Article:

Brook, R., Bramley, O., Makhov, D. et al. (7 more authors) (Accepted: 2025) Rules of triplet state electron impact neutral dissociation in plasma from molecular dynamics simulations and an electrophore model. Journal of Vacuum Science & Technology A. ISSN 0734-2101 (In Press)

Supplementary material:
Rules of triplet state electron impact neutral dissociation in plasma from molecular dynamics simulations and an electrophore model

Running title: Triplet State Electron Impact Dissociation in Plasma

Running Authors: Brook et al.

Ryan Brook [1,a)] Oliver Bramley [2], Dmitry V. Makhov [1], Anna Nelson [2], Gregory Armstrong [1], Joseph Yong [1], Ezri Saunders [1], Johnny de Viggiani [1],
Jonathan Tennyson [2,3] and Dmitrii V. Shalashilin [1,b)]

[1]School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom

[2]Quantemol Ltd., 320 City Road, The Angel, London EC1V 2NZ, United Kingdom
[3]Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom

a) Electronic mail: cm18rb@leeds.ac.uk
b) Electronic mail: d.shalashilin@leeds.ac.uk

Our previous letter[4] showed that relaxation to the lowest triplet state is very fast and, therefore, the trajectories run on the lowest lying triplet state are sufficient to produce valid data leading to accurate conclusions. While spin-flip TD-DFT was employed to properly manage the multiple excited triplet states and the non-adiabatic coupling between them, it is natural to employ a cheap and simple standard DFT method when only one lowest triplet state is considered. In order to test the consistency, trajectories are first run at 5000 K using spin-flip TD-DFT before rerunning the same initial conditions without the inclusion of spin-flip. After confirming that both spin-flip and non-spin-flip simulations yield sufficiently comparable results, we then proceed to run trajectories at lower temperatures using only the much cheaper standard DFT force calculations.

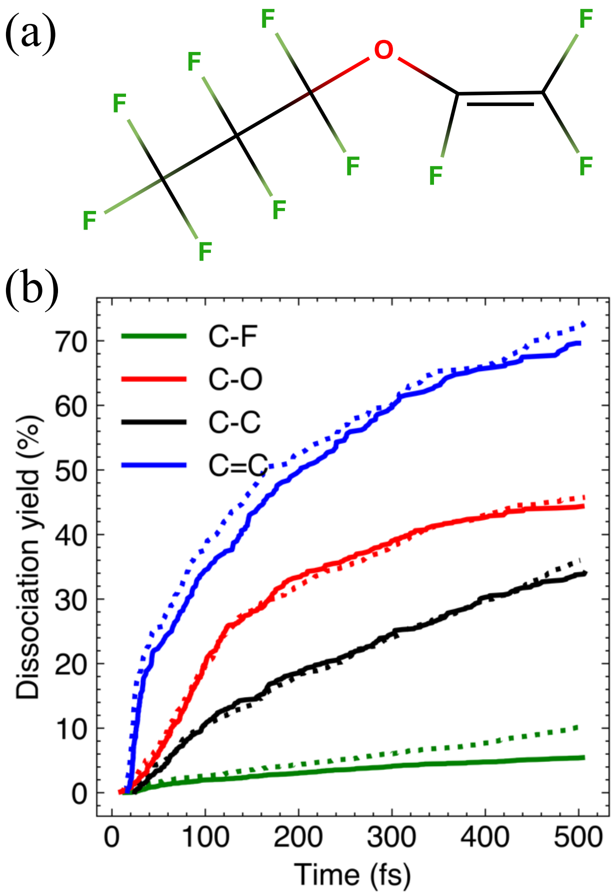

FIG S1. (a) Molecular structure of PPVE and (b) the total number of bonds broken in PPVE over 400 trajectories. The inclusion of spin-flip (dotted line) in the force calculations is compared with simple DFT force calculations (solid line).

The results shown in Figure 34 indicate that using standard DFT instead of spin-flip TDDFT force calculations does not change the order of the bond breaking nor overly affect the number of bonds broken for each bond type. For most type of bonds considered, the difference in average number of bonds broken per trajectory is negligible, though with standard DFT consistently reporting slightly under the more expensive spin-flip TD-DFT calculations. However, the major difference is that of the C-F bonds, where the difference between the two methods results in a factor of difference of approximately 2, reducing from an average of 0.10 per C-F bond per trajectory to an average of 0.05 per C-F bond per trajectory.

Table S1. Average number of C-F bonds broken for each carbon in PPVE for trajectories ran with spin-flip TDDFT and the same trajectories ran with standard DFT. The standard DFT yield is then represented as a percentage of the yield using spin-flip DFT.

Bond	Average number of bonds broken per trajectory (spin-flip)	Average number of bonds broken per trajectory	Standard DFT yield (% of spin-flip DFT yield)
C#1-F	0.031	0.015	48.0%
C#2-F	0.040	0.019	47.0%
C#3-F	0.070	0.022	30.7%
C#4-F	0.43	0.30	70.2%
C#5-F	0.1	0.057	40.7%

Table 1. compares the two different forms of DFT in terms of how often a C-F bond breaks for each carbon in PPVE. Interestingly the biggest difference is in the number of C#3-F bonds, where standard DFT only produces 30.7% of the bond breaking when compared to spin-flip TDDFT, indicating how standard DFT is less likely to break bonds after another bond on the central atom has been broken. This fact also demonstrates how effective the electrophore effect of both the oxygen and the C=C bond is as it's the C#4-F bond presents the smallest difference between spin-flip and non spin-flip calculations. When gathering statistics for dissociation pathways that involve multiple dissociations, the lower number of broken bonds may require a higher number of repeats to fully explore the space. However, the removal of spin-flip from our calculations allows for a reduction of computational cost of over 4x, overall allowing for the studying of a greater number of molecules at multiple temperatures more readily.

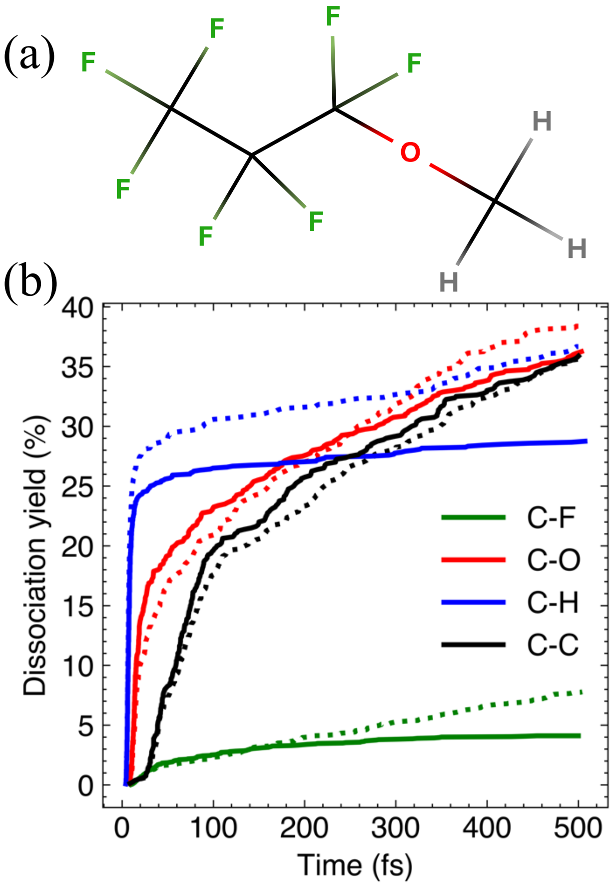

FIG S2. (a) Molecular structure of n-C4H3F7O and (b) the total number of bonds broken in n-C4H3F7O over 400 trajectories. The inclusion of spin-flip (dotted line) in the force calculations is compared with simple DFT force calculations (solid line).

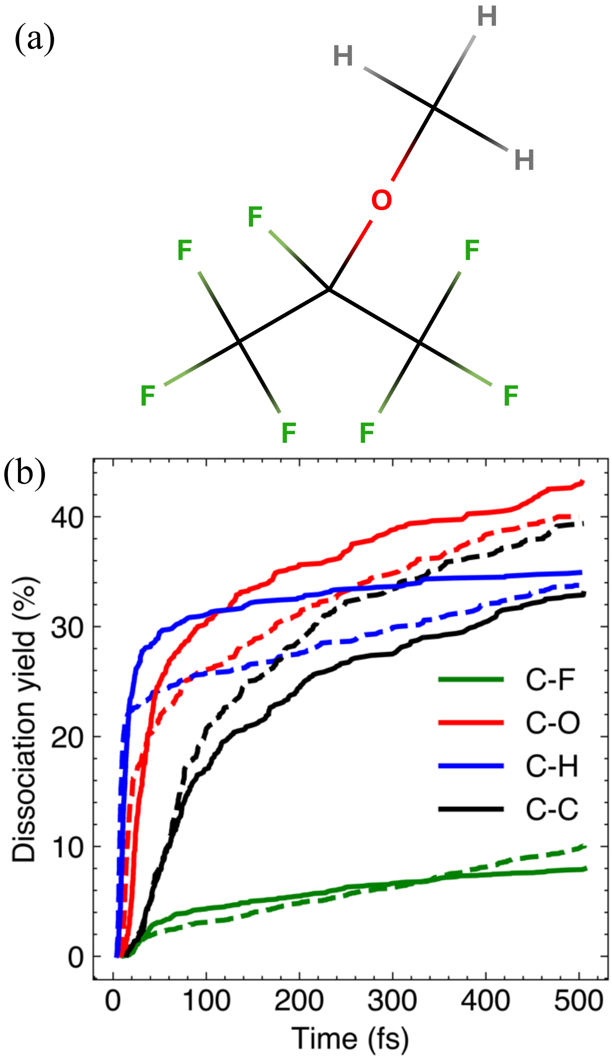

FIG S3. (a) Molecular structure of i-C4H3F7O and (b) the total number of bonds broken in i-C4H3F7O over 400 trajectories. The inclusion of spin-flip (dotted line) in the force calculations is compared with simple DFT force calculations (solid line).

Figure 35 shows the impact of spin-flip and non-spin-flip force calculations on the dissociation of n-$C_4H_3F_7O$ molecule. n-$C_4H_3F_7O$ presents a slightly larger difference within the C-O bond compared to the difference observed in Figure 34 but the final number of dissociations for the C-C bonds remains unchanged. For i-$C_4H_3F_7O$, Figure 36 similarly shows the difference between spin-flip and standard DFT, however the differences for both C-C and C-O bonds are larger when compared to the other molecules considered. Despite the fact that the average number of dissociations per trajectory of C-H bonds increase when removing spin-flip for i-$C_4H_3F_7O$ but decrease when removing spin-flip for n-$C_4H_3F_7O$, for both molecules, the C-H behavior has less dissociations at late times without the inclusion of spin-flip. The fluoroether positional isomers similarly show a substantial difference due to there being seven C-F bonds present in both n-$C_4H_3F_7O$ and i-$C_4H_3F_7O$. The relative difference between the number of C-F bonds dissociated in n-$C_4H_3F_7O$ for spin-flip and non-spin-flip calculations is larger than the relative difference in i-$C_4H_3F_7O$, possibly due to the structure of i-$C_4H_3F_7O$ being more favorable to the dissociation of the C-F bonds, as discussed in Figure. 9.

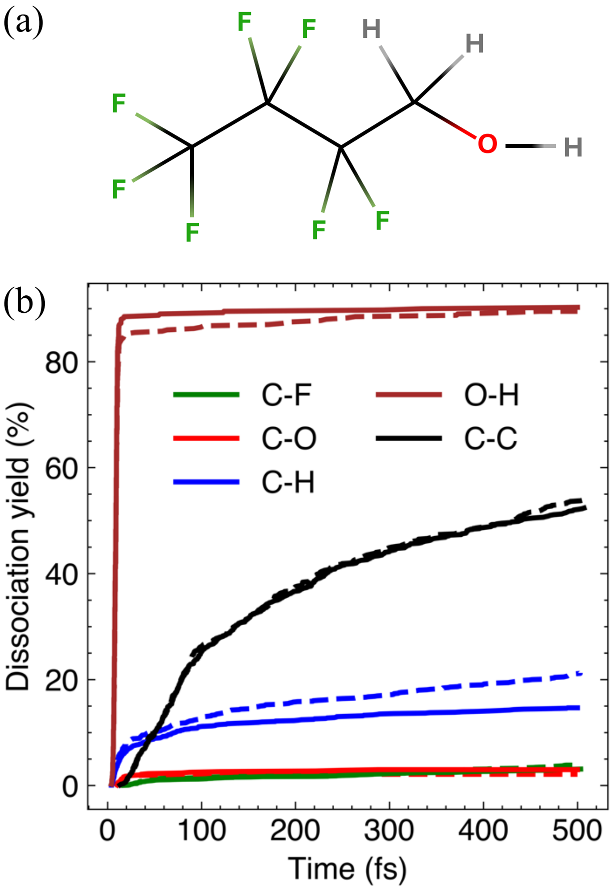

FIG S4. (a) Molecular structure of $C_4H_2F_7OH$ and (b) the total number of bonds broken in $C_4H_2F_7OH$ over 400 trajectories. The use of spin-flip TDDFT (dotted line) in the force calculations is compared with simple DFT force calculations (solid line).

The difference between the spin-flip and non-spin-flip calculations for the $C_4H_2F_7OH$ presented in Figure 37 is the smallest of all four molecules considered. For the O-H, C-C, C-F and C-O bonds, the difference in average number of dissociations per trajectories is negligible. The lower difference for the C-F bonds compared to PPVE or the ether isomers could be attributed to the lower number of flourines dissociating in the alcohol isomer. The difference in C-H bonds is fairly small as well, with fairly similar initial rapid kinetics, but with spin-flip TDDFT, more C-H bonds are broken after the initial rapid dissociative region of 50 fs, continuing the trend observed in the fluoroether, where the line of C-H bond dissociations flattens more without the inclusion of spin-flip.

As the trajectories run are entirely independent, they can be run in batches allowing the total number of trajectories to be decided by the method's own self convergence. A set number of trajectories can be run at a time until the change average number of bonds broken per 100 trajectories becomes negligible. Figure 38 compares the number of bonds broken per 100 repeats for a growing number of repeats. For all four bond types considered in PPVE, a low number of trajectories, such as 250, appears suitable as there is minimal variation from the average found with 500 trajectories, with the only exception being that of the C=C bonds at late time. However, as there is interest in studying the fragments that can appear after several bonds have broken in sequence, it is also important not only to have a consistent average in number of bonds broken, but also explore all of the possible likely dissociation routes. Therefore, a more significant number of trajectories is required to generate sufficient statistics from data that contains multiple iterations of different sequences in order to provide at least semiqualitative branching ratios.

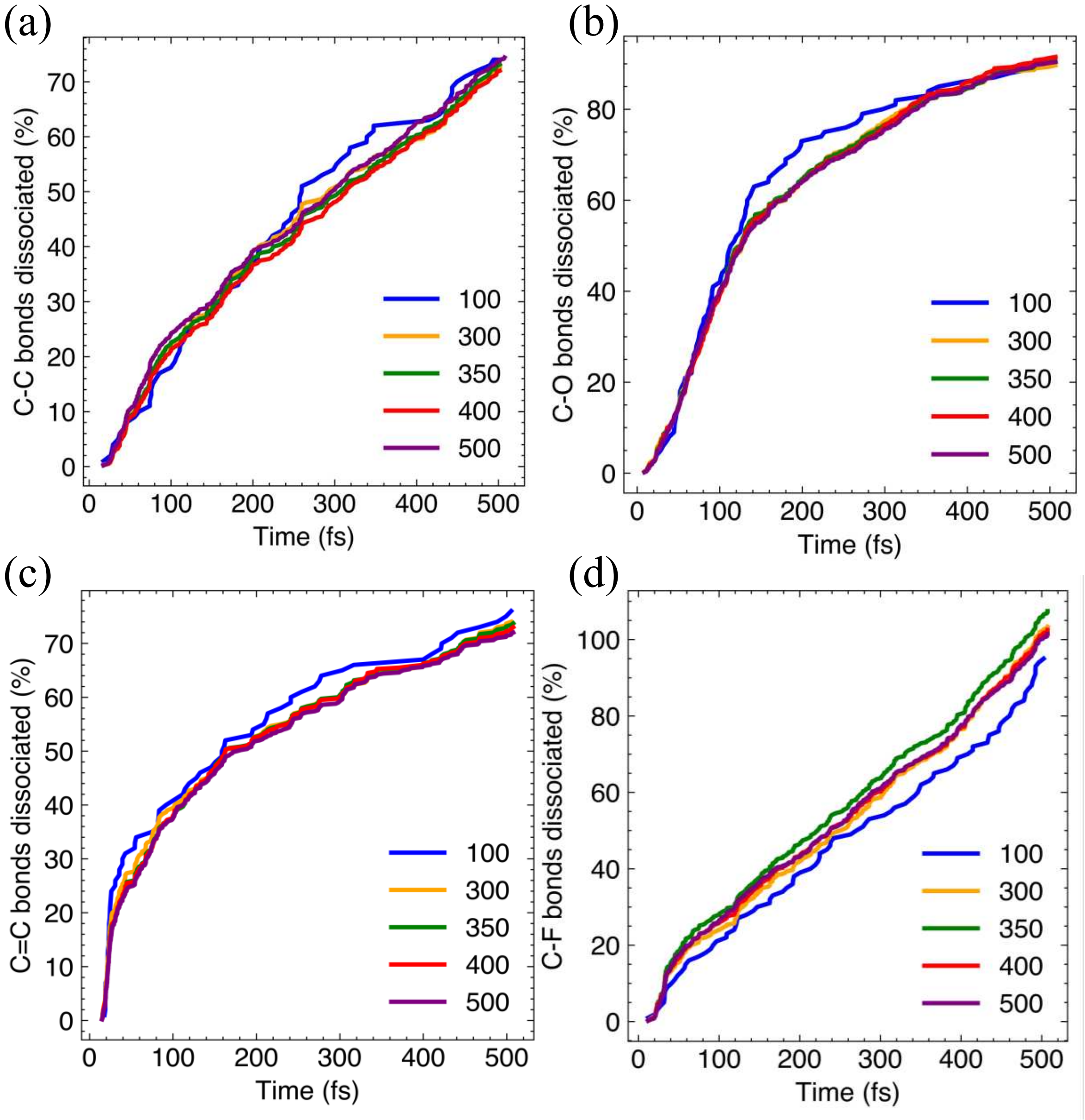

Fig S5. Dissociation yield for (a) C-C, (b) C-O, (c) C=C, (d) C-F bonds in PPVE per 100 trajectories for an increasing number of trajectories.