General Discussion

Prof. Hippler opened the discussion of the Introductory Lecture: (1) You showed a rectangular temperature profile during combustion in an engine. Would not this lead to a rectangular NO-profile both from thermal and prompt NO?

(2) How well can it be decided that the contribution of prompt NO to total NO is low, since the rate constant for $CH + N_2$ shows a strong non-Arrhenius behaviour and experiments under combustion conditions around 1000 K are lacking?

Prof. Wolfrum responded: (1) The rectangular temperature profile represents a 'snapshot' through the growing flame. Therefore, in the middle of the combustion chamber, where the flame started at the spark plug, hot gases have been present for the longest time. This temporal history is responsible for the increase of thermal NO towards the center of the combustion chamber.

(2) We are watching here an unsteady, growing flame. Residence times within the flame front are short compared to the time where thermal NO can be formed in the hot post-flame gases. The calculation checks if an additional contribution from NO formed directly in the flame front is necessary to explain the experimentally found profiles. Therefore, we did a phenomenological approach modeling prompt NO formation as an instantaneous process at the current flame front position. Flame conditions were assumed to be identical for all volume experiments when the flame front is crossing. Therefore, no temperature effects had to be included in the calculation. For details please refer to ref. 1.

1 C. Schulz, J. Wolfrum and V. Sick, *Twenty-seventh Symp.* (*Int.*) *Combust.*, The Combustion Institute, Pittsburgh, 1998, p. 2077.

Prof. Lin asked: We have recently shown by a high-level *ab initio* calculation that the prompt NO reaction, $CH + N_2$, produces the spin-allowed HNCN and H + NCN products,[1] instead of the commonly assumed, spin-forbidden HCN + N. Have you considered the new mechanism in your modeling?

1 L. V. Moskaleva and M. C. Lin, *Proc. Combust. Inst.*, 2000, **28**, 2393.

Prof. Wolfrum responded: As mentioned in the response to Hippler's question, no detailed information on rate constants was included in the simulation calculation presented here.

Dr Klippenstein opened the discussion of Prof. Casavecchia's paper: I was intrigued by your observation of what appears to be a highly non-statistical product branching in the $N(^2D) + CH_4$ reaction. To further investigate this possibility I have performed some direct dynamics simulations with the forces directly determined from B3LYP/6-31G* evaluations. Such simulations nicely complement statistical theories in that they are most feasible and most applicable to reactions occurring on a short time scale (*e.g.*, less than 1 ps) where statistical simulations are of dubious validity.

For the present simulations the initial conditions were chosen to correspond to a fixed C to N separation of 4.0 a_0, which roughly corresponds with the separation at the saddlepoint for the insertion of the N atom into a CH bond. The internal coordinates and conjugate momenta for the

vibrational modes of the CH_4 fragment were chosen quasiclassically with a random vibrational phase and the harmonic oscillator normal mode zero-point energy in each mode. The remaining coordinates and conjugate momenta were chosen randomly, as described in detail in our related work for the $CH_3 + O$ reaction.[1] While this choice of initial conditions does not exactly mimic the experimental conditions, it should still provide qualitatively meaningful predictions for the branching ratios.

Simulations were performed for a total angular momentum J of 25 at two different energies: 12.6 and 63 kcal mol^{-1}, in excess of the reactant's zero-point energy. A time step of 0.5 fs was employed for each of the 47 and 33 trajectories completed for these two energies. The results of these simulations are given here in Table 1.

Qualitatively these results are in good agreement with your experimental observations. In particular, there is a larger than expected branching to the higher energy $CH_3N + H$ channel, and this branching increases with increasing energy. Furthermore, the numerical values for the relative branching are of a similar magnitude to the experimental observations. The simulations also predict minor branching to other unexplored product channels such as $CH_3 + NH$.

As you suggest in your paper, the increased production of the $CH_3N + H$ channel over likely statistical theory expectations appears to be related to a correlation between the insertion and dissociation processes. Indeed, the average timescale for the H atom loss is much shorter for those trajectories that produce CH_3N (50 fs being fairly typical). Furthermore, in many instances the $CH_3N + H$ producing trajectories appear to proceed directly from insertion to bimolecular products.

The question I have for you is whether one can reconcile this direct short time nature of the trajectories that produce $CH_3N + H$ with the observed anisotropy in the centre-of-mass (CM) angular distributions?

1   T. P. Marcy, R. R. Díaz, D. Heard, S. R. Leone, L. B. Harding and S. J. Klippenstein, *J. Phys. Chem. A*, 2001, **105**, 8361.

Prof. Casavecchia responded: I am very glad to learn that direct dynamics simulations have become feasible for a polyatomic reaction such as $N(^2D) + CH_4$. Your results are indeed very interesting; in particular I notice that there really is a good qualitative agreement between your theoretical predictions and the results of our crossed molecular beam investigations as a function of collision energy, *i.e.*, the branching to the less exoergic $CH_3N + H$ channel is found also theoretically to be higher than expected on statistical grounds and to increase with increasing energy. Your theoretical work contributes considerably to the understanding of the dynamics of this multichannel reaction. Specifically, your finding that $CH_3N + H$ formation is prompt, following the insertion of the $N(^2D)$ atom into the C–H bond of methane, can help to rationalize the shape of the experimental center-of-mass angular distribution. In fact, an isotropic angular distribution, as that found for the CH_3N channel in our study, is usually attributed (at least for simple A + BC reactions) to a reaction micromechanism implying a long-lived-complex formation, *i.e.* a CH_3NH complex whose lifetime is significantly longer than its rotational period. This would be in line with the deep potential well of CH_3NH. However, an isotropic angular distribution can also have other

Table 1 Results of simulations performed for total angular momentum $J = 25$ at two different energies in excess of the reactants zero point energy

Product	Branching	
	$E = 12.6$	$E = 63.0$
$CH_2NH + H$	0.55	0.34
$CH_3N + H$	0.27	0.41
$NH + CH_3$	0.11	0.13
$HCNH + H_2$	0.07	0.03
$H_2CN + H_2$	0	0.06
$NH_2 + CH_2$	0	0.03

interpretations, especially for 'insertion' reactions. An isotropic angular distribution could also arise from a combination of two dynamically different 'direct' micromechanisms, one leading to backward scattering (arising from small impact parameter collisions) and the other leading to forward scattering (arising from large impact parameter collisions). But perhaps, more likely than that, the formalism derived for simple, limiting cases, is not valid here since, once the N atom has inserted into one of the four equivalent CH bonds, the geometry of the intermediate changes dramatically, and the memory of the initial direction of the reagents is lost. As a result, the intermediate is likely to fragment isotropically in space. The time scale of a 'direct' mechanisms is sub-picosecond, i.e., of the time-scale of molecular vibrations. The theoretical results of Klippenstein suggest that this is indeed the case. Interestingly, the fact that the $P(E_T')$ distribution for the $CH_3N + H$ forming channel corresponds to a large fraction (more than 40%) of total available energy released in translation, indicates that the energy release is not statistical and since no potential barrier is theoretically predicted to exist in the exit channel,[1] this is consistent with a CH_3NH intermediate which dissociates promptly, on a short time scale, before energy randomization can take place, i.e. the reaction proceeds via a 'direct' mechanism. In conclusion, although CH_3NH is very stable with respect to $CH_3N + H$ products, the mechanism of formation of CH_3N appears to be via a direct insertion of N into the CH bond followed by prompt NH bond cleavage. The fact that the CM angular distribution is isotropic (backward–forward symmetric) is still consistent with the short time nature of the reactive trajectories, as found in your theoretical investigation (see above).

1 Y. Kurosaki, T. Takayanagi, K. Sato and S. Tsunashima, *J. Phys. Chem. A*, 1998, **102**, 254.

Dr Kaiser said: The almost isotropic (flat) angular distribution in the case of the $CH_4 + N(^2D)$ reaction could have an alternative explanation. For example, it might be a superposition of two direct reaction mechanisms: mechanism I is dictated by relatively large impact parameters leading to a 'forward' scattered contribution; mechanism II is dominated by small impact parameters giving rise to a 'backward' scattered component, i.e. possibly via a transition state including a penta-coordinated carbon atom (Fig. 1). These transition states are well known in 'classical' organic chemistry; their contribution to the PES and hence the reactive scattering signal of CH_3N and should be investigated computationally.

Prof. Casavecchia replied: Although the superposition of two direct reaction mechanisms may be an alternative explanation, this is not the only other possible rationalization of an isotropic angular distribution (see my response to Dr Klippenstein previously). Actually, since we find the
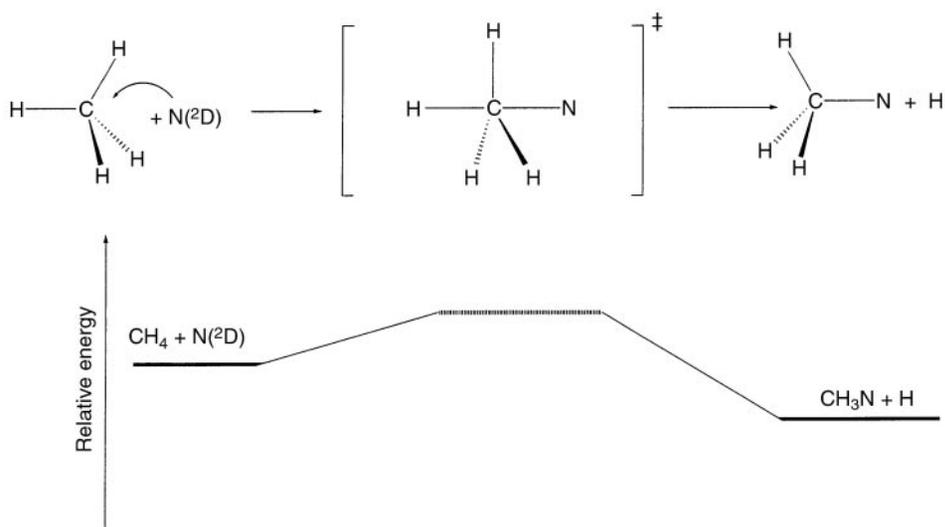
Fig. 1   The $CH_4 + N(^2D) \rightleftharpoons CH_3N + H$ reaction.

CM angular distribution of CH_3N to be isotropic in a wide range of collision energies (from 21.3 to 63.2 kJ mol^{-1}), it is unlikely that two different micromechanisms, one resulting from small impact parameter collisions and the other from large impact parameter collisions, give rise to a constant amount of backward and forward scattering, respectively, as a function of collision energy; in fact, one would expect an increasing forward scattering with increasing E_c, something which is not found experimentally. In addition, although transition states with a penta-coordinated carbon atom exist and may play some role also in this reaction, we note that detailed *ab initio* molecular orbital calculations of the potential energy surfaces for the $N(^2D) + CH_4$ reaction found that $N(^2D)$ 'inserts' into the C–H bond of methane.[1] Of course, a theoretical treatment of the dynamics using classical trajectory calculations on the global potential energy surface of this reaction, when a global CH_4N surface will become available, is desirable to fully characterize the reaction dynamics.

1   Y. Kurosaki, T. Takayanagi, K. Sato and S. Tsunashima, *J. Phys. Chem. A*, 1998, **102**, 254.

Prof. Golden asked: Can the difference in branching ratio of CH_3N and CH_2NH be due to symmetry and other factors that contribute to the *A*-factors (density of states at the transition states)?

Prof. Casavecchia answered: This is an interesting comment. Such factors could also be important. A detailed theoretical investigation of this reaction is however desirable to explore what is the role of energy and symmetry factors *vs.* dynamics. I notice that previous statistical (RRKM) considerations by Takayanagi and coworkers[1] did not find branching to the higher energy CH_3N + H channel to be important, while the direct dynamics treatment of Klippenstein provides quite opposite results. Clearly, dynamics is at play in this multichannel reaction.

1   Y. Kurosaki, T. Takayanagi, K. Sato and S. Tsunashima, *J. Phys. Chem. A*, 1998, **102**, 254.

Prof. Kohse-Höinghaus said: I would like to comment on the observation of hydrogen-deficient compounds in low-pressure flames. We have seen C_4H_2 and C_6H_2 in propene–oxygen, pentene–oxygen and acetylene–oxygen flames at 50 mbar, in particular these compounds (and C_8H_2) have been observed in fuel-rich acetylene flames used for diamond deposition.[1] While their dependence on flame stoichiometry may be quite well predicted using the combustion mechanism by Miller and Melius[2] with a few addenda,[3] the C_4H_2 concentration is underpredicted by about a factor of 10 (ref. 4) and the C_6H_2 concentration by about two orders of magnitude.[5]

1   A. G. Löwe, A. T. Hartlieb, J. Brand, B. Atakan and K. Kohse-Höinghaus, *Combust. Flame*, 1999, **118**, 37.
2   J. A. Miller and C. F. Melius, *Combust. Flame*, 1992, **91**, 21.
3   J. A. Miller, personal communication to B. Atakan, 1999.
4   K. Kohse-Höinghaus, A. Löwe and B. Atakan, *Thin Solid Films*, 2000, **368**, 185.
5   A. Löwe, PhD thesis, University of Bielefeld, Germany 1999.

Prof. I. W. M. Smith commented: I share with Prof. Casavecchia and Dr Kaiser, a strong interest in the reaction between $C(^3P)$ atoms and C_2H_2. The experiments reported here by Prof. Casavecchia confirm the importance of the 'spin-forbidden' channel to $C_3(X\,^1\Sigma_g^+) + H_2$ which appears to be competitive with the 'spin-allowed' channel to C_3H + H. As pointed out in the paper by Casavecchia, and co-workers, the reaction to $C_3(X\,^1\Sigma_g^+) + H_2$ is likely made possible by the long lifetime of the strongly bound triplet propargylene intermediate allowing intersystem crossing to the singlet surface and subsequent separation to $C_3(X\,^1\Sigma_g^+) + H_2$. There would seem to be an opportunity for theory of two kinds. First, the lifetime of the triplet state is likely to be strongly dependent on energies of the triplet products: l-C_3H + H and c-C_3H + H, and any barriers along the paths leading to these products. Can theory define these energies more closely than has been done so far? I note that the values quoted in the paper (from ref. 63) show these reactions to be very slightly exothermic, whereas the calculations of Guadagnini *et al.* (ref. 58) appear to suggest that they are very slightly endothermic. Second, very exact RRKM calculations on this system would be valuable. Such calculations should help not only to establish the lifetimes of the triplet propargylene and also the branching ratios, both between $C_3(X\,^1\Sigma_g^1) + H_2$ and C_3H + H, and between l-C_3H + H and c-C_3H + H, but also how those branching ratios depend on tem-

perature over a wide range. This information would be useful in models of both combustion and interstellar cloud chemistry.

Prof. Casavecchia responded: Yes, I agree with Prof. I. W. M. Smith that there is a need for a determination more accurate than the existing ones of the energetics of the various channels of the $C(^3P) + C_2H_2$ reaction, as well as of exact RRKM calculations in order to provide estimates of branching ratios as a function of temperature. From an experimental point of view, we plan to study this reaction both at lower and higher collision energies than that ($E_c = 29.3$ kJ mol^{-1}) reported in our paper[1] in order to explore how the branching ratio between $C_3H + H$ and $C_3 + H_2$ formation varies with collision energy. From experiments at very low E_c (4 kJ mol^{-1} or less) we also hope to be able to explore the branching ratio between linear C_3H and cyclic C_3H formation. Accurate theoretical values of the energetics of the corresponding reaction channels would be valuable in the data analysis.

1 P. Casavecchia, N. Balucani, L. Cartechini, G. Capozza, A. Bergeat and G. G. Volpi, *Faraday Discuss.*, 2001, **119**, 27.

Dr Bergeat opened the discussion of Dr Kaiser's paper: You have reported a new experiment which allows you to detect the $C_3 + H_2$ channel of the $C + C_2H_2$ reaction. How have you increased your sensitivity? Have you any idea or estimation of the branching ratio of the $C_3 + H_2$ and $C_3H + H$ channels?

In our fast-flow reactor, at 300 K and 1 Torr, we have found a branching ratio less than 0.53 ± 0.04 for the $H + C_3H$ channel, by comparison with the H production by the $C + H_2S$ reaction.[1,2]

(1) May you agree with this estimation?

(2) May you estimate the sensitivity of your experiments for the other C, C_2 and C_3 + hydrocarbon reactions?

1 A. Bergeat and J. C. Loison, *Phys. Chem. Chem. Phys.*, 2001, **3**, 2038.
2 N. Galland, F. Caralp, M. T. Rayez, Y. Hannachi, J. C. Loison, G. Dorthe and A. Bergeat, *J. Phys. Chem. A*, in press.

Dr Kaiser responded: (1) The very first study of the $C–C_2H_2$ system was performed with the old setup of the 35″ machine (1994–1997) employing diffusion pumps and oil lubricated roughing pumps. Therefore, the background at $m/z = 37$ and 36 was very high. Further, a significant background at $m/z = 36$ came from elastically scattered C_3 which was in the primary beam. Last but not least, the filament in the electron impact ionizer consisted of a tungsten wire coated with carbon; this contributed to the background at $m/z = 36$ as well. The new setup (after the machine was moved from Berkeley to Taiwan) had significant improvements. The filament was replaced by thoriated iridium. In addition, the detector system was equipped with a closed cycle helium refrigerator cold head (4.5 K) which lowered the pressure to $< 8 \times 10^{-13}$ mbar. Second, no diffusion pumps were used; only magnetically suspended turbo molecular pumps for the main chamber as well as both source chambers were utilized, and the main chamber was backed with an oil-free scroll pump. Third, all cables inside the machine were replaced by Teflon-coated wires which had a very low out gassing rate. Fourth, a second 4.5 K cold shield was placed between the interaction region and the chopper wheel. All these four improvements reduced the background at $m/z = 36$ significantly (the only background arises from electronic background which can be eliminated). Finally, the carbon source was modified: the atomic carbon number density was enhanced, and—at the same time—the contribution of C_3 to the elastically scattered background was minimized. These factors together allow a detection of the $C_3 + H_2$ channel which could not have been observed before.

(2) At a collision energy of 16.6 kJ mol^{-1}, it is about 30–40%. However, it is not feasible to compare this branching ratio to ones obtained from kinetic studies. As you pointed out in your paper, your experiments were not performed under single collision conditions. So numerous processes can complicate the true 'binary picture' of a collision as present in crossed beam setups. These are, for example: (a) third body reactions and hence a stabilization of long lived reaction intermediates, (b) collision induced inter-system crossing. So one always has to be very careful to compare these bulk studies with crossed beam data.

(3) As you know, the reactions of atomic, ground state carbon have rate constants in the order of 10^{-10} cm^3 s^{-1}. On the other hand, kinetic data suggest that reactions of tricarbon with unsaturated hydrocarbons are very slow (about 10^{-12} cm^3 s^{-1} and smaller); please refer to the literature cited in our paper presented at this meeting. Based on our experiments, the reaction of tricarbon with acetylene to form atomic hydrogen and CCCCCH is endothermic by about 80 ± 9 kJ mol^{-1}. Therefore, if the scattering experiments are performed at a collision energy of, let's say, 100 kJ mol^{-1}, this channel is open. But the scattering signal of the heavy fragment is confined to a very narrow angular range due to the low amount of energy which can channel into the translational degrees of freedom. So we can say that in principle, once the collision energy is larger than the endothermicity of a channel, this one can be detected in crossed experiments—even if the rate constants from bulk experiments (for example at room temperature) indicate that the reactions are very slow.

Prof. Casavecchia said: With reference to the paper by Kaiser *et al.*, I have a few questions regarding the results for the reaction $C(^3P) + C_2H_2$.

(1) You studied this reaction a few years ago and published the results in several articles.[1–4] Although you never showed TOF spectra at $m/z = 36$ in refs. 1–4, you always stated that the TOF and angular distributions at $m/z = 36$ were identical to those measured at $m/z = 37$, and this result lead you to the conclusion that $C_3H + H$ formation is the only reaction pathway taking place in the $C(^3P) + C_2H_2$ reaction, while formation of $C_3 + H_2$, a spin-forbidden channel, was clearly not occurring. However, I notice that the signal-to-noise of the TOF spectra at $m/z = 37$ reported in the previous articles[1–4] is similar to that exhibited in the spectrum at $m/z = 36$ shown in Fig. 11 of your paper.[5] Since the detector background is expected to be lower at $m/z = 36$ than at $m/z = 37$ (because of the ^{37}Cl isotope), I would have expected you to see the fast peak at $m/z = 36$, attributable to the $C_3 + H_2$ channel, also in the previous experiments. Then the first question is: why didn't you see the two peak structure, as that shown in Fig. 11, in the previous[1–4] measurements?

(2) In your pulsed C beams, obtained by laser ablation of graphite,[6] you have reported the presence of a large concentration of C_2 and C_3, with C_3 being 2.5 times more abundant than C when Ne is used as seeding gas, and 25% of C when He is the seeding gas.[3,6] As a matter of fact, using these beams you can study the reactive scattering of C_2 and C_3, which is the subject of your paper at this meeting. Since we know that C_3 does not react with C_2H_2 at $E_c = 16.6$ kJ mol^{-1}, having a threshold at $E = 80$ kJ mol^{-1},[5] the second question is then: Why don't you see elastically scattered C_3 from the C_2H_2 beam in the TOF spectrum at $m/z = 36$ at $E_c = 16.6$ kJ mol^{-1}? Elastically scattered C_3 should appear as a strong fast peak in the spectrum. I am very puzzled by the absence of the C_3 elastic peak in your spectrum of Fig. 11. What is the explanation? You report in your paper that you have measured TOF spectra from 12 to 72 degrees: can you show us the complete set of data, which are required to derive the CM product translational energy distribution shown in Fig. 12? Furthermore, when you say (footnote 40 in ref. 5) that close to the beam you have an elastic background, what do you mean? You are measuring TOF spectra and if you have elastically scattered particles, these should appear in the spectrum as a peak!

(3) You say that the results at $m/z = 36$ are different from those at $m/z = 37$. Can you show us the corresponding laboratory angular distributions at $m/z = 37$ and $m/z = 36$ that you have used to obtain the results shown in Fig. 12.?

(4) The authors say that by subtracting the collision energy from the high energy cut-off of the $P(E_T)$ (shown in Fig. 12), the reaction is found to be exothermic by 140–150 kJ mol^{-1}, and that this value is in good agreement with a reaction energy of 130–135 kJ mol^{-1} calculated from thermodynamical data (ref. 41). However, if one takes the thermodynamical data, which are rather accurate, one actually finds that the exoergicity of the reaction $C(^3P) + C_2H_2 \rightarrow C_3 + H_2$ is 100–105 kJ mol^{-1}, a value much lower than the value of 140–150 kJ mol^{-1} derived from your experiment. How do the authors explain this significant difference?

Finally, we would like to emphasize that our experiments on the $C(^3P) + C_2H_2$ reaction reported at this meeting,[7] although carried out using C beams containing both $C(^3P)$ and $C(^1D)$, allow a clean determination of the dynamics of the two competing reaction pathways leading to $C_3H + H$ and $C_3 + H_2$ formation. The reason is due (a) to the fact that our continuous C beams do not contain any detectable amount of C_3 which, elastically scattered, would represent a serious inter-

ference in the measurements of reactive signal at $m/z = 36$, and (b) to the high signal-to-noise of the experiment which permitted very clearly differences between the angular distribution at $m/z = 37$ and $m/z = 36$ (see Fig. 11a of ref. 7). Once the data at $m/z = 37$, corresponding to the $C_3H + H$ channel, are analyzed with great sensitivity to derive the CM angular and translational energy distributions for $C_3H + H$ formation from $C(^3P)$ and $C(^1D)$, the data at $m/z = 36$, which are partly derived from fragmentation of the C_3H product detected at $m/z = 37$, can also be analyzed in detail by adding to the components derived from the $m/z = 37$ data analysis, a new component corresponding to the new reaction channel contributing to the $m/z = 36$ signal, that is the $C_3 + H_2$ channel. We have derived a ratio of cross sections $\sigma(C_3 + H_2)/[\sigma(C_3 + H_2) + \sigma(C_3H + H)]$ of 0.3 at $E_c = 29.3$ kJ mol^{-1}. What is the ratio derived at $E_c = 16.6$ kJ mol^{-1} in your study? It would be interesting to know it in order to see how the above branching ratio varies with collision energy.

1 R. I. Kaiser, Y. T. Lee and A. G. Suits, *J. Chem. Phys.*, 1995, **103**, 10395.
2 R. I. Kaiser, C. Ochsenfeld, D. Stranges, M. Head-Gordon, Y. T. Lee and A. G. Suits, *Science*, 1996, **274**, 1508.
3 R. I. Kaiser, C. Ochsenfeld, M. Head-Gordon, Y. T. Lee and A. G. Suits, *J. Chem. Phys.*, 1997, **106**, 1729.
4 R. I. Kaiser, C. Ochsenfeld, D. Stranges, M. Head-Gordon and Y. T. Lee, *Faraday Discuss.*, 1998, **109**, 183.
5 R. I. Kaiser, T. N. Le, T. L. Nguyen, A. M. Mebel, N. Balucani, Y. T. Lee, F. Stahl, P. v. R. Schleyer and H. F. Schaefer III, *Faraday Discuss.*, 2001, **119**, 51.
6 R. I. Kaiser and A. G. Suits, *Rev. Sci. Instrum.*, 1995, **66**, 5405.
7 P. Casavecchia, N. Balucani, L. Cartechini, G. Capozza, A. Bergeat and G. G. Volpi, *Faraday Discuss.*, 2001, **119**, 27.

Dr Kaiser responded: The identity of the TOFs which was stated in the previous articles refers to the *reactively* scattered product. As you know, this does not refer to the background from inelastically scattered tricarbon molecules. There was a significant contribution of $m/z = 36$ from elastically scattered tricarbon in the very first study of this reaction back in Berkeley. For further details, please refer to my answer to Dr Bergeat's question. However, it should be really stressed that there is—in the case of multiple fits—always space for flexibility. Check for instance the data on the backward scattered channel in the C–C_2H_4 system. This backward scattering is very difficult to explain. If this pathway really exists, it should rather be forward–backward symmetric or—as the collision energy increases—forward-scattered.

Dr Bergeat said: The C + C_2H_2 reaction leads to H + C_3H and H_2 + C_3 channels. The last channel is spin forbidden and the adduct lying on the path leading to H + C_3H is quite long-lived, allowing time for inter-system crossing (ISC) (calculations were performed by your group[1,2] and others[3,4]). Our results (less than 53% of H atom produced by the reaction) and the estimation of Casavecchia *et al.* (presented here) under single collision conditions confirm that the ISC is facilitated. However, the C + methylacetylene reaction leads to the formation of around 79% of H atoms. Your previous experiment and the experiment of Casavecchia showed that there is no H_2 elimination. In your article, you mentioned the possibility of an ISC to lead to the formation of CH_4. As the exit channels leading to H + C_3H_3 are strongly exothermic (-177, -132 and -54 kJ mol^{-1}), while in the case of C + C_2H_2, the H elimination is nearly athermic (-1.5 and -8.6 kJ mol^{-1}), do you think that the ISC could be efficient? The experiment of Casavecchia shows that no H_2 is formed. Is it connected with the small ISC probability or with the barrier on the potential energy surface and the possibility of CH_4 production?

1 C. Ochsenfeld, R. I. Kaiser, Y. T. Lee, A. G. Suits and M. Head-Gordon, *J. Chem. Phys.*, 1997, **106**, 4141.
2 A. M. Mebel, W. M. Jackson, A. H. H. Chang and S. H. Lin, *J. Am. Chem. Soc.*, 1998, **120**, 5751.
3 J. Takahashi and K. Yamashsita, *J. Chem. Phys.*, 1996, **104**, 6613.
4 R. Guadagnini, G. C. Schatz and S. P. Walch, *J. Phys. Chem. A*, 1998, **102**, 5837.

Dr Kaiser replied: You cannot compare the H_2 loss channel in the HCCCH intermediate (C–C_2H_2 system) with the H_2 loss pathway from the $HCCCCH_3$ intermediate (C–CH_3CCH system)! The H_2 channel in the acetylene reaction is similar to the CH_4 loss pathway in the methylacetylene reaction. No one expects H_2 loss from $HCCCCH_3$; but a CH_4 elimination might be feasible—if ISC takes place.

Dr Klippenstein said: A BAC-MP4 theoretical study of the decomposition of vinylacetylene (CH_2CHCCH) by Melius *et al.* indicated that the H loss channel actually lies significantly higher in energy than both the $H_2 + HCCCCH$ and $HCCH + H_2CC$: channels.[1] Thus, it is somewhat surprising that you conclude that there are no H_2 products in the $C_2 + C_2H_4$ reaction. This could be due to a looser bottleneck for the H atom loss channel in combination with the high energy of the chemical activation process you have studied. However, I suspect that statistical theories would still predict a significant fraction (*e.g.* 10%) in the other channels. Can you comment on what is the maximum branching to the H_2 channel that is allowed by your experiments.

1 C. F. Melius, J. A. Miller and C. M. Evleth, *Twenty-fourth Symp. (Int.) Combust.*, The Combustion Institute, Pittsburgh, 1992, p. 621.

Dr Kaiser replied: The data on C_2–C_2H_4 presented here are the first data on this system obtained using the crossed beam technique. We mentioned that a detailed data analysis is 'in progress'; we have about 30 Mbyte additional data on C_2–C_3 reactions—at higher signal-to-noise ratio as presented here; unfortunately, they have not been analyzed yet. So stay tuned to find out what these data will tell.

Dr Kaiser addressed Prof. Casavecchia: Recent crossed beam reactions of $C(^1D)$ with unsaturated hydrocarbons acetylene, methylacetylene, propylene and ethylene[1,2] at high collision energies of 48–104 kJ mol^{-1} showed that they follow direct reaction dynamics. Further, all systems are dominated by a $C(^1D)$ *vs.* H exchange pathway to form C_3H, n-C_4H_3, C_4H_5 isomers and C_3H_3 (propargyl). Based on these results it is surprising that Casavecchia *et al.* could not detect any reactive scattering signal from $C(^1D)$ with C_2H_4. Although their collision energy is lower than 48 kJ mol^{-1}, electronic structure calculations predict[2] that at least an H atom elimination pathway should be observable. Since Casavecchia *et al.* performed their experiments with continuous beams of similar velocity, speed ratio and composition, $C(^1D)$ should be present in each beam. Is there any explanation why no reactive scattering signal was observed in the $C(^1D)$–C_2H_4 system?

1 R. I. Kaiser, A. M. Mebel and Y. T. Lee, *J. Chem. Phys.*, 2001, **114**, 231.
2 R. I. Kaiser, T. L. Nguyen, A. M. Mebel and Y. T. Lee, *J. Chem. Phys.*, submitted June 2001.

Prof. Casavecchia responded: Kaiser *et al.*[1] have recently reported a study of the reaction $C(^1D)$ + C_2H_2 at high collision energies ($E_c = 45$ kJ mol^{-1} and 109 kJ mol^{-1}) using pulsed C beams generated by laser ablation of graphite. In their study at the lowest E_c, the C beam appears to contain both $C(^3P)$ and $C(^1D)$, while at the highest E_c only $C(^1D)$.[1] We find it surprising that in that study[1] the C beam corresponding to $E_c = 109$ kJ mol^{-1} is estimated to contain exclusively $C(^1D)$: some $C(^3P)$ should always be present on the basis of simple electronic partition function arguments. In fact, the experimental data at $E_c = 109$ kJ mol^{-1} (see Fig. 4 of ref. 1) do not really permit one to exclude some contribution to C_3H + H formation also from the $C(^3P)$ reaction. We have studied the same reaction at $E_c = 29.3$ kJ mol^{-1} using a continuous beam of C atoms obtained by radio-frequency discharge in a dilute mixture of CO_2 in He and from the analysis presented here,[2] the ratio of concentration of $C(^1D)/C(^3P)$ in the beam appears to be much smaller than in the experiment of Kaiser *et al.*[1] at $E_c = 45$ kJ mol^{-1} (compare Fig. 11(a) of ref. 2 with Fig. 3 of ref. 1; these figures show the relative contribution of $C(^3P)$ and $C(^1D)$ reactions to the same C_3H product detected at $m/z = 37$).

In his comment, Kaiser says that in a similar study on the reaction $C(^3P, {}^1D) + C_2H_4$ at $E_c = 48$–104 kJ mol^{-1} similar results on the $C(^1D)$ reaction were obtained.[3] Unfortunately, the work is not published yet and we don't know what is the relative signal attributable to the $C(^1D)$ and $C(^3P)$ reactions at $E_c = 48$ and 104 kJ mol^{-1}. Presumably, at the lowest E_c the contribution of $C(^1D)$ is again considerably larger than that of $C(^3P)$, while at the highest E_c all the reactive signal is attributed to $C(^1D)$, as in the case of the $C(^3P, {}^1D) + C_2H_2$ reaction. We have studied the C + C_2H_4 reaction at $E_c = 8.8$, 15.9 and 29.7 kJ mol^{-1}. Since the $E_c = 29.7$ kJ mol^{-1} data (see Fig. 11(c) in ref. 2) have been obtained by using a beam similar (*i.e.*, CO_2 seeded in He) to that used for the $C(^3P, {}^1D) + C_2H_2$ experiment (see Fig. 11(a) in ref. 2), we would have expected some contribution also from $C(^1D)$ to the C_3H_3 signal. However, the $m/z = 38$ and $m/z = 39$ angular and TOF distributions could be well fit without invoking any ^1D contribution (see Fig. 11(c) in ref. 2).

Since the best-fit of the angular distribution measured at $m/z = 38$ (and characterized by rather small error bars) is slightly underestimating the last two experimental points at small angles (see Fig. 11(c) in ref. 2), after we submitted the *Faraday Discussion* paper presented here we studied the same reaction at the higher E_c of 37.8 kJ mol^{-1} by using the same C beam while accelerating the C_2H_4 beam by the seeded beam technique. The experimental laboratory angular distribution at $m/z = 38$ is shown in Fig. 2. As can be seen, because of the different kinematics, we are now able to observe the complete fall-off of the angular distribution also at small angles and, clearly, the small angle intensity cannot be accounted for by invoking only the reaction channels leading to $H_2CCCH + H$ and $H_3CCC + H$ from the reaction of $C(^3P)$, as was the case at the lower E_c of 8.8–29.7 kJ mol^{-1}: a small, additional contribution is now needed to fit the data at small angles. In fact, the dashed line in Fig. 2 corresponds to a contribution from the reaction $C(^1D) + C_2H_4 \rightarrow C_3H_3$(propargyl) $+ H$, in a relative amount, with respect to the $C(^3P)$ contributions (dotted and dashed-dotted lines), which is comparable to what we have observed in the $C + C_2H_2$ reaction at the slightly lower E_c of 29.3 kJ mol^{-1}. These results may suggest that the relative cross section $^1D/^3P$ is somewhat different in the reactions with C_2H_2 and C_2H_4, and/or that the $C(^1D)$ concentration in the experiment with C_2H_4 was lower than in that with C_2H_2, something plausible because the radio-frequency power conditions and backing pressure were not exactly the same in the two experiments. Another possible reason for a small $C(^1D)$ contribution to the $C_3H_3 + H$ channel is that the $C(^1D)$ reaction can also lead to other, competitive product channels, as for instance to $C_2H_2(X\,^1\Sigma_g^+) + CH_2$, which has an exoergicity comparable to the $C_3H_3 + H$ channel. Indeed, photodissociation of ground state singlet C_3H_4 (allene) at 157 nm (corresponding to a total available energy similar to that of our experiments) has shown that the C–C bond cleavage channel is sizeable (relative yields for the H, H_2, and CH_2 formation processes were determined to be 1 : 0.15 : 0.27).[4] Since in the experiment at $E_c = 29.7$ kJ mol^{-1} we did not observe the complete fall-off of the lab angular distribution at small angles, and the CM angular distribution from the $C(^1D)$ reaction is expected to be significantly forward peaked (as at $E_c = 37.8$ kJ mol^{-1}), a small contribution of $C(^1D)$ also to the results at $E_c = 29.7$ mol^{-1} cannot be ruled out; however, this contribution would be quite small. On the whole, the results seem to suggest that the relative contribution of $C(^1D)$ increases with E_c with respect to that of $C(^3P)$. This is supported by the fact that the angular distribution at $E_c = 8.8$ kJ mol^{-1} can very well be fitted without invoking any $C(^1D)$ contribution.[5] It should be noted that we were able to observe the fall-off to zero both at small and large angles in the angular distribution at this low E_c,[5] and its width would be quite sensitive to the extra available energy (121.9 kJ mol^{-1}) carried by the
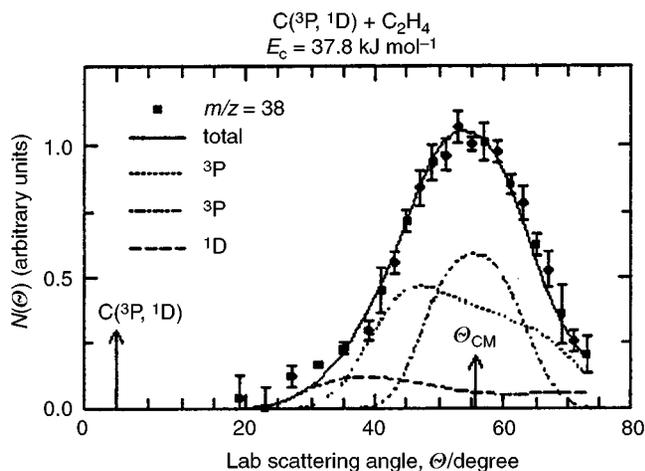
Fig. 2 Product ($m/z = 38$) laboratory angular distribution from the $C(^3P, ^1D) + C_2H_4$ reaction at $E_c = 37.8$ kJ mol^{-1}. The solid line is the total best-fit, dotted and dotted-dashed lines are the contributions (dotted: propargyl formation; dotted-dashed: cyclopropenyl and propyn-1-yl formation) from the $C(^3P)$ reaction, and dashed line is the contribution to propagyl formation from the $C(^1D)$ reaction.

electronically excited C(^{1}D) atom. Also note that the C beam used for the 8.8 kJ mol^{-1} experiment is obtained by seeding CO_2 in Ne and has been shown, from studies of the C(^{1}D) + H_2 reaction,[6] to contain both C(^{3}P) and C(^{1}D).

So, we do not see appreciable C(^{1}D) contribution to the H-displacement channel at $E_c = 29.7$ kJ mol^{-1}, and we start to see a small amount of it at $E_c = 37.8$ kJ mol^{-1}, because our C beam contains little C(^{1}D) (relative to C(^{3}P)) with respect to the pulsed beam used by Kaiser *et al.* at $E_c = 48–104$ kJ mol^{-1}.

Finally, we note that even invoking a small C(^{1}D) contribution in order to fit the data at $E_c = 37.8$ kJ mol^{-1}, the small angle intensity cannot be entirely reproduced (see Fig. 2). This suggests that the H_2 elimination channel may also have some importance in this reaction; in fact, it can be noted that the data in Fig. 2 have been recorded at $m/z = 38$ ($C_3H_2^+$)since the signal-to-noise ratio was higher than at $m/z = 39$ ($C_3H_3^+$). The experimental data shown in Fig. 2 have been obtained by using a very dilute (2%) mixture of C_2H_4 in He, which reduced significantly the signal level given a $m/z = 39$ angular distribution with large error bars. We plan to repeat the experiment with a more concentrated mixture of C_2H_4 in He and plan to compare the $m/z = 39$ and $m/z = 38$ angular distributions to verify whether they are identical (in this case the $m/z = 38$ signal would come only from fragmentation of C_3H_3 in the detector ionizer, corresponding only to the H-displacement channel) or somewhat different at small angles (in this case the $m/z = 38$ signal would partially come from a dynamically different channel, that corresponding to H_2 elimination and leading to $C_3H_2 + H_2$). In regard to the last point, we note that photodissociation of singlet C_3H_4 at 157 nm has been found to lead to both H and H_2 elimination with a ratio of 1 : 0.15,[4] and H_2 elimination from a chemically activated C_3H_4 complex may well occur also.

All this indicates that the dynamics of the C(^{3}P, ^{1}D) + C_2H_4 reaction are rather complex and accurate data at several collision energies are crucial to disentangle them in detail.

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Prof. Plane addressed Dr Kaiser and Prof. Casavecchia: Both of these molecular beam techniques require a high flux of radicals in one of the crossed beams. These are made either by high-powered microwave dissociation (Casavecchia) or by laser ablation of a solid target (Kaiser). Presumably highly excited metastable states are produced by both techniques. What is the evidence that they do not play a significant role in forming the observed reaction products?

Prof. Casavecchia responded: In general, we generate radical beams by high-power, high-pressure radio-frequency discharge.[1–4] In the case of nitrogen and carbon atoms, as well as in the case of oxygen atoms, both ground state (N(^{4}S), C(^{3}P) and O(^{3}P)) and excited state metastable (N(^{2}D), C(^{1}D) and O(^{1}D)) atoms are contained in the beam. However, the nitrogen atom reactions discussed in our paper[5] are endoergic for N(^{4}S) while exoergic for N(^{2}D), so we are only observing products from the excited state atom reactions. In contrast, in the case of C atom reactions, those discussed here[5] are exoergic for both C(^{3}P) and C(^{1}D); in particular, the reactions with unsaturated hydrocarbons are known to be fast both for C(^{3}P) and C(^{1}D). In this case, we observe contributions to formation of the same reaction product from both C(^{3}P) and C(^{1}D). As discussed in our paper,[5] by measuring accurately product angular and velocity distributions and relying on energy and momentum conservation, we are able to separate the distinct contributions of C(^{3}P) and C(^{1}D) to the formation of a given product. This in the past was also done successfully for O atom reactions, such as O(^{3}P, ^{1}D) + H_2S.[1,6] For instance, in the reaction C + CH_3CCH, the C(^{3}P) and C(^{1}D) contributions to formation of $C_4H_3 + H$ are clearly visible in both the laboratory angular and TOF distributions (see Fig. 11(b) of ref. 5), and the CM product angular and translational energy distributions have been derived for both C(^{3}P) and C(^{1}D) reactions (see Fig. 12(b) in ref. 5 for the $P(E_T')$). In conclusion, excited atoms, if present in the beam, do also contri-

bute, in general, to forming the observed product. The extent of the contribution depends on the relative concentration and relative reactive cross section of excited and ground state atoms; this may vary from system to system. Finally, the presence of excited species in these discharge generated beams, although experimentally may in some cases represent a complication when one wishes to study the ground state reactions, offers the exciting opportunity of exploring the reaction dynamics of electronically excited (metastable) atoms, such as $C(^1D)$.

But perhaps you were wondering about the possible role of even more highly excited metastable states, such as $O(^1S)$, $N(^2P)$ and $C(^1S)$. Although these more highly excited states may actually be present in our beams, though in lower concentration than $O(^1D)$, $N(^2D)$ and $C(^1D)$, we have never found evidence of their contribution. Please note that because of the much higher energies involved, their contribution to the observed products would be noticeable in the width of the product angular distribution as well as in the product velocity distributions. This is not surprising since it is well known that $O(^1S)$, $N(^2P)$ and $C(^1S)$, despite their much higher energy content, are much less reactive than $O(^1D)$, $N(^2D)$ and $C(^1D)$, respectively. The reason being that those very excited reactants do not correlate adiabatically with ground state products (for instance, see ref. 1 for O atoms).

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Dr Kaiser responded to Prof. Plane: Yes, laser ablation of solid targets will certainly produce metastable and even long-lived, highly excited Rydberg states. However, the great advantage of pulsed beams compared to continuous sources is that these excited states can be eliminated. Note that excited states are only present in the fast part of the pulsed beam. For example, $C(^1D)$ is present only if the carbon beam is faster than about 3000 m s^{-1}. Likewise, vibrationally excited CN radicals are only present at velocities of more than about 2000 m s^{-1}. However, a chopper wheel located after the ablation zone and after the skimmer can select a part of the pulsed beam in which no metastable species are present. Note that in some cases we can select a fast pulse of the beam to study the reactions of electronically excited species, such as carbon atoms.

Dr Whitaker communicated to Prof. Casavecchia and Dr Kaiser: In the conclusion of their paper Casavecchia *et al.* stress that their recent achievements in the study of elementary reactions by crossed molecular beam (CMB) methods has been made possible by developments in continuous supersonic beam sources and yet Dr Kaiser in his presentation of the equally impressive results obtained for the reactions of di- and tri-carbon with unsaturated hydrocarbons was at pains to point out the importance of pulsed molecular beam sources. Although clearly it is difficult to produce C_2 and C_3 in a continuous beam source for excited atomic reactants. My question to both Prof. Casavecchia and Dr Kaiser is, what are the advantages and disadvantages of each of these sources?

Prof. Casavecchia communicated in response: Continuous and pulsed beam sources have both advantages and disadvantages, depending on the application.[1] Usually, one wishes to use pulsed beams in conjunction with pulsed laser beam generation and/or pulsed laser detection schemes, for obvious reasons. In contrast, in crossed beam experiments with electron-impact ionization mass spectrometric detection, because of the continuous nature of the detection scheme, one wishes, in general, to use continuous beams, for duty cycle reasons, and this has always been done since the development of the technique.[1] However, pulsed beams can also be successfully used in reactive scattering with electron-impact ionization mass spectrometric detection, as the pioneering work of Gentry and coworkers and Lee and coworkers on the $D + H_2$ reaction demonstrated.[2]

More recently, a great deal of reaction dynamics studies have been carried out in Lee's group[3–6] using pulsed beams of C, CN and $O(^1D)$, and in Davis's group[7] using pulsed beams of a variety of transition metal atoms. The main difference, from a practical point of view, between using continuous or pulsed beams in this type of experiments is that with continuous beams one measures directly the product angular distribution by modulating with a tuning fork chopper one of the two beams for background subtraction. Since typical counting times are 50–100 s per angle, by taking 4–5 angular scans one obtains readily angular distributions over a fine grid of angles with high accuracy and small error bars (typically, 1–3%). Then, product velocity distributions are measured by the TOF technique at selected laboratory angles (typical counting times being 20–120 min depending on signal intensity). Since the area of each TOF spectrum at a given lab angle corresponds to the intensity of the angular distribution at that angle, the various TOF spectra can be normalized to an accurate angular distribution. In contrast, in experiments with pulsed beams, one measures only TOF spectra at selected angles (at least, in the applications seen so far), and then derives the product angular distribution by integrating the TOF spectra at each angle. Since the measurement of a TOF spectrum requires a considerable amount of time (from the order of 5–10 min to hours, depending on signal intensity) and 4–5 scans are needed to derive an angular distribution, during this extended period of time fluctuations of experimental conditions may occur. Although this can be taken into account (*i.e.*, by time normalization), the resulting angular distribution is often measured on a sparce grid of angles and is characterized by sizeable error bars (typically 10%).

Of course, there can be valid reasons, and often advantages, for using pulsed rather than continuous beams in CMB experiments with mass spectrometric detection. For instance, photolysis is usually a clean way of generating atoms and radicals, and there may not be other ways to generate these species efficiently in a continuous fashion. For example, generation of $O(^1D)$ by 157 nm laser photolysis of O_2 is very efficient and clean and this has permitted beautiful work in recent years by Yang and coworkers.[6] One great advantage of using pulsed beams is the very low gas consumption: this permits one to carry out studies with isotopically marked pure reagents that are not usually possible using continuous beams. Pulsed laser ablation is perhaps the only way to generate beams of transition metals.[7] Generation of C atoms by pulsed laser ablation is well established since the development of an efficient beam source by Costes *et al.*;[8] this has permitted one to study in recent years the dynamics of a large variety of C atom reactions with unsaturated hydrocarbons.[3,4] However, the error bars of the angular distributions derived for these reactions are often significantly larger than those we have obtained using our newly developed continuous beams of C atoms (compare for instance the results on $C + C_2H_2$ and $C + C_2H_4$ presented here by us[9] and the corresponding results obtained using pulsed C beams[4]). In addition, measurements of angular distributions with continuous beams are typically much faster. On another note, pulsed beams of C atoms generated by laser ablation of graphite are heavily contaminated by C_2 and C_3 species, and perhaps higher C_n clusters.[3,4] However, while this may represent a complication in studies of some C atom reactions, it offers the opportunity of studying the reactive scattering of C_2 and C_3, as reported here by Kaiser *et al.*[10]

In conclusion, there are not in general strict prescriptions on the use of pulsed or continuous beams in CMB experiments with electron-impact ionization mass spectrometric detection. Both types of beams can be used with various degree of success, resolution and accuracy.

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Dr Kaiser communicated in response to Dr Whitaker: The advantages of pulsed beams are as follows.

(1) Pulsed beams are very versatile, and can produce almost any reactive species. Carbon containing radicals for instance C_2D, C_2H_3, C_3H_3 and C_6H_5 which have been easily produced in pulsed beams *in situ* (C_2D), *via* photolysis (C_2H_3 and C_3H_3) and flash pyrolysis (C_6H_5) are extremely difficult to produce in continuous (CW) beams *via* discharge techniques.

(2) Coupling a chopper wheel with a pulsed source allows one to select a part of the pulse and hence get rid of highly excited metastable species in the beam. This is difficult in continuous beams as ground state and excited species might coexist.

(3) The *in situ* production of the cyano and ethynyl radicals *via* pulsed laser ablation of graphite seeding the ablated species in nitrogen or deuterium carrier gas allows us to produce an intense beam of hydrocarbon radicals. This method can be extended very easily to use nitrogen as a carrier gas of ablated boron atoms. This produces a supersonic beam of BN radicals, which are very difficult to make with continuous beams. Likewise, the carbon rod in the pulsed source can be replaced by any material in a rod form—even metals. CW beams might have great difficulties in producing supersonic beams of refractory metal atoms.

(4) Due to the excessive gas load, CW beams require a significant pumping setup and hence large capital investment. The gas load of pulsed beams is lower, and the costs are relatively moderate—especially if the beam sources are going to be operated under completely hydrocarbon-free conditions. Likewise, pulsed valves allow one to perform reactions with expensive reagents, for example deuterated molecules. Except HD of D_2, these experiments might be not fundable for CW sources.

(5) Further developments of the detection schemes in crossed beam setups will certainly involve pulsed laser techniques. Therefore, pulsed sources can always be coupled with pulsed laser detection/production techniques. However, if quasi-continuous, tunable VUV light from, for example, the Advanced Light Source will be used to photoionize the reactively scattered products, CW sources provide a larger duty cycle compared to pulsed valves.

Prof. I. W. M. Smith said: My question is addressed to Dr Kaiser and to others in the audience of a theoretical bent. It concerns the relative reactivities of $C_2(X\,^1\Sigma_g{}^+)$ and $C_3(X\,^1\Sigma_g{}^+)$ to alkenes and alkynes. The experiments and calculations of Kaiser and co-workers, along with those of others, demonstrate that $C_2(X\,^1\Sigma_g{}^+)$ adds to simple unsaturated hydrocarbons over a surface without a potential energy barrier. On the other hand, the addition $C_3(X\,^1\Sigma_g{}^+)$ to the same species is impeded by a substantial barrier. Is there any relatively simple theoretical reason for this large difference in behaviour? The question is not only important in relation to understanding these particular reactions, but also it might help us make sensible guesses at the rate coefficients for other reactions of alkenes and alkynes.

Dr Kaiser responded: Regarding the C_3 reactions, our paper said 'that signal was observed if the collision energy is higher than …'. This means (a) there is an entrance barrier, (b) the reaction to form the observed channel is endothermic or (c) there is an entrance barrier and the reaction to form the observed channel is endothermic. One possibility to understand the different reactivities of dicarbon *vs.* tricarbon might (and it is only a suggestion!) be based on the molecular orbitals in C_2 and C_3, respectively. Both carbon clusters have a $^1\Sigma_g{}^+$ electronic ground state. However, dicarbon has an empty, energetically low lying $3\sigma_g{}^+$ orbital (LUMO, lowest unoccupied molecular orbital) which could be an 'acceptor' for the π electrons of the hydrocarbon. On the other hand, the LUMO of tricarbon is energetically very high, and therefore, might make it difficult to act as an 'acceptor' for the π electrons of the hydrocarbons (this could result in a lower reactivity). I agree, this explanation is only very qualitative.

Dr Mebel added: The reason why C_2 is more reactive toward unsaturated hydrocarbons than C_3 is the following. C_2 has a low lying excited electronic state; the singlet–triplet energy gap in C_2 is less than 2 kcal mol^{-1}. On the contrary in C_3 the energy difference between the ground and first excited electronic states is large. The presence of low-lying excited state usually results in higher reactivity. In this view, one can expect that C_n species with even n should be more reactive than those with odd n.

Prof. Pilling commented: The papers of Casavecchia and Kaiser have shown the determination of channel yields under single collision conditions, with excellent resolution. For applications to combustion, we need to be able to convert this information into rate coefficients, but this is difficult without considerable theoretical analysis. It would be of considerable value to be able to use molecular beam data, and results from reaction dynamics experiments and *ab initio* calculations also, in evaluations of reaction rate data for combustion and atmospheric applications. At present this is not routinely possible, but some way needs to be found to provide the theoretical input into the evaluation process, in order to use a wider range of both experimental and theoretical information.

Prof. S. C. Smith responded: The great value of the crossed-beam data is that it provides 'cleaner' data against which to validate theory, which can then be used to work through *via* calculations to rate constants. Checking theory against thermal data always involves additional uncertainties, particularly in relation to the energy transfer parameters. Crossed-beam data under collisionless conditions provides an important alternative source of validation of parameters which are then used in the theory to go on and calculate rate constants.

Dr Klippenstein said: Ion chemists have been using beam data in theory and modeling of reaction kinetics for many years.

Prof. Casavecchia said: With reference to Prof. Pilling's comment, I fully agree that ways need to be found to better exploit molecular beam data in kinetic evaluations. Unfortunately, this aspect is not trivial because beam experiments are usually carried out under well defined relative collision energy conditions and with (at least partial) quantum state control. At present, the main contribution of our kind of experiments to kinetic evaluations stems from the fact that we can identify unambiguously the primary reaction products and also determine their relative importance under the specific conditions of the experiment. Then the ratio of integral cross sections at a given relative velocity can be approximated to the ratio of rate constants at the temperature corresponding to that average relative velocity.

Prof. Troe commented: In order to make these scattering experiments more useful to kineticists, it would be helpful to have at least a semiquantitative estimate of the absolute cross-sections. The difficulty in obtaining these are well known. Nevertheless, even some tentative information would be helpful.

Dr Kaiser responded: As you know, it is very difficult and time consuming to measure absolute cross sections with currently existing crossed beam setups. However, with significant capital investment and laser based detection/calibration techniques it will certainly be feasible to provide absolute cross sections in modified crossed beam setups in the future.

Prof. Casavecchia responded to Prof. Troe: I agree with Prof. Troe on the usefulness of absolute cross sections for kinetics use. Unfortunately, this is one of the most difficult quantities to measure in scattering experiments with neutral particles. Still, the procedure of using the small angle elastic scattering to calibrate the absolute reactive scale, as it has been used in the past, at least for simple A + BC reactions,[1] may be extended also to polyatomic reactions, if an estimate of the long range van der Waals interaction can be obtained (for instance, from theory or semiemirical rules). The uncertainty of this procedure was typically of a factor of two.[1] Despite the additional complication of heavy fragmentation under electron impact for polyatomic species, it should be possible, with

some effort, to derive semiquantitative estimates of integral reactive cross sections also for polyatomic reactions, as those discussed here.

1   C. H. Becker, P. Casavecchia, P. W. Tiedemann, J. J. Valentini and Y. T. Lee, *J. Chem. Phys.*, 1980, **73**, 2833, and references therein.

Dr Seakins† commented and opened the discussion of Dr Loison's paper: We have studied the kinetics and products of the $CH + O_2$ reaction for some time. There is much in the interesting results of Bergeat *et al.* that we would agree with, but there are some significant differences.

There is agreement in two respects. (a) The overall rate coefficient $(4.40 \pm 0.52) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. (b) There is significant H atom production.

We note three differences. (a) We observe $\sim 90\%$ H atom production. (b) Questions about the 20% yield of OH (although this is partially based on the work of Okada *et al.*, ref. 11 of the paper presented here by Loison). (c) Questions about the significant production of HCO.

Methodology: Bromoform ($CHBr_3$) is photolysed at 248 nm and concentrations of either CH or H are observed by laser induced fluorescence, the latter at 121.6 nm. Fig. 3 (presented here) shows that the kinetics of H atom production (from methane) and CH removal are well correlated, *i.e.* that the H is being produced in the same reaction as CH is removed. This observation is important as the photolysis of bromoform can lead to a variety of other reactive products.

We use a calibration reaction $CH + CH_4 \rightarrow C_2H_4 + H$ to avoid the need for measuring absolute concentrations. The H atom branching ratio is obtained by comparing the final H atom signal strengths (Fig. 4a).

The photolysis of bromoform also has an H producing channel. We account for this by removing any CH with nitrogen ($CH + N_2 \rightarrow HCN_2$) to give us a baseline signal.

In order to make a final quantitative comparison we need to account for the differing signal strengths in the presence of oxygen or methane. We calibrate the system by photolytically generating identical [H] from H_2S photolysis in the presence of either oxygen or methane. (Fig. 4b).

Results: After accounting for both prompt H atom formation and calibrating for both methane and oxygen we measure a branching ratio of H atoms from the $CH + O_2$ reaction of $90 \pm 15\%$. Our current experiments cannot differentiate between H atoms produced from the $H + CO_2$ or
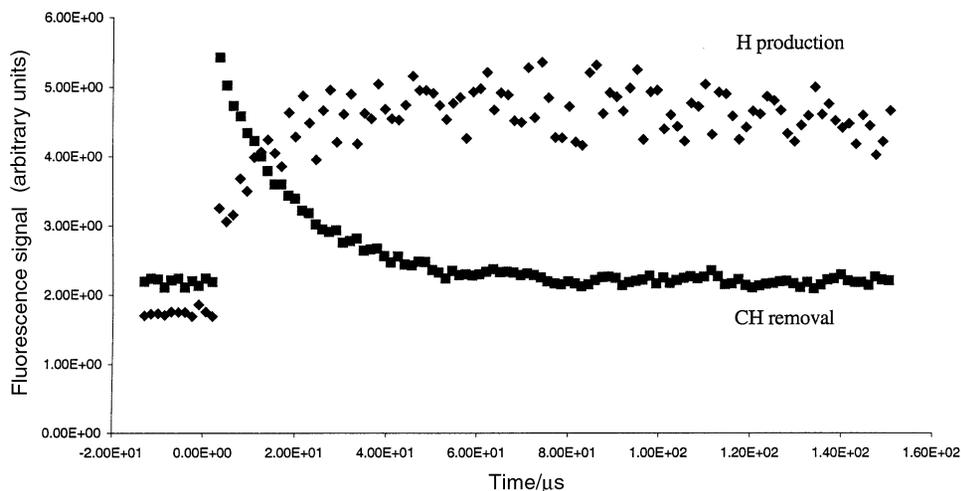
Fig. 3   Correlation of CH removal and H atom production from the $CH + CH_4$ reaction.

† Also Dr M. Blitz (University of Leeds), Dr H. Qian (University of Leeds) and Mr K. McKee (University of Leeds).
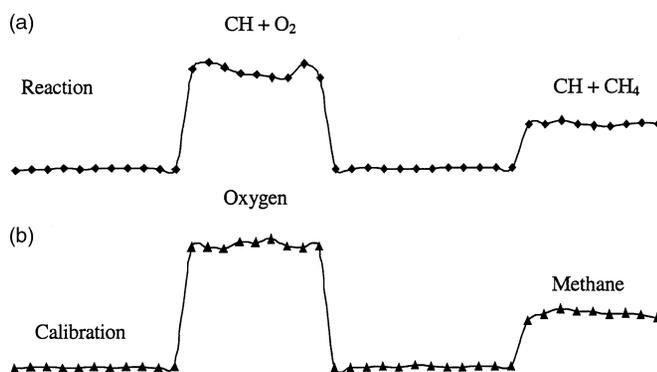
Fig. 4 (a) H atom signals obtained from CH + O$_2$ and CH + CH$_4$. The signal from the CH + CH$_4$ reaction is lower due to absorption of 121.6 nm radiation by methane. (b) Calibration signals for identical [H] in the presence of oxygen and methane.

H + O + CO channel and therefore any comparisons must be with the sum of channels 1 and 4 of Loison's paper, presented here.

Issues and questions: (a) Our current results are incompatible with the 60% yields of channels 1 and 4 reported in Loison's paper.

(b) Could the authors discuss the possibility of C$_2$H reactions influencing their measurements? Any C$_2$H produced in the injector or in the reactor by CH + CH $\rightarrow$ C$_2$H + H could influence yields *via* C$_2$H + O$_2$ $\rightarrow$ HCCO + O, this could lower the H : O ratio. A description of corrections for H atoms produced in the reactor is given in section 3.2 of their paper but no reference is made to corrections for the C$_2$H co-product.

(c) Relative atom yields put onto an absolute basis by comparison with the complex CH + NO reaction. How much uncertainty does this introduce?

(d) The observation of a significant HCO yield is interesting considering the reaction exothermicity and the weak H–CO bond. Does the partial stabilization of HCO under the 2 Torr conditions of the experiment give any information about this channel of the reaction (partition of energy to HCO, lifetime of HCO, ΔE_d)?

(e) Although it is not possible to probe the complete rovibrational manifold of the OH product, do you have any idea about the vibrational distribution?

The experiments discussed in Loison's paper and in this contribution are complex. Error bars are significant and therefore the discrepancies may not be that significant. The two techniques are complementary in approach, a combination of the results may offer the possibility of unravelling the product distribution of this complex and interesting reaction.

Dr Loison responded: During the photolysis of CHBr$_3$ products other than CH(X $^2\Pi$) are produced such as CH(a $^4\Sigma^-$) CHBr, ..., these other products being reactive with O$_2$ and not with CH$_4$ (for example CH(a $^4\Sigma^-$) + O$_2$: $k = 2.6 \times 10^{-11}$ molecules^{-1} cm^3 s^{-1} and CH(a $^4\Sigma^-$) + CH$_4$: $k < 0.07 \times 10^{-11}$ molecules^{-1} cm^3 s^{-1} (ref. 1)) they could be responsible for an extra H production in the CHBr$_3$/O$_2$/hv = 248 nm system *vs.* CHBr$_3$/CH$_4$/hv = 248 nm. Then I think that your result of 90 $\pm$ 15% of H atoms production is greatly influenced by these secondary reactions.

C$_2$H is indeed produced in the micro-furnace and in the fast flow reactor with a maximum ratio of 15% *vs.* the CH production. As C$_2$H + O$_2$ could give H and O atoms, and as the global rate constant of the C$_2$H + O$_2$ is equal to 3.0 $\times$ 10^{-11} molecules^{-1} cm^3 s^{-1}, we studied this reaction, producing C$_2$H by C$_2$HCl$_3$ + 3K. We found, in preliminary results, that about 35% of H atoms and 25% of O atoms are produced in the C$_2$H + O$_2$ reaction. Then this reaction could contribute less than 6% of H atoms and 4% of O atoms in the CH + O$_2$ reaction studies in our experimental conditions and then is included in the systematic error.

We compare the H atom production of the CH + O$_2$ reaction not only with CH + NO reaction, but also with CH + CH$_4$ and CH + H$_2$ reactions (this correction has been made in the article).

HCO has been probed by LIF (laser induced fluorescence) using the B(0,0,1)–X(0,0,0) transition near 251.5 nm, and no vibrational hot band has been detected. Nevertheless, no systematic study on the vibrational distribution HCO has been made, and therefore we don't know the energy partition precisely. The branching ratio of 8–30% on HCO production has been found with the supposition that the HCO probed was relaxed at 300 K. The lifetime of HCO above its dissociation barrier is very short (less than 1 ps) but HCO could have a very long lifetime. In our experiment we probe only HCO(0,0,0) relaxed at 300 K and in this state it's lifetime is much more than the time scale of the fast flow reactor which is typically 1 ms. Then we found that 60% of the HCO is dissociated in H + CO, and 40% is stabilized by collisions at 300 K. Of course at combustion temperature, the part of HCO dissociated will be higher.

The CO + OH channel is exothermic by 6.92 eV and only the $v'' = 0$ and a part of $v'' = 1$ could be probed by LIF due to predissociation of the excited state and we didn't try to probe OH by LIF. The only information on the OH energy distribution is the absence of the Meinel bands (ref. 31 of our paper) which are overtone transitions in fundamental state of OH in the 550–850 nm range, indicating that the high vibrational levels ($v'' = 4$–9) of OH (X $^2\Pi$) are not strongly populated.

Even if this reaction seems simple, it appears quite complex to study and we agree with Dr Seakins that complementary approaches will help provide a good description of the CH + O_2 reaction.

1   *J. Phys. Chem.*, 1992, **96**, 5685.

Dr Bergeat said: Your results on the CH + O_2 reaction are based on the comparison with the CH + CH_4 reaction. Can you confirm that the CH + CH_4 reaction leads only to H + C_2H_4 ? The CH production is performed by photolysis of $CHBr_3$. What are the other products of the photolysis? The source was used by other groups to study C, CBr, CHBr .... Have you any estimation of the secondary reaction contributions (like CHBr + CH_4, CBr + CH_4 ...)? Have you any idea of the quartet CH production and contribution in your experiment?

Dr Seakins replied: As far as we are aware H + C_2H_4 is the sole channel for the reaction. The negative temperature dependence of the overall kinetics of the CH + CH_4 reaction rules out the endothermic CH_2 + CH_3 reaction. One other possible set of exothermic products would be C_2H_3 + H_2, however, this would require either a three or four centered elimination reaction from an ethyl intermediate and we do not believe that this would compete with the simpler H atom elimination. Strictly speaking our reported yields are referenced to the H atom yield from the CH + CH_4 reaction, and whilst we believe this to be 100%, the possibility of other minor channels does exist.

Bromoform is not an ideal source for photolysis, as there will be other photolysis products, but we believe it is the best available for our technique. Our rationale for ignoring the effects of such species is two-fold. Firstly the kinetics of CH removal and H atom production are well correlated. Halogenated species such as CHBr or CBr are likely to react on a slower timescale than the more reactive CH radical. Secondly, the most likely elimination channel from the formation of any halogenated intermediate product would be the elimination of a bromine atom, rather than an H atom. Thus for both kinetic and mechanistic reasons, we believe that secondary reactions of bromoform co-photolysis products will not affect our H atom yield.

We have not looked at the effects of quartet CH on H atom production and this is something that we should address. Once again, however, the correlation of H atom production and CH(X) removal seems to indicate that the dominant source of the observed H atom production is the CH(X $^2\Pi$) radical.

Dr Klippenstein commented: The CH + O_2 system is again amenable to direct dynamics simulations due to the great exothermicity of the various product channels. In these simulations the classical equations of motion for the nuclei are solved *via* numerical propagation with the time dependent forces directly determined from *ab initio* quantum chemical simulations. The B3LYP/6-31G* method, which generally provides at least a qualitatively meaningful description of the global energetics, was again employed for the direct determination of the forces.

For this system, I have focused on the question of the branching between the various product channels for the dynamics on the doublet electronic state. The procedures employed are essentially identical to those described in my comment on the $CH_4 + N(^2D)$ reaction. 48 trajectories were propagated, with a typical trajectory lasting for 100–200 fs. The trajectories were initiated at a CH to O_2 center-of-mass separation of 4.0 a_0 and were terminated when any atom–atom separation exceeded 10.0 a_0.

For $J = 25$, at an energy of 12.6 kcal mol^{-1} above the zero-point energy of the reactants, these simulations predict a branching of $0.42 : 0.25 : 0.19 : 0.15$ for the $CO + OH : HCO + O : CO_2 + H : CO + O + H$ channels. Interestingly, there appears to be a highly non-statistical branching to the much less exothermic $HCO + O$ channel. Correspondingly, it is not necessary to incorporate a significant contribution from the quartet state to explain your observed population in the $HCO + O$ channel.

However, one should note that these trajectory predictions are for the nascent distribution. In many instances the HCO molecules are produced with an internal energy that exceeds the dissociation threshold. As a result, longer timescale observations would find less HCO and more $CO + O + H$. By the same token, we also observe that even some of the OH fragments have an internal energy that exceeds its dissociation threshold and some of the CO_2 fragments might also. Thus, a direct correlation with your experimental results should also consider the internal energy distribution and ultimate fate of the nascent products.

Dr Loison replied: The direct dynamics simulations made by Dr Klippenstein are very interesting. The main difference with our work is the fact that the doublet surface could lead to the $HCO + O$ channel, for 25% on one doublet surface and thus between 6 and 12% on the total of the reaction. This is not a major change and should be confirmed. The most surprising result is the ratio of $OH + CO$ *vs.* $H + CO_2$. This may be due to the fact that at 4.0 Å the long range part of the $CH + O_2$ potential could not be described by the B3LYP/6-31G* method. I think that these calculations should take into account the two doublet surfaces with precise description of the long range part. The calculation of energy distribution of the nascent products should also be very interesting.

Prof. Kohse-Höinghaus asked: (1) I wonder how clean your source of CH really is—would reactions including $K + O_2$ or O with bromoform affect your chemistry?

(2) The overall reaction rate of $CH + O_2$ in your paper is found to be independent of temperature at high temperatures (*i.e.* approximately 2000 K). It is intriguing to see that Desgroux *et al.*, in their paper to be presented at this meeting, discuss their CH measurements in a low pressure flame, in agreement with previous work, with respect to a potential temperature dependence of the $CH + O_2$ reaction in this temperature range around 2000 K. Would this finding indicate a conflict with your investigation?

Dr Loison replied: We do not make any investigation at high temperature and extrapolation of measurements to temperatures above 1000 K should be done with great care. The overall reaction rate of $CH + O_2$ is equal to 5.5×10^{-11} molecules^{-1} cm^3 s^{-1} (ref. 1) in the 300–2000 K range, but the direct measurements are only in the 15–700 K temperature range. Two recent combustion experiments[2,3] find a rate constant of 1.2–1.6×10^{-10} molecules^{-1} cm^3 s^{-1} near 2000 K. That could be due to the crossing of the first $^4A''$ surface (repulsive in C_s symmetry) and the second $^4A'$ surface (coming from $CH(a^4\Sigma^-) + O_2(^3\Sigma^-)$) this crossing being avoided in C_1 symmetry leading to an entrance channel with a quite high barrier, and thus this channel will be open only at high temperature.

1   *J. Phys. Chem. Ref. Data*, 1992, **21**, 411.
2   M. Rohrig, E. L. Petersen, D. F. Davidson, R. K. Hanson and C. T. Bowman, *Int. J. Chem. Kinet.*, 1997, **29**, 781.
3   M. W. Markus, P. Roth and T. Just, *Int. J. Chem. Kinet.*, 1996, **28**, 171.

Prof. Plane asked: The method of using atomic K to strip Br atoms successively from $CHBr_3$, thereby producing CH radicals, is very elegant. One possible problem may arise from having to

mix $CHBr_3$ with an excess of K. The remaining K will enter the flow tube and recombine with O_2 to produce KO_2. Does this play a significant role in the observed kinetics?

Dr Loison replied: In our source, K–bromoform and O_2 are in separated parts. We produce CH in a microfurnace with only $CHBr_3$, K and He with an excess of K (typically 1 mTorr in the microfurnace). Then the only K reactions in the microfurnace are $CHBr_3 + 3K \rightarrow CH + 3KBr$. Some of the K could escape from the microfurnace (less than 0.1 mTorr), with CH radicals, but the only possible reaction of K is adduct production such as $K + O_2 + M \rightarrow KO_2 + M$, $K + O + M \rightarrow KO + M$, $K + CH + M \rightarrow KCH + M$ reaction with rate constant equal to 8×10^{-30} cm^6 molecule^{-2} s^{-1} for the $K + O_2 + N_2$ and then at 1.4 Torr (4.6×10^{16} molecule cm^{-3}) we estimate the global rate constant of this reaction with He as a bath gas to be 2.0×10^{-13} molecule^{-1} cm^3 s^{-1} and thus negligible under our conditions for the consumption of any species (O_2, O, H or CH) and the small amount of KO_2 adduct produced (less than 0.003 mTorr) will not perturb the reaction (for example the $KO_2 + H \rightarrow HO_2 + K$ or $KO_2 + O \rightarrow O_3 + K$ are absolutely negligible as KO_2 is at least 300 times less concentrated than O_2, even if the global rate constant of this reaction is equal to the $CH + O_2$ one.

Dr Miller commented: An important finding of this paper is the theoretical result that the reaction can occur on both the doublet and quartet surfaces *with no energy barrier*. I wonder if this might be the reason that the shock tube experiments (ref. 19 and 20 of the paper) yield rate constants that are much higher than those of the low-temperature experiments (ref. 6, 12 and 13 of the paper). Perhaps the reaction takes place predominantly on the doublet surface at low T, with both surfaces contributing at high T.

Prof. Pilling opened the discussion of Dr Miller's paper: Miller and coworkers have discussed the application of eigenvector, eigenvalue analysis to master equations. The following comments refer to the process of relating the eigenvalues to the rate coefficients for the chemical system under study.

For reactions involving a single reactive process, such as dissociation, the unimolecular rate coefficient can be equated to the modulus of the eigenvalue of smallest magnitude, λ_1, so that $k_{uni} = -\lambda_1$. The eigenvalues of larger magnitude are related to collisional relaxation processes and refer to the relaxation of the system to a steady state population distribution over the energy states. Problems arise at high temperatures, especially for molecules with small dissociation energies, because λ_1 becomes so large that it is comparable in magnitude with the larger eigenvalues and the separation of chemical and collisional timescales is no longer possible: the system does not relax to a steady state distribution on a time short compared with dissociation and the reaction rate coefficient cannot simply be equated to $-\lambda_1$.[1] This problem also applies to more complex multi-well systems and has been discussed by Tsang *et al.*[2] in relation to alkyl radical isomerisation and dissociation.

For reactions with several wells and reaction channels, and with the eigenvalues related to chemical reaction well separated from those associated with collisional relaxation, a matrix G_{chem} can be factored out whose eigenvalues are related to the rate coefficients for the component chemical reactions. This relationship can be direct, with the modulus of the eigenvalue equal to the first order rate coefficient, or may be more complicated. The question arises as to what affects this relationship and how easily can the rate coefficients be related to the eigenvalues.

For the purposes of this comment, it is easiest to consider a more general situation of a complex reaction whose kinetics are defined by the coupled rate equations $(dc/dt) = G_{chem} c$ where c is a vector of concentrations of chemical species and G_{chem} is a matrix of first order (or pseudo first order) rate coefficients connecting the species; we order c according to the lifetimes of the species, with the shortest-lived occurring first. The diagonal elements of the matrix are minus the sum of the first order rate coefficients for removal of the species. The lower triangular section of G_{chem} contains the rate coefficients for processes that 'feed forward' from shorter-lived to longer-lived species, while the upper section relates to 'feed back' processes from longer- to shorter-lived species. If all the elements in the upper triangular section of G_{chem} are zero, *i.e.* if there is no feed back, the moduli of the eigenvalues of the matrix are identical to the diagonal elements and the relationship between the eigenvalues and the rate coefficients is a simple one. This situation

remains true for species with only zero elements in the upper section of the appropriate row of G_{chem} and is approximately true if the species responsible for the feed back are *much* longer lived than the species under consideration.[3] In all other situations, the relationship is more complex. This situation arises in two of the posters we have presented, on alkyl radical isomerization and dissociation,[4] and on $H + SO_2$.[5] It is important that the problem is analysed to define chemical networks that can describe the system and to provide the associated rate coefficients. We have done this through a classical kinetic analysis of the coupled rate equations,[4,5] but this is not the only, or even the most direct, way. The component rate coefficients may depend on both temperature and pressure and must be represented in a form that can be used readily by combustion modelers—presumably a Troe or modified Troe format.

1 H. O. Pritchard, *The quantum theory of unimolecular reactions*, Cambridge University Press, 1984.
2 W. Tsang, V. Bedanov, M. R. Zachariah, *Ber. Bunsen-Ges. Phys. Chem.*, 1997, **101**, 491.
3 N. Bell, M. J. Pilling and A. S. Tomlin, *J. Phys. Chem.*, submitted.
4 L. D. Jones, L. C. Jitariu, I. H. Hillier, S. H. Robertson and M. J. Pilling, poster presented at this meeting.
5 M. A. Blitz, K. J. Hughes and M. J. Pilling, poster presented at this meeting.

Dr Miller responded: I agree, more or less, with everything you say. We have discussed in several places how to extract rate coefficients from an eigenvector/eigenvalue analysis (*e.g.* ref. 18 and 36 of our paper, the paper itself and my comment following the paper by Frankcombe and Smith). In ref. 36 we extracted pressure and temperature dependent rate constants in the Troe format for the three reactions,

$$C_2H_5 + O_2 \rightarrow C_2H_5O_2,$$

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2,$$

and

$$C_2H_5O_2 \rightarrow C_2H_4 + HO_2.$$
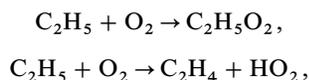
With the corresponding equilibrium constants, these three rate constants completely describe our master equation results to reasonable accuracy.

Although I have wavered on this point at times, I believe that, as long as Δx_R is -1 in eqn. (29) of the paper for some eigenvector of G, that eigenvector describes an elementary reaction (perhaps with several product channels), and the associated eigenvalue can be used to extract the corresponding phenomenological rate constants. Such an identification is legitimate, in my opinion, even though the products indicated by eqn. (29) may require a complex to pass over several potential wells and suffer many collisions over each of those wells.

Prof. Troe said: For kinetics modellers it would be helpful not only to have energy profiles from the given calculations but also rotational constants (or structures) and frequencies at the stationary points. In this way, the provided rate calculations could be modified, adapted or corrected whenever new information or better methods become available. Likewise centrifugal barriers $E_0(J)$ should be given explicitly for the addition processes such that proper falloff curves for the addition processes including anharmonicity effects could be calculated.

Dr Miller replied: We would be happy to provide rotational constants and vibrational frequencies upon request. In fact, we could simply provide the VARIFLEX input files. However, centrifugal barriers are determined implicitly and used internal to the code; they are not part of the input.

Prof. Golden said: The question of how evaluators should represent data for modelers, prompts me to point out that evaluation of data needs considerably more support. This difficult task must be undertaken by researchers with experimental experience. It seems a colossal waste of resources to fill journals and the web with unevaluated data. Researchers themselves and funding agencies must put a higher value on these activities.

Prof. Troe addressed Dr Miller: (1) You show that there are shallow entrance wells in some addition reactions of O_2. Are these kinetically relevant? Are the determining activated complexes the inner maxima?

(2) Why do the 2-d and 1-d master equation calculations of the addition reaction in the low pressure limit give such different results? Could you provide the limiting termolecular rate constants?

Dr Miller replied: (1) The inner maximum is the bottleneck.

(2) Although the 2-d master equation predicts non-equilibrium J distributions, I believe the major effect is simply one of conserving angular momentum between the molecule and the transition state, *i.e.* a certain amount of '$BJ(J + 1)$' energy is tied up in conserving angular momentum and cannot be used to break the bond. Remember that our formulation is in terms of E and J, where E is the *total energy* of the molecule, and not in terms of ε and J, where ε is the energy in the active degrees of freedom. In the latter formulation, one would expect the 2-d model to give larger rate constants than the 1-d model, because the effective rotational constant is smaller at the transition state than for the molecule, thus freeing some 'rotational energy' to be used to break the bond.

In the present problem k_0 (2-d) at $T = 295$ K is 2.97×10^{-30} cm^6 molecule^{-2} s^{-1} and k_0 (1-d) is 1.12×10^{-29} cm^6 molecule^{-2} s^{-1}. The difference is a factor of about 3.8.

Prof. S. C. Smith said: (a) There is a perturbational extension of the Smith–Gilbert rotationally averaged master equation which deals with weak-collisional relaxation of the angular momentum. This is described in ref. 1 in the context of ion–molecule association modelling.

(b) Have you explored the possibility of applying the Smith–Gilbert rotationally averaged master equation for multi-well systems?

1 S. C. Smith, M. J. McEwan and R. G. Gilbert, *J. Chem. Phys.*, 1989, **90**, 1630.

Dr Miller responded: (a) I am aware of your paper, but I prefer our variant of the original Smith–Gilbert method. By taking E and J as the independent variables in the master equation, rather than ε and J, we are able to take into account weak-collisional relaxation of the angular momentum approximately with a method that is as simple mathematically as the Smith–Gilbert strong-J model.

(b) If either the Smith–Gilbert rotationally averaged master equation or our variant of it is used unaltered in a problem where reaction must be allowed to take place in both directions, detailed balance is not satisfied and significant errors can result. This situation occurs because extra terms appear in the equations when one sums the 2-d master equation over J. However, it should be possible to solve the resulting equations in this case by an iterative procedure, but we have not yet attempted to do this.

Prof. Lin said: The energy transfer step-size you employed for N_2, $\langle \Delta E_{down} \rangle = 500$ cm^{-1}, seems rather large to me. In our recent modeling of the OH + CO reaction, we obtained a value of 250 cm^{-1} for N_2.[1] A similar value (270 cm^{-1}) has been used by Gilbert and coworkers[2] for the decomposition of C_4H_9Br.

1 R. S. Zhu, E. W. G. Diau, M. C. Lin and A. M. Mebel, *J. Phys. Chem.*, accepted.
2 T. C. Brown, K. King and R. G. Gilbert, *Int. J. Chem. Kinet.*, 1988, **20**, 549.

Dr Miller answered: We deduced $\langle \Delta E_d \rangle = 500$ cm^{-1} from modeling the fall-off curve of Atkinson and Hudgens (ref. 16 of the paper) at 295 K using the 2-d master equation and assuming a single exponential-down model for the energy transfer function; we also used Lennard-Jones potentials to calculate Z, the collision rate. In a similar analysis of $H + O_2 + N_2 \rightarrow HO_2 + N_2$ at room temperature, we deduced a value of $\langle \Delta E_d \rangle = 300$ cm^{-1}. For $H + NO + N_2 \rightarrow HNO + N_2$ we deduced $\langle \Delta E_d \rangle \approx 500$ cm^{-1}. However, in both these cases the difference between 300 cm^{-1} and 500 cm^{-1} was less than 20% in the rate constant. Moreover, I do not think it unreasonable that different molecules could transfer different quantities of energy in collisions with N_2, particularly if larger molecules are concluded to transfer more energy than smaller ones. The values of $\langle \Delta E_d \rangle$ that we (and everyone else) deduce from modeling dissociation/recombination reactions

apply only to energies of the molecule near the dissociation limit. The value of $\langle \Delta E_d \rangle$ probably depends on just how high the dissociation limit is above the ground state. My point is that $\langle \Delta E_d \rangle$ is not a fundamental constant for a given collider gas.

Your question brings to mind a more practical issue. Typically, one deduces $\langle \Delta E_d \rangle$ from an RRKM/master equation model using a single exponential-down energy transfer function, a harmonic-oscillator/rigid-rotor model to calculate the density of states, and Lennard-Jones potentials to calculate Z. All three of these assumptions could be questionable under certain conditions. Including anharmonicities will cause the $\langle \Delta E_d \rangle$ values inferred to be slightly smaller, perhaps more than slightly in some cases. Clearly, $\langle \Delta E_d \rangle$ depends somewhat on the form of $P(E,E')$, although such a dependence may be more important for chemically activated or photo-activated systems than for thermally activated ones. Also, Z may not be accurately described by Z_{LJ}. Classical trajectory calculations[1,2] seem to indicate that Z should be about 25% or more larger for ordinary colliders and that it may depend on E and J as well as T. Experiments[3] clearly show that Z should be *much larger* if water is the collider. A slightly more subtle effect, commonly omitted from analyses, is that $\langle \Delta E_d \rangle$ may depend on $J^{1,4,5}$ as well as E and T.

1 N. J. Brown and J. A. Miller, *J. Chem. Phys.*, 1984, **80**, 5568.
2 G. Lendvay and G. C. Schatz, in *Advances in Chemical Kinetics and Dynamics. Vol. 2: Vibrational Energy Transfer Involving Large and Small Molecules*, ed. J. R. Barker, JAI Press, Greenwich, CT, 1995, p. 481.
3 K.-J. Hsu, J. L. Durant and F. Kaufman, *J. Phys. Chem.*, 1987, **91**, 1895; K.-J. Hsu, S. M. Anderson, J. L. Durant and F. Kaufman, *J. Phys. Chem.*, 1989, **93**, 1018.
4 A. Gelb, *J. Phys. Chem.*, 1985, **89**, 4189.
5 S. Nordholm and H. W. Schranz, in *Advances in Chemical Kinetics and Dynamics. Vol. 2: Vibrational Energy Transfer Involving Large and Small Molecules*, ed. J. R. Barker, JAI Press, Greenwich, CT, 1995, p. 245.

Prof. Wolfrum opened the discussion of Dr Taatjes' paper: Did you observe the formation of heterocyclic compounds due to isomerization steps in your experiments?

Dr Taatjes responded: We are unable to directly observe the formation of heterocycles in our experiments. However the amount of OH suggested by the non-unity yield of HO_2 in our experiments, and implied by separate OH LIF measurements in our laboratories, is broadly consistent with the heterocycle branching fractions deduced from literature measurements of the initial products of butyl + O_2 reactions.[1]

1 See, *e.g.*, R. W. Walker and C. Morley, in *Low-Temperature Combustion and Autoignition*, ed. M. J. Pilling, *Comprehensive Chemical Kinetics*, Elsevier, Amsterdam, 1997, vol. 35, p. 1–124, and extensive references therein.

Prof. Griffiths asked: (1) In order to understand the chain branching processes that occur during alkane oxidation at low temperatures in a quantitative way, it is important to establish the extent to which RO_2 isomerises to QOOH and then dissociates to generate OH radicals, or acquire another O_2 to create diperoxy species. Are you able to deduce this information from your fraction Φ (Table 2) that leads to HO_2 radicals?

(2) From your data are you able to quantify the kinetic origins of the much greater reactivity of n-butane relative to that of isobutane leading to spontaneous ignition?

Dr Taatjes answered: The HO_2 yields measured in our experiments are an effective yield for the overall oxidation. They reflect a competition between HO_2 elimination from RO_2 and other removal processes for RO_2 and are not necessarily directly interpretable as the branching fraction of an elementary reaction. The rise in HO_2 yields with temperature in the transition region represents the onset of thermal instability of the RO_2 species. Further, the production of OH, which occurs to a significant extent in the butyl + O_2 reactions, tends to produce HO_2 eventually because of the regeneration of butyl radicals *via* the OH + butane reaction. Nevertheless, the fact that the yield of HO_2 remains significantly below 100% even at the highest temperatures of this study implies a contribution from other bimolecular channels, *i.e.*, isomerization to QOOH, followed by dissociation to OH + heterocycle (or by reaction with O_2, also producing OH). A qualitative, though naïve, estimate of the branching to these channels is given by $(1 - \Phi_{total})$ at temperatures above the transition region, which would suggest OH fractions of approximately

15–20% near 700 K. However, because the recycling reaction of OH with butane will tend to inflate the HO_2 yield, the true branching fraction will be larger than this estimate. For comparison, initial product measurements imply $\sim 35\%$ branching to OH-producing channels from *n*-butyl and *sec*-butyl reactions with O_2 at 753 K.[1,2] A positive activation energy for branching to oxirane + OH relative to $C_2H_4 + HO_2$ has been observed in the ethyl + O_2 reaction,[3] and might also be expected for the analogous channels in the butyl + O_2 reactions. Combined modeling of time-resolved OH measurements and our HO_2 signals from Cl-initiated butane oxidation may permit a more precise branching determination.

As to the different ignition behavior of the two butane isomers, the present experiments using Cl-initiated oxidation provide only qualitative suggestions. The individual butyl isomers may not be formed by Cl-initiation in the same ratio as occurs in spontaneous ignition, so direct quantitative comparison between the two systems can be difficult. For example, the combustion behavior of isobutane may have a larger contribution from the *tert*-butyl radical (which produces almost exclusively alkene + HO_2 in its reaction with O_2) than does our Cl-initiated oxidation. However, we certainly hope that our calculations, coupled with validation on test systems such as Cl-initiated oxidation, can contribute to improved modeling of ignition and related phenomena.

1   R. R. Baker, R. R. Baldwin, A. R. Fuller and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 736.
2   R. R. Baker, R. R. Baldwin and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 756.
3   R. R. Baldwin, I. A. Pickering and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 2374.

Prof. Golden asked: Can there be any contribution from the simple abstraction process?

Dr Miller responded: We have calculated the abstraction rate constant for alkyl + O_2 reactions only for ethyl + O_2. In this case the abstraction has a barrier of ~ 18 kcal mol^{-1}, and the rate constant is about a factor of ten smaller than that for the $C_2H_5 + O_2 \rightleftharpoons C_2H_5O_2^* \rightarrow C_2H_4 + HO_2$ mechanism at 2000 K. The abstraction is even less significant at lower temperatures.

Dr Seakins communicated to Dr Taatjes: One complication in your analysis of experimental data is the generation of multiple butyl and propyl fragments during the initial chlorine atom abstraction. What effect does this have on the quantitative data that can be obtained from the experimental results?

One possible method of eliminating this would be to use the less reactive, and hence more selective bromine atom to initiate the reaction. For example at 621 K, Br atoms react with n-butane and isobutane to give 96 and 98% of *sec*-butyl or *tert*-butyl respectively.[1] The disadvantage is that the rate coefficients are significantly slower than for Cl atom abstraction, but if your signals are not affected by hydrocarbons, then you can drive the pseudo-first-order rate coefficient to comparable levels by increasing the butane concentrations. The high activation energies of bromine atom reactions will however limit the temperature range of study. Bromine atoms react in a similar manner to chlorine with methanol[2] so you would still in principle use the same calibration reaction.

1   P. W. Seakins, M. J. Pilling, J. T. Niiranen, D. Gutman and L. N. Krasnoperov, *J. Phys. Chem.*, 1992, **96**, 9847.
2   S. Dobe, T. Berces, T. Turanyi, F. Marta, J. Grussdorf, F. Temps and H. Gg. Wagner, *J. Phys. Chem.*, 1996, **100**, 19864.

Dr Taatjes communicated in response: The production of multiple isomers is a complication for detailed quantitative modelling. The derivation of structural effects on isomerization and elimination pathways in RO_2 would be greatly facilitated by measurements on individual isomers. In this connection the use of Br initiation is an excellent suggestion. We had briefly considered the use of bromine atoms but were daunted by the relatively low rate coefficients for Br + hydrocarbon reactions. However, as you point out, the Br-initiated scheme would become more useful precisely in the elevated temperature range where the important kinetic phenomena of QOOH formation and HO_2 elimination occur. We will certainly consider this method in our future studies.