

Electronic supplementary information to
"Theoretical OH-stretching vibrations in dravite"

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I- Lattice dynamic of OH stretching vibrations in molecular coordinates

The lattice dynamic of molecular crystals has been reviewed by Califano et al. (1981) who provide a general treatment of the relations between the dynamical equations expressed in Cartesian coordinates and those expressed in molecular coordinates. In the present case, the system is described by a collection of OH stretching oscillators interacting with each other but decoupled from the other degrees of freedom. Following Califano et al. (1981), each isolated oscillator is characterized by its harmonic eigenfrequency ω and normal stretching coordinate $q^{m\mu}$, where m and μ are the index related to the cell and to the oscillator position in the cell, respectively. The total crystal potential V is a sum of intermolecular and intramolecular contributions. Considering pairwise harmonic interactions between oscillators at positions $m\mu$ and nv , it has the form:

$$V = \frac{1}{2} \sum_{m,n} \sum_{\mu,\nu} \left[F \begin{pmatrix} m & \mu \\ n & \nu \end{pmatrix} + \delta_{mn} \delta_{\mu\nu} \omega^2 \right] q^{m\mu} q^{nv} \quad \text{Eq. 1}$$

where the interaction coefficients $F \begin{pmatrix} m & \mu \\ n & \nu \end{pmatrix} = \left[\frac{\partial^2 V}{\partial q^{m\mu} \partial q^{nv}} \right]_0$ are computed at equilibrium positions and are only defined for $\mu \neq \nu$ if $m=n$. They are real quantities whose magnitude decreases as a function of the distance separating the oscillators. Imposing periodic boundary conditions to a macroscopic parallelepiped comprising N crystal cells, the symmetrized normal coordinates of the isolated oscillator μ are constructed as:

$$q^\mu(\mathbf{k}) = N^{-\frac{1}{2}} \sum_m q^{m\mu} e^{-i\mathbf{k}\mathbf{R}_m} \quad \text{Eq. 2}$$

where the vector \mathbf{R}_m corresponds to the lattice position of the m^{th} cell and \mathbf{k} is the phonon wavevector specifying an irreducible representation of the translational group. For each \mathbf{k} vector, the eigenvalue equations describing the interacting oscillators are then:

$$\sum_{\nu} D \begin{pmatrix} \mu \\ \nu \end{pmatrix} | \mathbf{k} \rangle e(\nu | p \mathbf{k}) = \omega_{p\mathbf{k}}^2 e(\mu | p \mathbf{k}) \quad \text{Eq. 3}$$

where p is the phonon branch, $\omega_{p\mathbf{k}}^2$ the eigenfrequency and $e(\mu | p \mathbf{k})$ the μ^{th} coordinate of the corresponding normalised eigenvector. In Eq. 3, the dynamical matrix coefficients $D \begin{pmatrix} \mu \\ \nu \end{pmatrix} | \mathbf{k} \rangle$ are defined by:

$$D \begin{pmatrix} \mu \\ \nu \end{pmatrix} | \mathbf{k} \rangle = \sum_n \left[F \begin{pmatrix} 0 & \mu \\ n & \nu \end{pmatrix} + \delta_{0n} \delta_{\mu\nu} \omega^2 \right] e^{i\mathbf{k}\mathbf{R}_n} \quad \text{Eq. 4}$$

For $\mathbf{k}=0$ (i.e., at the center of the Brillouin zone), the dynamical matrix defined by Eq. 4 is symmetric, with diagonal coefficients equal to ω^2 and out-of-diagonal coefficients determined by the bilinear couplings between different oscillators. In the present case, the primitive cell contains three $^{\text{V}}(\text{OH})$ oscillators related to each other by 3m symmetry. The 6 out-of-diagonal coefficients of the 3x3 dynamical matrix have the same value, here noted f . Its diagonalization results in one and two degenerate transverse optical modes belonging to the A_1 and E representations, respectively. At the first order in f/ω^2 , the splitting of the A_1 and E modes is 3λ , with $\lambda=f/2\omega$, thus providing a measure of the pairwise interactions between the oscillators. If the dominant interactions occur within the primitive cell (containing a single 3(YZZ) cluster), the description is formally equivalent to that of the potential coupling of three equivalent X-H groups in a C_{3v} molecule, where X is a heavier atom (e.g., Halonen and Child, 1983).

References

- Califano, S., Schettino, V., and Neto, N.: Lattice Dynamics of Molecular Crystals, Lecture Note in Chemistry, Springer, Berlin, ISBN: 978-3-540-10868-9, 1981.
- Halonen, L. and Child, M. S.: Local mode theory for C_{3v} molecules: CH_3D , CHD_3 , SiH_3D , and SiHD_3 , J. Chem. Phys., 79, 4355, <https://doi.org/10.1063/1.446317>, 1983.

II- Supplementary tables and figures

Table S1: Theoretical OH stretching frequencies (ω_{OH} , cm^{-1}) of dravite obtained using the full dynamical matrix (DM) of the rhomboedral primitive cell and using a partial DM of the rhomboedral primitive cell restricted to the atomic displacements of the 4 OH groups.

mode	ω_{OH} full DM	ω_{OH} partial DM	difference (cm^{-1})
$\nu_{\text{(OH)}} A_1$	3653.528	3653.429	- 0.099
$\nu_{\text{(OH)}} E$	3653.634	3653.515	- 0.119
$\omega_{\text{(OH)}}$	3856.001	3855.979	- 0.022

Table S2: Theoretical OH stretching frequencies (ω_{OH} , cm^{-1}) of the hexagonal dravite cell obtained using the full dynamical matrix (DM), a partial DM restricted to atomic displacements of OH groups and a smaller partial DM restricted to the OH groups belonging to a single 3(YZZ) cluster.

mode	ω_{OH} full DM	ω_{OH} partial DM	difference (cm^{-1})	mode	ω_{OH} average*	ω_{OH} single cluster	difference (cm^{-1})
$\nu_{\text{(OH)}} A_1$	3652.045	3651.946	-0.099	$\nu_{\text{(OH)}} A_1$	3652.41	3652.28	-0.13
$\nu_{\text{(OH)}} A_1$	3652.580	3652.462	-0.118	$\nu_{\text{(OH)}} E$	3653.04	3653.24	0.20
$\nu_{\text{(OH)}} A_1$	3652.595	3652.477	-0.118	$\omega_{\text{(OH)}}$	3856.31	3856.23	-0.08
$\nu_{\text{(OH)}} E$	3652.736	3652.627	-0.109				
$\nu_{\text{(OH)}} E$	3652.998	3652.888	-0.110				
$\nu_{\text{(OH)}} E$	3653.377	3653.263	-0.114				
$\omega_{\text{(OH)}}$	3856.290	3856.266	-0.024				
$\omega_{\text{(OH)}}$	3856.303	3856.280	-0.023				
$\omega_{\text{(OH)}}$	3856.329	3856.305	-0.024				

* average frequencies of full DM modes with corresponding symmetry.

Table S3: Theoretical relative energy, OH stretching frequency (ω_{OH}) and O-H bond length ($d(\text{OH})$) of dravite hexagonal cells displaying Al-Mg inversion. Data for ideal dravite are also reported for comparison. The Y sites occupied by a Al and Z sites occupied by Mg are specified with the labels indicated on Fig. S1. N is the number of symmetrically equivalent configurations. The relative energy of the models is defined with respect to ideal dravite.

model	^Y Al	^Z Mg	N	rel. energy (kJ/mol)	OH label	ω_{OH} (cm ⁻¹)	$d(\text{OH})$ (Å)	OH label	ω_{OH} (cm ⁻¹)	$d(\text{OH})$ (Å)
dravite	-	-	1	0	W	3856	0.9589	V1, V2, V3	3653	0.9724
Mg_Al	a	1	6	13.4	W	3811	0.9615	V3	3656	0.9721
								V2	3653	0.9723
								V1	3599	0.9749
Mg_Al_2	a	2	6	40.5	W	3780	0.9630	V2	3683	0.9700
								V3	3655	0.9722
								V1	3583	0.9765
Mg_Al_3	a	3	6	48.9	W	3811	0.9615	V2	3679	0.9702
								V3	3651	0.9724
								V1	3591	0.9761
2_1	a, b	1, 2	3	58.1	W	3757	0.9647	V3	3656	0.9721
								V1, V2	3588	0.9755
2_2	a, b	1, 3	6	54.5	W	3775	0.9639	V3	3653	0.9723
								V1	3592	0.9752
								V2	3583	0.9757
2_3	a, b	1, 4	6	87.8	W	3780	0.9637	V3	3682	0.9700
								V1	3594	0.9752
								V2	3570	0.9772
2_4	a, b	1, 5	6	87.0	W	3779	0.9637	V3	3681	0.9700
								V1	3588	0.9755
								V2	3579	0.9768
2_5	a, b	1, 6	6	74.8	W	3771	0.9640	V3	3653	0.9723
								V1	3612	0.9730
								V2	3580	0.9767
2_6	a, b	3, 6	3	58.9	W	3787	0.9632	V3	3648	0.9725
								V1, V2	3590	0.9754
2_7	a, b	4, 5	3	152.4	W	3775	0.9638	V3	3716	0.9672
								V1, V2	3578	0.9768
2_8	a, b	5, 6	6	98.1	W	3797	0.9628	V3	3678	0.9702
								V2	3585	0.9765
								V1	3580	0.9759
2_9	a, b	3, 5	6	89.2	W	3794	0.9629	V3	3678	0.9702
								V2	3587	0.9755
								V1	3577	0.9768
3_1	a, b, c	1, 2, 3	6	142.8	W	3768	0.9647	V2	3601	0.9735
								V1	3574	0.9761
								V3	3567	0.9773
3_2	a, b, c	1, 2, 4	6	125.8	W	3766	0.9648	V3	3583	0.9757
								V1	3578	0.9760
								V2	3570	0.9764
3_3	a, b, c	1, 3, 5	2	116.2	W	3767	0.9648	V1, V2, V3	3576	0.9760

Fig. S1: Dravite cluster viewed along the [001] direction. a,b, and c: Y sites, 1-6: Z sites, V_1 , V_2 , V_3 : V sites occupied by OH group. Purple grey triangles: BO_3 groups. White spheres: H atoms. Red spheres: oxygen atoms.

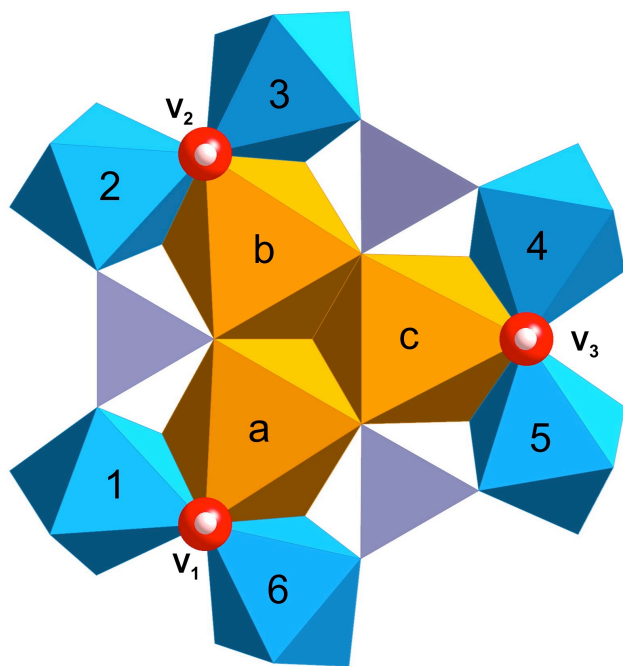


Fig. S2: Relation between theoretical OH stretching frequency (ω_{OH} , Table S1) and OH bond length ($d(\text{OH})$, Table S1) for models of dravite displaying Al-Mg inversion.

