1 Probing properties of molecule-based

interface systems: general discussion and

Discussion of the Concluding Remarks

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Zhi Li, Nian Lin, Trolle Linderoth, Natalia Martsinovich, Martin Nalbach,

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(600:[600]600) Ioan Bˆaldea opened a general discussion of the paper by

Angelika K¨uhnle: Congratulations on the nice work. You mentioned the case of

elevated temperatures, did you study more systematically the impact of temperature

(T)? And how T-variations possibly affect the distance histogram?

Angelika K¨uhnle replied: Thanks for the question. We are currently investigating

the impact of temperature on the distance distributions. In principle, there

are two effects: at low temperatures, the molecules might not be mobile enough

and the stripes will not adopt their optimum position. Thus, the distribution will

have a larger standard deviation. For elevated temperatures, “excited states” can

also be accessed, i.e., a small modulation in the energy landscape due to repulsion

might not be detectable above a certain temperature.

(601:[601]601) Ioan Bˆaldea said: Maybe in the experimental histograms (e.g.

the blue bars in Figs. 3a, 3b, 3c, DOI: 10.1039/C7FD00089H) you can disentangle

the physical effect(s) from the geometrical effects (grey bars in those gures) and

focus on the (T-dependence of the) former. Anyway, presenting quantitative

results on the effect of temperature on distance histograms would be interesting

also for a theorist aiming to compare with your data.

Angelika K¨uhnle replied: The grey bars represent the stripe distance distribution

that would be detected for randomly placed, non-interacting stripes. We

show the comparison with our results to demonstrate that a repulsive force must

exist between the stripes. We use the experimental data (blue bars) to get an

estimate for the dipole moment strength that is needed to arrive at the

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experimentally obtained distance distribution. Regarding the temperaturedependent

experiments, you are absolutely right. We are currently working on

this point.

(602:[602]602) Markus Lackinger asked: Would you please explain how the

geometric distribution is derived in more detail?

Angelika K¨uhnle answered: The geometric distribution is the distribution to be

applied when you have two possible outcomes (in our case “row” versus “no row”)

and the probability of nding a row (and of not nding a row) is the same for all

lattice sites. You can nd a detailed derivation in the Supporting Information of

the publication by Julia Neff.1

1 J. L. Neff, H. S¨ongen, R. Bechstein, P. Maass, and A. K¨uhnle, Long-Range Order Induced by

Intrinsic Repulsion on an Insulating Substrate, J. Phys. Chem. C, 2015, 119, 24927.

(603:[603]603) Nian Lin queried: Have you done coverage-dependent analysis

of chain–chain separation distribution to see how the separation changes?

Angelika K¨uhnle replied: Yes, we have studied this.1 The stripe-to-stripe

distance distribution is a direct function of the coverage. The more molecules

you put on the surface, the closer the stripes get. What you also see in this analysis

(Fig. 3 in the above-mentioned publication) is that the standard deviation of the

distribution gets broader for decreasing coverage. However, the standard deviation

is always signicantly smaller than the standard deviation of the corresponding

distribution of randomly placed, non-interacting stripes (Fig. 4a in the

above-mentioned publication), which is by the way an alternative way of identifying

the presence of a repulsive interaction in our system.

1 J. L. Neff, H. S¨ongen, R. Bechstein, P. Maass, and A. K¨uhnle, Long-Range Order Induced by

Intrinsic Repulsion on an Insulating Substrate, J. Phys. Chem. C, 2015, 119, 24927.

(604:[604]604) Nian Lin continued: You have this dipole–dipole repulsion; how

does this affect the length of the chains? Would the repulsion shorten the chains?

Angelika K¨uhnle replied: This is a very interesting point. Yes, both the width

and the length of the molecular aggregates are steered by the balance between the

short-range attraction and long-range repulsion in the respective directions.

Therefore, as mentioned in my presentation, analyzing the island width and

length distributions should allow us to elucidate the details of the (oen anisotropic)

molecule interaction potential. We currently follow this idea with the

structures formed from 3-EBA molecules.

(605:[605]605) Steven De Feyter commented: You have looked at quite a large

number of molecules, and you selected four of them to discuss. Do you have any

idea about their orientation with respect to the substrate? What is the effect of

different substituents? How does their orientation affect the repulsive inter-row

interactions?

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Angelika K¨uhnle responded: For some of the molecules tested, we have by now

a rather detailed understanding of the binding conguration to the surface

thanks to the efforts of our theory partners.1–3 However, for the 3-HBA presented

here, the present DFT calculations remain inconclusive so far. For the point I

want to make here, however, I think it is important to note that the specic

adsorption of the molecule towards the surface is not so decisive. Any binding

towards the surface, no matter how simple or complex, will be associated with the

formation of an electrical dipole perpendicular to the surface. This is the only

point that matters.

Regarding the effect of different substituents, we aim to gain insights by

systematically changing both number and nature of functional groups on

a benzene core. We have, for example, studied all six isomers of dihydroxybenzoic

acid.4 The result shows that although the molecules are seemingly similar, the

self-assembled structure can vary substantially for many different reasons. For

example, the acidity of the molecule is an important parameter as a low pKa value

is oen associated with a structural transition, which we associate to a change in

binding from dominating molecule–molecule to a balanced molecule–molecule

and molecule–surface interaction.1

1 C. Paris, A. Floris, S. Aeschlimann, M. Kittelmann, F. Kling, R. Bechstein, L. Kantorovich,

and A. K¨uhnle, Increasing the Templating Effect on a Bulk Insulator Surface: From

a Kinetically Trapped to a Thermodynamically More Stable Structure, J. Phys. Chem. C,

2016, 120, 17546.

2 Chunyan Guo, Yu Wang, Markus Kittelmann, Lev Kantorovitch, Angelika K¨uhnle and

Andrea Floris, Mechanisms of covalent assembly on a bulk insulating surface, J. Phys.

Chem. C, 2017, 121, 10053.

3 A. Richter, V. Haapasilta, C. Venturini, R. Bechstein, A. Gourdon, A. S. Foster and A.

K¨uhnle, Diacetylene polymerization on a bulk insulator surface, Phys. Chem. Chem. Phys.,

2017, 19, 15172.

4 Julia L. Neff, Markus Kittelmann, Ralf Bechstein, and Angelika K¨uhnle, Decisive Inuence

of Substitution Positions in Molecular Self-Assembly, Phys. Chem. Chem. Phys., 2014, 16,

15437.

(606:[606]606) Steven De Feyter asked: Have you tried deposition of the

molecules at the water/calcite interface? If so, what is the effect? Did you observe

any adsorption?

Angelika K¨uhnle answered: Thanks for this very relevant question. Yes, we

investigated many of the molecules that formed beautiful structures on calcite

(10.4) kept in UHV also at the calcite–water interface. Actually, it was Martin

Nalbach sitting here in the audience who tried a lot of them. However, for most of

these small benzoic acid derivatives, Martin showed that none of them could form

a nice self-assembled structure at the calcite–water interface. This nding again

underlines the impact of the solvent on molecular self-assembly. The poster

presented by Martin showing the assembly of benzopurpurine (BPP) at the

calcite–water interface illustrates the complexity of the situation in liquids.

Ongoing molecular dynamics simulations carried out by Paolo Raiteri suggest

that BPP, which forms a self-assembled structure, does not anchor to the calcite

surface directly. So, you cannot understand the self-assembly process at the solid–

liquid interface without considering the impact of the solvent and, in particular,

the interfacial solvation structure. This makes the situation rather complex and

hampers a direct transfer of knowledge gain in UHV to the situation in liquids.

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We clearly lack understanding and predictive power when it comes to solid–liquid

interfaces.

(607:[607]607) Giovanni Costantini queried: Have you studied the effect of

molecular coverage on the width of the molecular chains?

Do the molecular chains thicken before they are “pushed together” by

increasing coverage? I believe this could give you information on the interplay

between repulsive and attractive interactions regulating the self-assembly of these

systems.

Angelika K¨uhnle answered: Yes, we have studied the coverage dependence.

You nd that the molecular rows move closer as a function of coverage as the

average stripe-to-stripe distance is a direct function of the coverage. The molecular

double rows of 3-HBA do not get wider because the structure is dened by the

internal structure. We do see, however, that the rows are pushed together.

In this context, the result from 3-EBA is interesting, because this molecule

shows islands with (1x1) internal structure. As mentioned in my talk, we want to

use this molecule to do exactly what you propose, namely get insights into the

balance of short-range attraction and long-range repulsion by analyzing the

island length and width distribution.

1 J. L. Neff, H. S¨ongen, R. Bechstein, P. Maass, and A. K¨uhnle, Long-Range Order Induced by

Intrinsic Repulsion on an Insulating Substrate, J. Phys. Chem. C, 2015, 119, 24927.

(610:[610]610) Trolle Linderoth commented: Your data demonstrate that there

is repulsion between the 1D molecular chains on the calcite surface. But could you

be more specic about what is being repelled? In Fig. 2 (DOI: 10.1039/

C7FD00089H), you show a series of AFM images which demonstrate that the

chains do not move on the surface but rather there is a continuous decay/growth

process with new nucleation events occurring where presumably the repulsive

interactions involve the individual molecular species during this process and

create, for instance, an enhanced nucleation possibility at some optimum

distance from another chain. Could you clarify if this is the way we should think

about the underlying dynamics?

Angelika K¨uhnle responded: We cannot follow the nucleation event in our

AFM images, however, I think it is important to note that we did an experiment

where we deposited additional molecules to a sample where stripes were already

present (with a stripe-to-stripe distance distribution associated with the initial

coverage). In such a case, the stripes have to re-assemble to adjust to the increased

coverage aer the second deposition. Indeed, aer the second deposition, the

stripes have adopted their stripe-to-stripe distance distribution from the

increased coverage. This experiment indicates that the rows can move. We do not,

however, think that the rows move as a whole. From the AFM movie, our

understanding is that the rows form by attachment and detachment of diffusing

monomers (or perhaps clusters consisting of a certain critical monomer number).

Thus, when considering the existence of a row at a given position, the electrostatic

potential built up by this row will dictate the nucleation of a new row in the

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neighborhood. We used this picture for our simplied Monte Carlo simulations

explained in the Supporting Information of the publication by Julia Neff.1

1 J. L. Neff, H. S¨ongen, R. Bechstein, P. Maass, and A. K¨uhnle, Long-Range Order Induced by

Intrinsic Repulsion on an Insulating Substrate, J. Phys. Chem. C, 2015, 119, 24927.

(611:[611]611) Rasmita Raval asked: Question 1, what is understood about the

impact that molecules have on calcite surfaces? In biomineralisation, calcite

surfaces can be restructured substantially by adsorbing molecules.

Question 2, do Monte Carlo simulations give an indication of the strength of

the interactions that could yield the self-assembly stripes? Does one have to

assume strong electrostatic repulsion? Presumably, weaker repulsive interactions

would yield the same behaviour?

Angelika K¨uhnle answered: Regarding your rst question, many of these

benzoic acid derivatives are known to restructure the surface when added to the

solid–liquid interface. In UHV, however, we have not observed massive restructuring

of the surface upon adsorption of these molecules.

Regarding your second question, correct, the electrostatic interaction needed

can be explained by dipole–dipole repulsion of dipoles perpendicular to the

surface that are reasonable for adsorption-induced dipoles. Our MC simulations

yield a value for On\*p of 30 Debye, which can be achieved, e.g., with molecules

forming a dipole moment of 5 Debye and a critical stripe length of 7 nm.

(612:[612]612) David Amabilino said: Beautiful work, thanks for the presentation.

Regarding the last point, you said you nd it hard to think of something

other than electrostatics, but in one way that’s surprising – there’s a whole range

of length scales between your strips, but on the other hand, charges are very

localised on your surface. This reminds me of a case on much larger molecules,1

they saw stripes, direction of growth of an aggregate, and they saw a very strict

dependence on concentration. There, their explanation of that was a dewetting

phenomenon from the surface, which in a way could come from nucleation and

directional growth. Could that phenomenon (bearing in mind the relatively

hydrophobic thing on a quite polar surface you’ve got here) explain your results?

1 R. van Hameren, P. Sch¨on, A.M. van Buul, J. Hoogboom, S.V. Lazarenko, J.W. Gerritsen, H.

Engelkamp, P.C. M. Christianen, H.A. Heus, J.C. Maan, T. Rasing, S. Speller, A.E. Rowan,

J.A. A. W. Elemans and R. J. M. Nolte, Science, 2006, 314, 1433-1436.

Angelika K¨uhnle replied: Thanks for this suggestion. I want to stress that we

take care to exclude correlated growth effects. The explanation I presented is

based on thermodynamics, not kinetic effects. We verify this for example by

deposition of further molecules on a sample were there are already stripes

present. When you add more molecules, the stripe distance distribution is

changed to the new coverage, demonstrating sufficient mobility for the stripes to

adapt to the new situation. Therefore, the observed stripe-to-stripe distance

distribution is most likely not an effect that is caused by kinetic effects during

growth.

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(613:[613]613) David Amabilino continued: The formula you present explains

the phenomenon, I agree, perhaps you might put a number of factors in there;

given you’re using a surface with very localised charges, can you justify that

something on top of that very charge localised surface (that is insulating) can

mediate an electrostatic interaction over such a long range?

Angelika K¨uhnle replied: I do not want to claim that the ordering we observe

must originate from electrostatic repulsion of dipoles. The point I want to make

is, however, that electrostatic repulsion can be a possible explanation. In the

beginning, I thought that electrostatic repulsion would not be sufficient to explain

repulsion over a 16 nm distance. But a simple back-of-the-envelope estimate1

shows that the dipole moment needed to explain the ordering seen for 3-HBA can

be explained by dipole moments with reasonable dipole moment strength. So,

this explanation appears most appealing to me.

At present, I cannot think of another equally obvious origin. But they might be

there.

1 J. L. Neff, H. S¨ongen, R. Bechstein, P. Maass, and A. K¨uhnle, Long-Range Order Induced by

Intrinsic Repulsion on an Insulating Substrate, J. Phys. Chem. C, 2015, 119, 24927.

(614:[614]614) Robert Jones opened a general discussion of the paper by Karl-

Heinz Ernst: The terphenylcorannulene (TPC) shown in Fig.1 b and c (DOI:

10.1039/C7FD00109F), has three outer edge benzo rings, as well as six C6 rings at

the bottom of the bowl. For isolated adsorbed molecules, where there are no

interactions between TCP molecules, STM showed that the cup shaped molecule

adsorbs with the middle of the outer edge benzo ring parallel to the surface. i.e.

the cup adsorbs on the middle of its edge and stands up on the surface. You say

that a constraint of the central terphenyl C6 ring is required in an AMBER force

eld calculation to achieve the experimentally observed tilting of the molecule.

Could you comment a little more on why the bonding of the isolated molecule

occurs via this middle outer edge benzo group, rather than via one of the inner C6

rings?

Karl-Heinz Ernst responded: I can only speculate. The middle ring of the terphenyl

group being parallel is strongly suggested by the STM contrast. The

AMBER calculations were performed to see if the PI-PI interaction, as suggested

by the geometric alignment in the dimer, is indeed also the result of the calculation.

But with AMBER we got a little bit “less” tilted conguration, not

compatible with the observation. Hence the constraint (Surface–molecule interaction

is oen not well described in force eld calculations, but in few cases works

quite well).

Now why the middle ring? All I can say is that it might be due to minimalization

of the Pauli repulsion. There must be optimum binding of the aromatic

molecule and the electrons of a metal pushing away from the adsorbate spot.

Certainly a matter of polarizability.

(615:[615]615) Marco Sacchi commented: Wonderful results. In order to

understand the relative importance of vdW interactions and dipole–dipole

interactions, what is the intermolecular distance in the calculations? I agree that

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buckybowls are fairly big molecules, therefore I suppose that the unit cell has

been chosen to be as large as possible. Also, is there strong charge transfer from

the surface to the molecule?

Karl-Heinz Ernst responded: See Fig. 1. It was a 16 by 20 Angstrom cell.

No, there is no charge transfer (judged by the density of states calculation),

only rearrangement of the charge due to Pauli repulsion.

(616:[616]616) Brandon Hirsch asked: How do these molecules begin to stack

into the 3D structure?

Karl-Heinz Ernst answered: Some of these bowls (corannulene and pentamethylcorannulene)

were found to show surface-assisted bowl-in-bowl stacking.

This has not been observed as 3D crystals. See ref. 1.

1 Bauert, T., Baldridge, K. K., Siegel, J. S., and Ernst, K.-H., Surface-assisted bowl-in-bowl

stacking of nonplanar aromatic hydrocarbons, Chemical Communications, 2011, 47,

7995–7997.

(617:[617]617) Giovanni Costantini said: You were saying that if you increase

the coverage, at some point the molecules are forced together. Is it possible that

this is happening together with a rearrangement of the molecule? Maybe a situation

where the molecules are slightly less (or more) parallel to the surface,

thereby effectively reducing the Pauli repulsion induced dipole?

Karl-Heinz Ernst responded: Actually, the pi–pi interaction is already stronger

than the dipole–dipole interaction, because we see them joining together at low

coverage. Within the possibilities of STM, we did not see a reorientation. From

calculations with helicons, we also see, that pi–pi interaction is stronger than

Fig. 1 Representation of the 16 by 20 °A unit cell.

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dipole–dipole repulsion. Interface dipoles induced by Pauli repulsion depend

strongly on polarizability. For metals this is usually large. But the same applies to

depolarization, when two molecules come closer. So I do not see a strong dipole–

dipole repulsion mechanism here.

(618:[618]618) Giovanni Costantini continued: Have your done DFT calculations

for a monolayer? I think it would be extremely interesting to see whether the

closeness of neighbouring molecules, and thus the increased dipole–dipole

repulsion, induces a (potentially slightly) different adsorption conguration that

reduces the Pauli repulsion and thus also the magnitude of the dipole.

Karl-Heinz Ernst answered: No we haven’t. I believe that is a very expensive

calculation, if feasible at all.

Because we see already for small clusters and dimers a very close arrangement

in experiments, dipole–dipole repulsion (of this type of Pauli repulsion induced

interface dipole) does not seem to come into play. Calculations for pentahelicene

show a similar effect for monomers (4.5 Debye). Pentahelicene dimers just show

a push-back effect for the entire dimer (7.5 Debye), as if the two entities would

fuse together.

(619:[619]619) Peter Beton commented: I was also going to ask about whether

some of the effects we heard in the previous talk were relevant to this ordering in

view of the induced dipole. You mentioned in the introduction that these materials

are potentially relevant for organic transistors or photovoltaics. Have they

actually been used in that form? Is the material available in quantities that might

allow some kind of systematic study? Also, what might be the advantages?

Replacing PCBM?

Karl-Heinz Ernst replied: The better solubility should make them more

interesting than PCBM. However, the matching of electronic levels of acceptor

and donor in photovoltaics has not been successful so far. We tested corannulene

versus pentacene in an organic transistor set-up. Pentacene was much better.

Corannulene might become available in sufficient quantities, because an

upscaled synthesis scheme has been presented recently.

(620:[620]620) Robert Jones remarked: Figure 4(a) (DOI: 10.1039/C7FD00109F)

shows a beautiful rectangular array of over 100 TPC molecules surrounded by

a large area of disordered molecules. It is striking that within the image, there

appears to be no other highly ordered arrays of TPC molecules but with smaller

numbers of molecules. One might have expected to see a distribution of sizes for

the ordered structures. Could you comment on why there is such a large difference

between random structure and one large, very highly ordered structure?

Karl-Heinz Ernst replied: This can be explained by a low rate of nucleation. The

probability of having a nucleus that allows further growth was, at that coverage,

low.

In the area shown, only one nucleus formed at a certain temperature. (Note

that is was a cooling experiment, so the temperature was falling permanently.)

With temperature falling further, the 2D gas then solidied into a disordered

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"glass". Due to limited mobility, at that temperature, no further nucleation and

growth was possible. We have seen this oen for other systems at low or intermediate

coverages.

(621:[621]621) Rasmita Raval opened a general discussion of the paper by Neil

Robinson: Thank you for your nice talk. You talk about T1 timescales. Did you

consider T2 timescales? Are they not important in this system?

Neil Robinson responded: T1 and T2 are sensitive to different frequencies of

molecular motion. In particular, T1 is sensitive to motions occurring at the Larmor

frequency (u0 f magnetic eld strength) and above, T:1

1 ¼ J(u0) + 4J(2u0),

while T2 is sensitive to slower motions, such as those occurring at zero frequency,

T:1

2 ¼ 3J(0) + 5J(u0) + 2J(2u0). In the present work we have chosen to observe T1

relaxation at high magnetic eld in order to access fast molecular dynamics,

which may be associated with molecular tumbling motions. We have not probed

T2 relaxation in the current experiments. T2 is an interesting parameter in terms

of probing the dynamics of molecules at catalyst surfaces; for example, the

sensitivity of T2 relaxation to slow molecular motion gives measurements access

to the translational motions of molecules across the pore surface. In particular, T2

measurements may be combined with T1 relaxation analysis – either through

separate experiments on the same system, or through the use of two-dimensional

relaxation correlation experiments – in order to generate a T1/T2 ratio. It has

recently been shown that such a metric provides a quantitative measure of surface

affinity.1 However, the measurement of T2 relaxation times associated with

adsorbed species is far from trivial at high magnetic eld. A particular problem is

the existence of internal magnetic eld gradients, which are generated by

differences in magnetic susceptibility across the solid–liquid interface. Diffusion

through these internal gradients leads to enhanced rates of T2 relaxation.2 As

a result, it is typical that only an effective T2 may be measured for liquid-saturated

porous media investigated at high eld. In turn, T1/T2 ratios are typically established

at low or intermediate magnetic eld strengths, rather than the high eld

used in this particular work. Although techniques to correct for the presence of

these internal gradients exist, such methods are highly non-trivial.3 It would be

very interesting to perform low eld T1/T2 measurements on the systems I have

described in order to assess the differences in surface affinity upon hydroxyl

passivation.

1 D’Agostino, C., Mitchell, J., Mantle, M. D. and Gladden, L. F., Interpretation of NMR

Relaxation as a Tool for Characterising the Adsorption Strength of Liquids inside Porous

Materials, Chem. Eur. J., 2014, 20, 13009–13015.

2 Mitchell, J., Chandrasekera, T. C., Johns, M. L., Gladden, L. F. and Fordham,

E. J., Nuclear magnetic resonance relaxation and diffusion in the presence of

internal gradients: The effect of magnetic eld strength, Phys. Rev. E, 2010, 81,

026101.

3 Mitchell, J. and Chandrasekera, T. C., Understanding generalized inversions of nuclear

magnetic resonance transverse relaxation time in porous media, The Journal of Chemical

Physics, 2014, 141, 224201.

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(623:[623]623) David Amabilino commented: Thanks for the talk. You’ve

shown nicely how this works for porous materials. A big problem, I guess you’ve

picked up over the last couple of days, is that a lot of us are working with

monolayers. Looking at those spectroscopically, e.g. with XPS, is very challenging.

I know people who have looked at monolayers with, e.g. EPR. How could your

techniques help study adsorption in the kind of system that’s more a at surface

than a porous one?

Neil Robinson replied: Although the general theory of surface sensitive relaxation

in saturated porous media relies on the fast exchange of molecules between

bulk and adsorbed states, there is nothing I can see, theoretically, to prevent the

investigation of monolayer coverage over at surfaces. In this case, the observed

relaxation would move from the biphasic fast exchange description of Brownstein

and Tarr (as described in our paper, DOI: 10.1039/C7FD00098G), to the observation

of only surface relaxation. A similar condition would be found in liquidsaturated

microporous media, where very small pore diameters mean only

surface-bound species are present. That being said, NMR is an inherently

insensitive spectroscopic technique. The limiting factor in performing NMR

measurements is oen gaining adequate signal (or more correctly, signal-to-noise

ratio, SNR) during the experimental time available. SNR is a complex function of

NMR-active nuclear spin density within the sample, magnetic eld strength,

gyromagnetic ratio of the spins under observation, and the number of repeat

scans used throughout a given experiment. The high porosity of uid-saturated

meso- and microporous media is necessary to provide adequate SNR in systems

where we have an interest in the relaxation of adsorbed species, and the high

surface-to-volume ratios associated with such structures, combined with the

enhanced rates of relaxation at the pore surface, ensures the surface sensitivity of

such measurements. The investigation of monolayer and sub-monolayer coverages

on at surfaces may therefore prove difficult, simply due to the lack of

nuclear spins present across the surface of interest. The polarization achieved by

a given magnetic eld strength may, however, be dramatically enhanced beyond

thermodynamically accessible states by so-called hyperpolarization techniques,

leading to greater SNR.1 The proton (1H) hyperpolarization of hydrocarbon

species would typically involve synthesis of the molecule of interest through

a heterogeneous hydrogenation reaction, involving the reaction of a gaseous feed

with parahydrogen using an immobilized paramagnetic catalyst.2 Furthermore,

the SNR of 13C NMR experiments – the relaxation of which has been shown to be

useful in determining adsorbate orientation3 – may be enhanced by transferring

polarization to the carbon nucleus from neighbouring protons.4–5

One condition I would like to stress is that the surfaces investigated should not

be ferromagnetic or contain signicant quantities of paramagnetic ions, as

interactions with paramagnetic species will have dramatic effects on the relaxation

characteristics of molecules under investigation.6–7

1 Barskiy, D. A. et al., NMR Hyperpolarization Techniques of Gases, Chem. Eur. J., 2017, 23,

725–751.

2 Bouchard, L.-S. et al., Para-Hydrogen-Enhanced Hyperpolarized Gas-Phase Magnetic

Resonance Imaging, Angewandte Chemie International Edition, 2007, 46, 4064–4068.

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3 Vecino, P. A. et al., Determining adsorbate conguration on alumina surfaces with 13C

nuclear magnetic resonance relaxation time analysis, Phys. Chem. Chem. Phys., 2015, 17,

20830–20839.

4 Morris, G. A. and Freeman, R., Enhancement of nuclear magnetic resonance signals by

polarization transfer, J. Am. Chem. Soc., 1979, 101, 760–762.

5 Doddrell, D. M., Pegg, D. T. and Bendall, M. R., Distortionless enhancement of NMR

signals by polarization transfer, Journal of Magnetic Resonance, 1982, 48, 323–327.

6 McDonald, P. J., Korb, J.-P., Mitchell, J. and Monteilhet, L., Surface relaxation and

chemical exchange in hydrating cement pastes: A two-dimensional NMR relaxation study,

Phys. Rev. E, 2005, 72, 011409.

7 D’Agostino, C., Br¨auer, P., Charoen-Rajapark, P., Crouch, M. D. and Gladden, L. F., Effect

of paramagnetic species on T1, T2 and T1/T2 NMR relaxation times of liquids in porous

CuSO4/Al2O3, RSC Adv., 2017, 7, 36163–36167.

(624:[624]624) David Amabilino remarked: In EPR, you cut the square surface

into lots of pieces and put one on top of the other and then put the stack into the

spectrometer. I wonder if that could be used with a kind of NMR spectroscopy,

perhaps using T2, but for sure it is a challenge, but could be useful.

Neil Robinson answered: Stacking surfaces of interest and trapping molecules

between them sounds like a porous structure is being generated. If this is the

case, then relaxation experiments may well be applied in order to probe the

dynamics of adsorbate molecules in such a system. The issue of low SNR may

again arise due to the small number of spins present within each molecular

monolayer; however, this limitation may be circumvented to some extent by using

many layers stacked upon one another, leading to a reasonable number of spins

being present within the sample as a whole. I would be more tempted to use T1

rather than T2, however, as the T2 relaxation associated with such a system may

well be too rapid to measure.

(626:[626]626) Sebastian Schwaminger said: You now work with a completely

saturated system, but usually do mass transport effects also affect the tumbling of

molecules in your measurements? Concerning your system, do pore sizes have

a stronger effect on the molecular movement than the surface groups?

Neil Robinson replied: Interestingly, it has been observed in previous work

(using unpassivated oxides) that changes to T1 relaxation and the molecular selfdiffusion

coefficient are not independent upon imbibition of a liquid throughout

a mesoporous network.1 While relaxation in the bulk liquid does indeed contain

an intermolecular contribution associated with molecular self-diffusion, this

contribution is not necessarily present within saturated mesoporous solids. Here

we typically observed only relaxation associated with the adsorbed surface layer,

diffusion through which will be slow.

To a large extent, it is not the pore size which affects the effective self-diffusion

coefficient of liquids through a porous system. Rather, such dynamics are far

more susceptible to the interconnectivity of the porous network – which may be

somewhat dependent on the pore sizes present – dened by a dimensionless

metric known as the tortuosity. Non-negligible adsorption interactions occurring

between functional molecules and hydroxylated pore surfaces have been shown to

signicantly alter the observed self-diffusivities of such molecules, relative to the

tortuosity of the porous structure,1 and we are currently performing pulsed-eld-

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gradient NMR diffusion experiments on the materials discussed in order to

quantify the inuence of passivating alkyl groups on such interactions.

1 D’Agostino, C., Mitchell, J., Gladden, L. F. and Mantle, M. D., Hydrogen Bonding Network

Disruption in Mesoporous Catalyst Supports Probed by PFG-NMR Diffusometry and NMR

Relaxometry, J. Phys. Chem. C, 2012, 116, 8975–8982.

(627:[627]627) Robert Jones commented: The DRIFTS spectra in Fig. 1 (DOI:

10.1039/C7FD00098G) clearly show that the OH stretch reduces in intensity when

the surfaces have been passivated. However, as the scans are relative changes in

absorbance, it is not clear whether this is a partial or a complete removal of the

peak. Could you comment on whether the OH signals were completely extinguished,

implying complete passivation of the surface, or whether some OH

signal remained aer passivation, implying that there was still some concentration

of surface OH within the pores.

Neil Robinson replied: Making decisive conclusions concerning whether

complete passivation was achieved is unfortunately not a trivial task using

DRIFTS, even from examination of the individual spectra before and aer

passivation, due to the complex nature of the baseline. I include, as an example,

the raw absorption data gathered from our anatase titania samples in the

attached Fig. 2. Indeed, quantitative analysis using DRIFTS is notoriously difficult,

requiring reproducibly-milled and packed particles below 1 mm in diameter,

high sample dilution, and conversion of the acquired absorbance data using the

Kulbeka-Mulk equation. In the present work, samples were ground by hand using

a pestle and mortar, and without detailed analysis of the resulting particle size

distribution. It is therefore ill-advised to attempt a quantitative analysis of our

spectra, which we present only as a qualitative conrmation of successful

hydroxyl passivation. It is worth noting that the currently established theory of

Fig. 2 Diffuse reflectance infrared spectra of anatase titania pre- and post-passivation.

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surface relaxation predicts a subtle dependence on surface hydroxyl coverage. In

particular, the inuence of surface hydroxyl density on our observed relaxation is

likely to be magnetic eld dependent. At high magnetic eld strength, as used in

the present work, T1 relaxation is deemed to be dominated by fast motions such

as molecular tumbling. The prefactors in eqn (1) from our paper (DOI: 10.1039/

C7FD00098G) are therefore related to the intramolecular dipole–dipole

coupling of protons in the liquid phase (although it should be noted that at no

point have we used this equation analytically). At low magnetic eld strength,

however, relaxation is sensitive to slower motions. In the case of liquid-saturated

mesoporous solids, the two-dimensional translation of adsorbed molecules

across hydroxylated pore surfaces becomes a dominant source of relaxation. A

general spectral density expression for relaxation rates under such conditions has

been developed by Korb and co-workers (see, for example, ref. 1) and applied to

catalyst surfaces by Mitchell et al..2 Here, the spectral density prefactor is directly

dependent on the number of relaxation sinks (adsorption sites) at the surface,

which will be related to the number of surface hydroxyl groups (although not

necessarily directly proportional, due to the possibility of polydentate adsorption

sites involving rotationally mobile surface hydroxyls). This being said, it was not

the purpose of the present work to explore relaxation as a continuous function of

hydroxyl coverage. Such work would best be performed on a single oxide rather

than across a range of different materials. Although beyond the scope of the

current work, a low eld investigation of the inuence of surface hydroxyl density

on methanol relaxation would be enlightening.

1 S. Godefroy, J.-P. Korb, M. Fleury and R. G. Bryant, Phys. Rev. E, 2001, 64, 021605.

2 J. Mitchell, L. M. Broche, T. C. Chandrasekera, D. J. Lurie and L. F. Gladden, J. Phys. Chem.

C, 2013, 117, 17699–17706.

(629:[629]629) Karl-Heinz Ernst opened a general discussion of the topics

discussed during the session: Coming back to calcite. I call myself a stereochemist

and I wonder how exactly modication of surface morphology is achieved

by modiers, like tartaric acid. Is it just the footprint of the molecules or rather

the free energy situation at step edges? And wouldn’t it be very interesting to study

this kind of molecules?

Angelika K¨uhnle responded: Many people study the impact of organic modi-

ers (amino acids, peptides, polymers and others) on the surface morphology of

calcite. You can nd a wide range of results depending on the specic molecule

used, e.g., polar step edges that get stabilized1–2 or surface reconstructions with

etch pits that greatly differ from the thermodynamically most stable rhombohedral

shape.

So far, however, we largely lack predictive power. We have not studied tartaric

acid yet. However, my guess would be that we do not see a change in the calcite–

water interface when adding tartaric acid. But – as I said – we need to test as we do

not have predictive power so far.

1 M. Nalbach, S. Klassen, R. Bechstein, and A. K¨uhnle, Molecular Self-

Assembly Versus Surface Restructuring During Calcite Dissolution, Langmuir,

2016, 32, 9975.

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2 R. Momper, M. Nalbach, K. Lichtenstein, R. Bechstein, and A. K¨uhnle, Stabilization of

polar step edges on calcite (10.4) by the adsorption of Congo Red, Langmuir, 2015, 31,

7283.

(631:[631]631) Angelika K¨uhnle commented: We have studied a large range of

organic molecules at the calcite–water interface. A major nding is that results

obtained from UHV investigations cannot be directly transferred to the solid–

liquid interface. The presence of the water molecule severely alters the situation.

We have to consider effects like molecule deprotonation depending on the

solution pH, complexation with calcium ions that inevitably exist in solution

when immersing a calcite crystal. Also, the details of the hydration structure at the

surface is decisive. Again, the example of benzopurpurine shown on Martin

Nalbach’s poster nicely illustrates this: at the calcite–water interface, the molecules

do not even anchor to the calcite directly but appear to “oat” on top of the

second hydration layer as indicated by ongoing molecular dynamics simulations.

Moreover, at the calcite–water interface, we oen observe a massive restructuring

of the surface by the presence of additives (e.g. in ref. 1). Many of these effects are

poorly understood and we are currently not in the status to predict what to expect

when adding a given molecule to the calcite-water interface.

1 Nalbach, S. Klassen, R. Bechstein, and A. K¨uhnle, Molecular Self-Assembly Versus Surface

Restructuring During Calcite Dissolution, Langmuir, 2016, 32, 9975.

(632:[632]632) Karl-Heinz Ernst noted: Tartaric acid is a strong calcite modi-

er, like other dicarboxylic acids such as maleic acid, aspartic acid or gamma

carboxyl glutamic acid, as has been shown in the work of Stephen Mann et al..

(634:[634]634) Karl-Heinz Ernst remarked: We and others have shown that the

metal-UHV is a very nice model system for macroscopic rearrangements of the

system. Amino acids on Cu, for example, induce upon annealing, strong stereochemical

effect by restructuring and stabilizing only certain facets. Similar effects

have been observed in the biomineralization of calcite and calcium oxalate

crystallizing in the environment of tartaric acid with certain peptides.

(635:[635]635) Angelika K¨uhnle said: When discussing the impact of organic

molecules on the calcite morphology, we might also want to differentiate between

work where an existing at (10.4) surface is reconstructed by the presence of

organic molecules and studies in which crystals grow from a supersaturated

calcium carbonate solution in the presence of organic additives. Also for the

latter, a large body of literature exists.

(636:[636]636) Karl-Heinz Ernst contributed: But it is hard to control purity and

avoid crystallization effects due to impurities.

(700:[700]700) Zhi Li opened a general discussion of the paper by Federico

Rosei: I have a question about the substrate effect. You mentioned that the

organometallic chains follow certain directions, therefore, have you evaluated or

what do you expect the impact of the substrate, with different orientation index, to

be on the polymerization efficiency, based on the polymer length?

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Federico Rosei responded: While systematic studies on the effect of the

substrate are not available, various molecules have been studied on different

substrate orientations, such as 1,4-diiodobenzene (dIB), which we studied on

Cu(111), Cu(100) and Cu(110).1 In all cases, polyparaphenylene chains were obtained,

however, as also reported in the present work (DOI: 10.1039/C7FD00099E)

and by Vasseur et al.,2 the orientation and length of the PPP chains on the surface

can strongly affect their properties, such as band gap. The surface is therefore to

be considered as a parameter controlling the reaction, not only due to its catalytic

effect but also in terms of the directions of the surface atoms in driving the

molecular assembly. In this perspective, vicinal surfaces could allow the chains to

grow in only one direction,3 while different geometries (square or hexagonal)

would have more symmetrical outcomes. However, we must stress two points:

rst, the symmetry of the substrate is usually taken as equal to the symmetry of

the formed polymer, in order to make the surface a good template for the polymerization

reaction; second, we showed that the diagonal polymers are exactly

commensurate with the surface (both having single units distant 0.44 nm along

the [1–12] direction). Being commensurate with the surface reduces the

mismatch, which is favourable to obtain longer-range defect-free structures.

1 J. Lipton-Duffin, O. Ivasenko, D. Perepichka and F. Rosei, Small, 2009, 5, 592–597.

2 G. Vasseur, Y. Fagot-Revurat, M. Sicot, B. Kierren, L. Moreau, D. Malterre, L. Cardenas, G.

Galeotti, J. Lipton-Duffin, F. Rosei, M. Di Giovannantonio, G. Contini, P. Le F`evre, F.

Bertran, L. Liang, V. Meunier and D. F. Perepichka, Nat. Commun., 2016, 7, 10235.

3 A. Saywell, J. Schwarz, S. Hecht and L. Grill, Angew. Chem. Int. Ed., 2012, 51, 5096–5100.

(701:[701]701) Zhi Li continued: If you don’t use Cu or Ag substrates, but use

a different one (e.g. h-BN, graphite) for the polymerization reaction. Do you expect

that the reaction can still proceed as well as on Cu or Ag substrates by adding

external Cu or Ag.

Federico Rosei responded: Nudge-Elastic Band calculation of the Ullmann

reaction from single molecules to organometallic dimers or networks suggests

that the reaction can proceed both via incorporating the surface adatoms or with

the molecules “extracting”atoms from the substrate.1–2 Adding Cu or Ag atoms to

a less reactive surface (such as HOPG) could therefore lead to dehalogenation, as

it was demonstrated by Zhou et al.,3 who reported the formation of various

organometallic species on Au(111) by depositing extrinsic Ni and Ag atoms. The

reaction, however, would be controlled and limited by the number of available

catalytic adatoms, which would also remain on the surface as unwanted side

products of the reaction aer polymers are formed. In addition, depending on the

interaction between the surface and the extrinsic metal atoms, the polymerization

reaction could also be hindered. The size, arrangement and order of these added

catalytic centers/clusters to the surface could also play a key factor in limiting the

order of the formed polymer. Another possible way would be to avoid the use of

metallic catalysts in the reaction, for example by directly obtaining the polymerization

on bulk insulators, via thermal- or UV-induced dehalogenation. An

example has been shown by Kittelmann et al.,4 who reported the formation of

polymers using an Ullmann-like reaction on CaCO3. This path could, however,

introduce different challenges, for example a lower adsorption energy or sticking

coefficients of the molecular layer on the insulating surface compared to metallic

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substrates, or inversely mediating new reaction paths which could lead to the

dissociation of the molecules before they can undergo the desirable reaction.

1 J. Bj¨ork, F. Hanke and S. Stafstr¨om, J. Am. Chem. Soc., 2013, 135, 5768–5775.

2 D. Barton, H.-Y. Gao, P. A. Held, A. Studer, H. Fuchs, N. L. Doltsinis and J. Neugebauer,

Chem. - Eur. J, 2017, 23, 6190–6197.

3 X. Zhou, F. Bebensee, Q. Shen, R. Bebensee, F. Cheng, Y. He, H. Su, W. Chen, G. Q. Xu, F.

Besenbacher, T. R. Linderoth and K. Wu, Mater. Chem. Front., 2017, 1, 119–127.

4 M. Kittelmann, M. Nimmrich, R. Lindner, A. Gourdon and A. K¨uhnle, ACS

Nano, 2013, 7, 5614–5620.

(702:[702]702) Markus Lackinger asked: Could you explain the shis of C 1s

that you observe with Fast-XPS? I would be particularly interested in the origin of

the overall shi that is observed upon conversion from the organometallic to the

covalent state.

Federico Rosei answered: The overall shi is due to the conversion of C–Cu to

C–C bonds. Shown by Di Giovannantonio et al.,1–2 the C 1s core level spectrum of

1,4-dibromobenzene (dBB) on Cu(110) at RT can be deconvoluted into three

different components, one at lower binding energy (BE), assigned to carbon

atoms bound to copper (283.2 eV), and the peaks at the higher BE (283.8 eV and

284.2 eV) attributed to the remaining carbon atoms in the phenyl group. These

peaks originate from the non-equivalent positions of phenyl carbons with respect

to the copper substrate. Aer polymerization, the peak at 283.2 eV disappears,

and two new components at 284.4 eV and 285.1 eV are found. These components

are at higher BE compared to their organometallic counterparts, as expected and

calculated by Bj¨ork et al..3 Each spectrum (a single line of the Fast-XPS map)

presents the combination of these ve peaks depending on the progress of the

reaction. The observed shi of the Fast-XPS is therefore due to the transition from

the organometallic to polymer. The shape of the curve is related to the kinetic of

the reaction, which for dBB on Cu(110) follows a nucleation-and-growth mechanism.

4 While the same overall shi is found for all the studied molecules, it can

be seen that the shape of this transition differs depending on the halogen (in

particular for iodine-containing molecules), which therefore affects the reaction

kinetics.

1 M. Di Giovannantonio, M. El Garah, J. Lipton-Duffin, V. Meunier, L. Cardenas,

Y. Fagot Revurat, A. Cossaro, A. Verdini, D. F. Perepichka, F. Rosei and G.

Contini, ACS Nano, 2013, 7, 8190–8198.

2 M. Di Giovannantonio, M. El Garah, J. Lipton-Duffin, V. Meunier, L. Cardenas,

Y. Fagot-Revurat, A. Cossaro, A. Verdini, D. F. Perepichka, F. Rosei and G.

Contini, ACS Nano, 2014, 8, 1969–1971.

3 J. Bj¨ork, F. Hanke and S. Stafstr¨om, J. Am. Chem. Soc., 2013, 135, 5768–5775.

4 M. Di Giovannantonio, M. Tomellini, J. Lipton-Duffin, G. Galeotti, M.

Ebrahimi, A. Cossaro, A. Verdini, N. Kharche, V. Meunier, G. Vasseur, Y. Fagot-

Revurat, D. F. Perepichka, F. Rosei and G. Contini, J. Am. Chem. Soc., 2016, 138,

16696–16702.

(704:[704]704) Jonathan Davidson commented: A recent area of research

interest has been using halogen bonding to create supramolecular assemblies. An

example of a molecule used would be 1,4-Diiodotetrauorobenzene. Ullmann

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coupling presents a possible unwanted side reaction in studies of halogen

bonding assemblies on metal surfaces. Have you performed or are you aware of

any work studying similar uorinated halobenzenes on coinage metals?

Federico Rosei responded: The use of halogen bonding as a driving force to

grow and stabilize supramolecular networks is a vivid eld of research, which

allows the formation of both 2D and 3D self-assembled crystals.1 The halo

terminal groups could, however, be subjected to various reactions, such as

nucleophilic substitutions, elimination-addition and Grignard reactions. The

dehalogenation which drives the Ullmann reaction makes it undesirable for

forming supramolecular assemblies. The dehalogenation step of the Ullmann

reaction is dependent on both the substrate/metallic species and halogen, while

only some of these combinations yield room temperature dehalogenation. In the

present work, we observe that Cl–C bonds are mostly intact at RT on Cu, while I–C

and Br–C are readily dissociated. Regarding the case of uorinated halobenzenes

on transition metals, Blake et al.2 studied the interaction of 1-uoro-4-

bromobenzene (FBB) with Cu(111), and found out that C–Br dissociates at RT,

while the C–F bonds remain intact. NEXAFS analysis also showed that the uorophenyls

were tilted from the surface, conrming that the reactivity of uorinated

halobenzenes on copper is lower than halobenzenes with other halogens. A

conscious choice of the involved halogens and metal substrates could therefore

prevent such unfavourable side reactions.

1 L. C. Gilday, S. W. Robinson, T. A. Barendt, M. J. Langton, B. R. Mullaney and

P. D. Beer, Chem. Rev., 2015, 115, 7118–7195.

2 M. M. Blake, S. U. Nanayakkara, S. A. Claridge, L. C. Fern´andez-Torres, E. C.

H. Sykes and P. S. Weiss, J. Phys. Chem. A, 2009, 113, 13167–13172.

(705:[705]705) Alex Saywell queried: With regards to the “Fast XPS” data that

you present; what is the temporal resolution that you are able to obtain? In your

opinion, what is the limiting factor for time-resolved XPS and do you see scope for

developing this as a way to access information on reaction kinetics for various onsurface

systems?

Federico Rosei responded: The reported Fast-XPS spectra were achieved at the

ALOISA beamline on the Elettra synchrotron, in the snapshot mode with a 2D

delay-line detector. The data were collected with a rate of one spectrum per one

second, with a photon ux of 1012 ph s\_1 0.02%BW\_1. In this system, the limiting

factor to achieve a statistically good signal is given by the small aperture angle (2\_

FWHM) of the electron analyzer. Increasing the size and the luminosity of the

analyzer would easily allow the acquisition rate of 10 Hz. Faster rates, however,

require a ux increase, with the drawback of radiation damage of the molecules,

which becomes a problem at 1013 ph s\_1. From the technical point of view, the 2D

delay-line detector is currently limited by the deadtime of 10 msec for emptying

its buffer memory, whereas the electronics themselves (reading and conversion)

would allow rates in the kHz range. Fast-XPS could therefore be applied to study

on-surface reactions of different molecules, for example NH3 dissociation on Si1

and hydrogenation of graphene on Ir(111)2. The physical limits of this technique

allows us to study the reactions which take place in the order of 10–100 msec,

therefore strongly reducing the range of applications. Faster reaction kinetics

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would require a different experimental approach, e.g. pump-and-probe

techniques.

1M. Satta, R. Flammini, A. Goldoni, A. Baraldi, S. Lizzit and R. Larciprete, Phys.

Rev. Lett., 2012, 109, 036102.

2 R. Balog, M. Andersen, B. Jørgensen, Z. Sljivancanin, B. Hammer, A. Baraldi, R. Larciprete,

P. Hofmann, L. Hornekær and S. Lizzit, ACS Nano, 2013, 7, 3823–3832.

(706:[706]706) Markus Lackinger said: Relatively swi acquisition of XP spectra

relies on the high radiation intensities available at synchrotron facilities. How can

you exclude effects of radiation damage in such a experimental setting? Do you

have to take special precautions such as, e.g., constantly moving the sample

during spectra acquisition?

Federico Rosei replied: At the ALOISA beamline a photon ux of 1012 ph s\_1

0.02%BW\_1 was used to perform the experiments, while keeping the sample at

a grazing angle of 4\_, which further spreads the beam over an illuminated area of

3 \_ 0.1 mm2. Such ux density is not extremely damaging for our molecules and

we could therefore analyze our samples without the need to constantly move the

sample during acquisition. For every molecule, however, damage tests were performed,

by repeating and comparing the same C 1s scan aer long expositions,

without any indication of beam damaging in the data. In particular, the beam

could be problematic when studying molecular multilayers or intact halobenzenes,

as it is shown in Di Giovannantonio et al.,1–2 where beam exposition

caused a partial dehalogenation of a multilayer of dBB on Cu(110).

1 M. Di Giovannantonio, M. El Garah, J. Lipton-Duffin, V. Meunier, L. Cardenas,

Y. Fagot-Revurat, A. Cossaro, A. Verdini, D. F. Perepichka, F. Rosei and G.

Contini, ACS Nano, 2013, 7, 8190–8198.

2 M. Di Giovannantonio, M. El Garah, J. Lipton-Duffin, V. Meunier, L. Cardenas,

Y. Fagot-Revurat, A. Cossaro, A. Verdini, D. F. Perepichka, F. Rosei and G.

Contini, ACS Nano, 2014, 8, 1969–1971.

(708:[708]708) Nian Lin asked: Comparing the NEXAFS data of the organometallic

state with the polymerized chains, do you conclude that the phenyl rings

in the organometallic state are more tilted with respect to the substrate? Why?

Federico Rosei answered: The NEXAFS spectrum of a at benzene should

present only one p\* transition.1 Nevertheless, our NEXAFS data shows that the

organometallic systems present two clear p\* transitions, labeled as p\*

1 and p\*

2 in

our work (DOI: 10.1039/C7FD00099E). Geometrical distortion of the ring could

produce a symmetry reduction, which, as a consequence, would give rise to the

p\*

2 components.2 The two resonance components for chemisorbed phenyl rings

(or derivatives), due to geometrical distortion3 or to the formation of new electronic

states,4 have been previously reported in the literature.

1 M. X. Yang, M. Xi, H. Yuan, B. E. Bent, P. Stevens and J. M. White, Surf. Sci.,

1995, 341, 9–18.

2 L. G. M. Pettersson, H. °Agren, Y. Luo and L. Triguero, Surf. Sci., 1998, 408, 1–

20.

3 J. St¨ohr, NEXAFS spectroscopy, Springer-Verlag Berlin Heidelberg, 1992.

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4 M. Weinelt, N. Wassdahl, T. Wiell, O. Karis, J. Hasselstr¨om, P. Bennich, A.

Nilsson, J. St¨ohr and M. Samant, Phys. Rev. B, 1998, 58, 7351–7360.

(710:[710]710) Markus Lackinger commented: In your NEXAFS spectra, the

resonance at higher photon energies was assigned to a C 1s to p\*

2 transition. Yet,

we observe similar features on Ag(111) that however appear to be related to the

organometallic state. How condent are you that this assignment is correct and

do you think acquisition of additional spectra at various incidence angles would

be suitable to clarify this?

Federico Rosei replied: The observed p\*

2 resonance is connected to a nonplanarity

of the phenyl rings, and is observed more prominently for 1-bromo-4-

chlorobenzene (BCB) and 1,4-dichlorobenzene (dCB) at RT, for which we know

that the organometallic chains contain out of plane Ph–Cl segments (from STM

data). This resonance is strongly reduced aer annealing at 150 \_C, with the

curves being virtually indistinguishable from the RT spectra of the other

precursors. Aer annealing at 230 \_C polymers are formed, and the observed

p\*

2 resonance is completely suppressed, suggesting the planarity of the PPP

polymers and the absence of C–metal bond. Therefore, these features seem to be

related to organometallic states, and their reduction upon polymerization for all

the ve studied systems strengthen this point. Acquiring additional spectra at

different incidence angles could not provide additional important information.

(711:[711]711) Steven De Feyter remarked: The fact you observe a halogen

dependent behavior, is this good or bad in view of controlling the synthesis?

Federico Rosei responded: Identication of the parameters which control

a reaction is to be seen as a positive nding. The dependence of dehalogenation

and polymerization temperatures on the halogen presents in the reactants could

be used to lead distinct pathways with various products. For example, as shown by

Lafferentz et al.,1 a hierarchical growth can be obtained by controlling the key

factors in the reaction. This is the scope of reaction kinetics and its benets in

fundamental and applied sciences, as if “playing with the knob” to control the

outcome. However, while opening possibilities, having more parameters in the

ground adds more complexity to the study, to control and a priori predict, which

might be challenging and possibly unfavorable.

1 L. Lafferentz, V. Eberhardt, C. Dri, C. Africh, G. Comelli, F. Esch, S. Hecht

and L. Grill, Nat. Chem., 2012, 4, 215–220.

(713:[713]713) Robert Jones noted: One hypothesis put forward for the inuence

of the halogens on the reaction, is that the halogen adsorbs on top of the Cu

atom that links two phenyl groups together. Can you outline what the experimental

evidence is for this? In particular, as each phenyl group produces one

halogen atom when the –Cu– linkage is formed, only half the available halogen

atoms can be located on the linking Cu, the other half must be elsewhere. Does

this accord with the STM images?

Federico Rosei replied: The hypothesis of halogen atoms adsorbed on top of

the organometallic copper bridges was proposed by Di Giovannantonio et al.1 for

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the adsorption of dBB on Cu(110), based on qualitative matching between the

experimental STM data and the DFT simulated images. Furthermore, the on-top

halogens accounted for the 2-to-1 stoichiometric ratio of Br to Ph in the unit cell

(four Br on-top and four Br adjacent to the four phenyls in the OM chains). Low

temperature STM images, however, show that Br and Cl atoms can also be found

outside the molecular networks, on areas of the surface free of molecules, which

weaken the idea of keeping the on-top halogens to maintain the stoichiometry. A

possible experimental hint of the presence of the on-top halogens could be the

additional components at RT which are present in the Br 3d and Cl 2p spectra,

and are strongly reduced aer polymerization. Core-level shi calculations are

currently ongoing to further explain this point.

(715:[715]715) Yuri Diaz Fernandez opened a general discussion of the paper

by Marco Sacchi: It’s quite interesting that you have found consistent results for

the adsorption congurations for 3 of the corrections and not for 1? Can you

comment in the wider context of the selection of the modelling conditions?

Marco Sacchi answered: Yes, we were also quite surprised by the relative

consistency of the DFT results across the various vdW correction schemes

employed. The TS and TSSCS methods are essentially very similar, with exception

of the screening term, therefore we assume that, to a rst approximation, the

screening corrections are not essentials for capturing the corrugation of the PES

of benzene on Cu(111).

(716:[716]716) Ana Sanz Matias asked: According to the computational results,

the differences in adsorption energy between the adsorption sites are very small.

For instance, in Table 2 (DOI: 10.1039/C7FD00095B) the differences between the

bridge and the HCP and FCC hollow sites are well below 0.05 eV. To which extent

can you draw conclusions (i.e. regarding the adsorption site or the diffusion

mechanisms) from these values?

Marco Sacchi responded: It is very difficult to determine a priori the “error bar”

for DFT calculations, given the fact that the performance and accuracy of a DFT

calculation generally varies according to the specic surface system investigated.

In our experience (see for instance: ref. 1–4), the precision of DFT calculations for

aromatics adsorbed on metal surfaces is surprisingly good for most systems,

therefore we believe that DFT is able to quantify the small energy corrugation of

benzene/Cu(111).

1 M. Sacchi, S. J. Jenkins, H. Hedgeland, A. P. Jardine and B. J. Hinch, The

Journal of Physical Chemistry C, 2011, 115, 16134–16141.

2 B. A. J. Lechner, H. Hedgeland, J. Ellis, W. Allison, M. Sacchi, S. J. Jenkins and B. J. Hinch,

Angew. Chem. Int. Ed., 2013, 52, 5085–5088.

3 B. A. J. Lechner, M. Sacchi, A. P. Jardine, H. Hedgeland, W. Allison, J. Ellis, S. J. Jenkins, P.

C. Dastoor and B. J. Hinch, The Journal of Physical Chemistry Letters, 2013, 4, 1953–1958.

4 H. Hedgeland, M. Sacchi, P. Singh, A. J. McIntosh, A. P. Jardine, G. Alexandrowicz, D. J.

Ward, S. J. Jenkins, W. Allison and J. Ellis, The Journal of Physical Chemistry Letters, 2016, 7,

4819–4824.

(717:[717]717) Ana Sanz Matias commented: You have calculated benzene

diffusion barriers and adsorption energies, and future work on vibrational

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frequencies is also mentioned in the manuscript. Have you considered combining

this information into a kinetic Monte Carlo model to investigate the dynamics of

the diffusion process?

Marco Sacchi answered: Yes, we have indeed considered this line of research

for other surface systems, such as diffusion of glycine on Cu(110),1 but not for

benzene on Cu(111), since the dynamics of this system are relatively simple and

other approaches (such as molecular dynamics) could be employed.

1 M. Sacchi, D. J. Wales and S. J. Jenkins, Phys. Chem. Chem. Phys., 2017, 19,

16600–16605.

(718:[718]718) Rasmita Raval queried: Does the direction in which the beams

are aligned with regard to the surface matter and, if so, can information on

diffusion along particular axes of the surface be captured?

Marco Sacchi answered: Yes, HeSE measures only along one crystallographic

direction, corresponding to the azimuthal scattering angle, at a time.1 By rotating

the crystal you can measure in other directions, and the ratio of the diffusion rates

in the different directions will give an idea of the ratio of the variation in the

corrugation heights. In this case, we only measured in the. The measured

Arrhenius barrier, however, isn’t expected to vary between the azimuths (as

motion in the directions also project on the for instance).

1 G. Alexandrowicz, A. P. Jardine, P. Fouquet, S. Dworski, W. Allison and J. Ellis, Phys. Rev.

Lett., 2004, 93, 156103.

(719:[719]719) Natalia Martsinovich remarked: You have calculated diffusion

barriers in quite good agreement with experiment, but found less good agreement

in adsorption energies. In the well-known Grimme’s dispersion correction, you

can tune the strength of the dispersion interaction by changing the value of the s6

parameter. In your opinion, what is the way forward in achieving accuracy in

calculations of weak interactions? Is it useful to make this semi-empirical

correction even more empirical by tuning the coefficients, e.g. by tting to

known experimental data, or is it preferable to develop new functionals with

dispersion interactions embedded in them?

Marco Sacchi responded: From a philosophical point of view, I think we should

strive to keep the level of empiricism in the vdW corrections as minimal as

possible, therefore I would not recommend to tune the C6 coefficient to obtain

a desired adsorption energy, but to use more advanced vdW treatments, such as

MBD or vdW+DF.

(720:[720]720) Neil Robinson said: I have a general question about the use and

application of dispersion corrections in DFT calculations containing multiple

adsorption environments. How transferable is the use of a specic dispersion

correction across surfaces with different electronic structures? For example, in an

example calculation containing a supported metal nanoparticle embedded within

an oxide surface, are there different considerations which must be made for the

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inuence of the dispersion correction on the interaction of adsorbates with the

two different surfaces present within the system?

Marco Sacchi replied: The intensity of the vdW corrections should depend only

on the specic elements that compose the surfaces and, generally, on the local

chemical environment or oxidation state of each atom present in the system. I

think that the presence of multiple adsorption environments, for instance in

metal oxides with embedded metal nanoparticles, should not be an obstacle for

most modern dispersion correction schemes or long-range corrected XCfunctionals.

Clearly, accounting for many body corrections and screening

contributions would also be important for these systems.

(721:[721]721) Robert Jones commented: The density functional theory (DFT)

calculations with van der Waals corrections seem to give the work function

change of the surface aer adsorption rather accurately. Can these be applied in

a straightforward way to other molecular adsorbate systems on metals to provide

similar work function change predictions? Or is a certain level of parameterisation

needed for each system to achieve this level of accuracy?

Marco Sacchi responded: Yes, as far as I know, the work function and dipole

moment calculations can be applied successfully to other molecular adsorbate

systems without parameterisation.

(722:[722]722) Giovanni Costantini queried: Could you comment on what the

problems are with molecules which are less planar, therefore typically lying less

close to the surface and being less hybridised with the states of the substrate? In

particular, on the importance of the self-interaction problem in DFT and on the

ways to overcome it.

Marco Sacchi answered: I do not have specic experience with self-interaction

problems in large organic molecules adsorbed on surfaces. Historically, vdW

corrections have been tested for aromatic dimers as well as for graphite layer

interactions, therefore I do not think that the size of the adsorbate or its orientation

would necessarily cause huge problems. Clearly, charge transfer and

multipole effects could become more important for vertically oriented molecules

at high coverage, therefore one would need to accurately test DFT against quantitative

experimental measurements in order to insure that the precision of the

vdW corrections is maintained.

Discussion of the Concluding Remarks

(723:[723]723) Steven Tait opened the discussion of the Concluding Remarks:

A question to all: In the closing remarks, Prof. Amabilino and I have discussed ve

themes to summarize our meeting: developing a rulebook for molecular

adsorption, diffusion, and assembly; polymorphism; nucleation – observing and

exploring; going from simple, well-dened systems to complex, ill-dened

systems; and rationalizing multiple analytical inputs with theory. As we look

toward the future development of this research eld, which challenges and

opportunities are exciting and engaging to you? We would particularly like to have

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the students and postdocs contribute to this discussion to identify the key themes

that seem exciting to them.

Neil Robinson responded: I would like to see a greater emphasis placed on the

investigation of applied systems, as well as potential applications of fundamental

topics. Much of the work discussed here has been focused on very ideal adsorbate

systems. As has been alluded to in the closing remarks, I feel that we should not,

as a community, be put off by the idea of confronting the messy, non-idealised

systems found in the many industrial applications of complex surfaces; indeed,

quite the opposite. As someone who is currently writing a PhD thesis in this area, I

certainly feel the need to have a strong argument for the possible applications of

the surfaces and adsorbate structures I have investigated. A concentration on the

applied elements of surface science is also favourable in terms of attracting

funding, which is something our community has struggled with in recent years.

(728:[728]728) David Amabilino asked: Could you give an example of an

applied system that is in need of analytical probing and solutions from the

knowledge we have of complex molecular systems at surfaces and interfaces?

Neil Robinson replied: Polar isomers exhibiting identical physical properties

can have very different responses to functionalised surfaces exhibiting hydrophilic

or hydrophobic properties. Thus, the separation of complex mixtures using

porous membrane materials with tailored surfaces is an area that could show real

promise in terms of industrial applications.

(724:[729]729) Brandon Hirsch addressed David Amabilino and Steven

Tait:The future of surface science will likely expose valuable insights into kinetically

trapped states and concepts on non-equilibrium systems. This work, and

the individual molecular detail that our eld provides, is one of the remaining

frontiers of science. However, I believe that in the future the eld will also begin to

recognise the extent to which our measurements are perturbing the nal state of

the system. In particular at liquid/solid interfaces, where dynamics are incredibly

important, these concepts are likely to become much more prevalent than the few

cases already seen in literature and those that were highlighted at the conference

by Prof. Flood and Prof. De Feyter.

David Amabilino answered: The variation of temperature in assembly of

molecules on surfaces is likely to reveal a great deal about “trapped” states.

Ostwald ripening has been observed in monolayer systems that have not reached

a place near their thermodynamic minimum. That is true for physisorbed

systems. But these cases can be the “easy” ones. For chemisorbed systems, the

kinetic trapping determined by covalent bond formation means that trapped

states abound, and cannot mature, and in these cases the conditions of deposition

are very important. They are somewhat easier to study in the sense that they

are less prone to measurement perturbation.

The question actually raises an interesting point about chemisorption and

physisorption, that comes back to the question of the rulebook for interactions.

There is clearly a grey area where deposition under certain conditions leads to

stable structures that are characteristic of chemisorbed states, but that can evolve

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under temperature variation, more characteristic of a physisorbed state. Finding

the sweet spot for this kind of annealing is a challenge and great opportunity to

prepare complex structures.

(733:[733]733) Steven Tait said: A question addressed to all, but especially the

students and postdocs: we have discussed the idea of developing a rulebook for

molecular assembly at surfaces at several points during the meeting. How can we

do a better job at distilling observations about specic systems into generally

useful principles about molecular assembly that could aid others in the predictive

design of new systems? When you study the research literature, what are key

pieces of information that you would expect should be available, but have not

been reported or compiled?

(734:[734]734) Nerea Bilbao commented: I nd it important to keep working

and focusing our efforts on completing and developing a rulebook on the effects

of surfaces on molecules and molecular assemblies. A better understanding on

the forces that govern surface reactions, or surface-supported self-assembly, will

help us control and design, in a better way, the chemical systems we are aer.

(736:[736]736) Sebastian Schwaminger noted: It’s sometimes challenging to

nd the right analytics for every system. Therefore, it is necessary to develop new

techniques to get new insights and new points of view towards a system. Coming

back to what K.-H. Ernst said, how nobody has imagined the development of an

ambient pressure XPS in the past and right now it is unimaginable to think about

techniques like ambient pressure PEEM, but who knows what is going to happen

in the future? Ambient P. Challenges of the future. Furthermore, it is very challenging

to nd someone who can actually perform the analytics needed to

describe a certain system which might be completely different to what he is doing.

Thus the knowledge transfer between different disciplines/analysis techniques is

crucial to the understanding of many phenomena.

(737:[737]737) Martin Nalbach remarked: For studying molecules at the solid–

liquid interface, in my case particularly the calcite (10.4)–water interface, in situ

AFM does not tell you the exact arrangement of the molecules at step edges or on

terraces. Further experimental techniques, as well as support from theory, would

be very helpful to achieve more insights into the adsorption behavior on the

molecules.

The solvent itself is a molecule and can strongly interact with the substrate

surface. Therefore, it is very important to also consider the surface–solvent

interaction as well as the arrangement and order of the solvent molecules at the

interface when studying the inuence of molecules on the substrate surface.

(738:[738]738) Jonathan Davidson said: My supervisor, Stuart Clarke, made

a comment about this earlier, but I would like to reiterate that diffraction techniques

are oen underutilised in surface science. STM and related scanning

probe techniques are inherently invasive. For example, in DFT simulations using

periodic boundary conditions, such as in the paper presented by Marco Sacchi

(DOI: 10.1039/C7FD00095B), a “vacuum gap” of 15–20 angstroms between the

bottom of one layer and the top of another is generally considered necessary to

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avoid interference between adjacent layers. However, as Brandon Hirsch’s paper

(DOI: 10.1039/C7FD00104E) pointed out, the tip–sample distance in STM experiments

can generally be considered as being on the order of 10 angstroms, and

can be even less. Thus, even in the absence of a signicant bias voltage, the tip will

be perturbing the surface relative to simulations. Diffraction and related techniques

provide a non-invasive method to evaluate surface structure and can help

validate results from scanning probe techniques, bridging the gap between these

techniques and simulations.

David Amabilino responded: That is true, diffraction techniques can be useful,

mainly for seeing periodic structures I would say (although that is oen the case

for STM too), and especially LEED has proven vital as shown by people in this

discussion and others (for example ref. 1–3). Helium diffraction has also been

used for the study of SAMs.4

1 J. Stettner and A. Winkler, Characterization of Alkanethiol Self-Assembled Monolayers on

Gold by Thermal Desorption Spectroscopy, Langmuir, 2010, 26, 9659–9665.

2 T. Yokoyama, M. Kawasaki, T. Asari, S. Ohno, M. Tanaka and Y. Yoshimoto, Adsorption

and self-assembled structures of sexithiophene on the Si(111)-3—O\_3—O3\_3-Ag surface,

The Journal of Chemical Physics, 2015, 142, 204701.

3 Sanchez-Arenillas M. and Mateo-Marti, E., Pyrite surface environment drives molecular

adsorption: cystine on pyrite(100) investigated by X-ray photoemission spectroscopy and

low energy electron diffraction, Physical Chemistry Chemical Physics, 2016, 18, 27219–

27225.

4 E. Albayrak and M. F. Danisman, Helium Diffraction Study of Low Coverage Phases of

Mercaptoundecanol and Octadecanethiol Self-Assembled Monolayers on Au(111)

Prepared by Supersonic Molecular Beam Deposition, J. Phys. Chem. C, 2013, 117, 9801–

9811.

(740:[740]740) Yuri Diaz Fernandez commented: One of the recurrent themes

over the conference was the importance of disorder and how it could drive the

formation of ordered phases. We are currently lacking complementary analytical

tools to characterize the dynamics of disordered phases and phase boundaries in

2-dimensions. Translating into 2D probing techniques already established for 3-

dimensional material chemistry systems (e.g. total scattering pair distribution

function analysis) may bring a step change in our ability to understand complex

molecular processes at surfaces.

(741:[741]741) Karl-Heinz Ernst noted: New methods are not only important to

understand the properties or inuence of disordered phases. Over the last 100

years, aer XRD was revolutionarily introduced and told us there are actually

atoms, we thought we had a single crystal. Electron microscopies then revealed

recently that we don’t have a single crystal, although XRD suggested this, but

rather a polycrystalline sample, but all crystallites are more or less aligned

equally. See the aragonite example in ref. 1.

1 X. Li and Z. Huang, Phys. Rev. Lett., 2009, 102, 075502.

(743:[743]743) Karl-Heinz Ernst continued: And defects especially play a role at

surfaces. Aer preparation of surfaces with much lower step density, for example,

the dissociative sticking probability of molecules like water on Pt(111) became

orders of magnitude smaller.

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(744:[744]744) Rasmita Raval remarked: What is quite clear is that the eld of

complex molecules at surfaces will require a broad and deep discipline base in

order to ourish and reach its fullest potential. For example, the need for the

rigour of surface science and a multi-technique approach is vital to capture the

multifaceted aspects of these systems. The need for the methodology, insights

and concepts of organic and supramolecular chemistry is also clear. In addition,

we need to bring in the functionality focus that the materials scientist and

engineer have, alongside the complexity that is inherent in the biological system.

Theory will be instrumental in capturing the structure, kinetics and thermodynamics

of these systems. Finally, we will need to embrace the big data and

information space that science is currently generating. I feel that there is a real

need to broaden the minds of all researchers in the eld, from professor to

student, so that we possess sufficient breadth and depth to address the challenges

in the eld. This would allow us to grasp the advances in other elds and lever

that knowledge into ours, and will avoid reinventing the wheel that keeps

occurring across science.

(745:[745]745) Angelika K¨uhnle added: Along this line, I think we still have to

learn to better combine the worlds of physicists and chemists. There is still

a rather different view on many things and a different way of describing the

situation. For example, I have the impression that when considering disorder and

entropic effects in molecular self-assembly physicists can learn a lot from

chemists and vice versa.

(746:[746]746) Steven Tait asked: Much of the work that we have discussed in

this meeting is truly inter-disciplinary. This creates a real challenge in the design

of our training and education programs as the student researchers (and senior

researchers) need to have a depth of knowledge in more than one traditional eld

of study. What have you found to be effective methods in your training programs

to prepare researchers to work successfully in inter-disciplinary research elds? It

would be helpful to have both students and senior researchers respond to this

question so that we have both perspectives on the most effective strategies.

(747:[747]747) Trolle Linderoth noted: Regarding the previous comment concerning

better integration between chemistry and physics. At the Interdisciplinary

Nanoscience Center at Aarhus University (iNANO), since 2002 we have been

running interdisciplinary educational bachelor and master programmes in

nanoscience, encompassing both physics, chemistry and molecular biology.1 I

just wish to comment that the experience shows that this concept really works and

the students are able to pursue very interesting projects taking advantage of this

interdisciplinary breadth.

1 Mat. Today, 200811.

(749:[749]749) Marco Sacchi said: In my personal experience, I’ve collaborated

with physicists for more than 10 years and I enjoyed working on interdisciplinary

projects. I think it is fundamentally a question of keeping a exible mental attitude

and being able to enjoy the communication challenges given by the use of

different scientic language and terminologies in different communities. Also, I

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would like to add another great challenge we face in the surface science

community. From a theoretical point of view we have a theoretical “soware”

challenge that is the rationalisation and quantication of entropy, disorder,

complexity, solvent effects. But we also have a physical, “hardware”, challenge,

that is the limited amount of computer power available, especially on large

national HPC facilities. In the last decade, USA, Europe and China have consistently

increased the investment in HPC resources. The UK needs to urgently

increase its investment in computational power dedicated to materials and

surface science in order to remain competitive in these areas.

(751:[751]751) David Amabilino asked: Many examples of interfaces we’ve seen

in this meeting comprise molecules co-parallel with the adsorbent on which they

are deposited, but for many potential applications in different areas, like catalysis,

electronic devices, sensors and so on, the molecules are perpendicular to the

plane, and it is really tough to analyse that, although theory can model orientation

and order. Are there any ideas about how you could analyse, experimentally, these

areas of interfaces?

(752:[752]752) James Batteas commented: We are now investing heavily in high

precision, in situ techniques at TAMU, in particular in situ TEM methods that will

allow us to look at complex nanoparticle systems (such as catalysts), where it has

been shown that the interactions of solvents with nanoparticles can be followed.

We have also added a number of in situ nanomechanical testing tools. In general,

we feel that without moving more of our techniques to in situ based methods, we

can’t really address the issues we’re aer at the molecular level.

(753:[753]753) Mario Samperi remarked: I’d like to spend few words on two

different topics. Firstly, I strongly believe that we should always keep in mind how

extremely important the role of the solvent is on governing both the molecule–

molecule and molecule–substrate interactions. In this context, solvent mixtures

can represent an incredibly wide range of opportunities for achieving properties

and features that one solvent is not able to show in itself. As human beings behave

and interact with each other because of the environment in which they are in,

similarly the behavior of molecules is strongly imposed by the medium composition.

Secondly, I was considering how we approach supramolecular chemistry

differently when we move from solution to surface. One of the greatest challenges

for future research is to erect a solid bridge between chemistry on the surface and

in solution. The scientists awarded the Nobel Prize in Chemistry in 2016 have

shown us how to make catenanes, rotaxanes, how to utilize molecular recognition

and molecular self-assembly processes for the design and synthesis of devices at

the nanoscopic scale. Now we need to put them on surfaces, and make them work

together to create supramolecular machines.

(754:[754]754) Steven De Feyter noted: One of the important challenges is

understanding the role liquids or solvents play in supramolecular self-assembly at

the liquid–solid interface. The choice of the liquid is, in many cases, motivated by

technical considerations. For instance, only a small set of solvents are considered

for STM imaging at the liquid–solid interface, and few systematic studies are

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carried out. More in depth studies are needed, involving other techniques, to

shine light on the different roles the liquid environment plays.

(756:[756]756) Natalia Martsinovich commented: We also need to expand our

toolkit of theoretical methods. At the moment, most studies of self-assembled

systems in the literature use DFT. However, the use of DFT is limited by the

size of the systems. Force elds are used much less in this eld, but they are able

to treat much larger length scales and time scales. Notably, the DFT community

and the force eld/molecular dynamics community think in different ways, and

ask and answer different kinds of questions: while DFT calculations are largely

focused on obtaining structures and energies, molecular dynamics users thinks

in terms of order parameters and time correlation functions, and even diffusion

coefficients1 and entropy2 can be calculated. Therefore, force elds and molecular

dynamics calculations can be very useful, especially if we want to describe

complex systems, such as solid/liquid interfaces.

1 J. Wang and T. Hou, J. Comput. Chem., 2011, 32, 3505–3519.

2 J. Gaberle, D. Z. Gao, M. B. Watkins and A. L. Shluger, J. Phys. Chem. C 2016, 120, 3913–

3921.

Talat Rahman added: We should also not forget that DFT itself needs to be

reformed to include effects such as electron correlations which can have a large

impact on the characteristics of metal coordination centers, such as V or Fe, or on

oxide surfaces and nanostructures. Such developments are in the literature (for

example: ref. 1). Additionally, as has been discussed at this workshop, both

kinetic and dynamical (vibrational) effects need to be taken into consideration

together with insights from electronic structure calculations from DFT.

1 S. R. Acharya et al., Computation, 2016, 4, 34.

(757:[757]757) Claire-Marie Pradier addressed Steven Tait: May we come back

to the rst challenge you listed in the concluding remarks, what governs molecular

adsorption, diffusion and assembly. You showed a very interesting diagram

with different types of interaction between molecules on the surface. We should

consider interactions between molecules and the substrate too. There may be

competition or synergy when considering interactions between molecules, and

between molecule and substrate. Techniques to measure these interactions, and

their strength, apart from AFM, would be useful.

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