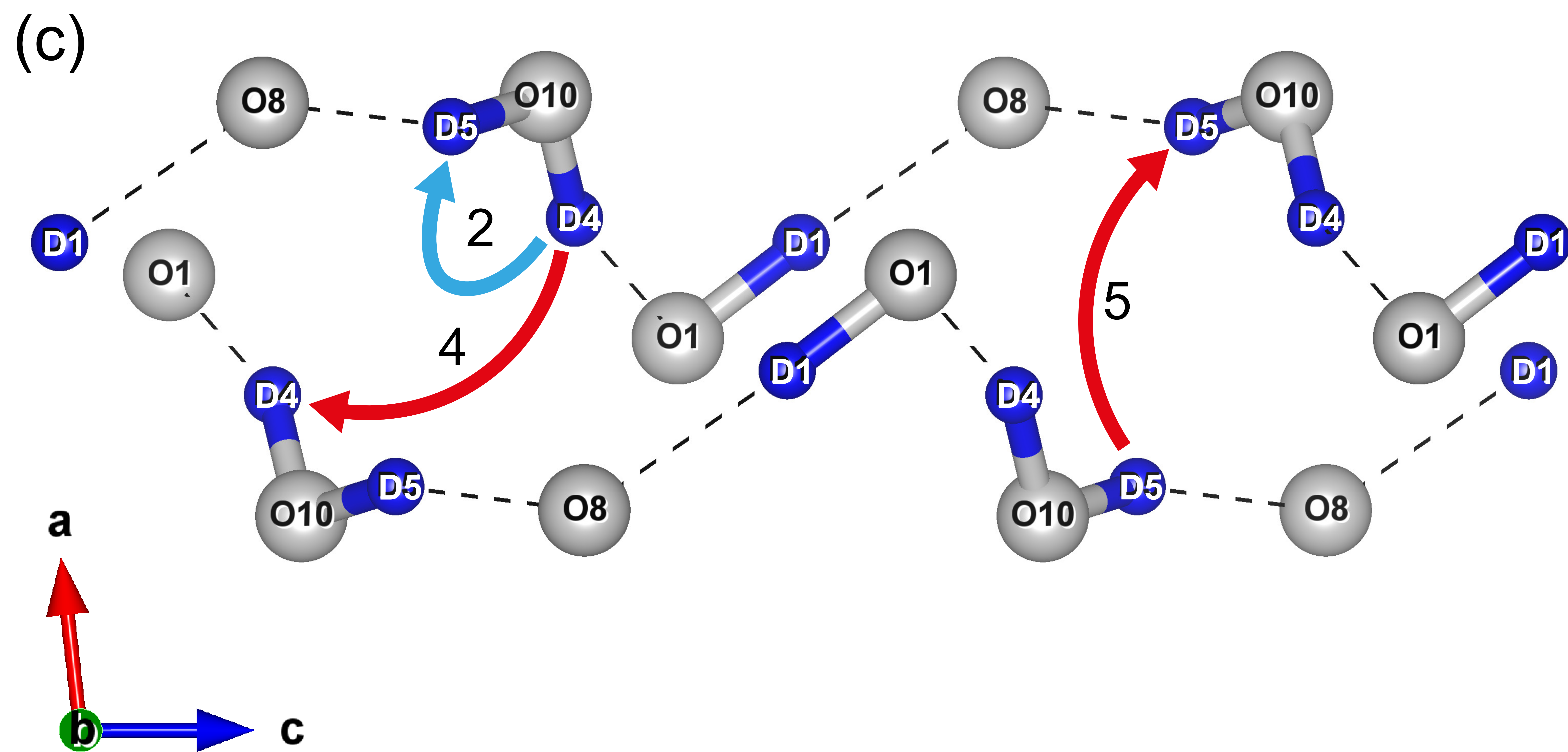
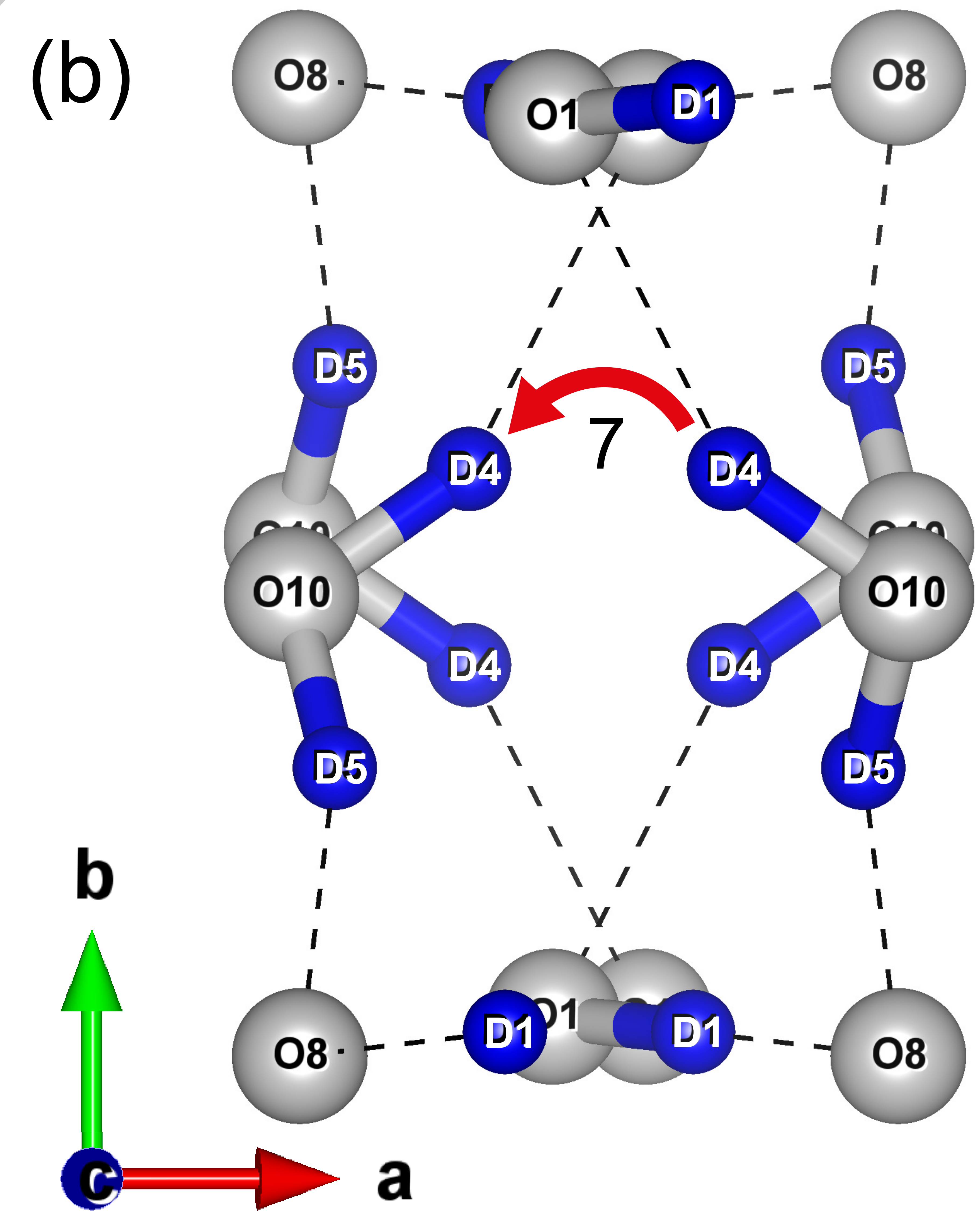
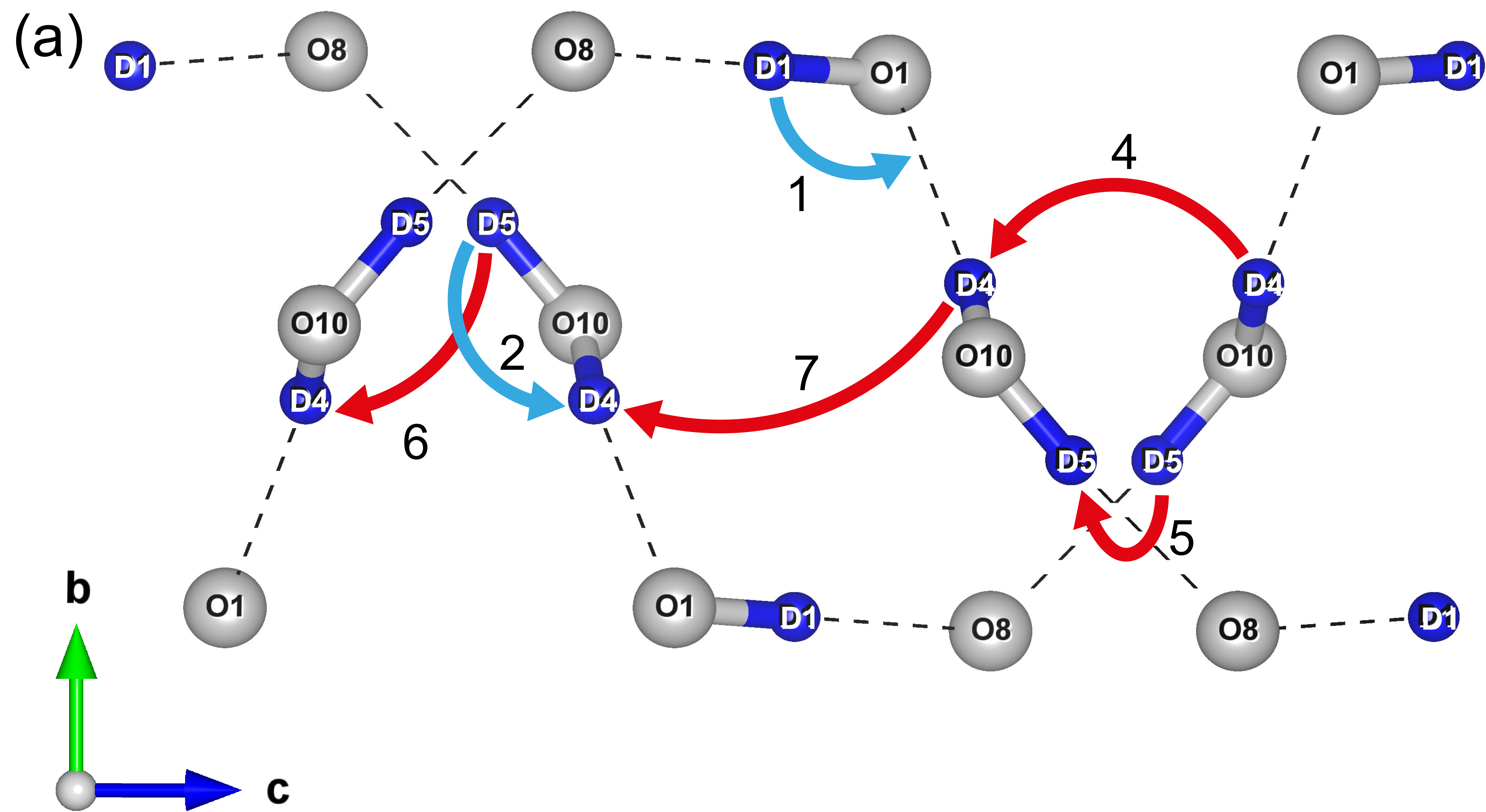
REFERENCES

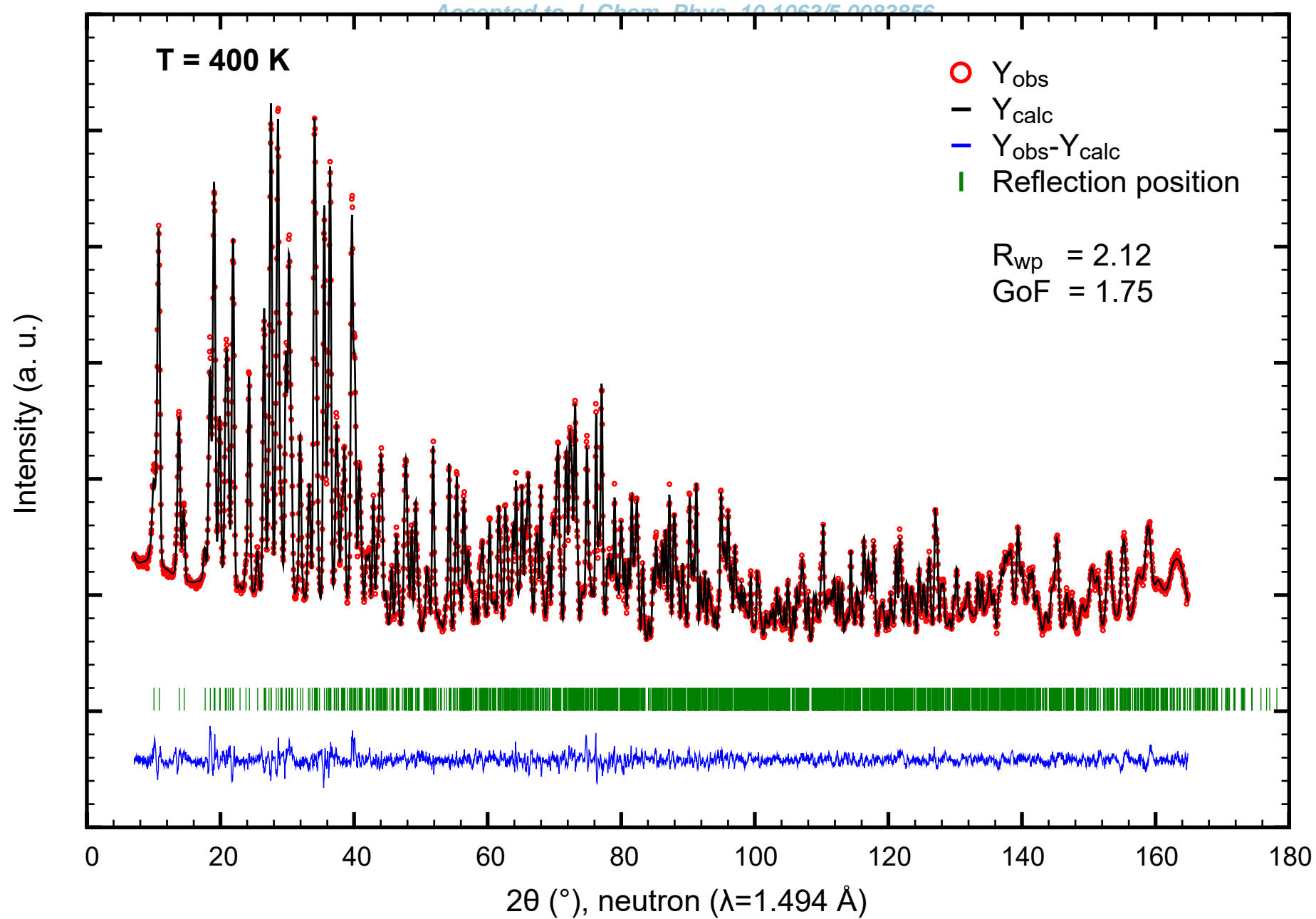
- Q. Chen and A. Braun, "Protons and the hydrogen economy," *MRS Energy & Sustainability* **4**, 80–83 (2017).
- A. Borgschulte, J. Terreni, E. Billeter, L. Daemen, Y. Cheng, A. Pandey, Z. Lodziana, R. J. Hemley, and A. J. Ramirez-Cuesta, "Inelastic neutron scattering evidence for anomalous H–H distances in metal hydrides," *Proceedings of the National Academy of Sciences of the United States of America* **117**, 4021–4026 (2020).
- S. Tao, L. Zhai, A. D. Dinga Wonanke, M. A. Addicoat, Q. Jiang, and D. Jiang, "Confining H_3PO_4 network in covalent organic frameworks enables proton super flow," *Nature Communications* **11**, 8–15 (2020).
- S. M. Haile, D. A. Boysen, C. R. I. Chisholm, and R. B. Merle, "Solid acids as fuel cell electrolytes," *Nature* **410**, 910–913 (2001).
- P. Colomban, ed., *Proton conductors: Solids, membranes, and gels-materials and devices*. (Cambridge University Press, New York, 1992) pp. 175,234.
- P. Colomban, "Proton conductors and their applications: A tentative historical overview of the early researches," *Solid State Ionics*, 125–144 (2019).
- A. C. Dupuis, "Proton exchange membranes for fuel cells operated at medium temperatures: Materials and experimental techniques," *Progress in Materials Science* **56**, 289–327 (2011).
- A. I. Baranov, "Crystals with Disordered Hydrogen-Bond Networks and Superprotonic Conductivity. Review," *Crystallography Reports* **48**, 1012–1037 (2003).
- Y. Matsuda, M. Yonemura, H. Koga, C. Pitteloud, M. Nagao, M. Hirayama, and R. Kanno, "Synthesis, crystal structure, and ionic conductivity of tunnel structure phosphates, $\text{RbMg}_{1-x}\text{H}_2\text{x}(\text{PO}_3)_3\cdot\text{y}(\text{H}_2\text{O})$," *Journal of Materials Chemistry A* **1**, 15544–15551 (2013).
- A. I. Baranov, L. A. Shuvalov, and N. M. Shchagina, "Superion conductivity and phase transitions in CsHSO_4 and CsHSeO_4 crystals," *JETP lett* **36**, 459–462 (1982).
- A. Ishikawa, H. Maekawa, T. Yamamura, Y. Kawakita, K. Shibata, and M. Kawai, "Proton dynamics of CsH_2PO_4 studied by quasi-elastic neutron scattering and PFG-NMR," *Solid State Ionics* **179**, 2345–2349 (2008).
- R. Blinc, V. Dimic, J. Petkovsek, and E. Pirkmajer, "Study of proton dynamics in paraelectric KH_2PO_4 by quasi-elastic cold neutron scattering," *Physics Letters A* **26**, 8–9 (1967).
- S. Ikeda, Y. Noda, H. Sugimoto, and Y. Yamada, "Dynamical properties of protons in KH_2PO_4 studied by incoherent neutron

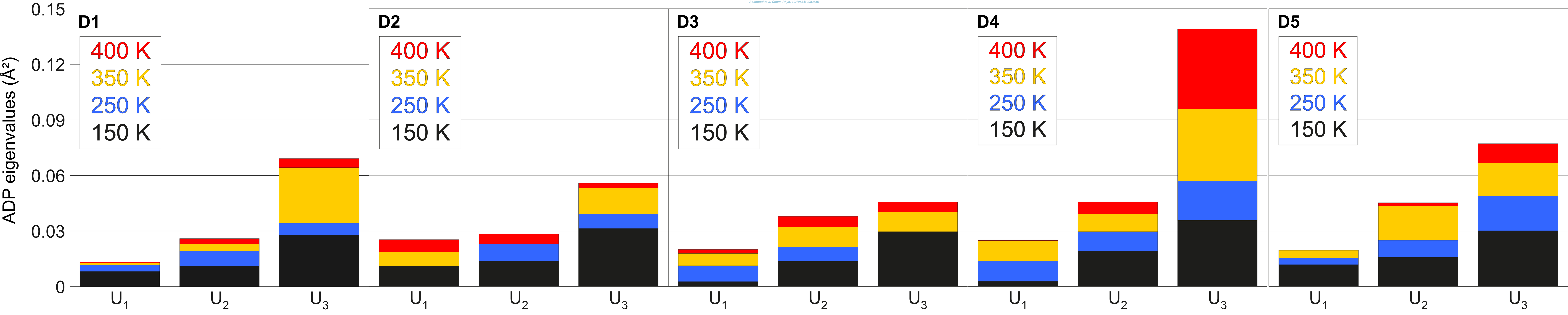
- scattering,” *Journal of the Physical Society of Japan* **63**, 1001–1008 (1994).
- ¹⁴A. Hartl, S.-H. Park, M. Hoelzel, N. Paul, and R. Gilles, “Proton conductivity in a hureaulite-type compound, $\text{Mn}_5[(\text{PO}_4)_2(\text{PO}_3(\text{OH}))_2](\text{HOH})_4$,” *Journal of Solid State Chemistry*, 290–302 (2019).
 - ¹⁵S.-H. Park, A. Hartl, D. Sheptyakov, M. Hoelzel, and A. Arauzo, “Structural Investigation into Magnetic Spin Orders of a Manganese Phosphatic Oxyhydroxide, $\text{Mn}_5[(\text{PO}_4)_2(\text{PO}_3(\text{OH}))_2](\text{HOH})_4$,” *Symmetry* **48**, 1688 (2021).
 - ¹⁶M. Baum, F. Rieutord, F. Juranyi, C. Rey, and D. Rébiscoul, “Dynamical and Structural Properties of Water in Silica Nanoconfinement: Impact of Pore Size, Ion Nature, and Electrolyte Concentration,” *Langmuir* **35**, 10780–10794 (2019).
 - ¹⁷X. Liu, Y. Li, J. Xue, W. Zhu, J. Zhang, Y. Yin, Y. Qin, K. Jiao, Q. Du, B. Cheng, X. Zhuang, J. Li, and M. D. Guiver, “Magnetic field alignment of stable proton-conducting channels in an electrolyte membrane,” *Nature Communications* **10**, 1–13 (2019).
 - ¹⁸G. Xing, T. Yan, S. Das, T. Ben, and S. Qiu, “Synthesis of Crystalline Porous Organic Salts with High Proton Conductivity,” *Angewandte Chemie - International Edition* **57**, 5345–5349 (2018).
 - ¹⁹H. Matsui and M. Tadokoro, “Eigen-like hydrated protons traveling with a local distortion through the water nanotube in new molecular porous crystals $\{\text{MIII}(\text{H}_2\text{O})_3(\text{TMA})\cdot 20\text{H}_2\text{O}\}_n$ ($\text{M}=\text{Co}, \text{Rh}, \text{Ru}$),” *Journal of Chemical Physics* **137**, 1–10 (2012).
 - ²⁰N. Zhang, Y. Song, J. Huo, Y. Li, Z. Liu, J. Bao, S. Chen, X. Ruan, and G. He, “Formation Mechanism of the Spiral-Like Structure of a Hydrogen Bond Network Confined in a Fluorinated Nanochannel: A Molecular Dynamics Simulation,” *Journal of Physical Chemistry C* **121**, 13840–13847 (2017).
 - ²¹M. Sadakiyo, T. Yamada, and H. Kitagawa, “Rational designs for highly proton-conductive metal-organic frameworks,” *Journal of the American Chemical Society* **131**, 9906–9907 (2009).
 - ²²M. A. Belyanchikov, M. Savinov, Z. V. Bedran, P. Bednyakov, P. Proschek, J. Prokleska, V. A. Abalmasov, J. Petzelt, E. S. Zhukova, V. G. Thomas, A. Dudka, A. Zhugayevych, A. S. Prokhorov, V. B. Anzin, R. K. Kremer, J. K. Fischer, P. Lunkenheimer, A. Loidl, E. Uykur, M. Dressel, and B. Gorshunov, “Dielectric ordering of water molecules arranged in a dipolar lattice,” *Nature Communications* **11**, 1–9 (2020).
 - ²³M. Busch, T. Hofmann, B. Frick, J. P. Embs, B. Dyatkin, and P. Huber, “Ionic liquid dynamics in nanoporous carbon: A pore-size- and temperature-dependent neutron spectroscopy study on supercapacitor materials,” *Physical Review Materials* **4**, 1–12 (2020).
 - ²⁴A. B. Yaroslavl'tsev, “Proton conductivity of inorganic hydrates,” *Russian Chemical Reviews* **63**, 429–435 (1994).
 - ²⁵Rigaku Oxford Diffraction UK Ltd, “CrysAlisPro,” (2015).
 - ²⁶V. Petříček, M. Dusek, and L. Palatinus, “Crystallographic computing system JANA2006: general features,” *Zeitschrift für Kristallographie-Crystalline Materials* **229**, 345–352 (2014).
 - ²⁷R. T. Azuah, L. R. Kneller, Y. Qiu, P. L. Tregenna-Piggott, C. M. Brown, J. R. Copley, and R. M. Dimeo, “DAVE: A comprehensive software suite for the reduction, visualization, and analysis of low energy neutron spectroscopic data,” *Journal of Research of the National Institute of Standards and Technology* **114**, 341–358 (2009).
 - ²⁸R. Böhmer, M. Maglione, P. Lunkenheimer, and A. Loidl, “Radio-frequency dielectric measurements at temperatures from 10 to 450 K,” *Journal of Applied Physics* **65**, 901–904 (1989).
 - ²⁹D. Marx and J. Hutter, *Ab initio molecular dynamics: basic theory and advanced methods* (Cambridge University Press, Cambridge, 2009).
 - ³⁰T. D. Kühne, M. Iannuzzi, M. D. Ben, V. V. Rybkin, P. Seewald, F. Stein, T. Laino, R. Z. Khaliullin, O. Schütt, F. Schiffmann, D. Golze, J. Wilhelm, S. Chulkov, M. H. Bani-Hashemian, V. Weber, U. Borštnik, M. Taillefumier, A. S. Jakobovits, A. Lazaro, H. Pabst, T. Müller, R. Schade, M. Guidon, S. Andermatt, N. Holmberg, G. K. Schenter, A. Hehn, A. Bussy, F. Belleflamme, G. Tabacchi, A. Glöck, M. Lass, I. Bethune, C. J. Mundy, C. Plessl, M. Watkins, J. VandeVondele, M. Krack, and J. Hutter, “CP2K: An electronic structure and molecular dynamics software package - quickstep: Efficient and accurate electronic structure calculations,” *J. Chem. Phys.* **152**, 194103 (2020).
 - ³¹J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, and J. Hutter, “Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach,” *Computer Physics Communications* **167**, 103–128 (2005).
 - ³²S. Goedecker and M. Teter, “Separable dual-space Gaussian pseudopotentials,” *Physical Review B - Condensed Matter and Materials Physics* **54**, 1703–1710 (1996).
 - ³³C. Hartwigsen, S. Goedecker, and J. Hutter, “Hartwigsen-1998,” *Physical Review B* **58**, 3641–3662 (1998).
 - ³⁴M. Krack, “Pseudopotentials for H to Kr optimized for gradient-corrected exchange-correlation functionals,” *Theoretical Chemistry Accounts* **114**, 145–152 (2005).
 - ³⁵J. VandeVondele and J. Hutter, “Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases,” *Journal of Chemical Physics* **127**, 1–9 (2007).
 - ³⁶J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple,” *Physical review letters* **77**, 3865 (1996).
 - ³⁷S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, “A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu,” *Journal of Chemical Physics* **132**, 1–19 (2010).
 - ³⁸G. Kresse and J. Furthmüller, “Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set,” *Phys. Rev. B* **54**, 11169–11186 (1996).
 - ³⁹G. Kresse and D. Joubert, “From ultrasoft pseudopotentials to the projector augmented-wave method,” *Phys. Rev. B* **59**, 1758–1775 (1999).
 - ⁴⁰M. Brehm and B. Kirchner, “TRAVIS - A free analyzer and visualizer for monte carlo and molecular dynamics trajectories,” *Journal of Chemical Information and Modeling* **51**, 2007–2023 (2011).
 - ⁴¹M. Brehm, M. Thomas, S. Gehrke, and B. Kirchner, “TRAVIS—A free analyzer for trajectories from molecular simulation,” *Journal of Chemical Physics* **152** (2020).
 - ⁴²W. Humphrey, A. Dalke, and K. Schulten, “VMD: visual molecular dynamics,” *Journal of molecular graphics* **14**, 33–38 (1996).
 - ⁴³H. Euchner, M. Mihalkovič, F. Gähler, M. R. Johnson, H. Schober, S. Rols, E. Suard, A. Bosak, S. Ohhashi, A. P. Tsai, S. Lidin, C. P. Gomez, J. Custers, S. Paschen, and M. De Boissieu, “Anomalous vibrational dynamics in the $\text{Mg}_2\text{Zn}_{11}$ phase,” *Physical Review B - Condensed Matter and Materials Physics* **83**, 1–17 (2011).
 - ⁴⁴M. Thomas, M. Brehm, R. Fligg, P. Vöhringer, and B. Kirchner, “Computing vibrational spectra from ab initio molecular dynamics,” *Physical Chemistry Chemical Physics* **15**, 6608–6622 (2013).
 - ⁴⁵T. Famprikis, P. Canepa, J. A. Dawson, M. S. Islam, and C. Masquelier, “Fundamentals of inorganic solid-state electrolytes for batteries,” *Nature Materials* **18**, 1278–1291 (2019).
 - ⁴⁶B. Frick, J. Combet, and L. Van Eijck, “New possibilities with inelastic fixed window scans and linear motor Doppler drives on high resolution neutron backscattering spectrometers,” *Nuclear Instruments and Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* **669**, 7–13 (2012).
 - ⁴⁷M. T. Telling, L. Clifton, J. Combet, B. Frick, S. Howells, and V. G. Sakai, “Lyophilised protein dynamics: More than just methyls?” *Soft Matter* **8**, 9529–9532 (2012).
 - ⁴⁸J. P. Embs, F. Juranyi, and R. Hempelmann, “Introduction to quasielastic neutron scattering,” *Zeitschrift für Physikalische Chemie* **224**, 5–32 (2010).
 - ⁴⁹F. Kremer and A. Schönhals, eds., *Broadband Dielectric Spectroscopy* (Springer, Berlin, 2002).

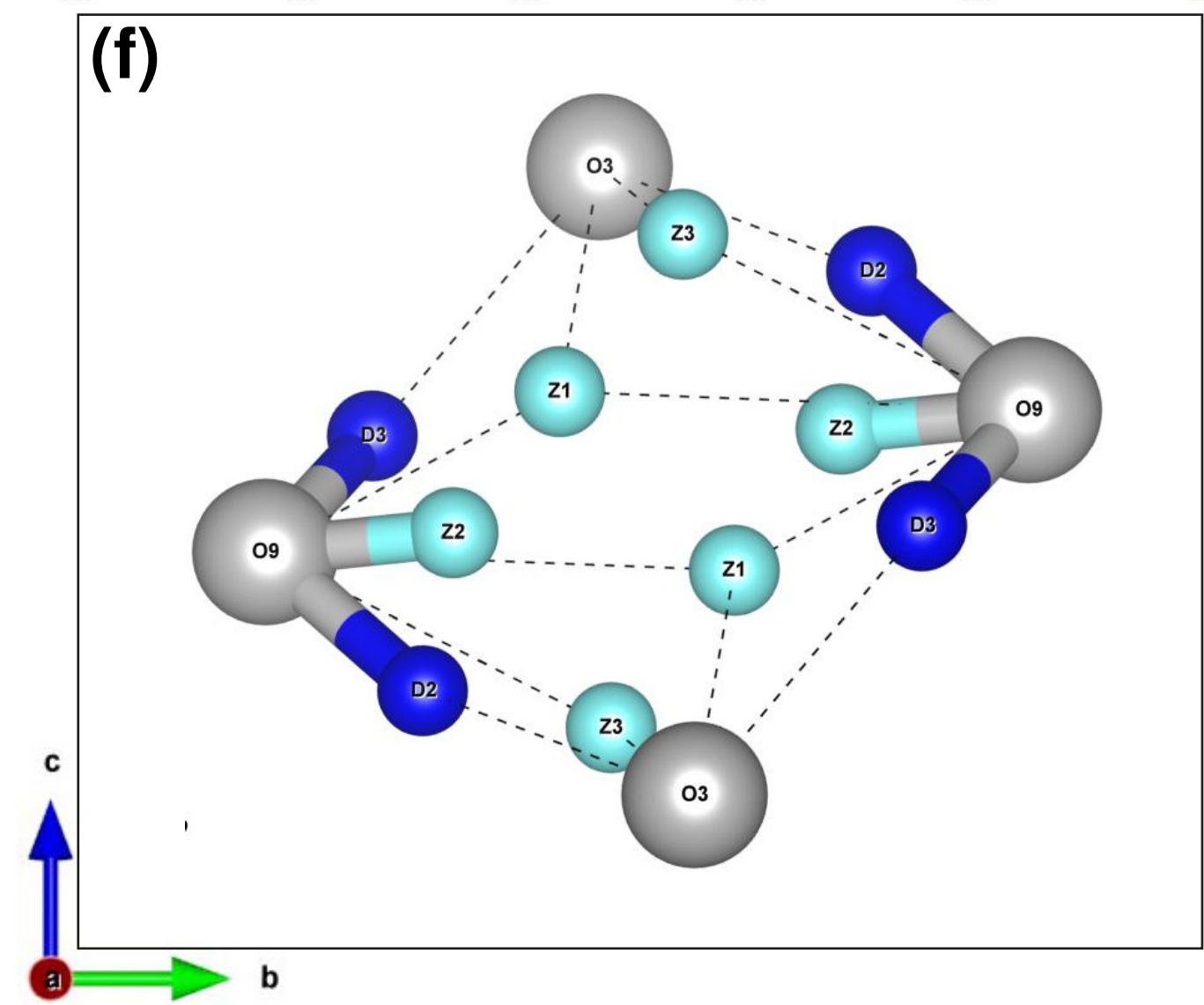
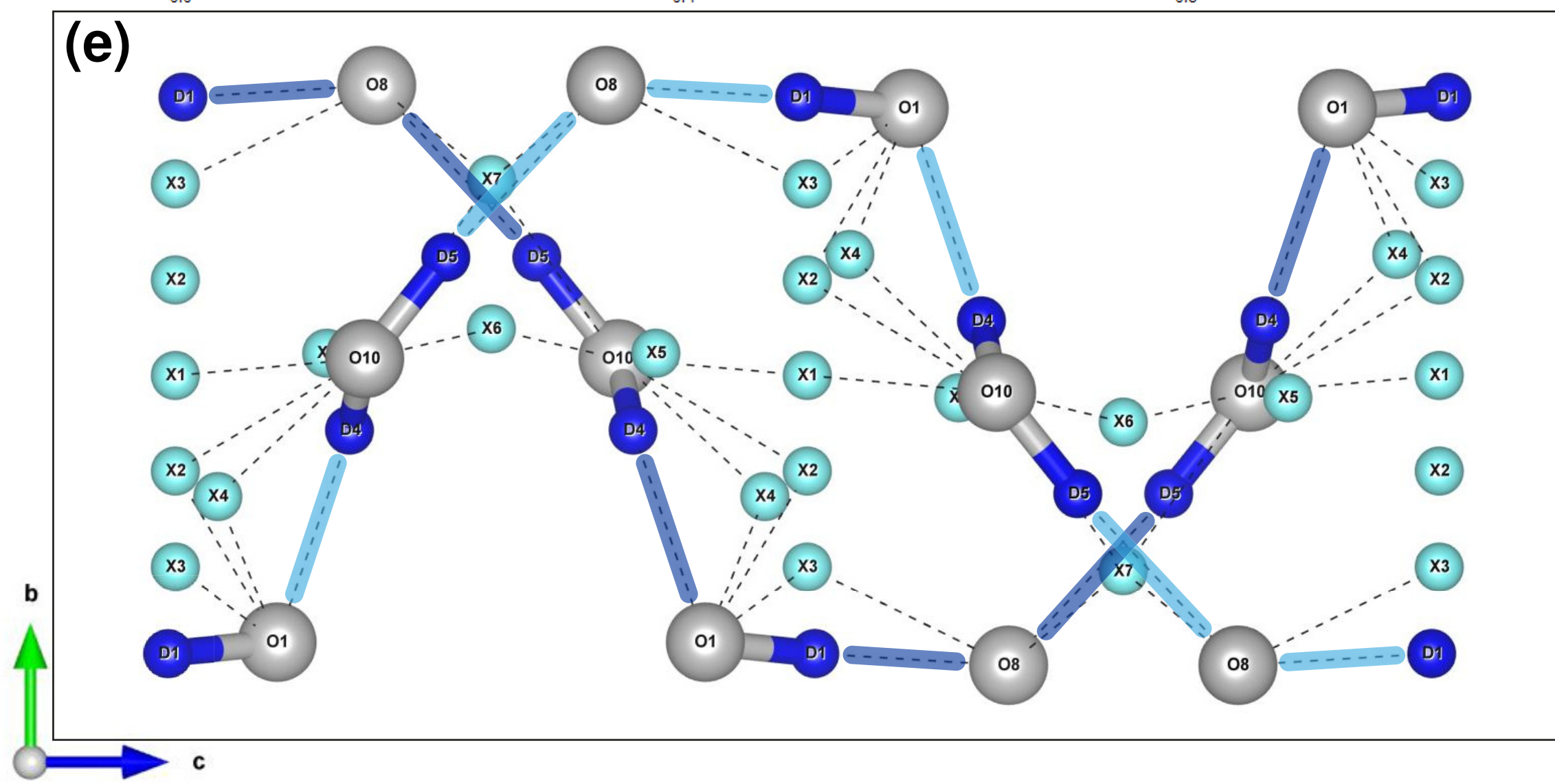
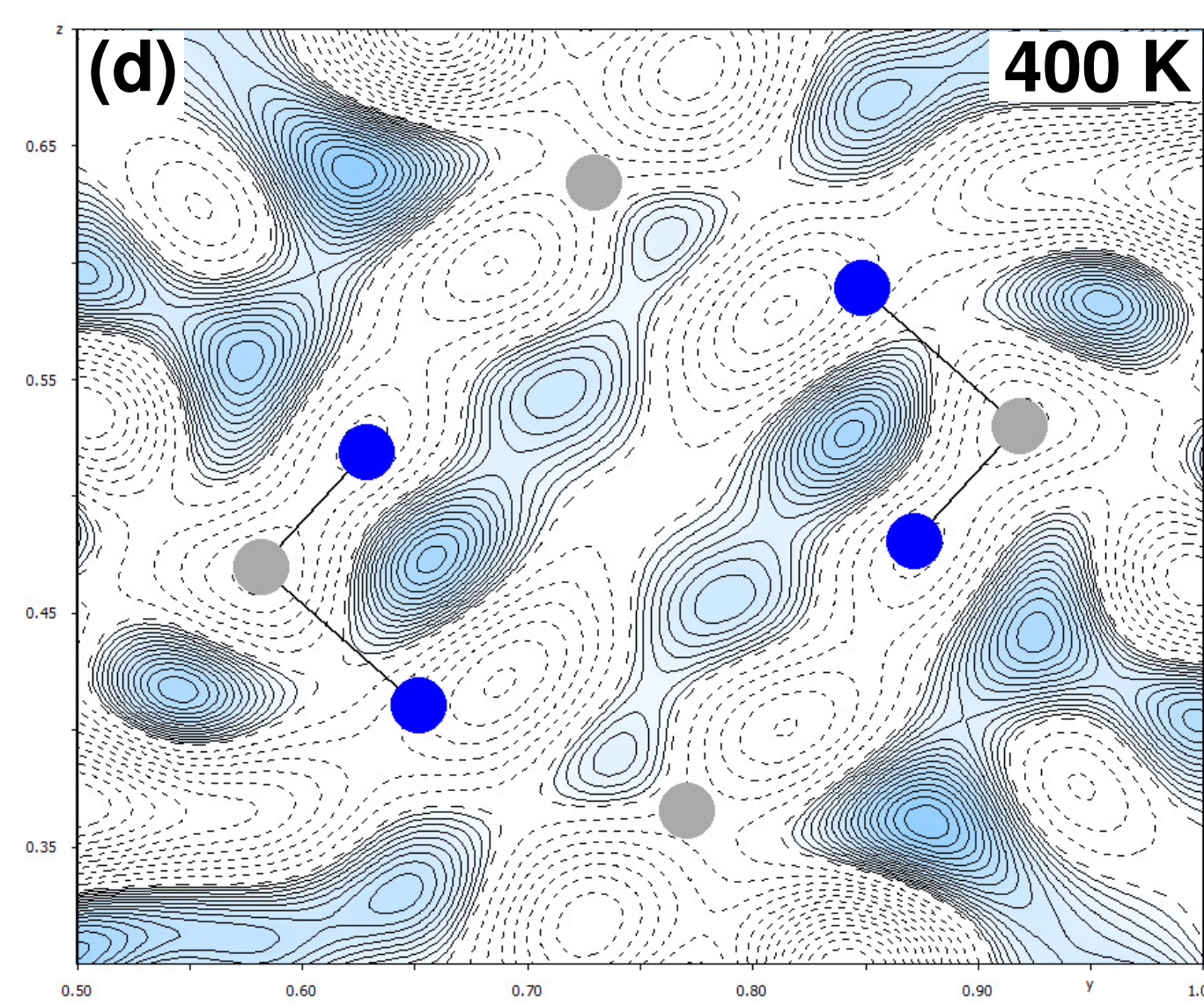
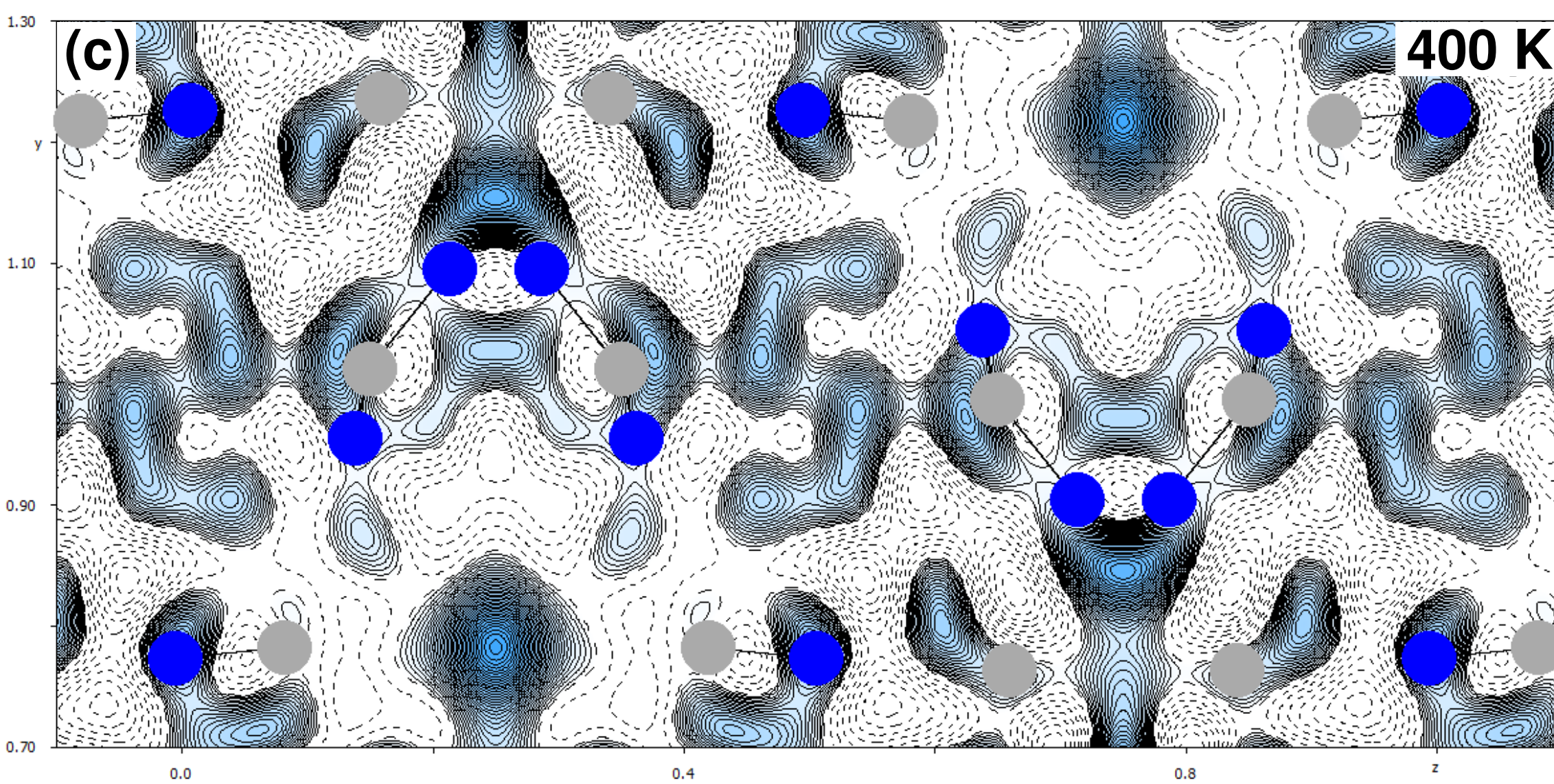
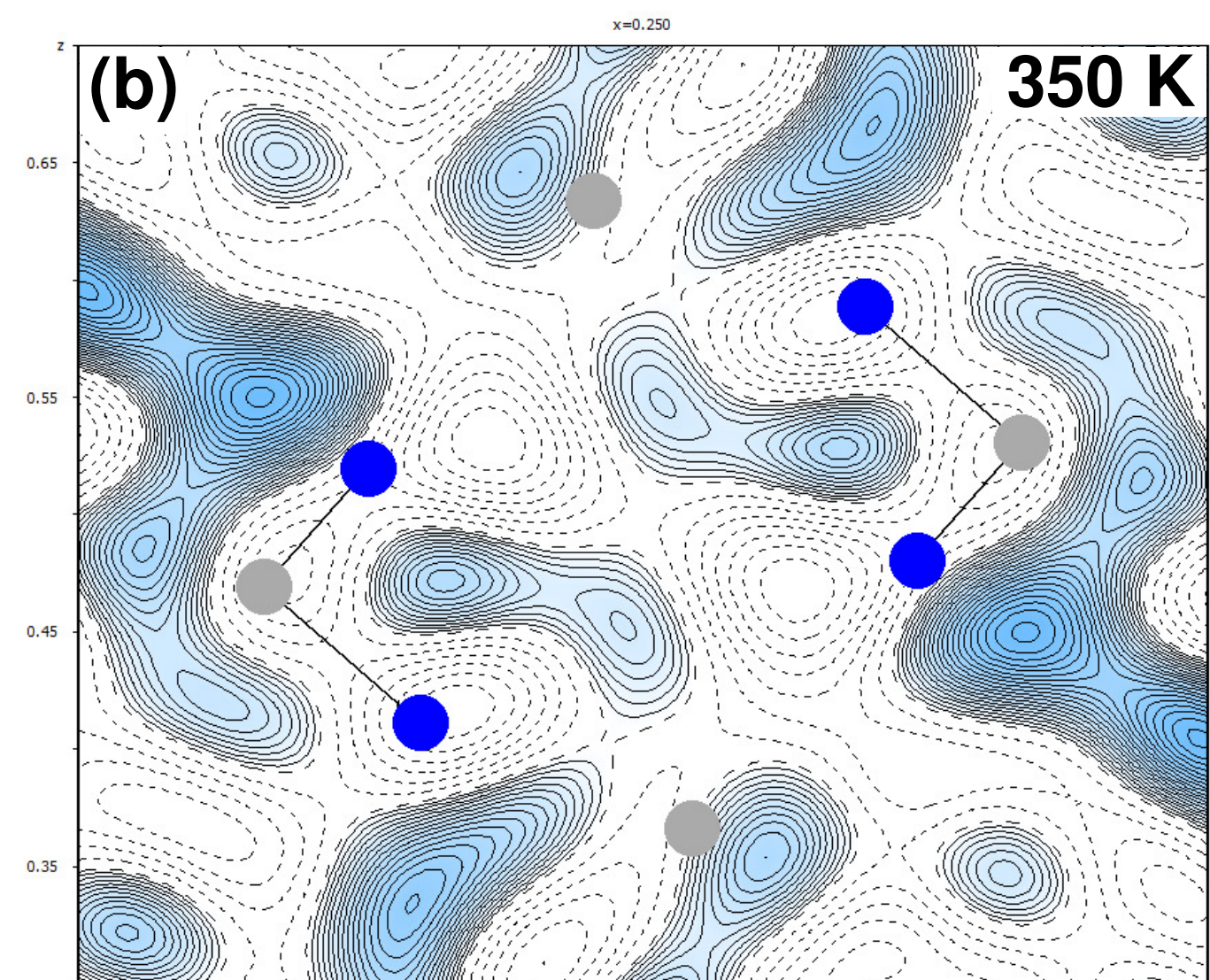
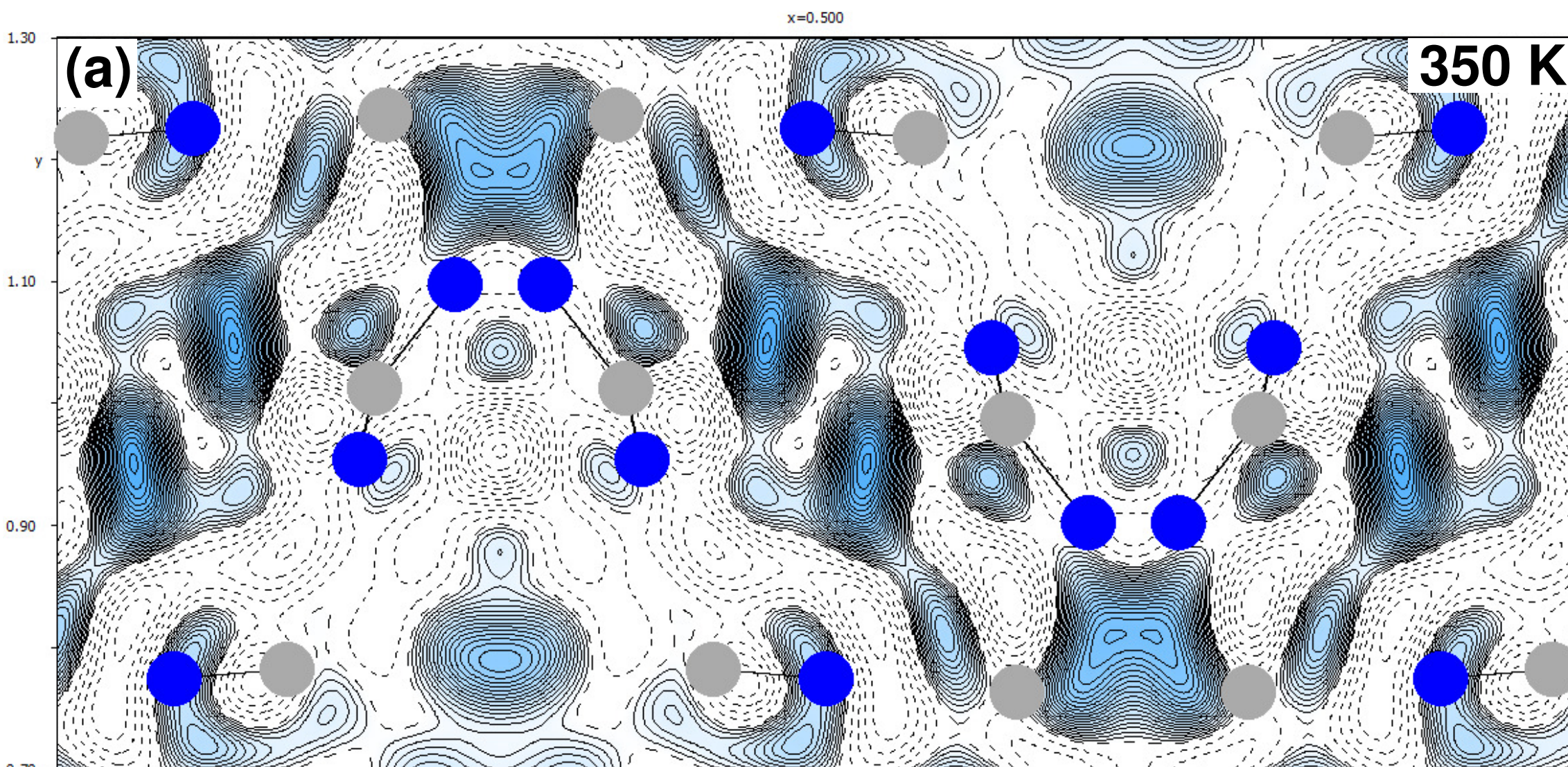
- ⁵⁰P. Lunkenheimer and A. Loidl, "Dielectric spectroscopy on organic charge-transfer salts," *Journal of Physics: Condensed Matter* **27**, 373001 (2015).
- ⁵¹P. Lunkenheimer, S. Krohns, S. Riegg, S. G. Ebbinghaus, A. Reller, and A. Loidl, "Colossal dielectric constants in transition-metal oxides," *European Physical Journal: Special Topics* **180**, 61–89 (2010).
- ⁵²S. Emmert, M. Wolf, R. Gulich, S. Krohns, S. Kastner, P. Lunkenheimer, and A. Loidl, "Electrode polarization effects in broadband dielectric spectroscopy," *European Physical Journal B* **83**, 157–165 (2011).
- ⁵³M. D. Ediger, C. A. Angell, and S. R. Nagel, "Supercooled liquids and glasses," *The Journal of Physical Chemistry* **100**, 13200–13212 (1996).
- ⁵⁴P. Lunkenheimer and A. Loidl, "Glassy dynamics: From millihertz to terahertz," in *The Scaling of Relaxation Processes*, edited by F. Kremer and A. Loidl (Springer International Publishing, Cham, 2018) pp. 23–59.
- ⁵⁵C. A. Angell, "Strong and Fragile Liquids," in *Relaxations in Complex Systems*, edited by K. L. Ngai and G. B. Wright (Springer, New York, 1985) pp. 3–11.
- ⁵⁶R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, "Non-exponential relaxations in strong and fragile glass formers," *The Journal of Chemical Physics* **99**, 4201–4209 (1993).
- ⁵⁷W. M. Du, G. Li, H. Z. Cummins, M. Fuchs, J. Toulouse, and L. A. Knauss, "Light-scattering study of the liquid-glass transition in propylene carbonate," *Phys. Rev. E* **49**, 2192–2205 (1994).
- ⁵⁸A. Faraone, D. V. Wagle, G. A. Baker, E. C. Novak, M. Ohl, D. Reuter, P. Lunkenheimer, A. Loidl, and E. Mamontov, "Glycerol hydrogen-bonding network dominates structure and collective dynamics in a deep eutectic solvent," *The Journal of Physical Chemistry B* **122**, 1261–1267 (2018).
- ⁵⁹S. Kämmerer, W. Kob, and R. Schilling, "Test of mode coupling theory for a supercooled liquid of diatomic molecules. ii. q -dependent orientational correlators," *Phys. Rev. E* **58**, 2141–2150 (1998).
- ⁶⁰W. Götze and T. Voigtmann, "Universal and nonuniversal features of glassy relaxation in propylene carbonate," *Phys. Rev. E* **61**, 4133–4147 (2000).
- ⁶¹M. Winkler, P. Lunkenheimer, A. Loidl, S.-H. Park, B. Röska, and M. Hoelzel, "Charge transport by global protonic conductivity and relaxational dynamics over hydrogen bonds in $\text{Fe}_2+\text{Fe}_3+3.2 (\text{Mn}_2+\text{Zn})_0.8 (\text{PO}_4)_3 (\text{OH})_{4.2} (\text{HOH})_{0.8}$," *Solid State Ionics*, 115240 (2020).
- ⁶²S. L. Hutton, I. Fehst, R. Böhmer, M. Braune, B. Mertz, P. Lunkenheimer, and A. Loidl, "Proton glass behavior and hopping conductivity in solid solutions of antiferroelectric betaine phosphate and ferroelectric betaine phosphite," *Phys. Rev. Lett.* **66**, 1990–1993 (1991).
- ⁶³Y. Feng, C. Ancona-Torres, T. F. Rosenbaum, G. F. Reiter, D. L. Price, and E. Courtens, "Quantum and classical relaxation in the proton glass," *Phys. Rev. Lett.* **97**, 145501 (2006).
- ⁶⁴N. H. Bashian, S. Zhou, M. Zuba, A. M. Ganose, J. W. Stiles, A. Ee, D. S. Ashby, D. O. Scanlon, L. F. Piper, B. Dunn, and B. C. Melot, "Correlated Polyhedral Rotations in the Absence of Polarons during Electrochemical Insertion of Lithium in ReO_3 ," *ACS Energy Letters* **3**, 2513–2519 (2018).
- ⁶⁵A. Hartl, *Proton motions in hydrogen bonds of phosphatic oxyhydroxides: the case of $\text{Mn}_2+[(\text{PO}_4)_2(\text{PO}_3\text{OH})_2](\text{HOH})_4$* , Master's thesis, Ludwig Maximilian University, Munich (2020).

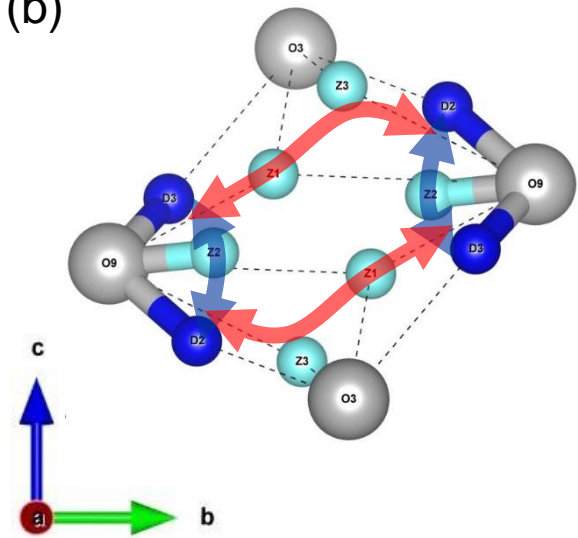


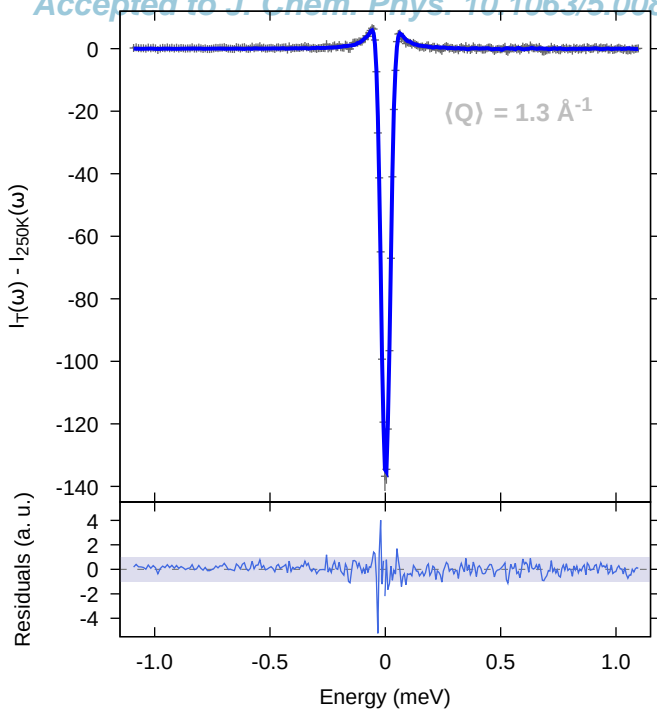


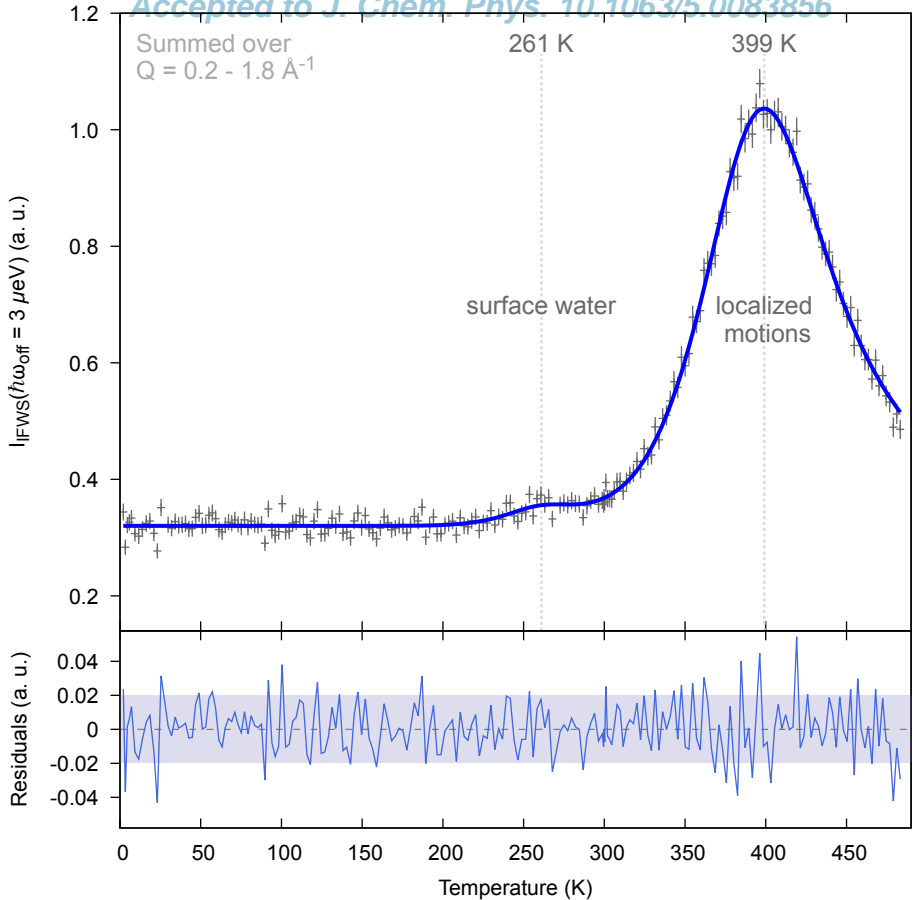


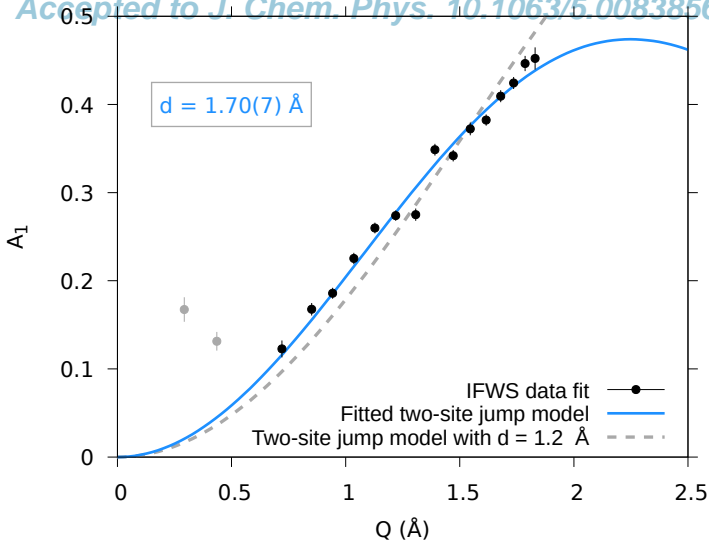


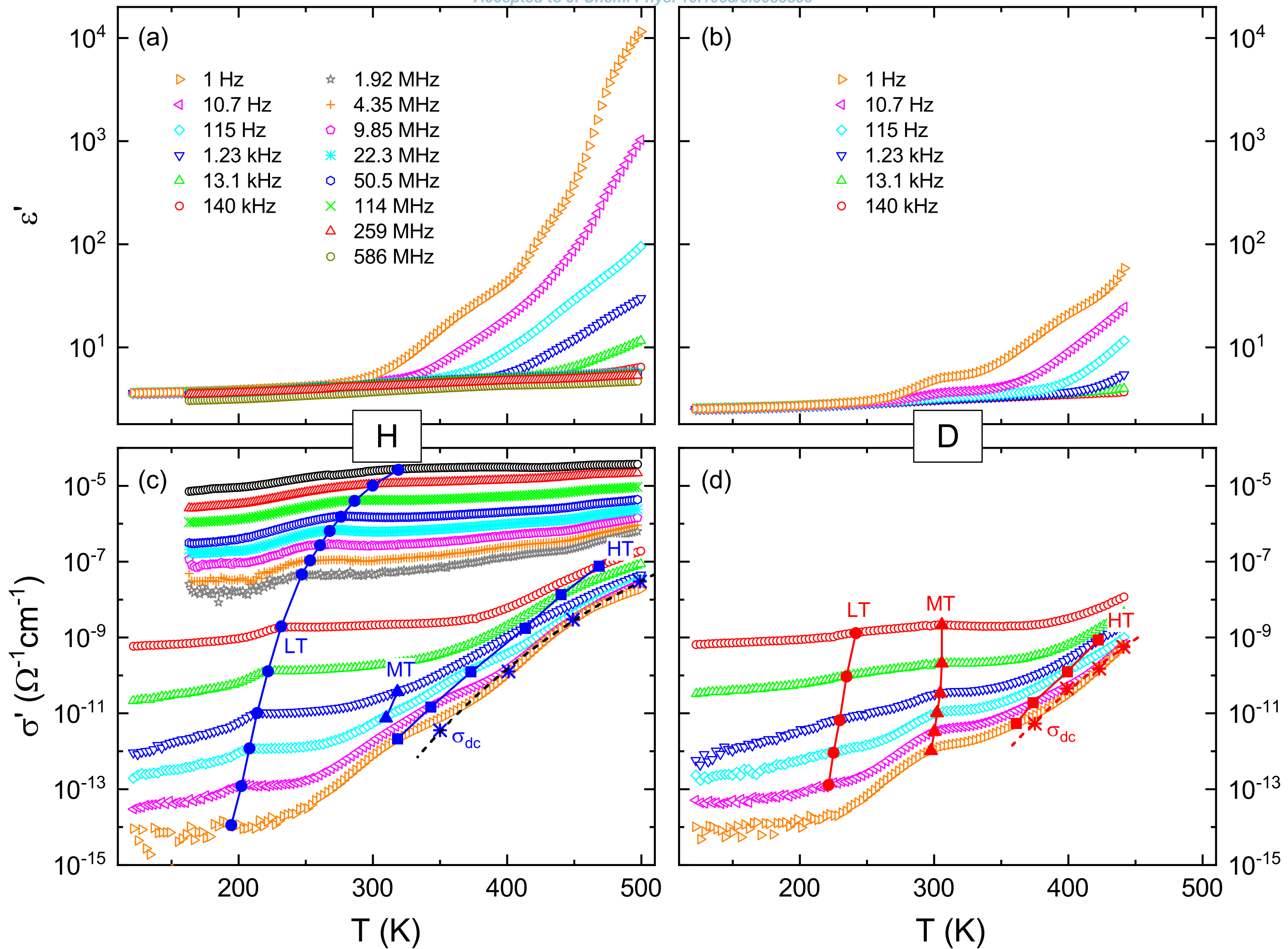


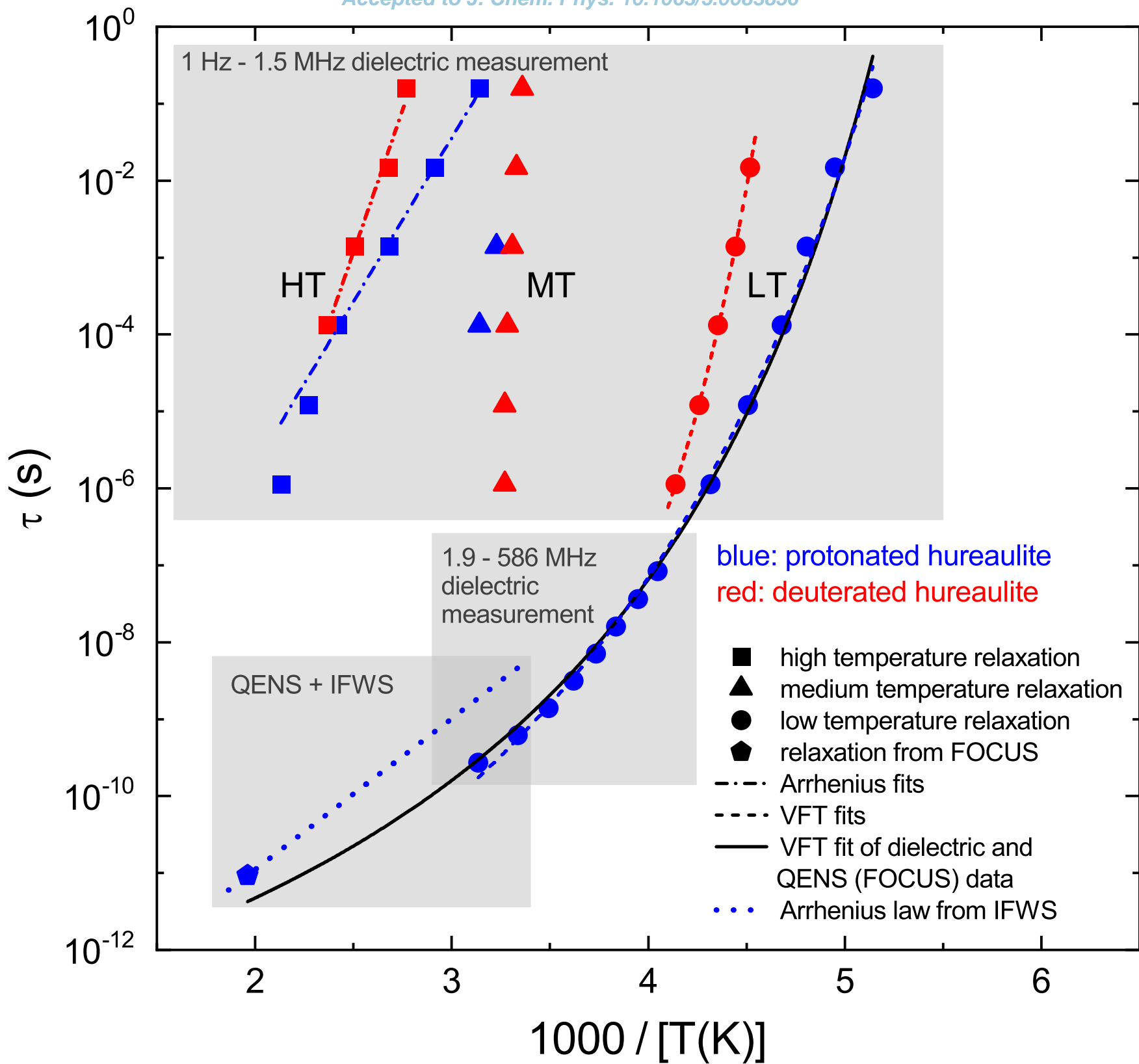


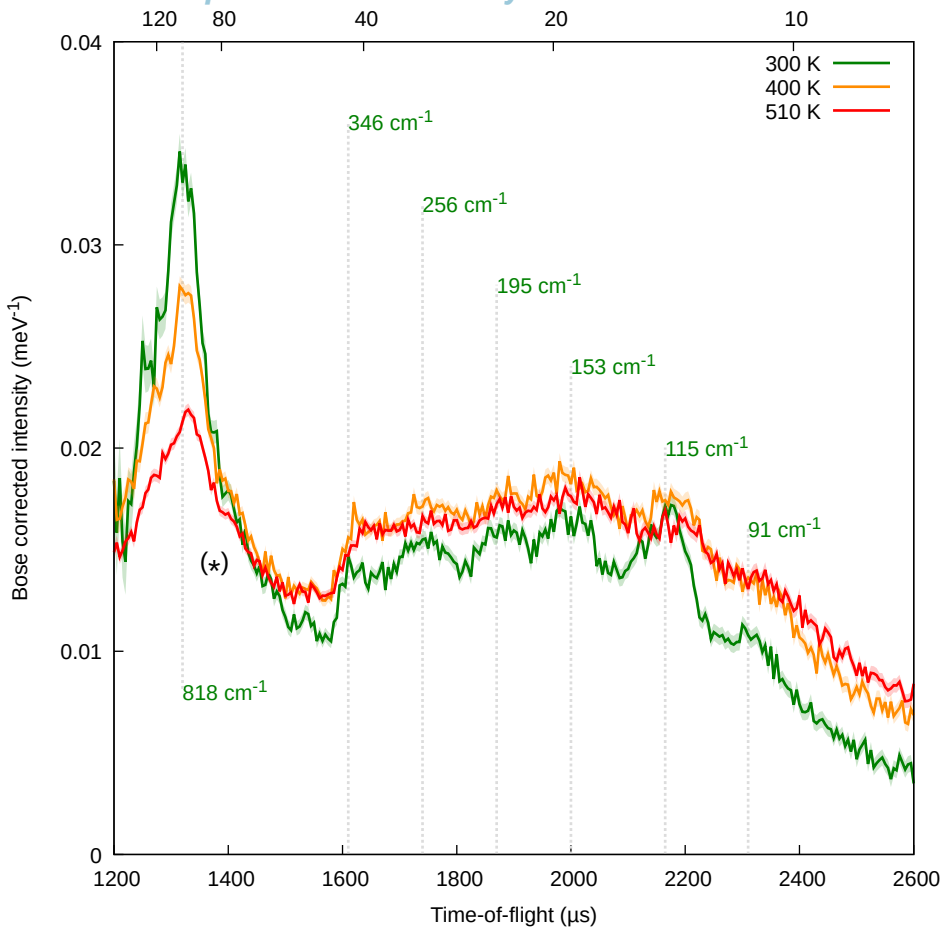












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