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Dynamics of hot electron generation in metallic nanostructures: general discussion

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Yonatan Sivan opened discussion of the introductory lecture by Naomi J. Halas: I have 3 comments, each addressing one of the key papers you presented.

(1) My first comment is regarding the theory paper.[1] In that paper, the authors calculated and plotted the electron excitation rate due to photon absorption, but claimed that it is actually the distribution itself. This is in principle not correct. Secondly, the calculation involved only the electron system, such that the energy flow into the phonons and environment was not correctly accounted for; specifically, this approach does not allow one to adjust the rate of heat flow from the phonons to the environment according to the particle size and shape. This leads, as we have shown in our paper (DOI: 10.1039/c8fd00147b), to quantitative errors in the electron distribution close to the Fermi energy. However, as we have also shown in our paper, a quantitative prediction for the distribution itself can effectively be obtained by multiplying the electron excitation rate by the e–e collision time. However, not only did the authors not do that, but they also did not plot the results on a logarithmic scale. Hence, it is impossible to know what the high energy electron population looks like, even qualitatively.

(2) As we showed during the poster session, my own presentation and in a paper we have submitted for publication (available on ArXiv[4]), the temperature measurement in the paper by Mukherjee *et al.*[2] was carried out far from where the reaction took place, thus underestimating the temperature rise and, therefore, the thermal contribution to the reaction. This means that the control experiment performed in that work was unfortunately meaningless. Furthermore, an Arrenhius fit to the data shows that the authors' claim that the activation energy in the

presence of Au nanoparticles is 1.8eV is incorrect; it also shows that all the data can be fit perfectly with the correct, intensity-independent activation-energy measured in the dark and with a correct evaluation of the reaction temperature.

(3) Finally, as we also showed during the poster session, my own presentation and in an accepted paper,[5] for the temperature measurement in the paper by Zhou *et al.*,[3] the thermal camera seemed to have been operated under the default settings, such that the temperatures were again underestimated. As we explained,[4,5] even if the temperatures were measured correctly, any slight difference between the pure thermal control (*i.e.* the data obtained in the dark) and the thermal contribution to the reaction in the photocatalysis experiment would be incorrectly interpreted as coming from the non-thermal (*i.e.* 'hot') electrons. In practice, not only are the spatial distributions of the temperature in these experiments quite different,[4,5] but also the exponential sensitivity of the reaction to the temperature amplifies these differences dramatically. Consequently, the conclusion drawn by the authors about the dominance of 'hot' electron effects over regular thermal effects is not supported by the obtained data.

1 A. Manjavacas, J. G. Liu, V. Kulkarni and P. Nordlander, *ACS Nano*, 2014, **8**, 7630–7638.
2 S. Mukherjee, F. Libisch, N. Large, O. Neumann, L. V. Brown, J. Cheng, J. Britt Lassiter, E. A. Carter, P. Nordlander and N. J. Halas, *Nano Lett.*, 2013, **13**, 240–247.
3 L. Zhou, D. F. Swearer, C. Zhang, H. Robatjazi, H. Zhao, L. Henderson, L. Dong, P. Christopher, E. A. Carter, P. Nordlander and N. J. Halas, *Science*, 2018, **362**, 69–72.
4 Y. Sivan, I. W. Un and Y. Dubi, 2019, arXiv:1902.03169 [physics.chem-ph].
5 Y. Sivan, J. Baraban, I. W. Un and Y. Dubi, Comment on "Quantifying hot carrier and thermal contributions in plasmonic photocatalysis", *Science*, 2019, **364**, eaaw9367.

Reinhard J. Maurer enquired: In your talk, you mentioned that plasmon-driven ammonia decomposition benefits from a reduced rate of ammonia desorption in comparison to thermal decomposition. I wonder how this relates to photo-induced ammonia desorption on copper, as studied by Gerhard Ertl and co-workers?[1] This is a process that is also understood to be driven by hot electrons in the metal and will contribute to desorption in the case of plasmonic catalysis.

1 T. Hertel, M. Wolf and G. Ertl, *J. Chem. Phys.*, 1995, **102**, 3414.

Naomi Halas replied: Yes, this work is very likely quite similar in that the process relies on desorption induced by electron transitions. However there are substantial differences in that one cannot generate hot electron populations directly on a bulk metal substrate sample as one can by optical illumination of subwavelength metal structures.

Priyank Vijaya Kumar asked: In comparison to an aluminium catalyst, does an aluminium–palladium catalyst produce higher HD reaction rates in your experiments? Do you have an estimate for this value?

Naomi Halas responded: Yes it most certainly does, by about 2 orders of magnitude. That is not clear in our presentation of the data because we focused instead on the difference in wavelength dependence of the HD yield. However, it isn't even close, because H_2 and D_2 dissociate spontaneously on Pd and the hot electrons in that system desorb the dissociated species; this was confirmed by E. A. Carter and her group.

Stefan Maier queried: What are the main design criteria for plasmonic catalysts? If you want to design an efficient plasmonic catalyst for a given reaction where do you start?

Naomi Halas answered: If one takes the antenna–reactor strategy, which is modular, then one has many options regarding reactor sites for binding reactants to the complex, as well as antenna tunability to address binding energies for bond dissociation. The weak link here is theory; there are only a few groups that address these problems in adsorbate levels and binding energies quantitatively.

Chao Zhan remarked: In the demonstration of antenna–reactor complexes, Pd is used as the reactor. However, as we know, Pd itself has a plasmonic effect. Can it be used to prove that it is the nanoantenna effect? Maybe it is required to extend the 'reactor' to another metal or metal oxide that does not have SP properties. Confirmation is also needed that there is no charge transfer between the antenna and reactor.

Naomi Halas replied: Yes, Pd has a weak plasmonic response but it does certainly have one. In the geometry we used, the antenna NP was much larger than the Pd NPs. The antenna NP already has a larger cross section and, with a larger size relative to the Pd, its optical properties dominate those of Pd. Here we take advantage of the ability of Pd for the barrierless dissociation of H_2 on its surface. We have also extended this general concept to other types of reactors, such as metal oxide layers. In the case of Al NPs, they have a 2–4 nm thick oxide layer and therefore it is highly improbable that there is any charge transfer between the antenna and the reactors.

Jhon Quiroz communicated: My question regards the antenna–reactor photocatalyst design. If I understood well the first example concerning the Al–Pd antenna reactor, both the plasmonic and catalytic components are not in direct contact. However, in the second example concerning the Cu–Ru photocatalyst intimate contact is suggested, producing an alloy. Could you please shed light on which design is more efficient or promising?

Naomi Halas communicated in reply: That is a very good question. They both have their merits. Because the reactive sites of Pd and Ru are different and because we have not tried them out on the same reaction we do not have a direct comparison. Since the reactor sites are different for the two complexes I don't think there is a way to compare them. However, if you were to synthesize both types of antenna–reactor complexes with the same reactor sites, one could make a direct comparison. Still, the properties of the specific reaction one ran would be very important in distinguishing the two A–R types from one another and assessing how one may perform better than the other. One thing is clear however, and that is that the Al-based A–R complex has a tunable plasmon resonance and the Cu plasmon is not nearly as tunable due to the more complex electronic structure of Cu and how this effects the plasmon resonant energy in this material.

Javier Aizpurua opened discussion of the paper by Jacob B. Khurgin: Your paper is very nice, and very helpful for obtaining the numbers and orders of magnitude of the rates of decay of hot electrons due to the different mechanisms. Most of the estimations are made for highly symmetric and homogenous bulks and surfaces, where you provide a nice description of each scattering mechanism, for example of a slab or a spherical particle. However, when one comes to realistic surfaces, these can show bumps, rough areas, or even atomic-scale protrusions, which can cause surface scattering processes to become more complicated. What happens when we have less-symmetric systems and angstrom-scale nano-features? How can we develop similar descriptions for systems of a few nanometers in size, or beyond these symmetric systems, in order to find out what the hot electrons do in those more extreme systems?

Jacob Khurgin responded: Thank you for this great question. I think that this theory stands for structures that have features larger than $1/\Delta k$ or v_{Fermi}/ω, which corresponds to a couple of nanometers. You can simply find the field and the emission will more or less follow the strength of the field normal to the surface. However, for smaller features this all starts breaking down and so probably the only correct way to handle this is to use a full atomistic model. A comparative study of two models would be great! However the general conclusion—that smaller features help—will stand; in the end all we need is to violate (relax) momentum conservation by all means possible.[1]

1 M. Grajower, U. Levy and J. B Khurgin, *ACS Photonics*, 2018, **5**, 4030–4036.

Jeremy Baumberg remarked: Your paper describes a very nice picture, and is very helpful. Since it is semi-classical, I wonder whether you have considered what happens in surfaces with sharp surface asperities such as vertices, edges or bumps (adatoms). It would seem that you can cast the theory to look at electron focussing (I suspect they will be beamed normal to the surface). Your theory also suggests that these are the places where hot electron emission would be strongest, since the field penetration is strongest. This would suggest that this semi-classical picture for catalysis also implies that there are active sites at step-edges, adatoms and vertices. This is an intriguing conclusion. Your comments about this would be very interesting, and could lay out a programme for tackling this.

Jacob Khurgin answered: Thank you for this intriguing question. I would not call my theory "semi-classical" as the only "classical" aspect is that the electric field is not quantized. Quantizing the field would not reveal anything new for applications in detection and catalysis. You are correct about the beaming—it does take place. In the text I derive an expression in which I show that the hot carriers inside the metal are generated proportional to some function (depending on the mechanism) of the cosine of the angle (Fig. 7a in DOI: 10.1039/c8fd00200b). Therefore, if you have a protruding (convex) feature on the surface I expect the carriers to spread out as the field tends to be normal to the surface. However, a concave feature will indeed cause focusing. Regarding the second half of your question, my belief is that the field is strongly affected by the presence of adatoms; in general any sharp feature further violates momentum conservation and increases hot electron emission.

Phillip Christopher commented: Very nice descriptions exist of how the electronic states of atoms at metal surfaces and adsorbates hybridize upon bond formation from a quantum mechanical perspective. The works of J. Norskov and many others have demonstrated these pictures over the past 2 decades based on density functional theory calculations.[1,2]

1 B. Hammer and J. K. Norskov, *Nature*, 1995, **376**, 238–240.
2 J. K. Norskov, F. Abild-Pedersen, F. Studt and T. Bligaard, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 937–943.

Jeremy Baumberg responded: Indeed, there are many works on the electronic states of adsorbates at surfaces, but my comment is about doing this for real systems where there is solvation, ionic double layers which respond to localised charges, Au atom movement *etc.* These are not typically included in such calculations, and certainly not in the systematic manner that is needed for the work presented here.

Julian Gargiulo asked: Where would "resistive losses" fit in the presented framework where absorption is led by carrier generation? Is there any energy transfer mechanism from the plasmon to the lattice without carrier generation?

Jacob Khurgin replied: "Resistive losses" as described in simple Drude theory at high (optical) frequencies should be described correctly with both energy and momentum conservation and not using phenomenological damping constants. This is exactly what is done in my work (see DOI: 10.1039/c8fd00200b), in which I show how phonon and impurity assisted transitions become Drude-like at low frequencies. It is important to understand that an intraband transition can only take place from an occupied state to an empty state and that the energy must be conserved. Using Drude theory for high frequencies without thinking about it is absolutely wrong. For example, Drude theory does not include electron–electron scattering contributions; this is correct at low frequencies but absolutely wrong at optical frequencies, as has been shown in numerous experiments dating back to the 1970s. In summary, there is no separate resistive contribution—it is already taken into account in my theory. Including it would lead to double counting, which has in fact been done in the literature.

Jie Liu queried: From a theoretical point of view, what is the difference between nanoparticles at room temperature and at higher temperatures (*e.g.* 1000 degrees)? Will plasmonic absorption change at all?

Jacob Khurgin answered: Yes, it will change with temperature, but only one contribution to the total phonon assisted absorption will increase. Since this absorption dominates at low optical frequencies, the relative change will be very large proportional to $(kT)^n$, where n can be as high as 4. However, when $\hbar\omega \gg kT$, the change will not be that large (maybe a factor of 2–3).

Niclas Sven Mueller remarked: Your study is mostly concerned with single nanoparticles. Can I also apply your theory to nanoparticle oligomers with plasmonic hot spots? If so, how would your advice and summary on the last page of your paper change? Would you still suggest using nanoparticles that are smaller than the effective mean free path?

Jacob Khurgin responded: Thank you for your question. Yes, I believe that the general conclusion will stand—you want to generate hot carriers at the surface and not deep inside. The theory is applicable to oligomers; of course having hot spots increases photoemission. In the end the total emission is increased with the surface to volume ratio (equation 50 in the text). Having hot spots will cause a change in the spatial distribution of the emitted carriers, which may be very important if you manage to have the molecules attached there.

Anatoly Zayats commented: Absorption of complex nanostructures will be different as, for example, an oligomer may have both bright and dark modes, thus light may be trapped more efficiently in the dark modes.

Jacob Khurgin replied: Yes, I agree. However my work is not really concerned with how much light gets absorbed, but more with what kinds of carriers are excited (in terms of energy and momentum) and what happens to them. The more light gets trapped the more carriers are excited, but their distribution does not change. In general, whether let's say 50% or 100% of light gets absorbed matters very little when considering that of all the photo-excited carriers, less than 0.1% will ever succeed in performing any useful function and not end up as just heat.

Sylwester Gawinkowski asked: In real situations, we very rarely have flat walls. How does the roughness of the metal–semiconductor interface affect the directionality of hot electrons?

Jacob Khurgin answered: Yes, I agree. In general the electrons will tend to move more or less normal to the walls locally. For more about roughness please refer to my previous work.[1]

1 M. Grajower, U. Levy and J. B Khurgin, *ACS Photonics*, 2018, **5**, 4030–4036.

Reinhard J. Maurer queried: In your paper, you conclude that phonon-assisted hot-electron generation is only moderately useful for photocatalysis. At the interface, the electronic structure will not be purely metallic due to the existence of adsorbates. Multi-phonon decay, multi-phonon-electron-coupling-induced decay and coupling of phonons and electrons with adsorbate vibrations have been shown before to be important energy dissipation channels. How do these different surface-dominated absorption processes fit into your analysis?

Jacob Khurgin responded: Thank you for your question. First and foremost, as I mentioned in my talk I am not really an expert on photocatalysis and so my conclusions are more relevant for hot electron emission, *i.e.* for detection and photovoltaics. Having said this, all that I meant was that phonon-assisted hot carrier generation occurs everywhere in the material and that this reduces the fraction of hot carriers reaching the surface. I agree entirely that hybridization between the metal and absorbate plays a very important role. However, once hybridization takes place there is no need for phonons to achieve the absorption of photons/plasmons as the momentum conservation impeding intraband absorption in the metal is broken. Therefore, there is no need for phonons to absorb the light. When it comes to decay, phonons do of course play a role, which I have never denied.

Jeremy Baumberg asked: Is your optimal hot electron system then not dense small nanoparticle aggregates, but perhaps instead a gold foam in order to allow the diffusion of reactants and products, and to use all of the gold as surface electrons with optimal penetration and absorption of light?

Jacob Khurgin replied: You are absolutely correct. However, one must be careful to avoid a situation whereby the outer layers of the gold foam screen the field so that it does not penetrate the inner layers.

Matteo Parente opened discussion of Phillip Christopher's paper: You depict the CID mechanism as a direct electron transfer from the metallic nanoparticle to an acceptor state of a molecule adsorbed on its surface. In other publications, the CID mechanism is depicted as an electron excitation from the HOMO to the LUMO of the molecule adsorbed on the surface of the metallic nanoparticle. In this latter case, the CID would look more like a near field effect. Could you explain why you prefer the first way of depicting it?

Phillip Christopher answered: The cartoon depiction we presented is too simplified. My picture of this situation is essentially a combination of the two ideas you describe. When a molecule chemisorbs to a metal surface, states of the molecule and metal will hybridize. The picture I have of CID is near field enhancement of electronic transitions involving these hybridized metal–molecule states. In these situations it isn't quite right to think of these transitions as a metal-to-molecule electron transfer, as seen in MLCT for organometallic complexes, because the states involved in electronic transitions have both metal and molecule character. However, it is possible that the states are localized more on either the metal or molecule and this probably plays a role in dictating how the excitation induces nuclear motion in the system.

Chao Zhan addressed Phillip Christopher and Sebastian Schlücker :In SERS, when the molecule interacts strongly with the plasmonic nanostructure, non-EM effects including CE/CT will contribute to the total enhancement. This has been widely investigated and can be separated into three types. Type I is a result of a charge transfer between the probe molecule and the surface. Type II involves the formation of surface complex which can be considered as new molecules that have new electronic transitions in resonance with the incident light, resulting in a resonant Raman process. Type III is photon-induced charge transfer from the plasmonic structure to the molecule, as has been observed in some electrochemical Raman spectroscopy experiments. However, usually there are no chemical reactions. Chemical interface damping does not mean a plasmon-mediated chemical reaction. For PMCR, excited carriers should have longer retention times for the reactants to take part in the reaction. Nevertheless, the excited carriers in the CT of PERS quickly decay back to the metal or the 'surface complex' on a femtosecond timescale. Additionally, in order to prove the existence of chemical interface damping, looking at only the absorption, scattering or extinction is not enough, and so more experiments are needed. For example, we can use the electrochemical method to regulate the Fermi level of the plasmonic nanostructure in order to prove its relation to the molecular energy level.

Phillip Christopher replied: I agree. Those interested in plasmon-induced catalysts can learn a lot from the many results and theoretical constructs existing in the SERS literature. The idea of using electrochemical approaches to learn more about these processes is a great one. It should be done.

Sebastian Schlücker responded: I agree that electrochemistry is an excellent way of controlling the Fermi level of a plasmonic nanostructure. In addition, we should also aim to carry out wavelength-dependent studies, as far as they are experimentally accessible (at least for a few fixed CW laser wavelengths or ideally a tunable CW laser source). A third important aspect in my opinion is to work on single nanostructures, *i.e.* single nanoparticles or single nanoantennas with defined structures.

Giulia Tagliabue queried: I notice that the absorption peak in your system is above 2eV, hence in a spectral region where interband transitions in Au are very strong. We also know that often molecule adsorption occurs through interaction with the d-band orbitals. Do you think that the two aspects are related? Can this give us some insight into the energetics of the process or any design guidelines? What would you expect to see in the case of a metal without a d-band, for example aluminum?

Phillip Christopher answered: This is an interesting point. It is important to note that similar measurements of chemical interface damping have been made for Au nanostructures with plasmon resonances of much lower energy (away from the interband threshold). Therefore, I am not sure whether the two aspects are related. I do think that the situation should look different for adsorbates on Al. The hybridized states created from molecule adsorption on Al will look quite different than those on Au/Ag/Cu, due to the involvement of the d-band, as you mentioned. This presumably would influence the probability of available electronic transitions associated with adsorbates being involved in plasmon decay processes.

Laura Torrente-Murciano remarked: Your paper nicely demonstrates that the adsorption of thiophenol on the surfaces of Au nanodisks reduces their extinction coefficient and affects the plasmon resonance energy. Based on this, would you expect a similar effect from the substrate upon which the plasmonic particles are supported? It seems to me that this is a generally disregarded point for understanding (and comparing) systems, especially in catalysis.

As a follow up question, do you think that it would be possible to use this effect in a beneficial manner?

Phillip Christopher responded: Absolutely there is an influence of the substrate. In some of the original work on CID, the influence of a SiO_2 matrix on plasmonic structures was examined, where the extent of CID is more significant than often seen with molecules. In addition, it has been shown that interfaces between plasmonic structures and semiconductors (not so different to many substrates used to support metal particles) can induce significant plasmon damping. For example, in Tim Lian's work[1] the strong interfacial damping induced by a semiconductor substrate has been shown to enable very efficient plasmon-induced electron transfer. Furthermore, Naomi Halas' work[2] has highlighted the importance of substrate composition for promoting plasmon-driven surface chemistry. As we learn more about these interfacial processes, we should be able to choose substrates to facilitate plasmon-mediated hot carrier transfer processes.

1 K. Wu, J. Chen, J. R. McBride and T. Lian, *Science*, 2015, **349**, 632–635.
2 S. Mukherjee, L. Zhou, A. M. Goodman, N. Large, C. Ayala-Orozco, Y, Zhang, P. Nordlander and N. Halas, *J. Am. Chem. Soc.*, 2014, **136**, 64–67.

Sebastian Schlücker asked: In contrast to the indirect mechanism, the direct mechanism depends, among other factors, on strong molecule–metal interactions including orbital coupling *etc.* Keeping this in mind, how universally applicable do you think the direct mechanism is with respect to establishing general design principles for plasmonic catalysis?

Phillip Christopher replied: In most catalytic processes on metal surfaces, reactants, intermediates or products will adsorb with energies of at least $\sim$0.5 eV. This is at the low end for adsorbates on optimal catalytic surfaces, but already requires significant hybridization between metal and molecule electronic states. Therefore, from this perspective it is not unreasonable to think that plasmon excitation of catalytic materials will often involve plasmon decay by transitions involving electronic states associated with adsorbates.

Madasamy Thangamuthu queried: What is the reason for using thiophenol? Is it to introduce covalent bonding with gold, which would correspond to the chemisorption of the adsorbate on the metal surface? If so, this should also work with L-cysteine, which has sulfur that can easily form a self-assembled monolayer on gold.

Why is an ultra high vacuum needed to carry out integrating sphere experiments? Would that also work under normal conditions with other thiol molecules on the gold surface?

A Xe light source is used in your study for the integrating sphere experiments, but it is claimed that the observed mechanism is consistent with the ultrafast studies reported in the literature. Both clearly have different working conditions and hence is it reliable to compare these?

Phillip Christopher answered: Thiophenol was used as a model system where we knew that we would be able to see the influence of adsorption on the optical properties of the plasmonic particles. The goal moving forward is to focus on more catalytically relevant molecules, *e.g.* alcohols, and to use the vacuum chamber in typical surface science experiments to follow how plasmon excitation induces chemical transformations and changes in the optical properties of the system under well defined conditions. The comment that the conclusions drawn from low intensity Xe probing and ultrafast studies seem to be consistent is from a mechanistic interpretation, not similarity in the measurements. Our measurements suggest that electronic states hybridized at the metal–molecule interface induce plasmon dephasing. This is consistent with inferences from ultrafast studies that show almost instantaneous charge transfer to interfacial species upon plasmon decay.

Yuri Diaz Fernandez remarked: I appreciate that the net variations that you observed after thiophenol deposition are small even with complete coverage of the surface. However, did you observe any dependence of the different spectroscopic contributions with the surface coverage as you cycled your deposition steps?

Phillip Christopher responded: Yes we did. Systematic damping of the surface plasmon resonance peak was observed as a function of coverage mostly following a Langmuir-type adsorption process. This can be seen in the inset of Figure 5A in our paper (DOI: 10.1039/c8fd00151k). We did not deconvolute the absorption and scattering contributions as a function of thiophenol coverage, but expect that the effect would be similar to the complete coverage case where the scattering spectrum was damped/broadened/shifted more significantly than the absorption spectrum.

Reinhard J. Maurer commented: In your work, you clearly distinguished between Landau damping (plasmon decay which leads to indirect electron transfer to the adsorbate) and chemical interface damping (plasmon decay which leads to direct electron transfer). The latter is an effect due to the hybridisation of localised adsorbate and delocalised surface states. I wonder how clearly these two conceptual processes can be separated in reality. In the case of strong hybridisation, the adsorbate state will hybridise with metallic states over a wide range of energies. This is definitely true for thiolate linkers. Therefore, only a small part of the probability distribution of an individual (hybridised) eigenstate will be localised at the adsorbate. It also becomes increasingly difficult to distinguish between adsorbate and substrate states. Whilst there is clearly an adsorbate-induced change in the hot-electron profile upon plasmon decay, it is not absolutely evident to me that this will also mean that more electrons will be directly transferred to electronic states localised at the adsorbate.

Phillip Christopher replied: I don't disagree that the situation is quite complicated. There are nice demonstrations[1] that the linewidth broadening (decreased lifetime) of plasmon resonances can be related to the formation of bonds between the metal surface and adsorbates or solid-state materials. This suggests that the electronic states associated with these interfacial bound species, or their influence on the metal electronic states, provide more effective pathways for plasmon decay. Therefore, while this is supportive of the idea that direct plasmon dephasing is driven by electronic transitions involving states associated with adsorbed species, there are other possible explanations.

1 B. Foerster, A. Joplin, K. Kaefer, S. Celiksoy, S. Link and C. Sönnichsen, *ACS Nano*, 2017, **11**, 2886–2893.

Bartlomiej Jankiewicz communicated: Have you carried out for comparison studies on the chemical interface damping induced by the adsorption of thiophenol derivatives with either electron withdrawing (EWG) or electron donating (EDG) groups? If so, did the substitution of thiophenol affect the measured scattering and absorption contribution to extinction? If not, do you expect to see any effect of substitution with other types of groups? What will happen if alkanethiol is used instead of thiophenol?

Phillip Christopher communicated in response: We have been carrying out these measurements. While it is too early to provide all of the details, we do see an influence of the R group substitution on thiophenol on the overall magnitude of the plasmon damping. This suggests that regulating the electronic structure of the metal–molecule electronic states controls how effectively these states participate in plasmon decay processes. It is also important to consider the packing density of adsorbed species, which should be different in the case of alkanethiols and thiophenol.

Bart de Nijs communicated: In your paper you mention that the surface damping by the molecules will increase if smaller metal structures are used as the number of molecules increases with respect to gold. Could you comment on how this effect relates to field localisation as well? For example, bringing two such metal objects very close together will not change the amount of gold but the field will be highly localised in the hot-spot between the disks. Would this effect then be the same or also be increased?

Phillip Christopher communicated in reply: This is a great point. The answer should be yes. The field localization at hot spots has been shown to enable enhanced hot carrier production due to surface scattering.[1] With the idea that hybridized metal–molecule states are likely to be involved in surface scattering when adsorbates on the metal surface are present, it is reasonable to consider that molecules in hot spots will be quite efficient at mediating the decay of surface plasmons through chemical interface damping.

1 L. V. Besteiro and A. O. Govorov, *J. Phys. Chem. C*, 2015, **120**, 19329–19339.

Jeong Y. Park opened discussion of the paper by Emiliano Cortés: In your technique, hot electrons are generated on metallic nanoparticles and then transferred to the molecule. These hot electrons cause the reduction of molecules into the fluorescent resorufin molecule, which can be detected *via* fluorescence measurements. Can we quantify the hot electron flux transferred to the molecules? If so, can we determine the efficiency of hot electron transfer, *i.e.* the ratio of the number of reduced molecules to the number of transferred hot electrons?

Emiliano Cortés answered: Efficiencies can be estimated, after agreeing upon a definition of efficiency. It is challenging to count or estimate the number of carriers, but it is possible to estimate the number of absorbed photons and converted molecules. We could then estimate the efficiency defined as the number of converted molecules per absorbed photon. In the solution experiments presented in our paper, the number of absorbed photons is equal to the irradiance of the laser multiplied by the absorption cross section and divided by the energy of one photon. The number of converted molecules can be estimated from the increments in the fluorescent signal. On the other hand, experiments at the single molecule level enable the counting of reduction events. This can be translated into reduction events (or transferred electrons)/absorbed photons. This could serve as an estimation of the number of 'useful' carriers, as long as the limiting regent is the carriers and not the molecules.

Ruben Hamans queried: In your simulations of the resistive losses, I see that the losses are typically higher in the middle of the particle than at the edges. However, your DNA-PAINT maps look very binary in that a particle is either fully covered with DNA strands or completely lacking DNA strands. Do you think that the DNA-PAINT method can eventually be used to gain a more quantitative understanding of the resistive losses in a single plasmonic particle?

Emiliano Cortés responded: We have previously shown that by performing a power-dependent mapping of the structure it is possible to resolve the initial steps of thiol-desorption in the Au structures (please see Figure 3g in our previous study).[1] As shown in that figure, the thiol-desorption reaction is initiated in the middle part of the rod, matching with the resistive losses map of the structure. It is also possible to quantify the number of Au–S bond cleavages from that power-dependence study.

1 S. Simoncelli, Y. Li, E. Cortés and S. Maier, *ACS Nano*, 2018, **12**, 2184–2192.

Zachary Schultz asked: There are some reports that the Fermi level changes in nanoparticles as a function of nanoparticle size. Your single particle measurements should be able to detect these changes. Have you looked into this effect and do you expect to see any changes?

Emiliano Cortés replied: This is an interesting point. We have not yet carried out size-dependence measurements in order to answer this question. Changes in the Fermi level are expected as a result of changes in the external applied potential, the size of the Au NP and the chemical composition at its interface.[1] However, in our experiments, negligible changes in the scattering spectra were observed with the applied potential unless polymerization took place, consequently changing the refractive index around the AuNP drastically (see Figures 1d (ii/iii) and S4 in a previous study by Pensa et al.).[2] This points towards dark-field microscopy not being the most suitable detection method for evaluating changes in the Fermi level alone, unless these changes trigger a process that modifies the local refractive index around the nanoparticle. The combination of electrochemistry and another optical detection method might be better suited for this purpose.

1 M. D. Scanlon, P. Peljo, M. A. Méndez, E. Smirnov and H. H. Girault, *Chem. Sci.*, 2015, **6**, 2705–2720.
2 E. Pensa, J. Gargiulo, A. Lauri, S. Schlücker, E. Cortés and S. A. Maier, *Nano Lett.*, 2019, **19**, 1867–1874.

A Mount enquired: What is the synthesis protocol and resulting thickness of the capping layer in Fig. 1b?

There appears to be an error in the redox equation (Fig. 1b(ii)), which doesn't have charge balance. I presume that the reduced PANI form should be shown schematically as [R–NH–] in order to be consistent with the product shown in Fig. 1c. In any case, isn't the actual redox reaction in this experiment more complicated, as 1e and 2e oxidation is known to occur in PANI? What complication(s) would this additional complexity introduce into your mechanisms? It is also well established for bulk PANI that there is asymmetry in the PANI CV. Indeed the CV in Fig 1b(ii) looks very similar to that of bulk PANI modified electrodes. The asymmetry in the redox peak is not assigned to irreversible electron transfer but a change in phase between the conducting, solvated, charged and hydrophilic oxidised form and the hydrophobic and compact semiconducting or insulating reduced form. In this case, as a change in the redox potential of PANI would be expected to reflect this change in form, would the delta lambda effect not be more likely to correlate with charge (redox composition) than with potential E?

Emiliano Cortés answered: Fig. 1b shows the optoelectrochemical response of a single gold nanoparticle covered with PANI. The aim of this experiment was to show that by using the setup depicted in Fig. 1a it is possible to follow the redox process at the single particle level. Details regarding the synthesis and characterization of AuNP@PANI are included in the experimental section of the paper (see 'Sample preparation for optoelectrochemical measurements' in DOI: 10.1039/c8fd00138c). The synthesis was carried out *via* chemical oxidative polymerization following the protocol described by Xing *et al.*[1] Briefly, oxidation of the aniline monomer was achieved in a strong acidic medium by using ammonium persulfate as a redox initiator at room temperature. The PANI thickness was estimated to be *ca.* 19 nm.

In the above context, we agree that the redox reaction associated with PANI is more complicated than the simple electron transfer that is usually sketched (*cf.* Fig. 1b(i)). As mentioned here, the charge transfer process has been proposed to occur in parallel to other phenomena such as the exchange of counter ions or solvent molecules and elastic deformation in the polymer film, among other examples.[2] However, all these phenomena contribute to the change in the dielectric constant of PANI, which is well known to be different for the two PANI forms studied here (fully reduced 'leucoemeraldine' and the partially oxidized 'emeraldine').[3] This change in the dielectric constant, which modifies the refractive index around the plasmonic nanoparticle, is what we are monitoring optically. Then, for the experiment depicted in Fig. 1b, the shifts in the scattering maximum wavelength ($\Delta\lambda_{max}$) are a consequence of the applied potential. Further experiments and assumptions must be carried out and made in order to satisfactorily correlate $\Delta\lambda_{max}$ with the exact redox composition of the polymer, *i.e.* the charge of the polymer along the applied potential window must be unambiguously determined.

On the other hand, Fig. 1c corresponds to plasmon-assisted aniline electropolymerization on single gold nanoparticles. Here, we study the influence of plasmon excitation on the onset potential that is needed to trigger the polymerization of aniline on single Au nanoparticles, *i.e.* we are focused on the initial step of the reaction shown in Fig. 1c(ii). Then, the composition and rate of polymerization would only affect the growing-slope of the curve $\Delta\lambda_{max}$ – E. In this case we have verified that very thin layers of PANI (less than 5 nm) can be detected optically due to the large difference in the refractive index between water (*i.e.* prior to polymerization) and PANI around the nanoparticle.

1 S. Xing, L. H. Tan, M. Yang, M. Pan, Y. Lv, Q. Tang, Y. Yang and H. Chen, *J. Mater. Chem.*, 2009, **19**, 3286–3291.
2 E. M. Andrade, F. V. Molina, M. I. Florit and D. Posadas, *Electrochem. Solid-State Lett.*, 2000, **3**, 504–507.
3 A. Baba, S. Tian, F. Stefani, C. Xia, Z. Wang, R. C. Advincula, D. Johannsmann and W. Knoll, *J. Electroanal. Chem.*, 2004, **562**, 95–103.

Laura Torrente-Murciano queried: This is a fundamental question directly related to this paper but also to a number of papers related to plasmonic catalysis discussed during the meeting.

If I had to compare plasmonic-driven catalysis with conventional photocatalysis (*e.g.* TiO2), in the latter case there are reduction and oxidation half-reactions that consume electrons and holes, respectively. However, on many occasions in the case of hot-electron driven catalysis, like in Fig. 3 of this paper (hot electron reduction of resazurin), only electrons are consumed. Where are these electrons coming from or, in other words, where are the holes going to?

Emiliano Cortés responded: In every reaction involving electron or hole transfer there must be a counter reaction fulfilling the redox cycle. In many cases the solvent could play that role, however, that might limit the rate of the reaction. This is a fundamental point to address the optimization of efficiencies in systems involving a charge transfer process. It is important to play with electron or hole scavengers in order to disentangle this point (see for example a previous study by Rao *et al.*)[1] Another possibility would be to split the redox reactions, as these occur in any electrochemical experiment (see our example in Fig. 1).

1 V. G. Rao, U. Aslam and S. Linic, *J. Am. Chem. Soc.*, 2019, **141**, 643–647.

Phillip Christopher replied: In many of the plasmon-mediated processes discussed in the literature, redox chemistry is driven that looks a lot like semiconductor photocatalysis. There can also be plasmon enhanced electrocatalytic processes, where a connection to an electrical circuit maintains charge neutrality. However, there is also another proposed process where an electron (or hole) transiently transfers to an adsorbed species. The transient transfer of charge induces forces on the molecule, which can result in the deposition of vibrational energy into a potential energy surface and induced chemistry. This sort of inelastic transient electron transfer is well-known in the surface science field as the Menzel Gomer Redhead (MGR) model, which was proposed in the mid 1960s for chemistry on metal surfaces induced by electron bombardment.

Yuri Diaz Fernandez asked: For the example of single particle spectroscopy detection of the photo-electrochemical polymerisation of PANI:

a) Did you observe non-specific electrochemical polymerisation on the ITO substrate?

b) How did you deconvolute the particle–surface polymerisation from the ITO polymerisation, considering that the effective refractive index and the plasmonic response will result from the combination of both?

Emiliano Cortés answered: As shown in Figure 1d (ii/iii) in Pensa *et al.*,[1] non-specific polymerization on ITO was not observed for illuminated Au nanoparticles below the electrochemical polymerization threshold E_{onset} ($E_{\mathrm{W}} = 0.68$ V). Only when the polymerization is electrochemically controlled, *i.e.* Ew ≥ 0.68 V, does the reaction take place over the whole electrode (ITO and Au NPs) and non-specific polymerization can be observed by dark-field microscopy.

As mentioned above, polymerization was only observed on Au NPs that were illuminated, meaning that PANI/ITO is only generated at the interface of AuNP/ITO. We have simulated this situation, as described in the supporting information of Pensa *et al.*[1] Briefly, 80 nm Au NPs surrounded by different thicknesses of PANI layer are placed on an ITO surface. The substrate is immersed in water. Numerical simulation shows a linear-like dependence of the maximum scattering wavelength on the thickness (see Figure S1). This trend is in line with experimental results where the PANI layer is increased around the Au NP by increasing either the illumination time or power (see Figure S5 in Pensa *et al.*).[1]

1 E. Pensa, J. Gargiulo, A. Lauri, S. Schlücker, E. Cortés and S. A. Maier, *Nano Lett.*, 2019, **19**, 1867–1874.

Yonatan Sivan enquired: Regarding your temperature control experiments, do you observe a signature unique to high energy non-thermal electrons and, if so, can you say how much energy goes into raising the temperature and how much goes into creating these non-thermal electrons?

Emiliano Cortés responded: We do not have an experiment where we can distinguish between high-energy non-thermal carriers and thermalized carriers. However, we have found that the effective energy contribution of the carrier to the photocatalytic effect (*i.e.* the energy that a carrier can transfer to a nearby molecule) depends on the excitation wavelength. This dependency has been measured at constant lattice temperature and at the single particle level.[1] If the temperature of the electrons was thermalized with the lattice (under our experimental conditions), our results would indicate that non-thermal electrons are driving the process. Regarding your last question, it is challenging to measure the steady state energy distribution between the lattice, thermal carriers and non-thermal carriers, and we have not done this yet.

1 E. Pensa, J. Gargiulo, A. Lauri, S. Schlücker, E. Cortés and S. A. Maier, *Nano Lett.*, 2019, **19**, 1867–1874.

Javier Aizpurua opened a general discussion of the papers by Jacob Khurgin, Phillip Christopher and Emiliano Cortés, and addressed Phillip Christopher: I am wondering what else we could do to access the dynamics of chemical reactions. Most of the current experimental approaches used by this community rely on optical spectroscopy to trace chemical reactions, but sometimes all we can detect is a small shift and/or broadening of an optical marking peak. This, sometimes, and after lots of nice control experiments and assumptions (for example an assumption of direct transfer), drives the main conclusions of the dynamics. One can detect a small percentage of change in the absorbance for instance, such as in your paper, and one can conclude with slight uncertainty regarding quenching. What can we do on top of this? What can we do to go beyond spectroscopy to address the dynamics? Can we simplify the systems and carry out real-time experiments in some way? What are the current efforts along these lines? This, of course, does not mean that the current information obtained *via* optical spectroscopy is not valuable or meritorious, as you have shown in your paper.

Phillip Christopher replied: There is work being carried out on very well defined systems that attempts to watch chemical transformations simultaneously with temporal and spatial resolution. This is a very tough task. Work with microscopy often does not have the required temporal resolution, while time-resolved work often does not have the required spatial resolution. Understanding the dynamics associated with processes like plasmon-mediated chemistry will likely require some insights to be gained from multiple experimental and theoretical approaches.

Naomi Halas asked: How can theorists move beyond the theory they are currently pursuing to also address the energies of adsorbates on surfaces, and to answer more of the questions we have regarding the processes and mechanisms of plasmonic photocatalysis? For accurate adsorbate energies, does this not involve extending theoretical efforts to include strategies such as embedded wavefunction approaches?

Javier Aizpurua answered: The theoretical challenge to address the energies involved in plasmonic photocatalysis, as well as the associated dynamics, is as demanding, if not more, than the experimental challenge. *Ab initio* efforts, together with molecular dynamic simulations, have been able to address some aspects of the energies of simple adsorbates, even in a dynamical way. However, those studies are restricted to 'good' metallic surfaces. In those studies, the density of states produced by plasmonic decay is still missing. To reconcile these two aspects would be a tremendous challenge, and I agree that theory is in need of a substantial methodological improvement to properly address all of the dynamical aspects of plasmon-induced catalysis.

Javier Aizpurua commented further: Although I encourage experimentalists to try to access the dynamics of reactions with more direct experimental techniques, I realize, and agree with Naomi Halas, that theory is in need of the same or even more development to address the challenges of plasmonically driven chemistry. In proper theoretical approaches, we would need to combine quantum chemistry with condensed matter physics on different timescales and for large systems, which is very challenging, and so this would also require a similar effort in theory.

Jeremy Baumberg returned to the discussion of the paper by Phillip Christopher: You use a thiol SAM and show that the optical properties change, which you ascribe to some sort of molecular hybridisation with gold. However it is known that at least 30% of Au atoms under such a thiol SAM are plucked out into adatom sites or staples between the S atoms. In this case, the roughness and surface electron states of the Au change drastically, and so we would already expect changes in the optical properties. Is this not what you see? Other techniques for probing the surface also have a tendency to move around these adatoms, so it is not clear whether other techniques, other than perhaps low temperature STM, are helpful for understanding this. Are there other techniques you would advocate that are gentle enough?

Phillip Christopher responded: Unravelling the roles of adsorbate-induced metal surface reconstruction and metal–molecule hybridized electronic states on plasmon decay and interfacial energy transfer is a very tough task, but could certainly teach us something. Both mechanisms make good sense as possible sources of enhanced surface scattering of electrons and plasmon decay. This could potentially be interrogated *via* variable temperature UV-Vis spectroscopy, where one might expect that at extremely low temperatures a metal surface would be kinetically trapped from reconstruction upon molecular adsorption, while reconstruction could occur at higher temperatures. However, the metal–molecule hybridization should also change upon surface reconstruction. In order to tease out these details, theory would likely be most effective once we can simultaneously describe plasmons and electronic structure with sufficient accuracy in a single calculation.

Sebastian Schlücker commented: The analysis of molecular adsorbates on plasmonic nanostructures requires experimental techniques to provide molecular/chemical specificity and surface selectivity. Such techniques are available, including SERS and vibrational SFG. However, theory is lacking behind in this respect. We therefore need strong support from our colleagues in theory who are able to reliably predict the properties of molecular adsorbates, in particular experimental observables such as vibrational spectra (surface-enhanced IR/Raman/fluorescence).

Emiliano Cortés replied: I agree with this comment and we should keep in mind that the excited states (vibrational and electronic) may play an important role in these transformations. We should be able to predict new reaction pathways if we know the energy landscape of the adsorbed molecules.

Jacob Khurgin also replied: I agree entirely. I am not sure that I can do much in this field but hopefully younger scientists can.

Rupert Oulton returned to the discussion of the paper by Phillip Christopher by communicating: Jacob Khurgin talked about the large density of states in metals, and Emiliano Cortés spoke of the relatively small number of molecules in comparison. Your paper even highlights this discrepancy. What is thus the intuitive picture for chemically induced damping?

There was also some discussion of the surface modification of gold by the molecule and electronic states of the molecule. Would it not be straightforward to rule out the role of electronic states by saturating them under high intensity illumination?

Phillip Christopher communicated in reply: The Landau damping process of plasmon decay and the generation of hot carriers that Jacob Khurgin discussed occurs due to the scattering of electrons off of the plasmonic nanostructure surface. In this case, the electronic transitions involved in the generation of the initial, nascent hot carriers will involve electronic states at the metal surfaces. The addition of adsorbates will specifically influence metal electronic states at the surface and further introduce new states due to hybridization. Thus, even though the number of molecules is small compared to the number of metal atoms, they are located at the surface where hot carrier formation initially occurs and will further introduce relatively localized electronic states that have a high probability of being excited during surface scattering.

Your idea of saturating these states through high intensity excitation is interesting. I would be worried that this would induce chemical transformations in the molecules, which would make analysis tough. Furthermore, the lifetimes of these excited states are very short (~few fs).

Emiliano Cortés provided a general comment: I think we should agree, sooner rather than later, on a set of basic principles for the field of hot-electron induced science. Otherwise we are at risk of reporting efficiencies that have been calculated in many different ways (which would make the data useless for benchmarking), or of reporting plasmonic photocatalysts that demonstrate no real impact or improvement over existing materials or technologies. Selectivity is a much more standardized concept, and it is clearer as to how to report it (% of each generated product). However, for efficiencies I think that we are already facing a problem. Taking into account all of the processes involved in a plasmonic photocatalyst, perhaps the ratio of (generated product(s) per gram of photocatalyst)/(total number of incident photons) could be a possible, rather simpler, metric that could be used to calculate the overall performance. There may be other options, but I think we should agree on this topic.

Jeremy Baumberg opened discussion of the paper by John C. Polanyi: You are making nice 'beams' on an atomic surface, but I am worried about constraining the molecular directions just along the lines of copper atoms. Does this not constrain the output directions of the products and so limit the type of reaction that you can do? Is this not like doing reactions on a chess board? How will this change the chemistry that is achievable? Can the molecules adapt and give you something useful, particularly if there are two products trying to head in different directions?

John Polanyi answered: We should have stressed that we are carrying out our reactions on an unmodified surface of a copper crystal, on which we and others have seen varied dynamics depending on the reagents. The surface beams are not due to irregularities in the surface. They are due to what I call 'funny walks'. We have previously reported a preference for CH_2, recoiling in the electron-induced reaction of CH_2I_2 on the same surface, Cu(110), to 'walk' on its residual bonds between the rows of Cu atoms.[1] In the present work we have another biradical, CF_2, walking (we call it 'ratcheting') directly along the close-packed rows of Cu atoms. Molecular dynamics showed that the reason for these specialized motions, in both cases, was a combination of linear recoil with a rocking motion. Linear momentum is essential to the overall motion. The rocking has a more subtle role, assisting in detaching the 'legs' of this walker successively from the surface as it proceeds along its path. What we have shown here is that this novel directional walking can be put to use in selecting the impact parameter in subsequent reactive encounters in which the walking 'projectile' strikes a fixed chemisorbed 'target'. The impact parameter is variable, and is determinable from the STM image. We can do something ‘useful’ (to use your term) by shedding light, as in Fig. 6 (DOI: 10.1039/c8fd00137e), on the dynamics of a reaction related to Fischer–Tropsch polymerization. It is true that we only do something ‘useful’ largely by accident.

1 A. Chatterjee, F. Cheng, L. Leung, M. Luo, Z. Ning and J. C. Polanyi, *J. Phys. Chem. C*, 2014, **118**, 25525–25533.

Michael Ashfold asked: What limits the range of collision energies that can be investigated with the ‘surface-molecular-beam’ method? The outcomes demonstrated in your paper involve the projectile and target species combining, or experiencing a non-reactive ‘near-miss’. Can you envisage studying a sufficiently exothermic reaction by this method that might yield two products and, if so, how might their recoil be constrained by registration with the underlying array of metal atoms?

John Polanyi responded: The upper limit of the collision energy in the case of the CF_2 ‘projectile’ is the energy released in the anti-bonding anionic state, as CF_2 recoils from the strongly surface-bound F-atom. This has been computed to be approximately 1.2 eV (see Fig. S2 of our previous study).[1] This is, therefore, our maximum possible collision energy. The CF_2 cools thereafter as it travels increasing distances along a copper row towards a target. One can see the effect of this cooling in the experimental results of Fig. 3b for CF_2 directed at zero impact parameter at a stationary chemisorbed CF_2 target. In the case that the CF_2 projectile travel distance was only $\sim$10 Å, the reaction was found to give forward scattered C_2F_4 (this reaction product being scattered on the surface forward along the continuation of the direction of the incoming beam). If, however, the travel distance was increased to 30 Å, the cooled CF_2 was observed to give product C_2F_4 scattered largely backwards (back towards the origin of the beam). This is revealing of the molecular dynamics.

Returning to your question, this collision energy should suffice for barrier-crossing in some exothermic reactions. Preliminary results from our laboratory have indeed, as you suggest, shown evidence of exchange reactions at a selected impact parameter yielding two new products. It is a mistake to think that the product recoil in the present work is being artificially constrained; the reagents are coming together on an unmodified clean copper crystal. Reactions on such surfaces are known to provide a rich variety of outcomes.

1 K. Anggara, L. Leung, M. J. Timm, Z. Hu and J. C. Polanyi, *Sci. Adv.*, 2018, **4**, eaau2821.

Naomi Halas queried: The animation you showed in your presentation appeared to simulate bonds between copper and carbon forming and breaking on the surface. Is that what is really going on here? Why does the adsorbate molecule move across the surface?

John Polanyi replied: The animation that I showed did indeed simulate the ‘ratcheting’ recoil of CF_2, moving along a close-packed row of Cu atoms on Cu(110), and involving successive bonding to the copper atoms of the row. The clue to this binding came from our observation of the molecular dynamics of the successive shortening of the C–Cu separation as the travelling carbon end of CF_2 came atop a copper atom (single-bond from an sp^3 hybridised carbon) or subsequently between a pair of copper atoms (a pair of bonds from an sp^2 hybridised carbon). You have asked (sensibly) why CF_2 is moving along the row. This is because it was formed, following electron attachment, from an antibonding state of the CF_3^- anion in which $F.CF_2$ repulsion (the dot indicates the locus of the repulsion) leads to F bonding strongly to the surface and the CF_2 (in its ratcheting motion, discussed above) recoiling a substantial distance along the close-packed row of Cu atoms. The CF_2 recoil travel direction is opposite to a slightly (but visibly) stretched C–F bond directed along the Cu-row, which is the bond broken in electron-induced dissociation.

Reinhard J. Maurer enquired: How many electrons are typically transferred in a pulse? Can surface-molecular-beams be introduced with positive and negative bias voltage?

John Polanyi answered: We have shown *via* a study of reaction rate *versus* current (see Fig. S8 of our previous study)[1] that the electron-induced dissociation of CF_3 adsorbed on copper is a single-electron process. We typically used a current of a few nanoamps for several seconds to induce a reactive event. This translated into a yield of $\sim 10^{-11}$ reactive events per electron, at a bias voltage of +1.3 V, as reported here. Our experiments were restricted to positive surface bias since (as described in Section 2.2) we are able to compute approximate energy states for the CF_3 anion at the surface.

1 K. Anggara, L. Leung, M. J. Timm, Z. Hu and J. C. Polanyi, *Sci. Adv.*, 2018, **4**, eaau2821.

Phillip Christopher asked: In studies of molecular beams interacting with metal surfaces, there is often a question of whether energy dissipation from exothermic chemical events is dissipated through adiabatic or non-adiabatic mechanisms. In your demonstration of molecular beams on surfaces, do you have any thoughts as to whether the projectiles dissipate energy to the surface through adiabatic or non-adiabatic mechanisms?

John Polanyi responded: Our impulsive two-state (I2S) model (whose antecedents lie in the work of Menzel, Gomer and Redhead, the famous MGR) is able to describe the varied dynamics of electron-induced product recoil, as observed experimentally by STM. We reference examples in our paper. This model takes no account of non-adiabaticity. The CF_2 loses its energy to surface vibrations, *i.e.* to phonon excitation. Despite the neglect of non-adiabaticity, the dynamics (average recoil distances and recoil directions) resemble those observed for molecules engaged in long-range excursions and reactions at the surfaces studied. Of course, in reality, non-adiabaticity may nonetheless be involved, as your question suggests.

Bart de Nijs communicated: You mention in your article that you look for an anisotropic shape to identify the CF_3 molecule on the (110) surface. Do you have the resolution to determine the orientation of the molecule before breaking the molecular bond and launching the CF_2, or will the CF_2 occasionally be launched in the opposite direction?

John Polanyi communicated in reply: You are attentive. When our STM tip was working well we could indeed detect asymmetry in the image of the chemisorbed CF_3. This was indicative of the small extension in bond length of the C–F that pointed along a Cu-row, as compared with the other two C–F bonds. Electron irradiation at +1.3 eV (positive surface; threshold energy for reaction $\sim$0.9eV) resulted in a CF_2 'projectile' recoiling preferentially away from the extended-bond end of the parent CF_3 molecule.

Jacob Khurgin opened discussion of Reinhard J. Maurer's paper: The question is regarding which hot carriers are responsible for the catalysis; they can be 'primary' hot carriers excited by the decay of plasmons or they can be 'secondary' carriers that have experienced multiple electron–electron collisions and then thermalized with electron temperature T_e. I presume that since T_e is proportional to the incoming light intensity and the effect (catalysis or just electron emission) depends on the presence of hot carriers in the tail of the distribution, one would observe some kind of nonlinear effect/intensity dependence in the experiments if the secondary thermalized carriers were responsible for this effect. Has this been observed?

Reinhard J. Maurer answered: This is indeed an open question of debate. In our approach, we only capture thermalized electrons at elevated T_e. There are several instances in the literature in which a time-dependent change in T_e can correctly capture the measurable effects of light illumination, *e.g.* in light-driven desorption. However, there is also some experimental evidence from molecular beam scattering that suggests that 'primary' transient molecular excitations dominate molecule–metal energy transfer.

Phillip Christopher remarked: There are some very nice experimental results from the 1980s and 1990s, for example the work of Gerhard Ertl,[1] Wilson Ho[2] and David King,[3] that demonstrated power law dependences of reaction yield on photon flux for pulsed laser driven chemical processes at metal surfaces. Further observations of a transition from linear photon intensity dependence to 'superlinear' dependence have also been reported in similar studies. Two pulse correlation experiments have been carried out to demonstrate that in the superlinear regime the reactions occur on timescales that are much too fast (<1 ps after the pulse) to be explained by thermal (phonon mediated) processes.

1 M. Bonn, S. Funk, C. Hess, D. N. Denzler, C. Stampfl, M. Scheffler, M. Wolf and G. Ertl, *Science*, 1999, **285**, 1042–1045.
2 F. M. Zimmermann and W. Ho, *Surf. Sci. Rep.*, 1995, **22**, 127–247.
3 S. A. Buntin, L. J. Richter, R. R. Cavanagh and D. S. King, *Phys. Rev. Lett.*, 1988, **61**, 1321–1324.

Jacob Khurgin commented: I think you mean lattice temperature. Can they still be 'secondary electrons' after a few e–e collisions?

John Polanyi enquired: As you well know, there has been much interest over the years in the dynamics of collisional vibrational ladder-climbing, which, in order to lead to molecular dissociation, must compete with its converse, collisional vibrational de-activation. Your molecular dynamics studies of the hot-electron mediated dissociation of H_2 on Ag(111) should teach us new things about how this balance of opposing processes can result in molecular dissociation. Would you care to comment?

Reinhard J. Maurer responded: On the basis of our current results, we are not in a position to confidently comment on this matter. However, we find that electronic friction due to hot-electron effects is larger for vibrational motion than it is for rotational or translational molecular motion of the adsorbate. The result is that hot electrons selectively promote molecule–metal energy transfer into and out of the intramolecular stretch of H_2. In the case of a hot-electron-heated metal surface, this points towards a qualitative trend of increasing the probability of dissociation.

Javier Aizpurua asked: You have developed a very nice description of molecular scattering on metallic surfaces which combines molecular dynamics with *ab initio* inputs. In this combined description, you assume an initial trajectory of the molecules; how much do the results depend on the initial conditions of the molecule (orientation and velocity, for instance)? Regarding the lack of memory, what are your plans to improve the current description based on the Markovian approximation? Finally, you treat a perfectly flat surface, which is a very useful geometry, but how could you incorporate more complex surfaces or nano-antennas? In other words, how could we transfer this to incorporate localised plasmons in your interactions with the molecule?

Reinhard J. Maurer replied: We find that the initial conditions play an important role in determining the extent of hot-electron-driven molecule–metal energy transfer and the subsequent measurable reaction probabilities (see, for example, Fig. 3 in DOI: 10.1039/c8fd00140e). Our plan is to improve our current description to include memory effects by explicitly integrating over electronic friction at past times using a generalised Langevin dynamics approach. We believe that this will enable us to employ electronic friction-based approaches for hot-electron chemistry in cases where thermalised hot-electron distributions are the main cause of molecule–metal energy transfer. While we are free to use any periodic surface structure in our simulations, we are currently not able to capture the light-matter interaction that gives rise to plasmon resonances directly. Therefore, simulating nanopatterned surfaces as such might not correctly capture the ensuing plasmonic effects. To capture the effects of plasmon scattering on molecular states, we would certainly have to model non-thermalised electronic excitations giving rise to transient molecule–metal charge transfer. This is clearly beyond the capabilities of electronic friction theory.

Xiaofei Xiao remarked: Thank you for giving your presentation. Current numerical methods can address relatively simple simulations. However, simulations become harder as structures become more complex. Some problems, such as many-body systems, cannot be solved due to various reasons, such as insufficient memory. Machine learning may be a solution. I saw that you have already used machine learning in your project. My questions are:

(1) What are the advantages and disadvantages of using machine learning in physics?

(2) What kinds of problems do you think this method are suitable for?

(3) What is the future or outlook of this method in physics, especially in plasmonics and catalysis?

Reinhard J. Maurer answered: We have used machine learning in the form of feed-forward neural-networks to generate interpolations of total energies and electronic friction tensors from density functional theory (DFT) as a function of the molecular degrees of freedom. In doing so, we were able to retain the predictive capabilities of DFT while performing simulations of tens of thousands of reaction events—an absolute necessity to determine statistically meaningful predictions of measurable reaction probabilities. In chemical reaction dynamics, machine learning has become a powerful tool for extending the time- and length-scales of electronic structure methods. I believe that in the near future we will see many more applications to this end that will enable previously impossible applications of *ab initio* methods, such as the simulation of reaction dynamics in the context of plasmonics and catalysis. It is important to note that, for machine learning to produce reliable representations of *ab initio* methods, reliable and consistent training data of high-quality needs to be generated, which is highly non-trivial.

John Polanyi asked: In your study of the reactive scattering of H_2 at a metal, you considered the effect on energy transfer to the H_2 of molecular cartwheeling. I recall a previous Faraday Discussion (No. 62, on potential energy surfaces) during which it was noted that enhanced rotation would lead to a regime in which the time spent in the preferred geometry for energy transfer or a reaction was too short to permit the process to occur. Is this outside the range of j that you examined?

Reinhard J. Maurer responded: In this work, we studied initial conditions with rotational quanta up to $j = 5$. We find that the vibrational de-excitation probability ($\nu = 2$ to $\nu = 1$) increases slightly for $j = 5$, in comparison to $j = 0$. While the residence time on the surface is indeed shorter for higher rotational states, the molecular velocity is also larger, which, together with the electronic friction tensor, defines the nonadiabatic forces that act on the impinging molecule. The latter is the main reason why nonadiabatic molecule-to-surface energy dissipation is larger for higher rotational states. However, it should be noted that we find significant differences between different orientations. Fig. 3(a) in our paper shows the de-excitation probability for ($\nu = 2, j = 5, m_j = 0/5$) to ($\nu = 1, j = 5$) scattering, where $m_j = 0$ and $m_j = 5$ correspond to the cartwheel and helicopter orientations, respectively. The de-excitation probability and ensuing energy loss are much larger in the helicopter motion due to the increased surface residence time and the ability of the molecule to penetrate regions of the potential energy surface in which larger electronic friction forces act on the molecule.

Francesca Baletto queried: Adsorption might alter the metallic substrate too. Is there any specific reason for keeping the Ag-substrate fixed?

Are there any limitations to the use of MDEF for depicting the adsorption of small molecules such as, O_2, H_2O, H_2, OH, CO and CO_2 on different metallic (mono- and bi-metallic) substrates?

Reinhard J. Maurer replied: Principally, our methodology is not restricted to a particular adsorbate size or to a frozen surface. Using on-the-fly *ab initio* calculations, we could use any choice of system. The main limitation is the computational cost associated with the evaluation of electronic friction from density functional theory at each time step. This is why we have used a neural-network-based interpolation to construct a 6-dimensional (adsorbate degrees of freedom) tensor landscape of electronic friction based on DFT data, allowing us to perform many hundreds of thousands of simulations. We are currently developing an interpolation representation of tensorial friction that will allow us to go beyond the frozen substrate approximation.

Sebastian Rejman returned to discussion of the paper by John Polanyi: Why does the CF_2 travel somewhat further on the surface than the F-atom? At least from a consideration of conservation of momentum, it should be the other way around, as the CF_2 is a lot heavier.

John Polanyi answered: The alert group doing the experiments were as amazed as you are; you are right about the expectation from conservation of momentum. Why does the light F-atom barely recoil (4 Å on average), whereas CF_2 recoils a long distance (20 Å on average)?

My co-workers' subsequent calculation of the binding energies of the two fragments to the underlying copper explained the short recoil of F; its binding energy to the surface was large, 5.01eV, in comparison with 1.89eV for CF_2 (both computed at a short-bridge site, between a pair of Cu atoms along a Cu-row).

That still left a mystery as to why the CF_2 travelled so far. Molecular dynamics gave the answer. It involved the walking (we call it 'ratcheting') of the divalent CF_2 radical from one Cu atom to the next, directly along a copper row. We had previously seen something similar for a different diradical, methylene CH_2, recoiling this time from an I-atom to which it had been bound and walking in this case between copper rows.[1] Perhaps such 'funny walks' will turn out to be common, especially for recoiling polyvalent radicals which have two or more 'legs' on which to walk.

[1] A. Chatterjee, F. Cheng, L. Leung, M. Luo, Z. Ning and J. C. Polanyi, *J. Phys. Chem. C*, 2014, **118**, 25525–25533.

Conflicts of interest

There are no conflicts to declare.