Faraday Discussions
Cite this: *Faraday Discuss.*, 2022, **238**, 121

DISCUSSIONS

Collisional energy transfer: general discussion

Dmitri Babikov, Michael P. Burke, Piergiorgio Casavecchia, William H. Green, Alon Grinberg Dana, Hua Guo, Dwayne E. Heard, David Heathcote, Majdi Hochlaf, Ahren W. Jasper, Stephen J. Klippenstein, Marsha I. Lester, Carles Martí, Alexander M. Mebel, Amy S. Mullin, Thanh Lam Nguyen, Matthias Olzmann, Andrew J. Orr-Ewing, David L. Osborn, Patrick A. Robertson, Matthew S. Robinson, Robin J. Shannon, Oisin J. Shiels, Arthur G. Suits, Craig A. Taatjes, Jürgen Troe, Xuefei Xu, Xiaoqing You, Feng Zhang, Rui Ming Zhang and Judit Zádor

DOI: 10.1039/d2fd90048c

Robin J. Shannon opened discussion of the introductory lecture by Stephen J. Klippenstein: I was surprised and heartened by your success in using a statistical approach to treat roaming radical channels. Could you comment further on the reasons why statistical rate theory appears to be predictive for such dynamical processes?

Stephen J. Klippenstein answered: One does expect some dynamical effects, particularly with biases toward continuing to dissociate after passing the inner transition state. I think what my results indicate is that those biases are not as large as one might think. Overall, there is still an underlying, more or less statistical, sampling of the orientational motions. Notably, for more complex cases, such as the RO···OH fissions of the vinyl hydroperoxides arising from Criegee intermediates, the increased strength of the interactions in the van der Waals complex regime will lead to even more effective randomization of the motions.

Thanh Lam Nguyen asked: Could you comment on an earlier master equation (ME) work reported by Zachariah and Tsang,[1] where these authors computed flux rate coefficients (as expectation values) as a function of time and determined reaction rate constants at a pseudo steady-state condition (*i.e.*, $\mathrm{d}(k(T,p))/\mathrm{d}t \sim 0$)?

1 V. M. Bedanov, W. Tsang and M. R. Zachariah, *J. Phys. Chem.*, 1995, **99**, 11452–11457.

Stephen J. Klippenstein replied: Probably the best thing to do here is to simply refer you to an article by Miller *et al.* that specifically focuses on the connection between phenomenological rate coefficients and flux coefficients.[1] The bottom

line is that, anytime you think you have time-dependent phenomenological rate constants, you are probably confused about the meaning of phenomenological rate constants.

1 J. A. Miller, S. J. Klippenstein, S. H. Robertson, M. J. Pilling, R. J. Shannon, J. Zador, A. W. Jasper, C. F. Goldsmith and M. P. Burke, *J. Phys. Chem. A*, 2016, **120**, 306–312.

Matthias Olzmann remarked: In your talk and article (**https://doi.org/10.1039/d2fd00125j**), you mentioned that the angular momentum dependence of tunneling contributions is neglected in all current models. What do you have in mind? Just the tunneling through the (angular momentum-dependent) centrifugal barriers, or do you think that additional dynamic contributions may exist?

Stephen J. Klippenstein responded: As you suggest, the standard assumption about the effect of angular momentum on tunneling is that it simply modulates the barrier potential through the addition of geometry-dependent centrifugal energy. What Yuri has derived is a dynamical correction that properly considers the effect of angular momentum fluctuations along the instanton trajectory.[1] We have not yet implemented this in any calculations, so we do not have a sense of how much it differs in practice. But formally, at least, it is quite different.

1 Y. Georgievskii and S. J. Klippenstein, Entanglement Effect and Angular Momentum Conservation in a Nonseparable Tunneling Treatment, *J. Chem. Theory Comput.*, 2021, **17**, 3863–3885.

Rui Ming Zhang said: Hi Stephen, thank you for your wonderful lecture. I have a question: if all isomer wells merged with bimolecular sinks in a reaction system, how could we describe the phenomenological kinetics of this system? I agree with the "species-reduction" method for treating the merger in multiple-well reactions. But I still was wondering if it is appropriate to be applied to a single-well reaction, *e.g.*, a unimolecular dissociation reaction. For example, for a dissociation reaction, A → B + C, when the temperature is high enough, unimolecular A will be merged with bimolecular B + C, so then how could one describe the phenomenological kinetics of such a reaction?

Stephen J. Klippenstein responded: In that case, you should consider the reaction forming A. Suppose it is D + E → A. That reaction should then be replaced with the reaction D + E → B + C, *i.e.*, A should never show up in a mechanism.

Michael P. Burke addressed Rui Ming Zhang and Stephen J. Klippenstein: I wanted to comment on Rui Ming Zhang's question about how to treat the phenomenological kinetics of molecular entities whose chemical timescales are not well separated from the relaxational ones, and which are, therefore, 'merged' with other species instead of existing as distinct chemical species. In addition to treating their unimolecular reactivity *via* well-skipping reactions among bimolecular species and/or wells that exist as species, one can also treat their bimolecular reactivity *via* chemically termolecular reactions[1] and well-skipping

bimolecular reactions. I discuss this in greater detail in my *Faraday Discuss.* paper for this meeting (**https://doi.org/10.1039/d2fd00054g**).

1 M. P. Burke and S. J. Klippenstein, *Nat. Chem.*, 2017, **9**, 1078.

Hua Guo asked: Since the experiment uses a photon to prepare the initial state, do you need to worry about mode specificity when you do kinetics?

Marsha I. Lester responded: We have found no evidence of mode specificity for the different IR transitions of ˙QOOH observed. The unimolecular decay rates scale uniformly with energy, as anticipated by statistical unimolecular reaction theory. From a spectroscopic perspective, we observe a rotational band contour for each vibrational transition that can be simulated using computed rotational constants, the IR laser bandwidth, and a homogeneous broadening term consistent with intramolecular vibrational redistribution on a few ps timescale. For example, see Fig. 3 in our *Faraday Discuss.* paper (**https://doi.org/10.1039/d2fd00008c**), where simulations are shown using the Gaussian laser linewidth (0.9 cm^{-1}, gray) and a Lorentzian linewidth (1.7 cm^{-1}) arising from homogenous broadening (black). The latter is primarily attributed to rapid (*ca.* 3 ps) intramolecular vibrational redistribution (IVR), consistent with the density of vibrational states (*ca.* 100 states per cm^{-1}) at 3579.5 cm^{-1} corresponding to fundamental OH stretch (ν_{OH}) excitation.

Oisin J. Shiels continued discussion of the introductory lecture by Stephen J. Klippenstein: You showed that for low-pressure rate constants there is a cutoff when radiative cooling outcompetes collisional deactivation (**https://doi.org/10.1039/d2fd00125j**). Do you think the current methods used to calculate rates of radiative cooling are sufficient in this low-pressure regime or will anharmonic terms eventually have to be included to achieve perfect agreement between theory and experiments?

Stephen J. Klippenstein replied: The answer to your question depends on what you mean by 'sufficient'. In prior work with Rob Dunbar, I think we concluded that simple doubly harmonic approximations (harmonic frequencies, harmonic intensity) seemed to be sufficient to predict radiative emission rates to within about a factor of two.[1,2] If you wish to predict them more accurately than that then, yes, anharmonicities in both the vibrations and the dipole moments will be important. Furthermore, there are undoubtedly pathological cases where the doubly harmonic approximation will fail even more significantly.

1 S. J. Klippenstein, Y.-C. Yang, V. Ryzhov and R. C. Dunbar, Theory and Modeling of Ion-Molecule Radiative Association, *J. Chem. Phys.*, 1996, **104**, 4502–4516
2 Y.-P. Ho, Y.-C. Yang, S. J. Klippenstein and R. C. Dunbar, Binding Energies of Ag^+ and Cd^+ Complexes from Analysis of Radiative Association Kinetics, *J. Phys. Chem. A*, 1997, **101**, 3338–3347.

Dwayne E. Heard communicated: I had a general question about the use of master equation methods for simulating the kinetics of reactions at very low temperatures, which are being used both to compare with CRESU experimental results, and to predict behaviour beyond conditions that can be obtained in the

lab. For example, are the parameterisations for $\langle \Delta E_{down} \rangle$ as a function of energy still valid for use at temperatures, for example, in the range 10–50 K? Also, there are some precision challenges for very low temperature calculations; can you comment on those also?

Stephen J. Klippenstein communicated in reply: Your question about the meaningfulness of energy transfer parameterisations down to very low temperature is a good one. The behavior near room temperature is by now quite well established through numerous substantive comparisons of theory and experiment. Such comparisons generally do not exist for temperatures in the range from 10–50 K. I always wonder whether the transition to a regime where the van der Waals well depths exceed the temperature might somehow dramatically increase the energy transfer rates. Furthermore, one might wonder whether quantum effects somehow become important. Regarding your second question: I believe the precision challenges for low temperature calculations have largely been met. The exception to this would be the case where the temperatures are so low that rotational states should be treated quantum mechanically. At least, our MESS master equation code is not set up to handle that situation. However, for the most part, that is below 10 K. One exception to that is OH, where strong coupling of rotational and electronic motions extends the quantum effects to somewhat higher temperature.

Carles Martí opened the discussion of the paper by Ahren W. Jasper: Considering that you are computing the final total energy and angular momentum once the reactant and bath are sufficiently separated in a trajectory, how do you deal with the presence of long-lived adducts for which such analysis is not possible (**https://doi.org/10.1039/d2fd00038e**)? Is the ratio of adduct formation considerable? Have you come up with any methods for such cases?

Ahren W. Jasper replied: For systems involving so-called "chattering" collisions, the trajectories are run long enough for the systems to eventually dissociate, and the computed moments of the collision kernel therefore include these kinds of multi-collision effects. For cases where longer-lived complexes are formed, such as systems with deep van der Waals wells at low temperatures, complexation could be treated using a master equation. Much of our attention has focused on conditions at 300 K and above where complex formation is not typically important.

Thanh Lam Nguyen asked: Two questions: first, are there good physical reasons to select a P(E,J) kernel function (as you did), which does not include coupling terms between E and J? Second, how do you compute rotational energy levels for asymmetric molecules (like H_2O) because there is no analytical formalism?

Ahren W. Jasper responded: Our detailed collision kernel is not separable but instead includes a mixing angle that couples E and J. In my opinion, the details of the collision kernel are not so important so long as it is flexible enough to accurately reproduce the trajectory-based moments. Our choice of collision kernel seems to work, but other choices may work as well. I would expect the accuracy of

the predicted rate constants to depend on how well the moments are reproduced. Regarding the computation of rotational energy levels for asymmetric tops, in our master equation calculations, we average the two most similar rotational constants and use a symmetric top approximation. One could diagonalize a 3×3 matrix to generate accurate rotational levels for asymmetric tops, but it seems unlikely to be a noticeable improvement. For some cases, such as the HO_2 kinetics studied here, we employ rovibrational anharmonicity corrections computed using Monte Carlo phase space integrals that include this effect, along with other more important coupling effects.

Michael P. Burke remarked: Very nice talk and very nice work. It was particularly exciting to see your paper describe energy transfer calculations for the stronger baths, like water and CO_2, which enable the field to begin to address a number of outstanding questions. I was interested in your comments on mixture effects, where the bath gas is a multi-component mixture (instead of a pure bath gas). Much of what is known about bath gas mixture effects is based on 1D energy transfer only, where it was found that the stronger collider serves to maintain higher reactant populations at the energies just below the dissociation threshold and, in so doing, enhances the effectiveness of weaker colliders. Your 2D calculations suggest that stronger colliders also have the same effect for angular momentum, such that one might expect that proper 2D analysis might yield mixture effects that are stronger than earlier approximate 1D studies. Do you agree? At the same time, I was surprised that your calculations for pure H_2O agreed well with experimental determinations for H_2O rate constants, which are all based on experiments in mixtures that were not interpreted in a way that properly accounts for mixture effects. Do you have any thoughts on this?

Ahren W. Jasper replied: It is very interesting to see the magnitudes of the mixture effects that you are reporting, and it would seem likely that mixture effects would feature so-called "2D" angular momentum effects analogous to the effects we quantified for pure baths. For pure baths, these effects have a noticeable effect on k_0, typically lowering k_0 by a factor of two or three. These effects largely cancel out when looking at the ratio of k_0 for two different baths, however. Perhaps this cancellation of errors obscures the interpretation of some of the experimental comparisons.

Hua Guo asked: Your potential energy surface consists of the interaction potential and monomer potentials. If I understand it correctly, the monomer potentials are essentially force fields. This is probably a good approximation for molecules at the bottom of the potential well. What happens if molecules are closer to dissociation? Do you need to worry about the suitability of the force fields in describing the potentials near the dissociation limit?

Ahren W. Jasper answered: We often use molecular mechanics force fields to describe monomer potentials, but we sometimes fit special monomer potential energy surfaces. For HO_2, for example, where the H atom can hop back and forth between the O atoms at the energies of our calculations, we generated and employed a flexible HO_2 surface. We found only negligible differences in our computed energy transfer rates using this more accurate surface when compared

with results generated using a fixed-bonding molecular mechanics force field. It seems unlikely that collisional energy transfer will be sensitive to the treatment of the monomer potential near the threshold, particularly for systems with more than a few atoms and that are at thermal or hotter conditions. Empirically at least, it appears that, while the accuracy of the interaction potential is important, the monomer potentials can be handled much more approximately.

Judit Zádor asked: Carbon dioxide and water appear towards the end of the combustion process. Are combustion models sensitive to energy transfer with other species, such as radicals, which appear earlier during combustion and, if so, is it possible to easily extend these calculations to such potentially disparate sets of colliders?

Ahren W. Jasper replied: No radicals were considered here, but our theoretical approaches would be applicable. I would not expect radicals to behave very differently from similar closed-shell species. Differences might arise when the radical features a stronger orientation dependence in its interaction potential (perhaps due to preferential prereactive orientations associated with the radical site) than is usual for saturated closed-shell species. Finally, we note that the fuel itself may be an important collider early in combustion, and a few small fuel baths were considered here.

Jürgen Troe commented: This article provides a most useful report on today's possibilities to characterize collisional energy transfer in thermal unimolecular reactions by *ab initio* calculational methods. As many details of the treatment get lost during thermal averaging, it appears useful to focus attention on what survives. For inefficient energy transfer ("weak collisions"), it is known that the master equation takes the form of a Fokker–Planck-type diffusion equation, whose solution only depends on "diffusion coefficients", such as $\langle \Delta E^2 \rangle$ or $\langle \Delta E \rangle$, and overall collision numbers (for a one-dimensional master equation).[1–4] These quantities refer to all activating and deactivating (and not only to deactivating) collisions. The temperature dependence of these quantities is most relevant for practical calculations of low-pressure rate constants. Could you say more, *e.g.*, about $\langle \Delta E \rangle$? For instance, values of $\langle \Delta E \rangle$ have been fitted to experimental results for the dissociation of CH_4 in Ar up to about 4500 K and found to be nearly temperature independent.[5] Could you rationalize such empirical conclusions?

1 T. Bak and S. E. Nielsen, *J. Chem. Phys.*, 1964, **41**, 665.
2 J. C. Keck and G. F. Carrier, *J. Chem. Phys.*, 1965, **43**, 2284.
3 C. A. Brau, J. C. Keck and G. F. Carrier, *Phys. Fluids*, 1966, **9**, 1885.
4 E. E. Nikitin, *Theory of Thermally Induced Gas Phase Reactions*, Indiana University Press, Bloomington and London, 1966.
5 C. J. Cobos and J. Troe, *Z. Phys. Chem.*, 1992, **176**, 161.

Ahren W. Jasper responded: The present trajectory calculations for CH_4 (+Ar) predict $\langle \Delta E \rangle$ to be independent of temperature, with $\langle \Delta E \rangle = -20 \pm 10$ cm^{-1} from 300 to 4500 K. This prediction has a small absolute error relative to the numbers reported by Cobos and Troe[1] (-50 ± 10 cm^{-1}), but a large relative error. Because $\langle \Delta E \rangle$ is typically close to zero, trajectory-based approaches might always suffer from larger relative errors in $\langle \Delta E \rangle$ than in, say, $\langle \Delta E_d \rangle$, thus limiting their usefulness for predicting $\langle \Delta E \rangle$. Another confounding choice is the treatment of angular

momentum. In the trajectory averages reported above, the initial state J was thermally distributed, but other choices, such as transition-state-theory-based or other statistical distributions, might be more appropriate and would change the quantitative results. Both the smallness of $\langle \Delta E \rangle$ and the choice of the initial J state distribution might also obscure trends with respect to temperature. Both $\langle \Delta E_u \rangle$ and $\langle \Delta E_d \rangle$ show stronger temperature dependence, and it's hard to predict if their near cancellation for CH_4 (+Ar) should be expected in general. For other systems and colliders, we and others have found some small temperature dependence in $\langle \Delta E \rangle$.

1 C. J. Cobos and J. Troe, *Z. Phys. Chem.*, 1992, **176**, 161.

William H. Green asked: At first glance, it is surprising that Fig. 5a and b in your paper (**https://doi.org/10.1039/d2fd00038e**) are so curved, while Fig. 5c is so linear. A big part of the shape of Fig. 5a and b is because these are upwards transitions, and so are expected to be affected by the shape of $\rho(E)$, which would not give a linear semi-log plot. But I'd be interested in a further analysis of the shapes of these curves. Is there a simple explanation for why the curves in Fig. 5c are roughly linear in ΔE_{up}?

Ahren W. Jasper responded: The microcanonical activation rates shown in Fig. 5 of the paper include transitions where $\Delta E < 0$ and the rotationally adiabatic dissociation threshold E_J is lowered by more than ΔE, and exclude transitions where $\Delta E > 0$ and E_J is raised by more than ΔE. If we instead compute rates for "upward" collisions where $\Delta E > 0$ and ignore the effects of changes to E_J, the resulting curves indeed have much less curvature and are nearly independent of the initial rotational state.

Craig A. Taatjes asked: I am interested in your conclusions about the role of the initial state on the relative efficiency of different collision partners. You show that collision partners are more similar to each other near the dissociation threshold. Do you have a general reason for this? Are there any consequences for collision-partner dependence of branching fractions for cases where there may be a couple of thresholds that are close in energy? As a follow-up to my previous question – would there be an opportunity to change branching fractions by the choice of colliders?

Ahren W. Jasper responded: It is likely that branching depends on the choice of collider, even for colliders with similar overall efficiencies but different underlying details. The shape of the collision kernel is a sensitive function of the bath gas and should have a significant impact on branching, especially if the two channels differ in the angular momentum dependence of their thresholds.

Alon Grinberg Dana remarked: According to the paper (**https://doi.org/10.1039/d2fd00038e**), "…it seems unavoidable that *a priori* strategies are needed for predicting collisional energy transfer and its effect on k_0 and k_p…". Regarding Fig. 5c in the paper, it might seem possible to develop some intuition regarding the linear slope of the normalized k_0 *vs.* ΔE for the different colliders. Would you agree?

Ahren W. Jasper replied: I do hope that progress can be made rationalizing the microcanonical rate constants. I made some attempt at this and showed, for example, that the rigidity of the transition state controlled the J dependence of the microcanonical rate constants.[1] Regarding the relationship between reactivity and moments, the first-order moments are more predictive of reactivity for weak colliders, while the second-order moments are more predictive for stronger colliders. It may be that more than one moment is required for rationalizing energy transfer.

1 A. W. Jasper, Microcanonical rate constants for unimolecular reactions in the low-pressure limit, *J. Phys. Chem. A*, 2020, **124**, 1205.

Stephen J. Klippenstein asked: For colliders like H_2O with large ΔE_{down} values, the energy transfer may approach the strong collider limit. In this case, the overall rate is limited by the presumed form for the collision rate. Does this cause any trouble for your formalism? In particular, is your formalism somehow limited by the rate of a Lennard-Jones collider in the strong collider limit?

Ahren W. Jasper responded: When using the detailed collision kernel, the total collision rate is treated as one of its parameters that is optimized against the large set of double moments. This parameter is an important one for accurately reproducing the trajectory-based moments, and so it would seem to be constrained by them. The optimized values of the total collision rate often end up 20–50% larger than the Lennard-Jones collision rate, which is in agreement with estimates of total collision rates based on long-range forces and capture.

Xuefei Xu communicated: Hi Ahren, could you please comment on the potential influence of hydrogen-bonding interactions between bath gas molecules on collisional energy transfer when with water molecules as colliders at very low temperatures or high pressures? Is it possible that the average energy transfer parameters of the water molecules show a much different temperature dependence below room temperature? If we have to perform trajectory simulations for obtaining the collisional transfer rate at very low temperatures (for example, below 200 K), how important is it to include the quantum effects (zero-point energy and tunneling) in the simulations with water molecules as the bath gas? Thank you.

Dwayne E. Heard communicated a related question: For some reactions, particularly at lower temperatures, a molecule of water has been seen to act as a catalyst to speed up a reaction by lowering the barriers for a reaction, for example, *via* a chaperone-type mechanism. From your results, you see $k(H_2O)/k(Ar)$ of 40 for states below the threshold, and for room temperature. What would the situation be at temperatures down to 10–50 K? Can you comment on what the relative efficiencies of H_2O *versus* Ar and other bath gases are at very low temperatures, as I can imagine that these may be very different indeed?

Ahren W. Jasper communicated in reply: Responding to both Profs. Heard and Xu, at very low temperatures, the full-dimensional classical trajectory approach used here may not be appropriate. Instead, methods that freeze vibrations and

consider only rotational excitation and de-excitation are likely to be more useful. Complicating matters, very low-temperature collisions may feature new mechanisms, such as increasing contributions from multiple collision (sometimes called chattering) processes, including those promoted by hydrogen bonds. More generally, the effects of many-body collisions involving transient complexes are likely key for understanding low-temperature unimolecular kinetics. Simplifying matters on the other hand, unimolecular kinetics at very low temperatures are likely governed by just a few relevant reactant states at low J states and at energies very close to the threshold. When this is the case, collisional reactivity, such as the relative importance of H_2O and Ar, is perhaps dominated by their overall collision rates, which could be estimated in a variety of ways, and a detailed collision kernel may not be required.

Matthew S. Robinson opened the discussion of the paper by Amy S. Mullin: In the paper (**https://doi.org/10.1039/d2fd00068g**), you suggest a 3% excitation rate of the sample. How were you able to determine this experimentally?

Amy S. Mullin responded: An excitation rate of 3–5% was measured for CO and CO_2, based on the transient absorption measurements of the rotational distributions following the optical centrifuge (OC) pulse. The optical centrifuge prepares an inverted rotational distribution for each species. We used a tunable optical centrifuge to control the angular frequency at which molecules are released from the optical trap. We measured absorption intensities as a function of J, interpolated for states that were not measured, converted the fractional absorption intensities to number densities (based on an estimated interaction path length of the OC and IR beams) and summed over all states. The key to this measurement is knowing the J-specific IR absorption cross sections for the centrifuged molecules.

Matthew S. Robinson asked: Are you able to increase the amount of sample that you are able to excite, or do you have experimental limitations that would prevent you from doing so?

Amy S. Mullin responded: The fundamentals for optically centrifuging molecules are based on the induced dipole interaction between the molecule and the optical field. The molecule's polarizability anisotropy and optical field strength must both be large enough for effective centrifugation. There are experimental limits to the field strength based on the output power of our pulsed laser system. For some molecules, using full intensity optical pulses induces an optical filament, which interferes with the production of high-J molecules in the ground electronic state. Increasing the pressure can increase the population of high-J molecules, within limits. Increasing the pressure leads to increased collision rates, which, in turn, reduce the time window to observe the optically centrifuged molecules. Our experiments so far have been performed on an isotropic sample in a 300 K gas cell. We are currently exploring whether a pre-alignment pulse could be used to increase the overall trapping efficiency.

Patrick A. Robertson asked: Given the large energy associated with these high-J species, do you see reactive collisions or vibrational excitation in the rotational deactivation?

Amy S. Mullin replied: We have observed both reactions of optically centrifuged molecules and vibrational excitation in the rotational relaxation process. Here I outline 3 scenarios where we have observed no reactions, reactions, and vibrational excitation.

(1) No reactions: under relatively low pressure conditions of 10 Torr and below, we do not observe unimolecular dissociation of CO, N_2O, or CO_2. The full bandwidth of our optical centrifuge corresponds to a rotational frequency of 6×10^{13} radians per second and is capable of exciting CO to $J = 84$ (13 600 cm^{-1}), N_2O to $J = 378$ (60 000 cm^{-1}), and CO_2 to $J = 400$ (63 200 cm^{-1}). Optically centrifuged N_2O and CO_2 are energetic enough to dissociate, but their dissociation requires excitation to even higher J states because of the centrifugal barrier.

(2) Reactions: under pressures above 10 Torr, we have observed CO reactions that lead to C_2 formation initiated by optical centrifuge pulses.[1] The CO is electronically excited by multiphoton absorption and collisions lead to formation of the triplet a-state. The triplet a-state is involved in a two-step mechanism to form C_2, which is observed by Swan band emission. We control the number density of rotationally excited CO molecules by controlling the polarization of the optical pulses. Optical centrifuge polarization leads to larger number densities of high-J CO molecules by more than a factor of two, compared to dynamic polarization grating pulses. Larger numbers of high-J CO molecules lead to a reduction in C_2 products, showing that the reaction has a linear transition state structure.

(3) Vibrational excitation: we have observed vibrational excitation of CO_2 following an optical centrifuge pulse.[2] We saw transient appearance of three quanta in the bending mode in the $J = 43$ state. Large Doppler widths indicate that this state is populated by collisions during the rotational relaxation. We currently have experiments underway to investigate the vibrational distributions of collision products and their associated rotational distributions.

1 H. M. Ogden, T. J. Michael, M. J. Murray, Q. N. Liu, C. Toro and A. S. Mullin, *Phys. Chem. Chem. Phys.*, 2019, **21**, 14103.
2 L. Yuan, S. W. Teitelbaum, A. Robinson and A. S. Mullin, *Proc. Natl. Acad. Sci.*, 2011, **108**, 6872.

Patrick A. Robertson asked: Correlated rotational excitation has been observed in CO–CO collisions, where both species increase their respective J during a collision. Do you expect to find similar dynamics here, and why, or why not?

Amy S. Mullin answered: The time-dependent, high-J distributions of optically centrifuged CO show that up-collisions of centrifuged molecules to higher J states are negligible. Instead, down-collisions are the dominant process. Correlated rotational excitation is observed when the collision energy is large enough to induce positive ΔJ transitions in both collision partners. This will generally be true for lower J states with smaller energy gaps. In the case of optically centrifuged CO with J values near 80, the energy gaps are near 300 cm^{-1}. Doppler profiles for the optically centrifuged molecules show that the centrifuge preferentially traps and angularly accelerates molecules with lower velocities. The larger energy gaps and lower velocities for high-J molecules combine to reduce the likelihood for correlated rotational excitation because the collision energy is insufficient to overcome the required energy needed to reach higher J states.

Patrick A. Robertson remarked: A high angular velocity relative to translational velocity feels somewhat analogous to a roaming trajectory, where a particle makes several orbits of a molecule on its journey towards a reaction. Could you comment on these similarities and differences, or perhaps some other relatable phenomena you might hope to find in these super-rotor systems?

Amy S. Mullin responded: You make an interesting observation about the similarities of the relative motions of rotation and translation in collisions of high-J molecules and the dynamics of roaming collisions. The high angular frequency of the centrifuged molecules affects the collision dynamics in several ways. High angular velocity inhibits relaxation of orientational anisotropy based on the classical physics of gyroscopes. We have observed this phenomenon in the relaxation of optically centrifuged CO and CO_2. The second effect is that the collisions lead to rotational and translational excitation of bath molecules, but the high-J molecules remain cool translationally. A third aspect of the dynamics is that the relative collision velocity has a notable effect on the energy transfer process by changing the rotational adiabaticity of the collisions. When He atoms are present as bath species, optically centrifuged CO_2 relaxes more quickly than when Ar atoms are present as quenchers.[1] For high-J CO_2 states, the average relative velocity of He–CO_2 collisions is larger than for Ar–CO_2 collisions. From the perspective of the rotating molecule, He atoms are able to have impulsive collisions within a time-frame that is short compared to the rotational period. In contrast, the Ar–CO_2 collisions are dominated by rotational motion that is faster than the relative translational velocity, and the presence of impulsive collisions is reduced. In a sense, the Ar–CO_2 collisions are less "sudden" because the angular velocity is relatively large.

1 M. J. Murray, H. M. Ogden and A. S. Mullin, *J. Chem. Phys.*, 2018, **148**, 84310.

Dmitri Babikov queried: Amy, regarding the state-to-state transition cross sections in Fig. 5 of your paper (**https://doi.org/10.1039/d2fd00068g**), are those theoretical or experimental? Did anyone try to do the calculations? What method did they use? I think we can compute those using the mixed quantum/classical theory. Thanks.

Amy S. Mullin replied: The state-to-state rate constants in Fig. 5 of the paper are based on double resonance experiments by Phipps *et al.*[1] They measured state-to-state rate constants for a number of J states of CO with $J = 0$–29, then fit their data to a statistical power exponential gap model. We used their fitting parameters and extrapolated values out to $J = 90$. I am not aware of theoretical studies of the state-to-state rate constants, and look forward to learning of your work in this area.

1 S. P. Phipps, T. C. Smith, G. D. Hager, M. C. Heaven, J. K. McIver and W. G. Rudolph, *J. Chem. Phys.*, 2002, **116**, 9281.

Hua Guo asked: CO is a very stable molecule, but could you use your method to induce chemical reactions? Have you seen any possible products from these collisions?

Amy S. Mullin answered: Despite the stability of CO, we have initiated bimolecular reactions of CO with the optical centrifuge and detected C_2 products with Swan band emission.[1] At pressures of 25 Torr and above, the intense field of the focused optical centrifuge beam induces multiphoton absorption ($n = 7$–8) to the CO B-state, which rapidly converts to the triplet a-state through collisions. The proposed mechanism includes two reactive steps. In the first, CO in the triplet a-state reacts with thermal CO to form CO_2 and a C atom. The second step is the reaction of the C atom and CO in the triplet a-state to form C_2 and O atoms.

1 H. M. Ogden, T. J. Michael, M. J. Murray, Q. N. Liu, C. Toro and A. S. Mullin, *Phys. Chem. Chem. Phys.*, 2019, **21**, 14103.

Hua Guo asked: Have you seen adducts forming? Species that show some sort of interaction, but not necessarily a product.

Amy S. Mullin replied: Apart from the strong-field-induced chemistry of CO, we have not observed the formation of adducts for optically centrifuged CO, CO_2, and N_2O.

Craig A. Taatjes queried: Have you seen vibrational excitation arising during the relaxation of your rotationally excited molecules?

Amy S. Mullin answered: We have observed CO_2 with 3 quanta in the ν_2 bending mode (with $J = 43$) following the optical centrifuge pulse.[1] The Doppler profiles are broad at 50 collisions (1100 K), consistent with being formed through collisions. The spectral bandwidth of the optical centrifuge pulses is not sufficient to form the vibrationally excited states directly through Raman excitation. The vibrational relaxation is slow compared to the rotational relaxation of the vibrationless ground state. This initial report of vibrationally excited products from collisions of optically centrifuged molecules does not represent a complete study, and experiments are currently underway to investigate this phenomenon more thoroughly.

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

David L. Osborn said: In Fig. 3(c) of the paper (**https://doi.org/10.1039/d2fd00068g**), you show the exponential decay of CO molecules with $J = 70$. If we simplify the situation by assuming that only $\Delta J = 1$ energy transfer may occur, then this level is being filled from $J = 71$ and depleted by transfer to $J = 69$. Because those state-to-state rates are likely quite similar, shouldn't this time trace look approximately like a steady-state population that is not decaying in time, rather than a rapidly decaying exponential as seen in the red trace of Fig. 3(c) of the paper?

Amy S. Mullin answered: In the limit of rotational energy transfer with $\Delta J = -1$ and similar rate constants for adjacent J states, one might expect a steady-state population in CO high-J states, as you say. However, the observed transient signals for the highest J states formed in the optical centrifuge exhibit exponential decay. This behavior results from three sources: down-collisions with absolute ΔJ

values that are larger than one, the minimal contribution of up-collisions with $\Delta J > 0$, and the vanishingly small number densities in higher J states. The time-dependent rotational populations give further insight into this phenomenon. Fig. 7 in our paper (**https://doi.org/10.1039/d2fd00068g**) shows that the linear fits overlap at a common J state without any constraints for both optical traps. If up-collision energy transfer was an important pathway, the fit results would not show such an overlap. The physical picture is clear: the high-J CO molecules formed in the optical centrifuge relax through a distribution of down-collisions that move the population to lower states. Lower down in the rotational ladder, the observed kinetics are quite different. For example, population increases are observed in $J = 29$ of CO (which is not thermally populated at 300 K) and the transients show quasi-steady-state behavior. The population appearing in $J = 29$ initially comes from excitation of the thermal bath molecules, and then later from the cascade of centrifuged molecules that are relaxing. Steady-state behavior is observed when the appearance rate is balanced by collisional relaxation, until the system eventually returns to thermal equilibrium. The kinetics of the high-J portion of the initial distribution give us a unique window to measure relaxation kinetics with minimal competition from up-collisions.

Andrew J. Orr-Ewing asked: How directly comparable do you think your measurements are with the master equation modelling, given that your experimental method produces a highly oriented sample of rotationally excited CO molecules, whereas the modelling assumes an isotropic spatial distribution of angular momentum vectors?

Amy S. Mullin responded: You make an interesting observation and raise a good question. Once the oriented rotors are released from the optical trap, they undergo collisions with an isotropic ensemble of bath molecules. Our Doppler profiles show that collisions of the high-J CO rotors lead to both rotational and translational energy gains in the bath molecules, but the high-J rotors retain their narrow profiles, indicating that they do not gain translational energy through collisions. As time elapses after the centrifuge pulse, the relative velocity of the overall sample increases as energy is partitioned into translation during the relaxation process. The master equation modelling is based on coupled rate equations for rotational energy transfer, and the simulation does not account for the translational energy gains in the sample. Therefore, the experiments and modelling should be most similar at early times after the centrifuge pulse, before the translational energy gains occur.

Andrew J. Orr-Ewing asked: To expand on my question a little more, in your experiments, the rotationally excited CO molecules are prepared in a narrow distribution of m_J states and so are rotating like propellers all pointing in similar directions in the lab frame. Do their collisions with an isotropic bath gas differ from what would be expected if all m_J states were equally populated (so the directions of rotation are randomized in the lab frame)?

Amy S. Mullin replied: For a single high-J rotor, the value of m_J should have no affect on the collision dynamics in an isotropic bath. A CO rotor with $J = 80$ and $m_J = 80$ rotates in a plane that is orthogonal to the plane of rotation for a rotor

with $J = 80$ and $m_J = 0$. If the bath is isotropic, the plane of rotation will not affect the energy transfer dynamics. For an ensemble of oriented rotors, however, the energy transfer dynamics are expected to be anisotropic. Translational energy gain in scattered bath molecules is likely to be found in the plane of rotation, which will affect subsequent collisions. Simulations by Steinitz, Prior, and Averbukh[1] show that collisions in an ensemble of oriented rotors lead to the generation of macroscopic vortex gas flows. If all m_J states were equally populated, no such vortex would be generated.

1 U. Steinitz, Y. Prior and I. S. Averbukh, *Phys. Rev. Lett.*, 2012, **109**, 033001.

Andrew J. Orr-Ewing queried: If very specific stereodynamics of the collisions of the bath gas CO molecules with the high-J CO rotors are required for the J-changing collisions, might these specific interactions be undersampled in an experiment with highly oriented CO rotors compared to the master equation models?

Amy S. Mullin responded: The master equation simulations solve for the overall relaxation kinetics based on state-to-state (STS) rate constants for rotational energy transfer. In this case, we extrapolated data from double resonance experiments on CO with $J = 0$–29 by Phipps *et al.*[1] to get STS rate constants up to $J = 90$. If specific stereodynamics are required for J-changing collisions of high-J CO rotors, the simulations will not account for this requirement. On the other hand, if the STS rate constants for high-J rotors are smaller than the extrapolated values, the master equation simulation would mirror the slower relaxation for the undersampled interactions.

1 S. P. Phipps, T. C. Smith, G. D. Hager, M. C. Heaven, J. K. McIver and W. G. Rudolph, *J. Chem. Phys.*, 2002, **116**, 9281.

Arthur G. Suits asked: Do you see anisotropy in the Doppler profiles for the collisional populated levels? Can you look for this?

Amy S. Mullin answered: So far, we have measured Doppler profiles with the IR probe beam crossing the optical centrifuge beam. This configuration measures the velocity components in the xy-plane in which the molecules are optically centrifuged. We measure decreasing translational energies as J increases. It is likely that recoil energy from collisions is larger in the xy-plane, given the oriented angular momentum of the centrifuged molecules. We have experiments underway now to measure Doppler profiles perpendicular to the plane of centrifugation.

Dwayne E. Heard communicated: Knowledge of the rates of rotational energy transfer at very low temperatures is needed in order to derive column densities and, hence, molecular abundances from telescope observations. This is particularly important for CO, which is used to infer a number of other astrophysical parameters. Is the J dependence that you observe experimentally, and, for example, is shown in Fig. 4(a) of the paper (**https://doi.org/10.1039/d2fd00068g**), taken into account by astronomers in determining CO abundances?

Amy S. Mullin communicated in reply: The *J*-dependent rate constants we report are likely applicable in astronomical environments in cases where high-*J* states are populated. Under cold astronomical conditions, number densities in high-*J* states are negligible and the associated rotational energy transfer rates will also be negligible. Astronomers use rotational distribution measurements to account for molecular column densities. As an example, CO has been measured in protostar outflows, and bimodal rotational distributions are reported with temperatures of 100 K (major component) and 350 K (minor component).[1] Their analysis includes states with *J* below 20. In other work on exoplanet environments, there is evidence for rotational distributions with temperatures above 1000 K, leading to emission from unassigned high-*J* rotational states. See, for example, ref. 2. In these environments, it will be important to characterize the collisional dynamics of high-*J* molecules.

1 Y.-L. Yang, J. D. Green, N. J. Evans II, J.-E. Lee, J. K. Jørgensen, L. E. Kristensen, J. C. Mottram, G. Herczeg, A. Karska, O. Dionatos, E. A. Bergin, J. Bouwman, E. F. van Dishoeck, T. A. van Kempen, R. L. Larson and U. A. Yıldız, *Astrophys. J.*, 2018, **860**, 174.
2 P. F. Bernath, *Philos. Trans. R. Soc., A*, 2014, **372**, 20130087.

Dwayne E. Heard communicated: What is the outlook for extending your experiments for molecules like NO, or even the OH radical, for which a lot of previous work on rotational energy transfer (RET) has been done, and for which spin–orbit propensities would be interesting to examine over a wide range of initially excited rotational states?

Amy S. Mullin communicated in reply: The mechanism for trapping and angularly accelerating molecules in an optical centrifuge involves an induced dipole interaction between the optical field and the polarizability anisotropy of the molecule. Based on our CO experiments, we expect that NO will have similar trapping efficiencies. Hydrides, such as OH and water, have substantially smaller polarizability anisotropies and the extent to which they are trapped and angularly accelerated is also reduced. It would be very interesting to investigate spin–orbit propensities in rotational energy transfer for a range of excited rotational states.

Craig A. Taatjes communicated: In many quantum systems, it is assumed that behavior approaches the classical limit at high levels of excitation. Going to high quantum numbers is not necessarily the same as having Planck's constant go to zero, but do you anticipate (or are you looking for) ways in which the rotor system becomes "more classical" at these levels of excitation?

Amy S. Mullin communicated in reply: This is an interesting question for molecules in high-*J* rotational states. A common form of the correspondence principle informs us that quantum systems behave classically when the quantum number is large. While this is the case for vibrational states, it does not hold true for rotation. Rotational energy increases as *J*-squared, and the energy gaps between states increase linearly with *J*. Thus propensities for collisional energy transfer decrease as a function of *J*, and orientational anisotropy decay lifetimes increase with *J*. Our experiments show that rotational energy transfer rates decrease as *J* increases and the energy gaps exceed the average thermal energy.

David Heathcote communicated: In Fig. 12 of the paper (https://doi.org/10.1039/d2fd00068g), there seem to be some J states that have higher anisotropy than the neighbouring states (the orange bands in Fig. 12(a), for example). My initial assumption would be that this is the result of some form of quantum effect, but would you be able to comment further? In addition, some states, such as $J = 64$ and 65 in Fig. 12(b), appear to lose their initial anisotropy more rapidly than other states shown in the figure. Could you comment on this?

Amy S. Mullin communicated in reply: The observed variations in orientational anisotropy values between adjacent states in Fig. 12 of the paper are most likely caused by experimental uncertainties. There are two sources of uncertainty: one is from the measurements themselves, and the second is the interpolation for states that were not measured directly. It is unlikely that the deviations are the result of quantum effects. At the time of our measurements, the system will have undergone decoherence decay through dephasing and collisions.

Dmitri Babikov opened the discussion of the paper by Xiaoqing You: Hi, how appropriate would the quality of these PESs be for the calculations of rotational state-to-state transitions? I am asking because I am interested in employing these surfaces for the description of rotational state-to-state transitions in PAHs using a recently developed mixed quantum/classical theory. A relevant paper on benzene + He is given as ref. 1. For this paper,[1] we used a relatively old PES from the literature, but we are interested in trying your PES (https://doi.org/10.1039/d2fd00058j) for these kinds of calculations. Thanks.

1 B. Mandal, C. Joy, A. Semenov and D. Babikov, Mixed quantum/classical theory for collisional quenching of PAHs in the interstellar media, *ACS J. Earth Space Chem.*, 2022, **6**, 521.

Xiaoqing You answered: Thank you very much for your question. I notice that your recent paper focused on the collisional quenching and excitation of astrochemically important molecules. The objective of our paper is to obtain effective Lennard-Jones parameters for predicting macroscopic quantities, such as binary diffusion coefficients. We assume the intermolecular potential between a target molecule A and a bath gas molecule M can be calculated as the sum of pairwise atom–atom interactions, which are described by a modified Buckingham potential (referred to as exp-6). Both A and M are fixed at the equilibrium structures, and, therefore, we do not evaluate the internal (rotational and vibrational) states of molecules as you did in your paper. I also notice that the translational motion of collision partners was described classically using the mean-field trajectories, and I wonder if that could be evaluated using our approach.

Feng Zhang queried: Can you give more comments on the differences between the Lennard-Jones potentials of long chain-like molecules and aromatic compounds?

Xiaoqing You responded: Thank you very much for the question. For molecules of similar mass, the atoms on the edge are farther away from the center of mass for a long chain-like molecule than a disc-like aromatic molecule, and,

therefore, the intermolecular potential between a long chain-like molecule and a bath gas molecule is more anisotropic than that between a disc-like aromatic molecule and the bath gas molecule. Consequently, the Lennard-Jones collision diameter for the chain-like orientation is the largest, which can be seen from the three-dimensional surfaces of the collision diameters.

William H. Green said: These intermolecular potentials are important for diffusion and many other properties. The shapes matter, *e.g.*, collisional energy transfer is sensitive to the shape of the repulsive wall, so Lennard-Jones might not be the best choice. Have you compared your calculations to other properties beyond those covered in the paper, such as viscosities?

Xiaoqing You responded: Thank you very much for your comments. We agree with your points. Our focus is on obtaining effective Lennard-Jones parameters for predicting transport properties, which might not be the best choice for collisional energy transfer. We would like to compare our results with other properties, such as viscosities, however, the intermolecular force field we use in this paper describes the interactions between hydrocarbons and bath gases only. To calculate other properties, such as viscosities, a combining rule must be applied, which may bring uncertainty. We will look into this issue in future work.

Judit Zádor remarked: In Fig. 2 of the paper (**https://doi.org/10.1039/d2fd00058j**), the repulsive part of the exp-6 intermolecular potential is much steeper than that of the *ab initio* one. Are the calculations sensitive to this part of the potential and, if so, how does it influence the results?

Xiaoqing You answered: Thanks for the question. The Lennard-Jones parameters obtained in our work are determined from the roots and well depths of intermolecular interaction potentials at different orientations. Consequently, it is not required to obtain a highly accurate intermolecular potential energy surface at all intermolecular distances, except for the region where the root and well depth are to be found.

Alexander M. Mebel asked a follow-up question to Judit Zádor's comment: Will the Lennard-Jones (L-J) parameters obtained in your work be sensitive with respect to the level of theory used for the calculations of the interaction potential? In particular, in your paper (**https://doi.org/10.1039/d2fd00058j**), you have compared the parameters obtained from your force field calculations with DFT results with the M062X functional and with CCSD(T)/CBS. Can further validation be provided by using DFT potentials from Head-Gordon's group (wB97XD), which better describe the long-range interaction? For larger systems, new local correlation methods like DLPNO-CCSD(T) are now available, which exhibit linear scaling and, hence, can be applied to large systems, describing in the meantime the full coupled-cluster results closely.[1] The use of these methods would allow you to provide further validation of your results for larger PAH systems and to establish the sensitivity of the L-J parameters σ and ε with respect to the theoretical method and assess possible error bars for these parameters.

1 J. Chai and M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620.

Xiaoqing You answered: Thank you very much for the question and suggestions. The Lennard-Jones parameters obtained in our work are determined from the roots and well depths of intermolecular interactions at different orientations. Consequently, it is not required to obtain highly accurate intermolecular potential energy surfaces at all intermolecular distances, except for the region where the root and well depth are to be found. Although the results reported in this paper seem to be satisfactory, we will further validate the intermolecular potentials using wB97XD and DLPNO-CCSD(T) as suggested in future work, for establishing the sensitivity of the L-J parameters σ and ε with respect to the theoretical method and assessing possible error bars for these parameters.

Majdi Hochlaf said: I have a comment and then a question.

Comment: Our experience in computing multidimensional potential energy surfaces for weakly bound complexes shows that virial coefficients are less sensitive to the quality of the potentials since they can be considered as "macroscopic" quantities. So, averaged L-J potentials, ignoring the anisotropy, should work. However, pressure-broadening coefficients are extremely sensitive to the anisotropy of the potentials, in particular those involving doubly degenerate vibrational modes. So the L-J potentials proposed in this paper (**https://doi.org/10.1039/d2fd00058j**) should be adapted to take into account strong anisotropic effects.

Question: Can you use these L-J potentials for dynamical studies in astrophysical conditions (low temperature, $T \sim 5$ K)?

Xiaoqing You responded: Thank you very much for your comments. The main purpose of our study is to obtain effective Lennard-Jones parameters for predicting macroscopic quantities, such as binary diffusion coefficients. We noticed that the anisotropy of potential energy surfaces does affect the results to some extent. Therefore, we compare the results of different averaging rules and try to find the most reliable and efficient method for getting the effective collision diameters and well depths. I agree that other quantities, such as pressure-broadening coefficients, are extremely sensitive to the anisotropy of the potentials, and the strong anisotropic effects should be considered in that case. As to your question, let me clarify our assumption. We assume the intermolecular potential between a target molecule A and a bath gas molecule M can be calculated as the sum of pairwise atom–atom interactions, which are described by a modified Buckingham potential (referred to as exp-6). Both A and M are fixed at the equilibrium structures, and, therefore, we do not evaluate the change of states of the molecules. It would be very interesting to explore whether our approach can be used to perform dynamical studies in astrophysical conditions.

Piergiorgio Casavecchia remarked: Two basic questions must be properly addressed concerning the procedure adopted in the paper (**https://doi.org/10.1039/d2fd00058j**).

The first question regards the use of the classical Lennard-Jones (L-J) model to represent the radial dependence of the intermolecular interaction. It is well-known that the L-J model exhibits an excessive repulsion at short range, and a too strong attraction at long range (asymptotically a factor of two larger with respect to the true value). Our group demonstrated that the L-J model is unable to simultaneously describe scattering cross sections, measured under resolution conditions appropriate to resolve quantum interference effects in the scattering, and this suggested to us the adoption of an Improved Lennard-Jones (ILJ) function, that removes most of the L-J inadequacies and maintains a relatively simple formulation (it involves only an additional parameter with respect to the L-J model) with analytical first and second derivatives. Its formulation is:[1]

$$V_{\mathrm{ILJ}}(r) = \varepsilon\left[\frac{m}{n(r)-m}\left(\frac{r_m}{r}\right)^{n(r)} - \frac{n(r)}{n(r)-m}\left(\frac{r_m}{r}\right)^{m}\right] \quad (1)$$

where ε and r_m are the depth and location of the potential well, respectively, associated with the pair of interacting partners. In addition, $m = 6$, $m = 4$ and $m = 1$ must be adopted for neutral–neutral, ion–neutral, and ion–ion pairs, respectively. The term $n(r)$ shows a dependence on the separation distance r, defined as:

$$n(r) = \beta + 4.0\left(\frac{r}{r_m}\right)^2 \quad (2)$$

The parameter β relates to the hardness of the two interacting fragments and, for typical non-covalent interactions, it is usually selected in the range of values from 7 to 9. A preliminary β value can be estimated from the softness s (defined as the cubic root of the electronic polarizability) and exploiting the following empirical relation:[2]

$$\beta = 6 + \frac{5}{(s_{\mathrm{i}} + s_{\mathrm{j}})} \quad (3)$$

The formulation of the second (negative) term in eqn (1) includes, in a simple and appropriate form, the radial dependence of the balance of all the leading long-range, attractive contributions with their proper damping effects. Therefore, ILJ provides asymptotically a long range attraction consistent with the experimental and theoretical results of each interaction pair.[1]

1 F. Pirani, S. Brizi, L. F. Roncaratti, P. Casavecchia, D. Cappelletti and F. Vecchiocattivi, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5489.
2 M. Capitelli, D. Cappelletti, G. Colonna, C. Gorse, A. Laricchiuta, G. Liuti, S. Longo and F. Pirani, *Chem. Phys.*, 2007, **338**, 62.

Xiaoqing You answered: Thank you very much for your comments. The objective of our paper is to obtain effective Lennard-Jones parameters for predicting macroscopic quantities, such as binary diffusion coefficients by using the Hirschfelder–Bird–Spotz (HBS) equation, which follows the Chapman–Enskog theory and combines with the Lennard-Jones 12-6 intermolecular potential function to determine the binary diffusion coefficient. If the intermolecular potential function is changed to another form, then a new equation for calculating binary diffusion coefficients may need to be derived first. Moreover, the Improved Lennard-Jones formula is more complex and may be more accurate than the Lennard-Jones 12-6 potential, however, it still needs to be verified

whether it is more appropriate for combustion cases. We will look into this problem in future work.

Piergiorgio Casavecchia added: The second question related to your paper (**https://doi.org/10.1039/d2fd00058j**) concerns the use of the Lorentz–Berthelot (LB) combination rules to estimate the potential parameters of an asymmetric system from those of the symmetric pairs. It has been demonstrated that such rules provide reasonable potential parameters only for cases involving partners with very similar electronic polarizability and whose basic interaction components are of the same nature (essentially van der Waals components).[1]

Correlation formulas (CF), of more general validity with respect to LB rules, are given in terms of the polarizability α (expressed in Å^3) of the interacting partners i and j.[1] They were proposed about 30 years ago and are useful to estimate the basic potential parameters. Their simplest formulations are:[1]

$$C_{6\text{eff}}\left(\text{eV Å}^6\right) = 15.7\frac{\alpha_\text{i}\cdot\alpha_\text{j}}{\sqrt{\frac{\alpha_\text{i}}{N_\text{i}}}+\sqrt{\frac{\alpha_\text{j}}{N_\text{j}}}}$$

where $C_{6\text{eff}}$ is an effective long-range attraction coefficient, which includes the role of the leading C_6 coefficient and of the higher-order terms. N is an effective number of electrons that control the polarization of each interacting partner;

$$r_m\left(\text{Å}\right) = 1.767\frac{{\alpha_\text{i}}^{1/3}+{\alpha_\text{j}}^{1/3}}{\left(\alpha_\text{i}\cdot\alpha_\text{j}\right)^{0.095}}$$

and

$$\varepsilon(\text{meV}) = 0.72\cdot\frac{C_{6\text{eff}}}{{r_m}^6}$$

It is interesting to note that all correlation formulas have been suggested by a phenomenological method, and the one defining r_m has been recently confirmed for symmetric noble gas dimers by a refined quantum mechanical treatment.[2] Such correlation formulas have also been extended to systems involving neutral partners with completely different structures, ions, open-shell atoms, and free radicals (see ref. 3 and 4, and references therein).

Both ILJ and CF have been largely exploited to calculate collision integrals of interest for transport properties in planetary atmospheres and plasmas of applied interest (see, for instance, ref. 5 and 6, and references therein).

Recently, the combined use of the ILJ and CF with state-of-the-art *ab initio* calculations of the interaction permitted researchers to obtain, in analytical form, the multidimensional potential energy surface (PES) describing the intermolecular interaction in the dimer of a prototype polycyclic aromatic hydrocarbon (PAH), such as coronene, which is an important intermediate in soot formation. Such a PES has been adopted in an evolutionary algorithm to define the geometry and stability of nanostructures formed by coronene clusters.[7,8]

1 R. Cambi, D. Cappelletti, G. Liuti and F. Pirani, *J. Chem. Phys.*, 1991, **95**, 1852.
2 D. V. Fedorov, M. Sadhunkhn, M. Stöhr and A. Tkatchenko, *Phys. Rev. Lett.*, 2018, **121**, 183401.
3 F. Pirani, G. S. Maciel, D. Cappelletti and V. Aquilanti, *Int. Rev. Phys. Chem.*, 2006, **25**, 165.

4 F. Nunzi, G. Pannacci, F. Tarantelli, L. Belpassi, D. Cappelletti, S. Falcinelli and F. Pirani, *Molecules*, 2020, **25**, 2367.
5 A. Laricchiuta, G. Colonna, D. Bruno, R. Celiberto, C. Gorse, F. Pirani and M. Capitelli, *Chem. Phys. Lett.*, 2007, **445**, 133.
6 A. Laricchiuta, D. Bruno, M. Capitelli, C. Catalfamo, R. Celiberto, G. Colonna, P. Diomede, D. Giordano, C. Gorse, S. Longo, D. Pagano and F. Pirani, *Eur. J. Phys. D*, 2009, **54**, 607.
7 M. Bartolomei, F. Pirani and J. M. Marques, *J. Phys. Chem. C*, 2017, **121**, 14330.
8 C. F. O. Correia, J. M. C. Marques, M. Bartolomei, F. Pirani, E. Maçôas and J. M. G. Martinho, *Phys. Chem. Chem. Phys.*, 2021, **23**, 1500.

Xiaoqing You answered: Thanks very much for the comment and suggestions. We are interested in modelling high-temperature combustion processes, which are very complex, and the intermolecular interaction potential is just one aspect of it. Instead of introducing an overly complicated calculation method, we are trying to simplify the problem as much as possible, while meeting the accuracy requirements. The performance of using the Hirschfelder–Bird–Spotz (HBS) equation and the Lorentz–Berthelot combination rules seems to be good enough for combustion problems, so it needs to be verified whether the ILJ and CF are effective for improving precision. Following the suggestions, we will adopt the ILJ and CF in follow-up studies to verify if these formulas are more appropriate for combustion problems.

Piergiorgio Casavecchia concluded: In regard to the paper (**https://doi.org/10.1039/d2fd00058j**), we believe that using the Improved Lennard-Jones potential model[1] and the correlation formulas (based on electronic polarizabilities) of Pirani and coworkers,[2] it will be possible to derive reliable and transferable interaction potential parameters for PAHs interacting with themselves, and with He and N_2.

In general, we wish to recommend the kinetics community to use the Improved Lennard-Jones model[1] and Pirani's correlation formulas[2,3] in place of the simpler (and not sufficiently accurate) Lennard-Jones 12-6 potential and the Lorentz–Berthelot combination rules.

1 F. Pirani, S. Brizi, L. F. Roncaratti, P. Casavecchia, D. Cappelletti and F. Vecchiocattivi, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5489.
2 R. Cambi, D. Cappelletti, G. Liuti and F. Pirani, *J. Chem. Phys.*, 1991, **95**, 1852.
3 F. Pirani, G. S. Maciel, D. Cappelletti and V. Aquilanti, *Int. Rev. Phys. Chem.*, 2006, **25**, 165.

Ahren W. Jasper commented: I enjoyed reading your paper. When we explored the σ/ε model, we found that no single set of L-J parameters performed well over a broad range of temperatures.[1] In Fig. 5 of the paper (**https://doi.org/10.1039/d2fd00058j**), you show good performance of your new η/ξ method below 1000 K, with larger errors for the simpler σ/ε model. The magnitude of your reported errors for the σ/ε model agrees with what we reported in our paper at similar temperatures for some different systems. There we showed that the performance of the σ/ε method improved at higher temperatures (see Fig. 4–6 from our paper[1]). Through comparisons with full-dimensional trajectories, we attributed this temperature-dependent error to the neglect of anisotropy, and this earlier result would suggest that the η/ξ approach might perform less well than the σ/ε model at higher temperatures than those considered in your comparisons. Furthermore, if anisotropy is important, as suggested by our study, it would seem to limit the accuracy of isotropic L-J models no matter how they are parametrized.

1 A. W. Jasper, E. Kamarchik, J. A. Miller and S. J. Klippenstein, *J. Chem. Phys.*, 2014, **141**, 124313.

Xiaoqing You replied: Thanks for letting us know that the performance of the σ/ε method improved at higher temperatures, and that this temperature-dependent error might be attributed to the neglect of anisotropy according to the full-dimensional trajectory results. In our work, we have not performed full-dimensional trajectory studies, but we evaluate the performance of different ways for obtaining effective Lennard-Jones parameters for *n*-alkanes[1] and PAHs (this work in **https://doi.org/10.1039/d2fd00058j**) by comparing with experimental diffusion data and those computed using the Green–Kubo formula (ongoing work). Our results demonstrate the overall good performance of the η/ξ method for all these molecules, although they have very different anisotropy. Inspired by the comments, we will pay more attention to the results at higher temperatures, where no experimental data are available, but the Green–Kubo formula can be applied.

1 H. Mo, X. You, K. H. Luo and S. H. Robertson, *Phys. Chem. Chem. Phys.*, 2022, **24**, 10147.

Alon Grinberg Dana made a general comment: In the context of determining which wells are significant and should appear in a pressure-dependent PES, I would like to point out a software developed at MIT called Arkane (**https://greengroup.mit.edu/arkane**).[1] In addition to other features, this software may assist in efficiently (no *ab initio* computations required, though may be added) estimating which wells and path reactions are significant for a given PES.

1 A. Grinberg Dana *et al.*, Automated Reaction Kinetics and Network Exploration (Arkane): A Statistical Mechanics, Thermodynamics, Transition State Theory, and Master Equation Software, 2022, DOI: 10.26434/chemrxiv-2022-4klsm.

David L. Osborn returned to the discussion of the papers by Ahren W. Jasper and Amy S. Mullin: We heard in Prof. Mullin's talk that collisional energy transfer becomes less efficient as a molecule becomes more rotationally excited. This result seems reasonable given that the energy gap between adjacent rotational levels increases with increasing rotational excitation. I would like to know whether Prof. Mullin or Dr Jasper have any insights from their work on the effect of extreme rotational excitation if the super-rotor instead is a reactant in a chemical reaction. Should we expect reactivity to be suppressed or enhanced compared to the same bimolecular reaction in which both partners have room temperature rotational energy distributions?

Amy S. Mullin replied: We have investigated the role of high-J excitation in bimolecular reactions of CO(J) that ultimately form C_2. The proposed mechanism involves two bimolecular reaction steps, each involving CO in the triplet a-state. By controlling the polarization of the optical pulses, but not the spectral bandwidth, we changed the number density, but not the distribution, of rotationally excited CO molecules made in the optical trap. Optical centrifuge pulses generate at least two times more high-J CO molecules than pulses from a dynamic polarization grating. We found that a higher population of rotationally excited CO leads to a reduction in the C_2 products.[1] In this case, rotational energy in the

reactants reduces the reaction probability, as expected for reactions with a linear transition state structure. Other types of reactions could well be enhanced by reactant rotation, if the rotational motion accesses additional transition state structures that lead to reaction products.

1 H. M. Ogden, T. J. Michael, M. J. Murray, Q. Liu, C. Toro and A. S. Mullin, *Phys. Chem. Chem. Phys.*, 2019, **21**, 14103.

Ahren W. Jasper replied: I don't have any direct insight for these systems. As a general comment, adding energy of any kind typically increases reactivity, while adding a lot of one type of energy can discourage the sharing of energy and decrease reactivity. I suppose for some reactions one might see a maximum in reactivity with increasing rotational state.

Hua Guo added: The effect of reactant rotation, particularly in super-rotor states, is not well-known. It is intuitive to imagine inhibitory effects by such a fast-rotating reactant, but there are other examples pointing to an opposite effect. A group at Northwestern University has shown a large enhancement of reactivity by super-rotator states.[1] This is due to the transition state that has its reaction coordinate aligned with the reactant rotational mode. I think there are cases where rotational energy may enhance or inhibit reactivity.

1 S. Venkataramanababu, A. Li, I. Antonov, J. Dragan, P. Stollenwerk, H. Guo and B. C. Odom, Rotational control of reactivity: Reaction of SiO^+ ions in extreme rotational states, *Nat. Commun.*, submitted.

David L. Osborn answered: Thank you for this insight to other recent experiments.

Matthias Olzmann addressed Amy S. Mullin: If you performed your experiments with a gas that has a small spin–orbit splitting, like NO, would it be possible to detect transitions between different spin–orbit states?

Amy S. Mullin responded: In principle, it is possible to optically centrifuge a molecule such as NO and investigate transitions between different spin–orbit states. The polarizability anisotropy of NO is large enough for it to be optically trapped and angularly accelerated. One challenge with our experiments is that NO has small IR absorption cross sections, so it is an ideal candidate for transient IR absorption probing.

Conflicts of interest

There are no conflicts to declare.