TU Graz

COMPUTATIONAL CHEMISTRY DAY 2023

RB

Characterization of diamondoid clusters emerging in helium nanodroplets

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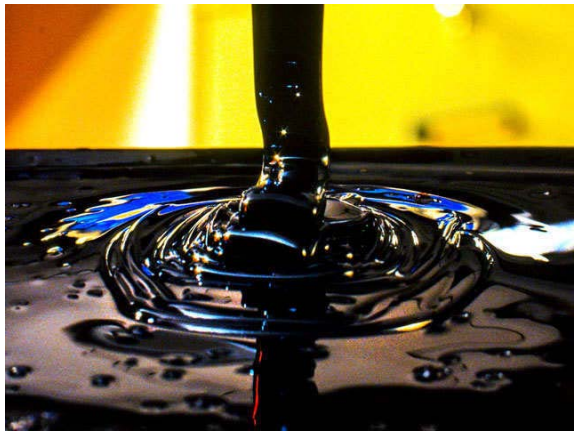
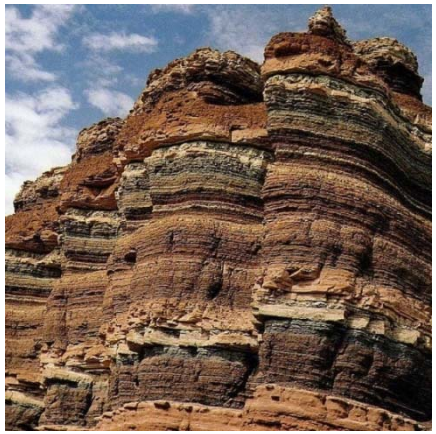
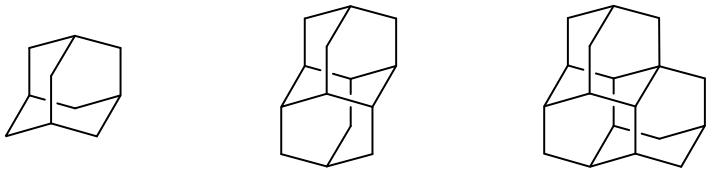
16. 09. 2023

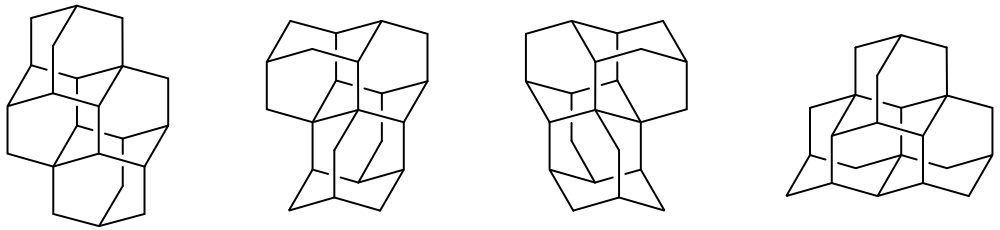




lower diamondoids

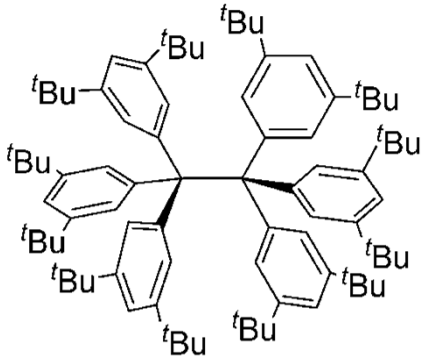


higher diamondoids

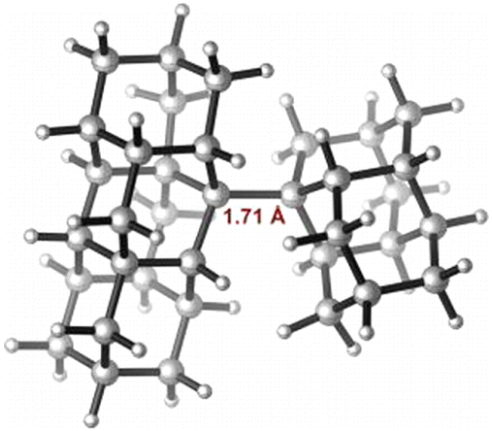


London dispersion

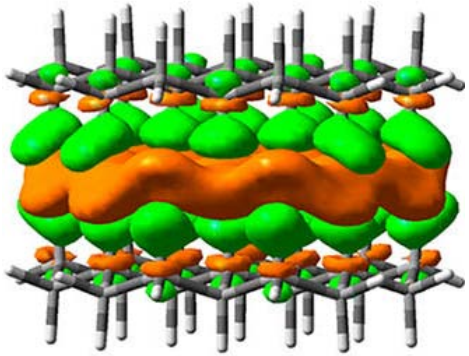
- acting in molecules due to interactions between induced dipoles
- the effect grows with the number of atom pairs that are interacting
- pronounced in bulky, polarizable molecules



- hexaphenylethane stabilized with *t*Bu groups

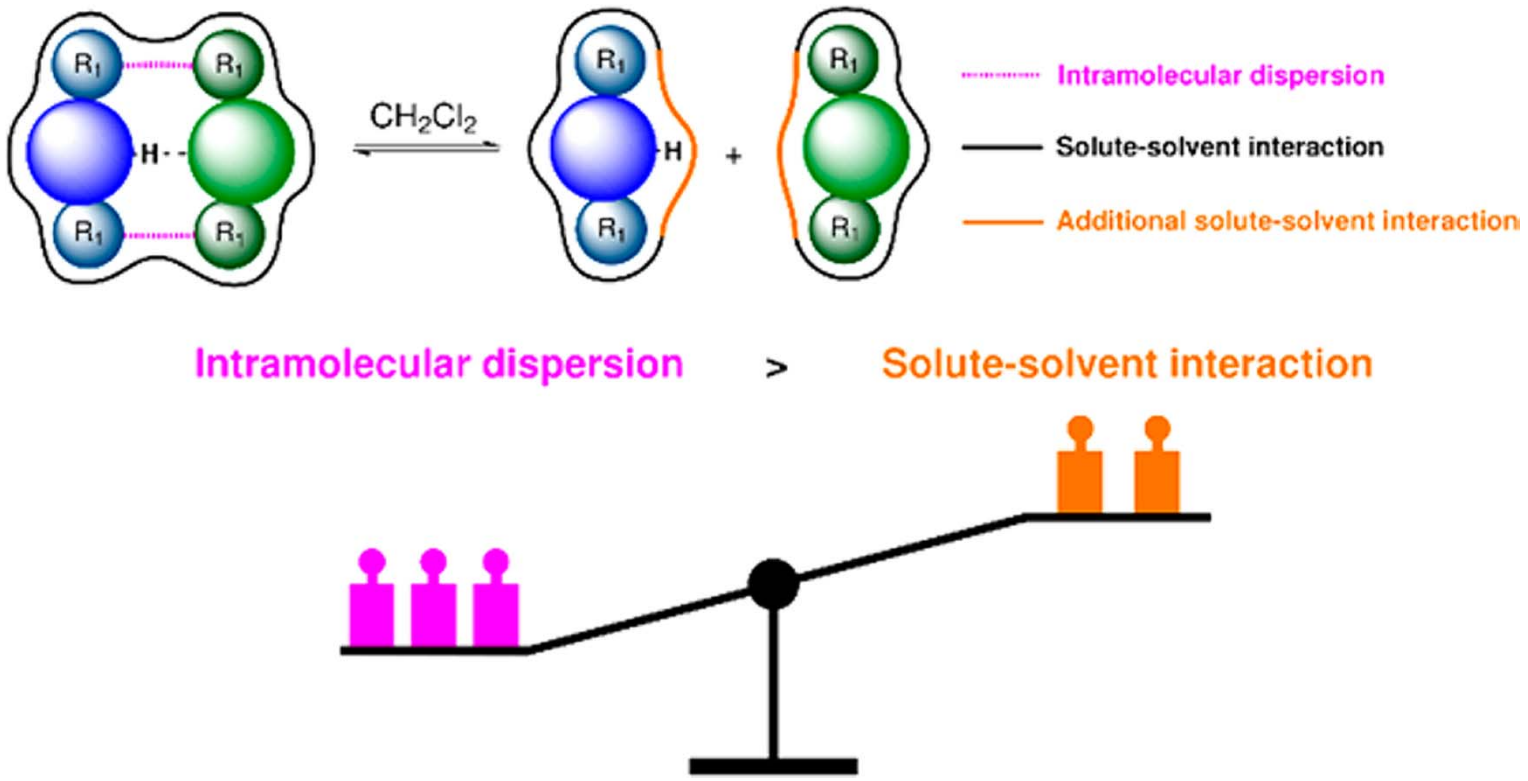


- the longest known alkane C–C bond



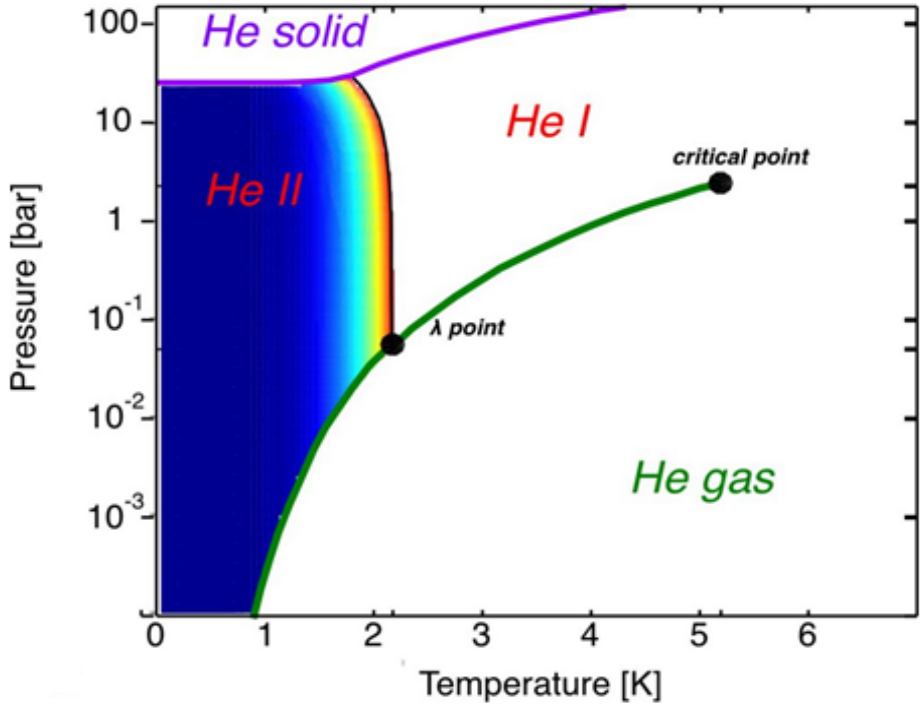
- important in σ–σ interactions of graphane

J. P. Wagner, P. R. Schreiner, *Angew. Chem., Int. Ed.* **2015**, *54*, 12274; C. Wang, Y. Mo, J. P. Wagner, P. R. Schreiner, E. D. Jemmis, D. Danovich, S. Shaik, *J. Chem. Theory Comput.* **2015**, *11*, 1621; S. Grimme, P. R. Schreiner, *Angew. Chem., Int. Ed*. **2011**, *50*, 12639; A. A. Fokin, L. V. Chernish, P. A. Gunchenko, E. Y. Tikhonchuk, H. Hausmann, M. Serafin, J. E. P. Dahl, R. M. K. Carlson, P. R. Schreiner, *J. Am. Chem. Soc.*, **2012**, *134*, 13641.



- going from the gas phase to a CH_2Cl_2 solution, attenuation of inter- and intramolecular dispersion by solvent is quite large (about 70%!)

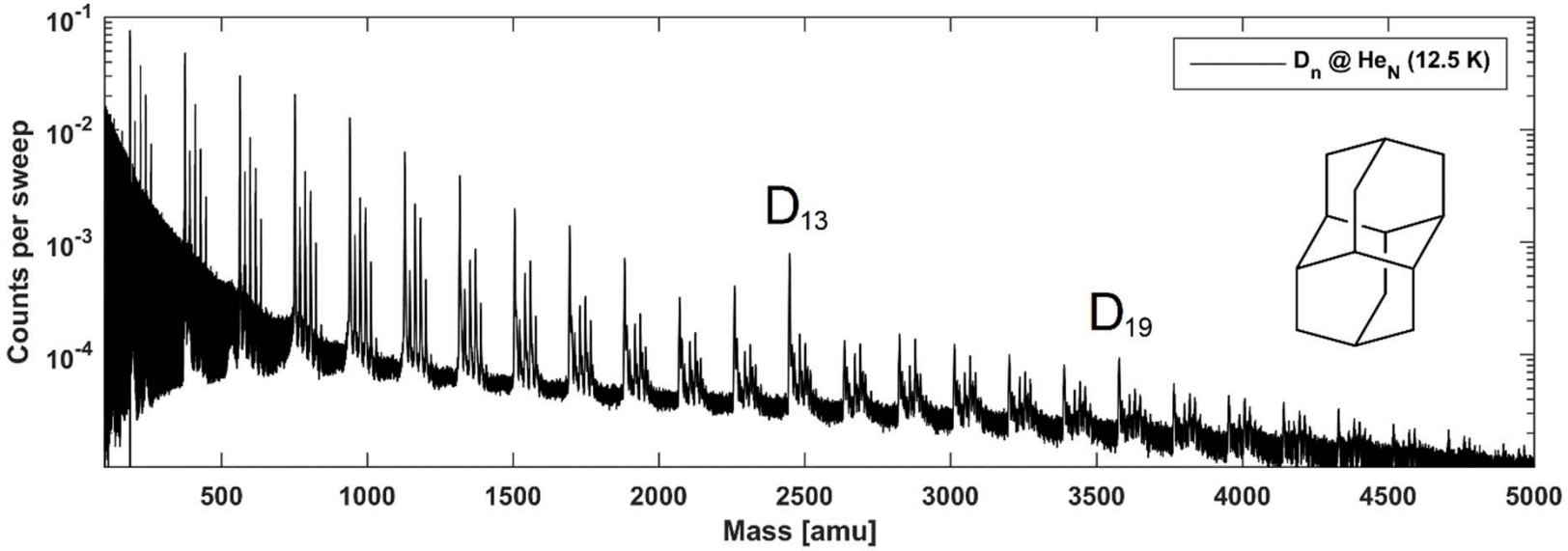
R. Pollice, M. Bot, I. J. Kobylianskii, I. Shenderovich, P. Chen, *J. Am. Chem. Soc.*, **2017**, *139*, 13126.



Phase diagram of ^{4}He

- helium II is superfluid
- suitable for generating **helium nanodroplets** (**HND**s)

- HNDs => small reaction chambers where large clusters can form
- produced by expanding gaseous helium into high vacuum at cryogenic temperatures
- negligible perturbative effect on dopant molecules
- ideal medium for trapping weakly binding van der Waals complexes



A recorded mass spectrum of He droplets doped with diamantane. Clusters with n = 13 and n = 19 units of diamantane show a higher abundance, suggesting increased stability. E_{el} = 90 eV, I_{em} = 6.8 µA, T_{He} = 12.5 K, p_{He} = 60 bar.

➢ emergence of ***magic number*** **clusters**

Experimental setup at *TU Graz*.

J. Alić, R. Messner, F. Lackner, W. E. Ernst, M. Šekutor, *Phys. Chem. Chem. Phys.* **2021**, *23*, 21833.

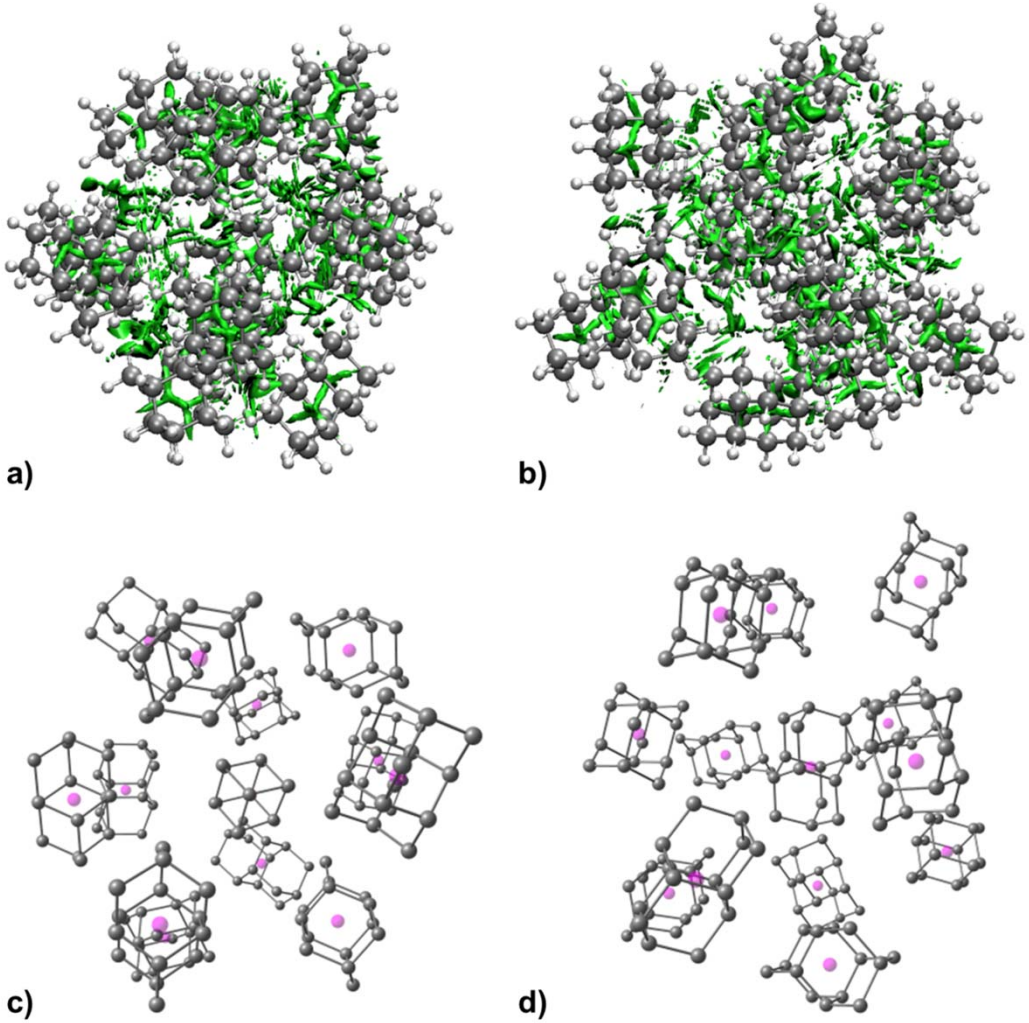
- constrained metadynamics (MTD) simulation
- semi-empirical quantum mechanical GFN2-xTB method
- DFT for single point energies

Table 1 Interaction energies, ΔH(0 K), of diamantane clusters in kcal mol^{-1} [a,b]

Level of theory	CL2	CL13	CL19
GFN2-xTB	−6.0	−72.6	−114.4
HF-3c	−7.6	−94.6	−149.4
PBEh-3c	−8.1	−102.0	−152.8
B3LYP-gCP-D3(BJ)/def2-TZVPP	−8.4	−96.8	−149.5
B3LYP-gCP-D3(BJ)-ABC/def2-TZVPP	−8.0	−87.7	−135.4
ωB97X-gCP-D3(BJ)/def2-TZVPP	−6.6	−93.3	−144.5
TightPNO-DLPNO-CCSD(T)/cc-pVTZ	−7.5	n.d.	n.d.

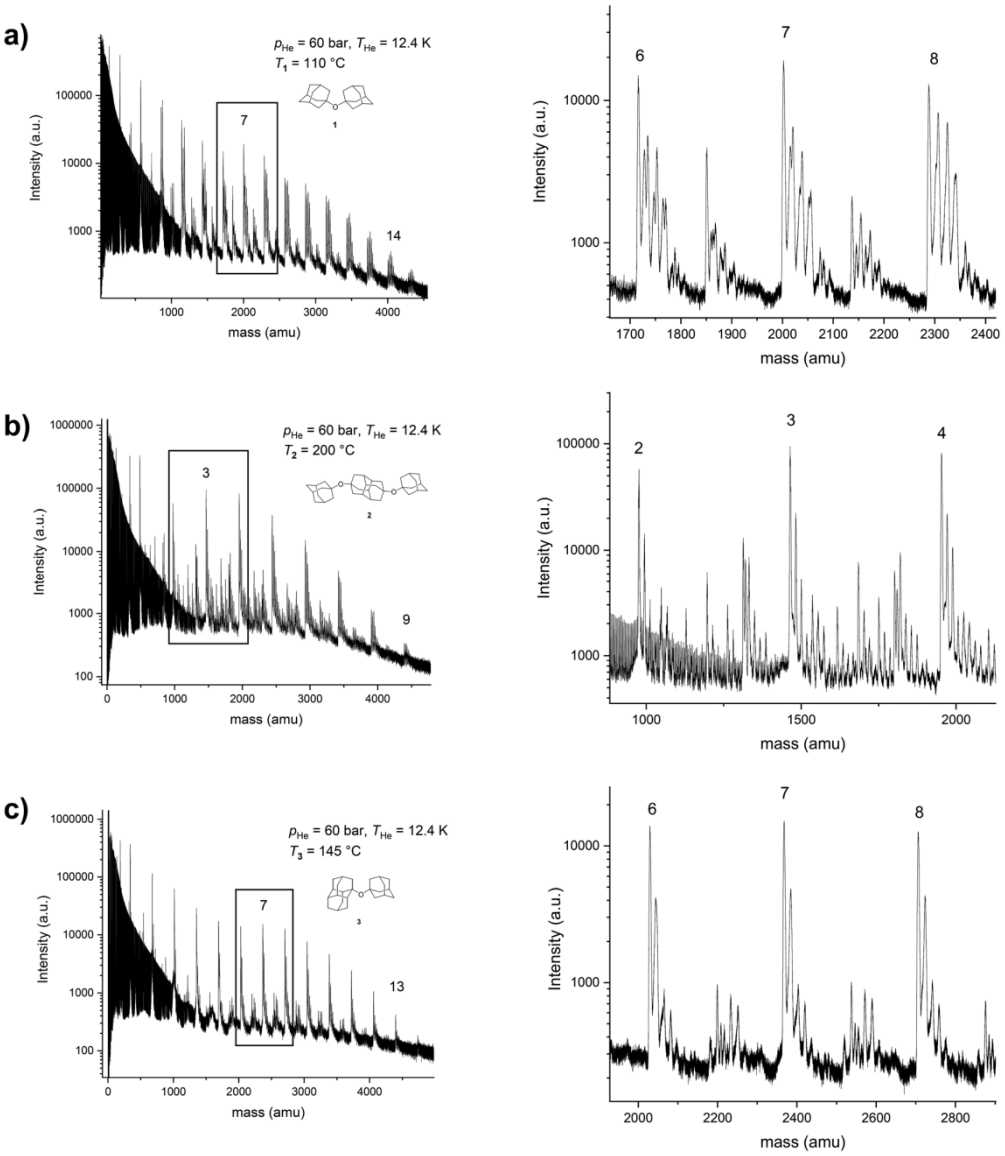
[a] Interaction energies are defined as a difference between the energy of the cluster and the energy of the corresponding number of diamantane moieties. [b] *ZPVE* taken from GFN2-xTB computations.

J. Alić, R. Messner, F. Lackner, W. E. Ernst, M. Šekutor, *Phys. Chem. Chem. Phys.* **2021**, *23*, 21833.

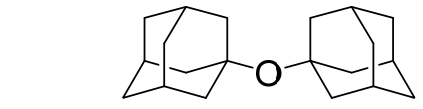


NCI plots of the computed structure of **CL13** with non-covalent interactions depicted in green, a) top view, b) side view.

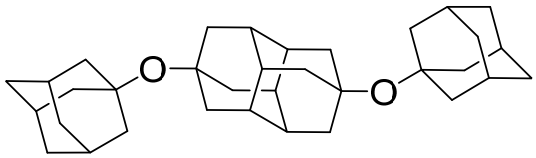
J. Alić, R. Messner, F. Lackner, W. E. Ernst, M. Šekutor, *Phys. Chem. Chem. Phys.* **2021**, *23*, 21833.



Diamondoid ethers



1



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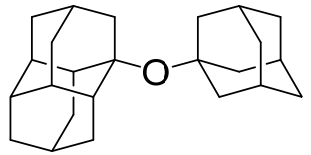
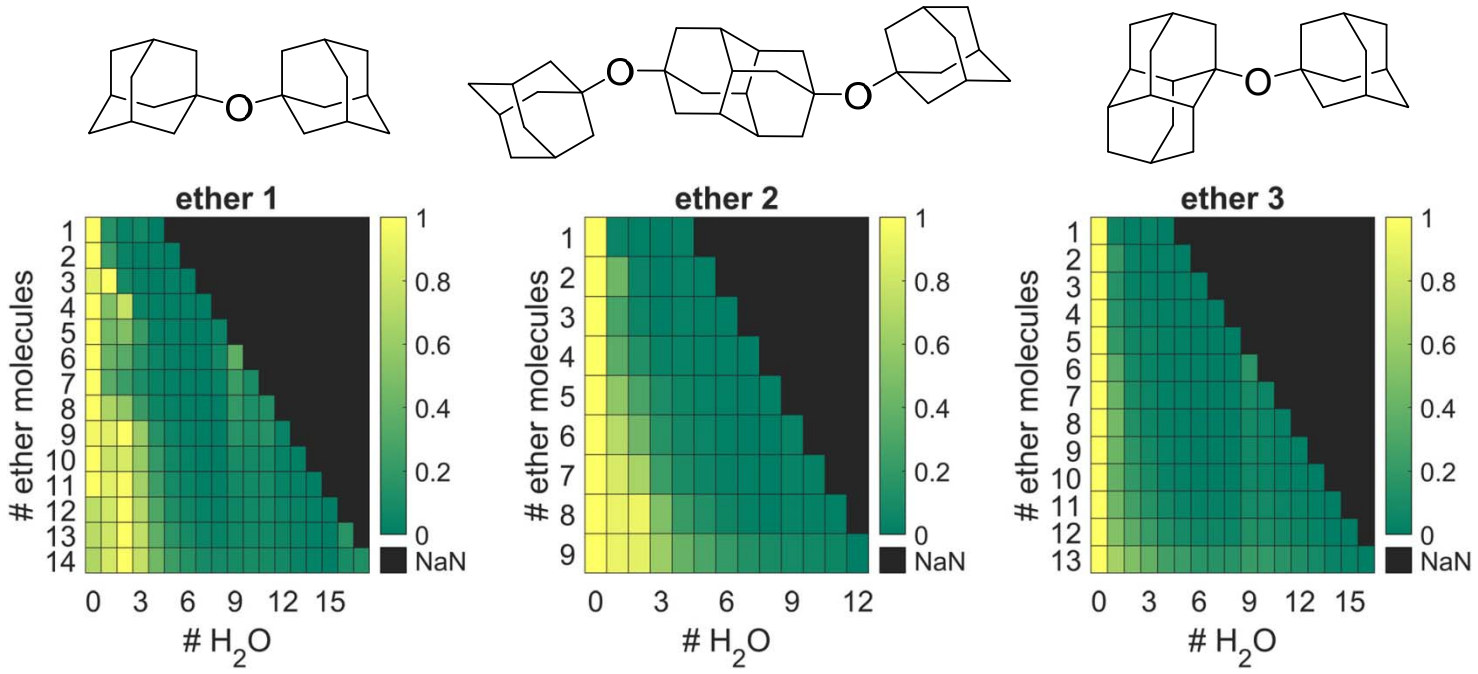


3

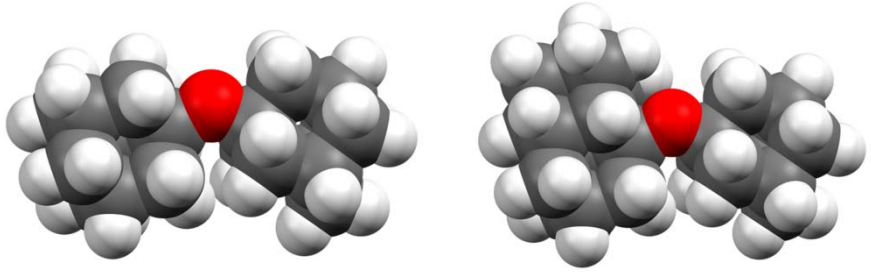
Mass spectra of He droplets doped with diamondoid ethers.

J. Alić, R. Messner, M. Alešković, F. Küstner, M. Rubčić, F. Lackner, W. E. Ernst, M. Šekutor, *Phys. Chem. Chem. Phys.* **2023**, *25*, 11951.

Diamondoid ethers

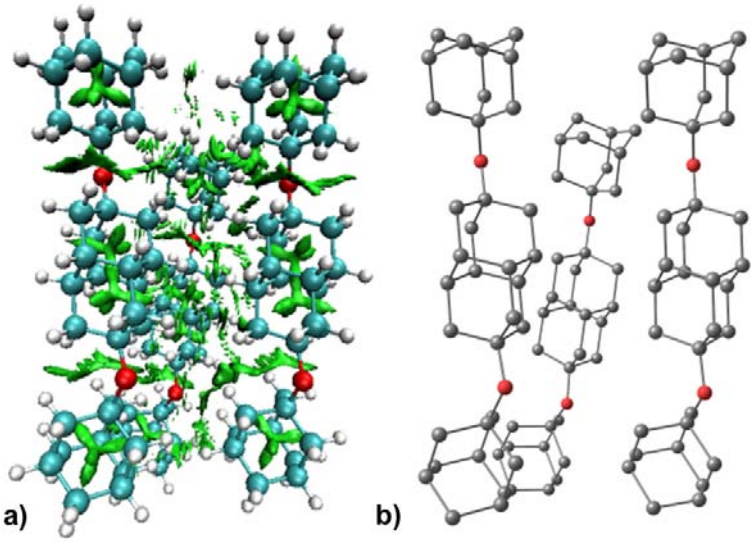


- the least water in ether **3** clusters => ether O shielding with appended cages

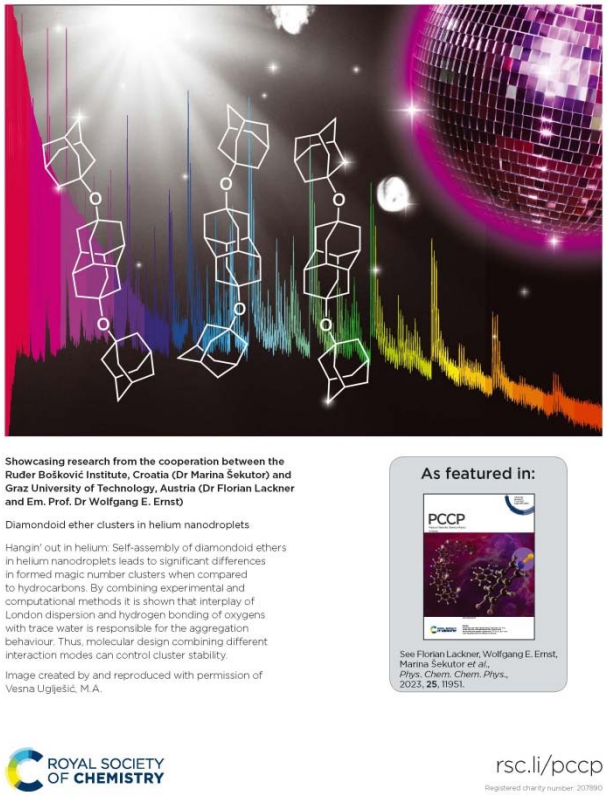


J. Alić, R. Messner, M. Alešković, F. Küstner, M. Rubčić, F. Lackner, W. E. Ernst, M. Šekutor, *Phys. Chem. Chem. Phys.* **2023**, *25*, 11951.

Diamondoid ethers

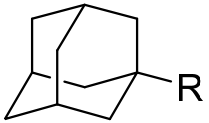


Non-covalent interactions (NCI) plot of a computed ether cluster structure **CL2**.

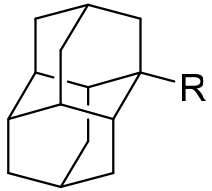


J. Alić, R. Messner, M. Alešković, F. Küstner, M. Rubčić, F. Lackner, W. E. Ernst, M. Šekutor, *Phys. Chem. Chem. Phys.* **2023**, *25*, 11951.

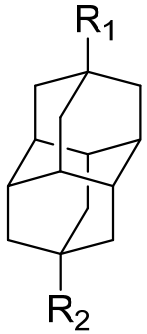
Diamondoid acids



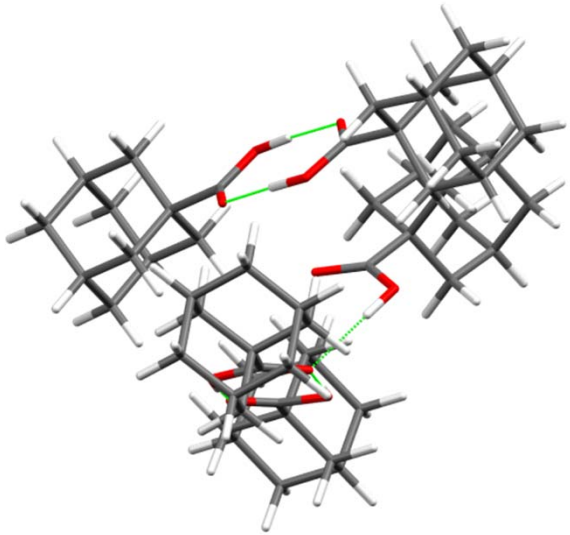
1a, R = COOH
1b, R = OH

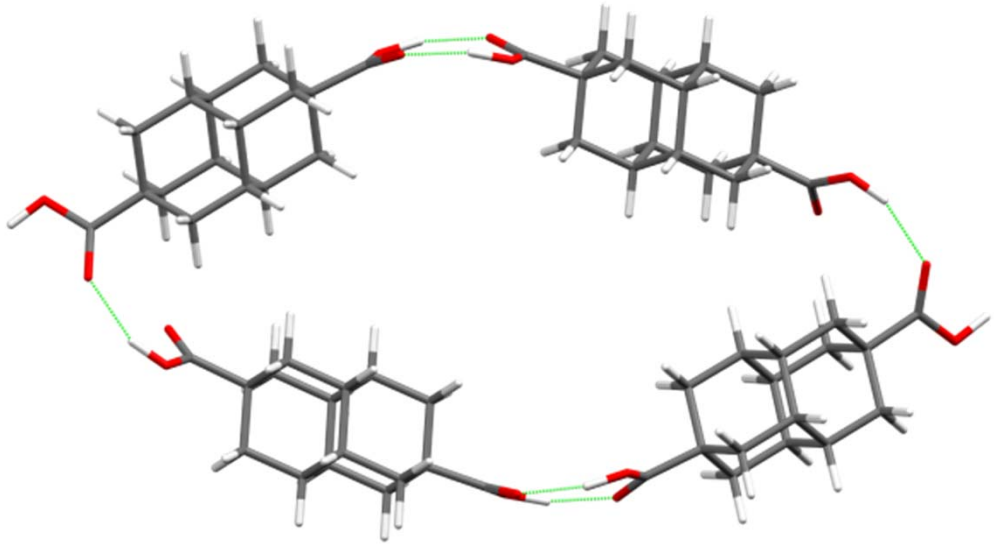


2a, R = COOH
2b, R = OH



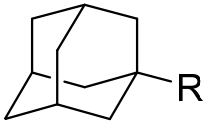
3a, R_1 = H, R_2 = COOH
3b, R_1 = H, R_2 = OH
4a, R_1 = R_2 = COOH
4b, R_1 = R_2 = OH



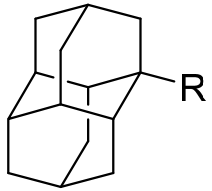


Representations of the minimized geometries of acid clusters **1aCL5** and **4aCL4**
CREST computations, iterative meta-dynamic sampling (NCI-iMTD mode)

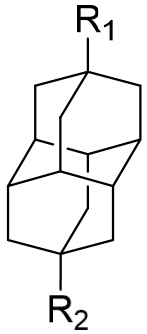
Diamondoid alcohols



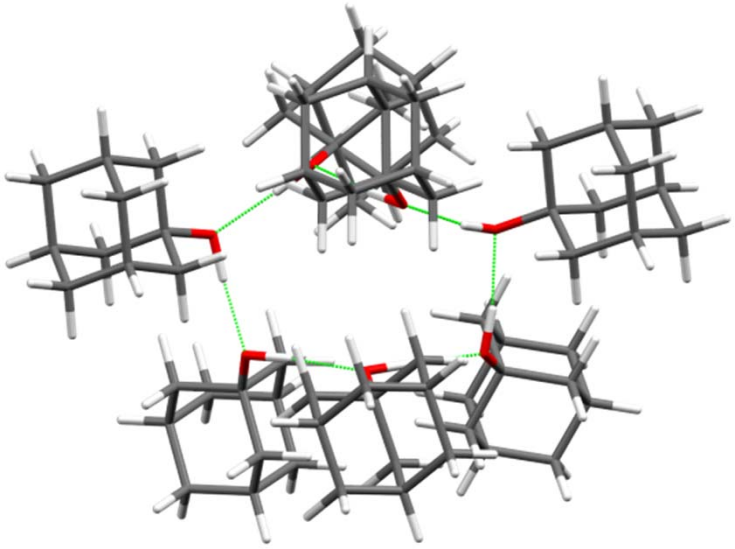
1a, R = COOH
1b, R = OH

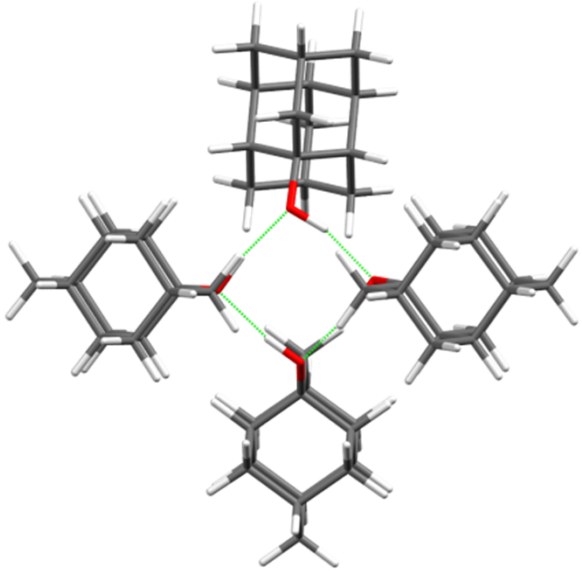


2a, R = COOH
2b, R = OH



3a, R_1 = H, R_2 = COOH
3b, R_1 = H, R_2 = OH
4a, R_1 = R_2 = COOH
4b, R_1 = R_2 = OH



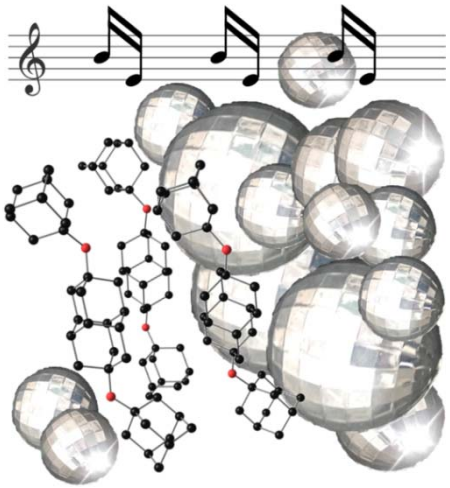


Representations of the minimized geometries of alcohol clusters **1bCL7** and **2bCL4**
CREST computations, iterative meta-dynamic sampling (NCI-iMTD mode)

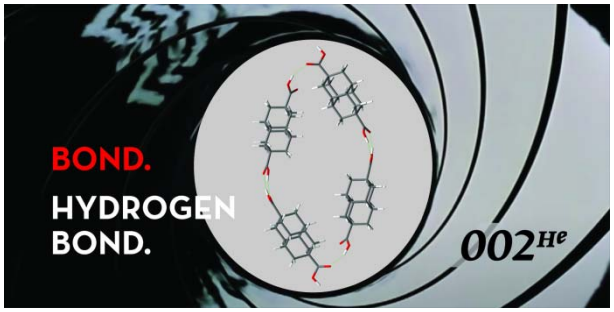
M. Alešković, F. Küstner, R. Messner, F. Lackner, W. E. Ernst, M. Šekutor, *Phys. Chem. Chem. Phys.* **2023**, *25*, 17869.

Summary

- HNDs => ideal medium to explore weakly-bound clusters
- diamondoids as dispersion energy donors => spontaneous cluster formation
- magic number clusters identified and characterized
- computations provided feasible cluster structures
- beyond single diamondoid cages => diamondoid covalent assemblies bridged with heteroatoms
- reverse micelle formation by diamondoid alcohols in HNDs
- power of inherently weak forces in aggregation processes => bulk matter formation



Hangin' out in helium…

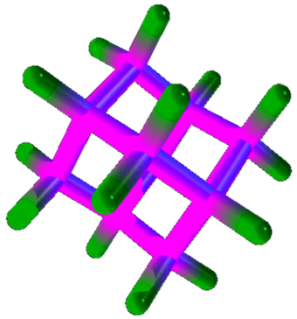


Acknowledgements

Dr. Jasna Alić Stolar
Dr. Marija Aleškoović
Prof. Mirta Rubčić

Em. Prof. Dr. Wolfgang E. Ernst
Dr. Florian Lackner
Dr. Roman Messner
Florian Küstner

Croatian Science Foundation (**UIP-2017-05-9653**)
and the Austrian Science Fund (**P30940 -N36**)



Thank you for your attention…