Enclosure 1b. Category 1 Application form 2015 – English version

APPLICATIONS ARE PREFERABLY DRAWN UP IN ENGLISH. AN ENGLISH TRANSLATION HAS TO BE ENCLOSED WITH APPLICATIONS SUBMITTED IN DUTCH.

The application form is available in Dutch on the website https://vscentrum.be/.

Title of the application:

Structural transformations during dehydroxylation reactions of UiO-66 type metal-organic frameworks; an extension with normal mode analysis

Name and first name of the applicant:

Vandichel Matthias

Institution:

Ghent University

Research group / department:

EA17, Center for Molecular Modeling

Title / position:

FWO postdoc

email address:

Matthias.Vandichel@Ugent.be

Total computing time that is needed, in node days:

2726

Total disk storage that is applied for (in GiB):

480 GB

1. Title of the research project (with IWETO or FRIS link if available) within the framework of which computing time is applied for:

Increasing the catalytic activity of metal-organic frameworks by tailor-made modifications (FWO postdoc mandate Matthias Vandichel)

Combined experimental and computational study of electronically modulated metal-organic framework (MOF) catalysts, FWO project 3G048612 between COK (Prof. Dirk De Vos) and CMM (Prof. Veronique Van Speybroeck)

2. Describe your research project in short. Explicitly mention the scientific questions that you are planning to address and the overall scientific goals of the project. (max. 1 A4 in Arial 12):

Metal-Organic Frameworks (MOFs) are crystalline nanoporous materials composed from both inorganic metal(oxide)s and organic linkers, with possible applications in gas separation/adsorption, catalysis, etc. In this project we aim at understanding the dehydroxylation behaviour of the MOF UiO-66 (Zirconium terephthalate), with structural formula $Zr_6O_4(OH)_4[BDC]_6$ (BDC=terephthalate). When placed in vacuum at high temperatures, this material loses its hydroxyl (OH) groups (***Figure 1***).

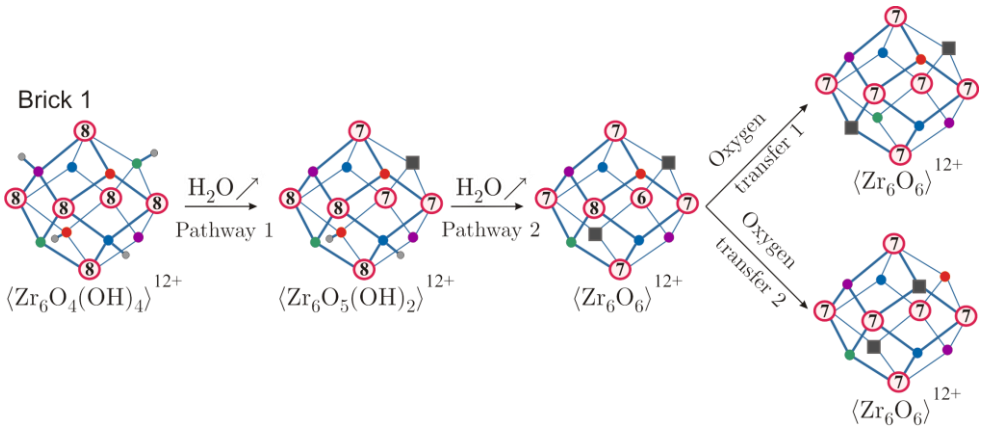

Figure 1*: Dehydroxylation processes can start from* $\{Zr_6O_4(OH)_4\}^{12+}$*. Coordination numbers of the different Zr-atoms are given (encircled).*

Terephthalate defects result in catalytical activity of the UiO-66 materials (F.Vermoortele, M.Vandichel et al. Angewandte Chemie Int. Ed., 51(20), 4887-4890, 2012 and JACS 135 (31), 11465–11468, 2013). In the case of

such structural defects (missing terephthalates), the inorganic bricks have a different formula, for example $[Zr_6O_5(OH)_3]^{11+}$ or, $[Zr_6O_6(OH)_2]^{10+}$, and their dehydroxylation behaviour will be different. For the $[Zr_6O_6(OH)_2]^{10+}$ brick, there exist even 3 different isomeric possibilities, dependent on where the two terephthalate defects are located. It is highly important to investigate dehydroxylation processes, as these lead to more catalytically active UiO-66 type materials. In this project, we want to refine the approach on our previous TIER1-project (Structural transformations during dehydroxylation reactions of UiO-66 type metal-organic frameworks), where we computed minimum energy pathways for a variety of dehydroxylation reactions using climbing image Nudged-Elastic Band (cNEB) simulations. More specifically, we would like to exploit the results of the previous TIER1-project to examine the stability of the periodic models along the reaction path. To that end, we need to determine more precisely the local minima and transition states that could be located by the NEB search of the previous TIER1-project. This improved precision is mandatory for the normal mode analysis (NMA), which is necessary to get to free energies.

Using standard density functional calculations with the PBE-D3 functional we will further optimize the local minima and transition states along the obtained minimum energy pathways. Therefore, these optimized structures will be submitted to a normal mode calculation (or frequency calculation), to yield both the frequencies and the elastic tensor. With these properties of the various states, we can compute free energy differences and see how the material stability changes along the reaction path. Accounting for the elastic tensor in the partition function of the structures will also enable us to see these more subtle effects in the free energy profile.

We will obtain detailed insight into the active sites after such a dehydroxylation treatment and their energetic relevance. Furthermore, this active site information – highly relevant for the Zr-MOF community – can then be used for further computational studies.

3. Provide an abstract (10 lines) for scientific communication on the website in layman's terms. See also item 13 of this application form.

In this project, we want refine the results obtained in our previous Tier1-project (Structural transformations during dehydroxylation reactions of UiO-66 type metal-organic frameworks), where we computed minimum energy pathways for a variety of dehydroxylation reactions using climbing

image Nudged-Elastic Band (cNEB) simulations. More specifically, we would like to refine this approach and further optimize the local minima and transition states along the obtained minimum energy pathways. Therefore, these optimized structures will be submitted to a normal mode calculation (or frequency calculation), to yield both the frequencies and the elastic tensor. With these properties of the various states, we can compute free energy differences and see how the material stability changes along the reaction path. Accounting for the elastic tensor in the partition function of the structures will also enable us to see these more subtle effects in the free energy profile.

4. Financing institution or channel, financing the research project in full or in part (FWO, BOF, IWT, EU, ...): Please attach the confirmation letter as enclosure (see instructions in enclosure 4 “EasyChair proposals submission procedure”).

Personal FWO postdoc fellowship of Matthias Vandichel, confirmation letter can be found at the end of the file.

FWO project 3G048612, confirmation letter can be found at the end of the file.

5. Name and email address of the promoter(s) of the research project:

Dr. ir. Matthias Vandichel, email: matthias.vandichel@ugent.be

Prof. Dr. ir. Veronique Van Speybroeck, email: veronique.vanspeybroeck@ugent.be

6. Billing address to which the payment invoice will be sent to:

Matthias Vandichel

Center for Molecular Modeling

Technologiepark 903

9052 Zwijnaarde

7. Persons mandated by the Applicant to compute on the Tier1 within the framework of the present project: Please provide for every person:
   - name and first name
   - institution
   - research group / department

- title / position
- experience of using HPC resources in the past (Tier0/Tier1/Tier2 infrastructure in Belgium and abroad)

Matthias Vandichel

Ghent University

EA17, Center for Molecular Modeling

FWO-postdoc

vsc40048

Experience with TIER1 and TIER2 infrastructure of UGent

Julianna Hajek

Ghent University

EA17, Center for Molecular Modeling

PhD fellow

vsc40880

Experience with TIER1 and TIER2 infrastructure of UGent

Veronique Van Speybroeck

Ghent University

EA17, Center for Molecular Modeling

Professor

vsc40021

Experience with TIER2 infrastructure of UGent

8. Explain why this project needs to run on a Tier1 system, why the machine you have requested is suitable for the project and how the use of the system will enable the science proposed (max. ½ A4 in Arial 12).

This work is a continuation of our previous TIER1-project and involves (1) optimizations and (2) frequency computations to obtain detailed free energy profiles of dehydroxylation reaction paths. Due to the size of the systems and the amount of calculations the project goes beyond what can comfortably be done (within a reasonable timeframe) on a TIER2 cluster. The queuing times for such large jobs can easily go up to one week, and

this project requires 210 of this type of calculations. We need the TIER1 cluster to be able to finalize this work.

9. Justify the number of node days requested. This should include information such as: number and nature of computing tasks, software used, and the sequence in which they will be performed. Indicate for each typical computing task the required resources:

   - wall clock time (note that 3 days is the maximal wall clock time for any job; checkpointing should be used for longer run times)
   - memory (maximum 64 GiB/node)
   - number of nodes
   - number of CPU cores
   - disk space (estimated volume in GiB and the total number of files); make a clear distinction between usage of Tier2 DATA/HOME partitions and the Tier1 SCRATCH partition
   - number of tasks, and an indication of how many such tasks would be submitted concurrently.

   This information should take the form of a table (an example is provided as Table 2 in the appendix). Provide additional descriptions of the computing tasks and comments as needed. Resource estimates should be preferably based on the results of actual calculations on Tier1 (via, e.g., a Starting Grant) for system/problem sizes that are on par with those of the intended computing tasks (e.g., same mesh sizes, actual molecular system, …). If not, provide the name, architecture, #cores, memory, etc. of the machine that was used to obtain these results and explain how you have calculated/rescaled the wall clock times, number of cores, etc.

   (max. 1 A4 Arial 12).

Our previous TIER1-project concerned 15 water removal trajectories in periodic unit cells (**system size**: 192 up to 228 atoms). Each water removal pathway contains typically 4 local minima and 3 transition states (7 states in total). To complete our study, we want to optimize 60 local minima and 45 transition states. Remark that the procedure to optimize transition states can be quite cumbersome, and involves typically an initial frequency computation to find the normal mode corresponding to the transition state, followed by the transition state optimization. For each

structure, a full frequency computation is required to determine free energy differences. We simulated optimization and frequency calculations during our previous TIER1-project, and this enabled us to make a good estimate of the number of node days we need for this proposal. An optimization of a local minimum takes typically 2-4 node days (dependent on system size), while a transition state optimization costs on average at least 16-18 node days. The frequency computations will cost between 10-12 node days. With this information, we can estimate the total node days needed (**Table 1**).

Table 1: Estimated node days for the project (1 node = 16 cores).

	#days x #nodes (per calculation)	Total computational time (total node days)
Opt (60)	4 x 1	240
Opt TS (45)	18 x 1	810
Freq (105)	3 x 4	1260 + 33%*
Total		**2726**

*In 33% of the calculations, there are small residual imaginary frequencies and therefore we need some additional computational time to get rid of them in another subsequent frequency computation.

We will apply a gamma-only version of VASP for all the intended optimizations and frequency computations, which leads to a speed up of almost 100% compared with the normal VASP versions (tested during the previous TIER1-project).

Optimizations can be performed on one node (16 cores), so the scaling of these calculations is optimal.

Frequency computations need to be performed on 4 nodes in order to finish before the wall time limit (72 hours) as we cannot resubmit unfinished calculations (not yet implemented in the current versions of VASP). Because of parameters mentioned in the INCAR file (NPAR), the scaling efficiency with respect to a single node calculation is higher than 80% [1].

Based on this information and initial VASP-benchmark calculations from our previous TIER1-project, we could make a fair estimate of the computational time needed (**Table 1**) and the memory use (**Table 2**).

Together, this yields 2310 node days. Due to the size of the systems and the amount of calculations this project is perfectly suitable for the TIER1-cluster.

Table 2: Estimated memory storage

	SCRATCH storage / calculation (GB)	Total scratch storage (GB)
Opt (60)	1.5	90
Opt TS (45)	4	180
Freq (105)	2	210
Total		**480**

10. Describe the software required to perform the computing task(s). Please clearly provide the following per item in this regard:

    - a reference to the software's web page
    - the software license system (open source, GPL, etc.)
    - if there is no free academic use of the software, state which license makes the installation and the use valid on the Tier1 by the Applicant (+ add a copy of the signed license)
    - if need be, which license server will be used (name + IP address)
    - whether the software is already available on the Tier1 (see https://vscentrum.be/nl/Tier1-rekenen) and, if this is not the case, compilation and installation instructions (possibly with reference to existing Tier2 installation)

    Provide the results of scaling tests that were conducted with this software, preferably on Tier1 (using, e.g., a Starting Grant) for system/problem sizes that are on par with those of the intended computing tasks (e.g., same mesh sizes, actual molecular system, …). If not, provide the name, architecture, #cores, memory, etc. of the machine that was used to obtain these results.
    Provide both a table and scaling plot such as table 1 and plot 1 in the appendix (max. 2 A4 in Arial 12).

VASP 5.3.3

- http://www.vasp.at
- License: see at the end of the file
- The software is already available on the TIER1 infrastructure.

We cannot provide scaling tests, since we use mostly single node calculations with exception for the normal mode calculations where we specify 4 nodes, which is required in order to have a finished job within the wall time of 72h. Of course, we use INCAR parameters, such as NPAR and NCORE to optimize the scaling behavior in case of multi-node calculations [1].

11. Describe how you will manage the resources requested in the period during which the task is to be performed. What usage pattern do you anticipate (similar usage on monthly basis, bursts, …)?

Jobs will be submitted manually in a stepwise manner, as there many intermediate results need to be visualized and checked.

12. List the granted computing time allocations to the promoter(s) of this research project, on the Flemish Tier1 system, as well as other Tier1 and Tier0 systems. Also, describe the scientific output obtained within the framework of computing time that was granted during the past two years on the Flemish Tier1 or on other Tier1 or Tier0 supercomputers. DOI links are sufficient.

“Unraveling reaction pathways on UiO-66 type systems with metadynamics” 4432 node days granted to Matthias Vandichel (01/11/2013 to 28/02/2014).

“Modeling aldol condensations in metal-organic frameworks with hybrid functional calculations” 2304 node days granted to Julianna Hajek (04/07/2014 to 31/12/2014).

“Structural transformations during dehydroxylation reactions of UiO-66 type metal-organic frameworks” 4720 node days granted to Matthias Vandichel (15/11/2014 to 30/04/2015).

Scientific output:

Active site engineering in UiO-66 type metal-organic frameworks by intentional creation of defects: a theoretical rationalization. DOI: http://dx.doi.org/10.1039/C4CE01672F

Mechanistic study on aldol condensations on UiO-66 and UiO-66-NH2 metal organic frameworks, Julianna Hajek, Matthias Vandichel, Dirk De Vos, Michel Waroquier, Veronique Van Speybroeck, submitted

Au@UiO-66: a base free oxidation catalyst, Karen Leus, Patricia Concepcion, Maria Meledina, Matthias Vandichel, Abdessamad Grirrane, Dolores Esquivel, Stuart Turner, Dirk Poelman, Michel Waroquier, Veronique Van Speybroeck, Gustaaf Van Tendeloo, Hermenegildo García, Pascal Van Der Voort, submitted

Unravelling reaction pathways systems with metadynamics, in preparation

13. Are the applicants of this application bound by a confidentiality agreement? If so, the title and the abstract of this application will not be published on the website of the Hercules Foundation / Flemish Supercomputer Center.

no

References:

[1] Specialist course on efficient use of VASP, University of Antwerp, 23-24th of October 2014
https://vscentrum.be/neutral/events/2014/introduction-to-vasp

Should you have any questions or encounter any difficulties during the electronic submission of an Application, please contact by e-mail:
Associatie KU Leuven: hpcinfo@kuleuven.be
Associatie Universiteit Gent: hpc@ugent.be
Associatie Universiteit Hogescholen Antwerpen: hpc@uantwerpen.be
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For the other institutions: marc.luwel@herculesstichting.be

Appendix: Example tables and plots

Table 1

# nodes	# cores	absolute timing (s)	speedup	# cores x timing
16	256	189.6	1.0000	
32	512	99.0	1.9154	
64	1024	55.6	3.4088	
128	2048	30.8	6.1376	

Plot 1

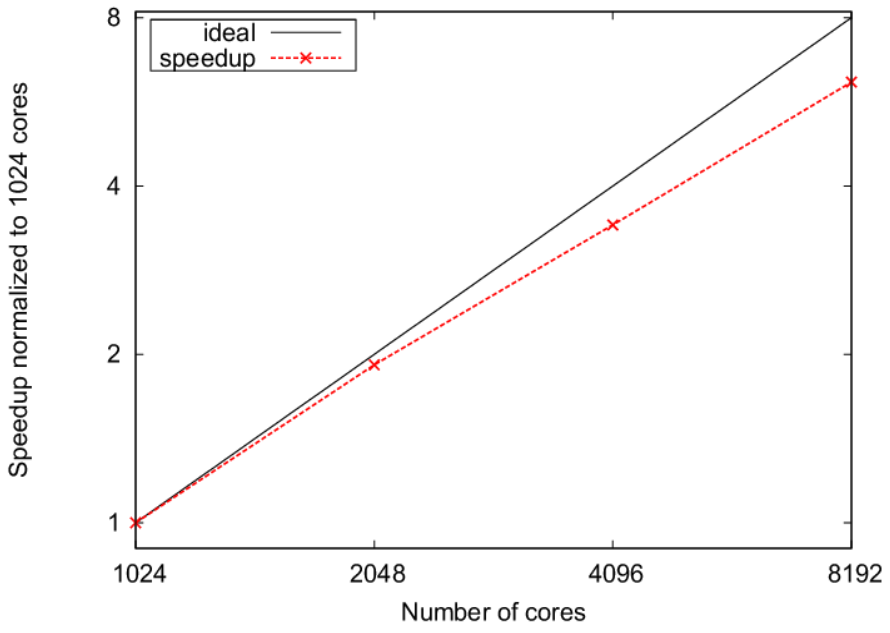

Table 2

	Node day calculation							Storage volume estimate	
Computational task	# of such tasks	Wall clock time (days) per task	# Tier1 nodes per task	# node days per task	# CPU cores per task	Memory usage (GiB) / node per task	OpenMP / MPI / hybrid / vSMP	Tier2 DATA/HOME volume (GiB) + number of files	Tier1 SCRATCH volume (GiB) + number of files
Task1	A	B	C	= A x B x C					
Task2	A	B	C	= A x B x C					

Fonds Wetenschappelijk Onderzoek
Research Foundation – Flanders

Prof. Dirk De Vos
Katholieke Universiteit Leuven
Oppervlaktechemie en Katalyse
Kasteelpark Arenberg 23
3001 LEUVEN

uw kenmerk	ons kenmerk	contact	datum
	05_05 G.0486.12	bio@fwo.be cult@fwo.be wt@fwo.be gm@fwo.be med@fwo.be interdisciplinair@fwo.be	16 november 2011

Betreft: **Toekenning project G.0486.12**

Geachte professor,

De Raad van Bestuur van het FWO heeft uw bovenvermelde aanvraag voor een onderzoeksproject goedgekeurd. De bijgevoegde overeenkomst werd opgesteld volgens het reglement van de Onderzoeksprojecten van het FWO.

Graag wil ik u hierbij feliciteren met de toekenning van het door u aangevraagde onderzoeksproject.

Mag ik u vragen alle exemplaren te ondertekenen, één kopie voor u te bewaren en mij het origineel samen met de overige kopie(ën) per kerende post terug te sturen.

De toegekende toelage is beschikbaar voor zover de financierende overheden hiervoor de nodige middelen vrijmaken. Onderzoek waarvoor medisch ethisch advies noodzakelijk is, kan pas starten als de onthaalinstelling hierover positief advies uitbrengt.

Slechts uitzonderlijk kan, met akkoord van het FWO, de oorspronkelijke bestemming van dit krediet worden gewijzigd.

Tenslotte vraag ik u met aandrang om op uw publicaties steeds te vermelden dat ze tot stand kwamen met de financiële steun van het FWO. Vacatures gekoppeld aan onderzoeksprojecten kunnen bekend worden gemaakt via de FWO-website. U kan het vacaturebericht aan het FWO bezorgen via communicatie@fwo.be. Aanvullend kan het nuttig zijn om dergelijke berichten ook te publiceren via de Euraxess website van de Europese Commissie: http://ec.europa.eu/euraxess/ .

./..

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../..

Fonds Wetenschappelijk Onderzoek
Research Foundation – Flanders

Voor bijkomende inlichtingen kan u steeds terecht bij uw dossierbeheerder. De e-mailadressen zijn voor de Biologische Wetenschappen: bio@fwo.be, voor de Cultuurwetenschappen: cult@fwo.be, voor de Gedrags- en Maatschappijwetenschappen: gm@fwo.be, voor Wetenschap en Technologie: wt@fwo.be, voor de Medische Wetenschappen: med@fwo.be en voor het Interdisciplinair onderzoek: interdisciplinair@fwo.be.

Hoogachtend,

dr. ir. Elisabeth Monard
secretaris-generaal

Bijlagen: 2

Kopie: Prof. Veronique Van Speybroeck

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De heer Matthias Vandichel
Maandagveld 8
8500 KORTRIJK

FWO VLAANDEREN
Fonds Wetenschappelijk Onderzoek
Research Foundation – Flanders

uw kenmerk	ons kenmerk	contact	datum
	63893 12F5214N	bio@fwo.be cult@fwo.be wt@fwo.be gm@fwo.be med@fwo.be interdisciplinair@fwo.be	26 juni 2013

Betreft: **Toekenning Postdoctoraal Onderzoeker 2013-2016**

Geachte heer,

De Raad van Bestuur heeft u vandaag aangesteld als Postdoctoraal Onderzoeker met ingang van 1 oktober 2013 tot en met 30 september 2016. Het reglement vindt u als bijlage.

Graag wil ik u feliciteren met deze aanstelling als Postdoctoraal Onderzoeker van het FWO.

In het kader van de verdere administratieve opvolging van uw aanstelling zal het FWO u nog vóór 19 juli 2013 een arbeidsovereenkomst bezorgen.

Voor bijkomende inlichtingen kan u steeds terecht bij de dossierbeheerder van uw wetenschapsgebied op bovenvermeld e-mailadres.

Tenslotte vraag ik u met aandrang om op uw publicaties steeds uw titel Postdoctoraal Onderzoeker van het FWO te vermelden.

Ik wens u veel succes toe in uw verdere onderzoeksloopbaan.

Hoogachtend,

dr.ir. Elisabeth Monard
secretaris-generaal

Bijlage: 1

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WWW.FWO.BE

SOFTWARE LICENSE AGREEMENT FOR THE USE OF VASP5.2 BY ACADEMIC INSTITUTIONS

The Universität Wien, Austria (UW in the following) and
Ghent University, Belgium (UG in the following) [1]
conclude the following agreement:

(1) The UG acquires a non-exclusive academic license for the use of the software-package VASP (Vienna ab-initio simulationprogram) for ab-initio local-density-functional total-energy and molecular-dynamics calculations, versions VASP5.2 and VASP4.6, by the research group Functional Nanomaterials (FUNNANO)[2]. Under this licence the use of the software is restricted to a maximum of six researchers or students, all belonging to this research group and to the same organisatorial unit and working at the same location. The licence does not cover the use of VASP by external collaborators working at other institutions.

(2) The license covers access to the source-code, the program documentation and to the data-base for ultrasoft pseudopotentials and PAW-potentials. UW reserves the exclusive property of the software. It declines any liability for the software and any responsibility for the results of calculations produced with the program. The license does not cover any maintenance service for the software or support for its implementation.

(3) The license is not transferable to another research group of UG without the written agreement of UW. UW reserves the right to refuse authorization of such a transfer. A transfer to a research group not belonging to UG is excluded.

(4)The UG guarantees that the software or parts thereof shall not be made accessible to third parties without the explicit written consent of UW. Access to the code and to the data-base shall be made available through an account of the UW. The UG guarantees that the password for this account will be known only to one contact-person and shall not be communicated to temporary co-workers or guests. All installations of the source code, the executable or the data-base must be copy-protected and accessible only to the authorized users.

[1] Please insert here the name of the institution concluding this agreement with UW. This institution must be a legal person and the agreement must be signed by an authorized representative of this institution. Define the acronym (replacing .....) under which this institution is referred to in the text of the agreement.

[2] Please insert here the name and affiliation research group for which the license is acquired

SOFTWARE LICENSE AGREEMENT FOR THE USE OF VASP5.2 BY ACADEMIC INSTITUTIONS

(5) If VASP is used as the basis of further methodological or software-development, UG agrees to make these additions available to UW. UW will also be entitled to include these additions in further releases of VASP.

(6) In future publications of work performed using VASP, the use of the software shall be properly acknowledged, e.g. in the form
"The calculations have been performed using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) developed at the Institut für Materialphysik of the Universität Wien [1-3]."
[1] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
If the PAW-version is used, reference will be made to
[2] G. Kresse and D. Joubert, Phys. Rev. **59**, 1758 (1999).
If special features implemented in VASP will have been used, reference should be made to the relevant publications as listed on the VASP home-page.

(7) The UG accepts to pay to UW a licence fee Euro 4.000,- (fourthousand Euro). The licence fee is strongly discounted and applies only to academic institutions with undergraduate teaching.

(8) The licensee will use VASP exclusively for non-profit research. If VASP is used in contractual research in cooperation with or for industry or for military institutions, the financial conditions will have to be re-negotiated.

(9) UW declares that it has the full power and authority to grant the rights granted in this agreement without the consent of any other person, and that the license and use of the software by the licensee will not in any way constitute an infringement or other violation of any copyright, proprietory right or any other rights of any third party.

(10) Any disputes arising from the license agreement are subject to the laws of the Republic of Austria.

(11) The terms of this agreement shall prevail any terms or conditions of the licensee.

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For the Universität Wien:

Jürgen Hafner
Fakultät für Physik, Universität Wien
Sensengasse 8/12, A-1090 Wien, Austria

Date

For the UG

Name (in print): Michel Waroquier
Institution: Faculty of Sciences, Ghent University

Address: Technologiepark 903, BE-9052 Zwijnaarde, Belgium

Date: 26 January 2010

For the research group entitled to use VASP5.2:

Name (in print): Veronique Van Speybroeck (FUNNANO)