Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

Unveiling anharmonic coupling by means of excited state ab-initio dynamics: application to diarylethenes photoreactivity

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Table 1: Main structural parameters computed for the CHD molecule from the ground state and excited states AIMD. Values are reported in Å as mean ± st. dev.

	TRJ S_0	**TRJ I S_1**	**TRJ II S_1**	**TRJ III S_1**
CC1	1.55 ± 0.03	1.60 ± 0.04	1.60 ± 0.04	1.60 ± 0.04
CC2	1.47 ± 0.03	1.42 ± 0.02	1.42 ± 0.02	1.42 ± 0.03
CC3	1.54 ± 0.03	1.52 ± 0.04	1.52 ± 0.02	1.52 ± 0.03
CC4	1.54 ± 0.03	1.52 ± 0.03	1.52 ± 0.02	1.52 ± 0.04
CC5	1.37 ± 0.02	1.42 ± 0.03	1.42 ± 0.02	1.42 ± 0.03
CC6	1.37 ± 0.02	1.42 ± 0.03	1.42 ± 0.02	1.42 ± 0.03
CC7	1.45 ± 0.03	1.42 ± 0.03	1.42 ± 0.02	1.42 ± 0.03
CC8	1.45 ± 0.03	1.42 ± 0.03	1.42 ± 0.02	1.42 ± 0.03
CC9	1.37 ± 0.03	1.40 ± 0.03	1.40 ± 0.02	1.40 ± 0.03
CC10	1.37 ± 0.03	1.40 ± 0.03	1.40 ± 0.02	1.40 ± 0.03
CS11	1.77 ± 0.03	1.76 ± 0.03	1.76 ± 0.02	1.76 ± 0.03
CS12	1.77 ± 0.04	1.76 ± 0.03	1.76 ± 0.03	1.76 ± 0.04
CS13	1.87 ± 0.04	1.84 ± 0.04	1.84 ± 0.03	1.84 ± 0.04
CS14	1.87 ± 0.05	1.84 ± 0.04	1.84 ± 0.03	1.84 ± 0.04
CC15	1.51 ± 0.03	1.50 ± 0.03	1.50 ± 0.02	1.50 ± 0.03
CC16	1.51 ± 0.03	1.50 ± 0.03	1.50 ± 0.02	1.50 ± 0.04
CC17	1.56 ± 0.03	1.56 ± 0.03	1.56 ± 0.02	1.56 ± 0.03
CC18	1.56 ± 0.03	1.56 ± 0.03	1.56 ± 0.02	1.56 ± 0.03

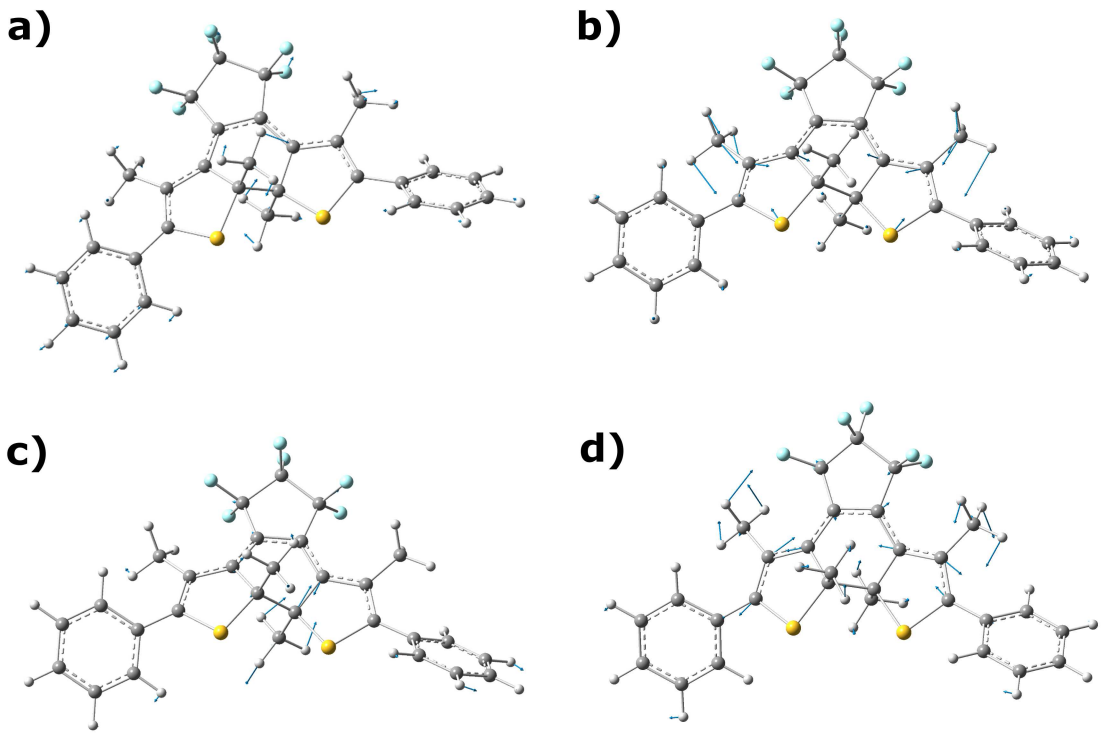

Figure 1: Sketch of CHD normal modes corresponding to harmonic frequency values calculated in S_1: a) wagging mode b)-d) stretching modes

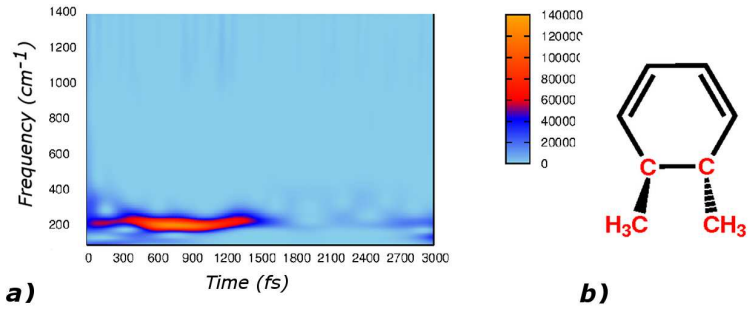

Figure 2: a) 2D wavelet map of the methyl wagging motion in excited state. b) Cyclohexadiene unity of CHD, with the atoms partecipating to the methyl wag (AIMD Frequency 200 cm^{-1}) highlighted in red.

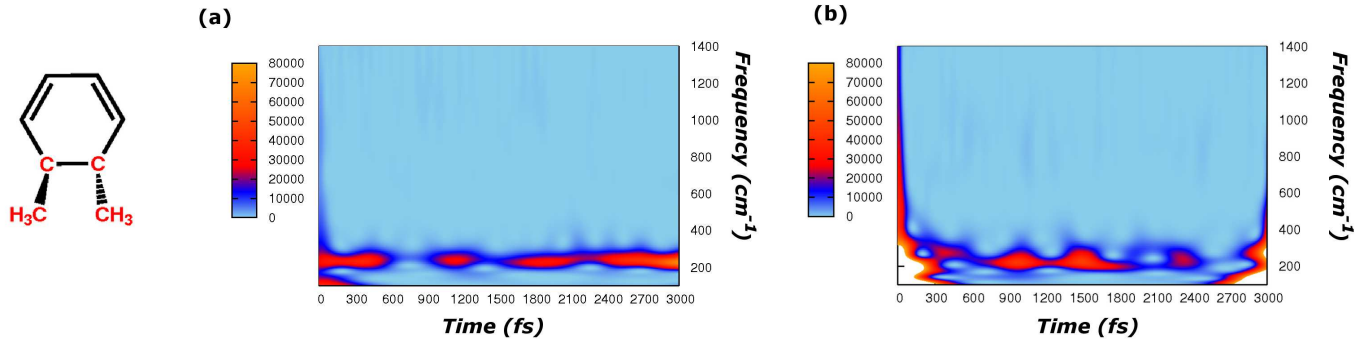

Figure 3: a) 2D wavelet map of the methil wagging motion in the excited state from TRJ II. b) 2D wavelet map of the methil wagging motion in the excited state from TRJ III.

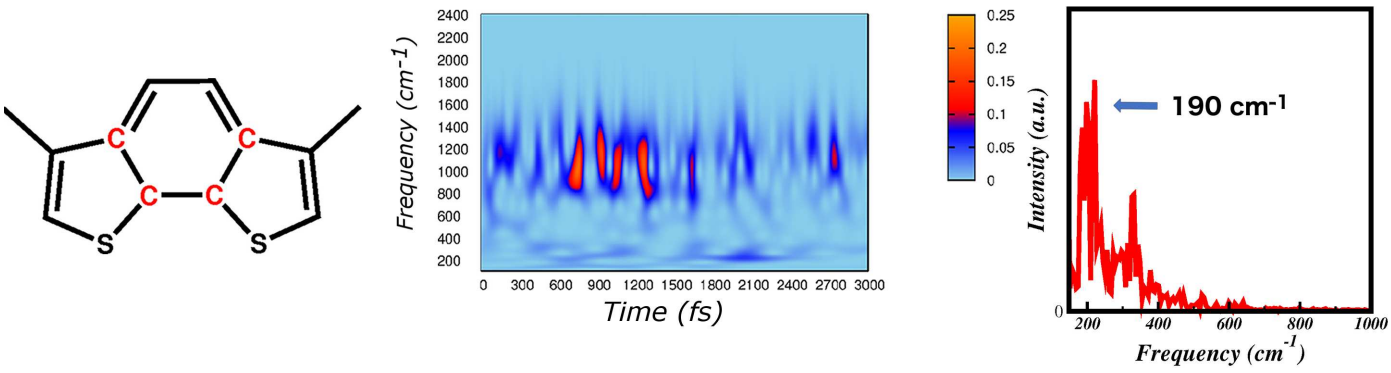

Figure 4: Left panel: 2D wavelet map of the *CC* stretching localized on cyclohexadiene unity. Central panel: Atoms in red participate to the *CC* stretching (AIMD Frequency 1186 cm^{-1}). Right panel) Discrete Fourier Tranform of the intensity oscillations.

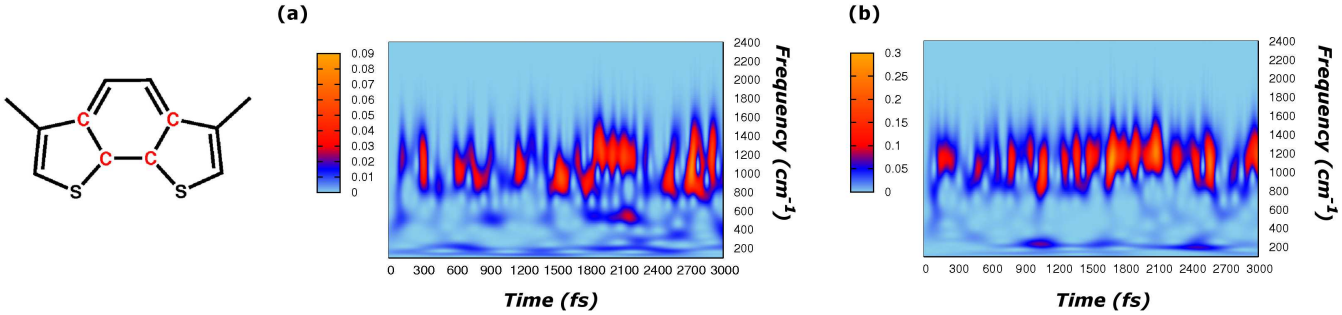

Figure 5: a) 2D wavelet map of the CC stretching localized on cyclohexadiene from TRJ II. b) 2D wavelet map of the CC stretching localized on cyclohexadiene from TRJ III.

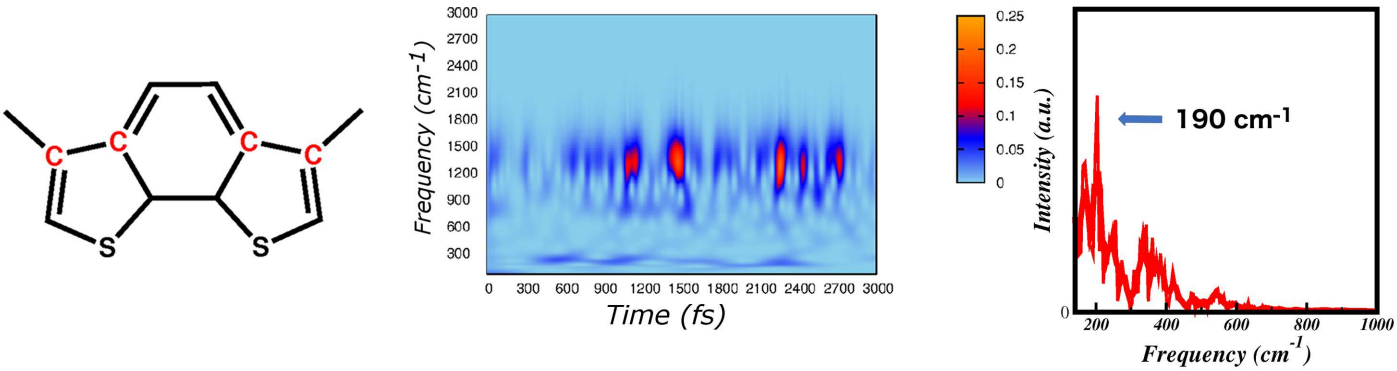

Figure 6: Left panel: 2D wavelet map of the *CC* stretching localized on thiophene rings. Central panel: Atoms in red participate to the *CC* stretching (AIMD Frequency 1380 cm^{-1}).Right panel: Discrete Fourier Tranform of the intensity oscillations.

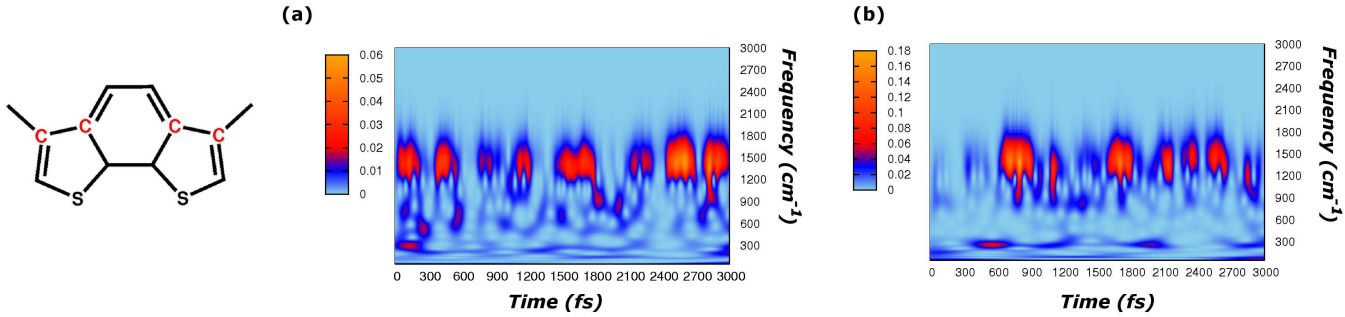

Figure 7: a) 2D wavelet map of the CC stretching localized on thiophene ring from TRJ II. b) 2D wavelet map of the CC stretching localized on thiophene from TRJ III.

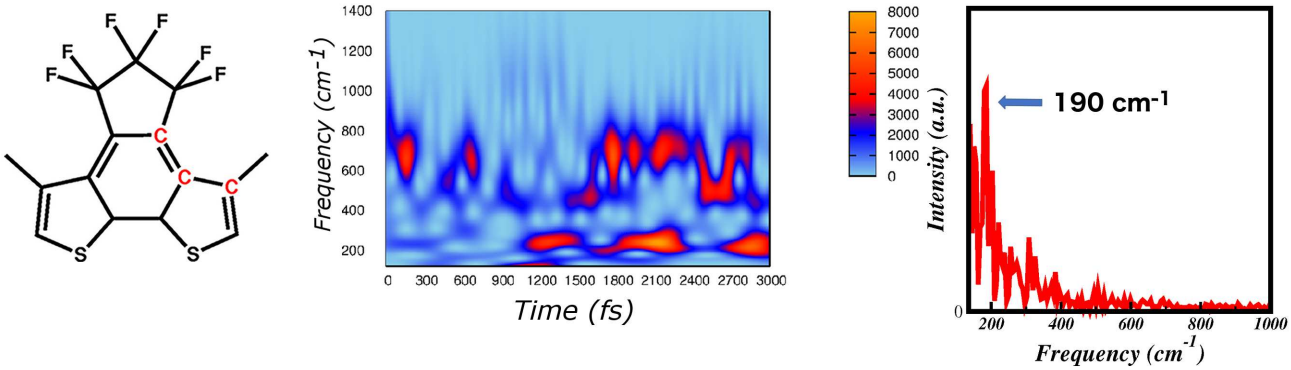

Figure 8: Left panel: 2D wavelet map of the *CCC* bending localized on cyclohexadiene and thiophene rings. Central panel: Atoms in red participate to the *CCC* bending (AIMD Frequency 469 cm^{-1}). Right panel: Discrete Fourier Tranform of the intensity oscillations.

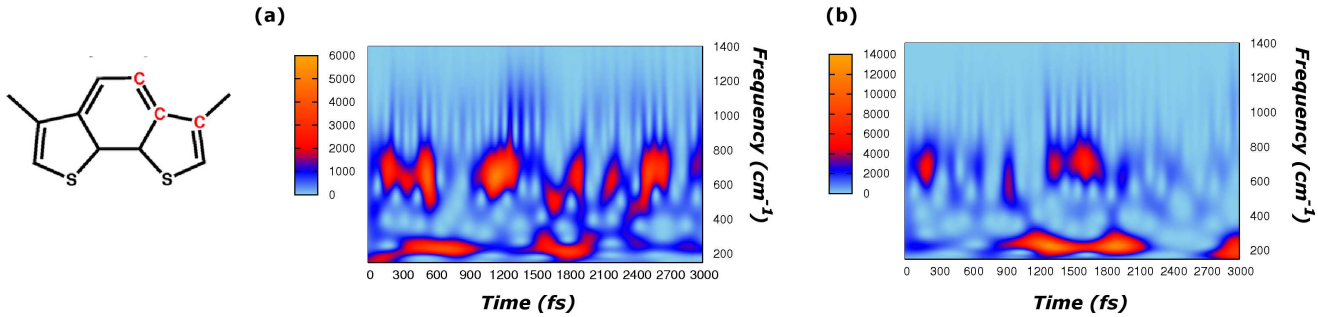

Figure 9: a) 2D wavelet map of the CCC bending localized on cyclohexadiene and thiophene rings from TRJ II. b) 2D wavelet map of the CCC bending localized on cyclohexadiene and thiophene rings from TRJ III.