Electronic Supplementary Information for: Setting up the HyDRA blind challenge for the microhydration of organic molecules

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Profiles of the ten monohydrates and their acceptor molecules (Table S1, Figure S1) chosen as the training set for the HyDRA challenge. The profiles include some key references and routinely computed and experimental properties which can be helpful in assessing the results of a chosen strategy to predict the hydrogen-bonded water OH stretching fundamental. For the computations, the B3LYP method with the D3 dispersion correction including three body term (abc) is combined with the def2-TZVP basis set in the double-harmonic approximation, using the ORCA quantum chemistry package. The training set was selected from proposals listed under qmbench.net, The proponents are listed in the profiles and the estimated wavenumber accuracy is based on their information.

We do not claim that the monohydrate structures shown in the profiles are the global minimum arrangements, but they correspond to the lowest structure found for the employed computational approach and are consistent with the indicated literature data.

Table S1: Alphabetically ordered acceptor molecules with their three-letter acronym and CAS registry number.

acceptor molecule	abbreviation	CAS RN
Acetone	ACE	67-64-1
Acetophenone	APH	98-86-2
Aniline	ANL	62-53-3
Cyclobutanone	CBU	1191-95-3
Dibenzofuran	DBF	132-64-9
Di-*tert*-butyl nitroxide	DBN	2406-25-9
Imidazole	IMZ	288-32-4
o-Cyanophenol	OCP	611-20-1
1-Phenylethanol	POH	98-85-1
1,2,4,5-Tetrafluorobenzene	TFB	327-54-8

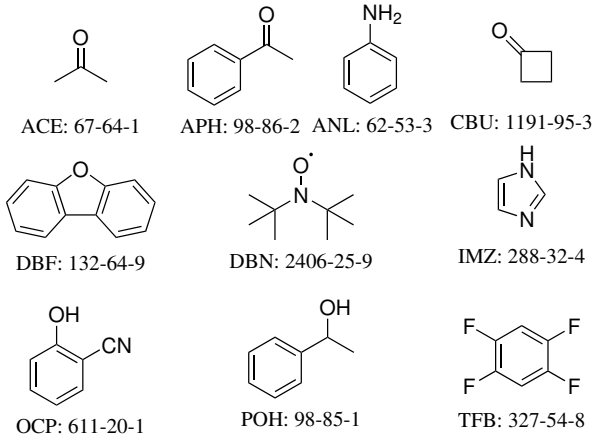
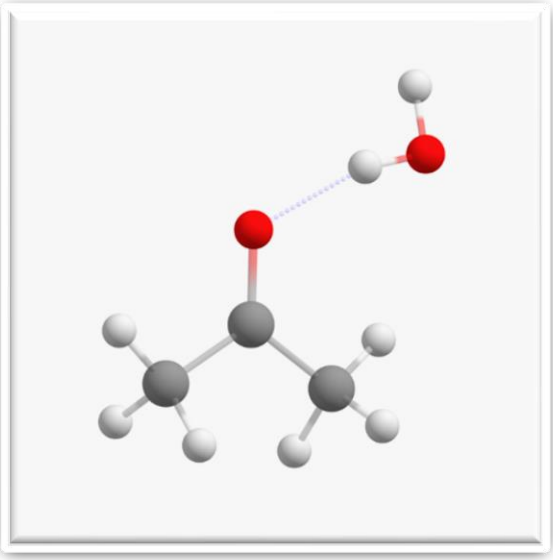


Figure S1: Alphabetically ordered structural formulas of the ten acceptor molecules from Table S1.

Acetone



CAS-No.	67-64-1
molecular formula	C_3H_6O
molecular weight /g mol^{-1}	58.08
calc. lowest monomer wavenumber/cm^{-1}	14*

Dimer:

exp. OH_b wavenumber / cm^{-1}	3538[1]
estimated accuracy / cm^{-1}	<1
calc. OH_b wavenumber / cm^{-1}	3613*
calc. OH_b band strength / km mol^{-1}	452*

Proposing and supporting researchers:

Taija L. Fischer Hannes C. Gottschalk Till Wagner
Martin A. Suhm Arman Nejad

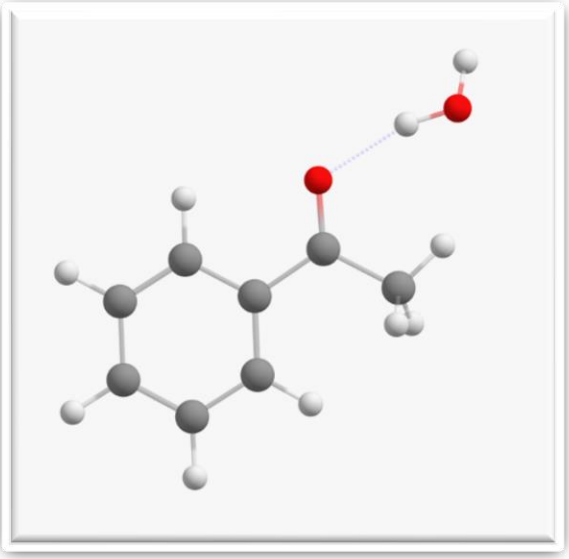
References:

[1-IR] Fischer, T. L.; Wagner, T.; Gottschalk, H. C.; Nejad, A.; Suhm, M. A. A Rather Universal Vibrational Resonance in 1:1 Hydrates of Carbonyl Compounds, *J. Phys. Chem. Lett.* **2021**, *12(1)*, 138−144. (DOI: 10.1021/acs.jpclett.0c03197)

[2-IR@Matrix] Zhang, X. K.; Lewars, E. G.; March, R. E.; Parnis, J. M. Vibrational spectrum of the acetone-water complex: a matrix isolation and FTIR and the theoretical study, *J. Phys. Chem.* **1993**, *17*, 4320−4325. (DOI: 10.1021/j100119a012)

* Calculation Method: B3LYP abc D3BJ def2-TZVP double harmonic

Acetophenone



CAS-No.	98-86-2
molecular formula	C_8H_8O
molecular weight /g mol^{-1}	120.15
calc. lowest monomer wavenumber/cm^{-1}	27*

Dimer:

exp. OH_b wavenumber / cm^{-1}	3536[1]
estimated accuracy / cm^{-1}	<1
calc. OH_b wavenumber / cm^{-1}	3609*
calc. OH_b band strength / km mol^{-1}	633*

Proposing and supporting researchers:

Taija L. Fischer Hannes C. Gottschalk Till Wagner
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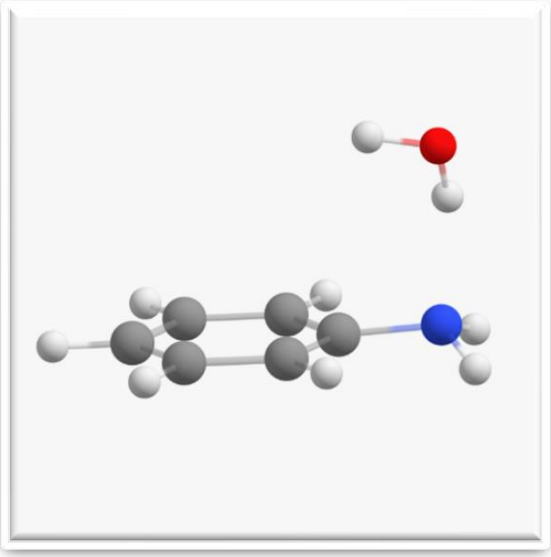
References:

[1-IR] Fischer, T. L.; Wagner, T.; Gottschalk, H. C.; Nejad, A.; Suhm, M. A. A Rather Universal Vibrational Resonance in 1:1 Hydrates of Carbonyl Compounds, *J. Phys. Chem. Lett.* **2021**, *12(1)*, 138−144. (DOI: 10.1021/acs.jpclett.0c03197)

[2-Microwave] Lei, J.; Zhang, J.; Feng, G.; Grabow, J.-U.; Gou, Q. Conformational preference determinded by inequivalent n-pairs: rotational studies on acetophenone and its monohydrate, *Phys. Chem. Chem. Phys.* **2019**, *21*, 22888−22894. (DOI: 10.1039/C9CP03904)

* Calculation Method: B3LYP abc D3BJ def2-TZVP double harmonic

Aniline



CAS-No.	62-53-3
molecular formula	C_6H_7N
molecular weight /g mol^{-1}	93.13
calc. lowest monomer wavenumber/cm^{-1}	220*

Dimer:

exp. OH_b wavenumber / cm^{-1}	3524[1]
estimated accuracy / cm^{-1}	1
calc. OH_b wavenumber / cm^{-1}	3637*
calc. OH_b band strength / km mol^{-1}	314*

Proposing and supporting researchers:

José A. Fernández
Iker León
Imanol Usabiaga

References:

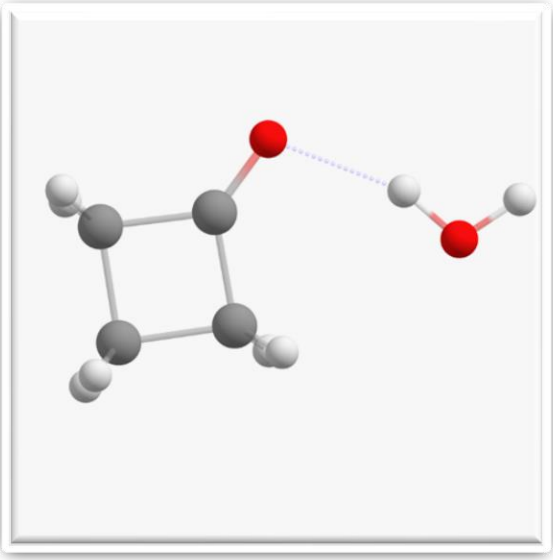
[1-IR-UV] Leon, I.; Arnaiz, P.F.; Usabiaga, I.; Fernandez, J. A. Mass resolved IR spectroscopy of anline-water aggregates, *Phys. Chem. Chem. Phys.* **2016**, *18*, 27336. (DOI: 10.1039/c6cp04373a)

[2-Microwave] Spoerel, U.; Stahl, W. The Aniline-Water Complex, *J. Mol. Spectrosc.* **1998**, *190*, 278−289. (DOI: 10.1006/jmsp.1998.7600)

[3-REMPI] Piani, G.; Pasquini, M.; López-Tocón, I.; Pietraperzia, G.; Becucci, M.; Castellucci, E. The aniline-water and aniline-methanol complexes in the S_1 excited state, *Chem. Phys.* **2006**, *330*, 138−145. (DOI: 10.1016/j.chemphys.2006.08.004)

* Calculation Method: B3LYP abc D3BJ def2-TZVP double harmonic

Cyclobutanone



CAS-No.	1191-95-3
molecular formula	C_4H_6O
molecular weight /g mol^{-1}	70.09
calc. lowest monomer wavenumber/cm^{-1}	402*

Dimer:

exp. OH_b wavenumber / cm^{-1}	3548[1]
estimated accuracy / cm^{-1}	<1
calc. OH_b wavenumber / cm^{-1}	3636*
calc. OH_b band strength / km mol^{-1}	362*

Proposing and supporting researchers:

Taija L. Fischer Hannes C. Gottschalk Till Wagner
Martin A. Suhm Arman Nejad

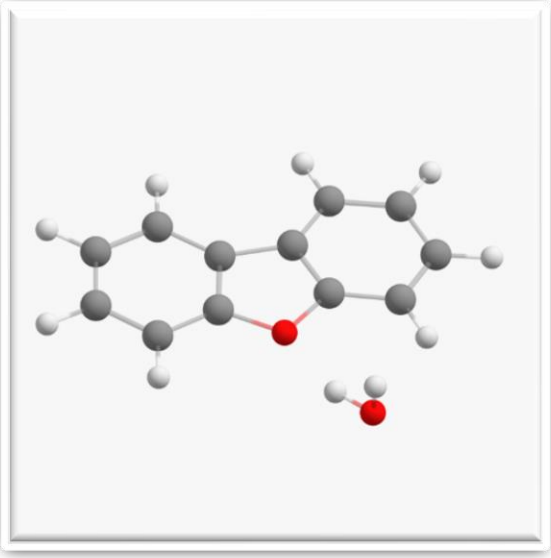
References:

[1-IR] Fischer, T. L.; Wagner, T.; Gottschalk, H. C.; Nejad, A.; Suhm, M. A. A Rather Universal Vibrational Resonance in 1:1 Hydrates of Carbonyl Compounds, *J. Phys. Chem. Lett.* **2021**, *12(1)*, 138−144. (DOI: 10.1021/acs.jpclett.0c03197)

[2-Microwave] Melandri, S.; Maris, A.; Giuliano, B. M. ; Caminat, W. Water-ketones hydrogen bonding: The rotational spectrum of cyclobutanone-water, *J. Chem. Phys.* **2005,** *123*, 164304. (DOI: 10.1063/1.2078767)

* Calculation Method: B3LYP abc D3BJ def2-TZVP double harmonic

Dibenzofuran



CAS-No.	132-64-9
molecular formula	$C_{12}H_8O$
molecular weight /g mol^{-1}	168.19
calc. lowest monomer wavenumber/cm^{-1}	105*

Dimer:

exp. OH_b wavenumber / cm^{-1}	3623[1]
estimated accuracy / cm^{-1}	<1
calc. OH_b wavenumber / cm^{-1}	3738*
calc. OH_b band strength / km mol^{-1}	181*

Proposing and supporting researchers:

Dominic Bernhard
Markus Gerhards

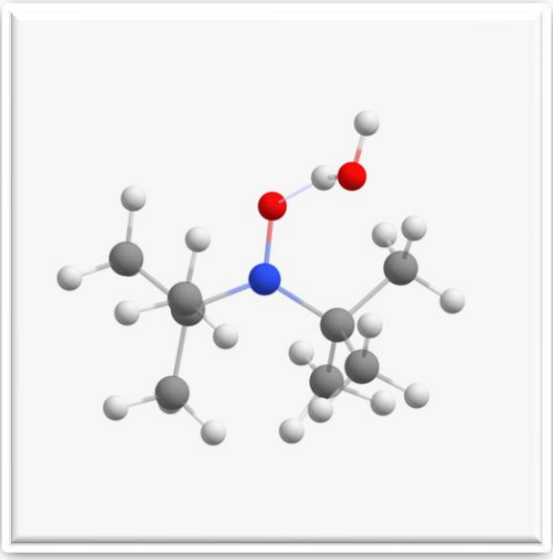
References:

[1-FTIR/IR-UV/Microwave] Bernhard, D.; Fatima, M.; Poblotzki, A.; Steber, A. L.; Pérez, C.; Suhm, M. A.; Schnell, M.; Gerhards, M. Dispersion-controlled docking preference: multi-spectroscopic study on complexes of dibenzofuran with alcohols and water, *Phys. Chem. Chem. Phys.* **2019**, *21*, 16032—16046.

[2-Fluorescence] Auty, A. R.; Jones, A. C.; Philips, D. Fluorescence excitation spectra and decay times of jet-cooled dibenzofuran and the dibenzofuran-water complex, *Chem. Phys. Lett.* **1984**, *112 (6)*, 529—533.

* Calculation Method: B3LYP abc D3BJ def2-TZVP double harmonic

Di-*tert*-butyl nitroxide



CAS-No.	2406-25-9
molecular formula	$C_8H_{18}NO$
molecular weight /g mol^{-1}	144.24
calc. lowest monomer wavenumber/cm^{-1}	56*

Dimer:

exp. OH_b wavenumber / cm^{-1}	3484[1]
estimated accuracy / cm^{-1}	2
calc. OH_b wavenumber / cm^{-1}	3578*
calc. OH_b band strength / km mol^{-1}	382*

Proposing and supporting researchers:

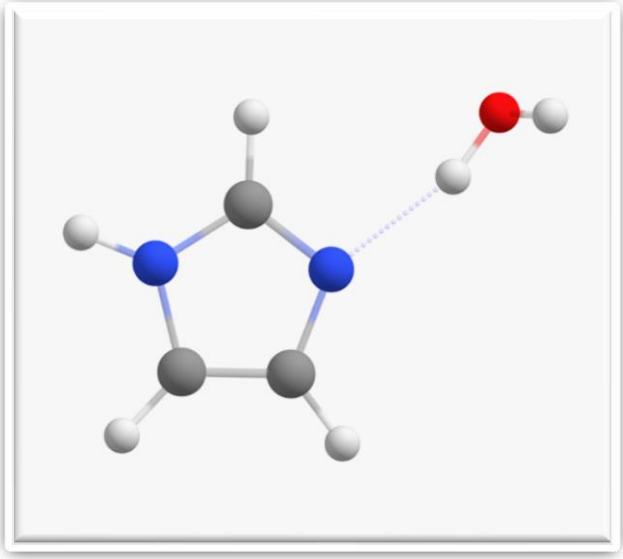
Elisa Bras
Taija L. Fischer
Martin A. Suhm

References:

[1-IR] Brás, E. M.; Fischer, T. L.; Suhm, M. A. The hydrates of TEMPO: Water vibrations reveal radical microsolvation, *Angew. Chem. Int. Ed.* **2021**, *60*, 19013–19017. (DOI: 10.1002/anie.202104496)

* Calculation Method: B3LYP abc D3BJ def2-TZVP UKS double harmonic

Imidazole



CAS-No.	288-32-4
molecular formula	$C_3H_4N_2$
molecular weight /g mol^{-1}	68.08
calc. lowest monomer wavenumber/cm^{-1}	517*

Dimer:

exp. OH_b wavenumber / cm^{-1}	3458[1]
estimated accuracy / cm^{-1}	2
calc. OH_b wavenumber / cm^{-1}	3537*
calc. OH_b band strength / km mol^{-1}	701*

Proposing and supporting researchers:

Julia Zischang
Martin A. Suhm

References:

[1-IR] Zischang, J.; Lee, J. J..; Suhm, M. A. Communication: Where does the first water molecule go in imidazole?, *J. Chem. Phys.* **2011**, *137*, 061102. (DOI: 10.1063/1.3624841)

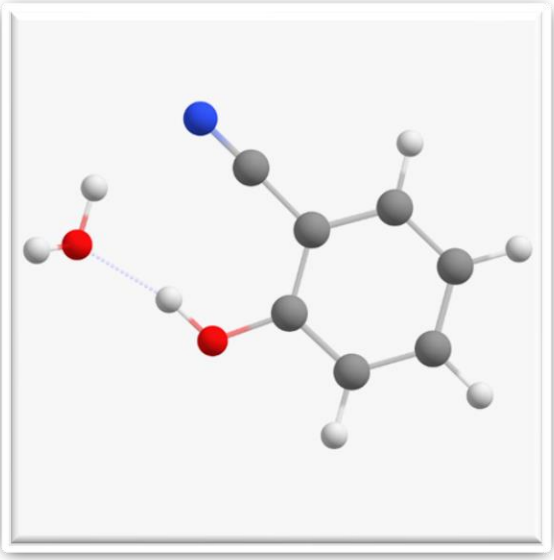
[2-Microwave] Gougoula, E.; Cole, D. J.; Walker, N. R. Bifunctional Hydrogen Bonding of Imidazole with Water Explored by Rotational Spectroscopy and DFT Calculations, *J. Phys. Chem. A* **2020,** *124*, 2649−2659. (DOI: 10.1021/acs.jpca0c00544)

[3-IR@He] Choi, M. Y.; Miller, R. E. Infrared Laser Spectroscopy of Imidazole Complexes in Helium Nanodroplets: Monomer, Dimer, and Binary Water Complexes, *J. Phys. Chem. A* **2006,** 9344−9351. (DOI: 10.1021/jp0624146)

[4-IR@Matrix] Van Bael, M. K.; Smets, J.; Schoone, K.; Houben, L.; McCarthy, W.; Adamowicz, L.; Nowak, M. J.; Maes, G. Matrix-Isolation FTIR Studies and Theoretical Calcilations of Hydrogen-Bonded Complexes of Imidazol. A Comparison between Experimental Results and Different Calculation Methods, *J. Phys. Chem. A* **1997**, *101*, 2397−2413. (DOI: 10.1021/jp963111)

* Calculation Method: B3LYP abc D3BJ def2-TZVP double harmonic

o-Cyanophenol



CAS-No.	611-20-1
molecular formula	C_7H_5ON
molecular weight /g mol^{-1}	119.12
calc. lowest monomer wavenumber/cm^{-1}	126*

Dimer:

exp. OH_b wavenumber / cm^{-1}	3595[1]
estimated accuracy / cm^{-1}	<1
calc. OH_b wavenumber / cm^{-1}	3684*
calc. OH_b band strength / km mol^{-1}	165*

Proposing and supporting researchers:

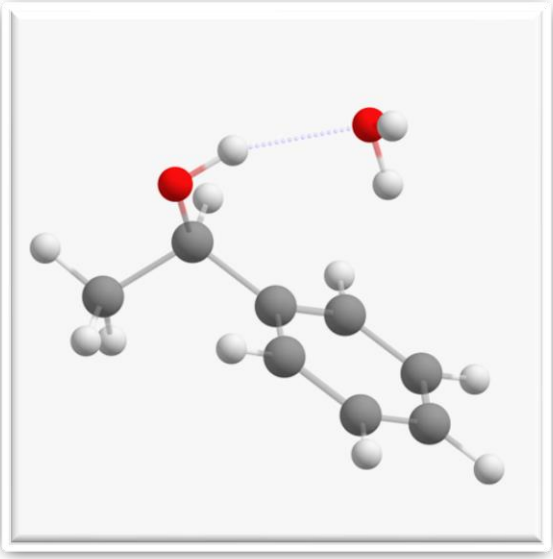
Anne Zehnacker
Michel Broquier
Valérie Brenner

References:

[1-IR] Broquier, M.; Lahmani, F.; Zehnacker-Rentien, A.; Brenner, V.; Millié, Ph.; Peremans, A. Hydrogen-Bonded Bridges in Complexes of *o*-Cyanophenol: Laser-Induced Fluorescence and IR/UV Double-Resonance Studies, *J. Phys. Chem. A* **2001**, *105(28)*, 6841−6850**.**

* Calculation Method: B3LYP abc D3BJ def2-TZVP double harmonic

1-Phenylethanol



CAS-No.	98-85-1
molecular formula	$C_8H_{10}O$
molecular weight /g mol^{-1}	122.16
calc. lowest monomer wavenumber/cm^{-1}	32*

Dimer:

exp. OH_b wavenumber / cm^{-1}	3620[1]
estimated accuracy / cm^{-1}	1-2
calc. OH_b wavenumber / cm^{-1}	3743*
calc. OH_b band strength / km mol^{-1}	81*

Proposing and supporting researchers:

Anne Zehnacker
Katia Le Barbu-Debus

References:

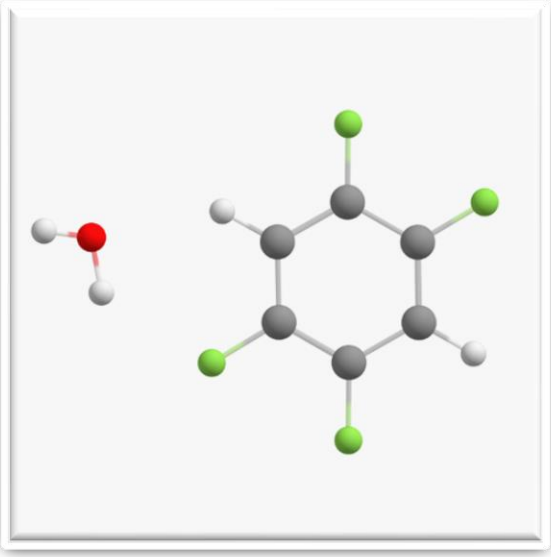
[1-IR-UV] Le Barbu, K.; Lahmani, F., Mons, M.; Broquier, M., Zehnacker, A. IR-UV investigation of the structure of the 1-phenylethanol chromophore and its hydrated complexes, *Phys. Chem. Chem. Phys.* **2001**, *3*, 4684−4688. (DOI: 10.1039/b105036m)

[2-IR] Gottschalk, H. C.; Fischer, T. L.; Meyer, V.; Hildebrandt, R.; Schmitt, U.; Suhm, M. A. A Sustainable Slit Jet FTIR Spectrometer for Hydrate Complexes and Beyond, *Instruments* **2021**, *5*, 12. (DOI: 10.3390/instruments5010012)

[3-R2PI] Giadrini Guioni, A.; Piccirillo, S.; Scuderi, D.; Satta, M.; Di Palma, T. M.; Speranza, M. Chirality and intermolecular forces: studies using R2PI experiments in supersonic beams, *Phys. Chem. Chem. Phys.* **2000**, *2*, 4139−4142. (DOI: 10.1039/b004138f)

* Calculation Method: B3LYP abc D3BJ def2-TZVP double harmonic

1,2,4,5-Tetrafluorobenzene



CAS-No.	327-54-8
molecular formula	$C_6H_2F_4$
molecular weight /g mol^{-1}	150.08
calc. lowest monomer wavenumber/cm^{-1}	129*

Dimer:

exp. OH_b wavenumber / cm^{-1}	3647[1]
estimated accuracy / cm^{-1}	1
calc. OH_b wavenumber / cm^{-1}	3778*
calc. OH_b band strength / km mol^{-1}	11*

Proposing and supporting researchers:

A. Fujii T. Ebata
V. Venkatesan N. Mikami

References:

[1-IR-UV] Venkatesan, V.; Fujii, A.; Ebata, T.; Mikami, N. A direct experimental evidence for an aromatic C−H···O hydrogen bond by fluorescence-detected infrared spectroscopy, *Chem. Phys. Lett.* **2004**, *394*, 45−48. (DOI: 10.1016/j.cplett.2004.06.101)

* Calculation Method: B3LYP abc D3BJ def2-TZVP double harmonic