

## Supplementary Information for "Is a Thin Mechanism Appropriate for Aromatic Nitration?"

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## 1 Electronic structure of liquid dichloromethane

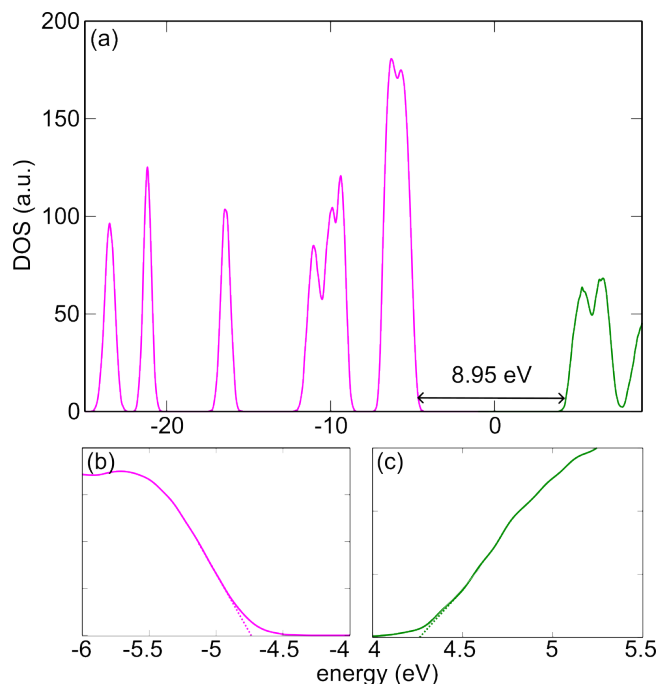


Fig. 1 (a) Electronic density of states (DOS) of liquid dichloromethane, averaged over the MD simulation. Energies are referred to the average electrostatic potential. Valence DOS in magenta and conduction DOS in green. DOS near (b) the valence band maximum and (c) the conduction band minimum. Dotted lines show the linear extrapolation of the low-energy wing of the DOS.

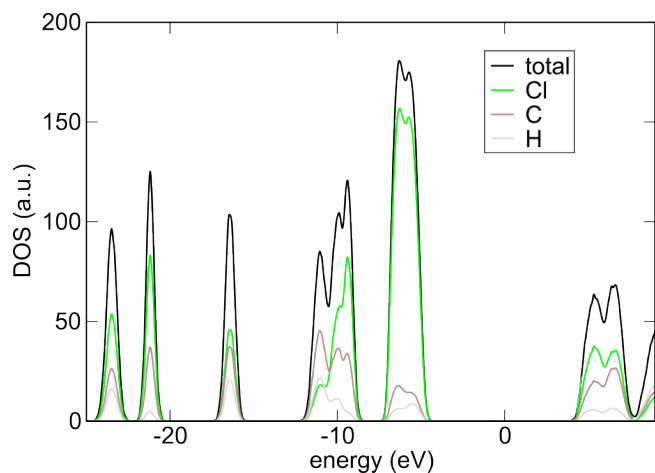


Fig. 2 Total and partial electronic DOS of liquid dichloromethane, averaged over the MD simulation. Energies are referred to the average electrostatic potential.

## 2 $\text{CH}_2\text{Cl}_2$ dimers

In order to verify that the achieved  $\text{PBE0}(\alpha_K)$  functional can correctly describe the intermolecular interactions in condensed-phase  $\text{CH}_2\text{Cl}_2$ , we consider, as a test case, the energetics of dimers in different configurations (A-E, cf. Fig. S3), for which highly accurate coupled cluster results are available.<sup>1,2</sup> To this end, we

perform single-point calculations on the structural models reported in Ref. 2. In Table S1, we collect the relative energies of the different dimers referred to that of the A structure, predicted to be the most stable from CCSD(T) calculations.<sup>2</sup>

Table 1 Relative energy (kJ/mol) of the B-E dimers of  $\text{CH}_2\text{Cl}_2$ , referred to that of the A dimer at different levels of theory. CCSD(T) values from Ref. 2 are reported for comparison.

	B	C	D	E
PBE	-1.6	1.8	0.9	0.3
PBE0	-1.5	1.8	1.0	0.4
$\text{PBE0}(\alpha_K)$	-1.3	1.8	1.2	0.5
$\text{PBE0}(\alpha_K) + \text{rVV10}$	0.04	1.4	4.6	4.1
CCSD(T) (Ref. 2)	0.3	1.5	4.8	3.9

The constructed  $\text{PBE0}(\alpha_K)$  functional fails to deliver the correct energetics of the dimers, with no significant difference if compared to the standard PBE<sup>3</sup> or the semi-local PBE<sup>4</sup> functional. In fact, van der Waals interactions are known to play a key role in determining the stability of such a weakly interacting dimer.<sup>2</sup> Therefore, we include non-local electron correlation in our functional self-consistently via the rVV10 scheme, developed by Vydrov and Van Voorhis<sup>5,6</sup>, in line with a previous study.<sup>7</sup> The new  $\text{PBE0}(\alpha_K) + \text{rVV10}$  functional is found to deliver values in excellent agreement with the CCSD(T) calculations, with differences below 0.3 kJ/mol (cf. Table S1).

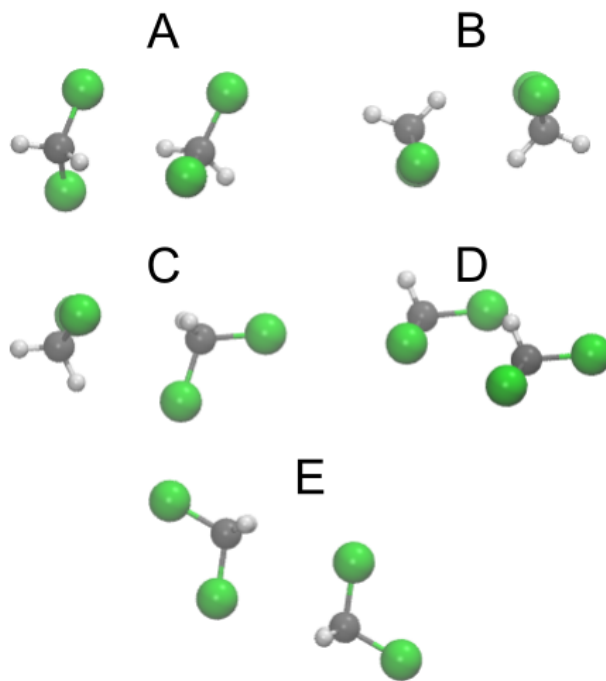


Fig. 3 Ball and stick representation of the different possible dimers of  $\text{CH}_2\text{Cl}_2$ . H in white, C in grey, and Cl in green.

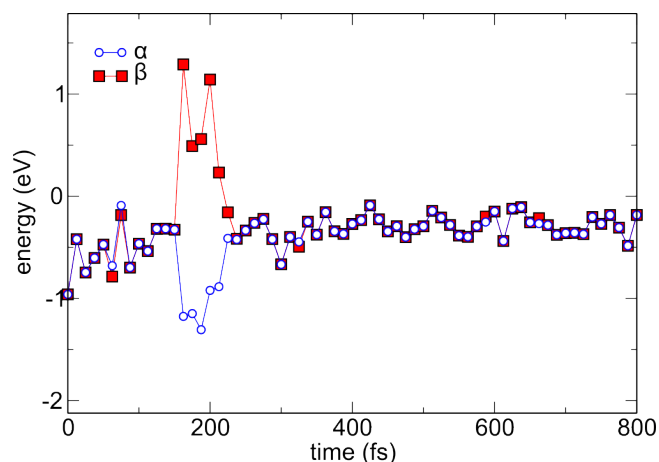


Fig. 4 Time-dependent Kohn-Sham lowest unoccupied energy levels for  $\alpha$  and  $\beta$  electrons during unrestricted-DFT MD simulation of the solvated  $\text{NO}_2^+$ -toluene complex. Energies are referred to the average electrostatic potential.

### 3 Time evolution of Kohn-Sham energy levels

### 4 Analysis of the time evolution for the $\text{NO}_2^+$ -toluene complex in ipso position

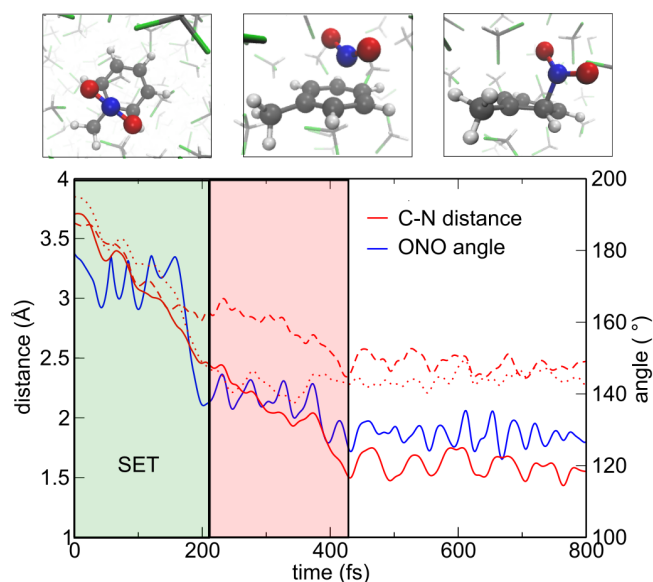


Fig. 5 Time evolution of (i) the distance between C atoms of toluene and the N atom of the nitronium cation and (ii) the ONO angle upon MD simulation. The bolder solid line indicates the distance with the para C atom, dashed and dotted lines for ipso and meta C, respectively. The simulation is initiated from a solvated  $\text{NO}_2^+$ -toluene encounter complex with N above the ipso C of the aromatic ring (top left), proceeds via electron transfer (green shaded area) and subsequent roaming of the  $\text{NO}_2$  radical between ortho and meta positions (red shaded area, top middle for an indicative configuration) and is concluded with formation of the  $\sigma$ -complex in ortho position (top right). H atoms in white, C in grey, Cl in green, N in blue, and O in red.

### 5 Energy profile of the MD simulation for the P1 and P2 complexes

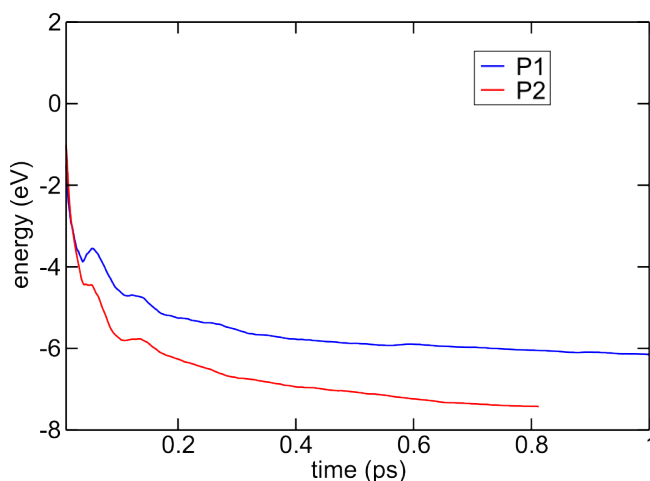


Fig. 6 Cumulative average of the total energy from the P1 and P2 MD simulations (Cf. main text).

### Notes and references

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