Electronic Supplementary Material (ESI) for Faraday Discussions.

Supplementary Information: Electron and nuclear dynamics following ionisation of modified bismethylene-adamantane†

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For the simulations in BMA[5,5] cation presented in Sections 3.4 and 4.3, the effect of the vibrational ground state delocalisation was taken into account by considering an ensemble of 500 nuclear geometries and velocities sampled from a Wigner distribution.

The results depending on the number of sampled geometries / velocities, we have checked that convergence is reached. Figure S1 shows the spin density averaged over the ensemble of sampled fixed geometries, as in Figure 6 of the article, for different sizes of samples: with 500 sampled geometries, the result is converged.

To take into account the nuclear motion, equation (4) was integrated calculating only the gradient without the coupled-perturbed corrections (with a time step of 0.05 fs) so that the 500 trajectories are computationally affordable. We have checked that for this molecule the results obtained with this method are in good agreement with the Hessian-based predictor-corrector algorithm. We compare the time evolution of the potential, kinetic and total energies for two Ehrenfest trajectories started at the minimum geometry of the neutral species with no kinetic energy (Figure S2) and at a sampled geometry (Figure S3): the curves are very similar and the total energy is conserved.

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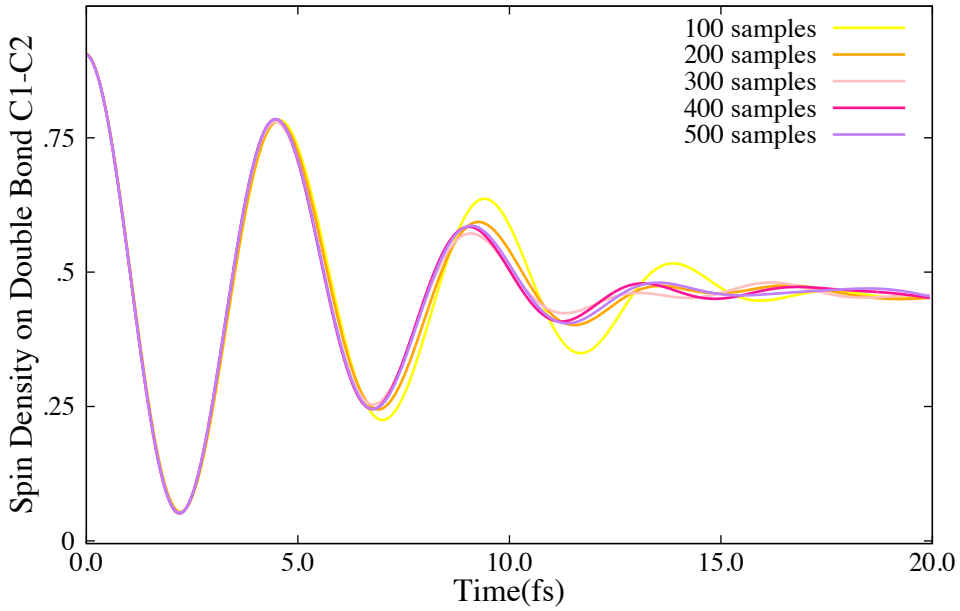

Fig. S1 Spin density oscillation amplitude averaged over ensembles of sampled fixed geometries, as in Figure 6 of the article, for different sizes of ensemble: 100, 200, 300, 400 and 500 geometries sampled from a Wigner distribution. The curves for the different sample sizes are superimposed up to 5 fs. The biggest change is obtained at longer time going from 100 to 200 geometries. There is no significant change going from 400 to 500 geometries, demonstrating that convergence has been reached.

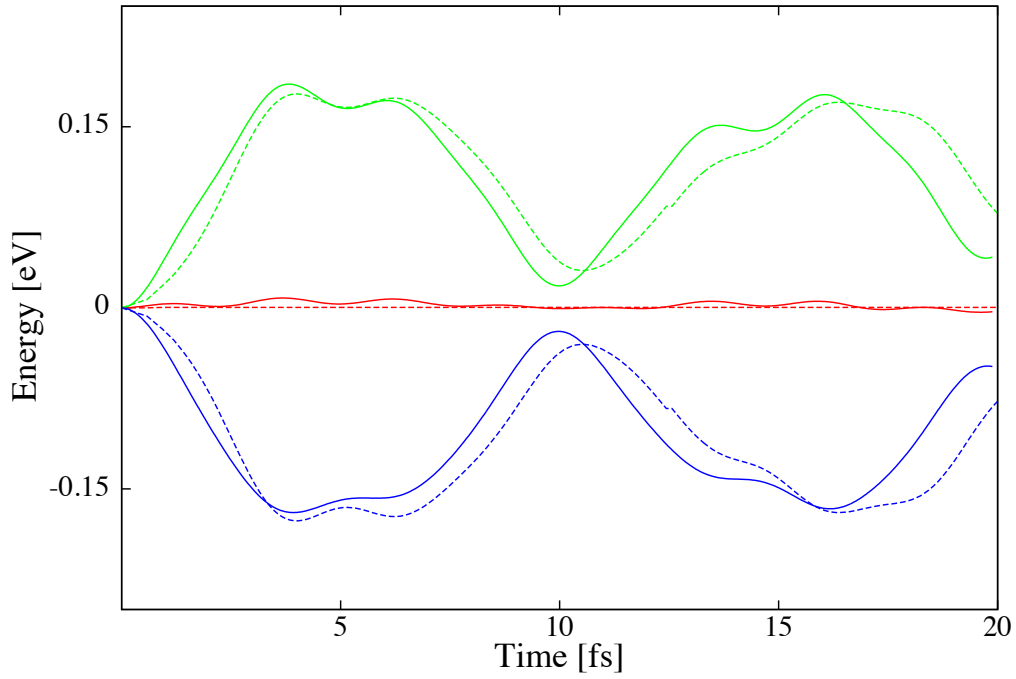

Fig. S2 Time evolution of the potential (in blue), kinetic (in green) and total (in red) energies. The dashed lines are obtained with the Hessian-based predictor-corrector algorithm, with a mass-weighted step size of 0.01 amu$^{1/2}$bohr (corresponding to a time step of approximately 0.1 fs). The solid lines are obtained with only the gradient computed without the coupled-perturbed corrections (with a time step of 0.05 fs). Simulations started at the minimum geometry of the neutral species with no initial kinetic energy.

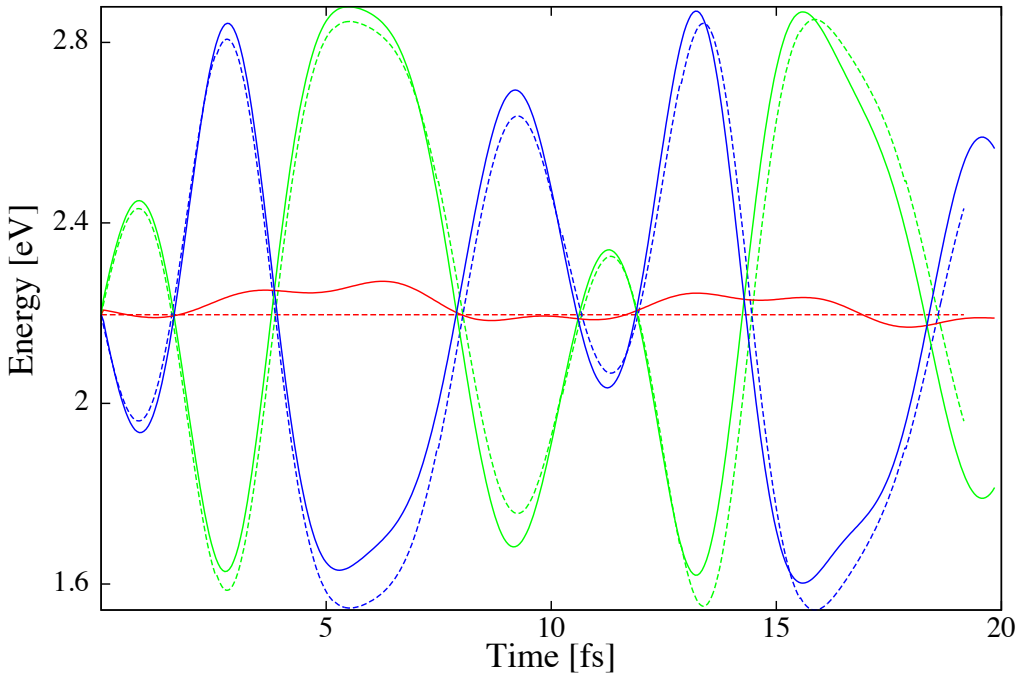

Fig. S3 Same as Figure S2 for simulations started at a geometry and velocity sampled from the Wigner distribution.