Faraday Discussions

Cite this: *Faraday Discuss.*, 2024, **251**, 313

Scattering of larger molecules – part 1: general discussion

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DOI: 10.1039/d4fd90019g

Viet Le Duc opened a general discussion of the paper by Astrid Bergeat: Why is it that the potential energy surface (PES) of HDO is so different from H_2O and D_2O (the back scattering in the case of HDO is much stronger than the other 2, from a calculation point of view)?

Astrid Bergeat responded: I'm not sure I understand correctly the question: there is no back scattering for HDO + Ne (no peak at 180° on the DCS). The contour plots Fig. 5 of our paper (**https://doi.org/10.1039/d3fd00168g**) are the surfaces of HDO–Ne, H_2O–Ne or D_2O–Ne with R, Θ and φ defined in Fig. 4, the origins of the coordinate system corresponding to the center of mass of the HDO, H_2O or D_2O molecules. The PESs are thus different because the symmetry is lost and appears in a set of terms in the expansion of the potential that, in the case of H_2O and D_2O, are zero (related to the odd values of m).

Stefan Willitsch asked: Could you provide some insights into why the v_{10} term which is responsible for the observed back-scattering is so different in the D_2O + Ne potential compared to H_2O and HDO?

Astrid Bergeat replied: I have conferred with my co-authors, Ricardo Manuel García-Vázquez and Thierry Stoecklin, to provide this response. Within the Born–Oppenheimer approximation, the energies of the D_2O–Ne system are identical to those of the H_2O–Ne system for the same set of internuclear distances:

$$V_{D_2O\text{–}Ne}(R_{hw}, \theta_{hw}, \varphi_{hw}) = V_{H_2O\text{–}Ne}(R_w, \theta_w, \varphi_w),$$

where the subscripts hw and w, refer to heavy water and water, respectively. The spherical coordinates (R,θ,φ) describe the position of the Ne atom with respect to the origin of the molecular frame, which is located at the center of mass of D_2O or H_2O. The relationships between the two sets of coordinates are given by the following equations:[1]

$$R_w = R_{hw}[1 + t^2 - 2t\cos(\theta_{hw})]^{(1/2)}\cos\text{-}(\theta_w) = ([t - \cos\text{-}(\theta_{hw})]R_{hw})/R_w\varphi_w = \varphi_{hw}$$

where $t = |\Delta z_{cm}|/R_{hw}$, and $|\Delta z_{cm}| = 0.012\ a_0$ is the displacement of the center of mass from one system to the other. The difference between the v_{10} term in water and in D_2O can be understood by noting that the relatively small value of $|\Delta z_{cm}|$ results in relatively small values of t while changing both the magnitude and the sign of the $\cos(\theta)$ term. As v_{10} is directly proportional to $\cos(\theta)$, its sign is also changed, going from attractive in the case of water–Ne to repulsive for D_2O–Ne. More details can be found in ref. 1.

1 R. M. García-Vázquez, O. Denis-Alpizar and T. Stoecklin, *J. Phys. Chem. A*, 2023, **127**, 4838–4847.

Stefan Willitsch said: Can you comment on the density of your HDO beam in the scattering region and whether water clusters in the beam could have any effects on your results?

Astrid Bergeat answered: The reservoir tank, which contains liquid water, is maintained at an external temperature of 45 °C. The valve reservoir is at 320 K, thus slightly above the reservoir tank temperature to prevent condensation of water. The water vapour pressure at these temperatures is low, and the total pressure in the reservoir is approximately 11 bar of Ne. I should recognized that even if the cooling is rapid in the supersonic expansion to form the molecular beam, which normally avoids condensation, dimers may be formed, *i.e.*, a weakly bound van der Waals structure: the carrier gas is Ne in our studies, and the well for HDO–Ne is only 65 cm^{-1} deep. However, no signal was detected at higher *m*/*z* than those of water ions, and no shift or new ionisation wavelength was observed. Furthermore, the characteristics of the beams (in particular the velocity, which is sensitive to the gas mass) are identical with or without water. It is commonly observed that a large cluster binding energy enhances the formation of clusters, which release their condensation energy into the beam, thereby limiting translational cooling. This would lead again to a change in the characteristics of the beam.

In conclusion, there is no evidence of significant amounts of water clusters in the beam. This was also the case for our previous studies on $D_2O + H_2$, where the agreements with theoretical calculations were excellent.

Pablo G. Jambrina commented: Thank you for your very nice presentation.

I have a question regarding the equilibrium energies and geometries of the Ne–H_2O, Ne–HOD and Ne–D_2O complexes shown in Table 2. As the centre of mass of the three complexes is slightly different, the potential energy surfaces (PESs) will also be slightly different when plotted as a function of the centre of mass dependent coordinates. However, for a given geometry (in internal coordinates) we should get the same *ab initio* energy (at least if we work within the Born–Oppenheimer approximation). So my question is, why are the equilibrium internuclear distances different for the H_2O and D_2O complexes?

On the same topic, because of the difference in the centre of mass, the contour plots shown in Fig. 5 of your paper (**https://doi.org/10.1039/d3fd00168g**) should be slightly different. However, I would expect them to show the same features, albeit with slightly different values of θ and φ. However, for Ne + H_2O there is a barrier at (140,0) and (140,180) that is not present for Ne + D_2O, why is that?

Astrid Bergeat replied: I have conferred with my co-authors, Ricardo Manuel García-Vázquez and Thierry Stoecklin, to provide this response. The geometries depicted in Table 2 of our paper (**https://doi.org/10.1039/d3fd00168g**) refer to the spherical coordinates of the Ne atom with respect to the molecular center of mass frame of, respectively, H_2O, D_2O and HDO. As the three centres of mass are not identical, the spherical coordinates of the minimum configuration are also different.

Differences in energy between the three systems are not only a function of θ and φ but also of R. The contour plots presented in Fig. 5 were made for the same value of $R = 3.2$ Å while the equilibrium value of R is not the same for the three systems (see Table 2). The features observed in the three plots are then different as they are associated with slightly different geometries. However, the Ne–HDO/D_2O/H_2O contour plots still exhibit strong similarities. The upper part of the HDO plot is strikingly similar to that of H_2O, while the lower part of the HDO plot is very similar to the D_2O one. The barrier observed at ($\Theta = 140°$, $\varphi = 0°$) and ($\Theta = 140°$, $\varphi = 180°$) for Ne–H_2O is only observed at ($\Theta = 140°$, $\varphi = 180°$) for Ne–HDO and is absent of the D_2O contour plot for this peculiar geometry.

Roland Wester asked: In the collision of HDO with Neon into the 1_{01} state, the error bars of the absolute cross section (Fig. 11 of your paper) are substantially larger than the error bars for the absolute cross section for scattering into the 1_{11} state (Fig. 8). What is the reason for that? Did you average fewer measurements or did you have to subtract a background?

Astrid Bergeat responded: Several points should be considered:

The wavelengths used to probe the HDO rotational levels by (2 + 1) REMPI are given in Table 1 of the electronic supplementary information file accompanying our paper (**https://doi.org/10.1039/d3fd00168g**). Unfortunately, if the line strength to probe HDO(1_{01}) is almost twice that for HDO(1_{11}), the width is also multiplied by 2.6. This leads to a significant reduction in intensity (almost divided by 2) for HDO(1_{01}) compared to HDO(1_{11}) for the same population.

Furthermore, the signal resulting from inelastic collisions is so small that it differs only slightly from the background signal. This is due to the small amount of HDO(1_{01}) population in the beam. To obtain the cross-sections, we have to subtract the background signal and thus to combine the uncertainties ($\sqrt{(u(\text{signal})^2 + u(\text{background})^2)}$). In the case of HDO($1_{11}$), the background signal is almost null (no population of HDO(1_{11}) in the water beam). Consequently, the background uncertainty is also negligible compared to the signal uncertainty.

Christopher Reilly opened a general discussion of the paper by Dmitri Babikov: What should be the effect of vibrationally excited states on collisions where vibrational excitation is energetically forbidden? Under what conditions would you expect the possibility of transient occupation of these states to have a significant influence on your vibrationally elastic scattering cross sections?

Dmitri Babikov answered: My understanding is that closed channels at higher energy should be added to the basis set if there is a chance that their energy is significantly lowered in the interaction region due to attraction between the collision partners. Quantitatively, the vibrational excitation quantum in water molecule is over 1000 wavenumbers, while the attractive interaction between the water molecule and the hydrogen molecule is on the order of 100 wavenumbers. Therefore, it seems unlikely that the molecule–molecule interaction would be sufficient to stabilize the excited vibrational states causing their transient population. I don't think that they need to be added to the rotational basis set employed for our calculations.

Astrid Bergeat remarked: In the calculations of the rotationally inelastic scattering in the $H_2O + H_2$ system in your paper (**https://doi.org/10.1039/d3fd00166k**), are you introducing any vibrational states for the water molecule? Do you take into account any coupling or resonances? At the highest collision energies (<12 000 cm^{-1}), several vibrational states are possible (symmetric stretching (ν_1 = 3657 cm^{-1}), bending (ν_2 = 1595 cm^{-1}), and asymmetric stretching (ν_3 = 3756 cm^{-1})). Thus how will these vibrational states modify your rotational inelastic cross-sections?[1,2]

[1] J. Tennyson *et al.*, *J. Quant. Spectrosc. Radiat. Transfer*, 2013, **117**, 29–58.
[2] A. Bykov *et al.*, *J. Mol. Spectrosc.*, 2001, **205**, 1–8.

Dmitri Babikov replied: If the vibrational states of water molecules are introduced into the model, they will have to be computed first, using some (probably an approximate) rotation–vibration Hamiltonian. This can create the couplings and resonances you mentioned. As I responded in the previous question, we would like to follow this route, but have not started yet as of now. One can hypothesize that allowing molecules to vibrate during the collision with a projectile will result in slightly lowered values of rotational state-to-state transitions, because the inclusion of vibrations makes the rotor "softer", which results in weaker interactions during the encounter and smaller values of rotationally inelastic state-to-state transition probabilities.

Astrid Bergeat queried: Are you planning to do any calculations with rovibrationally excited water molecules? Your calculations up to a high collision energy are important for the observations in the astrophysical environments where the local thermal equilibrium (LTE) conditions are not reached. Indeed, the kinetic temperature may be high due to shocks and stellar winds, for example. A. Baudry and coworkers[1] report H_2O radio lines excited at energy levels in the range ~3900–9000 K (~2700–6300 cm^{-1}). The ATOMIUM consortium group has observed several masers, H_2O being vibrationally excited up to 2 quanta in the bending mode.

[1] A. Baudry *et al.*, *Astron. Astrophys.*, 2023, **674**, A125.

Dmitri Babikov responded: Yes, the inclusion of bending mode of water into the basis set of internal states is within the scope of our project. It requires further code development and testing, by comparing the results of MQCT (mixed quantum/classical theory) for the coupled rotational–vibrational quenching against available full-quantum calculations.

George C. Schatz asked: It is impressive how well your results show the exponential fall off that is commonly found for energy transfer. Some of your results show deviations for large energy transfer, typically bending down compared to the exponential. In past work I have found that this result can be found in other simulations of energy transfer.[1]

[1] G. C. Schatz and G. Lendvay, *J. Chem. Phys.*, 1997, **106**, 3548–3557, DOI: 10.1063/1.473451.

Dmitri Babikov replied: Thank you for pointing this out.

George C. Schatz commented: The Billing method can fail when the energy transfer is a reasonable fraction of the kinetic energy. This would lead to deviations from correct results for the high delta E tail of the energy transfer distributions. Is this an issue for your results?

Dmitri Babikov responded: So far, we did not notice any significant deviations of our MQCT results from the accurate full quantum results. But thank you for bringing this up. Here is what we can do. Since we have a large number of individual state-to-state transition cross sections for the processes with various values of delta E, we can check whether a systematic trend exists between the delta E and the errors of MQCT method (computed as differences between cross sections or rate coefficients obtained using MQCT and those of the full quantum benchmark data). We did not check this correlation, but we can easily do that. Thank you.

Amy S. Mullin asked: We have investigated collisions of optically centrifuged CO molecules with rotational excitation up to $J = 80$. We have used state specific rate constants for $J = 0$–29 to model the high-J relaxation using master equation modeling, but the model predicts significantly faster relaxation than is observed in the experiments and the reasons remain an open question.[1] To what extent can your scattering code be used for CO–CO collisions of high J molecules? Please comment on the current situation and what the future prospects are for running such calculations.

[1] M. R. Laskowski, T. J. Michael, H. M. Ogden, M. H. Alexander and A. S. Mullin, *Faraday Discuss.*, 2022, **238**, 87–102.

Dmitri Babikov responded: We are interested in the CO + CO system and have already done some MQCT calculations for $J = 0$–15.[1] We are eager to undertake a new study of CO + CO collisions up to $J = 29$, but this will require further optimization of the code and would be a challenge from the computational cost perspective. Still, this should be doable using the mixed quantum/classical theory approach. From these new calculations for $J = 29$ we would have a better idea about what it would take to tackle $J = 80$.

[1] D. Bostan *et al.*, *Phys. Chem. Chem. Phys.*, 2024, **26**, 6627–6637.

Alec M. Wodtke said: Do you see possibilities to apply your mixed quantum-classical methods in atom and molecule scattering from surfaces? There are very few calculations in this field that go beyond the classical trajectory level. There are important problems where your methods might help. (1) Adiabatic scattering of polyatomic molecules – see work of Rainer Beck for example. Here inelastic vibrational and rotational scattering is observed specifically on metals and on graphene surfaces. (2) Electronically nonadiabatic scattering. Molecular vibrational relaxation is known to excite electron hole pairs in metals for example. The Born–Oppenheimer failure may be treated by frictional methods employing classical Langevin-dynamics or by surface hopping methods again using classical dynamics for nuclear degrees of freedom. As far as I know there have be none (or at least very few) calculations where the vibrational degree of freedom is treated quantum mechanically. This work has been recently reviewed.[1]

[1] I. Rahinov, A. Kandratsenka, T. Schäfer, P. Shirhatti, K. Golibrzuch and A. M. Wodtke, *Phys. Chem. Chem. Phys.*, 2024, **26**, 15090–15114, DOI: 10.1039/d4cp00957f.

Dmitri Babikov responded: I can see ample opportunities for the mixed quantum/classical theory in molecule-surface scattering, simply because this is a general approach to molecular dynamics. For electronically adiabatic (ro-vibrationally inelastic) scattering we would have to reformulate our theory in the space-fixed reference frame, because our present formulation uses advantages of the body-fixed reference frame, very useful for the molecule–molecule scattering but inappropriate for the molecule–surface scattering. An expansion onto electronically adiabatic processes is also possible, as we illustrated in the past.[1]

[1] D. Babikov, F. Aguillon, M. Sizun and V. Sidis, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1999, **59**, 330–341.

Hua Guo asked: Can the MQCT approach calculate product angular distributions? What are the technical difficulties?

Dmitri Babikov replied: In principle yes, but so far, we tried to compute differential cross sections only for $j = 0$ initial state of diatomic molecules. It worked fine.[1] For more complicated cases, one has to implement transformation from the body-fixed reference frame employed in our code, to the lab-fixed reference frame. This requires further development of the MQCT code.

[1] B. Mandal, A. Semenov and S. Babikov, *J. Phys. Chem. A*, 2018, **122**, 6157–6165.

Max McCrea opened a general discussion of the paper by Jérôme Loreau: Your paper (https://doi.org/10.1039/d3fd00180f) mentions the differences in the inversion splitting in ammonia for the different vibrational levels. However, inversion splitting also changes with rotational level. Is this included in your calculation, and how much of a difference do you think it would make either way?

Jérôme Loreau answered: There is indeed a small dependence of the inversion splitting on the rotational level of ammonia. This is not explicitly taken into account since we construct our basis of vibrational wave functions only once, for the ground rotational state. Introducing this dependence fully would require different vibrational wave functions for each rotational state, which is not currently feasible computationally. Part of this effect is recovered through the fact that we use at least four vibrational wave functions in our calculations. The mixing of wave functions corresponding to different vibrational states in the scattering calculations leads to a dependence on j and k. It should be noted that the dependence of the inversion splitting on j and k is a rather weak dependence, so its effect on the cross sections will be small.

O. A. Krohn asked: Thank you for a nice presentation of this very interesting work. As the motivation and interpretation of your results is derived from the inversion splitting of ammonia, I was curious if you had a comment on the expected differences for the scattering cross section in the case of ND_3–He *vs.* NH_3–He? Have you considered exploring the system of ND_3–He?

Jérôme Loreau responded: We have already explored the ND_3–He collisional system in the case of rotation–inversion transitions in the ground vibrational state[1] and discussed the differences with NH_3–He. We have not yet investigated rotation–inversion transitions of ND_3 in the first excited umbrella state, but one might expect smaller differences than for NH_3 since the tunnelling splitting in the excited state is much smaller (3.5 cm^{-1} compared to 35.2 cm^{-1} for NH_3). We can also expect larger vibrationally-inelastic cross sections since the energy difference between the $v = 0$ and $v = 1$ umbrella vibrational states is smaller for ND_3 than for NH_3 (747 cm^{-1} compared to 949 cm^{-1}).

1 J. Loreau and A. van der Avoird, *J. Chem. Phys.*, 2015, **143**, 184303, DOI: 10.1063/1.4935259.

Viet Le Duc said: Can this calculation be used to calculate the vibrational energy transfer of ND_3, or other isotope mixes of ammonia, such as ND_2H and so on? What are the difficulties in doing so, or it is straight forward?

Jérôme Loreau answered: Vibrational energy transfer in ND_3–He collisions can be treated with exactly the same methodology and an umbrella potential adapted to describe the vibrational levels of ND_3. This has already been done for rotation–inversion transitions (see *e.g.* ref. 1 and 2). Partially deuterated ammonia can certainly be investigated as well, although in this case an additional complication comes from the fact that the molecule is now an asymmetric top, which requires the use of adapted rotational basis functions.

1 J. Loreau and A. van der Avoird, *J. Chem. Phys.*, 2015, **143**, 184303, DOI: 10.1063/1.4935259.
2 O. Tkac, A. K. Saha, J. Loreau, D. H. Parker, A. van der Avoird and A. J. Orr-Ewing, *J. Phys. Chem. A*, **119**, 5979, DOI: 10.1021/jp5115042.

Roland Wester asked: How general do you expect the strong increase of the vibrational quenching rate coefficient to be when the temperature is increased? We have studied vibrational quenching of C_2^- ions in collisions with molecular hydrogen[1] and different rare gases.[2] While the rate coefficient increases somewhat for helium collisions between 10 and 100 kelvin, it remains fairly constant, albeit significantly larger, for collisions with argon. Would you expect a similar behavior for ammonia?

1 M. Nötzold, R. Wild, C. Lochmann, T. Rahim, S. Purushu Melath, K. Dulitz, B. Mant, J. Franz, F. A. Gianturco and R. Wester, *Phys. Rev. Lett.*, 2023, **131**, 183002.
2 B. P. Mant, F. A. Gianturco, R. Wester, E. Yurtsever and L. González-Sánchez, *Phys. Rev. A*, 2020, **102**, 062810.

Jérôme Loreau responded: The strong increase of the vibrational quenching rate coefficient when the temperature is increased is expected to be general for van der Waals complexes. This follows from the increase of the cross section with increasing energies (outside the resonance region). The interpretation is that rovibrational relaxation is inefficient unless the short range (repulsive) region of the potential energy surface (PES) can be reached, since this is the region where the PES depends the most on the vibrational coordinate. This becomes more likely with increasing energy, and this behaviour has indeed been observed for collisions of polyatomic molecules with He atoms such as CO_2–He,[1] and CH_3–He,[2] in addition to NH_3–He discussed here. The same effect would thus be expected for Ar atoms as well, but it could possibly be occurring at higher energy.

Regarding the much larger vibrationally-inelastic cross section (or rate coefficient) for C_2^- + Ar compared to C_2^- + He/Ne, we do not believe that the effect will be as drastic for NH_3. It is of course difficult to generalize since C_2^- is an ion while NH_3 is neutral, but overall we can say that (1) rotationally-inelastic cross sections are larger for collisions with Ar than with He, since the well in the PES is much deeper (see *e.g.* ref. 3 and 4 for the case of NH_3-rare gas PESs and collisions), and (2) for efficient vibrationally-inelastic transitions reaching the short-range part of the PES is required.

In the case of C_2^- + Ar, the well of the PES is much deeper and its minimum occurs at a smaller distance than for C_2^- + He, so the effects add up. In the case of NH_3–Ar the PES is deeper than for NH_3–He (but the difference is not as large as for C_2^- + Ar compared to C_2^- + He), however the minimum of the PES occurs at a larger distance.[4] Reaching the short-range would thus be more difficult and the two effects should somewhat compensate each other. It is difficult to conclude without doing the explicit calculations, but we would expect the effect of substituting Ar to He in collisions with NH_3 to be less pronounced than in the case of C_2^-.

1 T. Selim, A. Christianen, A. van der Avoird and G. Groenenboom, *J. Chem. Phys.*, 2021, **155**, 034105, DOI: 10.1063/5.0058576.
2 Q. Ma, P. J. Dagdigian and M. H. Alexander, *J. Chem. Phys.*, 2013, **138**, 104317, DOI: 10.1063/1.4794167.
3 J. Loreau, J., Liévin, Y. Scribano and A. van der Avoird, *J. Chem. Phys.*, 2014, **141**, 224303, DOI: 10.1063/1.4903047.
4 J. Loreau and A. van der Avoird, *J. Chem. Phys.*, 2015, **143**, 184303, DOI: 10.1063/1.4935259.

Christopher Reilly communicated: You rationalize your observed trends in vibrationally elastic rotation–inversion transitions in terms of the energy differences between the initial and final states. I was curious if there were in addition any dynamical considerations influencing the transition probabilities. Would it be accurate, in the simplest picture, to think of conversion between even and odd parities as the accumulation of a 180 degree phase shift in the wavefunctions of the inverted and non-inverted molecular frameworks? If so, what collision conditions would act to enhance or suppress such phase shifts?

Jérôme Loreau communicated in reply: The energy differences are only used to explain the similarities and differences between specific rotation–inversion transitions in the first excited vibrational level compared to the ground vibrational level. The transition probability for a transition between a symmetric (+) and antisymmetric (−) state can be related to specific terms in the expansion of the PES in spherical harmonics (see *e.g.* ref. 1 and 2) and thus directly depends on the interaction with the He atom.

A way to enhance or suppress these transitions would be through alignment of the ammonia molecule. The + and − inversion states are symmetric and antisymmetric (respectively) linear combinations of the two ammonia equilibrium structures. These are stationary states, which get mixed in collisions. For instance, orienting the molecule such that the collision occurs on the nitrogen atom side, you would get a maximum mixing since this specific orientation corresponds to a well-defined equilibrium structure. This should enhance the inversion-changing transitions.

1 K. B. Gubbels, S. Y. T. van de Meerakker, G. C. Groenenboom, G. Meijer and A. van der Avoird, *J. Chem. Phys.*, 2012, **136**, 074301, DOI: 10.1063/1.3683219.
2 J. Loreau and A. van der Avoird, *J. Chem. Phys.*, 2015, **143**, 184303, DOI: 10.1063/1.4935259.

David Heathcote asked a general question: Tying in with the opening lecture yesterday regarding the importance of collaboration of experiment and theory (Schatz *et al.*,https://doi.org/10.1039/d4fd00015c), this is a question to the theoreticians among you. What experiment or experiments would you like to be carried out to direct or support your work?

Jérôme Loreau answered: An experiment that probes cross sections as a function of the collision energy for ro-vibrational collisional excitation or relaxation of a polyatomic with state-to-state resolution would be fantastic. Probing the regime of energy where resonances are present would lead to an even more sensitive test of the quality of theoretical methods. Measurements of differential cross sections for this process would lead to even more insight.

Astrid Bergeat replied: According to my colleague Alexandre Faure, for reactive collisions, an experiment controlling the quantum state of the reactant and the state-distribution of the products would be particularly constraining for theory.

It should be noted that theoreticians also request experimental results on vibrational inelastic collisions.

David W. Chandler returned to the discussion of the paper by Jérôme Loreau: As the number of resonant structures becomes very large for molecule–molecular collisions at low collision energies does measuring them lose importance as one would have a very difficult time assigning the structures to a particular barrier of quantum state? I note that in the lecture of Dr Astrid Bergeat that the resonance structures she calculates for the collisions of H_2 with the 000 band of HOD are very small and diffuse. They would seem to be extremely hard to both observe and match experimentally considering the uncertainty in both experiment and theory.

Jérôme Loreau replied: Indeed, for heavier collisional systems the resonance structure becomes more complex, with overlapping resonances that are associated to different quantum states.[1,2] They become harder to distinguish experimentally but measuring cross sections at low collision energy still provides a stringent test for theory even if all resonances cannot be separated. In addition, based on calculations it is still possible to assign these resonances to specific quantum states and to identify whether they are shape or Feshbach resonances.

1 Q. Ma, A. van der Avoird, J. Loreau, M. H. Alexander, S. Y. T. van de Meerakker and P. J. Dagdigian, *J. Chem. Phys.*, 2015, **143**, 044312, DOI: **10.1063/1.4927074**.

2 M. Ben Khalifa and J. Loreau, *Mon. Not. R. Astron. Soc.*, 2024, **527**, 846, DOI: **10.1093/mnras/stad3201**.

Dwayne Heard returned to the paper by Dmitri Babikov: In general there is a scarcity of experimental data for the energy removed per collision by different bath gases as a function of energy of the excited molecule – a parameter needed to describe collisional energy transfer within master equation formulations of transition state theory.

Dmitri Babikov answered: We are aware of this, and one reason for our research is to fill this gap. In the past, we used a somewhat different formulation of mixed quantum classical theory to determine the value of energy removed per collision for the recombination reaction that forms ozone.[1]

1 M. V. Ivanov and D. Babikov, *J. Chem. Phys.*, 2016, **144**, 154301.

Dwayne Heard asked: When calculating the rate coefficient at 25 K, can the exponential energy gap law still be applied to treat collisional energy transfer?

Dmitri Babikov responded: I think that in the low temperature range, when the kinetic energy is comparable to the energy difference between the rotational eigenstates, one has to use cross sections for the individual state-to-state transitions, rather than the energy-gap model.

Dwayne Heard queried: When there are multiple, deep energy wells within the potential energy surface of a chemical reaction, master equation approaches need to use energy grains of a particular width. The parameter needed is delta E down, the average amount of energy removed per collision (or an equivalent for collisional excitation), as a function of energy within the vibrationally excited molecules. It is too complex to use the detailed state-to-state cross-sections that you have presented in your paper. Can you please comment on whether some sort of parameterisation could be developed to describe the collisional energy transfer for real systems (combustion, atmospheric, astrochemical) which can include your state-to-state cross-sections?

Dmitri Babikov replied: Yes, of course, one future direction of this project is to obtain a parametric dependence of cross section in the form of equation given on the last page of section 5 of the paper (**https://doi.org/10.1039/d3fd00166k**). As we emphasized in the paper, our results indeed show the exponential dependence of cross section on the energy gap ΔE, but they also indicate very clearly that besides the energy gap, the change in the rotational angular momentum ΔJ and the change in the asymmetric top "quantum number" $\Delta\tau$, all play important roles. Therefore, our parametrization may be somewhat more complicated than a simple one-dimensional energy-gap model. The approach we promote would be a three-dimensional energy gap model, where the value of the cross section would depend exponentially on ΔE, ΔJ and $\Delta\tau$, with appropriately chosen parameters.

Hua Guo made a general comment: I would like to comment that the gap laws might fail completely when the collision involves a long-lived intermediate complex. Such a complex might be supported for example by hydrogen bonds between HF molecules. In this case, the long lifetime of the complex facilitates efficient energy transfer between the two collision partners, leading to the failure of gap laws.[1] There is a breakdown of energy transfer gap laws revealed by full-dimensional quantum scattering between HF molecules.

1 D. Yang, J. Huang, X. Hu, H. Guo and D. Xie, *Nat. Commun.*, 2019, **10**(1), 4658, DOI: 10.1038/s41467-019-12691-8.

Jérôme Loreau replied: There are indeed many exceptions to gap laws. Even in the case presented in our paper, for which the PES is very shallow compared to the HF–HF PES, the energy gap laws cannot fully explain the magnitude of the cross sections when comparing rotation–inversion transitions within $\nu = 1$ compared to $\nu = 0$.

Dwayne Heard responded: Many thanks for that comment. In that case, the breakdown of the energy transfer gap laws may partly account for why transition state theory, when implemented using master equation approaches, is not able to reproduce experimental measurements of rate coefficients at very low temperatures (down to around 20 K) made using a Laval nozzle apparatus. In some cases long-lived complexes are formed in the entrance channel to the reaction.

Dmitri Babikov answered: I agree and would like to add that the long-lived complex is a classical analogue of quantum scattering resonance. In this case, found typically at low collision energy, quantum effects are not negligible. The amount of kinetic energy in the system is comparable to one quantum of excitation, in which case you cannot ignore state quantization and must use cross sections or rate coefficients for individual quantum state-to-state transitions.

Kang-Kuen Ni remarked: I would like to make a comment regarding collision resonances for light *vs.* heavy systems. For atom–molecule collisions at ultralow temperatures (typical translational energy of less than one micro Kelvin), the ultracold community found that there are qualitative differences in magnetic scattering resonances among the realized systems of LiNa, NaK, KRb, and NaRb. For light species such as LiNa and NaK, resonances were resolved and can be assigned. For KRb and NaRb, resonances are overlapping and abundant. They have not been assigned. The very general understanding of such a trend is that the density of states of the system increases dramatically as the mass of the species increases.

Patrick Robertson opened a general discussion of the paper by Nathanael M. Kidwell: Is it possible to probe rotational alignment in your NO products, for example by varying the polarisation of the REMPI laser? If you could make this measurement, could you comment on how you might expect it to be impacted by different IR modes?

Nathanael M. Kidwell answered: Permutating the relative IR pump and UV probe beam polarizations enables one to extract the polarization parameters for transitions that are either parallel, perpendicular, or a coherent superposition of parallel and perpendicular. The polarization parameters determine the orientation and alignment of the distributions with respect to the recoil direction from dissociation. Using these polarization parameters, one can cast them into terms of physical quantities such as nonadiabatic transition probabilities. The IR action spectrum for NO–C_2H_6 complexes display transitions that are either parallel (ν_5 and $\nu_8 + \nu_{11}\|$) or perpendicular (ν_7 and $\nu_8 + \nu_{11}\perp$). In future experiments, we may consider alternating the relative polarizations of the IR pump and UV probe beams for different IR transitions that are either parallel or perpendicular. In doing so, one can envision determining nonadiabatic transition probabilities for NO photofragments.

Max McCrea commented: Your paper (**https://doi.org/10.1039/d3fd00176h**) mentions that the dynamics after vibrational excitation is seemingly independent of the symmetry of the mode excited. Is this something specific about those modes available, or a general independence of the symmetries of the modes?

Nathanael M. Kidwell replied: The dynamical signatures appear similar when IR activating NO–C_2H_6 with either the symmetric (ν_5) or asymmetric (ν_7) CH stretch. The conservation of energy and symmetry requirements shown for ν_7 in the paper are also met for ν_5. The homogeneous broadening of the ν_5 band was found to have an upper limit of ~9 cm^{-1}, whereas the corresponding value for the ν_7 transition was determined to be ~40 cm^{-1}, leading to vibrational predissociation lifetimes of ~590 fs and ~130 fs, respectively. The degree of coupling for the ν_5 and ν_7 CH stretch mode of NO–C_2H_6 to the intermolecular bond dissociation coordinate appears to be the main distinguishing factor in the dynamics. The coupling strength may be due to the form of each NO–C_2H_6 vibrational mode. The ν_7 asymmetric CH stretch appears to be more directly coupled to the dissociation coordinate since the vibrational predissociation lifetime is shorter when activating the ν_7 asymmetric CH stretch. The ν_5 mode is still moderately coupled, but to a lesser extent.

Chris Sparling asked: You used measured anisotropic parameters in your ion imaging data to give qualitative estimates of the predissociation lifetime of the NO–C_2H_6 complex. Within some axial recoil approximation, have you been able to *quantitively* determine the lifetime from the imaging directly?

Nathanael M. Kidwell replied: In the limit that the upper state lifetime of a molecule is very short, the value of β reaches its limiting value of +2 for a parallel transition. However, as the lifetime increases, the value of β decreases. When IR activating NO–C_2H_6, the main features in the NO product ion images have β values of ~+0.4. Using an axial recoil approximation, one may determine the lifetime from the ion images. Qualitatively, the NO product ion images from NO–

C_2H_6 fragmentation shown in Fig. 4 of the paper (**https://doi.org/10.1039/d3fd00176h**) are anisotropic, indicating the vibrational predissociation lifetime is shorter than the NO–C_2H_6 rotational period (τ_{rot} ~3.5 ps) determined from calculated rotational constants. In our paper, we quantitatively determined the vibrational predissociation lifetime from the NO–C_2H_6 IR action spectrum. Using the ν_7 spectral linewidth, the homogeneous broadening was found to have an upper limit of ~40 cm^{-1} from the rovibrational simulation fitting to the experimental data. Therefore, the vibrational predissociation lifetime when exciting the ν_7 asymmetric CH stretch is ~130 fs.

David Heathcote remarked: In Fig. 5 of your paper (**https://doi.org/10.1039/d3fd00176h**) you highlight a number of states in red which correspond to a prompt dissociation of the NO–C_2H_6 complex. Can you explain why these states might fall in such a narrow band?

Nathanael M. Kidwell answered: According to the energy gap law, it is expected that the dominant mechanism of energy exchange will be near-resonant vibration-to-vibration energy transfer from NO–C_2H_6 (ν_7) to the vibrational stretching modes of C_2H_6 (ν) and some degree of energy flow to the NO rotational levels within its $2\Pi_{1/2}$ and $2\Pi_{3/2}$ spin–orbit electronic states. The parallel and/or the perpendicular $\nu_8 + \nu_{12}$ levels of C_2H_6 appear to be the dominant accepting modes. The ν_8 mode in Fig. 3 is characterized as an umbrella mode of the three facial H-atoms of C_2H_6 oriented towards NO. The ν_{12} mode is portrayed as a buckling mode. Since the energy difference between the ν_7 level of NO–C_2H_6 and the $\nu_8 + \nu_{12}$ levels of C_2H_6 is small and the form of the normal modes are similar, energy flow will be maximized. Therefore, to conserve energy, the little remaining available energy flows to the near rovibrational levels of the NO co-fragment, leading to a narrow range showing anisotropic ion images.

Kenneth G. McKendrick said: I am interested in the source of the kinetic-energy spread in Fig. 4 of your paper (**https://doi.org/10.1039/d3fd00176h**). The distribution extends out beyond at least 2000 cm^{-1}. I wonder how this is compatible with the idea of the population being channelled into particular near-degenerate levels of ethane, as indicated in Fig. 5, and identified as being the $\nu_4 + \nu_{12}$ combination mode based on symmetry arguments? This would appear at face value to energetically incompatible with having the high levels of kinetic energy release in Fig. 4? Perhaps the near-degenerate states act as “gateway” levels, but the ethane ends up in a lower-energy final state?

Nathanael M. Kidwell replied: By conservation of energy, the peaks of the largest features in the TKER (total kinetic energy release) distributions in Fig. 4 coincide with the parallel and/or perpendicular $\nu_8 + \nu_{12}$ levels of C_2H_6. The form of the ν_8 mode (umbrella mode) closely resembles the form of the ν_7 asymmetric CH stretch mode of NO–C_2H_6. The ν_{12} vibrational mode of C_2H_6 is portrayed as a buckling mode in Fig. 5, which may account for the broadened TKER features in Fig. 4 possibly due to rotational excitation involving this buckling motion. However, it cannot be ruled out that other, nearby vibrational levels of C_2H_6 may be populated following fragmentation of NO–C_2H_6, leading to a tail in the TKER distribution.

Kenneth G. McKendrick asked: To follow my previous question, what distribution of internal states do you think would be found for the high-kinetic-energy component of the ethane products, if it were somehow possible to measure them directly?

Nathanael M. Kidwell responded: Through conservation of energy, as the relative translational energy (TKER) increases, the internal energy of C_2H_6 decreases (and *vice versa*) when the internal energy of NO is fixed, as it is in our experiments when detecting NO fragments. Although the dominant feature in the TKER distribution at low kinetic energy is assigned to the parallel and/or perpendicular $\nu_8 + \nu_{12}$ levels of C_2H_6, it is conceivable that the high kinetic energy tail can be attributed to either rotational and/or lower-energy vibrational levels of C_2H_6 that are also populated following fragmentation of NO–C_2H_6.

David W. Chandler addressed Nathanael M. Kidwell and Dmitri Babikov: Dr Kidwell, Have you measured the rotational distribution of the NO coming from the NO/C_2H_6 clusters? If you have this distribution can you use Dr Babikov's theory to predict the rotational energy distribution of the C_2H_6 molecule. Would having an estimate of the rotational distribution of the C_2H_6 allow you to better analyze your velocity distribution of the NO?

Nathanael M. Kidwell replied: We have measured the NO product state distribution from NO–C_2H_6 dissociation, and also for NO–CH_4, NO-propane, and NO-(*n*-butane) fragmentation that will appear in a future publication. The NO products from prompt NO–C_2H_6 dissociation predominantly occupy low-energy rotational levels, indicating little rotational excitation in NO products. The peaks of the TKER distributions overlap with the $\nu_8 + \nu_{12}$ levels of C_2H_6, yet the distributions have a high kinetic energy tail, suggesting that the C_2H_6 co-products have relatively high rotational excitation and/or occupy low-energy vibrational levels. For C_2H_6 rotational excitation, this is plausibly due to the impulse imparted to C_2H_6 as NO products depart from prompt NO–C_2H_6 dissociation. It would be very interesting to compare the experimental results to the rovibrational energy exchange predictions from Dr Babikov's mixed quantum/classical theoretical model to reveal the dynamics from NO and C_2H_6 collisions.

Dmitri Babikov responded: I would like to comment that the present version of the MQCT code was built to handle inelastic collisions that start with two collision partners occupying certain rotational eigenstates, but, in principle, the mixed quantum classical theory can be used to treat "half-collisions", such as dissociation of a molecule–molecule complex that gives two fragments with some distribution of the internal states. This would require further work on the MQCT theory and code.

Gilbert S. Nathanson asked: Would you please share your thoughts on the roles of vibrational modes 5, 7, 8, and 11 in Fig. 3 of your paper (**https://doi.org/10.1039/d3fd00176h**) in dissociating the NO-ethane cluster?

Nathanael M. Kidwell replied: The ν_8 and ν_{11} vibrational modes of C_2H_6 are asymmetric methyl deformation modes, where they involve in-phase and out-of-phase nuclear displacement, respectively. Additionally, the ν_5 mode is characterized as the out-of-phase symmetric CH stretch, while the ν_7 mode is assigned to the in-phase asymmetric stretch. The homogeneous broadening of the ν_8, ν_{11}, and ν_5 vibrational transitions are on the order of $\sim$9 cm^{-1}, and therefore appear to be only moderately coupled to the intermolecular bond dissociation coordinate of the NO–C_2H_6 complex. However, the ν_7 asymmetric stretch has a homogeneous broadening determined to be on the order of 40 cm^{-1} (τ_{vib} $\sim$130 fs) indicating that this mode is more conducive to NO–C_2H_6 fragmentation. Similarly, the analogous vibrational mode of NO–CH_4 was also demonstrated to lead to a comparable vibrational predissociation lifetime. Here, the prompt dissociation of NO–CH_4 was determined to take place *via* energy transfer to a near-resonant CH_4 vibrational level ($2\nu(4)$), resembling an umbrella mode. In the same fashion, the accepting $\nu_8 + \nu_{12}$ levels ($\parallel$ and/or $\perp$) of C_2H_6 also have nuclear displacement described with an umbrella mode. Since the ν_7 mode of NO–C_2H_6 and the $\nu_8 + \nu_{12}$ levels of C_2H_6 are nearby in energy with similar vibrational mode character, we attribute the prompt dissociation mechanism of NO–C_2H_6 to the analogous pathway observed for NO–CH_4.

Max McCrea opened a general discussion of the paper by Matthew L. Costen: You've used an onion peeling method to analyse your data here. Would a 3D velocity map ion imaging setup enhance the resolution of the experiment?

Matthew L. Costen responded: A 3D VMI approach would definitely help improve the analysis, although I would be cautious with describing it as improving the resolution. The resolution of the coincident rotational excitation is ultimately defined by the collision energy spread, arising from the spreads of speeds in the molecular beams and finite molecular beam collimation. The very elegant work of van de Meerakker and co-workers shows how clearly correlations can be determined using conventional VMI if the collision energy resolution is high enough.[1] However, in 2D "crushed" images the signal dependence on rotational angular momentum polarisation of the detected product is convoluted with the projection of the internal energy distribution of the unobserved product. In the analysis of our 2D-image experiments we can only use theoretical predictions (*e.g.* classical models of angular moment conservation) to simulate the effect of angular momentum polarisation in the basis images that are fitted to extract the differential cross sections. In contrast, imaging in 3D would enable the angular momentum polarisation and product-state correlations to be disentangled, and independently determined.

[1] Z. Gao, T. Karman, S. N. Vogels, M. Besemer, A. van der Avoird, G. C. Groenenboom and S. Y. T. van de Meerakker, *Nat. Chem.*, 2018, **10**, 469–473.

Nils Hertl said: In your paper (**https://doi.org/10.1039/d3fd00162h**), you discussed your findings also in the context of the scattering of NO in its electronic ground state with other molecules. I was wondering how different the PES (potential energy surface) between NO and CO_2 is when I have NO($X^2\Pi$) instead of NO($A^2\Sigma^+$)?

Matthew L. Costen replied: We calculated a range of cuts through the NO(X) + CO_2 van der Waal's PES at both PNO-CCSD(T) and CCSD(T) levels as part of our initial study of the NO(A,X) + CO_2 system.[1] Overall, the NO(X) + CO_2 PES is substantially less attractive than that for NO(A) + CO_2. The minima along the linear geometries, LinO and LinN, are <100 cm^{-1} for NO(X), and are at longer range than the 500–700 cm^{-1} deep wells observed for NO(A). In contrast, the T-shaped geometries TO and TN display stronger, shorter-range, attractive forces for NO(X) than for NO(A). This can be qualitatively rationalised based on selected molecular properties, *e.g.* NO dipole moment, CO_2 polarizability.

1 L. Craciunsecu, E. M. Liane, A. Kirrander and M. J. Paterson, *J. Chem. Phys.*, 2023, **159**, 124303.

Patrick Robertson asked: Can you comment on the generality of correlated rotational excitation in molecule–molecule scattering? Work from the Nijmegen group on NO(X) + CO (see *e.g.* ref. 1) indicated that scattering both colliders into higher rotational state required a closely matched rotational constant, but that doesn't apply here. Is this an NO(A) property, or simply that the picture is far more complex than those Nijmegen results might suggest?

1 Z. Gao, T. Karman, S. N. Vogels, *et al.*, Observation of correlated excitations in bimolecular collisions, *Nat. Chem.*, 2018, **10**, 469–473, DOI: **10.1038/s41557-018-0004-0.**

Matthew L. Costen responded: I think that the picture is more complex, as you suggest. The NO(X) + CO study by van de Meerakker and co-workers is an example of coincident rotational excitation with closely matched rotational constants in the collision partners.[1] But other studies by the same group show examples of coincident rotational changes where the collision partners have significantly different rotational constants.[2,3] I think that the "bigger-picture" point here is that there just isn't a very large sample of these measurements, and as a consequence we haven't had a chance to develop general predictive models. It should be a priority to perform more experimental and theoretical studies that broaden the range of collision systems, both exploring varying collision kinematics, and also different collider molecular structures. One of the motivations for studying collisions of NO(A) with CO_2 was the contrast of its "stick-shape" with the more near-spherical diatomics, CO, N_2 and O_2. Expanding the range of collision partners to include spherical rotors or asymmetric tops would be a significant step.

1 G. Q. Tang, M. Besemer, J. Onvlee, T. Karman, A. van der Avoird, G. C. Groenenboom and S. Y. T. van de Meerakker, *J. Chem. Phys.*, 2022, **156**, 214304.
2 G. Tang, M. Besemer, S. Kuijpers, G. C. Groenenboom, A. van der Avoird, T. Karman and S. Y. T. van de Meerakker, *Science*, 2023, **379**, 1031–1036.
3 G. Tang, M. Besemer, T. de Jongh, Q. Shuai, A. van der Avoird, G. C. Groenenboom and S. Y. T. van de Meerakker, *J. Chem. Phys.*, 2020, **153**, 064301.

Tibor Győri said: I am a little surprised that you are using a PNO-CC method for such a small system. Usually one would not use localized methods for a system that contains only five atoms, as generally the speedups from PNO and similar approximations are only expected to be significant for larger systems, so for small systems one might incur the (admittedly small) PNO truncation errors for very little benefit in terms of execution time.

Is using PNO-CCSD(T)-F12b instead of CCSD(T)-F12b profitable for this system?

Martin J. Paterson answered: As the triply even-tempered augmented basis set used in this study adds a lot of diffuse basis functions (needed for the NO Rydberg A state), the number of basis functions even for this small five atom system is, somewhat counterintuitively, 390. This means the perturbative triples correction over the full amplitude space is already very large. In a practical sense when running calculations, this affects memory usage particularly as using the PNO approximation reduces the memory usage roughly by the factor 15 to 20, in addition to significant speed-up for generating the complete PES. We therefore think that this saving in resources alone in conjunction with a minimal loss of accuracy is worthwhile. As benchmarked in our previous work,[1] this makes the exploitation of the PNO formalism highly profitable.

[1] L. Craciunescu, E. M. Liane, A. Kirrander and M. J. Paterson, Excited-state van der Waals potential energy surfaces for the NO($A^2\Sigma^+$) + CO_2 ($X^2\Sigma_g^+$) collision complex, *J. Chem. Phys.*, 2023, **159**, 124303.

Daniel M. Neumark asked: Although your angular distributions are dominated by forward-scattering, there is some back-scattered signal in many of your results. The overall angular distribution is reminiscent of an osculating collision complex. Do you think that is the explanation?

Matthew L. Costen answered: We have discussed the forward and backward scattered peaks in our paper in terms of glories, resulting from the deep attractive wells found on our *ab initio* potential energy surface. A backward glory results from collisions in a narrow range of impact parameters that undergo a complete reversal of direction, and end up focussed into a narrow range of final scattering angles with a maximum at 180°. In one sense, this does look somewhat like the forward-backward scattering observed in long-lived collision complexes.[1] However, the ratios of forward to backward scattering observed in our NO(A)-CO_2 collisions are very strongly forward biased, with the ($\theta = 0 : \theta = \pi$) ratio ranging from 45 : 1 for final rotational state, $N' = 5$, to 13 : 1 for $N' = 10$. Interpreting this within the osculating complex model, in which the collision complex dissociates on a timescale faster than the rotational period of the complex, leads to osculation angles, θ_{osc}, ranging from 40° to 55°.[2] These correspond to lifetimes of $\approx 1/6$ to $1/9$ of the complex rotational period. If we assume an NO–CO_2 complex arising from a collision at an impact parameter $b = 4.5$ Å (corresponding to the separation at the minimum of our calculated potential), and a relative velocity of 1100 ms^{-1}, we find it has a rotational period $\tau_R = 2.6$ ps. Hence the implied collision lifetimes range from 300 to 400 fs.

But is this a good picture for inelastic rotational energy transfer? I think that to some degree this is a semantic argument, but perhaps scattering calculations, *e.g.* QCT, could distinguish between these mechanistic interpretations.

[1] W. B. Miller, S. A. Safron and D. R. Herschbach, *Discuss. Faraday Soc.*, 1967, **44**, 108–122.
[2] M. K. Bullitt, C. H. Fisher and J. L. Kinsey, *J. Chem. Phys.*, 1974, **60**, 478–491.

Mark Brouard asked: Have you tried to look at the rovibrational states populated in NO(X) following electronic quenching of NO(A) by CO_2?

Matthew L. Costen responded: We have made quite extensive experimental attempts to detect the products of quenching in NO(A) + CO_2. This system has been previously studied using time-resolved IR emission by Hancock and co-workers, who observed extensive NO(X) vibrational excitation, as well as CO_2 vibrational excitation.[1] We looked for NO(X, $v = 0$) across a very wide range of rotational levels, from $j = 6.5$ to $j = 50.5$ predominately in F_2 spin–orbit states. We did not try to probe NO(X, $v = 1$), because photolysis of NO(X)-CO_2 van der Waal's clusters provided a very large background at NO(A-X)(1,1) probe wavelengths. Hancock and co-workers also suggested that a dissociative channel leading to CO(X) and O(^{3}P) may be significant. We therefore looked for O(^{3}P) *via* 2 + 1 REMPI around 225 nm.

However, we have seen no signals that can be definitively assigned to quenching in any of these measurements. Although the collision cross section for NO(A) quenching by CO_2 is comparable to the total cross section for rotational energy transfer in NO(A) (estimated at ≈ 60 Å^2), there are simply many more possible final states accessible upon quenching, given the NO(A) electronic energy is *ca.* 44 250 cm^{-1}. We believe that the quenched NO(X) population is simply too diluted across these product states to be detected above the background signals. We note that NO(X) from quenching of NO(A) by O_2 has been detected by REMPI-VMI by Kidwell and co-workers.[2] However, that experiment used a co-expansion of NO and O_2, with the quenching occurring in a significantly higher density environment than is provided in a crossed molecular beam experiment.

1 M. A. Burgos Paci, J. Few, S. Gowrie and G. Hancock, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2554.
2 K. J. Blackshaw, N. K. Quartey, R. T. Korb, D. J. Hood, C. D. Hettwer and N. M. Kidwell, *J. Chem. Phys.*, 2019, **151**, 104304.

Mark Brouard remarked: To follow on from this, what are the prospects of performing dynamical calculations (*e.g.*, trajectory surface hopping) on the potential energy surfaces determined in your paper?

Martin J. Paterson replied: Some preliminary work has been done to look at this. Initially we planned on the fly generation of PES, however this proved problematic due to the number of electronic states and the complexity of the wavefunctions in the non-adiabatic regions. We have now begun fitting the PESs to contrast wave packet simulations with trajectory surface hopping for the quenching process.

Arthur G. Suits commented: I am interested in your attempts to see the A state quenching in the NO product. We have recently looked at NO-argon collisions up to 1.4 eV, and we can readily observe $\Delta j = 59$ collisions. These are vibrationally elastic, however. In your case, of course, you have far more energy and a greater possibility for vibrational excitation. If one could anticipate the likely product vibrational state perhaps this could narrow the search. Have you done much in the way of probing the quenching channel directly?

Matthew L. Costen answered: As explained in the answer to Prof. Brouard, we have made a variety of attempts to probe the products of quenching directly, but so far have not been successful. The infra-red emission studies performed by

Hancock and co-workers determined that the NO(X) was highly vibrationally excited, with population detected as high as $v = 14$.[1] The recent theoretical work of Bridgers *et al.* provides evidence that the quenching pathways proceed through non-linear ON-OCO geometries that would lead to strong rotational torques on both fragments, as well as vibrational excitation of both.[2] This supports our proposal that the null observation of NO(X, $v = 0$, j) from quenching in our experiments is a consequence of dilution of the quenched population across a very high number of NO(X, v, j) states.

1 M. A. Burgos Paci, J. Few, S. Gowrie and G. Hancock, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2554.
2 A. N. Bridgers, J. A. Urquilla, J. Im and A. S. Petit, *J. Phys. Chem. A.*, 2023, **127**, 7228–7240.

Amy S. Mullin enquired: Are there any experimental tools to characterize the low impact parameter quenching collisions of NO(A)?

Matthew L. Costen responded: As I explained in response to Prof. Brouard and Prof. Suits, attempts to measure the products of quenching in our crossed beam apparatus have so far been unsuccessful. I also previously noted that the experiments of Kidwell and co-workers have successfully probed coincident energy disposal in NO(X) from quenching of NO(A) with O_2, and I believe that that experimental approach would also work in the NO(A) + CO_2 system.[1] An alternative approach that might work would be starting from an NO(X)-CO_2 van der Waal's complex, in analogy to experiments that have explored the photodissociation dynamics of NO(A,X)-CH_4 complexes.[2] However, I am not aware of any experiments to date that have studied either the NO(X,A)-CO_2 van der Waal's complex, or any quenching experiments that have been initiated from such complexes.

1 K. J. Blackshaw, N. K. Quartey, R. T. Korb, D. J. Hood, C. D. Hettwer and N. M. Kidwell, *J. Chem. Phys.*, 2019, **151**, 104304.
2 H. L. Holmes-Ross, J. R. Gascooke and W. D. Lawrance, *J. Phys. Chem. A*, **126**, 7981–7996.

Daniel R. Moon opened a general discussion of the paper by Michal Fárník: Could one expect a correlation between cluster size and your results, as larger clusters have a more extensive hydrogen-bonding network that may stabilise absorbed alcohols?

Michal Fárník answered: The absolute values of the uptake cross sections reported in our present work (**https://doi.org/10.1039/d3fd00160a**) correspond to the present cluster size, *i.e.*, the clusters composed on average of about 1–2 nitric acid molecules with about 6 water molecules. Larger clusters have larger geometrical sizes, and thus correspondingly larger uptake cross sections can be expected. However, the relative trend among the different alcohol molecules is rather given by the alcohol structure and the position of the OH group within the alcohol molecule. Thus, we expect the trends in the relative uptake cross sections to be conserved independent of the cluster size.

Daniel R. Moon asked: In atmospheric science, new particle formation is understood to result from reactions between acids and bases, such as ammonia and nitric acid. Given that your experiments involve nitric acid/water clusters, the question arises: what role does ammonia play in the dynamics of new particle formation?

Michal Fárník answered: In terms of Classical Nucleation Theory (CNT) the cluster is treated within the classical liquid drop model and its growth is accompanied by an increase of the Gibbs free energy until the drop reaches a certain critical radius of about one to a few nanometers, where the Gibbs free energy reaches its maximum, and then the energy decreases with further increases of the drop radius causing the aerosol particle to grow spontaneously. However, in the region of the small clusters below the critical radius, the clusters can form and decay in the collisions with the gas phase molecules in the atmosphere. The small cluster requires a stabilization mechanism in order to reach further growth towards the critical radius. The acid–base reactions can provide such a mechanism to stabilize the molecular cluster that can then grow further by adding molecules from the gas phase. We have investigated this process in a pickup experiment, where our hydrated nitric acid clusters picked up base dimethylamine molecules (DMA). The observed mass spectra were very different from the present pickup of alcohol molecules pointing to the acid–base reactions in the neutral clusters and their stabilization.[1]

[1] A. Pysanenko *et al.*, Molecular-level insight into uptake of dimethylamine on hydrated nitric acid clusters, *Environ. Sci.: Atmos.* 2022, **2**, 1292, DOI: **10.1039/d2ea00094f**.

Daniel R. Moon remarked: Rather than nitric acid–water clusters, is it possible to create clusters with relevance to new particle formation from organic precursors?

Michal Fárník replied: Indeed, different clusters can be created in our cluster sources and pickup of different molecules can be investigated. So far, we have focused on the acid clusters and the uptake of the organic precursors by them, *e.g.*, the present alcohols or isoprene, α-pinene and related molecules in our previous paper.[1] Nitric acid–water (NAW) clusters are special in terms of their mass spectra after the pickup of (some) molecules, which allow evaluation of the uptake cross sections. This property of the NAW clusters is exploited in the present paper (**https://doi.org/10.1039/d3fd00160a**) and our previous publications cited therein. On the other hand, pickup of bases (dimethylamine, ammonia) leads to acid–base reactions, and completely different spectra are observed, from which the uptake cross section cannot be evaluated but other relevant properties can be obtained as discussed in the answer to your previous question. Sulfuric acid–water (SAW) clusters are, perhaps, even more atmospherically relevant. We performed some pickup experiments with the SAW clusters, however, (a) they were difficult to produce and to keep the conditions stable, and (b) their mass spectra again did not allow the evaluation of the uptake probabilities. Recently, we have measured the uptake of different molecules by different polyaromatic hydrocarbon clusters.[2] Large clusters "several nanometres in diameter" were investigated and a different method was used to evaluate the relative uptake probabilities for different molecules after multiple uptake collisions. Similarly, we measured the relative uptake probabilities for different molecules by large water clusters (ice nanoparticles), evaluating the uptake from velocity measurements after a momentum transfer in multiple collisions.[3] Thus, we can perform different uptake experiments with different clusters of atmospheric organic precursors and we intend to continue this work in the future.

1 J. Lengyel *et al.*, Oxidation Enhances Aerosol Nucleation: Measurement of Kinetic Pickup Probability of Organic Molecules on Hydrated Acid Clusters, *J. Phys. Chem. Lett.*, 2020, **11**, 2101, DOI: 10.1021/acs.jpclett.0c00207.
2 V. Poterya *et al.*, Uptake of Molecules by Polyaromatic Hydrocarbon Nanoparticles, *ACS Earth Space Chem.*, 2024, **8**, 369, DOI: 10.1021/acsearthspacechem.3c00327.
3 J. Lengyel *et al.*, Uptake of atmospheric molecules by ice nanoparticles: Pickup cross sections, *J. Chem. Phys.*, 2012, **137**, 034304, DOI: 10.1063/1.4733987.

Patrick Robertson remarked: Is there a cluster size cut-off above which it is meaningful to consider a distinction between uptake into the bulk *versus* to the surface? Are you able to discriminate between surface *versus* bulk uptake experimentally?

Michal Fárník answered: Indeed, this is an important question in aerosol chemistry. However, our present hydrated nitric acid clusters are relatively small so that the distinction between surface and bulk is not quite meaningful. The picked-up molecules in our simulations are bound to the cluster surface since there is essentially no bulk part of the cluster. With (much) larger clusters, the molecules could be picked-up on the surface and eventually diffuse or react into the cluster interior. In the past, we did some experiments where we have photodissociated molecules in clusters by UV laser and measured the fragments by velocity map imaging [*e.g.*, ref. 1 and 2]. From the images, we were able to deduce (to some extent) whether the fragment molecule emerged from the cluster bulk or from the surface and how the molecule was oriented on the cluster. In principle, similar photodissociation experiments can be performed for other clusters, but it is always difficult and the evidence is rather indirect.

Also, calculation of the pickup of molecules by larger clusters could provide some insight into the question of if the molecules penetrate or react into the cluster bulk. We performed such an experimental and theoretical study for hydrogen peroxide picked up by large argon and water clusters,[3] and we saw different behaviour for the molecule on/in these clusters. However, in the present case, we expect that the alcohols with longer aliphatic chain (butanol, pentanol) will remain at the surface of the cluster independent of its size due to their amphiphilic nature and known partial immiscibility with water.

1 J. Fedor *et al.*, Velocity map imaging of HBr photodissociation in large rare gas clusters, *J. Chem. Phys.*, 2011, **134**, 154303, DOI: 10.1063/1.3578610.
2 V. Poterya *et al.*, Imaging of hydrogen halides photochemistry on argon and ice nanoparticles, *J. Chem. Phys.*, 2014, **141**, 074309, DOI: 10.1063/1.4892585.
3 J. Poštulka *et al.*, Bimolecular reactions on sticky and slippery clusters: Electron-induced reactions of hydrogen peroxide, *J. Chem. Phys.*, 2022, **156**, 054306, DOI: 10.1063/5.0079283.

Stuart R. Mackenzie asked: Thank you for this very interesting and clearly written paper. As you highlight you demonstrate very impressive agreement of experiment and calculation, particularly in the trends for the sticking probability.

The challenges of working on neutral clusters, with no mass selection in the parent, are clear.

These are comparatively strongly-bound molecular clusters, but can you say a bit more about how confidently you can ignore fragmentation in the electron impact/TOF detection stage? At some points you seem to suggest that fragmentation might be significant for the naked parent clusters but not affect the pickup products.

Michal Fárník answered: Thank you for your positive evaluation of our work. Indeed, you are right, the cluster fragmentation after the electron ionization has to be considered in the evaluation of our experimental data. Since we obtain the uptake probability by integrating the mass peak series with and without the alcohol molecules as the ratio of these integrals, we have to make sure that the alcohol molecules do not evaporate from the cluster upon ionization. In our previous two investigations,[1,2] we have measured the cluster velocities corresponding to the different fragment ion peaks, and we have shown that the clusters yielding fragment ions with the alcohol molecules were, indeed, significantly slower due to the momentum transfer in the uptake collisions. On the other hand, only a very small shift of the velocity was measured for the "clean" fragment ion peaks without the adsorbed molecules. The small shift corresponded to the momentum transfer in grazing non-sticking collisions as shown in our present paper. We have done the velocity measurements for the pickup of methanol and two other alcohols – unfortunately, we could not repeat them for all the molecules within the present investigation. Nevertheless, the very similar character of all the mass spectra suggests the same behavior for all the studied molecules. Thus, these measurements demonstrated that the alcohol molecules did not evaporate upon electron ionization from the hydrated nitric acid clusters. On the other hand, the same measurements also suggested that some cluster fragmentation upon ionization took place, since the measured change in the velocity always corresponded to a larger cluster mass than the mass of the cluster ion fragment, for which the velocity was measured. Therefore, we believe that some water molecules evaporate upon ionization, nevertheless, that does not influence our evaluation of the uptake probability as long as the alcohol sticks to the cluster ion fragment, which seems to be the case.

1 A. Pysanenko *et al.*, Uptake of methanol on mixed HNO_3/H_2O clusters: an absolute pickup cross section, *J. Chem. Phys.*, 2018, **148**, 154301, DOI: **10.1063/1.5021471**.
2 J. Lengyel *et al.*, Oxidation Enhances Aerosol Nucleation: Measurement of Kinetic Pickup Probability of Organic Molecules on Hydrated Acid Clusters, *J. Phys. Chem. Lett.*, 2020, **11**, 2101, DOI: **10.1021/acs.jpclett.0c00207**.

Dwayne Heard said: The determination of a sticking probability *versus* impact parameter, a sort of opacity function for sticking, is a really interesting result from this paper (**https://doi.org/10.1039/d3fd00160a**). Also, the agreement with theory is very impressive so it seems you understand the fundamental processes well. I think these fundamental data do provide the basis for calculating some useful parameters that could be incorporated into atmospheric models, for example nucleation rates of aerosols or aerosol growth (condensation) rates. Can you calculate the nucleation rate or growth rate from your data? *i.e.* For a given temperature, can you calculate from the opacity function the rate of the "sticking events" and growth of the particle? This is something that can be measured in the laboratory and so you could then compare with this?

Another question is whether the presence of alcohol on the cluster could accelerate the rate of water vapour uptake on the surface – or rather decelerate the rate of water vapour uptake? It is water vapour, which is far more abundant in the atmosphere, which controls the rate of growth of a new particle – *e.g.* towards cloud condensation nuclei. Can you please comment on this? Can you measure or calculate using theory the sticking probability of water vapour itself when an alcohol or another oxygenated OVOCs is present on the surface? This could be useful for the treatment of the growth of small nanoclusters.

Michal Fárník replied: Thank you for your interest in our results and for these important questions. Our experiments have been motivated by the aerosol formation in the atmosphere, and we were hoping that our data could be implemented in some atmospheric modelling. Since we have no experience with the atmospheric models, we were not planning to do the modelling ourselves, but so far, we have not heard of anybody else implementing our data. We have already been thinking about evaluating the aerosol growth rates from our uptake cross sections, but honestly, we do not know how to do that. We could see a clear qualitative correspondence between our cross sections and the rate constants measured by other groups. For example, our group measured uptake cross sections for water (and other atmospheric molecules) on large water clusters (ice nanoparticles).[1] The cross sections turned out to be significantly larger than the cluster geometrical cross sections. Signorell's group measured association rate constants for small water clusters.[2] These rates were also significantly larger than the collision rates corresponding to the geometrical size of the clusters. Thus, there is a clear qualitative agreement of the measured uptake cross sections with the association rates, however, we were not able to evaluate the association rates from our cross sections to make a quantitative comparison. There might be a way to incorporate into the nucleation models the detailed molecular-level understanding of the uptake processes delivered by our experiments and simulations, but we would like to collaborate with some experts on aerosol nucleation on that.

Concerning the second part of your question, we have not tried pickup water on the cluster which already contained alcohol molecules. In principle, such experiments could be done, since we have multiple pickup cells in series in our apparatus. We have done some experiments, where we pick up two different bases, ammonia and dimethylamine, on the hydrated nitric acid clusters. Some preliminary results have been published,[3] and they show that changing the ordering in the pickup (*i.e.* first ammonia and then DMA or *vice versa*) does not change the result. We could try the uptake of an alcohol and water, but we can already foresee quite a few experimental complications. Perhaps, trying simulations in the first place would be more feasible.

1 J. Lengyel *et al.*, Uptake of atmospheric molecules by ice nanoparticles: pickup cross sections, *J. Chem. Phys.*, 2012, **137**, 034304, DOI: **10.1063/1.4733987**.
2 C. Li *et al.*, Extraction of monomer-cluster association rate constants from water nucleation data measured at extreme supersaturations, *J. Chem. Phys.*, 2019, **151**, 094305, DOI: **10.1063/1.5118350**.
3 M. Fárník, Bridging Gaps between Clusters in Molecular-Beam Experiments and Aerosol Nanoclusters, *J. Phys. Chem. Lett.*, 2023, **14**, 287, DOI: **10.1021/acs.jpclett.2c03417**.

Dwayne Heard addressed Michal Fárník and Eva Pluhařová: When the alcohol lands on surface of the cluster and is incorporated, does it sometimes kick out a water molecule?

Michal Fárník responded: Yes, these processes happen. We cannot distinguish them in our experiment but we can see them in the simulations. For example, in the present article (**https://doi.org/10.1039/d3fd00160a**), Fig. 4 shows the uptake events in the solid red circles, while the light red circles correspond to the uptake with water evaporation. It can be seen that the water evaporation follows the uptake of methanol only in a few percent of cases, but the uptake of *tert*-butanol is followed by the evaporation in about 10% of the uptake events. Similar graphs for all the investigated alcohol molecules are shown in the ESI of our paper. In any case, the uptake with water evaporation is much less frequent than the uptake without any evaporation. Perhaps my theory colleagues, who actually did and analyzed these simulations, can add a comment.

Eva Pluhařová replied: I would like to add that interestingly, in a few no-sticking trajectories, we have seen the water leaving the cluster attached to the alcohol molecule.

Daniel M. Neumark said: When an alcohol is picked up by the cluster, what is the extent and time scale of any subsequent solvent (*i.e.* water) evaporation? Does the presence of evaporation affect your mass spectra to any significant extent?

Michal Fárník responded: In our simulations, we see evaporation of at most one water molecule on a ps time scale. However, this process is not frequent (see Fig. S7 in the ESI of **https://doi.org/10.1039/d3fd00160a**). For methanol, it occurs only in less than 4% of cases and at most it reaches about 10% cases for *tert*-butanol and 1-pentanol. On the other hand, the cluster ion fragment series with the picked-up alcohol in the experimental spectra have the same shape as the series without the pickup, but are shifted by one water molecule (see Fig. 3 and S4 in the ESI of **https://doi.org/10.1039/d3fd00160a**). This suggests that the water is replaced by the alcohol in the uptake process and the water evaporation can take place within 0.6 ms corresponding to the flight time of the cluster from the pickup cell to the ionizer of the TOF. In any case, the mass spectra are not affected to a significant extent by the water evaporation after the uptake of the alcohol, but can be affected by the cluster fragmentation after the ionization as explained in our answer to the question from Stuart R. Mackenzie. We see experimental evidence for more than one water molecule evaporating after the electron ionization in the velocity measurements, which reveal the momentum transfer. However, this does not influence our evaluation of the uptake probability as long as the cluster ion fragments with and without the alcohol molecules are influenced to the same extent by the ionization and the alcohol is not evaporated from the cluster upon the ionization. This is suggested by the same shape of the fragment ion series with and without the alcohol, and it has been proved by the velocity measurements.

Jennifer Meyer asked: Michal, great agreement between experiment and theory. Most of the alcohols you investigated follow a general trend with carbon chain length or branching. What makes 1-propanol special? The integral cross section for 1-propanol is higher than for ethanol in the simulations and on the same level as for ethanol in the experiment. That is against the general trend. What is special about 1-propanol that its reactivity is enhanced or is it the other way around and the reactivity of ethanol is somehow inhibited?

Michal Fárník responded: The agreement in the qualitative trends of the relative uptake cross sections between our experiments and calculations was surprising even for us. The present work is reassuring that our methods actually provide a realistic description of the uptake processes. The difference between the experiment and simulations in the case of 1-propanol was actually on the level of agreement that we expected, and rather exceptional was the agreement for the other alcohols. We can only hypothesize here, why the uptake cross section 1-propanol exceeds the monotonous trend in dependence on the chain length. The uptake of the molecule is a result of several effects acting in opposite directions and partly cancelling each other. The increasing size of the molecule increases the geometrical cross-section and thus the uptake, but the increased momentum and decreased availability of the anchoring OH group act in the opposite way. This might lead to a not perfectly monotonous dependence of the uptake on the chain length.

Pablo G. Jambrina said: Thank you for your very nice presentation. In the paper you show an excellent agreement between theory and calculations, which is really impressive considering that the calculations were carried out using MD (*i.e.* at a force-field level of theory). I would like to ask about the sensitivity of the results to the forcefield parameters (*i.e.* whether they change significantly with the forcefield) and also about the sensitivity to the partial charges assigned to the alcohols.

Eva Pluhařová responded: Thank you for your positive reaction. We tested two force-fields for water, namely TIP3P and SPC/E, the differences were negligible. The atomic partial charges of the alcohol molecules do not come from one source and, in addition to that, in several cases we had to assign partial atomic charges as described in the Methods of our paper (**https://doi.org/10.1039/d3fd00160a**). All parameters all available here **https://data.narodni-repozitar.cz/heyrovsky/datasets/jq7fm-k2x81**. As an example, the span of the partial charges for the H atom of the OH group is 0.3976 to 0.4389 and for the O atom of the OH group −0.7598 to −0.6666. The results seem robust within this range of values of partial charges.

Pablo G. Jambrina commented: Thank you for your response. As far as I understand, the results shown in panel b of Fig. 7 of your paper (**https://doi.org/10.1039/d3fd00160a**) for each alcohol are averaged over the different initial structures extracted from the initial MD simulation. How strong was the dependence of the results on the initial structure used? Would you have obtained a similar agreement with the experiments by considering only one of these structures?

Eva Pluhařová replied: Yes, the error bars in Fig. 7 originate not only from many different mutual initial orientations of the alcohol and the cluster, but also from different structures of the aqueous nitric acid cluster. This is also true for the error bars in Fig. 4, 5 and 6. The analysis of the data for each cluster give slightly different absolute values of the cross-section for each cluster, but the trends for the alcohol series are preserved.

Gilbert S. Nathanson asked: Could you please speculate on the uptake of gas-phase alcohol molecules at low cluster temperatures and translational energies representative of the troposphere? Do you think that the alcohol molecules would spend enough time on the clusters at these conditions for the OH group to reorient and find surface hydrogen bonding sites even if the alkyl chain is long?

Michal Fárník answered: This is a very good question, since the collision energy in our experiment and simulations correspond to the experimentally measured cluster velocity of 1800 m s^{-1}. The molecules at atmospheric temperatures 200–300 K are 5–10 times slower, corresponding to collision energies up to 100 times smaller. This can change the game significantly. For example, the molecule approaching the cluster much more slowly might have time to reorient itself with the anchoring OH group towards the cluster leading to more sticking collisions. Longer contact with the cluster can have a similar effect. Thus, the uptake probabilities will be probably larger at the lower temperature. However, they will increase for the smaller molecules as well, and the question is, to which extent this effect will smear out the differences in the pickup between the different molecules. We guess that the qualitative trends observed in our experiment and simulations will be preserved to a certain extent. We cannot prove that experimentally, but we can perform at least some of our simulations in the future at lower velocities to check if that is the case. Thank you for the interesting proposal.

Eva Pluhařová responded: In addition to Michal's response, I would like to add that there is a recent simulation study of properties of water and argon clusters by the group of Jiri Kolafa.[1] They showed that the cluster pickup cross section increases with decreasing velocity of the incoming molecule or atom.

1. M. Klíma, D. Celný, J. Janek and J. Kolafa, *J. Chem. Phys.*, 2023, **159**, 124302, DOI: **10.1063/5.0166912.**

Jennifer Meyer said: Why does the opacity function (reaction probability) make such large changes at impact parameters of about 0.6–0.8 nm for methanol as well as for *tert*-butanol (Fig. 4 of your paper **https://doi.org/10.1039/d3fd00160a**). Up to an impact parameter of 0.6 nm the curves irrespective of (non)reactive channel are rather smooth. Is that "jump" related to the (physical) size of the cluster? Should there not be a larger difference between the two alcohols?

Michal Fárník replied: The probability of the observed processes exhibits very similar behavior not only for methanol and *tert*-butanol (Fig. 4 in **https://doi.org/10.1039/d3fd00160a**) but for all the investigated molecules (see Fig. S7 in the ESI). There is a relatively sharp increase in the dependence corresponding to the "direction change" (green curve) at between 0.6 and 0.8 nm for all the molecules. On the other hand, the steep increase is not exactly the same for all the molecules and the dependence on the carbon chain length can be seen in Fig. S7 in the ESI. For methanol it is a step-like function rising sharply at 0.6 nm, but this increase is smoother and more gradual for the larger molecules. Similarly, the "short contact" (blue curve) exhibits a sharp maximum at 0.6 nm for methanol, while for the larger molecules there is a maximum too, but the dependence is broader and smoother. The shape of these curves is determined by interplay of three factors: (1) the size (geometrical cross section) of the clusters in our simulations; (2) the size of the molecules that increases with the chain length; (3) the mass of the molecule, which also increases with the chain length and means that the heavier molecules can escape the attractive potential of the cluster more easily than the light ones. The factors (2) and (3) can cancel each other to some extent and factor (1) is independent of the molecule. This can explain why the calculated curves have similar character for all the molecules. In any case, they are result of the simulations where the size, mass and interaction potential for of the different molecules were taken into account.

Nadia Balucani communicated: Is it possible to measure or quantify the temperature of the clusters (or their internal energy) in your experiments?"

Michal Fárník communicated in reply: This is, indeed, a very important but difficult question. We cannot determine the cluster temperature in our experiment. Usually, the clusters generated in supersonic expansions are assumed to be relatively cold, *e.g.*, for large Ar clusters the temperature of about 30 K was determined experimentally by electron diffraction experiments.[1] Temperatures of pure large water clusters between 80 K and 200 K were reported in the literature,[2–6] based on various models and measured by different spectroscopic techniques. Based on these numbers and similar temperatures reported in the literature for other molecular clusters, we can speculate that the present hydrated nitric acid clusters should be relatively cold. Therefore, we assign the velocities of the hydrated nitric acid clusters from the Maxwell distribution at 150 K. However, we have no experimental proof of the cluster temperature.

1 J. Farges, *et al.*, Structure and temperature of rare gas clusters in a supersonic expansion, *Surf. Sci.*, 1981, **106**, 95.
2 J. Brudermann, *et al.*, Isomerization and melting-like transition of size-selected water nonamers, *J. Phys. Chem. A.*, 2002, **106**, 453.
3 N. Gimelshein, *et al.*, The temperature and size distribution of large water clusters from a nonequilibrium model, *J. Chem. Phys.*, 2015, **142**, 244305.
4 C. Hock, *et al.*, Calorimetric observation of the melting of free water nanoparticles at cryogenic temperatures. *Phys. Rev. Lett.*, 2009, **103**, 073401.
5 J. Boulon, *et al.*, Experimental nanocalorimetry of protonated and deprotonated water clusters, *J. Chem. Phys.*, 2014, **140**, 164305.
6 M. Fárník and J. Lengyel, Mass spectrometry of aerosol particle analogues in molecular beam experiments, *Mass Spec. Rev.*, 2018, **37**, 630.

Peter D. Watson communicated: In Fig. 3b and c, each of the integrated intensities presents with an onset and peaks for a given degree of hydration except for the $HNO_3(H_2O)_nH^+$ which decreases from $n = 1$. Does this result from coordination but not dissociation of the nitric acid in small hydrated clusters?

Michal Fárník communicated in reply: The mass spectra of the hydrated nitric acid clusters have been discussed in detail previously – first by Castleman *et al.*[1], then in our previous papers.[2] The $HNO_3(H_2O)_nH^+$ series originates from the $HNO_3(H_2O)_N$ neutral precursors. For the small N, these neutral clusters contain the HNO_3 molecule in non-dissociated form and their abundance decreases with N. Correspondingly, the abundance of the cluster ion fragments $HNO_3(H_2O)_nH^+$ decreases with n. For N larger than a certain threshold size N_{th}, the HNO_3 molecule is assumed to be acidically dissociated in the neutral $HNO_3(H_2O)_N$ cluster. The presence of the ion pair in the cluster can increase the ionization cross section due to the formation of a dipole in the cluster. This would lead to the increase of the $HNO_3(H_2O)_nH^+$ ion signal from certain n corresponding to the fragment of the neutral cluster with N_{th} water molecules. Alternatively, the ion pair and corresponding dipole formation in the neutral can increase the interaction of the cluster with the water molecules in the supersonic expansion leading to a more efficient $HNO_3(H_2O)_N$ cluster generation for $N > N_{th}$. This would again lead to the increase in the corresponding $HNO_3(H_2O)_nH^+$ fragment ion abundances. Thus, the observed decrease and subsequent increase of the $HNO_3(H_2O)_nH^+$ ion intensities in the spectra is explained by the acidic dissociation. For the clusters with more HNO_3 molecules, their threshold size for the acid ionization corresponds to smaller N_{th}. Besides, they are less abundant in the neutral beam. Therefore, we can see only the increase of the corresponding $HNO_3(H_2O)_nH^+$ fragment ion intensities, which occurs due to the acid dissociation in the neutral precursor. More detailed discussion and corresponding threshold sizes can be found in the above cited articles. However, it is worth noting that there might be still some small ambiguities concerning this model and the actual threshold sizes, since the original Castleman's work assumed the evaporation of only an OH group upon the cluster ionization, while our pickup experiments suggested that more water molecules might be evaporated upon ionization. Nevertheless, the qualitative arguments based on the acidic dissociation causing the general mass spectrum shape remain valid and they seem to hold also for the mass spectra after the alcohol uptake.

1 B. D. Kay *et al.*, Studies of gas-phase clusters: The solvation of HNO_3, in microscopic aqueous clusters, *Chem. Phys. Lett.*, 1981, **80**, 469.
2 J. Lengyel *et al.*, Nucleation of Mixed Nitric Acid–Water Ice Nanoparticles in Molecular Beams that Starts with a HNO_3 Molecule, *J. Phys. Chem. Lett.*, 2012, **3**, 3069.

Dwayne Heard said: In recent years there have been some papers regarding the spontaneous formation of radicals at the surface of an aerosol – which may form OH, HO_2 or other reactive species.[1–5]

Extending these ideas to your paper, if you had an alcohol on the surface and you had a strong electric field, and this is calculated to be larger for smaller clusters, could you cleave the R–OH in the alcohol to form R + OH? Or is the OH^- (anion) to OH radical energetically easier? There is some debate regarding this mechanism – so I am interested in your thoughts on whether a significant electric field would influence your results – given already that you have a good comparison between experiment and theory? More generally I am interested in the presence of electric fields at surfaces and what the impact of this may be?

1 M. Angelaki *et al.*, Quantification and Mechanistic Investigation of the Spontaneous H_2O_2 Generation at the Interfaces of Salt-Containing Aqueous Droplets, *J. Am. Chem. Soc.*, 2024, **146**, 8327–8334.

2 K. Li *et al.*, Spontaneous dark formation of OH radicals at the interface of aqueous atmospheric droplets, *Proc. Natl. Acad. Sci. U. S. A.*, 2023, **120**(15), e2220228120.

3 N. H. Musskopf *et al.*, The Air–Water Interface of Water Microdroplets Formed by Ultrasonication or Condensation Does Not Produce H_2O_2, *J. Phys. Chem. Lett.*, 2021, **12**, 11422–11429.

4 J. K. Lee *et al.*, Spontaneous generation of hydrogen peroxide from aqueous microdroplets, *Proc. Natl. Acad. Sci. U. S. A.*, 2019, **116**(39), 19294–19298.

5 Y. Guo *et al.*, Spontaneous Iodide Activation at the Air–Water Interface of Aqueous Droplets, *Environ. Sci. Tech.*, 2023, **57**, 15580–15587.

Eva Pluhařová answered: Thank you for bringing these studies to our attention. They agree in the spontaneous formation of H_2O_2 or I_2 at the surface of small aqueous droplets, even though Musskopf *et al.*[1] points out the importance of the method of the generation of the droplets. Nevertheless, the accepted explanation is that the strong local electric field at the air/water interface triggers the charge separation in OH^- (anion) → OH (radical) + e^-. We think that the local electric field at the droplet interface would not influence the uptake of the alcohols much, especially given their velocities in our current setup which do not allow for complete reorientation of the molecule when it is passing by the cluster. If the velocities were much lower, the local field would probably increase the overall uptake, but we do not expect changes in the qualitative trends.

The key thing in the mentioned studies is the presence OH^- which results from the autoprotolysis of water, *i.e.* $2H_2O \rightarrow OH^- + H_3O^+$. The analogous reaction for the alcohols would be the OH bond dissociation: $ROH + H_2O \rightarrow RO^- + H_3O^+$, because alcohols are weak Brønsted acids. The C–O bond cleavage, you mentioned, is more difficult. However, the pK_α values of the alcohols are higher than that of water, so such a process is less likely. The next important factor is the presence of electron scavengers, such as O_2, which facilitate the charge separation and OH radical formation. Covering the surface of the droplet with the alcohol decreases the availability of O_2 at the interface which shall decrease the efficiency of the process.

Finally, the OH radicals have to recombine in order to form H_2O_2, but they are very likely to encounter C–H bond from the alkyl chain and cleave it upon formation of water which would further decrease the H_2O_2 yield.

1 N. H. Musskopf *et al.*, The Air–Water Interface of Water Microdroplets Formed by Ultrasonication or Condensation Does Not Produce H_2O_2, *J. Phys. Chem. Lett.*, 2021, **12**, 11422–11429.

Conflicts of interest

There are no conflicts to declare.