

A theoretical and experimental study of the crystal structure of $\text{H}_2\text{V}_3\text{O}_8$ [†]

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1 Supplementary Information

The crystal structure of $\text{H}_2\text{V}_3\text{O}_8$ was described¹ as being characterized by a nearly two-dimensional framework of V_3O_8 layers, comprised of three kinds of $[\text{VO}_n]$ polyhedra: two $[\text{VO}_6]$ octahedra and one $[\text{VO}_5]$ trigonal bipyramid. Units of edge-sharing octahedra pile up along the crystallographic **b**-axis and are connected by two edge-sharing trigonal bipyramids forming V_3O_8 layers in the *ab*-plane and stacked along the **b**-axis.

As the square pyramid and the trigonal bipyramid are closely related by the Berri-pseudo rotation, some authors may refer to this unit as trigonal bipyramid.

The electron diffraction patterns indicate that the $\text{H}_2\text{V}_3\text{O}_8$ fibers elongate along the **b**-axis.

A cut through the V-O bonds at 2.15 Å shows that the face-sharing octahedral coordination of vanadium atoms reduces to corner-sharing square pyramidal coordination, because the V(1)-O(1) bond, 2.180 Å, displaced along the **b**-direction, is longer than the other five bonds. Accordingly, the V_3O_8 framework can be described entirely by trigonal bipyramids, $[\text{VO}_5]$, which are alternatively corner- and edge-sharing in the (*ac*)-plane.

$\text{H}_2\text{V}_3\text{O}_8$ and $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ are likewise reported in literature to indicate the same compound, because of a lack of knowledge about the exact location of the hydrogen atoms in the lattice. A close look at the vanadium coordination in the monoclinic structure of V_3O_7 , space group $C2/c$, proposed by Waltersson², suggests that it does not share the identical structural features of the orthorhombic structure suggested by Oka¹ for $\text{H}_2\text{V}_3\text{O}_8$. In the monoclinic heptaoxide V_3O_7 , chains of edge-sharing square-based pyramids, $[\text{VO}_5]$, alternate by corner-sharing with the octahedra $[\text{VO}_6]$ along the crystallographic **c**-direction. The edge-sharing octahedra, $[\text{VO}_6]$, displaced on the (*ac*)-plane are corner-sharing along the crystallographic **b**-direction.

The Figure 1 shows a topview of the monoclinic V_3O_7 ² and the

orthorhombic $\text{H}_2\text{V}_3\text{O}_8$ ¹ structures, as they are reported in the references.

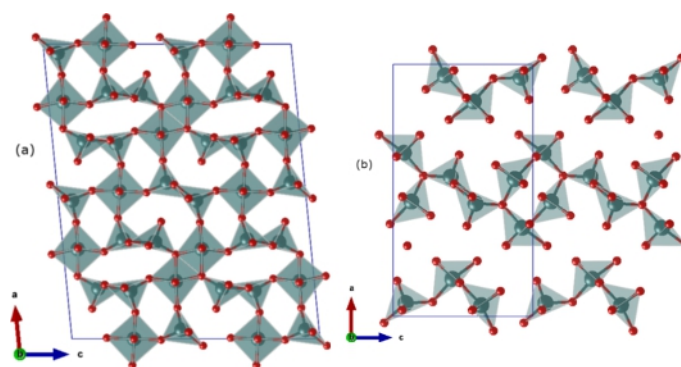


Fig. 1: (a) A top-view of the unit cell of the monoclinic structure of V_3O_7 ², symmetry space group $C2/m$. The average bond lengths of V-O bonds in $[\text{VO}_6]$ are 1.947 Å and 1.939 Å (distortion index of 0.056 in bond length); and in $[\text{VO}_5]$ are 1.813 Å and 1.825 Å (distortion index of 0.071 and 0.075 in bond length). (b) A topview of the $1 \times 1 \times 2$ cell of the orthorhombic $Pnma$ structure of $\text{H}_2\text{V}_3\text{O}_8$ ¹. By cutting through the V-O bond lengths at 2.15 Å, the edge-sharing octahedra¹, which pile up along the **b**-direction, become corner-sharing square pyramids with the average bond lengths of 1.901 Å (distortion index of 0.062 in bond length) and 1.893 Å (distortion index of 0.064 in bond length). The average bond lengths of V-O bonds in the other $[\text{VO}_5]$, corner-sharing trigonal bipyramids are 1.9001 Å and 1.830 Å (distortion index of 0.062 and 0.057 in bond length). The V(1)-O(3) bond length is the largest, 2.072 Å, while the V(2)-O(6) is 2.056 Å. The O(6) is the oxygen atom, which in our crystal structure prediction is bound to hydrogen atoms. The polyhedra of coordination of vanadium atoms are reported.

At DFT-D level of theory, the geometry optimization of the monoclinic structure of V_3O_7 ² resulted still monoclinic, after relaxing the atomic positions and the lattice parameters, but represented in the symmetry space group $C2/m$ (IT No 15), which differs from the $C2/c$ symmetry space group by the mirror plane. The number of formula units in the optimized structure is accordingly half of the reference structure. In the optimized structure the (1 0 0) plane passes through the six-fold coordinated vanadium atoms, which octahedra are alternatively corner- and edge-sharing units. In Table S.1 the structure data of the optimized monoclinic structure of V_3O_7 , symmetry space group $C2/m$ are reported.

The ribbon-like morphology of the V_3O_8 framework¹ is characterized by the corner-sharing units $[\text{VO}_5]$, aligned on the (*ac*)-plane and interconnected perpendicularly, along the **b**-direction

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Table 1: The atomic positions of the monoclinic structure of V_3O_7 , space group $C2/m$ (IT No 12), optimized at DFT-D level. The lattice parameters are: $a = 18.626 \text{ \AA}$, $b = 3.622 \text{ \AA}$, $c = 13.719 \text{ \AA}$, $\beta = 126.135$ degrees.

species	x	y	z	site
V(1)	0	1/2	0	2b
V(2)	0.5035	0	0.3840	4i
V(3)	0.3358	0	0.0653	4i
V(4)	0.6614	0	0.3290	4i
V(5)	0.2992	0	0.3400	4i
O(1)	0.0049	0	0.3894	4i
O(2)	0	0	0	2a
O(3)	0.7986	0	0.0573	4i
O(4)	0.2008	0	0.3608	4i
O(5)	0.2168	0	0.6315	4i
O(6)	0.3865	0	0.5937	4i
O(7)	0.3908	0	0.0029	4i
O(8)	0.2608	0	0.1979	4i
O(9)	0.5785	0	0.1813	4i
O(10)	0.4251	0	0.2213	4i
O(11)	0.4172	0	0.4250	4i

to the edge-sharing $[VO_5]$. If the structure of V_3O_7 converted into the $H_2V_3O_8$ structure by H_2O absorption, the reaction $V_3O_7 + H_2O \rightarrow H_2V_3O_8$ would involve the formation of a new V-O bond, unless to consider the water molecules simply coordinated into the V_3O_7 lattice by polarization interactions. In the latter case the V-O skeletons of V_3O_7 and V_3O_8 should perfectly match, unless water absorption can induce lattice distortion, besides eventually a volume expansion, but they do not. In addition, there is no direct group-subgroup relationship neither between the experimental ($C2/c$) nor the theoretically optimized V_3O_7 model ($C2/m$) between the monoclinic heptoxide, V_3O_7 and the orthorhombic framework of V_3O_8 ¹. Moreover, there are clear distinctions in terms of connectivities between the polyhedra in V_3O_7 and V_3O_8 framework¹. This means that there cannot be a continuous second order kind of transition on adding water to V_3O_7 to form $H_2V_3O_8$. On the other hand, lattice distortions induced upon water absorption have to be sufficient to turn into orthogonal the monoclinic lattice of V_3O_7 and accordingly change the edge-sharing polyhedra $[VO_6]$ in V_3O_7 into corner-sharing square pyramids, $[VO_5]$, being the octahedra $[VO_6]$ absent in V_3O_8 network. Our calculations of the absorption of H_2O in the monoclinic heptoxide, V_3O_7 , showed that it is an exothermic process, of which the enthalpy of absorption to form the orthorhombic $H_2V_3O_8$ is -68.07 kJ/mol of H_2O absorbed, calculated at DFT-D level and at (P, T) equal to zero, without accounting in for the zero-point energy and the thermal contributions. Although a detail understanding of water absorption in V_3O_7 requires a study on its own, our molecular dynamics calculations (NPT ensemble, P = 1 atm, T = 300 K) of the stoichiometric amount of H_2O in V_3O_7 to have formally $H_2V_3O_8$, revealed an interesting chemistry. In fact, the O-H bonds in H_2O split into OH, with the oxygen atom forming the new V-O bonds and H atoms bound to the oxygen atoms of the $[VO_6]$ octahedra. Accordingly, the MD calculations suggest the formation of hydroxyl group, which hydrogen atoms interact via hydrogen bonds.

In Figure 2 is shown a snapshot of a trajectory of the molecular dynamics of the system V_3O_7 (monoclinic structure) and the stoi-

chiometric amount of water to have the formulation $H_2V_3O_8$. For comparison the monoclinic structure of V_3O_7 optimized at DFT-D level is reported. Interestingly, by H_2O absorption the lattice turned almost orthogonal. In fact, the β angle in V_3O_7 changed from 126.14 degrees to 91.10 degrees. The hydroxyl group and hydrogen bonds are formed.

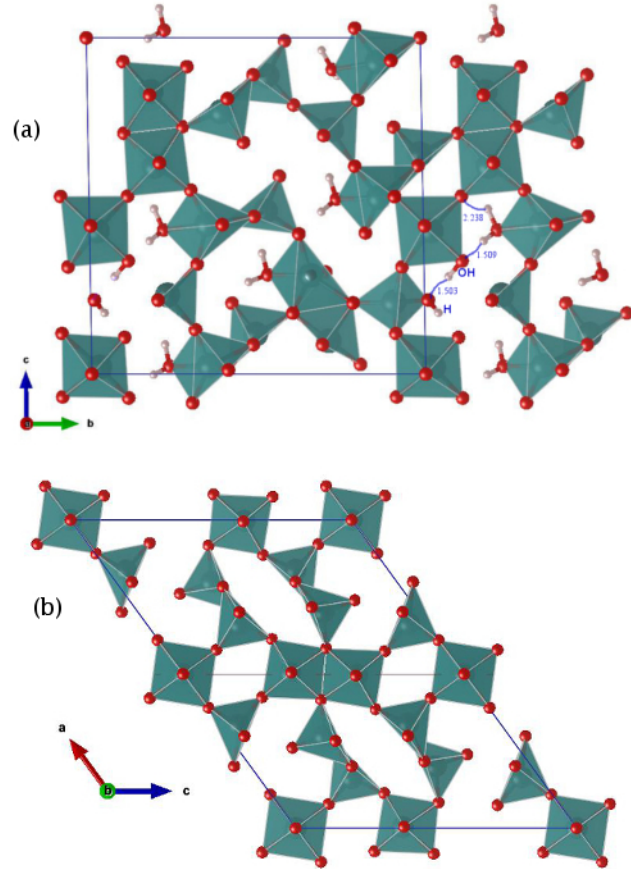


Fig. 2: (a) A snapshot (top-view) of the room-temperature molecular dynamics of the system $V_3O_7 + H_2O$. The O-H distances are in \AA . (b) A top-view of the monoclinic structure, $C2/m$, of V_3O_7 as optimized at DFT-D level. Representing colours: vanadium, green with the polyhedra of coordination; oxygen, red; hydrogen, white.

A Scanning Electron Micrograph (SEM) of the as-synthesised $H_2V_3O_8$ is shown in Figure 3.

The XRD pattern of the residual of the TG analysis at 690 K is reported in Figure 4. Several phases are present, among which the monoclinic structure of V_3O_7 .

References

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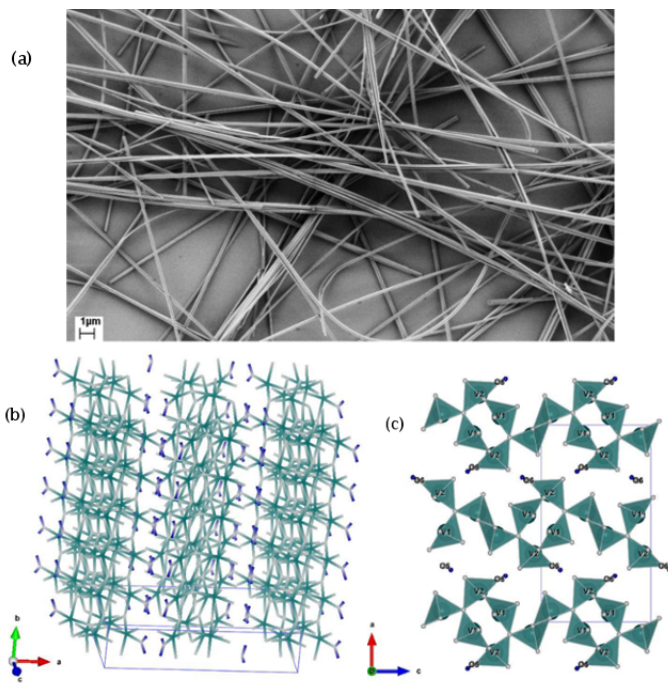


Fig. 3: (a) A SEM image of the bunched $\text{H}_2\text{V}_3\text{O}_8$ nanowires. (b) A 3D-view, in the wireframe representation, of $\text{H}_2\text{V}_3\text{O}_8$ (structure 1) showing the displacement of the wires along the crystallographic **b**-direction. (c) a top-view with the polyhedra of coordination of vanadium atoms cut through the V-O bond length of 2.30 Å. Representing colours: hydrogen, blue; vanadium, green; oxygen, grey.

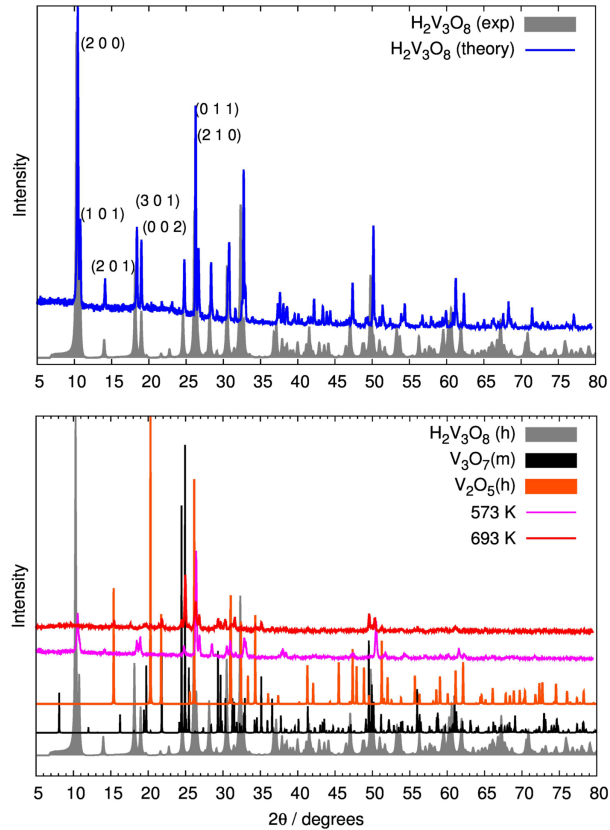


Fig. 4: A XRD pattern of the residual of the TG analysis at 690 K.