DISCUSSIONS

Scattering in extreme environments: general discussion

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Viet Le Duc opened a discussion of the paper by Kang-Kuen Ni: How will the relative orientation between two different KRb molecules affect the outcome of the nuclear spin coupling measurement? Will this measurement be done directly or indirectly, and if indirectly, will there be any contribution from the orientation effect that needs to be accounted for during data analysis?

Kang-Kuen Ni answered: The lab-frame orientations of the two KRb molecules are not controlled. The molecules are prepared at an ultra-low temperature and the collisions proceed with one unit of angular momentum (p-wave) because KRb molecules are indistinguishable fermions here. When a phase is applied to one of the KRb molecules, the collisions proceed with no angular momentum (s-wave) because the phase distinguishes the fermionic KRb molecules. As a consequence, there are rules related to angular momentum conservation to follow, but I don't believe there is an orientation effect.

Eva Pluhařová asked: What properties do the molecules need to have in order to perform such experiments? Would, for example, KI be suitable as well?

Kang-Kuen Ni replied: The experiment makes use of a system in which we can prepare a reactant initially in a single quantum state (an entangled nuclear spin state) and a reaction that conveniently exchanges atom partners. Also, coincident

detection of product pairs from the same reaction events is crucial to decipher non-trivial correlations. These are tools we now have available for ultra-cold KRb molecules. But the chemical phenomena may be more general than the specific case we study here (https://doi.org/10.1039/d3fd00175j). So I would say it's more about the tools available to really probe the underlying question, not necessary the specific properties of the molecules.

Christopher Reilly enquired: Can you describe what you would expect to be the physical mechanism that could drive decoherence during your chemical reaction?

Kang-Kuen Ni responded: Physical mechanisms of how nuclear spin couples to other degrees of freedom at short range, within the reaction complex, is precisely what we are hoping to learn. For example, nuclear spin can couple to mechanical angular momentum through nuclear quadrupole interactions. Other unknown mechanisms are yet to be explored! It is suffice to say that we know very little and we have to do the experiments to learn more and begin to decipher the underlying world.

Olivia A. Krohn remarked: Thank you for an excellent talk. I wondered under what conditions you are testing the coherence of the nuclear spin states. For example, are you moving the molecular clouds as you will in the experiment and testing coherence after? What do you expect to be the largest sources of decoherence in this system?

Kang-Kuen Ni answered: Thank you. I am testing the coherence of the nuclear spins in the stage of the reaction complex as atoms exchange partners. The coherence of the reactant nuclear spins (after we move clouds, *etc.*) is tested separately *via* a Ramsey experiment. This way we can tell whether decoherence occurs during reactant preparation or during reaction in the complex.

Arthur G. Suits commented: This is a fascinating proposal. Will there be some means to quantify the entanglement you hope to observe?

Kang-Kuen Ni replied: This is an excellent question. We believe the product state outcome, the coherent control of which is the aim in this paper (https://doi.org/10.1039/d3fd00175j), will allow us to quantify the entanglement of the spins of the reactants. But we would also like to measure the degree of entanglement of the product pairs, which would require a direct phase measurement on the product. We do not yet have a feasible scheme.

Hua Guo said: I was wondering if the dephasing can be controlled by taking advantage of the coupling between the nuclear and electronic spins. I understand that the current experiment is with singlet KRb, but I assume that it is possible to prepare triplet KRb. For these species, there will be hyperfine states that can presumably be prepared using the same procedure, but the involvement of the electronic spin might lead to much stronger coupling with nuclear dynamics. Additionally, rotationally excited triplet KRb will also induce additional coupling between the rotational angular momentum and the spins, which will make the situation even more interesting.

Kang-Kuen Ni responded: I certainly agree. This proposed approach (https://doi.org/10.1039/d3fd00175j) is a new way to scrutinize the role of nuclear spins in reactions, at short range. Usually we don't think of nuclear spin participating in reactions, but there are ways they may, for example, through coupling to electron spins or through nuclear quadrupole interactions for molecules in rotationally excited states. As an aside, ultracold triplet KRb molecules have been prepared (in prior work in 2008),[1] and one can certainly try these experiments as well.

1 K.-K. Ni, S. Ospelkaus, M. H. G. de Miranda, A. Pe'er, B. Neyenhuis, J. J. Zirbel, S. Koto-chigova, P. S. Julienne, D. S. Jin and J. Ye, *Science*, 2008, **322**, 231.

Roland Wester asked: What is the importance of the low translational temperature of the KRb molecules, or their possible quantum degeneracy, for the proposed studies of coherent superpositions of reaction products? Would it be possible to identify systems where such studies can be carried out at higher temperatures, *e.g.*, in molecular hydrogen?

Kang-Kuen Ni answered: I would say the key to the proposed study is single quantum state (including nuclear spins) preparation and coincident detection of products from the same collisional/reactive event. The low translation temperature is not important. I think it's possible to identify other systems, at higher temperature for the proposed study, but I don't know any right now.

Mark Brouard remarked: Thank you for your very thought-provoking paper (https://doi.org/10.1039/d3fd00175j). I was wondering whether you could comment on the likelihood of being able to see similar reaction interferometry effects in the case of electron spin. It has been found, for example, that collisions of molecules in $^2\Sigma$ states can often be treated on the basis that both nuclear spin and electron spin behave as spectators to the scattering.

Kang-Kuen Ni replied: That is a very interesting question. Anything is possible, but we won't know until we design an experiment and carry out a test of the outcome to see what nature gives us. The available time scale might be very short because electron spins themselves may be sensitive to environmental perturbation, such that we could not test the dynamics purely from the perspective of scattering. But one should try!

Alec. M. Wodtke enquired: What about vibrational coherence? Would there be a quantum imprint of coherence, or would it just look the same as a quasi-classical trajectory (QCT) simulation? Can you explain how we should think about this and if experiments to detect the quantum imprint of vibrational coherence might be possible?

Kang-Kuen Ni responded: That's a good question. There may be vibrational coherence, but I think it's much harder to prove it. In the KRb + KRb → K_2 + Rb_2 system, we found previously that the products are distributed among 57 energetically allowed channels (rotational pairs and no vibrational excitation).[1] We used coincidence detection to probe and see that the product distribution is

mostly statistical. It could be that the products are in the superposition of 57 states, but we couldn't feasibly show it. Now, the current paper (https://doi.org/10.1039/d3fd00175j) was established on top of nuclear spin coherence and the way we probed it was through measuring the parity of the correlated rotational states. So one might suggest that rotational states also have to be coherent and therefore possibly in a superposition of 57 states. But we have no way to prove it at the moment.

1 Y. Liu, M.-G. Hu, M. A. Nichols, D. Yang, D. Xie, H. Guo and K.-K. Ni, *Nature*, 2021, 593, 379–384.

Ajeet Srivastav commented: You mentioned in your talk that the product output depends on phase correlation between molecules. I would ask if any phase correlation exists where we do not have any product output or the reaction does not happen at all.

Kang-Kuen Ni answered: Just to clarify, the product state outcome is expected to depend on the phase correlation of the reactant molecules. One of the roles of the interferometer is to "witness" such a phase correlation.

Dmitri Babikov queried: Using your experimental approach, would it be possible to study the effect of phase shifts on non-reactive inelastic rotational state-to-state transitions in molecule–molecule collisions? I could imagine that the values of the rotational state-to-state transition cross sections or rate coefficients would be extremely sensitive to the amount of phase shift introduced between the two eigen-components of the initial state of one of the collision partners. Would it be possible to check this in experiments similar to yours?

Kang-Kuen Ni replied: I think this is very hard for the rotational state-to-state transitions. The reason is because we have not established rotational coherence and such transitions are much more energetic. We have previously studied rotational state-to-state products in a reactive process[1] and found 57 energetically allowed state outcomes. Therefore, seeing phase sensitive effects among these possibilities would be challenging currently.

1 Y. Liu, M.-G. Hu, M. A. Nichols, D. Yang, D. Xie, H. Guo and K.-K. Ni, *Nature*, 2021, 593, 379–384.

Gilbert M. Nathanson asked: Do you think that tuning cavity modes (in the manner of Ebbeson) might bring about additional coherent control in the proposed experiments?

Kang-Kuen Ni responded: That is an interesting thought. Maybe, but we have not thought about it. It will also depend on what degree of freedom tuning the cavity modes alters.

David Chandler said: The K_2Rb_2 reaction complex forms over a deep well and therefore has much energy and a "long lifetime" compared to internal energy redistribution. How do you anticipate that the well depth (energy content) and lifetime of the complex impact the maintenance of coherence in the reaction?

How important is the nature of the reaction? For instance, would an abstraction reaction have a better chance of maintaining coherence throughout the reaction?

Kang-Kuen Ni answered: I think an abstraction reaction should indeed have a better chance of maintaining nuclear spin coherence because there is less time for the different degrees of freedom of molecules to mix. The fact that the existence of the long lifetime complex did not disturb nuclear spin coherence in the one case checked is a pleasant surprise!

Daniel R. Moon opened a discussion of the paper by Helen Chadwick: Could the variation in surface phonon behaviour with temperature account for the temperature-related variations in polarisation effects observed in your measurements? Could one expect similar polarisation effects on stepped surfaces with different terrace orientations, such as Cu(211)?

Helen Chadwick replied: In answer to your first question, increasing the surface temperature will increase the phonon population, which will alter the apparent roughness of the surface that the H_2 molecules sample. This will affect the translationally inelastic scattering channel, which competes with the elastic scattering channel that we are measuring, and so could influence the polarisation effects that we observe as the surface temperature is changed.

And to answer your second question, I would expect there to be rotational orientation effects for scattering of H_2 from the stepped Cu(211) surface, but not that they would necessarily be the same as for the Cu(511) surface. The rotational orientation dependences that are observed are dependent on the surface plane, as shown by the contrasting results for the Cu(511) and Cu(111) surfaces, and the Cu(211) surface again has a different structure at the atomic level, and so the effects for the two stepped surfaces are likely to be different.

Nils Hertl remarked: In your paper (**https://doi.org/10.1039/d4fd00007b**), you showed that Cu(111) has no temperature dependence, whereas Cu(511) does. I was wondering why you have not used a flat Cu(100) surface instead of a Cu(111) surface, because the Cu(511) surface has Cu(100) terraces that are, in contrast to Cu(111), not close-packed and therefore more corrugated than Cu(111). Thus, I would speculate that you might also see a temperature dependence for Cu(100).

Helen Chadwick responded: We used a Cu(111) surface rather than Cu(100) as we have a Cu(111) surface in the lab and we don't have a Cu(100) surface! But yes, it would be interesting to compare the temperature dependence of scattering from a Cu(211) crystal (which has (111) terraces and (100) steps) with that on Cu(111) and likewise the results for Cu(511) with Cu(100), as then the comparison is much more focussed on what happens when steps are added to the surface.

Paul D. Lane enquired: For the stepped Cu(511) surface, do you see any difference in your scattering signals depending on how the surface is oriented with respect to the molecular beam? For clarity, I mean if you rotate the sample about the surface normal so that the molecular beam encounters up steps or down steps, does this change the scattering signal observed?

Helen Chadwick answered: The dependence of the scattering signal on the azimuthal angle has been studied previously[1] and the signal does indeed change as the orientation of the steps changes with respect to the incident molecular beam. It is likely that the temperature effects will also be different, but this hasn't been studied yet.

1 O. Godsi, G. Corem, Y. Alkoby, J. T. Cantin, R. V. Krems, M. F. Somers, J. Meyer, G. J. Kroes, T. Maniv and G. Alexandrowicz, *Nat. Commun.*, 2017, **8**, 15357.

David Heathcote queried: How might the metal used as the scattering surface affect the results of the scattering process you observe? I am mainly considering the change down the group, from Cu to Ag to Au, but would also be interested to hear about other relevant surface materials.

Helen Chadwick replied: We haven't studied rotational orientation effects for H_2 scattering from the other metals in the group, *i.e.*, from silver and gold, but there would be no reason to expect that these will be the same as we observe on the Cu(511) surface, although this is something that would need to be verified.

Geert-Jan Kroes commented: I have a question regarding your finding of low probabilities of Δm_J transitions in specular scattering, as reported in Fig. 6 of your paper (**https://doi.org/10.1039/d4fd00007b**). Could this be due to symmetry reasons? I think that for normal incidence, $|\Delta m_J| = 1$ or 2 transitions should be forbidden due to symmetry reasons: the plane group symmetry[1] associated with a Cu(111) surface should dictate that. In particular, the potential should be a sum of products of functions of X and Y that are linear combinations of plane wave functions, and functions that are linear combinations of spherical harmonics, and rotational functions that are linear combinations of $Y_{jm_j}(\theta,\phi)$ and $Y_{j-m_j}(\theta,\phi)$ should be pre-multiplied with functions of X and Y, and not the trivial function $f(X,Y) = 1$. For scattering with non-normal incidence, this selection rule probably does not hold, but a remnant of it might still be present. Have you considered this possibility?

1 T. J. Frankcombe, M. A. Collins and D. H. Zhang, *J. Chem. Phys.*, 2012, **137**, 144701, DOI: **10.1063/1.4757149**.

Helen Chadwick responded: The low probability of $\Delta m_J \neq 0$ transitions in specular scattering shown in Fig. 6 in the paper (**https://doi.org/10.1039/d4fd00007b**) is for the Cu(511) surface and is not measured at normal incidence. This observation could be due to a remnant of the selection rule, but we are not in a position to confirm this.

Geert-Jan Kroes asked: Concerning the exponential decay you see with surface temperature, in the signal of the initially cartwheeling molecules to the final cart-wheeling state in specular scattering – is that not simply Debye–Waller attenuation?

Helen Chadwick answered: Fig. 3 in the paper (**https://doi.org/10.1039/d4fd00007b**) shows Debye–Waller attenuation of the H_2 signals scattering from the Cu(511) and Cu(111) surfaces, but it has no information about the contribution that the different m_J states make to it. In the remainder of the paper, we study the temperature effects with initial and final m_J state

resolution, and as the surface temperature increases, the contribution that cartwheels make to the total scattered signal increases compared to that of helicopters (see the top right panel of Fig. 7 in the paper).

Mark Brouard said: I very much enjoyed your paper (https://doi.org/10.1039/d4fd00007b) on the magnetic selection and detection of polarized H_2 ($j = 1$). However, I wonder whether you could clarify one point for me. The discussion in the paper focusses very much on rotational *alignment*, but the H_2 molecule can also be *oriented*. Whilst I can understand that for an H_2 molecule approaching the surface in a helicopter configuration it would not matter whether the molecule was rotating clockwise or count-clockwise, unless the surface were chiral, that would not be the case for the approach of H_2 in a cartwheel configuration. In the latter case, I would expect that specular reflection of H_2 undergoing clockwise rotation (a top-slice approach, say) would be different to that for H_2 with counter-clockwise rotation (back-slice approach). Perhaps you could comment on that?

Geert-Jan Kroes remarked: I think Mark Brouard is referring to an experiment where the quantization axis would be perpendicular to the scattering plane, in which one could measure whether the scattered molecules display "topspin" or "backspin", looking at it from a tennis point-of-view.

Helen Chadwick responded: We define the quantisation axis for the scattering-matrix elements and the state-to-state scattering probabilities as the surface normal, as this is the convention that is used in theoretical calculations.[1] However, we can rotate the scattering-matrix elements we obtain so that they are defined with respect to a different quantisation axis. Therefore, it would be possible to use a quantisation axis that is perpendicular to the scattering plane (which would be along the y-axis in the frame of reference we use), which would allow us to distinguish between these two types of rotation (which would correspond to $m_J = 1$ and $m_J = -1$ with respect to the y-axis).

1 R. C. Mowrey and G. J. Kroes, *J. Chem. Phys.*, 1995, **103**, 1216–1225.

Hua Guo commented: I was wondering if the different behaviors of the helicopter and cartwheel rotations of H_2 are related to the existence of the dissociation channel on the Cu surface. There is ample evidence showing that inelastic scattering of molecules on metal surfaces can be influenced by the reaction channel.[1] The helicopter rotation would be able to access the reaction channel more easily than the cartwheel rotation.

1 X. Zhou, G. Meng, H. Guo and B. Jiang, *J. Phys. Chem. Lett.*, 2022, **13**(15), 3450–3461, DOI: 10.1021/acs.jpclett.2c00593.

Helen Chadwick answered: In the present work (https://doi.org/10.1039/d4fd00007b),we are studying rotationally and vibrationally elastic scattering of H_2 from a Cu(511) surface rather than inelastic scattering, but I believe the same principles apply, *i.e.*, molecules rotating like helicopters are more likely to access the reactive channel than cartwheels.[1] As this channel is stereospecific, it could well influence the trends that we see in the rotational orientation

dependence of the scattering. However, as mentioned in the paper, we see very little evidence of dissociation and therefore this is unlikely to fully account for the trends that we observe.

Additionally, ref. 1 suggests that helicoptering molecules are more likely to scatter into the higher order diffraction channels than cartwheeling molecules, which scatter into lower order channels, including specular, which could be consistent with what we are seeing. This also highlights the importance of other scattering channels, and the interplay between them, which will all play a role in the trends that we observe.

1 M. del Cueto, X. Zhou, A. S. Muzas, C. Díaz, F. Martín, B. Jiang and H. Guo, *J. Phys. Chem. C*, 2019, **123**, 16223–16231.

Bum Suk Zhao enquired: How do you anticipate the experimental outcomes to vary when altering the collision energy in your experiment, such as by decelerating hydrogen molecules or adjusting the incidence angles?

Helen Chadwick replied: Changing the collision energy can affect the outcome of the collision between the molecule and the surface in various ways, for example by providing enough energy for the molecule to overcome the activation barrier and react on the surface, or to undergo rotationally inelastic scattering (J state changing) rather than the rotationally elastic (J state conserving) collisions studied here (https://doi.org/10.1039/d4fd00007b). It will also affect the rotationally elastic channel, as the molecules will sample a different part of the molecule–surface interaction potential, which means they will experience different forces during the collision, which could lead to a different rotational orientation dependence of the scattering being observed.

Gilbert M. Nathanson queried: Do you think that collisions of H_2 molecules with a kink atom on a surface might convert the H_2 rotation between cartwheeling and helicoptering motions?

Helen Chadwick responded: Yes, this could happen, although it would depend on the underlying interaction potential between the molecule and the surface. Another interesting point is that many kinked surfaces are also chiral, which then means the surface no longer has reflection symmetry in the scattering plane. This means that clockwise and counterclockwise rotating helicopters ($m_J = \pm 1$) are no longer equivalent and can scatter differently. This adds a significant complexity to the analysis, as there are then more unique elements of the scattering matrix that can be extracted from the data.

Brianna R. Heazlewood communicated: You have identified a number of possible explanations for the variation in the scattering dynamics as the temperature of a stepped Cu(511) surface is varied — noting that competition from other channels is also likely to vary as a function of temperature. Could you comment on how you might test these different theories in the future?

Helen Chadwick communicated in reply: Work is currently on-going to try and assess how scattering into competing channels changes as a function of surface

temperature. Specifically, we have measured oscillation curves for the scattering of H_2 at the same incident energy into different diffraction channels for a (smaller) range of surface temperatures. The analysis of this data is a work in progress, but will help determine how the scattering dynamics into the elastic diffraction channels changes as a function of the surface temperature, which will complement the data for specular scattering presented here.

Whilst performing the measurements presented in the current manuscript (**https://doi.org/10.1039/d4fd00007b**), there was also some evidence of molecules dissociating on a Cu(511) surface. As part of a longer-term project that I am leading, there are plans to modify the apparatus to be able to perform reactivity measurements, which would then also provide insight into the stereodynamic preference of the reactive channel.

Geert-Jan Kroes said: With your new experiments, you are posing a new challenge to theorists, requiring a good description of weak interactions of molecules with surfaces. How do you think theorists will meet these challenges?

Helen Chadwick answered: I think with the ever-developing toolkit that theoreticians have access to, combined with the increasing expertise of theoreticians, these challenges will be met, even if there are a few wrong turns and dead ends along the way! But I also think that the measurements that we perform can help guide this, and indeed Gil Alexandrowicz is currently leading a research project, which is being done in collaboration with Mark Somers at Leiden University, to investigate whether it is possible to extract information about the molecule–surface interaction potential from the experimental data, rather than relying on theoretical methods to calculate them. The oscillation curves that are measured are extremely sensitive to the underlying potential, so it is possible that there are features in the measurements that are fingerprints to certain characteristics of the potential energy surface. This project aims to determine if this is the case, and if it is, whether these fingerprints can be used to obtain an empirical interaction potential.

Dan J. Harding asked: Is it possible to perform similar experiments with molecules other than H_2 and do you expect that this could provide more information about the surface? Are there currently instrumental limitations to experiments with other molecules?

Helen Chadwick replied: In principle it is possible to perform the experiment with any (small) molecules that have a nuclear and rotational magnetic moment. We have studied the rotationally inelastic scattering of D_2 from Cu(111) previously, specifically the $J = 2$ to $J = 0$ transition, and shown that the probability that the molecule is stopped from rotating by the collision is related to its rotational orientation as it approaches the surface.[1] Likewise, we have also studied translationally inelastic scattering of D_2 for $I = 2$, $J = 0$, where energy is transferred between the surface phonons and the molecule.[2] There are plans to extend these measurements to rotating H_2/D_2 molecules, which can then be used to probe phonon modes that are not visible to atomic scattering for symmetry reasons.[3]

It should also be possible to extend the measurements to polyatomic molecules, for example H_2O, NH_3 and CH_4. Previous work has shown that the different

states of water,[4] ethylene[5] and methane[5] can be separated by a magnetic hexa-pole, and we have done a proof-of-concept measurement that shows we can control and manipulate the rotational orientation (and nuclear spin) projection states of methane. However, going to polyatomic molecules represents a huge increase in complexity, due to the number of initial and final projection states that can be populated, and in that the Hamiltonian that is required to propagate the different states through the machine is less well characterised. Additionally, there are experimental limitations, for example the hexapoles have a fixed length and a fixed magnetic field strength, meaning that as the molecules get heavier, they will be deflected less and therefore we will have less of a population bias in the different projection states (although this can be countered to some extent by changing the velocity of the beam). The most significant limitation of the appa-ratus at the moment is that the custom-built detector[6] can only detect masses 2 to 4 and will need significant modifications to be able to detect higher masses. This can be overcome by using the alternative quadrupole mass spectrometer on the machine, but this is significantly less sensitive than the main detector, and so would limit the measurements to those with higher scattering intensity.

1 H. Chadwick, M. F. Somers, A. C. Stewart, Y. Alkoby, T. J. D. Carter, D. Butkovicova and G. Alexandrowicz, *Nat. Commun.*, 2022, **13**, 2287.
2 H. Chadwick and G. Alexandrowicz, *Phys. Chem. Chem. Phys.*, 2022, **24**, 14198.
3 G. Benedek, F. Traeger and J. P. Toennies, *Phys. Rev. Lett.*, 2005, **94**, 086103.
4 T. Kravchuk, M. Reznikov, P. Tichonov, N. Avidor, Y. Meir, A. Bekkerman and G. Alexan-drowicz, *Science*, 2011, **331**, 319.
5 C. Krüger, E. Lisitsin-Baranovsky, O. Ofer, P. A. Turgeon, J. Vermette, P. Ayotte and G. Alexandrowicz, *J. Chem. Phys.*, 2018, **149**, 164201.
6 M. Bergin, D. J. Ward, S. M. Lambrick, N. A. von Jeinsen, B. Holst, J. Ellis, A. P. Jardine and W. Allison, *Rev. Sci. Instrum.*, 2021, **92**, 73305.

Patrick Robertson opened a discussion of the paper by Stefan Willitsch: You attribute the increased dissociative ionisation product yield to dipole–dipole orientation in the *cis*-isomer aligning the molecular orbitals, associated with formation of the dissociative states of the ion, with the neon atom and shifting the entrance channel early in the reaction coordinate. However, you also show more strongly deflected low-*J* states, which are themselves more easily aligned. If you could *J*-select the *trans*-isomer, would you expect a similar alignment effect in this isomer through a dipole–quadrupole interaction? More generally, is this difference in reactivity reflective of a structural difference or a *J*-state selectivity difference, or a combination of the two?

Stefan Willitsch responded: For the *trans* isomer, we would expect alignment effects to be less pronounced because of the weaker quadrupole-induced dipole interaction. Indeed, we understand the difference in reactivity really to be a combination of both factors: it needs a sufficiently strong aligning interaction, which in this case is geometry dependent, and this alignment is most effective in low-*J* states, hence the rotational selectivity.

Patrick Robertson enquired: Do you know which orbitals are responsible for dissociative ionisation in this molecule? From my experience, ionisation of halogen lone pairs typically leads to C–X bond dissociation when a sigma bonding orbital electron fills the hole in the lone pair. This mechanism seems like it would

agree well with your dipole–dipole alignment conclusion, and so might we infer that these orbitals are involved in the dissociative ion states?

Stefan Willitsch answered: In the absence of knowledge of the relevant decay widths, we do not know exactly which electronic states, and hence orbitals, are responsible for the dissociative ionisation in this system. However, considering the large number of states between the first dissociation limit of the 1,2-dibromoethene (DBE) cation and the limit set by available energy in the experiment, it can be assumed that there will be several and that the products that we see originate from a variety of different channels.

Chris Sparling remarked: This is a beautifully designed experiment apparatus. I'm curious as to the choice of tilting the entire spectrometer to select out specific deflection coordinates – was this challenging to engineer? Is this a simpler approach than, say, translating the detection laser focal point?

Stefan Willitsch replied: The entire machine can be tilted with a precision of tens of micrometers – indeed, it takes a skilled workshop to engineer this mechanism. Note that we do not use a detection laser in the reaction experiments, so translating its focal point is not an option. For the sole purpose of recording density profiles of the deflected beam by, *e.g.*, photoionisation, one could indeed just translate the ionisation laser beam.

Nitish Pal queried: Can the isomerization be induced in DBE upon collision with Ne* and will it then impact the fragmentation pattern?

Stefan Willitsch responded: The DBE ions produced in the chemi-ionisation are internally hot and it is conceivable that some of them isomerise before fragmenting. Possibly, this has an effect on some of the fragmentation channels that we are seeing, but this is hard to ascertain in the absence of detailed calculations of the relevant potential energy surfaces and the dynamics on them.

Patrick Robertson asked: Using these electrostatic deflectors, has anyone ever tried to deflect molecules by optically pumping to an electronic excited state to induce a dipole and separate out molecules in this way?

Stefan Willitsch answered: Molecules like CO have been Stark decelerated by pumping them to different electronic states. I am not aware that this has been implemented in a deflection experiment yet, but it would certainly be conceivable.

Alexander Butler enquired: In reactions induced by chemi-ionisation, do you think the dynamics are influenced by an impulse from the scattered Neon atom? Or is the dominant factor the electronic state the cation is formed in, as in the case of dissociative photoionisation or electron ionisation?

Stefan Willitsch replied: In chemi-ionisation, the latter is clearly the more important factor.

Daniel M. Neumark commented: The alignment effects with the *cis*-isomer that you refer to in your work (**https://doi.org/10.1039/d3fd00172e**) presumably depend on the collision energy. Were you able to vary the collision energy? If not, what was its value?

Stefan Willitsch responded: The collision energy was 0.36 eV, as mentioned in the paper (**https://doi.org/10.1039/d3fd00172e**), and I agree that the alignment effects should depend on it. In this work, we did not vary the collision energy, but we could (and have done so in previous studies) by, *e.g.*, changing the seed gas of the molecular beams.

Jennifer Meyer queried: What is the density of the neutral reactant 1,2-dibromoethane after passing through the electrostatic deflector in the interaction region with the Ne* beam, *e.g.*, after selecting the *cis*-isomer? Can you envision investigating more complex reactions, like Diels–Alder, with this method compared to Penning ionization?

Stefan Willitsch answered: We have not specifically measured the DBE densities in the interaction region in this work, but based on previous studies in which we performed such measurements,[1] we estimate average densities on the order of 10^6–10^7 cm^{-3} in the gas pulse. Clearly, the number of collision events is low at such densities and one needs a sensitive detection method for the products to be able to study reactions under these conditions.

1 A. Kilaj, H. Gao, D. Rösch, U. Rivero, J. Küpper and S. Willitsch, *Nat. Commun.*, 2018 , **9**, 2096.

David W. Chandler asked: Is it possible to maintain the alignment or orientation of the molecules into the scattering apparatus by using a weak alignment field, as Steven Stolte and Maurice Janssen did for maintaining the orientation of methyl iodide and guiding it into a Velocity Mapped Imaging (VMI) dissociation machine?[1]

1 M. H. M. Janssen, J. W. G. Mastenbroek and S. Stolte, *J. Phys. Chem. A*, 1997, **101**(41), 7605–7613.

Stefan Willitsch replied: This is an intriguing idea. It will be difficult to implement in our current setup, in which the molecule still has to pass through two skimmers after the deflector. However, with suitable modifications of the apparatus, this should in principle be possible.

Roland Wester enquired: What do you expect to gain from measuring the angle- and velocity-differential scattering cross sections using the velocity map imaging spectrometer in your crossed-beam setup?

Stefan Willitsch responded: Primarily, we hope to gain further information on the reaction mechanism, *e.g.*, whether it is direct or complex-mediated, and on the cationic states generated in the electron transfer. For this purpose, we are currently implementing an electron–ion coincidence velocity-map imaging setup.

Michal Fárník said: This is probably not observed in the case of the dissociative ionization of DBE; however, is it, in principle, possible that the free electron is not ejected in the collision of Ne* with DBE, but the ion pair is formed yielding the Br^- anion and $C_2H_2Br^+$ cation? In such a case, would the energy required for the reaction be just lowered by the electron affinity of Br (3.36 eV), or is the energy requirement for the ion-pair formation higher? Is the ion-pair formation process allowed in your case energetically – and if that is the case, why it is not happening?

Stefan Willitsch answered: It is not inconceivable that intermediary ion-pair states are formed in the collision; however, we would not be able to detect them in the experiment, which is only sensitive to ionic products. Moreover, considering the high available energy of 16.7 eV in the system, any such ion-pair state would probably not be stable and further decay.

Hua Guo asked: Can you comment on if there are stereodynamics in such processes? If so, what would be the conditions for the stereodynamics to be observed?

Stefan Willitsch replied: Chemi-ionization cross sections depend on the overlap of atomic and molecular orbitals, so the effects that we are observing are inherently stereodynamic in character. In the present case, we conjecture that we observe signatures of stereodynamics in the dependence of the Penning-ionization rates on the rotational excitation of hydroquinone, which modulates the alignment of the collision partners.

Brianna R. Heazlewood communicated: In Fig. 2 of your paper (**https://doi.org/10.1039/d3fd00172e**), you present the density profiles of the molecular beam at deflector voltages of 0 kV and 35 kV, obtained by measuring the DBE ion yield as a function of the deflection coordinate. Complementing the experimental measurements, you also provide the simulated deflection profiles of *cis*- and *trans*-DBE. Could you comment on how you established the relative rotational state population distribution that gives rise to these simulated DBE profiles? As a related point, it would be very interesting to extract information on the rotational state-specific dynamics of the system. Given your ability to vary the rotational state distribution of *cis*-DBE with the deflector, is this something that might be possible in future work?

Stefan Willitsch communicated in reply: The rotational state populations are extracted from a fit of the simulated to the experimental density profiles of the deflected molecular beam obtained *via* photoionisation. Indeed, we can get information on rotationally specific dynamics in a similar fashion. Fig. 1 shows a simulation of the Penning ionisation (PI) reaction deflection profile of DBE + Ne* assuming (a) all rotational states contribute to the reaction according to their thermal population in the beam and (b) that the contribution of the lowest rotational states is reduced, with weights determined from a fit of the simulation to the experiment. The better agreement between experiment and simulation in (b) suggests that low rotational states show a reduced reactivity in PI, as discussed in the paper (**https://doi.org/10.1039/d3fd00172e**).
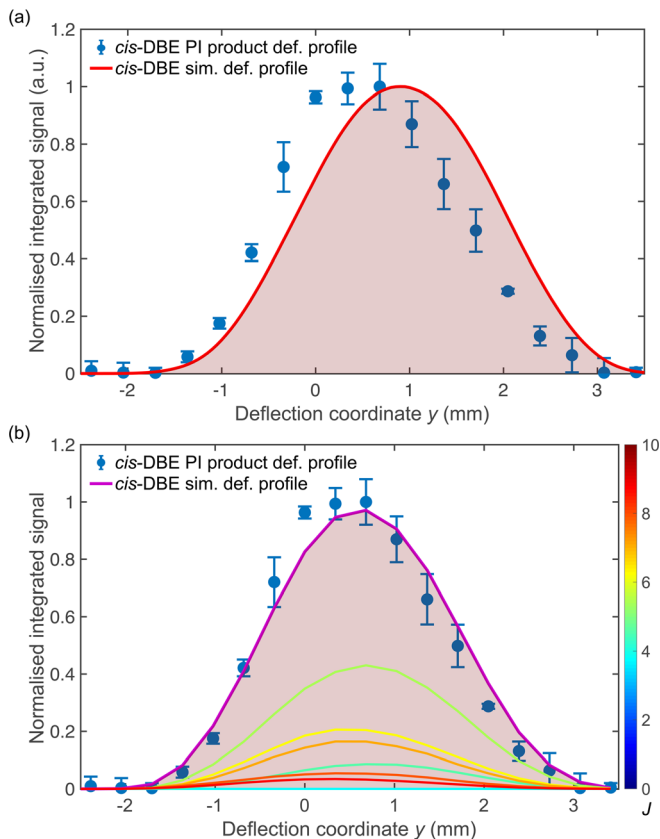
Fig. 1 Simulation of the PI reaction deflection profile of DBE + Ne*, assuming (a) all rotational states contribute to the reaction according to their thermal population in the beam, and (b) the contribution of the lowest rotational states is reduced, with weights determined from a fit of the simulation to the experiment.

Peter D. Watson communicated: Considering the degree of deflection of the *cis*-1,2-dibromoethene (where you form a fan based on the random orientation of the permanent dipole), would selecting for or pulsing a hexapole guide to align the molecules prior to deflection improve transmission or would you be too concerned with losses through the hexapole?

Stefan Willitsch communicated in reply: The electrostatic deflector is in many ways an alternative to an electrostatic hexapole selector. Implementing a hexapole to align the molecules before the electrostatic deflector would not help much, as the molecules are aligned in the deflector anyway. In contrast, it would rather lead to further losses, as you correctly observe.

Jan Fingerhut remarked: In your manuscript (**https://doi.org/10.1039/d3fd00172e**) you mention that you use a 1 : 1 mixture of *cis*, *trans*-1,2-dibromoethene. You use the electrostatic deflector to separate the *cis* and *trans* isomers by their dipole moment. You also mention that you can purify the mixture by using chromatography. My question is, why don't you use the

purified isomer from the beginning if you are separating the isomers later using the deflector anyway? Wouldn't working with the purified isomers give you better signal-to-noise because you don't have to separate the isomers anymore? Or is this to do with investigating the branching ratios of the isomers by colliding the excited Ne* atoms with both isomers at the same time?

Stefan Willitsch responded: In fact we did both, separating the isomers electrostatically *in situ* and purifying them chemically before introducing them into the setup. This was done with the aim to better disentangle rotational from conformational effects, as discussed in the paper (**https://doi.org/10.1039/d3fd00172e**). It is correct that the pure samples give a better signal-to-noise (S/N) ratio for the specific isomer compared to the mixture. However, generally the S/N ratio was readily sufficient so that this did not pose a limitation.

Max McCrea opened a discussion of the paper by Pablo G. Jambrina: In your paper (**https://doi.org/10.1039/d3fd00173c**) you have shown some very specific and granular data about the stereodynamics of the molecules at very low collision energies. As lower collision energies test potential energy surfaces (PESs) more than higher energies, how can you be confident in the quality of the PES to be able to draw these conclusions?

Pablo G. Jambrina answered: You are absolutely right. At very low collision energies (say below 0.1 K), the dynamics is extremely sensitive to any small features of the PES, so even small changes in the depth of any van der Waals well or in the long-range part of the potential (for example) will be reflected in the dynamics and will probably lead to differences in the absolute value of the cross section and/or in the value of the collision energy at which the resonances appear.

In ref. 1, we evaluated the sensitivity of the stereodynamics of the inelastic collisions between He and D_2 to the *ab initio* potential. Our results showed that, as far as the stereodynamics is concerned, our conclusions basically did not change with the PES used (although the position of the resonance did).[1]

1 P. G. Jambrina, M. Morita, J. F. E. Croft, F. Javier Aoiz and N. Balakrishnan, *J. Phys. Chem. Lett.*, 2022, **13**, 4064–4072, DOI: **10.1021/acs.jpclett.2c00587**.

Jérôme Loreau commented: Thank you for this nice presentation. I was wondering if you can easily estimate the maximum cross section enhancement (at resonance or off-resonance) that is achievable? Could you also comment on the level of control you might expect for collisions involving heavier molecules, where the resonance structure is usually denser and many resonances overlap?

Pablo G. Jambrina replied: Let's first assume a situation in which only one reactant can be polarized. In that case, the maximum value of the cross section that could be achievable would be $(2j + 1)$ higher than the isotropic cross section (σ_{iso}, corresponding to an unpolarized distribution of the internuclear axis or rotational angular momentum).[1] This situation would correspond to a case in which all "reactivity" comes from a pure state that we can prepare in the laboratory. Also in that case, if we could prepare a mixed state that does not include the "reactive" state, or a different pure state, the cross section would be zero.

When we applied the same argument to collisions between two aligned molecules, we find that the higher limit of the cross section is $(2j_{A+1})(2j_{B+1})\sigma_{iso}$, where j_A and j_B are the rotational quantum numbers of the two incoming molecules. At least for inelastic collisions, it is hard to imagine a situation where only one pure state could lead to the desired final state, so the maximum degree of control will be significantly smaller. However, this may change when we have shape resonances. Shape resonances are typically associated with a value of L, J, and sometimes even an Ω state (where Ω is the projection of j onto the incoming direction). It is therefore possible to achieve a higher degree of control at the resonances closer to the $(2j + 1)$ theoretical limit. In addition to the examples shown in our paper, for HD + H_2 collisions it was possible to "switch off" the 0.1 K resonance by appropriate alignment of HD.[2]

In the case of clusters of overlapping resonances, each characterised by different J, L and Ω, it is in principle possible to maximise some resonances while minimising others, leading to significant changes in the relative shape of the cluster of resonances. An example of this behaviour is shown in ref. 3 for H + HF using only three-vector correlations. By simultaneously aligning two molecules, there are two molecules that can be controlled, so in principle more exquisite control of the resonances could be achieved.

1 J. Aldegunde, F. J. Aoiz and M. P. de Miranda, *Phys. Chem. Chem. Phys.*, 2008, **10**, 1139, DOI: 10.1039/B716482C.
2 P. G. Jambrina, J. F. E. Croft, H. Guo, M. Brouard, N. Balakrishnan and F. J. Aoiz, *Phys. Rev. Lett.*, 2019, **123**, 043401, DOI: 10.1103/PhysRevLett.123.043401.
3 P. G. Jambrina, L. González-Sánchez, M. Lara, M. Menéndez and F. J. Aoiz, *Phys. Chem. Chem. Phys.*, 2020, **22**, 24943, DOI: 10.1039/d0cp04885b.

Mark Brouard enquired: I wonder if you could say anything further about the reason why the diatom–diatom stereodynamics changes so dramatically around the resonances shown in your paper (https://doi.org/10.1039/d3fd00173c)? In the diatom–diatom case I assume it is more complicated to provide an explanation for the stereodynamical preferences compared with that in the atom-diatom case, but at low collision energy perhaps it is still possible?

Pablo G. Jambrina responded: Shape resonances are sometimes associated with a single value of L, J, and sometimes even with a single value of the helicity, Ω, (the projection of j onto the relative velocity direction). When this is the case, it is possible to obtain a greater degree of control near the resonances than far from them, where more states contribute to the cross section to a similar extent. It is also sometimes observed that resonances are associated with a change in the collision mechanism. Also, parity may play an important role when there is a unique L and J value, if the prepared state does not match with the parity of the collision. The mechanistic explanation for a particular resonance (or off-resonance case) is encoded in the polarisation parameters. For an atom–diatom case (or for a diatom–diatom case where only one of the molecules is polarised), it is easier to extract the information from these parameters by plotting the stereodynamical portraits (distributions that graphically represent the dependence of the reaction dynamics on directions in space).[1] However, for the diatom–diatom case where both partners are polarised, it is not possible to plot the stereodynamical portraits, which makes the interpretation of the mechanisms more
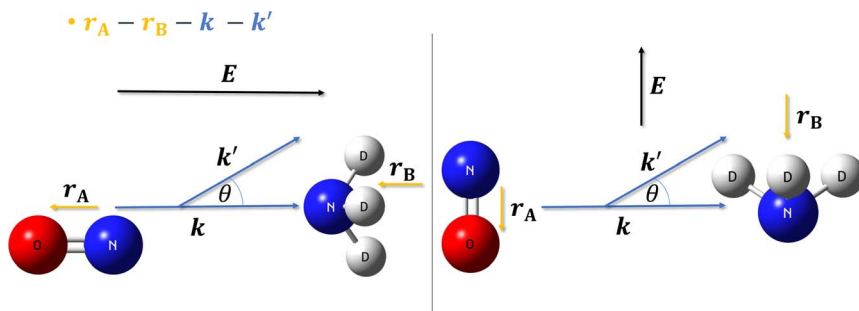
Fig. 2 4-Vector correlations – static electric field orientation.

difficult, and probably the closest we can get is to plot the asymptotic spatial distributions of the internuclear axes of the two partners that maximise the cross sections (as it is done in Fig. 4 of the paper (**https://doi.org/10.1039/d3fd00173c**)). The main polarisation parameters needed to interpret the collision mechanisms are shown in panel b of Fig. 1, 5, and 7 of the paper. For all cases, we observe strong oscillations in their values around the resonances, indicating a change in the collision mechanism.

1 F. J. Aoiz and M. P. de Miranda, in *Tutorials in Molecular Reaction Dynamics*, ed. M. Brouard and C. Vallance, RSC Publishing, 2010.

Max McCrea and **Matt Strutton** presented a set of slides:† Hi everyone. We're Matt Strutton and Max McCrea from the Brouard group at the University of Oxford. We work on the NDMS programme grant, which aims to push the field of molecular scattering towards bigger systems to expand its relevance towards real world problems. We carry out ultimate benchmarking experiments involving NO colliding with small molecules. We are interested in how polarisation of the collision partners before the collision impacts the outcome. We use electric fields to orient molecules prior to a collision. If we take both molecules' bond axis vectors, and the initial and final relative velocities, we are measuring or controlling 4 different vectors (Fig. 2), as Pablo just showed for angular momentum.

Our experiment is a cross molecular beam setup, using a hexapole to state-select our NO molecules. Our electric field is produced by 4 rods, 2 with a positive potential, and 2 with a negative potential. The ion images at the top of Fig. 3 show the result of NO scattering with Ar on either side of the molecule. We're adding in a double hexapole to our secondary molecular beam to allow us to state-select symmetric top molecules, which can then be oriented in the static field. We've also begun a collaboration with Gil Alexandrowicz and Helen Chadwick (whose presentation we've already seen) to install a magnetic hexapole system for our secondary molecular beam, in place of the double electric hexapole.

This will allow us to magnetically orient H_2 angular momentum before the collision, as you can see in Fig. 4. Hence, we will be able to independently control the orientation of both the NO bond axis and the H_2 angular momentum.

† Co-authored by Josh Featherstone and Mark Brouard. Based on work in collaboration with F. Javier Aoiz, Pablo Jambrina, Gil Alexandrowicz, Helen Chadwick, Martin Paterson, Chris Robertson and Dimitri Babikov.
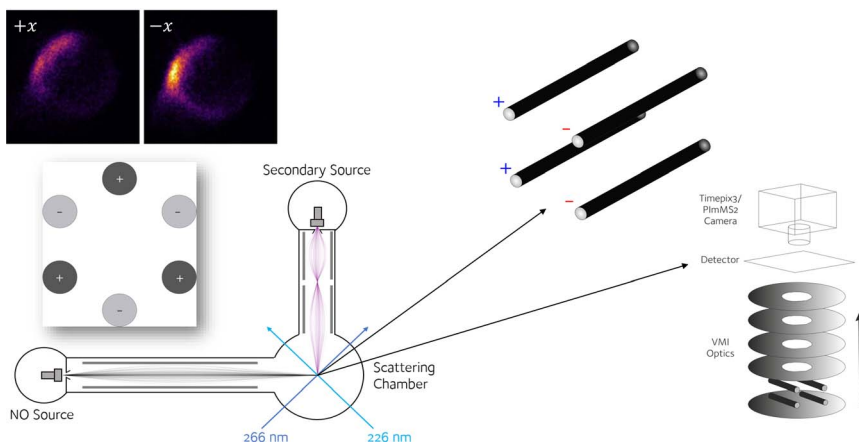
Fig. 3 Experimental implementation.[1]
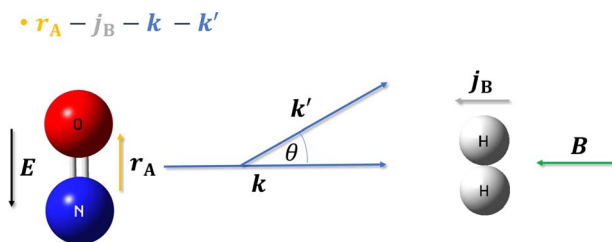
Fig. 4 4-Vector correlations – combining electric and magnetic field polarisation. See https://doi.org/10.1039/d4fd00007b for more on H_2 angular momentum polarisation using magnetic fields.

As we have seen in Pablo's paper (https://doi.org/10.1039/d3fd00173c), we can parameterise the effect of the orientation of molecules before a collision using polarisation-dependent differential cross sections (PDDCSs). Fig. 5 is an example of one that is relevant for the case of NO + H_2. When we orient the NO molecule using an electric field as shown, then if this polarization dependent differential cross section (PDDCS) ($O_{0,1-}^{\{1,1\}}$) is positive for a given transition, then that transition is more likely when the angular momentum of the H_2 molecule is directed in the +y direction (towards us in the drawn frame). If the PDDCS is negative, then the transition is more likely when the H_2 angular momentum is oriented in the −y direction (into the wall in the drawn frame).

We've carried out some time-independent scattering calculations using the HIBRIDON program suite and calculated this PDDCS, shown in the bottom right of Fig. 6. The top right shows the scattering angle integrated version of this, while the other two panels show the integral and differential cross sections. Our integral cross sections help us to identify the resonances seen here as sharp peaks, and the differential cross sections display the large effect these resonances have on angular distributions. In the bottom right, the resonances are also clear to see, with large changes of behaviour seen in rapid shifts from positive to negative, such as that at around 18 cm^{-1} in the forward scattering direction.
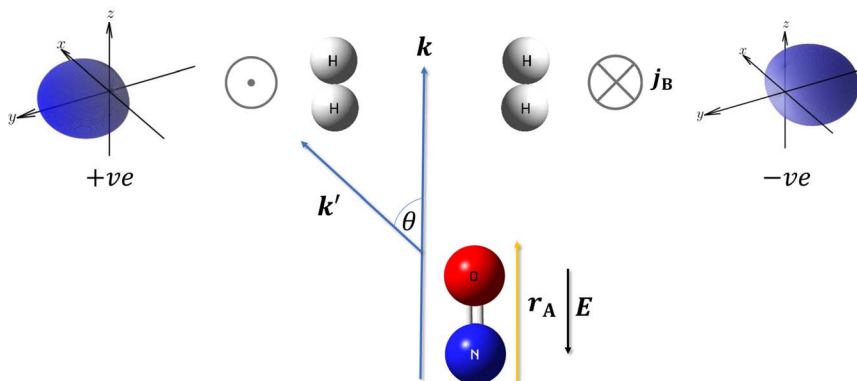
Fig. 5 A pictorial representation of an example interpretation of the $\left(O_{}^{\{1,1\}}\right)$ example PDDCS, corresponding to the simultaneous orientation of the bond axis vector of NO along the relative velocity vector, and orientation of the H_2 angular momentum vector in or out of the page as drawn.
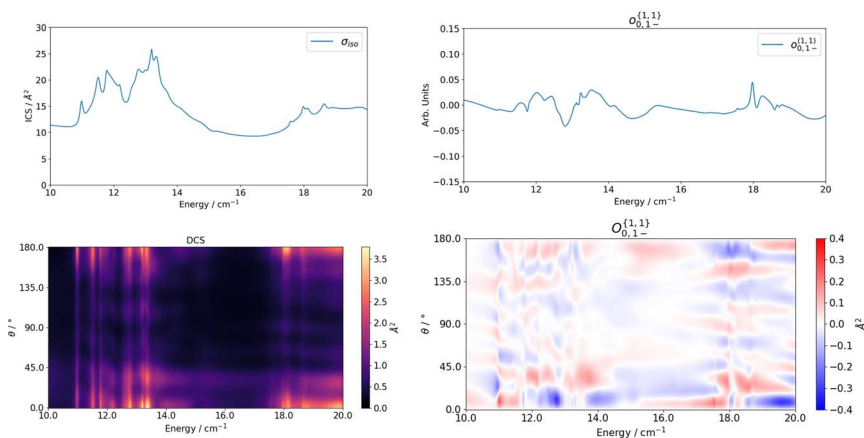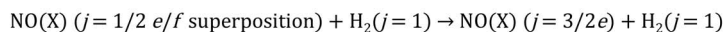
$$NO(X)\ (j = 1/2\ e/f\ \text{superposition}) + H_2(j = 1) \rightarrow NO(X)\ (j = 3/2e) + H_2(j = 1)$$

Fig. 6 Early quantum mechanical (QM) results for the $O_{0,1-}^{\{1,1\}}(\theta)$ example.

1 C. G. Heid, V. Walpole, M. Brouard, P. G. Jambrina and F. J. Aoiz, *Nat. Chem.*, 2019, **11**, 662–668

Christian T. Haakansson opened a discussion of the paper by Heather J. Lewandowski:‡ Have you considered adding functional groups to the neutral molecule in order to increase the dipole moment, for example adding an oxygen atom to the C_3H_4 molecule, in order to observe how this affects the formation of reaction complexes?

‡ Heather J. Lewandowski's paper was presented by Olivia Krohn, Sandia National Labs - CRF, Livermore, California, USA.

Heather J. Lewandowski answered: We have not considered adding functional groups. This would introduce additional structural differences that may impact the dynamics of the reaction in a way that obscures the effects of the isomeric dependence.

David Heathcote queried: Can you comment on whether the fact that O_2 has available vibrational and rotational modes, whereas Xe does not, is important here? I am particularly considering the energy transferred from the cation to the neutral hydrocarbon species, since a smaller amount of energy should be available from recombination of an electron with the O_2^+ cation than with the Xe^+ cation, since the equilibrium bond length changes between O_2 and O_2^+, and the O_2^+ may have undergone vibrational relaxation prior to scattering. I would be interested to hear your thoughts more generally as well.

Heather J. Lewandowski replied: For our previous work with $C_2H_2^+$,[1,2] we found that even with vibrational and rotational modes available, only one isomer of C_3H_4 formed a complex, indicating complex formation is not driven solely by the availability of these modes.

1 J. Greenberg, P. C. Schmid, J. H. Thorpe, T. L. Nguyen, K. J. Catani, O. A. Krohn, M. I. Miller, J. F. Stanton and H. J. Lewandowski, *J. Chem. Phys.*, 2021, **154**, 124310.
2 P. C. Schmid, J. Greenberg, T. L. Nguyen, J. H. Thorpe, K. J. Catani, O. A. Krohn, M. I. Miller, J. F. Stanton and H. J. Lewandowski, *Phys. Chem. Chem. Phys.*, 2020, **22**, 20303–20310.

Alexander Butler asked: Can the ability of O_2^+ and inability of Xe^+ to form a collision complex with isomers of C_3H_4 be rationalised by the possibility of π–π bonding in the O_2^+ case and the lack of a π bond in the case of Xe^+?

Heather J. Lewandowski responded: We do not believe this is the main mechanism that drives the differences in complex formation. Ultimately, our goal was to determine if each isomer for C_3H_4 would form a complex with O_2^+ unlike what was seen for $C_2H_2^+$. However, it is an interesting idea to explore theoretically.

Viet Le Duc enquired: What is the reasoning behind the choice to compare the reaction between Xe^+ and O_2^+? From what I understand, Xe^+ and other rare ion gases have a more similar electronic structure to each other than to O_2^+, and O_2^+, N_2^+ and CO^+ have more similarity than to Xe^+ (this of course is not very accurate to say, but the comparison still stands, in my opinion).

Heather J. Lewandowski answered: Our goal was to compare O_2^+ reacting with two different isomers of C_3H_4. We saw different behavior as compared to $C_2H_2^+$ reacting with different isomers of C_3H_4. To make sure these differences were not due to just available energy, we wanted to do a reaction with an ion with a similar ionization potential to O_2^+, but that would not likely form a complex. Xe^+ was a convenient atom with those characteristics.

Patrick Robertson remarked: In your previous paper on $C_2H_2^+$ with allene,[1,2] you attribute the lack of complex formation on Jahn–Teller distortions in the ionised allene. Do you expect the converse case to also be true, that when a Jahn–

Teller distorted ion is neutralised by charged transfer, its changing geometry impacts the dynamics of complex formation?

1 J. Greenberg, P. Schmid, J. H. Thorpe, T. L. Nguyen, K. J. Catani, O. A. Krohn, M. I. Miller, J. F. Stanton and H. J. Lewandowski, *J. Chem. Phys.*, 2021, **154**, 124310.
2 P. C. Schmid, J. Greenberg, T. L. Nguyen, J. H. Thorpe, K. J. Catani, O. A. Krohn, M. I. Miller, J. F. Stanton and H. J. Lewandowski, *Phys. Chem. Chem. Phys.*, 2020, **22**, 20303–20310.

Heather J. Lewandowski responded: We suggested that one possible reason for the lack of complex formation in the reaction of $C_2H_2^+$ with allene was due to the Jahn–Teller distortion, although there may be other reasons. It is interesting to consider if Jahn–Teller distortions upon neutralization could also impact complex formation. Future work would have to be done to understand if this is the case.

Alec. M. Wodtke queried: How can you rule out the possibility that other reaction channels, that do not explicitly show an atom from each reactant in the products, are not also undergoing a complex formation mechanism?

Heather J. Lewandowski answered: This is an interesting question. A product composed of atoms solely from one reactant does not directly inform you if a complex has formed or not. However, theoretical calculations and performing additional reactions can provide more information to make this distinction. For example, see ref. 1.

1 J. Greenberg, P. Schmid, J. H. Thorpe, T. L. Nguyen, K. J. Catani, O. A. Krohn, M. I. Miller, J. F. Stanton and H. J. Lewandowski, *J. Chem. Phys.*, 2021, **154**, 124310; ref. 8 in the original article.

Dwayne Heard asked: Which isotope of Xe^+ did you use to monitor the time dependence? If it was the sum of all isotopes, did you ever compare individual isotope masses to follow the time dependence of Xe^+, and if so did they agree well?

Heather J. Lewandowski replied: We added together all isotopes of Xe^+ for our analysis. We did not look at the time dependence of each isotope individually.

Dwayne Heard enquired: Can you please explain why you didn't fit the Xe^+ decays as you have done for the O_2^+ decays and also the products formed in the reactions?

Heather J. Lewandowski responded: The detection efficiency for Xe^+ is significantly lower (2–3 times lower) than for all other lighter masses in our trap for these experiments.

Dwayne Heard commented: This question is in two parts.
(i) You fit reagent decays for O_2^+ and the rise of the product masses, with a solid line in the figures being a fit to the kinetic equations. These equations contain the thermal rate coefficients, which are the parameters k that are varied. However, you did not report the values of k in the paper. What are the parameters k, and are they consistent with any previous data that have been measured, for

example at higher temperatures perhaps? What is the temperature for the collisions relevant for a thermal rate coefficient?

(ii) For the reaction of Xe^+ + allene, the Xe^+ signal is flat for a while at the beginning of the reaction, even though products are already being formed. What is the reason for this, as it ought to decay?

Heather J. Lewandowski answered: We measure the neutral gas density using an ion gauge, which can be inaccurate at low pressures. We did estimate the rate constants using the measured pressure and the rate constants are consistent with predictions from average dipole orientation theory. We do not believe the Xe^+ signal is constant at the beginning of the reaction, but rather there are just statistical fluctuations in the number of ions loaded and not all of the Xe^+ ions are detected by our time-of-flight mass spectrometer due to their large mass-to-charge ratio.

Daniel M. Neumark said: In the reactions of O_2^+ with allene and propyne, you find $C_3H_4^+$ to be a significant product. Do you know which isomeric cations are produced in each case? I realize that the experiment probably cannot distinguish, but perhaps Rice–Rampsberger–Kessel–Marcus (RRKM) calculations on your calculated potential energy surfaces would reveal the extent of isomeric scrambling in the product cations.

Heather J. Lewandowski replied: In each case, the $C_3H_4^+$ products are not experimentally distinguishable; however, this would be an interesting idea to explore theoretically.

Roland Wester remarked: Your article (**https://doi.org/10.1039/d4fd00005f**) states the assumption that charge transfer reactions follow a direct reaction mechanism without the formation of a long-lived complex. I can confirm this based on differential reactive scattering measurements that we have performed using a crossed-beam velocity map imaging spectrometer. Reactions such as Ar^+ + N_2, O_2 or CO,[1–3] are dominated by strong forward scattering, which is clear evidence for a direct mechanism.

1 S. Trippel, M. Stei, J. A. Cox and R. Wester, *Phys. Rev. Lett.*, 2013, **110**, 163201.
2 T. Michaelsen, B. Bastian, E. Carrascosa, J. Meyer, D. H. Parker and R. Wester, *J. Chem. Phys.*, 2017, **147**, 013940.
3 T. Michaelsen, T. Gstir, B. Bastian, E. Carrascosa, A. Ayasli, J. Meyer and R. Wester, *Mol. Phys.*, 2020, **119**, e1815885.

Heather J. Lewandowski responded: These are great examples of this mechanism. We will be sure to connect our work to these findings.

Roland Wester queried: How do you prepare the O_2^+ ions in your experiment? In particular, what do you know about the rotational and vibrational level population of the ions? Do you use, or have you considered using, quenching collisions or state-selective preparation?

Heather J. Lewandowski answered: The O_2^+ ions are prepared in the ground vibrational state *via* 2 + 1 resonance enhanced multi-photon ionization (REMPI)

(see ref. 1). We assume the rotational distribution is in thermal equilibrium with room temperature black body radiation even considering the lack of an electric dipole moment, since the reaction time scale is very long.

1 Y. Wu, Z. Zhang and S. F. Adams, *Chem. Phys. Lett.*, 2011, **513**, 191–194; ref. 27 in the original article.

Roland Wester asked: In order to better discriminate the signal at $m/z = 40$, have you considered investigating the isotopologues at $m/z = 41$ to clarify how much $C_3H_4^+$ and C_2O^+ is formed in the reactions with O_2^{+}? Would there be other opportunities to better separate the C_2O^+ channel?

Heather J. Lewandowski replied: We have used the fully deuterated C_3D_4 reactants to see $C_3D_4^+$ in our mass spectrum. Additionally, we have also created a Coulomb crystal of ^{44}Ca (along with using C_3D_4 reactants) and still saw growth at mass = 40, which we assume is C_2O^{+}, as there do not seem to be any other possible ions with that mass in our system. The results from this work will be presented in a future paper.

Tibor Győri commented: The theoretical work in your paper (**https://doi.org/10.1039/d4fd00005f**) is extensive and a large number of interesting new stationary points have been located using a density functional theory (DFT) method. I would like to kindly request publication of the final Cartesian coordinates of the optimized geometries presented in the paper, so that any interested theoretician may build upon this work, barrierlessly.

Beyond furthering research into these particular reactions, freely available stationary-point geometries are also an important resource for the development, testing and validation of theoretical methods, such as new DFT functionals.

One more dataset that I would also be interested in seeing, is a table of classical relative energies for the geometries in Fig. 6–8 in the paper (**https://doi.org/10.1039/d4fd00005f**). The paper does not explicitly state this, but I assume that the energies in the figures are adiabatic (zero-point energy (ZPE) inclusive), and for follow-up studies it would be useful to also have the classical (ZPE exclusive) data available.

If attaching such data to the article as electronic supplementary information (ESI) is no longer possible, the Zenodo service operated by CERN would also be a suitable way to ensure the long-term availability of this data and any further raw data that the authors may want to deposit.

Heather J. Lewandowski responded: We are currently working with collaborators to extend the level of theory and the range of the potential energy surface we explore. We will make sure to include the detailed results of those calculations in the forthcoming paper.

David Heathcote communicated: I have been considering one of the previous questions relating to orbitals. From inorganic chemistry, the 2p–2p orbital overlap is stronger than the 2p–5p orbital overlap. Does this have any relevance to the results you observe?

Heather J. Lewandowski communicated in reply: Orbital overlap is a contributory factor to the relative weakness of the carbon–xenon bond. In turn, the relative weakness of such bonds is likely to contribute to our findings, in that there is no barrierless exothermic pathway to the formation of a covalently bonded xenon complex. Ultimately, our goal was to determine if each isomer for C_3H_4 would form a complex with O_2^+, unlike what was seen for $C_2H_2^+$.

Nils Hertl opened a discussion of the paper by Amy S. Mullin: What limits your rotational excitation and can you push those limits to realise CO_2 dissociation through rotational excitation?

Amy S. Mullin answered: The extent of rotational excitation in an optical centrifuge depends on the spectral bandwidth of the Ti:sapphire pulses and the interaction strength of the molecules with the optical field. The centrifuge consists of a pair of oppositely chirped pulses, centered at 805 nm. Over the time of the pulse, the frequency difference between the pair of pulses increases linearly and sweeps through sequential Raman transitions from J to $J = 2$. Molecules gain rotational energy through this ladder of transitions. Once the intensity of the field becomes insufficient to ramp to the next $J + 2$ state, the centrifuged molecules have reached their ultimate J states. With our current bandwidth, we can excite CO_2 to near $J = 390$ with a rotational energy of around 7.4 eV. The thermodynamic bond dissociation energy is 5.5 eV, so there is enough energy for dissociation, but the rotation adds a significant centrifugal barrier, so additional energy is needed to break the bond by adding rotation. The ultimate J state for excitation also depends on the trapping strength, which is linearly proportional to the anisotropic polarizability of the molecules.

Nils Hertl enquired: Do you see vibrational excitation due to rotational relaxation in your experiments?

Amy S. Mullin replied: We observe vibrationally excited CO_2 molecules that are formed by collisions after the centrifuge pulse. Initially, the largest energy source is the ensemble of optically centrifuged molecules, and as collisions occur, translational energy is also available from collision products. Transient absorption profiles for a number of CO_2 vibrational modes have been observed, including three quanta in the bending mode.[1] The energy partitioning in the vibrational states we have looked at so far include a significant amount of translational energy, corresponding to an impulsive energy transfer mechanism.

1 L. Yuan, S. W. Teitelbaum, A. Robinson and A. S. Mullin, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 6872.

Patrick Robertson queried: Can you comment more on the deviation from the rigid rotor model that you observe around $J = 259$ and $J = 280$? Naively, we teach undergraduates that high rotational excitation couples into vibration, but this ignores complexities such as symmetry requirements. Are these deviations truly coupled rovibrational states or just coincidental degeneracies?

Amy S. Mullin responded: The presence of perturbations in the IR spectrum of the CO_2 Nu_3 fundamental transitions results from the symmetry, energy, and rotational quantum number of the (00^01) state. The vibrational symmetry is antisymmetric with exchange of the oxygen atoms. It can interact with other antisymmetric vibrations if the rovibrational energies are similar and the rotational quantum numbers are the same. The (11^10) vibration, with 1 quantum in the symmetric stretch and 1 quantum in the bend, is the perturbing state near $J = 257$. The (03^30) state, with 3 quanta in the bend, is the perturbing state near $J = 291$. The energy for the lowest J state of (11^10) is 270 cm^{-1} below the $J = 0$ state of (00^01) and the lowest J state of (03^30) is an additional 80 cm^{-1} lower. As such, these vibrational states are not Fermi-mixed in the way that one quantum of symmetric stretch mixes with two quanta of bend, leading to two separate J manifolds. In the case here, differences in the rotational constants for the (00^01), (11^10), and (03^30) states lead to J-specific mixing when the energies of two J states from different vibrations happen to become similar. The state-mixing is strongest when the energy difference is closest to zero, as is seen from the range of J states that are perturbed. In these regions, the states are coupled.

Daniel R. Moon said: Fig. 10a in your article (**https://doi.org/10.1039/d3fd00179b**) illustrates that the rate of change of the average angular momentum projection quantum number is less for the highest J state (282) compared to the other states. Could you provide more details on this?

Amy S. Mullin answered: The reduced relaxation rate for the average angular momentum quantum number of CO_2 $J = 282$ is a direct result of the initial distribution of rotational states prepared by the optical centrifuge pulse. For this data set, the optical centrifuged bandwidth was reduced so that the $J = 282$ state is the highest state populated (within our detection limits). On the time scale of our measurements, collisions induce population decay of the optically centrifuged molecules, which leads to some extent of lab-frame reorientation of their angular momentum vectors. The products of collisions move centrifuged molecules into lower J states, leading to average angular momentum projection quantum numbers that are less than that for $J = 282$. In this way, states with $J < 282$ have a source of reorientated molecules that feed into them, and their average projection quantum number decreases by collisions. Up-collisions that move population into $J = 282$ are unlikely because of the large energy gap. Therefore, for the $J = 282$ state, there is no source that brings in population of reoriented molecules through collisions, and the relaxation rate of average m_J is smaller than for the lower states.

Kenneth G. McKendrick remarked: I would like to ask about the efficiency of the stimulated-Raman optical-centrifuge pump process. Is this sufficient to excite a high-enough proportion of the CO_2 molecules for collisions of two high-J molecules to be probable? This would be feasible, at least in terms of overall number density, because the mean-free path at the pressures of the experiments would be shorter than the estimated diameter of the pumped volume.

If so, is there any signature of this *via* energy-pooling collisions, leaving one molecule in a significantly higher J-state than the highest levels that are pumped directly?

As a follow-up question, is there anything in the measurements that makes it possible to identify the source of intermediate-J molecules, *e.g.*, in $J = 92$? I mean by this whether they have been collisionally relaxed down after having been pumped to much higher J, or excited upwards from the thermal bath in collisions with high-J molecules. There is a conceptual difficulty with making this distinction when the pumped and thermal bath molecules are identical, because at least in principle no conservation laws are violated if in a collision between two CO_2 molecules they effectively switch quantum states and/or velocities. One possible way round this would be to have distinguishable pumped and collision-partner molecules. Can I ask if it is technically possible to rotationally excite one type of molecule, which is efficiently pumped by the optical centrifuge, in the presence of another that interacts only weakly or ideally not at all? I exclude the trivial case of, *e.g.*, a monatomic noble-gas partner, but consider a molecular partner that would be capable of being rotationally excited in the collisions with the pumped molecules. This presumably depends on a favourable arrangement of Raman cross sections.

Amy S. Mullin replied: (i) Regarding the number density of optically centrifuged molecules, and the possibility of collisions between two super-rotors: it is possible in our experiments that two high-J molecules can collide. The number density of excited CO_2 in our interaction volume is about 60% of the initial ensemble. The mean free path for collisions between two super-rotors is about 12 microns, which is smaller than the 100 micron beam diameter in the x-direction, and much smaller than the probe distance in the z-direction.

(ii) Regarding the idea of up-collisions of centrifuged molecules: we have looked for the outcome of collisions that move population into higher J states than are initially prepared by the centrifuge pulse. For the systems we have looked at, we see no evidence for up-collisions of the highest J states. State-to-state rate constants for the high-J states are skewed to down-collisions in large part by rotational energy gaps that increase linearly with J. For only moderately centrifuged molecules, my guess is that collisions could move centrifuged molecules into higher J states. This question can be investigated using a tunable optical centrifuge.

(iii) Regarding the source of intermediate J states: you raise an interesting question and one that we often consider. The molecules in scattering experiments rarely come with labels, which makes sorting out energy transfer dynamics challenging. However, there are some tools at our disposal to identify the molecules involved in the energy transfer using the tunable optical centrifuge and transient polarization spectroscopy. We measured very small alignment parameters for the CO_2 $J = 92$ molecules in these experiments, showing that they likely correspond to bath molecules that have been excited. The relaxation rates for alignment of centrifuged molecules are less than for population decay, and both are less than the collision rate. Your question could be answered in the following way. I envision experiments where the initial set of centrifuged molecules has quantum numbers that are far above those of the thermal bath. Measuring the time evolution of low-, mid-, and high-J molecules, along with their polarization, should provide some information about their origin. In our earliest optical centrifuge experiments, we used the full bandwidth of the centrifuge pulse to excite CO_2 to J higher than $J = 350$ and measured the rotational energy gain in the

300 K bath.[1] Combining this approach with polarization analysis, knowledge of the initial high-*J* population, and master-equation modeling will give clues about the species involved in the overall energy transfer process.

(iv) Regarding selective excitation: not all molecules are optically centrifuged with the same efficiency. It may be possible to look at energy transfer in bimolecular collisions with two different species, where only one has been optically centrifuged. In this case, it would be possible to perform such an experiment.

1 L. Yuan, S. W. Teitelbaum, A. Robinson and A. S. Mullin, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 6872.

Daniel M. Neumark asked: Why are the Doppler profiles for the highly excited rotational states so much narrower than those of the lower-lying states?

Amy S. Mullin responded: There are several possibilities for the difference in Doppler widths between low and high rotational states. It is clear from our data that the low-*J* states gain significant translational energies through non-resonant impulsive collisions. These molecules could start either as super-rotors and be on their way down to lower states, or they could be thermal bath molecules getting excited by super-rotors. For the systems we have looked at, the high-*J* states routinely have narrow Doppler profiles. If there are sufficient number densities of super-rotors, near-resonant energy transfer between super-rotors could occur and would result in very little energy being available for translation, along with small changes in rotation, leaving the high-*J* molecules with narrow Doppler profiles. The same observable for the high-*J* molecules would result from non-resonant energy transfer if the centrifuged molecules started off with sub-thermal profiles. We have experiments underway to establish initial pre-collision Doppler profiles, which will give us insight into the collision dynamics.

David W. Chandler enquired: Dr Mullin, if one would change the chirp of your laser beams, such that the laser beams had initially a large energy gap moving toward a small energy gap at the later part of the overlap of the beams, would you expect to be able to drive molecules to high vibrational levels in a manner similar to your present experiment where you drive molecules to high rotational levels? What would the issues be that might limit this vibrational pumping?

Amy S. Mullin answered: Dr Chandler, this method in principle could be an effective tool for sequential vibrational pumping. Given no restrictions on laser power or bandwidth, one could combine pairs of oppositely chirped pulses that start with an initial frequency difference that is larger than the fundamental vibrational transition and a final frequency difference that approaches zero. Vibrational anharmonicity ensures that subsequent vibrational Raman transitions to higher v states will be driven as the frequency difference becomes smaller. Practical considerations for such an experiment include the need for sufficient optical bandwidth to excite Raman active vibrational modes and for sufficient optical intensity at the ± frequencies required for the initial Raman transition.

Arthur G. Suits queried: Is it possible that the translationally cooler Doppler profiles for the centrifuged molecules arise from greater scattering out of the *x–y*

plane? I gather you believe instead that the centrifuge selects a translationally cooler portion of the distribution to begin with. What is the reason for this selectivity?

Amy S. Mullin replied: At this point, we do not have hard evidence that the centrifuged molecules start out cold relative to the thermal sample. We have some clues from depletion measurements that collisions with lower relative velocity have higher inelastic cross sections.[1] In these experiments, we observe depletion of CO_2 low-J states ($J = 0$ and 36) with Doppler broadening corresponding to translational temperatures of 130 K. In our paper here (https://doi.org/10.1039/d3fd00179b), we present a possible scenario to explain the lack of Doppler broadening in high-J states. If the centrifuged molecules start out translationally cold, their Doppler widths could appear near 300 K after they gain translational energy from non-resonant collisional energy transfer. Another possibility is that near-resonant energy transfer occurs between two super-rotor molecules, leaving little extra energy available for recoil. We currently have sufficient signal levels that we can make the high J Doppler measurements before collisions take place and establish the initial translational energies.

1 M. J. Murray, H. M. Odgen, C. Toro, Q. Liu, D. A. Burns, M. H. Alexander and A. S. Mullin, *J. Phys. Chem. A*, 2015, **119**, 12471–12479.

Alec. M. Wodtke commented: The obvious question here for chemistry concerns the nature of reactivity for such highly rotationally excited molecules. Can you suggest a target system that appears to be experimentally accessible? This should be a system that theoreticians could also work on.

Amy S. Mullin responded: To investigate the effect of high rotation on chemical reactions is an exciting prospect, yet poses a number of experimental challenges. The method of rotational excitation needs to be selective, so that both reactant species are not driven into high J states, and then there needs to be a detection scheme to observe the reactants. At this point, I cannot outline a scheme for such an experiment, but this is an active area of research interest. Support from theorists will be an important component as well.

Hua Guo said: It is generally believed that reactant rotational excitation inhibits reactivity due to an increased effective barrier. However, there is evidence of rotational enhancement of reactivity. Recently, Odom and coworkers have demonstrated that super-rotor states of SiO^+ are more reactive with H_2 than lower rotational states.[1] Our theoretical studies indicated that this can be attributed to the reaction coordinate of the dominant transition state with a large component in the SiO^+ rotational coordinate. This case suggests that rotational energy can indeed be used to promote reactions.[1]

1 S. Venkataramanababu, A. Li, I. O. Antonov, J. B. Dragan, P. R. Stollenwerk, H. Guo and B. C. Odom, *Nat. Commun.*, 2023, **14**(1), 4446, DOI: 10.1038/s41467-023-40135-x.

Amy S. Mullin answered: Thank you for mentioning this paper. For the one reactive system we have studied, $CO(J) + CO$, which ultimately forms C_2, we found

the opposite effect, namely that increasing the number density of high-J molecules by a factor of two decreased the reaction product signal by a factor of two.[1] Future work will no doubt reveal a wide range of behavior and deeper insight into energy and chemical reactivity.

1 H. M. Ogden, T. J. Michael, M. J. Murray, Q. Liu, C. Toro and A. S. Mullin, The effect of CO rotation from shaped pulse polarization on reactions that form C_2, *Phys. Chem. Chem. Phys.*, 2019, **21**, 14103.

Geert-Jan Kroes remarked: I would suggest an experiment in which you collide rotationally excited CO_2 with a copper surface. There is plenty of experimental evidence to suggest that rotational pre-excitation promotes reaction with surfaces.

Amy S. Mullin replied: It would indeed be exciting to combine optical centrifuge excitation with surface scattering.

Patrick Robertson commented: The idea of bimolecular reactions in these super-rotors always struck me as an analogue to roaming, where rather than an atom orbiting a potential, you have a stationary atom with an orbiting potential well, which the atom samples over and over again. This sort of dynamics might favour non-linear transition states.

Amy S. Mullin responded: Super-rotors have large angular velocities compared to a 300 K thermal sample. Their rotational periodicity is essentially proportional to the ratio of I/J, the moment of inertia over the rotational quantum number. Angular frequencies affect collisional energy transfer efficiencies. We have observed that CO_2 super-rotors are quenched more efficiently in collisions with helium than with argon.[1] The higher efficiency of quenching by helium is connected with its higher relative linear velocity. Reaction efficiencies of super-rotors will also likely be affected by the relative values of angular and linear velocities.

1 M. Murray, H. M. Ogden and A. S. Mullin, Importance of rotational adiabaticity in collisions of CO_2 super rotors with Ar and He, *J. Chem. Phys.*, 2018, **148**, 084310.

Hua Guo added: I am not sure if it is related to roaming, but a strong component of the reaction coordinate in the reactant rotational mode is known to promote reactivity, based on the Sudden Vector Projection model.[1]

1 H. Guo and B. Jiang, *Acc. Chem. Res.*, 2014, **47**(12), 3679–3685, DOI: **10.1021/ar500350f**.

Patrick Robertson asked: Beyond a need to accurately characterise the spectroscopy of these super-rotors in these extreme environments, is your detection method limited to transient IR? What are the limitations of generating and studying super-rotors in, for example, a mass spectrometer?

Amy S. Mullin replied: The detection of optically centrifuged molecules is not limited to transient IR detection. Coherent Raman scattering and ionization schemes with mass spectrometry are other approaches that have been used. Our interest in molecular energy transfer mechanisms makes transient IR probing very attractive as it provides an unprecedented level of detail of rotational, vibrational, electronic, and translational energies as they evolve in time.

Arthur G. Suits said: I would think these spectroscopic measurements for very high rotational levels would be of interest to astronomers examining exoplanet atmospheres. Have you found this to be the case, have any been in contact with you?

Amy S. Mullin responded: A number of exoplanets appear to have high temperature conditions and the presence of numerous unassigned lines. I am currently working with an exoplanet researcher on this topic. Other groups who have contacted me include researchers who model spectra in high temperature environments, including inputs for spectral databases.

David W. Chandler enquired: Dr Mullin, as you can drive rotational energy into your molecules up to the dissociation limit of the molecule (including a large centrifugal barrier), would the addition of your infrared detection photon then push such a metastable molecule over the dissociation barrier and dissociate the molecule, or is the rotational and vibrational energy in the molecule independent?

Amy S. Mullin answered: Dr Chandler, you pose an intriguing question. My prediction is that the addition of an IR photon could be used to induce dissociation if the molecule was poised for dissociation with energy and rotational quantum number J just below the reaction threshold. IR excitation to a $v = 1$ and $J + 1$ state could push it over the edge and induce a reaction. The key is to find that threshold state.

Alec. M. Wodtke remarked: One possible experiment that might be attractive would be to spin-up the molecules with the molecular centrifuge in a molecular beam, photo-ionize them and thereby remove a binding electron. This might lead to dissociation of the ion that could be observed with ion imaging. Such an experiment could have a very high S/N ratio and provide "knobs to turn", *e.g.*, photo-ionization wavelength and initial J excitation, as well as detailed dynamical information in the ion images.

Amy S. Mullin replied: Your proposal is interesting and suggests a number of possible systems to study. Using light as an additional knob to turn can open new opportunities and new scientific insights.

Joshua Wagner opened a discussion of the paper by Bum Suk Zhao: The maximum reflectivity of helium atoms scattering from epitaxial graphene on ruthenium is cited to be 20%,[1] while the blazed gratings used in this study (https://doi.org/10.1039/d3fd00155e) demonstrate reflectivity upwards of 50%. Could you summarize the surface dynamics that allow such a high reflection efficiency to be achieved in comparison to a single-crystalline surface?

1 G. Anemone, A. A. Taleb, S. D. Eder, B. Holst and D. Farías, *Phys. Rev. B*, 2017, **95**, 205428.

Bum Suk Zhao responded: In multiple edge-diffraction reflections, only atoms that do not collide with the half-plane surface contribute to the diffraction pattern and, hence, to the reflectivity. Therefore, surface dynamics as well as surface
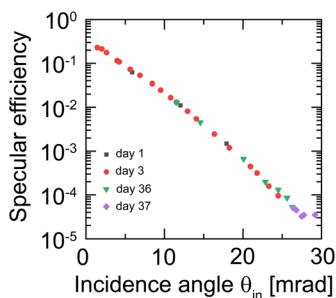
Fig. 7 Specular reflection efficiency of helium atoms scattering off a 1 µm-period grating.

roughness and defects appear to be much less relevant for the reflection than in classical reflection from a crystal surface.

Chris Sparling queried: Does the reflectivity of the grating degrade notably over time, and how stable is it over typical experiment timescales? If it degrades, could this be due to any non-reflected He sticking to the surface?

Bum Suk Zhao answered: We did not observe any variations in the reflectivity of any surface for at least a month in our atom scattering experiment under grazing incidence conditions, although the surfaces were kept in a relatively "bad" vacuum of 10^{-7} mbar. For example, Fig. 7 shows the specular reflection efficiency of helium atoms scattering off a 1 µm-period grating, in which the efficiency hardly varied over 37 days at least.

Christopher Reilly asked: How close does a helium atom get to the grating before it is turned around?

Bum Suk Zhao replied: Since multiple edge-diffraction reflection is a wave-like phenomenon, it might not be entirely appropriate to discuss a specific point where an atom "turns around" in classical terms. Some atoms can approach right above the grating edges, but the turning point is generally uncertain.

Viet Le Duc enquired: Will the helium beam show any form of constructive interference, like when light is reflected from a grating to form a diffraction pattern?

Bum Suk Zhao responded: There is indeed constructive interference due to the periodicity of the grating, leading to significant diffraction efficiencies as predicted by the multiple edge-diffraction reflection theory[1] for ideal parallel edges. Diffraction patterns resulting from multiple edge-diffraction have been observed by two groups,[2,3] thereby confirming that multiple edge diffraction is a *coherent* scattering mechanism. However, in our present work (**https://doi.org/10.1039/d3fd00155e**), we were unable to observe any diffraction peaks using the commercial gratings we employed. We attribute this lack of observable diffraction peaks to two main factors.

Firstly, the grating magnification significantly widens the diffraction beams that are scattered at larger angles, farther away from the surface, under grazing incidence conditions. This broadening reduces the visibility of these diffraction beams compared to the specular beam, as discussed in ref. 4–6.

Secondly, the imperfect edges of the commercial gratings, coupled with the interaction between atoms and the finite-width edges, attenuate the diffraction beam intensities from the theoretical values. This attenuation becomes more significant for beams that scatter at greater angles.

These two factors contribute to the infinitesimal peak height, obscuring the diffraction beams.

We are preparing a manuscript that includes a quantitative discussion of why we could not observe diffraction peaks from the commercial gratings.

1 E. Bogomolny and C. Schmit, *Nonlinearity*, 2003, **16**, 2035–2059.
2 H. Oberst, D. Kouznetsov, K. Shimizu, J. Fujita and F. Shimizu, *Phys. Rev. Lett.*, 2005, **94**, 013203.
3 J. H. Lee, L. Y. Kim, Y.-T. Kim, C. Y. Lee, W. Schöllkopf and B. S. Zhao, *Phys. Rev. Lett.*, 2019, **122**, 040401.
4 C. Palmer, *Diffraction Grating Handbook*, MKS Instruments, Inc., New York, 8th edn, 2020.
5 L. Y. Kim, D. W. Kang, J. C. Lee, E. Chae, W. Schöllkopf and B. S. Zhao, *arXiv*, 2023, preprint, arXiv:2311.12416, DOI: **10.48550/arXiv.2311.12416**.
6 L. Y. Kim, D. W. Kang, J. C. Lee, E. Chae, W. Schöllkopf and B. S. Zhao, *Phys. Rev. A*, 2024, **110**, 013313.

Vimala Sridurai commented: Prof. Zhao, this is very interesting work! Can you please comment on the following? When the gratings with multiple edge-diffraction reflection (MEDR) mirrors are used to focus matter waves of neutral atoms at grazing (or close to grazing) incidence angles, what is the expected resolution when these neutral atoms are employed in a scanning microscope?

These gratings seem to be more efficient with increased reflectivity in the grazing angle. So, does increasing the reflectivity have any particular effect on the resolution?

Bum Suk Zhao answered: We estimated a 90 nm resolution for He atoms of 56 pm wavelength with a 1 μm diameter micro-skimmer[1] and elliptical concave mirrors.[2] We could improve the resolution by applying an advanced Kirkpatrick–Baez (AKB) geometry developed in X-ray microscopy, which shortens the focal length by moving the principal plane.[3–5]

Since the AKB geometry consists of four mirrors, high reflectivity is mandatory for it. The AKB geometry decreases the effective focal length, which is beneficial for microscope resolution.

1 J. Braun, P. K. Day, J. P. Toennies, G. Witte and E. Neher, *Rev. Sci. Instrum.*, 1997, **68**, 3001–3009.
2 H. C. Schewe, B. S. Zhao, G. Meijer and W. Schöllkopf, *New J. Phys.*, 2009, **11**, 113030.
3 J. Yamada, S. Matsuyama, Y. Sano and K. Yamauchi, *Appl. Opt.*, 2017, **56**, 967–974.
4 J. Yamada, S. Matsuyama, I. Inoue, *et al.*, *Opt. Express*, 2019, **27**, 3429–3438.
5 J. Yamada, S. Matsuyama, I. Inoue, *et al.*, *Nat. Photon.*, 2024, **18**, 685–690.

Gil Alexandrowicz said: Since the reflection probability at grazing angles is relatively high and since the scattering is purely elastic (as evidenced by the helium trimer reflection), I wanted to suggest, as an application, using the mirror to bend/guide beams in bi-molecular collision experiments. In particular,

currently merged beams are used to create ultra-low energy collisions. This is currently done by choosing one collision partner as a controllable/steerable particle, for example metastable helium, which has an electronic spin and can be bent using magnetic fields. Using reflective mirrors such as the one shown in your work (**https://doi.org/10.1039/d3fd00155e**) and a small number of reflections, perhaps a beam could be effectively bent. The advantage would be that it would be much more generally applicable than magnetic- or electric-based manipulation, *i.e.*, it could open up cold collisions for species that haven't been accessible to experiments.

Bum Suk Zhao replied: We have considered a collision experiment involving an incident beam clipped by the grating and the reflected beam. The idea of using mirrors to guide a molecular beam for bi-molecular collision experiments is indeed intriguing.

Steven J. Sibener remarked: It would seem that you could apply a large-area curved reflective surface to use in microscopy based upon using a focussed atomic beam of helium. Your unique surfaces would appear to be ideal substrates for constructing a variety of neutral helium atomic beam microscopes. Please comment on this exciting possibility.

Bum Suk Zhao responded: We have demonstrated one-dimensional focusing of a helium atom beam using a cylindrical concave mirror based on quantum reflection.[1] Building on this, our research group has been considering the construction of a scanning helium microscope utilizing focusing mirrors, similar to KB (Kirkpatrick–Baez) optics used in X-ray microscopy.

So far, the optical components we have tested were commercially available ones. To achieve optimal resolution in our helium microscope, we recognize the need to precisely control the curvature and significantly enhance the reflectivity of the focusing components. This will likely involve custom fabrication and advanced surface engineering techniques.

1 H. C. Schewe, B. S. Zhao, G. Meijer and W. Schöllkopf, *New J. Phys.*, 2009, **11**, 113030.

Steven J. Sibener commented: Given the high reflectivity of your surface, I was curious if you are planning to carry out a double-scattering experiment. Here, you would scatter from one surface, and then aim the initially scattered beam onto a second highly-reflective surface. This arrangement would, in principle, allow you to prepare beams that conserve the *m*-state for very flat surfaces.

Bum Suk Zhao answered: I haven't considered a double-scattering experiment yet, but I am thrilled to hear about the various possible experiments using our method, as discussed here. The idea of using our highly reflective surfaces to manipulate atoms and molecules in such innovative ways is very exciting, because it could, possibly, open up new avenues for interesting experiments. We look forward to exploring these possibilities further.

Gilbert M. Nathanson queried: What do you believe is the smallest spatial resolution that can be achieved in a helium microscope?

Bum Suk Zhao replied: We estimated a 90 nm resolution for He atoms of 56 pm wavelength with a 1 μm diameter micro-skimmer[1] and elliptical concave mirrors.[2] We could improve the resolution by applying an advanced Kirkpatrick–Baez geometry developed in X-ray microscopy, which shortens the focal length by moving the principal plane.[3–5]

1 J. Braun, P. K. Day, J. P. Toennies, G. Witte and E. Neher, *Rev. Sci. Instrum.*, 1997, **68**, 3001–3009.
2 H. C. Schewe, B. S. Zhao, G. Meijer and W. Schöllkopf, *New J. Phys.*, 2009, **11**, 113030.
3 J. Yamada, S. Matsuyama, Y. Sano and K. Yamauchi, *Appl. Opt.*, 2017, **56**, 967–974.
4 J. Yamada, S. Matsuyama, I. Inoue, *et al.*, *Opt. Express*, 2019, **27**, 3429–3438.
5 J. Yamada, S. Matsuyama, I. Inoue, *et al.*, *Nat. Photon.*, 2024, **18**, 685–690.

Steven J. Sibener said: Another exciting aspect of your system would be to do either localized photoemission using electronically excited beams of helium, or even localized lithography. Surface ionization, such as with Penning processes, seems possible. Please comment on these possibilities.

Bum Suk Zhao responded: I am aware that Prof. Holst's group at the University of Bergen is working on lithography using a beam of metastable helium atoms.[1] Indeed, experiments involving photoemission and Penning ionization induced by localized collisions of metastable helium atoms are very interesting.

To focus metastable helium atoms effectively, we need to further improve the reflectivity of our surfaces. The strong interactions of metastable helium atoms are expected to decrease the reflectivity, especially for structures with finite widths at the edges.[2] Addressing this challenge is crucial for optimizing the performance of these experiments and unlocking their full potential.

1 T. Nesse, I. Simonsen and B. Holst, *Phys. Rev. Appl.*, 2019, **11**, 024009.
2 D. Kouznetsov and H. Oberst, *Phys. Rev. A: At., Mol., Opt. Phys.*, 2005, **72**, 0136176.

Conflicts of interest

There are no conflicts to declare.