

## Supplementary Information – HyDRA challenge

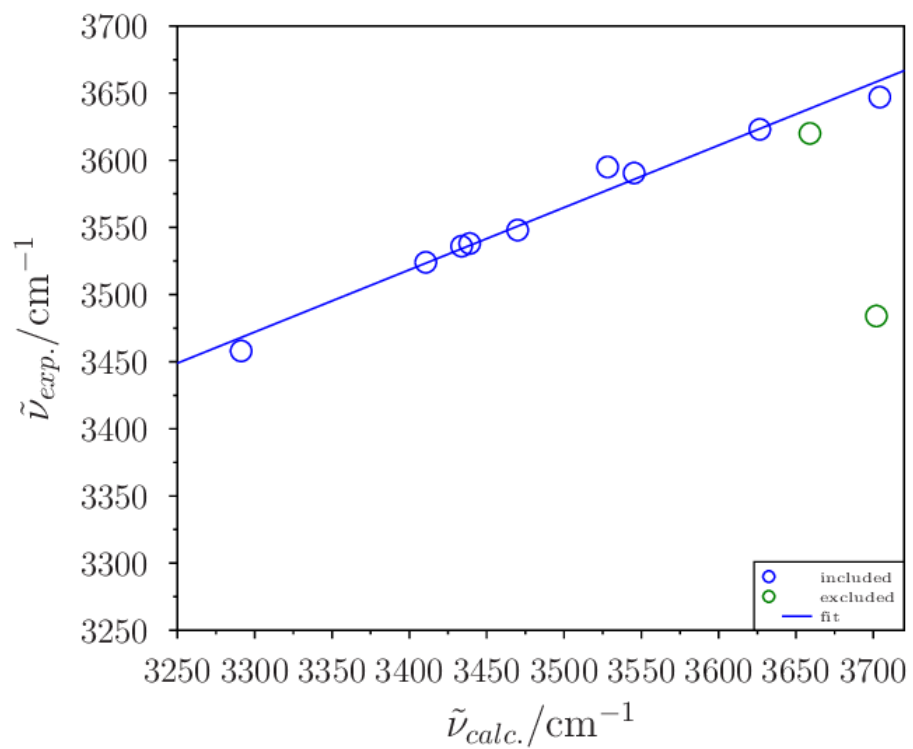
Fabian Dietrich [ORCID: 0000-0002-2720-3364, email: fabian.dietrich@ufrontera.cl]<sup>1</sup> and Vicente Cisternas [email: v.cisternas01@ufromail.cl]<sup>1</sup>

<sup>1</sup>Departament of Physics Science, Universidad de La Frontera, Francisco Salazar 01145, Temuco, Chile

### 1 Computational Details

For the generation of input structures, we used the CREST algorithm [1] of the xTB package [2]. The best geometry was used for further optimization with DFT methods. Therefore, we used QUANTUM ESPRESSO 6.3.0 [3]. The Kohn-Sham equations are solved using the projector augmented wave (PAW) approach for describing electronic core states and a plane-wave basis set setting the energy cutoff for the wave functions to 40 Ry and the kinetic energy cutoff for charge density and potential to 320 Ry. Electron exchange and correlation energies are calculated within the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE [4]) form using an ultrasoft pseudopotential (pbe-n-rrkjus\_psl.1.0.0.UPF). To consider van-der-Waals interaction, the dispersion correction D3 [5] was used. To avoid interaction between the aggregates and their images, the aggregates were placed in a box of  $10 \times 10 \times 10$  Å (for PCD, the box had to be extended to  $20 \times 20 \times 20$  Å). For the small boxes, the reciprocal-space k-point mesh of  $6 \times 6 \times 6$  are used, while the one for PCD was reduced to  $2 \times 2 \times 2$ . Frequency calculations were performed on these optimized structures.

The test systems were used to evaluate the used pseudopotential and the calculation method in general. Therefore, we plotted the calculated frequencies against the experimental ones as shown in figure 1. It can be seen that a simple scaling factor is not sufficient but a linear function has to be used. The obtained parameters of the linear fit were applied to the challenge set.



Fit  
 $y = 0.46350x + 1942.54$   
 $r^2 = 0.97795$

Figure 1: Calculated and experimental wavenumbers for the test set. Phenylethanol and di-tert-butyl nitroxid were not considered in the fit due to there bad optimized geometries.

## 2 Additional computed data (optional)

### 2.1 OH-stretching fundamentals for test set

Code	CAS	fundamentals (cm <sup>-1</sup> )	description
CON	502-49-8	3438.4	$\tilde{\nu}(\text{OH}_b)$
		3780.9	$\tilde{\nu}(\text{OH}_f)$
DMI	80-73-9	3404.2	$\tilde{\nu}(\text{OH}_b)$
		3780.2	$\tilde{\nu}(\text{OH}_f)$
FAH	50-0-0	3552.9	$\tilde{\nu}(\text{OH}_b)$
		3784.9	$\tilde{\nu}(\text{OH}_f)$
MLA	547-64-8	3351.1	asym. $\tilde{\nu}(\text{H-OH}_b + \text{MLA-OH}_b)$
		3424.9	sym. $\tilde{\nu}(\text{H-OH}_b + \text{MLA-OH}_b)$
		3771.5	$\tilde{\nu}(\text{OH}_f)$
PCD	125132-75-4	3409.5	$\tilde{\nu}(\text{PCD-OH}_b \cdots \text{OH}_2)$
		3564.1	$\tilde{\nu}(\text{PCD-OH}_b \text{ (intermolecular)})$
		3647.5	$\tilde{\nu}(\text{OH}_b \cdots \pi)$
		3779.8	$\tilde{\nu}(\text{OH}_f)$
PYR	110-86-1	3289.7	$\tilde{\nu}(\text{OH}_b)$
		3765.8	$\tilde{\nu}(\text{OH}_f)$
THF	109-99-9	3427.0	$\tilde{\nu}(\text{OH}_b)$
		3781.1	$\tilde{\nu}(\text{OH}_f)$
THT	110-01-0	3390.2	$\tilde{\nu}(\text{OH}_b)$
		3769.0	$\tilde{\nu}(\text{OH}_f)$
TPH	434-45-7	3611.0	$\tilde{\nu}(\text{OH}_b)$
		3777.6	$\tilde{\nu}(\text{OH}_f)$
TFE	75-89-8	3398.6	$\tilde{\nu}(\text{TFE-OH}_b \cdots \text{OH}_2)$
		3690.2	$\tilde{\nu}(\text{OH}_b \cdots \text{F})$
		3795.9	$\tilde{\nu}(\text{OH}_f)$

## 2.2 IR intensities and Raman scattering activities

Code	CAS	fundamentals (cm <sup>-1</sup> )	IR intensity ((D/Å) <sup>2</sup> /amu)
CON	502-49-8	3438.4	15.64
		3780.9	1.21
DMI	80-73-9	3404.2	24.38
		3780.2	1.22
FAH	50-0-0	3552.9	7.91
		3784.9	1.33
MLA	547-64-8	3351.1	2.69
		3424.9	22.02
		3771.5	1.15
PCD	125132-75-4	3409.5	11.23
		3564.1	1.12
		3647.5	2.33
		3779.8	2.06
PYR	110-86-1	3289.7	33.70
		3765.8	1.39
THF	109-99-9	3427.0	14.02
		3781.1	1.30
THT	110-01-0	3390.2	15.25
		3769.0	1.39
TPH	434-45-7	3611.0	11.95
		3777.6	2.84
TFE	75-89-8	3398.6	15.15
		3690.2	0.06
		3795.9	1.56

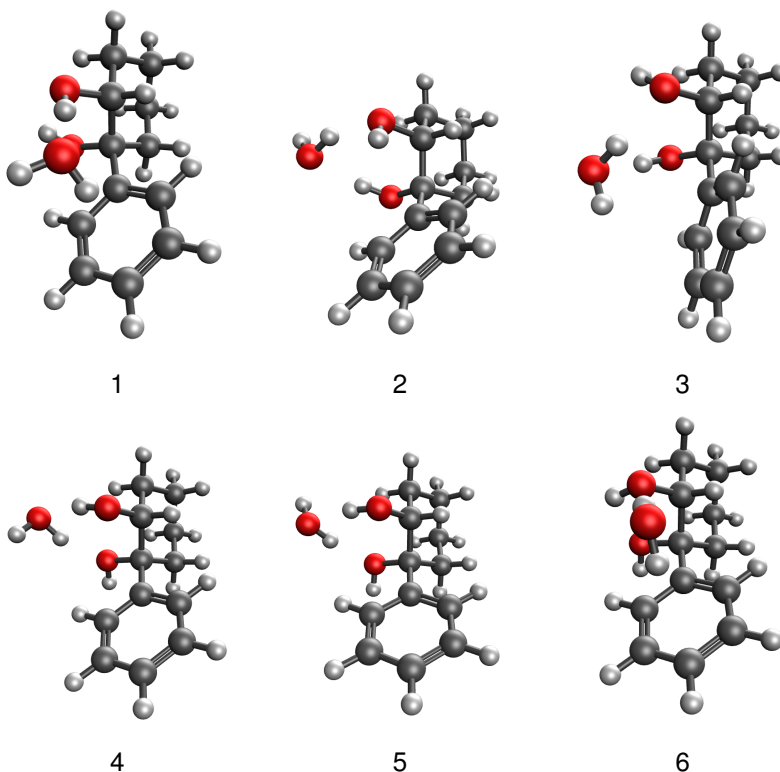
## 2.3 Isotopolog information

No further information has been made available.

## 2.4 Relative energies for local minima and spectral properties

The CREST algorithm provided six low lying structures for the PCD-water complex. To chose the best structure for the frequency calculation, these six were post-optimized with procedure described above and ordered in dependence of their energy. The motif describes the hydrogen-bond donor (d) and acceptor (a), respectively, from the viewpoint of the water molecule.

Nr.	motif	$E_{\text{rel}}/\text{kJ/mol}$
1	OH <sub>2</sub> (d) $\pi$ (a)	0.00
2	OH <sub>1</sub> (d)OH <sub>2</sub> (a)	0.60
3	OH <sub>1</sub> (d)OH <sub>2</sub> (a)	7.52
4	OH <sub>1</sub> (a)OH <sub>2</sub> (d)	14.99
5	OH <sub>1</sub> (a)OH <sub>2</sub> (d)	15.02
6	OH <sub>2</sub> (d) $\pi$ (a)	16.18



## 2.5 Other computed quantities for the training and test sets

No further information has been made available.

### 3 References

#### References

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