

## Scattering of larger molecules – part 2: general discussion

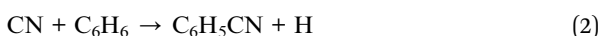
F. Javier Aoiz, Nadia Balucani,  Astrid Bergeat,  Alexander Butler, David W. Chandler, Gábor Czakó, Tibor Győri, Dwayne E. Heard, David Heathcote,  Brianna R. Heazlewood,  Nils Hertl, Pablo G. Jambrina,  Ralf I. Kaiser, Olivia A. Krohn,  Viet Le Duc,  Jérôme Loreau, Stuart R. Mackenzie,  Kenneth G. McKendrick,  Jennifer Meyer,  Gilbert M. Nathanson, Daniel M. Neumark, Rahul Pandey, Christopher Reilly, Patrick Robertson, George C. Schatz,  Steven J. Sibener, Arthur G. Suits,  Peter D. Watson,  Roland Wester, Stefan Willitsch, Alec M. Wodtke and Bum Suk Zhao

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**Daniel M. Neumark** opened discussion of the paper by Ralf I. Kaiser: Is there any evidence for the phenylethynyl radical in the interstellar medium, and is there a plausible mechanism for its formation?

**Ralf I. Kaiser** replied: So far, the phenylethynyl radical has not been detected in the interstellar medium. However, this does not mean that it is not present. The phenylethynyl radical has three sets of chemically inequivalent hydrogen atoms. Along with the hyperfine structure, the rotational spectrum is expected to be complex. This presents a challenge in terms of data accumulation times for the detection of phenylethynyl. However, considering the rapidly increasing number of detected hydrocarbons and their radicals in the Taurus molecular cloud (TMC-1), we should be confident that phenylethynyl should be detected in this decade through the GOTHAM or QUIJOTE observational line surveys.

Regarding potential formation pathways, crossed molecular beam experiments in our laboratory merged with electronic structure calculations showed that phenylethynyl can be formed in the bimolecular, barrierless and exoergic neutral–neutral reactions between ground state dicarbon ( $C_2$ ) and benzene ( $C_6H_6$ ) [eqn (1)].<sup>1</sup> Here, dicarbon acts like a pseudohalogen and reacts *via* addition–hydrogen atom elimination to the benzene ring similarly to the reaction of the cyano radical (CN) with benzene ( $C_6H_6$ ) [eqn (2)] forming cyanobenzene ( $C_6H_5CN$ ):<sup>2</sup>



Also, in photon rich regions, phenylethynyl might be produced *via* photodissociation of phenylacetylene. Recent experiments exploiting a two-photon absorption of D1-phenylacetylene ( $C_6H_5CCD$ ) at 243 nm observed both the atomic hydrogen (H) and deuterium (D) losses with a ratio of about 5:1.<sup>3</sup> Note that another absorption band exists at 6.4 eV (193.7 nm),<sup>4</sup> and many Rydberg states above exist as well. For this band, the absorbed energy would be  $617 \text{ kJ mol}^{-1}$ , which is sufficient to dissociate the acetylenic carbon–hydrogen bond, which has a bond energy of  $566 \text{ kJ mol}^{-1}$ .

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3 S. K. Shin, H. L. Kim and C. R. Park, *Bull. Korean Chem. Soc.*, 2002, **23**, 286–290.

4 L. Serrano-Andrés, M. Merchán and M. Jabłoński, *J. Chem. Phys.*, 2003, **119**, 4294–4304.

**Daniel M. Neumark** asked: The calculated barriers for ring formation are buried but the transition states must be quite constrained. Does this entropic effect limit the rate constant for product formation, *i.e.* once the intermediate **i1(d)** in Fig. 4 in the paper (<https://doi.org/10.1039/d3fd00159h>) is formed, does all of it go towards products or is the reverse reaction to reactants significant?

**Ralf I. Kaiser** responded: The entropic effect limits the rate constants for product formation and it is more significant for the multistep pathway toward **p1** than for the immediate H(D) loss to **p2**. In principle, the entrance intermediate **i1** can decompose back to reactants. However, this reverse channel was not included in our calculations as our main goal was to assess relative yield of various reaction products. Accurate calculations of the rate constant for the barrierless entrance reaction channel (in forward and reverse directions) are challenging and time-consuming as they require the use of the variable reaction coordinate transition state theory (VRC-TST).

**Stefan Willitsch** enquired: Do you have an estimate of the rotational and vibrational temperature of your radicals in the molecular beam? Can you comment on possible effects of the internal excitation of the radicals on the class of reactions you are studying?

**Ralf I. Kaiser** answered: For those radicals with established laser induced fluorescence (LIF) spectra such as methylidyne (CH), we can determine the rotational temperature to be  $14 \pm 1 \text{ K}$  for the vibrational ground state with less than 6% of the populations in  $v = 1$ .<sup>1</sup> However, the phenylethynyl radical has no LIF spectrum, so we were not able to determine the rotational and vibrational temperature.

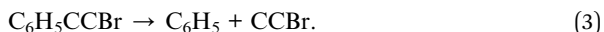
Recently, we explored the chemical dynamics of the test reactions of the phenylethynyl radical with allene ( $H_2CCCH_2$ ) and methylacetylene ( $CH_3CCH$ ) under single collision conditions in a crossed molecular beams machine and also computationally.<sup>2</sup> Here, the phenylethynyl radical was found to add without entrance barrier to the C1 carbon of the allene and methylacetylene reactants, resulting in doublet  $C_{11}H_9$  collision complexes. These intermediates underwent unimolecular decomposition *via* atomic hydrogen loss forming predominantly 3,4-pentadien-1-yn-1-ylbenzene ( $C_6H_5CCCHCCH_2$ ) and 1-phenyl-1,3-pentadiyne ( $C_6H_5CCCCCH_3$ ) in overall exoergic reactions ( $-110 \pm 8 \text{ kJ mol}^{-1}$

computationally *versus*  $117 \pm 22 \text{ kJ mol}^{-1}$  experimentally;  $-130 \pm 8 \text{ kJ mol}^{-1}$  computationally *versus*  $146 \pm 22 \text{ kJ mol}^{-1}$  experimentally) for the phenylethynyl-allene and phenylethynyl-methylacetylene systems. Therefore, within our error limits, we do not have evidence of any rovibrational excitation of the radical reactant.

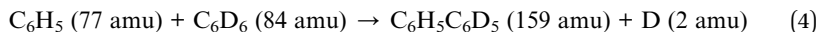
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**Astrid Bergeat** questioned: Have you fully characterized the minor products of your photolysis source? The main product is the photodissociation of the Br bond in the (2-bromoethynyl)benzene precursor, but are there any other small possibilities? What are the secondary products due to the impurities in the precursor?

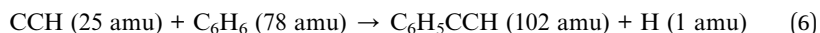
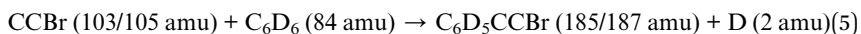
**Ralf I. Kaiser** replied: We also found that the (2-bromoethynyl)benzene precursor photodissociates to the phenyl radical ( $\text{C}_6\text{H}_5$ ) plus bromoethynyl (CCBr) [eqn (3)].



Phenyl radicals present in the primary reactant beam could react with D6-benzene to D5-biphenyl [eqn (4)]:<sup>1</sup>



Likewise, the bromoethynyl (CCBr) radical may react with D6-benzene to (2-bromoethynyl)-D5-benzene [eqn (5)] in a similar way as benzene ( $\text{C}_6\text{H}_6$ ) reacts with the ethynyl radical (CCH) to ethynylbenzene ( $\text{C}_6\text{H}_5\text{CCH}$ ) [eqn (6)]:<sup>2</sup>



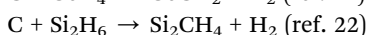
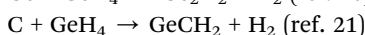
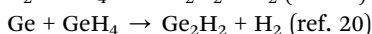
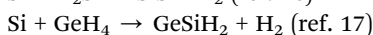
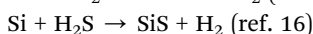
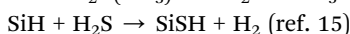
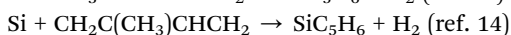
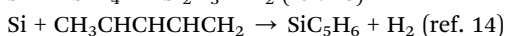
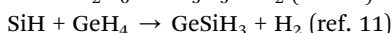
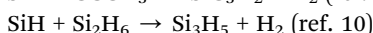
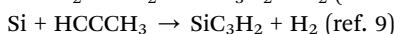
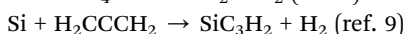
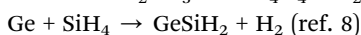
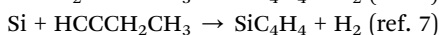
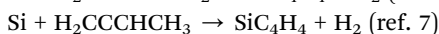
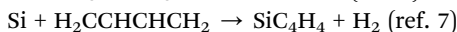
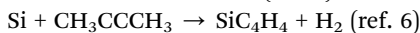
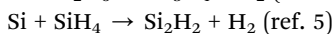
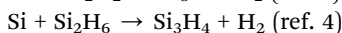
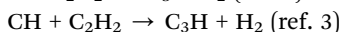
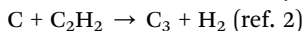
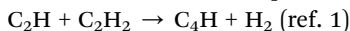
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**George C. Schatz** said: The pathway to grow graphite from hydrocarbons must ultimately require  $\text{H}_2$  elimination processes.

**Ralf I. Kaiser** responded: A more likely mechanism for the removal of hydrogen from the growing PAH is not  $\text{H}_2$  elimination but rather, direct H abstraction by a radical (*e.g.*, H atom) followed by another H atom loss which can be accompanied by cyclization (cyclodehydrogenation).

**George C. Schatz** enquired: Does  $\text{H}_2$  formation play a role in your experiments?

**Ralf I. Kaiser** replied: In the current system, we do not have any evidence of molecular hydrogen elimination. If molecular hydrogen is formed, we should see it – depending on sufficient branching ratios, kinematics, and hence signal-to-noise – as demonstrated in previous crossed molecular beams experiments:



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**David W. Chandler** requested: Dr Kaiser could you comment on other ways that people have suggested that large organic molecules can be formed in outer space such as formation on ice crystals or grains and the participation of resonantly stabilized radicals.

**Ralf I. Kaiser** answered: These are two separate, important questions in one. Each would deserve a comprehensive, chemically ‘correct’ review paper. This is certainly beyond scope of this *Faraday Discussion*. So, let us focus briefly on the participation of resonantly stabilized radicals first. Resonantly stabilized free radicals – radicals in which the unpaired electron is delocalized over multiple carbon atoms – such as the propargyl radical ( $\text{H}_2\text{CCCH}$ ,  $X^2B_1$ ) have been detected in the Taurus Molecular Cloud-1 (TMC-1) at significant fractional abundances of  $0.8 \times 10^{-8}$  to  $1.2 \times 10^{-8}$  with respect to molecular hydrogen.<sup>1,2</sup> TMC-1 is characterized by number densities of  $10^4 \text{ cm}^{-3}$  and temperatures as low as 10 K. In order for neutral–neutral reactions to proceed, these reactions must be bimolecular, have no entrance barriers, must be exoergic, and all transition states involved have to be located below the energy of the separated reactants.<sup>3–6</sup> Here, the bimolecular reaction of ground state carbon atoms ( $\text{C}$ ;  $^3P_j$ ) with ethylene ( $\text{C}_2\text{H}_4$ ) can rapidly form propargyl plus atomic hydrogen<sup>7</sup> at rates of a few  $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ .<sup>8</sup> The large fractional abundances of the propargyl radicals in TMC-1 indicate fast production mechanisms – as through the bimolecular reaction of atomic carbon with ethylene,<sup>7</sup> slow consumption pathways, or both. The reaction rates of propargyl radicals with closed shell hydrocarbons like acetylene ( $\text{C}_2\text{H}_2$ ),<sup>9,10</sup> ethylene ( $\text{C}_2\text{H}_4$ ),<sup>11</sup> and benzene ( $\text{C}_6\text{H}_6$ )<sup>12</sup> as prototype reactants of hydrocarbons carrying triple, double, and ‘aromatic’ bonds, respectively, from  $4.3 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$  to  $10^{-15} \text{ cm}^3 \text{ s}^{-1}$  at temperatures of 1100–1500 K are very low due to inherent entrance barriers to addition of 51, 52 and 59  $\text{kJ mol}^{-1}$ . This means reactions of propargyl radicals with closed shell hydrocarbons are irrelevant in TMC-1 at 10 K, but they could be important in high temperature circumstellar envelopes of carbon-rich Asymptotic Giant Branch (AGB) stars and planetary nebulae as their descendants holding temperatures of a few 1000 K.

So, what is the fate of propargyl radicals in TMC-1? Experimental studies of barrierless and exoergic atom–propargyl and radical–propargyl reactions are rare.

A crossed molecular beams reaction of ground state carbon atoms ( $C$ ;  $^3P_j$ ) with propargyl radicals revealed the formation of diacetylene ( $HCCCCH$ ) plus atomic hydrogen.<sup>13</sup> Molecular beams studies of the propargyl radical self-reaction<sup>14</sup> in a chemical microreactor suggest that if two propargyl radicals react under single collision conditions, phenyl radicals ( $C_6H_5$ ) plus atomic hydrogen may be formed, with internally excited phenyl radicals undergoing unimolecular decomposition through atomic hydrogen loss to *o*-benzynes ( $C_6H_4$ ). The recently established Propargyl Addition BenzAnnulation (PABA)<sup>15,16</sup> mechanism forms aromatics such as naphthalene ( $C_{10}H_8$ )<sup>15</sup> and anthracene ( $C_{14}H_{10}$ ) and phenanthrene ( $C_{14}H_{10}$ ),<sup>16</sup> respectively. These pathways involve the reaction of propargyl radicals with the benzyl radical ( $C_7H_7$ ) and with the 1'- and 2'-methylnaphthyl radicals ( $C_{11}H_9$ ). However, these pathways operate in conjunction with hydrogen-atom-assisted isomerization and hence are closed in TMC-1, but could be important in circumstellar envelopes of carbon-rich AGB stars. As shown in a chemical microreactor study, the reaction of the propargyl radical with the phenyl radical ( $C_6H_5$ ) leads – if only single collision conditions operate – to the indenyl radical ( $C_9H_7$ ).<sup>17</sup> In a more exotic twist, recent electronic structure calculations merged with astrochemical modeling<sup>18</sup> exposed that the reaction of tricarbon ( $C_3$ ;  $X^1\Sigma_g^+$ ) – formally a closed shell, but electron deficient reactant – with propargyl is very fast and generates in a bimolecular reaction at 10 K the ethynylbutatrienylidene molecule ( $CCCHCCCH$ ;  $X^1A'$ ). The latter is a high energy isomer of triacetylene ( $HCCCCCCH$ ) and was recently detected in TMC-1.<sup>19</sup> To sum up, the aforementioned studies showcased that bimolecular atom–propargyl and radical–propargyl radical reactions could be rapid and efficient under conditions in TMC-1 and might contribute to molecular mass growth processes of hydrocarbons in these extreme environments, but no coherent, systematic picture has arisen as of today on the reactivity of propargyl radicals under the conditions of TMC-1. This should be explored in future studies.

Let us move now to the second part, *i.e.* the question if large organic molecules can be formed in outer space such as the formation on ice crystals or grains. The short answer is: ‘Yes – even aromatics’.<sup>20–23</sup> We could stop here and just cite some review papers from our laboratory; this is done here anyway to provide newcomers to the field an opportunity to get a jumpstart on the complexity of chemistry in low-temperature ices.<sup>24,25</sup> But some additional thoughts are appropriate.

Interstellar grains can be described as interstellar nanoparticles with sizes of a few 100 nm.<sup>26,27</sup> These can be silicate-based (oxygen rich),<sup>28,29</sup> carbonaceous (carbon rich),<sup>30</sup> and may contain sulfides (sulfur-rich).<sup>31,32</sup> At 10 K in cold molecular clouds, these nanoparticles accrete ice layers of a few 100 nm thicknesses containing simple hydrides like water ( $H_2O$ ), ammonia ( $NH_3$ ), and methane ( $CH_4$ ), oxides (carbon monoxide ( $CO$ ), carbon dioxide ( $CO_2$ )), methanol ( $CH_3OH$ ), formaldehyde ( $H_2CO$ ), and even carbonyl sulfide ( $COS$ ) along with sulfur dioxide ( $SO_2$ ) as probed recently with the James Webb Space Telescope (JWST).<sup>33</sup> The recently proposed infrared detection of complex organics<sup>33,34</sup> such as ethanol ( $C_2H_5OH$ ), acetaldehyde ( $CH_3CHO$ ), formic acid ( $HCOOH$ ), and acetic acid ( $CH_3COOH$ ) is problematic and would not even hold up stringent requirements of an undergraduate organic-analytical chemistry midterm. Although recent laboratory experiments provide compelling evidence that these complex organics *should* be formed on interstellar ices,<sup>35–40</sup> scientific standards have to be followed, and complex organics cannot be ‘identified’ through single infrared

lines – not on Earth and not in space; they could be linked to functional groups, but not to individual, isomer-specific molecules.

Nevertheless, at 10 K, these complex ice mixtures on interstellar grains can be exposed to (non) ionizing radiation in the form of high energy Galactic Cosmic Rays (GCRs) penetrating even deep inside molecular clouds and also to Lyman- $\alpha$  photons (VUV) generated deep inside molecular clouds.<sup>3,24,41</sup> The exposure of simple molecules leads to suprathreshold atoms such as atomic hydrogen, carbon, nitrogen, and sulfur that have excess kinetic energies of a few electron volts. Reactions of these suprathreshold atoms can overcome barriers to reaction easily resulting in reaction rates orders of magnitude higher than their thermal counterparts.<sup>42</sup> Likewise, the exposure of these ices to VUV and GCRs also generate reactive radicals; if these radicals are in close proximity (neighborhood), they can recombine to form complex organics deep within<sup>22,24,25,43,44</sup> interstellar ices. Exploiting an isomer selective photoionization (PI) reflectron time-of-flight mass spectrometry (Re-TOF-MS) (condensed phase) analysis of those molecules subliming in the temperature programmed desorption (TPD) phase, multiple key classes of organic molecules have been identified in our laboratory; important species are compiled in Fig. 1–4 here.<sup>20,23–25,36,39,40,45–125</sup> It is important to highlight that GCRs penetrate throughout the ice-coated nanoparticles,<sup>24,41</sup> and evidence suggests that these processes form complex organics in the ‘bulk’ of the ices at 10 K, but not on the surface of those ices, despite ‘popular belief’. If the bulk ices can also store radicals, then these radicals may also recombine during the TPD heating phase, which simulates the transition from a molecular cloud to a hot-core stage. However, radical–radical recombination at 10 K may dominate the production, for instance in the case of acetaldehyde (CH<sub>3</sub>CHO).<sup>76</sup> Recently, laboratory experiments also demonstrated that thermal processing of interstellar analog ices<sup>126–128</sup> can form complex organics *via* Lewis acid–Lewis base reactions resulting in, *e.g.*, the ‘simplest’ amino acid,<sup>50</sup> hemiacetals,<sup>53</sup> and prebiotic chelating agents.<sup>51</sup>

Before concluding, it is interesting to deliberate on potential mechanisms how complex organics can be transferred from the 10 K ices into the gas phase of cold

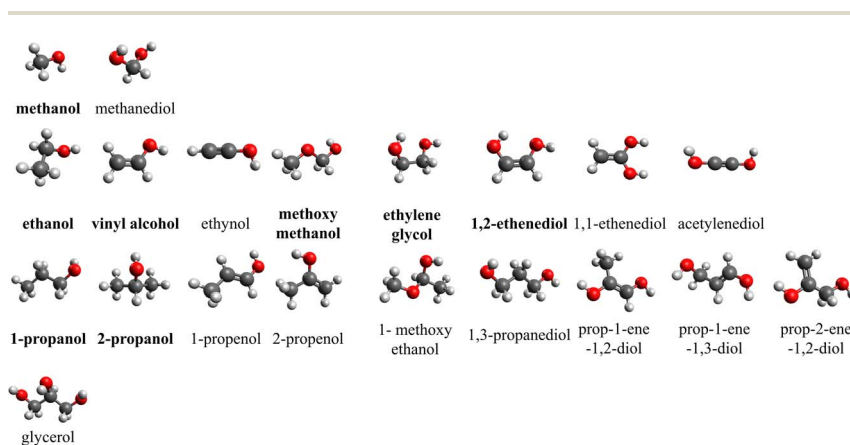


Fig. 1 Selected alcohols detected in our laboratory. Names in bold indicate these compounds have also been detected in astronomical environments.



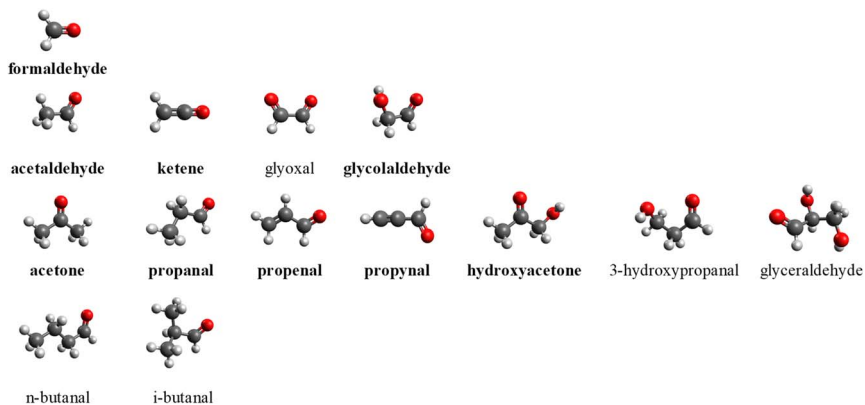


Fig. 2 Selected aldehydes and ketones detected in our laboratory. Names in bold indicate these compounds have also been detected in astronomical environments.

molecular clouds (still at 10 K) or in star forming regions, where temperatures can rise up to 300 K. As discussed above, the transition from a molecular cloud to a star forming region increases the temperature and hence leads to a fractionated sublimation of the molecules formed at 10 K and, to a minor fraction during the warm up phase, into the gas phase. However, the recent detection of complex organics such as acetaldehyde ( $\text{CH}_3\text{CHO}$ ), methyl formate ( $\text{HCOOCH}_3$ ), and dimethyl ether ( $\text{CH}_3\text{OCH}_3$ ) in cold molecular clouds such as TMC-1<sup>129,130</sup> suggests that this picture is incomplete, and mechanisms should exist – unless these complex organics are formed in the gas phase – which deliver complex organics into the gas phase from the grains at 10 K. Multiple pathways have been

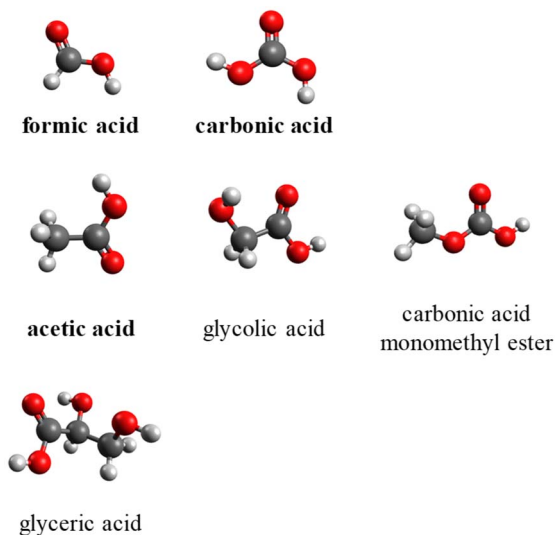


Fig. 3 Selected carboxylic acids detected in our laboratory. Names in bold indicate these compounds have also been detected in astronomical environments.



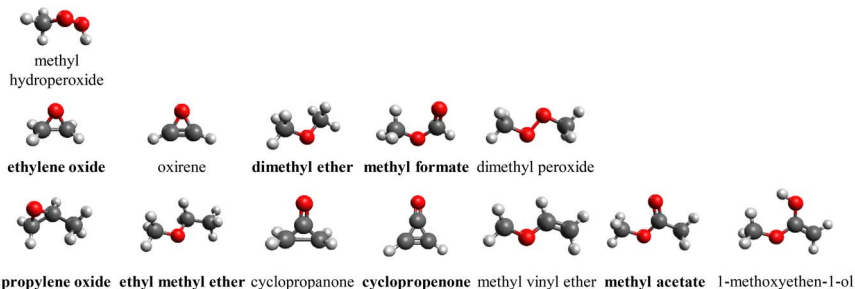


Fig. 4 Selected miscellaneous oxygen-containing organic compounds detected in our laboratory. Names in bold indicate these compounds have also been detected in astronomical environments.

suggested how complex organic molecules (COMs) might have been ejected from the icy grains into the gas phase.<sup>131–138</sup> First, a hypothesized photon desorption of organics, which is efficient at the edges of clouds, is negligible in the inner parts of clouds.<sup>139</sup>

A second hypothesis highlights the role of GCRs since high energy GCRs can penetrate deep into dense regions and induce sputtering of frozen molecules.<sup>133</sup> Third, chemical explosive desorption mechanisms in conjunction with a rapid ejection of accreted molecules through the release of ‘chemical energy’ from the reactions of radicals stored in the ice mantles has been offered.<sup>131,132,135,136,140–142</sup> Recent experiments identified hydrogen (H<sub>2</sub>) bursts accompanied by an ejection of up to 90% of solid samples during 9.0 MeV  $\alpha$ -particle (He<sup>2+</sup>) and 7.3 MeV proton (H<sup>+</sup>) irradiation of methane ices at 10 K *without* warming the sample.<sup>43</sup> Energetic electrons – formed in the track of GCRs penetrating interstellar ices – processing methane ices also induced a rapid emission of molecules into the gas phase.<sup>143–145</sup> These studies were expanded recently to repetitive grain-explosions in methane–carbon monoxide ices at 5 K.<sup>121</sup> Critical radical concentrations of up to a few percent induce rapid, radical–radical reactions accompanied by an ‘explosive’ ejection of organic matter into the gas phase. However, a spectroscopic tracing of these radical reactions at ultralow temperatures representing molecular clouds has not been reported to date.

Overall, laboratory experiments such as molecular beam studies (gas phase) and surface science experiments in conjunction with an isomer selective, universal detection of complex organics *via* photoionization (PI) reflectron time-of-flight mass spectrometry (Re-TOF-MS) (condensed phase) represent ideal approaches to systematically explore the formation of complex organics in the interstellar medium and also in our Solar System. These laboratory simulation experiments should follow the principle ‘Chemistry First’ and adhere to stringent physical chemistry requirements. Further, an incorporation of these data into astrochemical models requires intimate knowledge on fundamental principles of reaction dynamics, kinetics, and (non-equilibrium) radiation chemistry rather than adding laboratory results uncontrolled into even incomplete chemical reaction networks. After all, a chemically meaningful and hence correct output requires accurate input parameters<sup>146</sup> so that scientists can elucidate

fundamental gas-phase and ‘ice’ processes leading to complex molecules, such as organics of astrobiological relevance, in our Galaxy.

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**Roland Wester** asked: Based on your obtained translational energy distributions in the center-of-mass frame, you conclude the presence of a tight transition state for the reaction. Can you give more information on the line of argumentation and provide more details of the properties of this transition state?

**Ralf I. Kaiser** responded: The structure of the exit transition state is illustrated in Fig. 5 here. This is a relatively early (reactant-like) transition state with the H atom departing nearly perpendicularly with respect to the molecular plane.

**Jérôme Loreau** enquired: As far as I know, for cyclic molecules in the interstellar medium there is still a large discrepancy between the abundances inferred

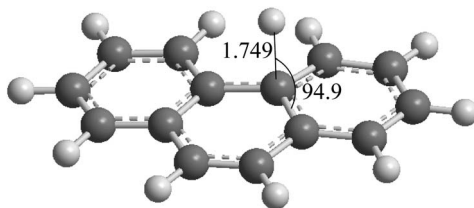


Fig. 5 Transition state for H loss leading to the observed product **p1**. The breaking bond length and angle are shown in Å and degree, respectively.

from radio astronomy and models. Do the reaction mechanisms illustrated here (partially) solve this discrepancy?

**Ralf I. Kaiser** replied: Yes, you are correct. There are large discrepancies by up to three orders of magnitude. Even for astronomical standards, three orders of magnitude is quite a significant deviation. These deviations are mainly based on chemically incomplete reaction networks, *i.e.* reaction pathways have been forgotten and hence not included and incorrect rates were used, and lack of chemical knowledge of the reaction dynamics and kinetics of elementary reactions. We are currently investigating the effects of the title reaction on the chemistry leading to aromatics in TMC-1.

**Tibor Györi** said: The final single-point energies of the stationary points are computed using a methodology based on the G3(MP2,CC)//B3LYP composite method. While it is an adequate method, G3 relies on canonical CCSD(T) and MP2 methods. Since the invention of G3, a number of notable efficiency-improving innovations such as DF/RI MP2, F12 explicit correlation and PNO methods have gained considerable traction.

For large systems like this, localized coupled-cluster methods may offer very substantial speedups and reductions in RAM and disk requirements. While one does have to be wary of PNO truncation errors, the savings from PNO may be great enough to enable the use of both a larger basis set and F12, potentially yielding significantly more accurate results at comparable cost.

For the system studied in this work, I would expect that a PNO-LCCSD(T)-F12/cc-pVDZ-F12 single-point energy computation should not take much longer than a few hours (depending on the choice of PNO thresholds and auxiliary basis sets) if run on a relatively modern machine that has 16 CPU cores and a fast SSD. Was the use of PNO-LCCSD(T)-F12 (or any other non-canonical *ab initio* method) considered for computing the final energies with greater efficiency and/or accuracy?

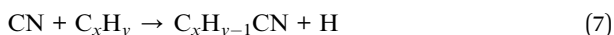
**Ralf I. Kaiser** responded: In a recent work,<sup>1</sup> we compared the performance of the DLPNO-CCSD(T) and G3(MP2,CC) methods for some reactions of aromatic growth and found a close agreement between them, with differences being normally within 3 kJ mol<sup>-1</sup>. The proposed explicitly correlated PNO-LCCSD(T)-F12/cc-pVDZ-F12 method is likely to be accurate and efficient for this system.

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**Roland Wester** asked: Have you considered studying reactions that form polar polycyclic aromatic species such cyanonaphthalene, which has been directly observed by radioastronomy? Would this be interesting to investigate?

**Ralf I. Kaiser** answered: For the past years, we have explored in crossed molecular beams experiments multiple reactions of cyano radicals with unsaturated hydrocarbons.<sup>1–16</sup> Essentially, these reactions have no entrance barrier and are overall exoergic. In simple terms, these pathways are initiated by an addition of the cyano radical with its radical center at the carbon atom followed by a dominant emission of a hydrogen atom leading to a nitrile, *i.e.* a cyano-substituted hydrocarbon [eqn (7)]:



Even for benzene, the reaction of the cyano radical with benzene forms cyanobenzene [eqn (8)]:<sup>15</sup>



In the case of naphthalene, based on the aforementioned experiments, it is easy to predict that the reaction of cyano radicals with naphthalene ( $\text{C}_{10}\text{H}_8$ ) forms 1- and 2-cyanonaphthalene plus atomic hydrogen. There are many other reactions of astrochemical relevance unexplored under single collision conditions, where we cannot predict 'on the paper' what the reaction products are. So although it would be good to 'see' experimentally that 1- and 2-cyanonaphthalene plus atomic hydrogen are formed, it is not on our high priority list of experiments. After all, the energetics to form 1- and 2-cyanonaphthalene are pretty close; therefore, reactions with partially deuterated naphthalenes have to be conducted.

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**Steven J. Sibener** requested: Ralf, could you please comment on the relation of your large molecular ensembles to the formation of polycyclic aromatic hydrocarbons (PAHs) and their associated contribution to diffuse interstellar bands? I would think that the barrierless additions could continue to synthesize ever larger molecular species in the astrochemistry environment.

**Ralf I. Kaiser** responded: First, multiple authors have proposed that PAHs and their derivatives such as ionized, substituted, (de)hydrogenated, and open-shell PAHs may contribute to the Diffuse Interstellar Bands (DIBs) – discrete absorption features superimposed on the interstellar extinction curve ranging from the blue part of the visible (400 nm) to the near-infrared (1.2  $\mu\text{m}$ ).<sup>1–9</sup> Since ‘diffuse’ also characterizes the current state-of-knowledge of the carriers of these DIBs, we opt to not dive into this often emotionally-led discussion on the origin of DIBs.

Second, indeed, barrierless additions could drive the synthesis of even larger molecules in astrochemical environments. Eight ‘global’ mechanisms leading to aromatics in the gas phase have been elucidated *via* molecular beams experiments merged with electronic structure calculations over the last decade.<sup>10</sup> These are (1) Hydrogen Abstraction acetylene Addition (HACA),<sup>11</sup> (2) Hydrogen Abstraction Vinylacetylene Addition (HAVA),<sup>12</sup> (3) Phenyl Addition dehydroCyclization (PAC),<sup>13</sup> (4) Methylidyne Addition Cyclization Aromatization (MACA),<sup>14</sup> (5) Radical–Radical Reaction (RRR),<sup>15</sup> (6) Propargyl Addition BenzAnnulation (PABA),<sup>16</sup> (7) Fulvenallenyl Addition Cyclization Aromatization (FACA),<sup>17</sup> and (8) Phenylethynyl Addition Cyclization Aromatization (PACA) (see our current paper <https://doi.org/10.1039/d3fd00159h>). Among them, only three mechanisms – (2), (4), and (8) – are bimolecular thus fulfilling the conditions of a rapid, efficient synthesis of aromatics in cold molecular clouds. Commencing with the phenyl radical, the Hydrogen Abstraction Vinylacetylene Addition (HAVA) pathway represents a plausible route to, *e.g.*, acenes and helicenes *via* barrierless ring expansions. This pathway does require multiple ring annulations to aromatic radicals, which can be accessed through photolysis of the closed shell aromatic precursor (Fig. 6). Computations also suggest that the barrierless ethynyl addition mechanism can lead to naphthalene moieties at low temperatures.<sup>18</sup>

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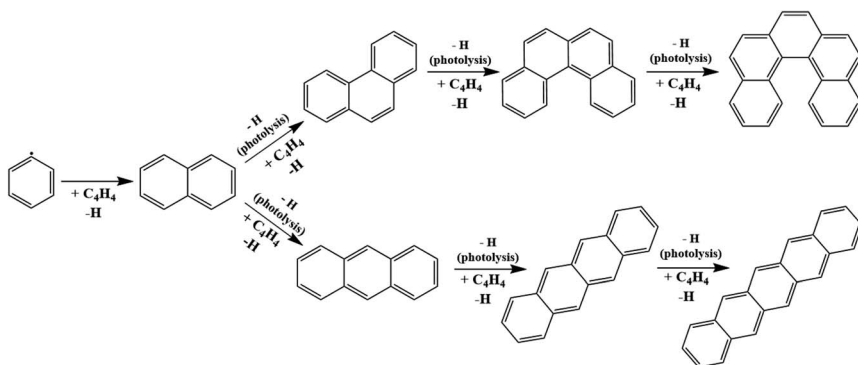


Fig. 6 The formation of acenes and helicenes from phenyl radical *via* HAVA pathways.

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**Steven J. Sibener** said: Perhaps you could comment on the relative importance of gas-phase chemistry *versus* heterogeneous chemistry on interstellar dust/ice leading to the syntheses that you have shown. In particular, can observations now sort out these relative contributions by pointing their telescopes at regions that do or do not have substantial presence of dust and icy substrates?

**Ralf I. Kaiser** responded: There is no general answer to this question. Please refer to the importance of the grain processing in my previous answer to the question from David W. Chandler; the aforementioned answer also highlights the role of gas phase processes to PAH formation.

**David Heathcote** opened discussion of the paper by Nadia Balucani: In our gas-phase electron–molecule crossed beam experiments, we see significant fragmentation of all species we have studied to date at 70 eV, and even with 17 eV electrons we usually see some fragmentation; with 17 eV electrons you can typically access the first few cationic states, some of which can be dissociative. If the ions are fragmenting prior to detection, I would expect this to affect the branching ratios recorded. How is the fragmentation of the ions produced from the scattering products accounted for in your work?

**Nadia Balucani** replied: We also see fragmentation at 17 eV. Indeed, the data shown in Fig. 3 and 4 of the paper (<https://doi.org/10.1039/d3fd00181d>) were measured using soft ionization at 17 eV in the case of  $m/z = 79$  and 65. Clearly, signal originating from the fragmentation of the heavy coproduct from the H-displacement channel is visible also at those masses. Nevertheless, since the

ionization takes place in the ionizer, the ions retain the scattering properties (namely, the distribution as a function of the scattering angle and recoil energy) of the neutral products formed at the collision center. The only difference in the cases of the time-of-flight spectra is associated with the ion flight time, but that can be easily accounted for since we know the extraction potential that accelerates the ions toward the entrance of the quadrupole mass filter. Finally, when we derive the product branching fractions, we consider the fragmentation pattern of each neutral product (see section 3.2.4 of the paper, section S2 of the supplementary information of the paper, and also ref. 1 and 2).

I would also like to remark that the use of soft electron impact ionization in our experiments does not prevent fragmentation and does not allow selective ionization working at the ionization threshold in most cases.<sup>1,2</sup> It is only a way to suppress or mitigate the contribution coming either from elastic scattering of interfering species (through their daughter ions) or background signal thus increasing the signal-to-noise ratio. In Fig. 7 here is shown a comparison of the TOF spectra recorded at  $m/z = 65$  for the scattering angles  $52^\circ$  and  $60^\circ$  (a similar picture is shown in the supplementary information of our paper for  $\Theta = 44^\circ$  and  $52^\circ$ , see Fig. S1). As can be seen, using 17 eV it is possible to measure the co-product  $C_6H_5O$  of the  $CH_3$ -elimination channel at its  $-28$  daughter ion  $m/z = 65$  in a clear manner, having suppressed the otherwise (at 70 eV) overwhelming contributions from elastically/inelastically scattered toluene.

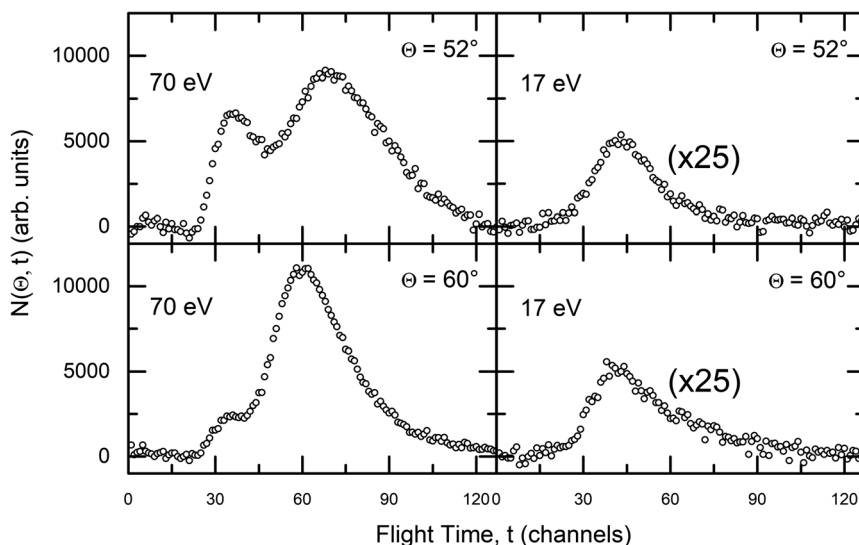


Fig. 7 TOF spectra for  $m/z = 65$  at  $\Theta = 52^\circ$  and  $60^\circ$  for the  $O(^3P, ^1D) + \text{toluene}$  reactions ( $E_c = 34.7 \text{ kJ mol}^{-1}$ ), employing hard (70 eV) (left panels) and soft (17 eV) (right panels) electron ionization. Signals at 70 eV include the dominant elastic/inelastic scattering contribution of toluene from the seeded oxygen beam, with the reactive signal being minor and buried under the much stronger elastic/inelastic components. Signals at 17 eV (which have been multiplied by a factor of 25 in the figure to make them visible) are only reactive signal, since elastic/inelastic contributions from dissociative ionization of toluene are suppressed. For toluene, the appearance energy of the  $C_5H_5^+$  daughter ion at  $m/z = 65$  is  $16.4 \text{ eV}$ .<sup>3</sup>

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**Nils Hertl** asked: In your experiments, you generate around 10% ( $^1\text{D}$ )O. Can you capitalise on that and perhaps separate those species from each other to perform experiments exclusively with either one or the other species to elucidate more details on the reaction mechanism?

**Nadia Balucani** answered: We tried several different gaseous mixtures of  $\text{O}_2$  in rare gases (namely, He, Ne, and Ar) with a varying percentage of  $\text{O}_2$  (up to 20%) and using a different stagnation pressure in the nozzle before the expansion or different radiofrequency power hoping to find the conditions to suppress the presence of the electronically excited  $^1\text{D}$  state. Unfortunately, in all cases we could verify that, in addition to atomic oxygen in the  $^3\text{P}$  ground state,  $\text{O}(^1\text{D})$  was also present in the beam. The test reaction to prove the presence of  $\text{O}(^1\text{D})$  is the one with  $\text{H}_2$  which is barrierless while the reaction of  $\text{O}(^3\text{P})$  has a threshold of ca.  $38 \text{ kJ mol}^{-1}$ , that is, much higher than the experimental collision energy used in our experiments.<sup>1,2</sup> In several cases, similarly to the case of the reaction with  $\text{H}_2$ , we took advantage of the fact that the reaction of  $\text{O}(^3\text{P})$  is too slow so that we could characterize the reaction mechanism of the  $^1\text{D}$  reaction only (e.g. the reactions with hydrogen halides<sup>3–5</sup>) while in some other cases we could see the onset of the  $\text{O}(^3\text{P})$  reaction by increasing the collision energy (this was the case for the  $\text{O}(^3\text{P}, ^1\text{D})$  reactions with  $\text{H}_2\text{S}$  for which the onset of the  $^3\text{P}$  reaction is at  $18 \text{ kJ mol}^{-1}$ , see ref. 6 and 7).

In all cases, since the energy content of the  $^1\text{D}$  state is quite large ( $190 \text{ kJ mol}^{-1}$ ), we have been able to disentangle the two contributions to the reactive signal and characterize their reaction mechanisms.<sup>8–12</sup> In a few cases, the large reactivity of  $\text{O}(^3\text{P})$  (which is dominant in the beam, being  $\geq 90\%$ ) provided the only significant contribution to reactive signal.<sup>13,14</sup>

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**Jennifer Meyer** enquired: I have a question regarding the number of product channels fitted to the angular distributions in the laboratory frame (Fig. 3 in the paper; <https://doi.org/10.1039/d3fd00181d>) or the time of flight distributions (Fig. 4 in the paper). For some of the channels the branching/contribution is so small (*e.g.* C<sub>6</sub>H<sub>8</sub> from O(<sup>3</sup>P) *via* intersystem crossing (ISC), light green curve) that I wonder how you determined that contribution. And how much the fit of the total experimental flux (black curve) really improves with that contribution included compared to not adding such a minor channel.

**Nadia Balucani** responded: In crossed molecular beam experiments with mass spectrometric and TOF detection, the product intensity as a function of the scattering angle,  $N(\Theta)$ , and as a function of the scattering angle  $\Theta$  and arrival time  $t$ ,  $N(\Theta, t)$ , is measured in the laboratory (LAB) system of coordinates. However, for the physical interpretation of the scattering data it is necessary to perform a coordinate transformation and move to the centre-of-mass (CM) reference frame.<sup>1–3</sup>

For the products of each reaction channel, the relation between LAB and CM product flux is given by

$$I(\Theta, \nu)_{\text{LAB}} = I(\theta, u)_{\text{CM}} \frac{\nu^2}{u^2}$$

where  $\Theta$  and  $\nu$  are the LAB scattering angle and velocity, respectively, while  $\theta$  and  $u$  are the corresponding CM quantities. Since the mass-spectrometric detector measures the number density of products,  $N(\Theta, t)$ , rather than the flux, the actual relation between the LAB density and the CM flux is given by<sup>1–3</sup>

$$N(\Theta, \nu)_{\text{LAB}} = I(\theta, u)_{\text{CM}} \frac{\nu}{u^2}$$

Because of the finite resolution of experimental conditions (angular and velocity spread of the reactant beams and angular resolution of the detector), the LAB to CM transformation is not single-valued and, therefore, analysis of the laboratory data is usually performed by forward convoluting tentative CM distributions over the experimental conditions. In other words, the CM angular and velocity distributions are assumed, averaged and transformed to the LAB frame for comparison with the experimental distributions and the procedure is repeated until a satisfactory fit of the experimental distributions is obtained.

When multiple reaction channels contribute to the signal at a given  $m/z$  ratio, a more complex situation arises.<sup>1–3</sup> By considering the product masses and the laws of conservation of linear momentum and total energy, it is possible to calculate the maximum CM speed that the products can reach and, therefore, to draw the limiting circles in the Newton diagram which define the range of LAB angles within which the products can be scattered. By considering the kinematics constraints and the appropriate CM distributions for each channel, it is possible to disentangle the contributions. In these cases, a weighted total CM differential

cross-section reflecting the various possible contributions is used in the data analysis of the LAB distributions for a specific  $m/z$ , that is:

$$I(\theta, u)_{\text{CM}} = \sum_i w_i \cdot [T(\theta) \times P(u)]_i$$

with the parameter  $w_i$  representing the relative contribution of the integral cross-section of the  $i$ -th channel determined during the best-fit procedure.

Because of the different mass combination of the products of each channel and, to a minor extent, because of their different enthalpy changes, the Newton circles can be very different (see Fig. 2 of the main paper; <https://doi.org/10.1039/d3fd00181d>). In the cases of small Newton circles, all the product flux will be confined into a very small LAB angular range while the same flux will spread over a much larger LAB angular range in the cases of large Newton circles. With the same reactive flux for two channels of those types, the enhancement given by the transformation Jacobian will result in a very intense signal in the laboratory system for the first case (albeit confined to a small angular range), while the second channel will have a signal with low intensity but spread over a much wider angular range. In other words, whenever we consider the heavy coproduct formed in H-displacement channels, the transformation Jacobian will greatly enhance the signal compared to the case of other channels in which the two coproducts have comparable masses.<sup>1–3</sup>

In the case of the reaction in question, the contribution deriving from the dissociative ionization of cresoxy (parent mass of 107 Da) formed in the H-displacement channel is also dominant at  $m/z = 79$ . For a similar reason, the  $\text{CH}_3$ -elimination channel also has an advantage over the channel that leads to CO (the masses of the two coproducts are 93 vs. 15 Da in the first case and 80 vs. 28 Da in the second case; furthermore, the  $\text{CH}_3$ -elimination channel has an exothermicity of  $100 \text{ kJ mol}^{-1}$  versus  $317 \text{ kJ mol}^{-1}$  for the ring contraction channel). That said, a deeper analysis of the TOF spectra demonstrates how the collection of sensitive data still allows one to derive the best CM functions also for the most unfavorable channels. Fig. 8 here shows a close-up of the fast portion of the TOF spectrum measured at  $\theta = 36^\circ$  for  $m/z = 79$ . The same TOF spectrum is shown in Fig. 4(b) of the main article, but in that case the peak of the distribution, essentially produced by the dissociative ionization of the molecular product of the H-displacement channel, squeezes the figure and does not allow us to appreciate what we see in the close-up. The right panel of Fig. 8 here shows the best fit we proposed and in which the channel associated with phenoxy formation from the  $\text{O}(^3\text{P})$  reaction *via* intersystem crossing is also present. In the left panel, that specific contribution has been removed. As is perfectly visible, in this region of the TOF spectrum the experimental intensity is larger than that of the simulated distribution in both cases, but on removing the contribution of the  $\text{O}(^3\text{P})$  channel, the fit of the experimental data is clearly worse. The indication is, if any, to increase its contribution because it is the only one with the right kinematic requirements to fill the missing intensity of the simulated spectrum.

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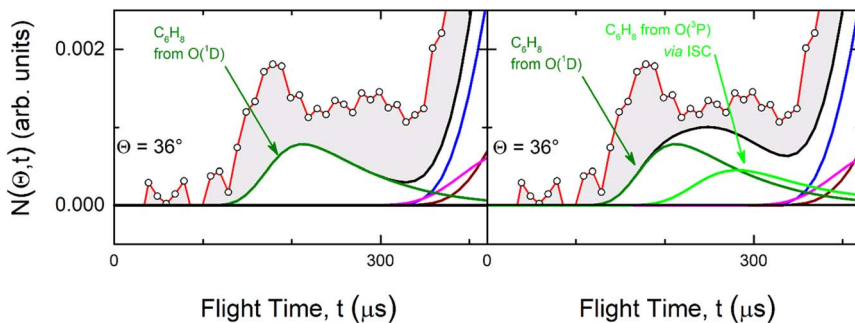


Fig. 8 A close-up of the fast portion of the time-of-flight spectrum recorded at  $m/z = 79$  and  $\Theta = 36^\circ$ . The dots represent the experimental data while the lines represent the global best-fit simulation (black lines) and the separate contributions at this  $m/z$  (the color code is the same as Fig. 4 of the main paper). The grey areas highlight the discrepancies between the simulated distributions and the experimental data. As clearly visible, the fit of the experimental points is significantly worse when the contribution associated with the formation of methylcyclopentadiene + CO from the  $O(^3P)$  reaction is removed.

**Daniel M. Neumark** said: Your observation the CO branching ratio for O + toluene is much smaller than that for O + benzene is very interesting. As you point out, this product can only occur on a singlet surface and thus requires intersystem crossing. Are the ISC probabilities different for the two reactions, or do the branching ratios reflect different dynamics on the singlet surfaces?

**Nadia Balucani** replied: The extent of ISC is similar in the cases of the two reactions: from the analysis of the experimental data, it accounts for 57% in the case of the  $O(^3P)$  + toluene reaction and 52% in the case of the  $O(^3P)$  + benzene reaction under very similar experimental conditions<sup>1,2</sup> (see also the main article (<https://doi.org/10.1039/d3fd00181d>)) (the experimental collision energy was  $34.7 \text{ kJ mol}^{-1}$  for the reaction with toluene and  $34.3 \text{ kJ mol}^{-1}$  for the reaction with benzene). The extent of ISC derived theoretically (simulating the crossed molecular beam experiments) is instead 50% for the  $O(^3P)$  + toluene reaction and 74% for the  $O(^3P)$  + benzene reaction<sup>1,2</sup> (see also the main article). However, while in the case of the reaction with benzene after ISC most of the reactive flux is channeled toward the ring-contraction mechanism with CO production, in the case of the reaction with toluene the  $\text{CH}_3$  elimination channel is competitive. To illustrate that I have reported in Fig. 9 here the main reaction pathways after the  $O(^1D)$  *ipso* addition on the singlet adiabatic potential energy surface (the complete potential energy surface is reported in the main paper). The *ipso* addition mechanism starts with the formation of  $^1W1$  intermediate that easily rearranges to  $^1W4$  which, in turn, can either (i) isomerize to  $^1W7$  and  $^1W10$  before dissociating into 1-methyl-1,3-cyclopentadiene + CO or (ii) dissociate into phenoxy +  $\text{CH}_3$  or (iii) dissociate into cresoxy + H. ISC from the *ipso* and *para* entrance wells can lead only to  $^1W1$  and  $^1W3$ , respectively, while ISC from the *ortho* entrance wells can lead either to  $^1W1$  or  $^1W2$  and ISC from the *meta* entrance well leads to  $^1W2$  and  $^1W3$  (see the main article). The ME simulations showed that following ISC to  $^1W1$  and  $^1W2$ , a large fraction (up to 80%) of the reaction flux leads to  $\text{CH}_3$  loss (see the main article). However, the reactivity on the singlet



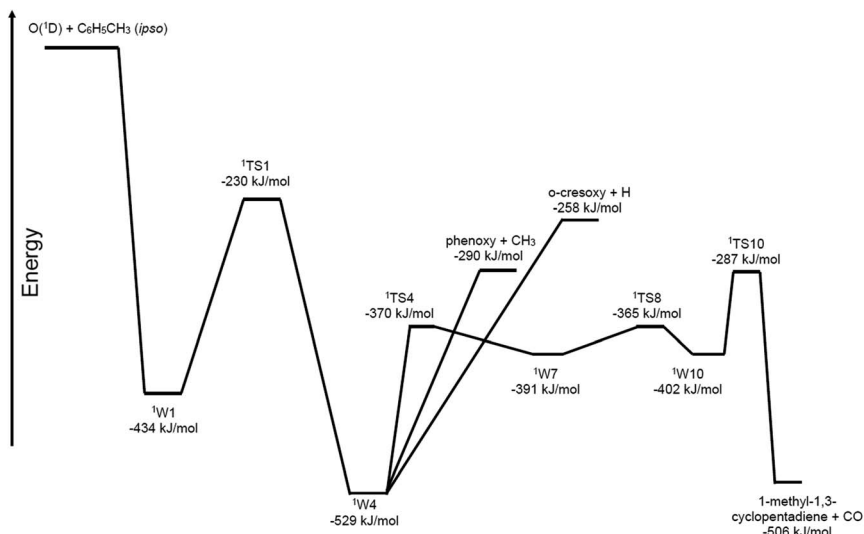


Fig. 9 Main reaction pathways after the O(<sup>1</sup>D) *ipso* addition on the singlet adiabatic potential energy surface.

potential energy surface (PES) differs when <sup>1</sup>W3 is formed by ISC (*para* addition). In this case isomerization to the precursor for CH<sub>3</sub> loss, <sup>1</sup>W4, is hindered by significant energy barriers and the main reaction channel is thus decomposition to CO and methylocyclopentadiene (see the main article). Overall, the phenoxy + CH<sub>3</sub> channel is favored along the singlet PES when the initial energy is that of the O(<sup>3</sup>P) reaction (see Table 1 of the main article). For the O(<sup>1</sup>D) reaction, instead, the two channels have roughly the same yield within the experimental uncertainty (0.43 ± 0.13 vs. 0.54 ± 0.27). The larger amount of the available energy when the reaction starts on the singlet PES or the different role of the four initial attacks can explain a larger yield of the CO channel for the adiabatic singlet reaction.

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**Rahul Pandey** communicated: What are the typical molecular beam densities in the experiments? Is careful density control necessary at the interaction region to manage single or multiple collision conditions during the experiment? Additionally, could multiple collision conditions lead to the multichannel reaction of toluene with atomic oxygen, particularly in the case of high densities?

**Nadia Balucani** communicated in reply: The basic characteristic of crossed molecular beam experiments is that the reactants are confined into distinct supersonic beams which cross each other only at the collision center allowing us to observe the consequences of many identical single bimolecular collisions. No collisions occur among the molecules/atoms inside the same beam after the supersonic expansion, since they are travelling in the same direction at (essentially) the same speed. Bimolecular collisions occur only at the collision center

where the two beams cross each other. Because of the finite dimensions of the two beams, the overlap occurs in a volume of about  $10\text{ mm}^3$ . There, the typical number densities of the beams of the transient species (radicals or atoms, but also unstable species like  $\text{C}_2$ ) are in the  $10^9$ – $10^{10}$  particles per  $\text{cm}^3$  range, while the number density can be as high as  $10^{12}$  particles per  $\text{cm}^3$  for the stable species. Given the small collision volume and the short residence time of the reactants in it, no multiple collisions are expected to occur, nor three body collisions. Collision volume aside, the pressure in the scattering chamber is kept at  $10^{-6}$  mbar under operating conditions, corresponding to a mean free path of more than 100 m.

**F. Javier Aoiz** addressed all the delegates:†

We would like to make a few comments related to the  $\text{O}(^3\text{P}) + \text{H}_2$  and  $\text{O}(^3\text{P}) + \text{D}_2$  reactions, and in particular on two aspects that have already been mentioned in this conference:

(a) How well does the ring polymer molecular dynamics approach account for tunnelling?

(b) How important is intersystem crossing (singlet–triplet), ISC, for this reaction?

We have recently carried out extensive calculations on the reaction dynamics of  $\text{O}(^3\text{P}) + \text{H}_2$  and  $\text{O}(^3\text{P}) + \text{D}_2$  to determine rate coefficients in the temperature range 200 K to 2500 K. The calculations were performed using fully converged time-independent quantum mechanics (TI QM), which is essentially exact within the Born–Oppenheimer approximation, quasiclassical trajectories (QCT) and ring polymer molecular dynamics (RPMD) on the two lowest lying adiabatic potential energy surfaces (PESs),  $1^3\text{A}'$  and  $1^3\text{A}''$ , calculated by Zanchet *et al.*,<sup>1</sup> which are more accurate than any previous PESs for this system.

The vibrationally adiabatic minimum energy path for the  $\text{O} + \text{D}_2$  reaction is considerably broader and has a slightly higher barrier than for the reaction with  $\text{H}_2$ . Therefore, the expected tunneling contribution to the reaction will be more important for the latter. This is supported by the respective crossover temperatures (the imaginary frequency over the Boltzmann constant) which is 100 K higher for the reaction with  $\text{H}_2$ . The agreement between the rate coefficients calculated by QM and RPMD is excellent for the reaction with  $\text{D}_2$  in almost the whole temperature range. For the reaction with  $\text{H}_2$  the agreement is very good above 500 K, but deviations are significant at lower temperatures. We have found that as a rule, RPMD reproduces almost perfectly the exact QM calculations above the crossover temperatures. In contrast, the QCT calculations largely underestimate the rate coefficients for the two isotopic variants due to its inability to account for tunneling which is not compensated for by the non-conservation of the zero-point energy. We conclude that RPMD is a reliable and indeed much more efficient method than QM calculation for determining rate coefficients and that tunneling above the crossover temperature is very well accounted for.

By careful comparison of the present QM results with the experimental values, we have found: (i) that the present state-of-the-art QM results on adiabatic PESs slightly underestimate the experimental results; and (ii) that the agreement of the

† Comment co-authored by M. Menéndez, A. Veselinova, A. Zanchet and P. G. Jambrina.

QM rate coefficients with the experimental results is somewhat worse for  $O + D_2$ . The most likely explanation for these discrepancies is that the calculations require a non-adiabatic treatment that couples triplet with singlet PESs. The greater effect of ISC for the  $O + D_2$  reaction is probably due to the wider barrier for this reaction leading to more effective crossing with the singlet PES, resulting in slightly larger cross sections.

1 A. Zanchet, M. Menéndez, P. G. Jambrina and F. J. Aoiz, *J. Chem. Phys.*, 2019, **151**, 094307.

**Alec M. Wodtke** opened discussion of the paper by Arthur G. Suits: I am wondering how you, as an experimentalist, use KinBot in your data analysis. It appears advantageous to have the automated discovery of reaction mechanisms, but I also see that the number of possible elementary steps appears to become overwhelming. How do you use the KinBot output with its overwhelming number of possible reactions to narrow down the possibilities and figure out what are the important pathways to product formation?

**Arthur G. Suits** replied: I should first note that we have not used the full power of KinBot in this study (<https://doi.org/10.1039/d4fd00009a>). In our initial paper involving  $S(^3P) + 1,3$ -butadiene (13BD), KinBot was used to give full predictions of the energy-dependent branching. That showed that thiophene should be the dominant product and thioketene should also be present. This motivated us to work hard to detect those products: we saw thiophene before with the focused laser, as we do here, and here we also detect thioketene in the flow as predicted. The full statistical calculations and kinetics can be done for the isoprene reaction as well but given time constraints we have not done this yet. However, even with the complicated S-isoprene PES, KinBot allowed us to identify dominant pathways and coproducts even when we could not make that determination from our results alone. For example, we initially assumed the 72 u product was thioketene by analogy with the 13BD result. KinBot clearly showed it was likely thioacrolein, and explained the low translational energy release as well. KinBot showed there are a handful of H loss radicals likely contributing to 99 u. I could go on. Let me just say as an experimentalist, I am a strong believer in KinBot and the power of computational tools to sharpen and guide our intuition.

**David W. Chandler** remarked: Dr Suits, I offer a comment on the KinBot program of Dr Zádor. I believe that it has been shown to be very efficient at finding transition states and saddle points on complex potential energy surfaces and has recently been extended to the study of reactions on surfaces for the development of catalytic mechanisms. This seems to be a very valuable tool for understanding complex chemistry of larger reactive systems.

**Arthur G. Suits** responded: I heartily agree.

**Dwayne E. Heard** asked: I really liked seeing the combination of two complementary methods being used in this paper (<https://doi.org/10.1039/d4fd00009a>) to study the same reaction, namely (1) the crossed molecular beam single collision method with velocity map imaging (VMI) and (2) the pulsed uniform flow Laval nozzle method which is at 20 K under thermal collision conditions

with a rotational spectroscopy method (chirped microwaves) which can see a large range of products. I had two questions:

(i) For the S + butadiene reaction you see thiophene as the main product – but for the thioketene just a weak signal – whereas for the pulsed flow you see the thioketene but not the thiophene despite it being predicted to be the main product. Can you please expand a little more on your explanation regarding the larger vibrational partition function for the thioketene which you say may be the reason why you do not see it.

(ii) Likewise for the S + isoprene reaction, you see thioformaldehyde with the chirped MW rotational absorption method, but not the other products – and again give the same reason. So again presumably formed with a lot of vibrational energy. Can you once again please expand.

**Arthur G. Suits** replied: From the translational energy release and the available energy ( $\sim 80 \text{ kcal mol}^{-1}$ ) in the thiophene channel for the butadiene reaction we can estimate about  $50 \text{ kcal mol}^{-1}$  in internal energy in thiophene, most of which will be in vibration. That would correspond to an enormous number of vibrational states. It will be cooled in the flow, but the vibrational degrees of freedom may not be cooled efficiently. Even if it is vibrationally cooled to 1000 K, this corresponds to a vibrational partition function over 300. This can account for the relative detection efficiency compared to thioketene. In the isoprene reaction we have not searched for many products in the chirped-pulse/uniform flow (CPUF) experiment but in that case the methyl thiophene, for example, has additional vibrational degrees of freedom. Furthermore, there is an additional challenge in that there are many more open product channels so the signals will be diluted further. Chirped-Pulse Fourier-Transform mmWave spectroscopy (CP-FTmmW) does not have the sensitivity of mass spectrometry or photoionization, but we are looking to ways to improve it. I can add these considerations generally do not play a role if we are monitoring a reactant in a kinetics experiment.

**Dwayne E. Heard** enquired: Have you considered trying to monitor the S atom, either directly or *via* a proxy (*e.g.* by adding something which reacts quickly with a small fraction of the S atoms to form a product you can detect) – then you could monitor the kinetics *via* the decay of the reagent. Secondly, can thioformaldehyde be detected *via* a fluorescence method perhaps?

**Arthur G. Suits** responded: We have not examined the prospects of detecting the sulfur atom for kinetics measurements. I can add that we recently demonstrated the use of sensitive resonant multiphoton ionization within a Laval flow.<sup>1</sup> This approach could be adapted to detect S(<sup>3</sup>P) although to-date we have only applied it to 1 + 1 ionization of NO. I do not know if the spectroscopy of thioformaldehyde is amenable to fluorescence detection. We do not currently make use of LIF in our laboratory.

1 S. Thawoos, N. Suas-David, R. Gurusinghe, M. Edlin, A. Behzadfar, J. Lang and A. G. Suits, Low temperature reaction kinetics inside an extended Laval nozzle: REMPI characterization and detection by broadband rotational spectroscopy, *J. Chem. Phys.*, 2023, **159**, 214201, DOI: [10.1063/5.0178533](https://doi.org/10.1063/5.0178533).

**Dwayne E. Heard** asked: Can you get any further information from the temporal rise of the products which you see from the pulsed uniform flow method – you have the basis of information for a rate coefficient determination if you know the isoprene or 1,3-butadiene concentration, and can vary these concentrations in a known way?

**Arthur G. Suits** answered: It is possible to do this if the products are not highly vibrationally excited. We have shown this in the past in a sampled flow.<sup>1</sup> However, to do this requires careful adjustment of the concentrations of the reactants as you know. To achieve pseudo first order conditions may require us to operate at  $S(^3P)$  densities that are quite low making detection problematic. We have not yet looked into how feasible that is for the present reactions.

1 R. M. Gurusinge, N. Dias, R. Krueger and A. G. Suits, Uniform supersonic flow sampling for detection by chirped-pulse rotational spectroscopy, *J. Chem. Phys.*, 2022, **156**, 014202, DOI: [10.1063/5.0073527](https://doi.org/10.1063/5.0073527).

**Stefan Willitsch** queried: How confident can one be that the KinBot algorithm finds all reaction pathways which are relevant under your experimental conditions?

**Arthur G. Suits** answered: I suggest one can be quite confident, certainly compared to the alternative of one's intuition. You raise the question of the experimental conditions, and that is important. Dr Zádor, as described in the paper (<https://doi.org/10.1039/d4fd00009a>), adjusted the thresholds for inclusion at various levels of theory to ensure that no relevant stationary points or products were neglected. For the present work KinBot was used just to characterize the potential energy surface. Once we have the PES, KinBot can also be used to calculate rate coefficients and solve the kinetic equations, and there one could include more experiment-specific aspects, like temperature and pressure, initial conditions, *etc.* and see which of the pathways dominate. This is the “Kin” in KinBot.

**Kenneth G. McKendrick** said: I was interested in the relative detection sensitivities for the thioketene product of the  $S(^3P) + 1,3$ -butadiene reaction. It was surprising to me, and perhaps to others, that chirped-pulse FTmmW detection had a higher signal-to-noise than “universal” ionisation-VMI detection.

Clearly, there are a number of factors that affect the result beyond the intrinsic sensitivity of the two methods. The ability, in principle, to ionise all product quantum states should strongly favour VMI over CP-FTmmW, which suffers from the “partition-function problem” of only detecting a single rotational quantum state amongst all those that are populated. There are also significant differences in collision energy: perhaps the thioketene channel is strongly favoured at the relatively low (average) kinetic energies in the uniform flow *versus* the high kinetic energies in the crossed-beam experiments?

The number densities may also be substantially different in these two types of experiment, as may be the probed volumes and hence the absolute numbers of molecules being detected in each case.

The signal is also of a different type – the crossed-beam data are distributed over a significant number of pixels in the VMI image, whereas the CP-FTmmW line intensity is a single, integral measure.

I am wondering how transferable the observations here might be to other reactions and different products? Is there some specific combination of properties at play in this particular case, or is this a more general phenomenon?

**Arthur G. Suits** responded: The short answer here is that in this case the energy of our photoionization laser for thioketene (and thiophene) is below the ionization energy of these molecules. We are relying on non-resonant 1 + 1 ionization or Rydberg states that may happen to be present to facilitate this. When we are above the ionization energy, as is the case for the 2*H*-thiophen-5-yl (2HT) radical (corresponding to H loss from the 13BD reaction or methyl loss from isoprene) we have excellent sensitivity, far beyond what could be achieved by chirped pulse Fourier transform microwave (CP-FTMW). I do not think the collision energy dependence is playing much of a role. In the flow experiments the endothermic channels (H loss for example) will be closed but these are relatively minor and the competition between thioketene and thiophene will not be strongly affected.

For CP-FTMW the partition function does play a major role but if the molecules are not vibrationally hot, and the rotational constants are not too small, then in the probed region at ~5 K the molecule may be distributed in just a few quantum states. For thioketene at 5 K the rotational partition function is 26. The reaction volume and reactant densities are much larger in our flow experiment than in the crossed-beam experiment as well.

With a tunable VUV probe the imaging experiment could gain a great deal more sensitivity for the closed-shell products but one must be mindful of ionizing the reactant molecules themselves which could overwhelm the desired signals.

**Brianna R. Heazlewood** enquired: I agree that it would be interesting to identify the relative branching ratios for the various C<sub>4</sub>H<sub>6</sub> isomers that could be formed alongside thioformaldehyde. Is this something you could potentially measure experimentally?

**Arthur G. Suits** answered: This would be challenging I think for any single method. CPUF could distinguish 1,2-butadiene, 1-butyne and methyl cyclopropane as these have reasonable dipole moments. *Trans*-1,3-butadiene has no dipole moment and that for the *gauche* (*cis*) species is likely too small for us to detect given the quadratic dependence of the signal on the dipole moment. Most of these would also be very challenging for mass spectrometry as the fragmentation patterns are similar. Tunable VUV photoionization could help but even there I fear similar photoionization yield curves in some cases would make it difficult unless a single product dominates. For answers here I think the best course would be to use KinBot or a related method to predict the branching and validate where possible with experiment. I think the theory–experiment synergy as we have shown here will be critical as we seek deeper insight into these more complex systems.

**Gilbert M. Nathanson** asked: Do you happen to know of any evidence for the production of sulfur atoms and their reactions in the troposphere?

**Arthur G. Suits** replied: I am afraid I do not. Perhaps one of the atmospheric chemists here can comment on this.

**George C. Schatz** said: Years ago my group studied intersystem crossing in both  $O + H_2$  and  $S + H_2$ .<sup>1,2</sup> In  $O + H_2$  the singlet/triplet crossing is near the top of the barrier, as Prof. Aoiz discussed earlier in this meeting, and this leads to a small contribution to the thermal rate coefficient for reaction due to formation of a singlet  $H_2O$  intermediate. For  $S + H_2$ , the corresponding singlet/triplet crossing occurs prior to the barrier on the triplet surface, leading to much more important contributions to the rate coefficient from singlet  $SH_2$  complex formation. However, even for  $S + H_2$ , the triplet channel is not completely negligible, especially at high temperature. Presumably this sort of dynamics would apply in the present study if you can detect the SH product. Are there opportunities for doing this?

1 M. R. Hoffmann and G. C. Schatz, *J. Chem. Phys.*, 2000, **113**, 9456–9465, DOI: [10.1063/1.1319937](https://doi.org/10.1063/1.1319937).

2 B. Maiti, G. C. Schatz and G. Lendvay, *J. Phys. Chem. A*, 2004, **108**, 8772–8781, DOI: [10.1021/jp049143o](https://doi.org/10.1021/jp049143o).

**Arthur G. Suits** responded: The H abstraction reaction is closed in the case of 13BD at our collision energy, but it is accessible and likely plays a role in the isoprene reaction. It could be accessed either on the triplet surface or the singlet. My belief is that the strongly attractive potential leading to the adduct likely means most of the action is on the singlet surface after ISC. Our observation of the singlet products supports that. But some H abstraction on the triplet surface is certainly possible. Unfortunately SH is present in the sulfur atom beam and H abstraction is very difficult to detect for the hydrocarbon radical because of interference from ionization of the parent molecule. Other means could be used to detect that channel and I suppose if any direct reaction is seen that could be ascribed to the triplet.

**Dwayne E. Heard** remarked: Regarding the photolysis of  $SO_2$  by Osborn and co-workers,<sup>1</sup> a wavelength of 193 nm was used, which would not reach the troposphere in Earth's current atmosphere (but present in the early atmosphere of Earth prior to formation of the ozone layer). However, this wavelength will be present in the stratosphere and  $SO_2$  can be injected into the stratosphere *via* volcanic eruption. However, the atmosphere lifetimes of 1,3-butadiene and isoprene are both short and there is unlikely to be significant concentrations of these species in the stratosphere.

1 D. Rösch, Y. Xu, H. Guo, X. Hu and D. L. Osborn,  $SO_2$  Photodissociation at 193 nm Directly Forms  $S(^3P) + O_2(^3\Sigma_g^-)$ : Implications for the Archean Atmosphere on Earth, *J. Phys. Chem. Lett.*, 2023, **14**(12), 3084–3091, DOI: [10.1021/acs.jpcclett.3c00077](https://doi.org/10.1021/acs.jpcclett.3c00077).

**Arthur G. Suits** responded: I agree there is no obvious immediate relevance of these reactions to the present atmosphere of Earth. Nevertheless, I think it is useful to be aware of these pathways in contemplating chemistry of planetary atmospheres both present and past.



**Arthur G. Suits** continued discussion of the paper by Ralf I. Kaiser: In our  $S(^3P) +$  alkene experiments with imaging we often detect adduct formation which can be seen at the center of mass velocity. Have you seen evidence of adduct formation in these experiments? For these high-dimensional systems I can imagine they might play a role. Even if you do not detect adducts directly, I can imagine if they decompose on the way to the detector it could impact the inferred product distributions (depending on the decay pathway) or their associated translational energy distributions. Have you ever considered these effects or thought about trying to model them?

**Ralf I. Kaiser** answered: For the present system, we could not detect any adducts. However, we could detect them in the carbon (C)/D<sub>6</sub>-benzene (C<sub>6</sub>D<sub>6</sub>),<sup>1</sup> boron (B)/D<sub>6</sub>-benzene (C<sub>6</sub>D<sub>6</sub>),<sup>2</sup> and D<sub>5</sub>-phenyl (C<sub>6</sub>D<sub>5</sub>)/phenylacetylene (C<sub>6</sub>H<sub>5</sub>CCH) systems.<sup>3</sup> Likewise, bimolecular collisions of ground state atomic silicon (Si) with diacetylene (C<sub>4</sub>H<sub>2</sub>) lead exclusively to adduct formation.<sup>4</sup>

- 1 R. I. Kaiser, I. Hahndorf, L. C. L. Huang, Y. T. Lee, H. F. Bettinger, P. v. R. Schleyer, H. F. Schaefer III and P. R. Schreiner, Crossed beams reaction of atomic carbon, C(<sup>3</sup>P), with d<sub>6</sub>-benzene, C<sub>6</sub>D<sub>6</sub>(X<sup>1</sup>A<sub>1g</sub>): Observation of the per-deutero-1,2-didehydro-cycloheptatrienyl radical, C<sub>7</sub>D<sub>5</sub>(X<sup>2</sup>B<sub>2</sub>), *J. Chem. Phys.*, 1999, **110**, 6091–6094.
- 2 F. Zhang, Y. Guo, X. Gu and R. I. Kaiser, A crossed molecular beam study on the reaction of boron atoms, B(<sup>2</sup>P<sub>j</sub>), with benzene, C<sub>6</sub>H<sub>6</sub>(X<sup>1</sup>A<sub>1g</sub>), and D<sub>6</sub>-benzene C<sub>6</sub>D<sub>6</sub>(X<sup>1</sup>A<sub>1g</sub>), *Chem. Phys. Lett.*, 2007, **440**, 56–63.
- 3 D. S. N. Parker, T. Yang, R. I. Kaiser, A. Landera and A. M. Mebel, On the formation of ethynylbiphenyl (C<sub>14</sub>D<sub>5</sub>H<sub>5</sub>; C<sub>6</sub>D<sub>5</sub>C<sub>6</sub>H<sub>4</sub>CCH) isomers in the reaction of D<sub>5</sub>-phenyl radicals (C<sub>6</sub>D<sub>5</sub>; X<sup>2</sup>A<sub>1</sub>) with phenylacetylene (C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>H; X<sup>1</sup>A<sub>1</sub>) under single collision conditions, *Chem. Phys. Lett.*, 2014, **595**, 230–236.
- 4 Z. Yang, S. Doddipatla, C. He, S. J. Goettl, R. I. Kaiser, A. W. Jasper, A. C. Gomes and B. R. Galvão, Can third-body stabilisation of bimolecular collision complexes in cold molecular clouds happen?, *Mol. Phys.*, 2024, **122**, e2134832.

**David W. Chandler** asked: What fraction of polycyclic aromatic molecules in space are made in the gas phase *versus* on surfaces or other mechanisms? And does your work impact these other mechanisms for large molecule production in space?

**Ralf I. Kaiser** replied: This is a very complex question. The answer depends on the PAH. Our recent comprehensive modeling studies – which are still under review – on PAH formation in TMC-1 can fully account for the gas phase formation of, *e.g.*, substituted naphthalenes such as cyano naphthalenes. Prior to our chemically complete model, the astronomy community thought that there must be some processes on the grains simply because the gas phase models cannot replicate the observed abundances. This is the key issue here: incomplete modeling networks lead to incorrect conclusions. So the reply to the question “Does your work impact these other mechanisms for large molecule production in space” is certainly YES, since the results from our gas phase studies in the laboratory can – so far for smaller, astronomically observed aromatics and their derivatives – be directly incorporated into astrochemical models of, *e.g.*, TMC-1 to “account” for the missing aromatics such as cyano naphthalenes.

**David Heathcote** opened discussion of the paper by Roland Wester: Would it be conceivable to run an experiment where the CH<sub>3</sub>I molecule could be oriented,

such that the differences in the nucleophile scattering from either the CH<sub>3</sub> end, the I end or the side of the molecule could be determined?

**Roland Wester** answered: We have once studied adiabatic laser alignment of CH<sub>3</sub>I molecules to prepare for such an experiment.<sup>1</sup> However, the degree of alignment over a finite interaction volume turned out to be too small to observe an effect on the reaction dynamics.

1 S. Trippel, M. Stei, C. Eichhorn, R. Otto, P. Hlavenka, M. Weidemüller and R. Wester, *J. Chem. Phys.*, 2011, **134**, 104306, DOI: [10.1063/1.3557822](https://doi.org/10.1063/1.3557822).

**Christopher Reilly** asked: How would you expect the branching ratios to change at lower CH<sub>3</sub>I rotational temperatures?

**Roland Wester** replied: In our experiments with CH<sub>3</sub>I, we use seeded beams that are only weakly supersonic in order to avoid the formation of dimers in the reactant beam. Therefore our translational temperatures in the co-moving frame typically range between 100 and 200 K and we expect the rotational temperatures to be similar. We have so far not been able to extract an influence of rotational excitation on the reaction dynamics or the branching ratios. Since most of the dynamics are influenced by fairly short-range interactions it is also not clear what to expect for the branching ratios from changing the rotational temperature. It would certainly be interesting to investigate this.

**Patrick Robertson** enquired: In the paper (<https://doi.org/10.1039/d3fd00164d>) you discuss the similarity of the methoxy anion to other smaller anions with respect to rotational alignment in the entrance channel, and the need to study anions which are larger still. I wonder if you've considered looking from the other direction, varying the dipole of the neutral collider? *E.g.* selecting a poorer leaving group?

**Roland Wester** responded: With methoxy anions we have so far only studied the reaction presented in this paper (<https://doi.org/10.1039/d3fd00164d>). With other anionic nucleophiles (fluoride, chloride, cyanide, hydroxide) we have studied various alkane halides, specifically methyl, ethyl, isopropyl, and *tert*-butyl halides with the halide atom being either chlorine or iodine. However, all of these species have a dipole moment between about 1.5 and 2.5 debye. Recently we have also studied nucleophilic substitution reactions with tri-fluoro ethyl iodide, which presumably has a lower dipole moment.<sup>1</sup> There we indeed observed a substantially reduced branching ratio for the nucleophilic substitution channel. QCT simulations for this reaction are currently underway in the group of Gábor Czakó, which will allow us to further explore the dynamics of this reaction.

1 T. Gstir, T. Michaelsen, B. A. Long, A. B. Nacsa, A. Ayasli, D. Swaraj, F. Zappa, F. Trummer, S. G. Ard, N. S. Shuman, G. Czakó, A. A. Viggiano and R. Wester, *Phys. Chem. Chem. Phys.*, 2023, **25**, 18711–18719, DOI: [10.1039/d3cp02110f](https://doi.org/10.1039/d3cp02110f).

**Stefan Willitsch** requested: Can you comment on the general role of the rotational motion of the molecules and possible alignment effects in the S<sub>N</sub>2 reactions you are studying?

**Roland Wester** responded: As also stated in my earlier reply to the question from Christopher Reilly, we have so far not been able to extract an influence of rotational excitation on the dynamics of  $S_N2$  reactions. Since most of the dynamics are influenced by fairly short-range interactions it is not clear what to expect for the branching ratios from changing the rotational temperature. Spatial alignment would certainly have a major impact, as nucleophilic substitution occurs primarily *via* a backside attack followed by a Walden inversion, which is a very stereoselective reaction path. However, so far no experiments have succeeded in studying such kind of reactions with aligned molecules.

**David W. Chandler** enquired: Dr Wester, would more insight into the dynamics associated with the  $S_N2$  reactions be obtained if one could selectively vibrationally excite the molecule? Do you have any plans to try such experiments?

**Roland Wester** replied: In my view this is a very interesting topic. In a series of articles, we have already studied the influence of the symmetric CH stretching vibration in  $CH_3I$  reacting with  $F^{-.1-3}$ . We found that this mode is mostly a spectator for nucleophilic substitution, only at higher collision energies it slightly enhances this reaction channel. In contrast, it strongly promotes proton transfer and slightly suppresses the higher energy channel of halide abstraction. Besides the symmetric CH stretching vibrations also other vibrational modes would be very interesting to study, in particular the  $CH_3$  umbrella and the CI stretching vibration. Both modes need lower photon energy to excite, which makes these experiments more demanding. Nevertheless, I hope that we will be able to investigate this in the future.

- 1 M. Stei, E. Carrascosa, A. Doerfler, J. Meyer, B. Olsaz, G. Czakó, A. Li, H. Guo and R. Wester, *Sci. Adv.*, 2018, 4, eaas954, DOI: [10.1126/sciadv.aas9544](https://doi.org/10.1126/sciadv.aas9544).
- 2 T. Michaelsen, B. Bastian, A. Ayasli, P. Strübin, J. Meyer and R. Wester, *J. Phys. Chem. Lett.*, 2020, 11, 4331, DOI: [10.1021/acs.jpcclett.0c01095](https://doi.org/10.1021/acs.jpcclett.0c01095).
- 3 T. Michaelsen, B. Bastian, P. Strübin, J. Meyer and R. Wester, *Phys. Chem. Chem. Phys.*, 2020, 22, 12382, DOI: [10.1039/d0cp00727g](https://doi.org/10.1039/d0cp00727g).

**Jennifer Meyer** said: Roland, looking at the branching ratio of the  $S_N2$  fast to  $S_N2$  complex (Fig. 1 and 2 in the paper (<https://doi.org/10.1039/d3fd00164d>)) both channels have a comparable contribution. Have you tried to evaluate the velocity distributions for the complex channel? That might not be possible in 3D mode due to the ill-defined velocities but an evaluation in 2D could give some mechanistic insights.

**Roland Wester** responded: Yes, we have also evaluated the velocity distributions for the events identified by time of flight as originating from long-lived reaction complexes. You are right a full three-dimensional analysis is not suitable, because the time-of-flight is not well defined due to the finite decay time of the complex. The two-dimensional velocity distributions are very spread out as expected for a long-lived complex. Along the axis of the relative collision velocity they show a slight offset from the origin towards forward scattering, which cannot be easily explained at present and needs further experimental investigation.

**Gilbert M. Nathanson** asked: Do you see evidence for formation of ethane and a carbon–carbon bond in the reaction of methoxy anion with methyl iodide?

**Roland Wester** answered: In our experiments we detect the ionic products from a reaction. In the case of ethane formation that would imply  $\text{IO}^-$  as the ionic co-product, an ion that we have detected in reactions of oxygen anions with methyl iodide.<sup>1</sup> This product would appear two mass units next to the  $\text{CH}_2\text{I}^-$  product ion in Fig. 1 of our paper (<https://doi.org/10.1039/d3fd00164d>). Our mass resolution would allow us to differentiate this, but this product has not been observed in the present study. Without knowing the exact energetics, I would also expect that this product lies significantly higher in energy than the other channels. It should also be dynamically hindered compared to the two observed channels.

1 A. Ayasli, A. Khan, T. Michaelsen, T. Gstir, M. Onćák and R. Wester, *J. Phys. Chem. A*, 2023, **127**, 5565–5571, DOI: [10.1021/acs.jpca.3c02856](https://doi.org/10.1021/acs.jpca.3c02856).

**Daniel M. Neumark** enquired: Do you expect any effects in the product branching ratio or angular distributions to arise if you excite any of the vibrational modes in the  $\text{CH}_3\text{O}^-$  anion? How feasible would such an experiment be, assuming that you knew the anion vibrational frequencies?

**Roland Wester** responded: So far there are no predictions for the studied reaction of vibrational mode-specific effects in the methoxy anion. One could speculate that the CO stretching vibration may have an impact on both proton transfer and nucleophilic substitution, while the CH vibrations will most likely be spectator modes.

To carry out such an experiment the methoxy anion would need to be pumped into excited vibrational levels prior to the interaction in the crossed-beam spectrometer. This could be achieved while the anions are located in the octupole ion trap, where they are pre-trapped in the present experiment for 40 ms to thermalize their rovibrational degrees of freedom. During this time, and using suitable buffer gas conditions to avoid vibrational quenching, the vibrational excitation could take place. Before using these ions for reactive scattering experiments, however, a spectroscopic characterization of the excited fraction needs to take place (see ref. 1 for details), e.g. using photodetachment spectroscopy as in our recent study of  $\text{C}_3\text{N}^-$ .<sup>2</sup>

1 M. Stei, E. Carrascosa, A. Doerfler, J. Meyer, B. Olasz, G. Czakó, A. Li, H. Guo and R. Wester, *Sci. Adv.*, 2018, **4**, eaas954, DOI: [10.1126/sciadv.aas9544](https://doi.org/10.1126/sciadv.aas9544).

2 M. Simpson, M. Nötzold, F. A. Gianturco, T. Michaelsen, R. Wild and R. Wester, *Phys. Rev. Lett.*, 2021, **127**, 043001, DOI: [10.1103/PhysRevLett.127.043001](https://doi.org/10.1103/PhysRevLett.127.043001).

**Alexander Butler** asked: How might excitation of the C–I stretch/ $\text{CH}_3$  umbrella mode of  $\text{CH}_3\text{I}$  affect the  $\text{S}_{\text{N}}2$ /proton transfer branching ratio and the ion yields from different  $\text{S}_{\text{N}}2$  mechanisms?

**Roland Wester** replied: It would be very interesting to investigate the CI stretching or the  $\text{CH}_3$  umbrella vibration. Both modes are expected to clearly

enhance the nucleophilic substitution reaction, as calculated using the sudden vector projection model, see Table 2 in ref. 1.

1 M. Stei, E. Carrascosa, A. Doerfler, J. Meyer, B. Olasz, G. Czako, A. Li, H. Guo and R. Wester, *Sci. Adv.*, 2018, **4**, eaas9544, DOI: [10.1126/sciadv.aas9544](https://doi.org/10.1126/sciadv.aas9544).

**Bum Suk Zhao** enquired: In your trial experiment investigating the effect of alignment on reactive collisions, how did you assess the degree of alignment? Did you employ fragmentation techniques or another method to quantify alignment? The high rotational temperature is known to mask the effect of adiabatic alignment.

**Roland Wester** answered: We studied adiabatic alignment of CH<sub>3</sub>I in the intense field of nanosecond near-infrared laser pulses.<sup>1</sup> In this work we characterized the degree of alignment using photodissociation and velocity map imaging of the iodine products ionized *via* REMPI. Comparing the data with theoretical results we also extracted the rotational temperature of the molecules to be  $12 \pm 1$  K. Importantly, we determined the degree of alignment over an extended volume in the supersonic jet, because this is the necessary information for future reactive scattering experiments with aligned molecules.

1 S. Trippel, M. Stei, C. Eichhorn, R. Otto, P. Hlavenka, M. Weidemüller and R. Wester, *J. Chem. Phys.*, 2011, **134**, 104306, DOI: [10.1063/1.3557822](https://doi.org/10.1063/1.3557822).

**F. Javier Aoiz** said: I gather from your paper (<https://doi.org/10.1039/d3fd00164d>) that you use the topography of the scattering angle–recoil velocity polar map of the products to assign the contributions of each mechanism to the total scattering signal. You assign backward or forward scattering to channels with a direct mechanism, low recoil velocities and isotropic scattering to indirect mechanisms, and sideways to a combination of mechanisms. However, even for fully resolved angular distributions for single rovibrational states, the polar maps may show the combination of backward, forward and sideways types of scattering. For non-state resolved, where many rovibrational states contribute to the reaction, the polar map may look like the superposition of different mechanisms when in fact there is only one. In general, how reliable is the assignment of mechanisms and channels based on inspection of the angle–velocity polar plots? I suspect that trajectory calculations have been very useful in assigning different mechanisms in S<sub>N</sub>2 reactions.

**Roland Wester** responded: Yes, the assignment of different regions of the differential scattering images to reaction mechanisms is an empirical assignment. It allows us to extract trends of the differential scattering cross section with collision energy and provides more compact data for further interpretation. In direct comparison with QCT simulations, such an assignment can be tested. For other substitution reactions, QCT simulations have supported such an assignment, see *e.g.* ref. 1.

1 J. Meyer, V. Tajti, E. Carrascosa, T. Györi, M. Stei, T. Michaelsen, B. Bastian, G. Czako and R. Wester, *Nat. Chem.*, 2021, **13**, 977–981.

**Rahul Pandey** communicated: What is the typical timescale of the long-lived collision complex in Fig. 1 of the paper (<https://doi.org/10.1039/d3fd00164d>)? Does higher beam density play any role in the formation of the long-lived collision complex due to multiple collisions?

**Roland Wester** communicated in reply: We estimate the time scale for the long-lived complex to be at least several if not several ten picoseconds. For a smaller nucleophilic substitution reaction ( $I^- + CH_3I$ ) we once investigated the decay of the intermediate complex by time-resolved photoelectron spectroscopy and found two lifetimes of 0.8 and 10 ps.<sup>1</sup> In the density regime employed in the present experiment we only have single collisions of the reactant ions with molecules from the neutral beam. Reaction probabilities are typically below  $10^{-5}$  and multiple collisions can therefore be neglected.

1 R. Wester, A. E. Bragg, A. V. Davis and D. M. Neumark, *J. Chem. Phys.*, 2003, **119**, 10032, DOI: [10.1063/1.1618220](https://doi.org/10.1063/1.1618220).

**Bum Suk Zhao** communicated: The paper<sup>1</sup> mentioned in your answer to my earlier question raises two questions. What fraction of colliding molecules was influenced by the alignment laser pulse? Do you think it is possible to estimate the alignment effect on reactive collision by lowering the rotational temperature to 1 K (ref. 2) and using a high-power long-pulse laser?<sup>3</sup>

1 S. Trippel, M. Stei, C. Eichhorn, R. Otto, P. Hlavenka, M. Weidemüller and R. Wester, *J. Chem. Phys.*, 2011, **134**, 104306.

2 L. Y. Kim, B. G. Jin, T. W. Kim, J. H. Lee and B. S. Zhao, *Sci. Adv.*, 2020, **6**, eaaz0682.

3 C. Maher-McWilliams, P. Douglas and P. F. Barker, *Nat. Photonics*, 2012, **6**, 386.

**Roland Wester** communicated in reply: In that work<sup>1</sup> we had to employ a focused nanosecond laser for alignment, the waist was 40  $\mu\text{m}$  and the pulse duration 7 ns (FWHM). In subsequent work<sup>2</sup> we estimated that in ion–molecule scattering with these alignment conditions about 0.6% of all scattering events would take place with target molecules affected by the alignment laser. This is mainly caused by the narrow laser beam compared to the impinging ions. Yes, with lower rotational temperatures a less focused laser beam could achieve the same degree of alignment over a larger volume, therefore that would make the search for alignment-induced chemical dynamics in crossed-beam collisions more feasible.

1 S. Trippel, M. Stei, C. Eichhorn, R. Otto, P. Hlavenka, M. Weidemüller and R. Wester, *J. Chem. Phys.*, 2011, **134**, 104306, DOI: [10.1063/1.3557822](https://doi.org/10.1063/1.3557822).

2 S. Trippel, PhD thesis, Universität Freiburg, 2010.

**Peter D. Watson** communicated: This may be only a point of clarification. Comparing the top and bottom panels of Fig. 4 in the paper (<https://doi.org/10.1039/d3fd00164d>): the top panel attributes relative intensities to different reaction mechanisms but the bottom panel does not. Is ‘Other’ attributed to particular reaction mechanisms or does it simply represent the complement of the stated mechanisms (*i.e.* Other = 1 – Indirect – Forward)?

**Roland Wester** communicated in response: In Fig. 4 in the paper (<https://doi.org/10.1039/d3fd00164d>) we show the yields for different mechanisms,

which are derived by integrating different parts of the two-dimensional differential scattering images (see also the last paragraph of the methods section in the paper). In our analysis we assigned the differential scattering images of the  $S_{N2}$  product channel to four different mechanisms (see the grey dotted lines in Fig. 3 in the paper). For the proton transfer channel, we separated the images into three different mechanisms (see the grey dotted lines in Fig. 5 in the paper). This assignment was led by visual inspection of the measured images. The error bars for the relative yields were obtained by varying the boundaries in the assignment, as explained in the methods section of our article.

**David Heathcote** opened discussion of the paper by Jennifer Meyer: Following a reactive collision between  $Ta^+$  and  $CH_4$ , how easily is the tantalum–carbon bond broken to re-liberate a  $Ta^+$  ion to allow activation of further  $CH_4$  molecules? Also, is there scope for  $Ta^+$  to act as a catalyst in forming carbon–carbon bonds?

**Jennifer Meyer** answered: In the reaction  $Ta^+ + CH_4$ , a tantalum carbene  $[Ta=CH_2]^+$ , *i.e.*, a covalent double bond to the tantalum, is formed. The bond dissociation energy (BDE) of the carbene bond has been measured at 4.81 eV.<sup>1</sup> It is known that further methane molecules are attached and/or activated if more methane molecules are available. At least one more methane molecule gets activated. A formal  $[TaC_2H_4]^+$  species is observed in experiments. If two carbene groups or C–C bond formation occurs, is still debated for a number of 5d elements.<sup>2–5</sup> In these experiments, molecular hydrogen  $H_2$  was assumed to be released and the hydrocarbon moieties were still attached to the transition metal ion. We plan to look into this, once we include the ion trap and can prepare the  $TaCH_2^+$  *in situ*.

I cannot envision tantalum as catalytic material because the tantalum oxygen, carbon, and nitrogen bonds are just too strong. Small molecules can be expected to be activated but then they are most likely stuck. But they make great model systems for us.

- 1 L. G. Parke, *et al.*, *J. Phys. Chem. C*, 2007, **111**, 17773.
- 2 A. Simon, *et al.*, *Int. J. Mass Spectrom.*, 2002, **219**, 457.
- 3 E. Sicilia, *et al.*, *Phys. Chem. Chem. Phys.*, 2017, **19**, 16178.
- 4 F. J. Wensik, *et al.*, *Inorg. Chem.*, 2022, **61**, 11252.
- 5 J. Kozubal, *et al.*, *J. Phys. Chem. A*, 2020, **124**, 8235.

**Viet Le Duc** enquired: Will the use of a second laser specifically for ionisation here be more efficient in generating ions than relying on only the ablation laser for non-resonance ionisation? Or the choice of ionisation here is more due to the technical difficulty?

**Jennifer Meyer** replied: Laser vaporization sources have a rather high ion yield despite it being a non-resonant process. We form a plasma which contains as the major constituents neutral species and then as minor fractions cations and anions. The source was initially developed to form cluster ions.<sup>1–4</sup> We operate the source to only form atomic ions and suppress cluster formation. The advantage is in the versatility of the source. We can produce different transition metal ions by changing the metal foil and do not rely on a second laser. A two laser scheme has been used on the neutral atoms formed in laser ablation which are subsequently



ionized by a resonant scheme. James C. Weisshaar and co-workers investigated reactions between nickel and cobalt ions and small aliphatic hydrocarbon molecules (C3–C4 carbon backbone).<sup>5,6</sup> Laser ablation was used to form neutral atoms which were entrained in an argon beam. Ions were formed by laser ionization within the interaction region of the velocity map imaging stack. A similar ionization scheme was used by Ng and co-workers to, for example, produce vanadium V<sup>+</sup> ions.<sup>7,8</sup> If one knows the resonant transitions, the ionization leads to a state selected ion beam.

We decided on the laser vaporization source for direct ion formation with the perspective to move to dimers and trimers but also to form small oxide or possible nitride cluster ions. We are moving into a different direction with the instrument as we want to form small reactive intermediates in the ion trap prior to scattering. Further, we will not have a direct line of sight between the ion source and the interaction region of the beams anymore and in the ion source region we currently have no direct access for a second laser beam.

- 1 M. A. Duncan, *Rev. Sci. Instrum.*, 2012, **83**, 041101.
- 2 T. G. Dietz, *et al.*, *J. Chem. Phys.*, 1981, **74**, 6511.
- 3 V. E. Bondybey and J. H. English, *J. Chem. Phys.*, 1981, **74**, 6978.
- 4 D. Proch and T. Trickl, *Rev. Sci. Instrum.*, 1989, **60**, 713.
- 5 E. L. Reichert and J. C. Weisshaar, *J. Phys. Chem. A*, 2002, **106**, 5563.
- 6 E. L. Reichert, *et al.*, *Int. J. Mass Spectrom.*, 2000, **195–196**, 55.
- 7 Y. C. Chang, *et al.*, *J. Phys. Chem. A*, 2019, **123**, 2310.
- 8 Y. C. Chang, *et al.*, *Phys. Chem. Chem. Phys.*, 2019, **21**, 6868.

**Patrick Robertson** asked: Much of your product scattering distribution is outside of the maximum available energy for the collision. In the manuscript (<https://doi.org/10.1039/d3fd00171g>), you cover all possible sources of this error very thoroughly. My question is, are you more confident in what the particular source(s) might be now? Given that you don't see the error in your Ta + CO<sub>2</sub> paper,<sup>1</sup> is this an issue specific to the mass balance of this reaction, or is it one you expect to encounter again?

- 1 M. Meta, M. E. Huber, T. Michaelsen, A. Ayasli, M. Ončák, R. Wester and J. Meyer, *J. Phys. Chem. Lett.*, 2023, **14**, 5524–5530.

**Jennifer Meyer** responded: We are rather confident that the source is the mass ratio (kinematics) of the reaction. We are currently running some further experiments with methane as a reactant (Zr<sup>+</sup> + CH<sub>4</sub>). The reaction has a much better mass ratio (Zr<sup>+</sup> *m/z* 90) and we will also check this reaction with CD<sub>4</sub>. We are very sensitive to the scattering angle, *i.e.*, the optimization of the ion beam. We expect this to be much better once the ion trap is put in place. Currently the ion source is in direct line of sight of the interaction region and any changes in the source (gas pressure, laser power) is picked up by the energy and orientation of the ion beam. This will be removed once the ions are stored in the trap and thermalized. They will have a new point of origin. We will also be able to make use of a diagnostic imaging detector along the ion beam path. To fully exclude such effects, we would have to redesign the instrument by putting in a larger detector in combination with different VMI settings or even a new electrode stack.

**Stuart R. Mackenzie** said: Very nice extension to your Ta<sup>+</sup> + CO<sub>2</sub> study<sup>1</sup> (with considerable added complexity). I have one comment and one question.

Comment: I do think it likely that you have some excited electronic states – it's hard to see how you can't with ablation (and the lack of selection rules) even if the spin–orbit manifolds do overlap. Certainly in a very similar source, we regularly see excited state effects, spectroscopically.<sup>2</sup> I don't think your helium carrier gas will help quench electronically excited states but seeding with a small fraction of a heavier rare gas (Ar, Kr) might help?

Question: Which other transition metals do you have in mind to try? Which might realistically show multi-state reactivity? One that won't but in which we have seen dehydrogenation of CH<sub>4</sub> is Au<sup>+</sup>, especially with vibrationally excited methane.<sup>3</sup> This could be a great system for your crossed beam apparatus.

1 M. Meta, *et al.*, *J. Phys. Chem. Lett.*, 2023, **14**, 5524, DOI: [10.1021/acs.jpcclett.3c01078](https://doi.org/10.1021/acs.jpcclett.3c01078).

2 See for example: E. M. Cunningham, *et al.*, *Phys. Chem. Chem. Phys.*, 2019, **21**, 13959, DOI: [10.1039/c8cp05995k](https://doi.org/10.1039/c8cp05995k).

3 A. S. Gentleman, *et al.*, *Topic Catal.*, 2018, **61**, 81, DOI: [10.1007/s11244-017-0868-z](https://doi.org/10.1007/s11244-017-0868-z).

**Jennifer Meyer** answered: We are aware of the possible contributions of electronically excited states in our ion beam. We estimated an upper limit of about 20%. We currently cannot fully quantify this contribution. In a different study (Ta<sup>+</sup> + CO<sub>2</sub>),<sup>1</sup> we varied the power of the ablation laser by almost doubling it and saw no changes in the velocity distributions. For the <sup>3</sup>Ta<sup>+</sup>, we would expect much more direct dynamics because we have a highly exothermic gas phase reaction, even more so than for the presented carbene formation. And we now know that the bottleneck for TaO<sup>+</sup> formation is the intersystem crossing and not the submerged transition state. We do not have trajectory simulations for the carbene formation yet but in case of dynamics of the excited state, I expect a similar behavior for both systems.

Helium certainly does not quench the excited states given our experimental conditions (pressure in the source region and time scales). Indeed, ion mobility can be used to separate spin states given the right conditions.<sup>2,3</sup> We could seed Ar or Kr into the expansion gas but I do not expect to see large effects. It is known that small molecules (N<sub>2</sub>, CO) are more efficient and have been used.<sup>4</sup> Seeding them into the expansion gas will not be beneficial in the present case but once we added the currently assembled ion trap, we could run some tests.

We are currently working with zirconium, which is expected to show two-state reactivity. We completed a first set of experiments with CO<sub>2</sub> and are in the process of running scattering experiments with methane.

The effects of vibrational excitation would be very interesting. The experiments are a great challenge for neutral–neutral scattering<sup>5,6</sup> and even more so for ion–molecule reactions.<sup>7</sup> It is technically feasible but nothing that can be done without some preparation. We would first need to overlap our neutral beam and the laser, implement a scheme to quantify the excited fraction in the neutral beam and find a scattering signal in the first place. And we would need an estimate of the expected effect to be sure we could see it. But sure it is a great idea to work towards.

1 M. Meta, *et al.*, *J. Phys. Chem. Lett.*, 2023, **14**, 5524.

2 Y. Ibrahim, *et al.*, *J. Phys. Chem. A*, 2008, **112**, 1112.

3 M. T. Bowers, *et al.*, *Science*, 1993, **260**, 1446.

4 M. A. Duncan, *Rev. Sci. Instrum.*, 2012, **83**, 041101.

5 F. Wang, *et al.*, *Science*, 2011, **331**, 900.

6 W. Zhang, *et al.*, *Science*, 2009, **325**, 303.

7 M. Stei, *et al.*, *Sci. Adv.*, 2018, **4**, eaas9544.

**George C. Schatz** commented: One area of interest in the chemistry community is the development of methods for separating mixtures of Ta and Nb. Typically this is done using ligands that bind selectively with one of the ions, or with electrochemistry where there are differences in redox behavior, but the differences between Nb and Ta are small due to their similar chemical properties.<sup>1</sup>

1 M. Furigay, *et al.*, *Inorg. Chem.*, 2022, **61**, 23–27, DOI: [10.1021/acs.inorgchem.1c02976](https://doi.org/10.1021/acs.inorgchem.1c02976).

**George C. Schatz** asked: One might imagine that the larger spin–orbit coupling of Ta would make it possible to separate these elements based on differences in reactivity. Assessing this would involve doing similar experiments to yours but with Nb. Can this be done and does this lead to differences in reactivity between the two elements?

**Jennifer Meyer** replied: We have not done reactive scattering experiments for  $\text{Nb}^+ + \text{CH}_4$ . But we have compared the reaction dynamics for the oxygen atom transfer reaction  $\text{M}^+ + \text{CO}_2 \rightarrow \text{MO}^+ + \text{CO}$  for Ta and Nb.<sup>1</sup> We see similar dynamical features for both reactions, which are dominated by indirect dynamics. We concluded that in both cases the reaction is trapped in the pre-reaction minimum on the quintet surface and that the bottleneck is the intersystem crossing. Based on this single comparison both metals behave very similar as mono cations regarding the dynamics of the oxygen atom transfer reaction. Our recent publication is a collaborative work with the team around Nick Shuman at the Air Force Research Lab in Albuquerque. They measured thermal rate constants at different temperatures using their selected ion flow tube instrument. The temperature dependence of the reaction of  $\text{Nb}^+ + \text{CO}_2$  is more pronounced than for  $\text{Ta}^+ + \text{CO}_2$  which could be related to the different spin–orbit coupling strength. We will need further input from trajectory simulations to confirm this.

1 M. E. Huber, *et al.*, *Phys. Chem. Chem. Phys.*, 2024, **26**, 8670, DOI: [10.1039/d3cp05549c](https://doi.org/10.1039/d3cp05549c).

**Olivia A. Krohn** said: Thank you for a great talk and discussion. My question is also in regard to characterizing potential excited state  $\text{Ta}^+$  that may be reacting in your system. A technique that we have used in ion traps is to expose trapped ions of unknown state to a molecule or atom with an ionization potential between the ground state and excited state energy and look for charge exchange. Have you have considered a method like this in order to characterize potential population of excited state  $\text{Ta}^+$ ?

**Jennifer Meyer** responded: I had a similar idea regarding the 3d elements, for which the spin state is even more important for the reactivity. The appearance energies for the different spin states can vary on the eV scale. Charge transfer seems very intriguing as it is commonly associated with high rates. In the crossed beam, I do not see this at the moment because of the experimental uncertainty in the ion beam energy in the case of tantalum. Here, we are talking about less than

400 meV in difference with the spin-orbit splitting leading to both spin manifolds energetically overlapping. However, we are currently in the process of assembling an ion trap. The trap will be operated at room temperature and we cannot trap for the extended times you can. But we can add a rather wide range of neutral reactants and run basic kinetics experiments. It is certainly worth a try and looking up some ionization energies. Thank you for pointing this out.

**Roland Wester** asked: Now that you have successfully studied reactions with tantalum ions, what are the prospects for reactive scattering experiments involving coinage metal ions, such as copper?

**Jennifer Meyer** answered: I originally planned the experiments with elements of the 3d series in mind. The reaction rates are somewhat lower than for 4d or 5d elements but they show a more pronounced state selective reactivity. The reactions are often associated with a barrier. This might allow us also more insights into possible contributions of electronically excited states because barriers for different states can vary on the scale of several eV. I personally have never worked with copper but I cannot see why we should not be able to produce  $\text{Cu}^+$  ions in our source. However, we will next focus on iron and cobalt in the near future.

**Jennifer Meyer** opened discussion of the paper by Gábor Czakó: Gábor, great work. I have a question related to the energy partitioning in the E2 channel. The opacity function, angular distributions and internal energy distributions show a remarkable similarity to results for  $\text{F}^- + \text{CH}_3\text{CH}_2\text{Cl}$ .<sup>1</sup> There, most of the additional collision energy is partitioned into the recoil of the two neutral products. Here, you show only the total translational energy (bottom row of Fig. 8 in the paper (<https://doi.org/10.1039/d3fd00161j>)). Have you analyzed which contribution exactly increases as function of collision energy? That is, is it the kinetic energy of the  $\text{Cl}^-$  or the recoil?

1 J. Meyer, V. Tatji, E. Carrascosa, T. Gyori, M. Stei, T. Michaelsen, B. Bastian, G. Czako and R. Wester, *Nat. Chem.*, 2021, **13**, 977, DOI: [10.1038/s41557-021-00753-8](https://doi.org/10.1038/s41557-021-00753-8).

**Gábor Czakó** replied: We computed the relative translational energy of the two neutral fragments ( $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_4$ ) to test our trajectory analyzer code. However, we have not analyzed these results in detail. Nevertheless, in the case of these neutral products, we determined the internal energy distributions for each fragment separately, as shown in Fig. 8 of the paper (<https://doi.org/10.1039/d3fd00161j>).

**Pablo G. Jambrina** asked: Thank you for the very nice presentation and congratulations on your work. It is relatively straightforward to distinguish between the different product channels just by analysing the distances in the last frames of each trajectory. However, it is not easy to distinguish between different reaction mechanisms when some of them give rise to the same products. How did you solve this problem? And was it unambiguous? Was it possible to assign all the trajectories to one of the mechanisms or was there a grey area?

**Gábor Czakó** answered: We developed numerical methods to distinguish between different reaction pathways. In the case of the double-inversion vs. front-

side attack  $S_N2$  mechanisms our method is described in ref. 1, while the *anti*-E2 and *syn*-E2 separation is discussed in ref. 2. In short, we follow the trajectories backward until we arrive to the transition-state (TS) region, which can be defined based on a characteristic distance. For  $S_N2$  reactions, at the TS we compute an attack angle, which is close to  $180^\circ$  for double inversion, where the second TS corresponds to Walden inversion or the angle is around  $90^\circ$  indicating front-side attack. In the case of the E2 channel, we compute a torsion angle, which is characteristic for *syn*- and *anti*-E2 TSs. These methods are almost unambiguous and we can usually assign each of the trajectories to one of the mechanisms. The unambiguity can be verified by plotting the TS attack angle or torsion angle distributions as we did in ref. 1 and 2. We found bimodal distributions, which enable the separation of the pathways based on the values of these angles.

- 1 P. Papp, V. Tajti and G. Czakó, *Chem. Phys. Lett.*, 2020, 755, 137780, DOI: [10.1016/j.cplett.2020.137780](https://doi.org/10.1016/j.cplett.2020.137780).
- 2 V. Tajti and G. Czakó, *Phys. Chem. Chem. Phys.*, 2022, 24, 8166, DOI: [10.1039/d2cp00685e](https://doi.org/10.1039/d2cp00685e).

**Pablo G. Jambrina** enquired: Thanks for the kind and clarifying answer. As far as I have understood, you calculated the TS for each trajectory. How was it calculated? Just as the maximum of the potential energy of a given trajectory?

**Gábor Czakó** responded: We always identify the transition-state (TS) region based on geometric conditions.<sup>1,2</sup> Energy can fluctuate between the kinetic and potential parts and also between the various vibrational modes, therefore, finding TSs in high-dimensional configurational spaces based simply on energy is not possible. In the case of the  $\text{OH}^- + \text{CH}_3\text{CH}_2\text{Cl}$  reaction (discussed in the paper (<https://doi.org/10.1039/d3fd00161j>)), following the C–Cl distance backwards from the final value is a good way to find the  $S_N2$  or E2 TS, which leads to the products.

- 1 P. Papp, V. Tajti and G. Czakó, *Chem. Phys. Lett.*, 2020, 755, 137780, DOI: [10.1016/j.cplett.2020.137780](https://doi.org/10.1016/j.cplett.2020.137780).
- 2 V. Tajti and G. Czakó, *Phys. Chem. Chem. Phys.*, 2022, 24, 8166, DOI: [10.1039/d2cp00685e](https://doi.org/10.1039/d2cp00685e).

**David W. Chandler** asked: Dr Czakó, as you calculate exactly which hydrogen atoms are involved in the various reactions would experiments using deuterated samples be of value for testing your calculations and if so what experiments would you like to see being done?

**Gábor Czakó** answered: As our simulations uncovered interesting pathways involving proton transfer between or within the reactants (<https://doi.org/10.1039/d3fd00161j>), experiments with deuterated or partially-deuterated reactants would be useful to probe these mechanisms. We found proton exchange between  $\text{OH}^-$  and  $\text{CH}_3\text{CH}_2\text{Cl}$ , which could be experimentally detected in the  $\text{OD}^- + \text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{OH}^- + \text{CH}_3\text{CHDCl}$  or  $\text{OH}^- + \text{CH}_3\text{CD}_2\text{Cl} \rightarrow \text{OD}^- + \text{CH}_3\text{CHDCl}$  reaction. As detection of ions is straightforward, these reactions could allow the experimental observation of the H/D-exchange process. Of course, the presence of  $^{17}\text{O}$  may complicate the experiments. We also found elimination (E2) pathways, which involve proton transfer from the  $\beta$  to the  $\alpha$  carbon atom. Here the experiments with  $\text{OH}^- + \text{CH}_3\text{CD}_2\text{Cl}$  or  $\text{CD}_3\text{CH}_2\text{Cl}$  could be interesting, where the  $\text{HDO} +$

$\text{CH}_2\text{CDH} + \text{Cl}^-$  or  $\text{H}_2\text{O} + \text{CD}_2\text{CDH} + \text{Cl}^-$  products could be observed in the case of  $\beta$ - $\alpha$  transfer, whereas the common E2 pathway would lead to  $\text{H}_2\text{O} + \text{CH}_2\text{CD}_2 + \text{Cl}^-$  or  $\text{HDO} + \text{CD}_2\text{CH}_2 + \text{Cl}^-$ , respectively. However, the experimental detection of the different E2 channels would be challenging, because these pathways result in the same ionic product and differ only in the neutral counterparts.

**Roland Wester** enquired: It was interesting to read that you observe the  $\text{Cl}^- (\text{H}_2\text{O})$  product channel in your study. What are the specific dynamics for the formation of this channel? Do you see differences between this reaction and the formation of  $\text{FHCl}^-$  in reactions of fluorine anions?

**Gábor Czakó** replied: We found trajectories leading to the  $\text{Cl}^- \cdots \text{H}_2\text{O}$  (see the current paper; <https://doi.org/10.1039/d3fd00161j>) and  $\text{Cl}^- \cdots \text{HF}$  (ref. 1 and 2) complexes in the  $\text{OH}^-$  and  $\text{F}^- + \text{CH}_3\text{CH}_2\text{Cl}$  reactions, respectively. In both cases the anion complexes are formed *via* the *syn*-E2 pathway and the dissociation of the complexes results in the E2 products ( $\text{Cl}^- + \text{H}_2\text{O}/\text{HF} + \text{C}_2\text{H}_4$ ). We found significantly larger cross sections for the  $\text{Cl}^- \cdots \text{H}_2\text{O}$  channel compared to the corresponding  $\text{Cl}^- \cdots \text{HF}$  pathway. In the case of the  $\text{Cl}^- \cdots \text{HF}$  products we computed internal energy distributions as well, which show that a large fraction of the complexes has higher internal energy than their dissociation limit,<sup>2</sup> thus, these complexes may exist in Feshbach resonance states, therefore, the timescale of the simulations or experiments could significantly affect the population of this channel.

1 J. Meyer, V. Tajti, E. Carrascosa, T. Györi, M. Stei, T. Michaelsen, B. Bastian, G. Czakó and R. Wester, *Nat. Chem.*, 2021, **13**, 977, DOI: [10.1038/s41557-021-00753-8](https://doi.org/10.1038/s41557-021-00753-8).

2 V. Tajti and G. Czakó, *Phys. Chem. Chem. Phys.*, 2022, **24**, 8166, DOI: [10.1039/d2cp00685e](https://doi.org/10.1039/d2cp00685e).

**Kenneth G. McKendrick** opened a general discussion: One of the intended themes of this *Faraday Discussion* was the proposition that information provided by scattering experiments might be increasingly useful to more-applied communities as the problems tackled become more complex and hence more representative of real-world problems. In this session, we have seen beautiful gas-phase results on systems that would be immediately recognisable as prototypical reactions by synthetic or catalytic chemists. However, they have been carried out under very different conditions, including much higher collision energies and in the absence of solvents. I would like to ask the speakers and others to comment on this point, which I pose as a question in two parts:

(a) Are there significant new things that have been discovered through the gas-phase scattering experiments that should be important to those working in more-applied fields?

And, if so, (b) in your experience, are they listening?

**Roland Wester** responded: Nucleophilic substitution reactions play major roles in chemical synthesis applications in the liquid phase. Our gas phase experiments cannot directly be compared to the dynamics in the liquid phase, even when microsolvated reactions are studied.<sup>1,2</sup> Nevertheless, some of the fast and direct dynamics observed in the gas phase may carry over into a solution phase environment. Furthermore, accurate QCT simulations can be

benchmarked with our highly differential experimental data in the gas phase and then applied with higher confidence to solvated environments.

- 1 R. Otto, J. Brox, S. Trippel, M. Stei, T. Best and R. Wester, *Nat. Chem.*, 2012, 4, 534, DOI: [10.1038/nchem.1362](https://doi.org/10.1038/nchem.1362).
- 2 B. Bastian, T. Michaelsen, L. Li, M. Ončák, J. Meyer, D. H. Zhang and R. Wester, *J. Phys. Chem. A*, 2020, 124, 1929, DOI: [10.1021/acs.jpca.0c00098](https://doi.org/10.1021/acs.jpca.0c00098).

**Jennifer Meyer** answered: In answer to (a): our model systems are quite far from applied catalysis research. Therefore, we talk about activation in a more general sense and not about catalysis. But it becomes more and more clear that if we want to model catalytic process from first principles/by rational design, we need more detailed knowledge on the factors influencing the intrinsic reactivity. However, our results are not directly transferable to the condensed phase. But we provide important benchmarking results especially for going beyond the stationary description.

In answer to (b): in my experience, the fact that if one makes a system smaller and smaller to design a model system may lead to complex properties that first need to be understood is often not really appreciated. Even in classic gas phase environments (atmospheres, interstellar medium) the fact that collisions are dynamic is often not considered in the modelling.

**Brianna R. Heazlewood** addressed Roland Wester: Continuing the broader discussion about future directions for the field, you mentioned the possibility of studying the reaction dynamics of larger molecules—including species that are of significant interest in organic chemistry. What challenges do you foresee in applying your experimental methods to larger systems? Can you predict when you may start to encounter systems that are too large to study, or where you cannot extract detailed information from your measurements?

**Roland Wester** responded: The most complex covalently bound negative ion that we have included in our nucleophilic substitution studies is the methoxy anion of the work presented here (<https://doi.org/10.1039/d3fd00164d>). In previous work we have also studied reactions of hydroxyl anions clustered to one or two water molecules.<sup>1</sup> Ions that are larger than these species are generally feasible, but may require some modifications of our mass spectrometry or the ion trap parameters. The main limitation may be the increased difficulty in interpreting the data. The largest neutral molecules we have studied so far in  $S_N2$  reactions are *tert*-butyl halides. Here, the preparation of larger molecules hinges on their volatility, because the molecules have to be seeded in a rare gas supersonic jet. Based on this we expect that several larger alkanes and also several aromatic or polyaromatic species can be also studied with this technique. Understanding and interpreting the differential scattering data will certainly be more difficult, but here, as already today, I expect the most detailed insight will arise from combined experimental and theoretical investigations.

- 1 R. Otto, J. Brox, S. Trippel, M. Stei, T. Best and R. Wester, *Nat. Chem.*, 2012, 4, 534, DOI: [10.1038/nchem.1362](https://doi.org/10.1038/nchem.1362).



**Brianna R. Heazlewood** remarked: In this session—and throughout the meeting—the interplay between theory and experiment has been highlighted. We have discussed the importance of benchmarking theoretical predictions with experimental measurements and considered what larger molecular systems might be experimentally studied in the future. In the discussion of your paper, Gábor (<https://doi.org/10.1039/d3fd00161j>), we heard about the information that can be gained from following the trajectories that yield a given set of products—enabling the branching ratios for different reaction pathways to be elucidated. Could you comment on whether you could study larger systems using this approach, and where the limit might be?

**Gábor Czakó** replied: Our  $S_N2$  reaction dynamics investigations started with 6-atom systems about 10 years ago. We developed the first full-dimensional high-level *ab initio* potential energy surfaces (PESs) for the  $F^- + CH_3X$  [ $X = F, Cl, Br, I$ ] reactions,<sup>1–5</sup> allowing efficient dynamics investigations with the quasi-classical trajectory method. Now we can study the 10-atom  $OH^- + CH_3CH_2Cl$  reaction in full-dimensionality (see our current paper (<https://doi.org/10.1039/d3fd00161j>)). In the past few years we carried out several methodological developments to make the PES construction more efficient, robust, and user-friendly. We developed the machine-learning-type ROBOSURFER program package<sup>5</sup> for automatic PES construction as well as the ManyHF method<sup>6</sup> and a Brueckner-coupled-cluster-based composite approach<sup>7</sup> to make the electronic structure part of the PES development more robust. Using these techniques, we have already developed a full-dimensional coupled-cluster PES for a 12-atom reactive system, and we will certainly be able to go beyond this limit in the near future.

1 I. Szabó, A. G. Császár and G. Czakó, *Chem. Sci.*, 2013, **4**, 4362, DOI: [10.1039/c3sc52157e](https://doi.org/10.1039/c3sc52157e).

2 I. Szabó and G. Czakó, *Nat. Commun.*, 2015, **6**, 5972, DOI: [10.1038/ncomms6972](https://doi.org/10.1038/ncomms6972).

3 I. Szabó, H. Telekes and G. Czakó, *J. Chem. Phys.*, 2015, **142**, 244301, DOI: [10.1063/1.4922616](https://doi.org/10.1063/1.4922616).

4 B. Olasz, I. Szabó and G. Czakó, *Chem. Sci.*, 2017, **8**, 3164, DOI: [10.1039/c7sc00033b](https://doi.org/10.1039/c7sc00033b).

5 T. Györi and G. Czakó, *J. Chem. Theory Comput.*, 2020, **16**, 51, DOI: [10.1021/acs.jctc.9b01006](https://doi.org/10.1021/acs.jctc.9b01006).

6 T. Györi and G. Czakó, *J. Chem. Phys.*, 2022, **156**, 071101, DOI: [10.1063/5.0080817](https://doi.org/10.1063/5.0080817).

7 D. A. Tasi, T. Györi and G. Czakó, *Phys. Chem. Chem. Phys.*, 2020, **22**, 3775, DOI: [10.1039/c9cp07007a](https://doi.org/10.1039/c9cp07007a).

## Conflicts of interest

There are no conflicts to declare.