

Supporting Information

Ultrafast Excited-State Decays in [Re(CO)₃(N,N)(L)]ⁿ⁺: Non-Adiabatic Quantum Dynamics

M. Fumanal, E. Gindensperger and C. Daniel

*Laboratoire de Chimie Quantique, Institut de Chimie Strasbourg, UMR-7177 CNRS/
Université de Strasbourg, 1 Rue Blaise Pascal BP 296/R8, F-67008 Strasbourg, France*

Table S1. Number of basis functions for the primitive basis as well as for the time-dependent (SPF) basis used in the MCTDH calculation for the lowest 14 electronic states of [Re(CO)₃(phen)(im)]⁺ when using the 15-modes model Hamiltonian described in the Results section of the main text.

Figure S1. Displacement contributions of the a' normal modes for each excited state (ES).

Figure S2. Energy-scaled contributions (in eV) of the a' normal modes for each ES.

Figure S3. Diabatic potential energy curves along the 20 Q_i most relevant a' normal modes.

Figure S4. Diabatic electronic populations as a function of time for different models considering the a'' normal modes at 90 and 475 cm⁻¹, the a' normal modes at 93, 439, 498 and 637 cm⁻¹, and an extra a' normal mode.

Figure S5. Diabatic electronic populations as a function of time, for different 5-modes models arising from the 6-modes Model-1 and excluding the normal mode indicated.

Figure S6. Kohn-Sham frontier orbitals of (a) [Re(CO)₃(phen)(im)]⁺ and (b) [Re(CO)₃(bpy)(im)]⁺ in water.

Figure S7. Kohn-Sham frontier orbitals of (a) [Re(CO)₃(phen)(Br)] and (b) [Re(CO)₃(bpy)(Br)] in water.



Figure S1. Displacement contributions of the a' normal modes for each excited state of $[\text{Re}(\text{CO})_3(\text{phen})(\text{im})]^+$ considered herein. The contribution of the modes between 770 - 1174 cm^{-1} and 2039 - 3653 cm^{-1} is negligible and not shown for the sake of clarity.

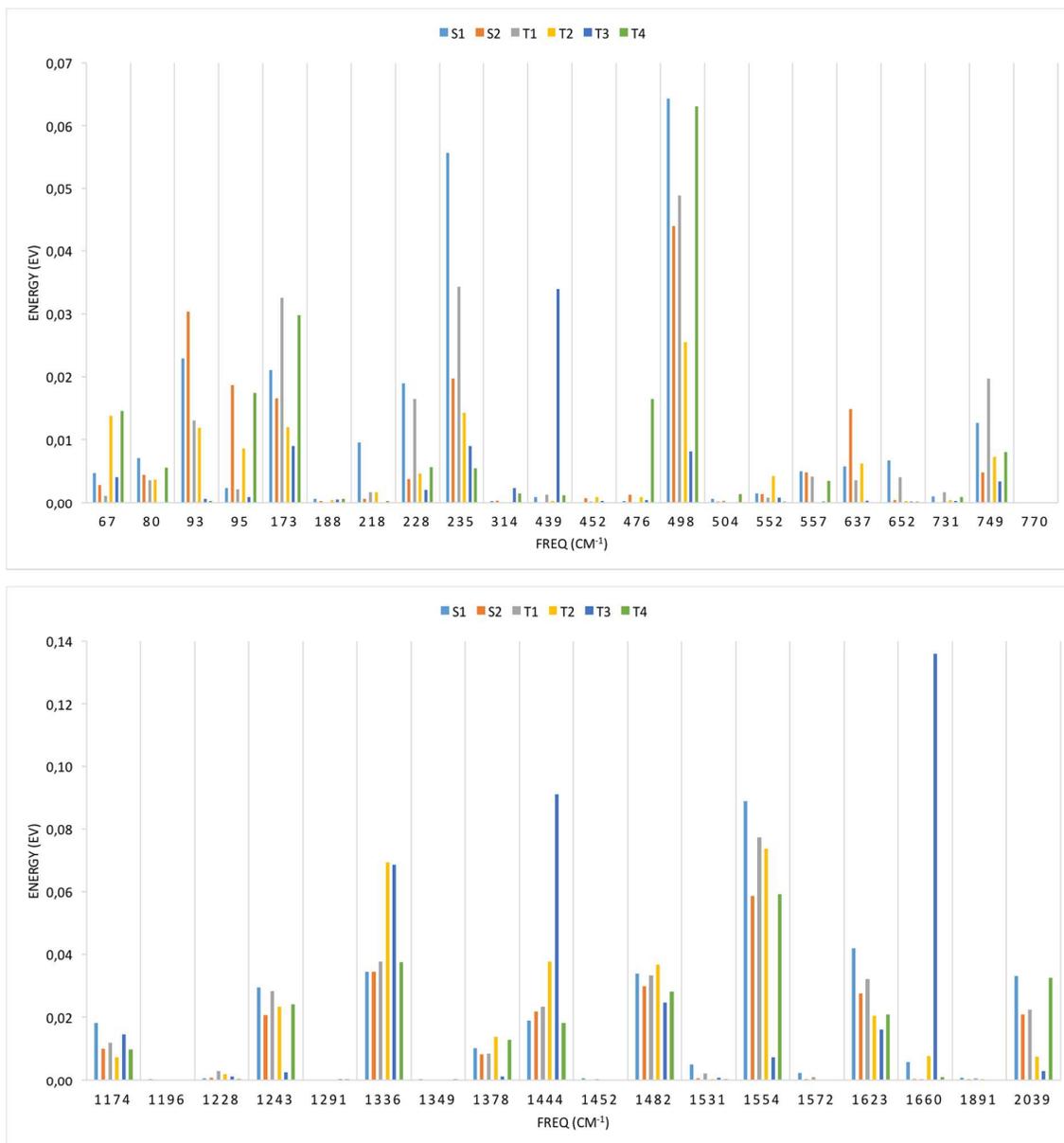
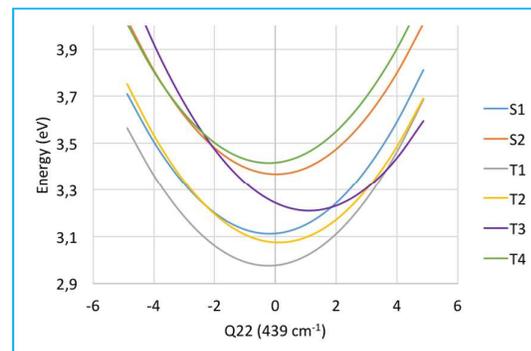
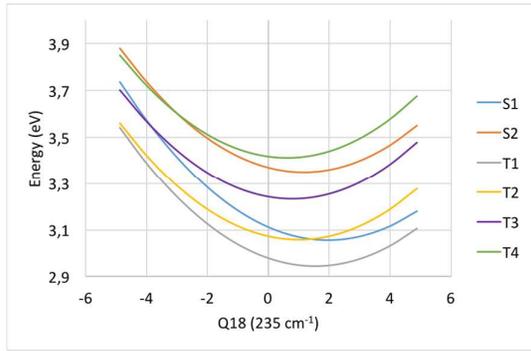
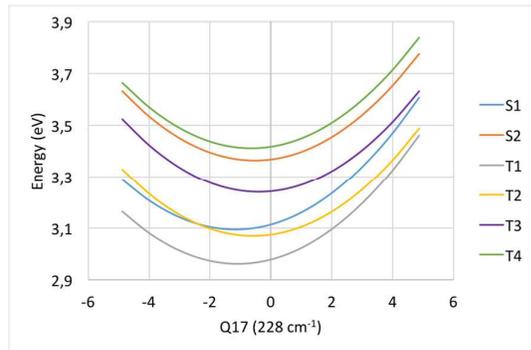
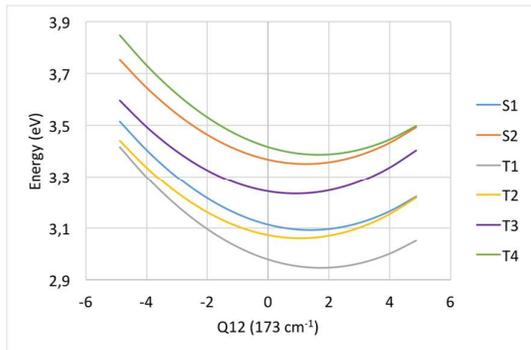
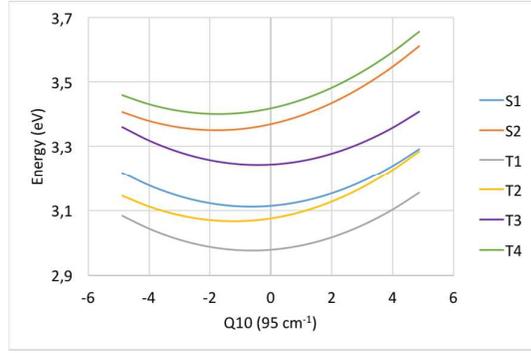
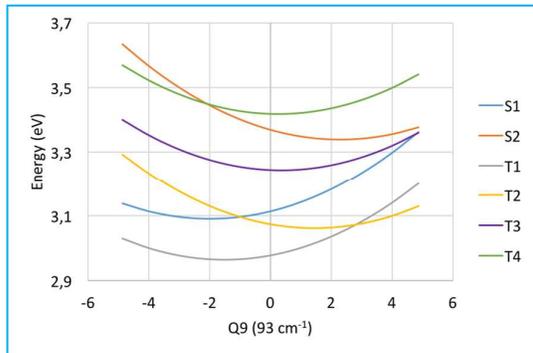
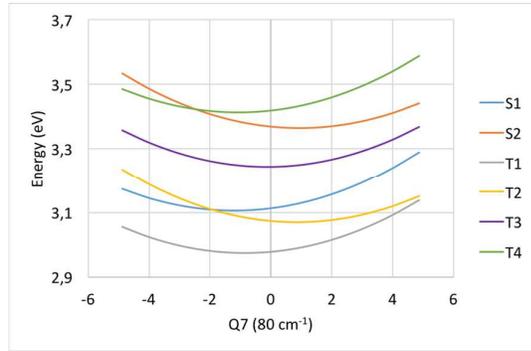
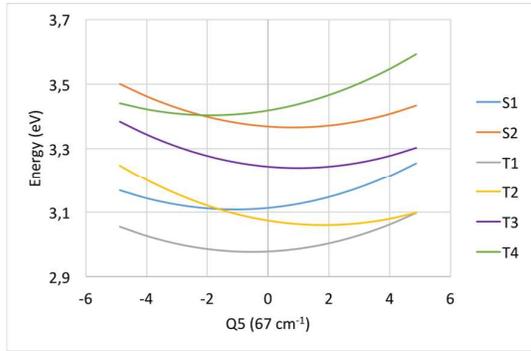
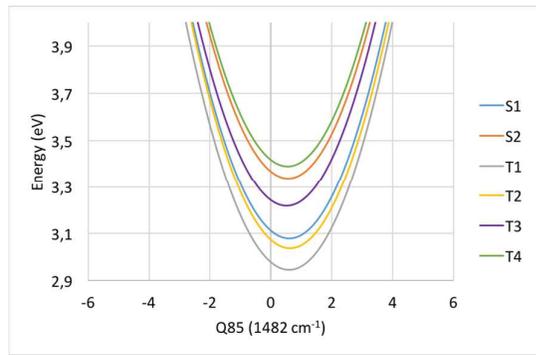
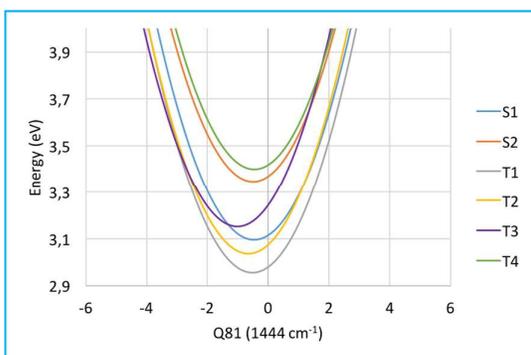
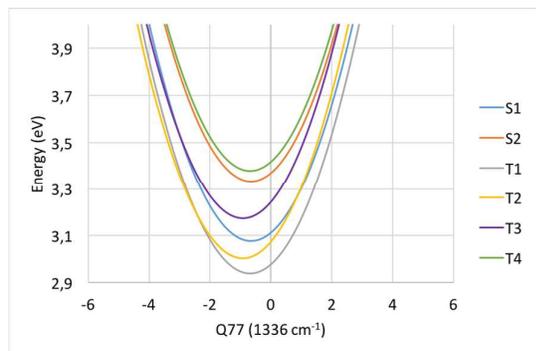
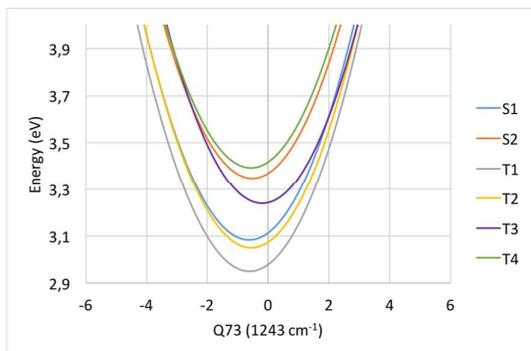
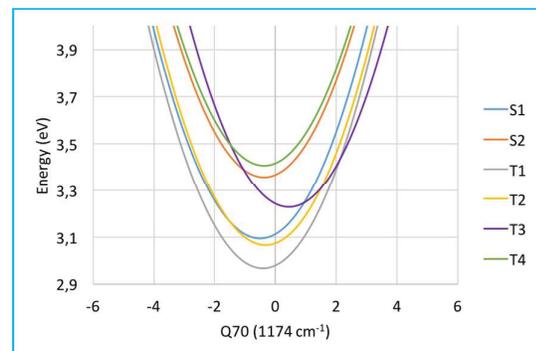
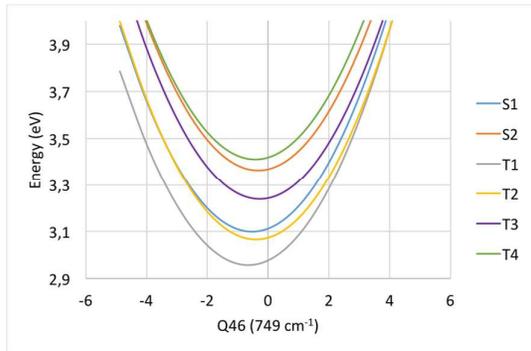
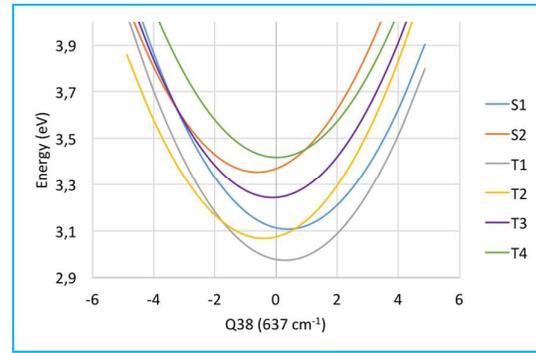
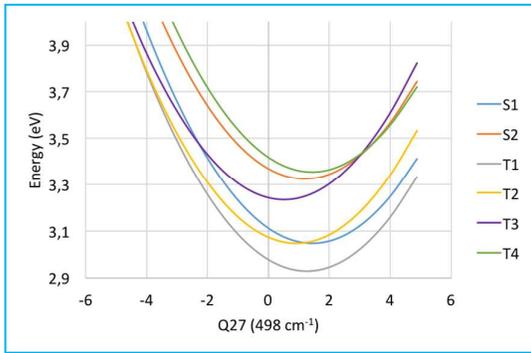


Figure S2. Energy-scaled contributions (in eV) of the a' normal modes for each excited state of $[\text{Re}(\text{CO})_3(\text{phen})(\text{im})]^+$ considered herein. The contribution of the modes between $770 - 1174 \text{ cm}^{-1}$ and $2039 - 3653 \text{ cm}^{-1}$ is negligible and not shown for the sake of clarity.





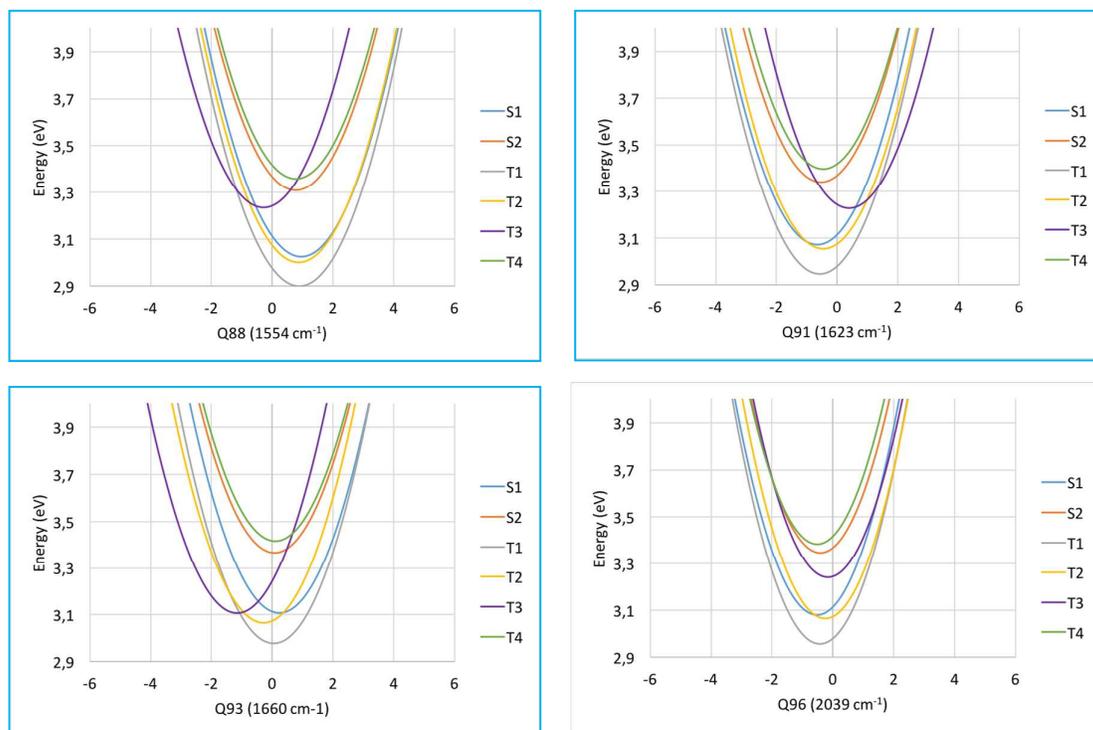
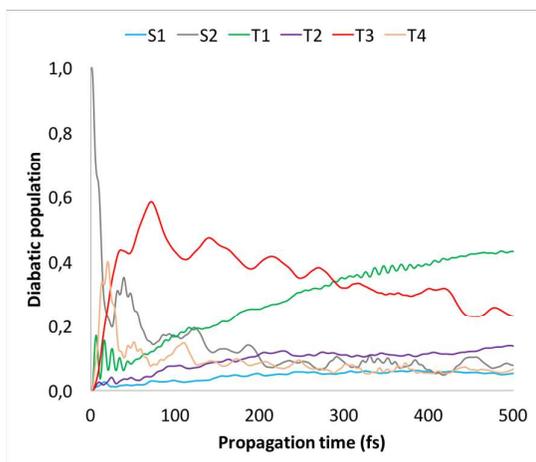
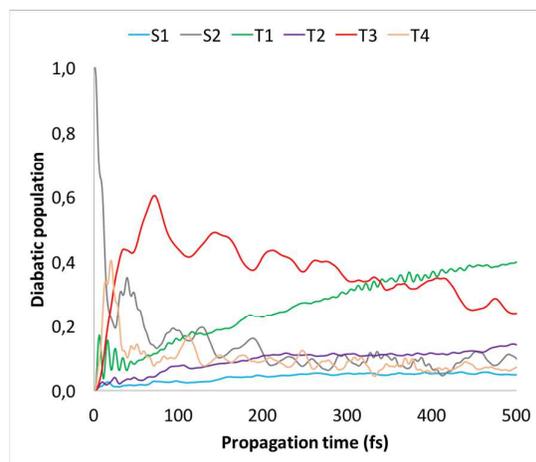


Figure S3. Diabatic potential energy curves along the 20 Q_i most relevant a' normal modes of $[\text{Re}(\text{CO})_3(\text{phen})(\text{im})]^+$. Each triplet state is triply degenerate.

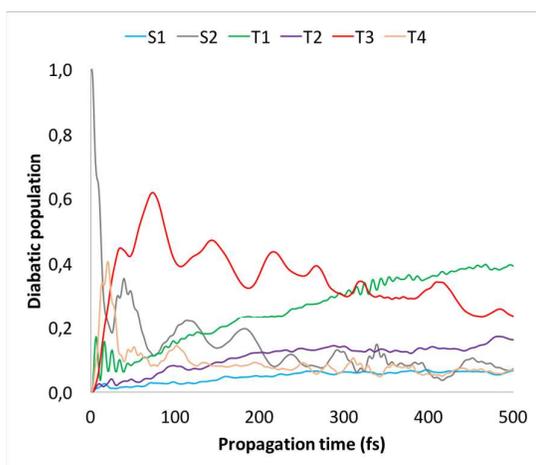
67 cm^{-1}



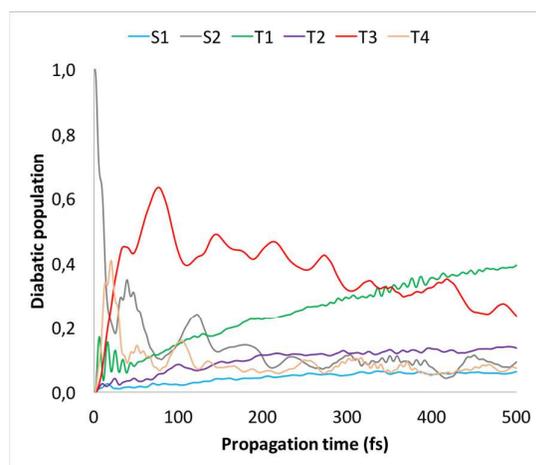
80 cm^{-1}



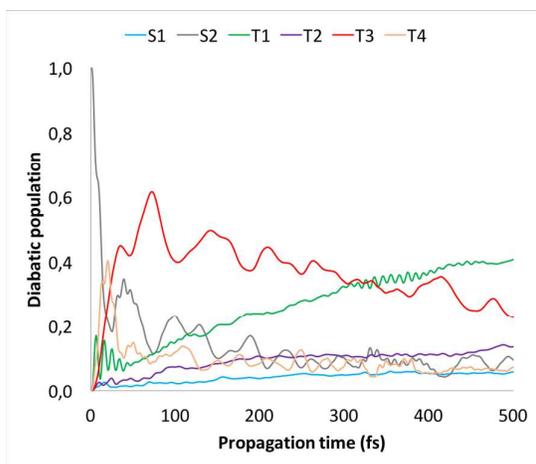
95 cm^{-1}



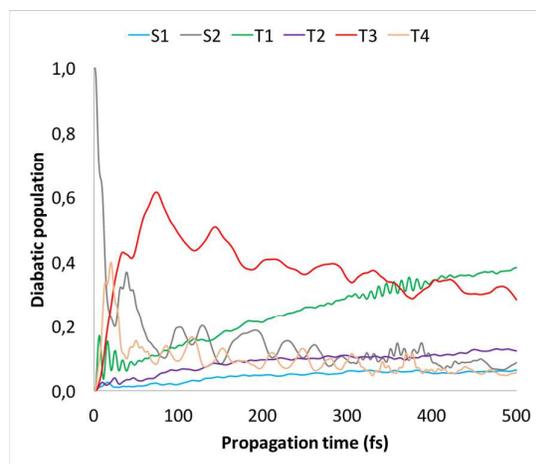
173 cm^{-1}



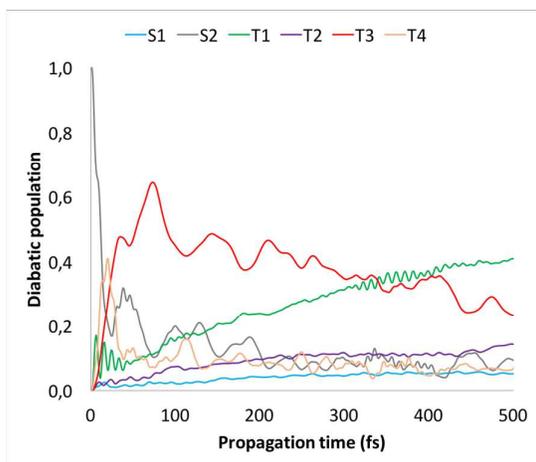
228 cm^{-1}



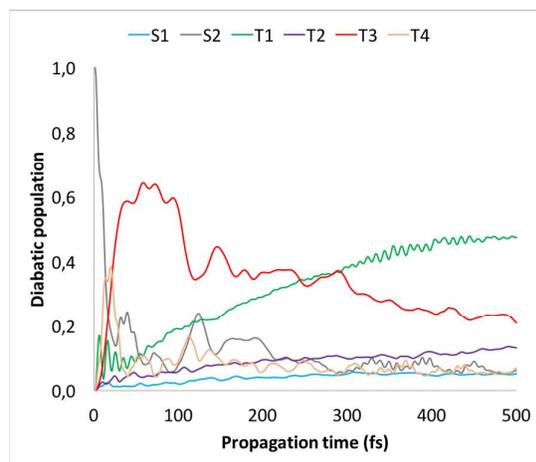
235 cm^{-1}



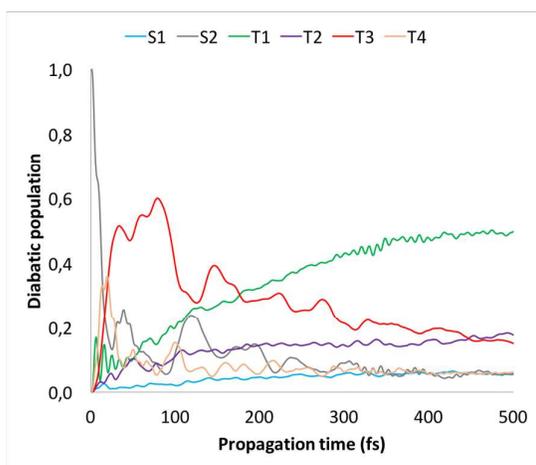
749 cm^{-1}



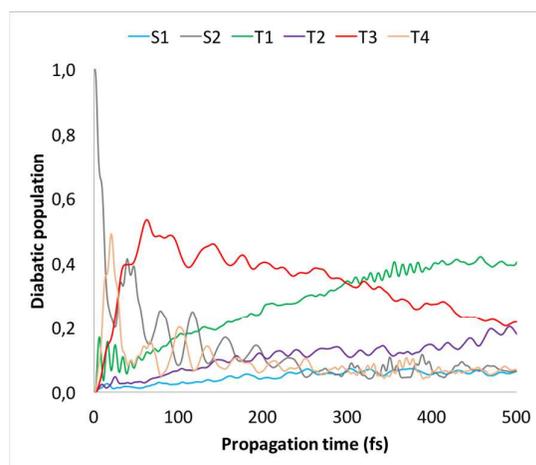
1174 cm^{-1}



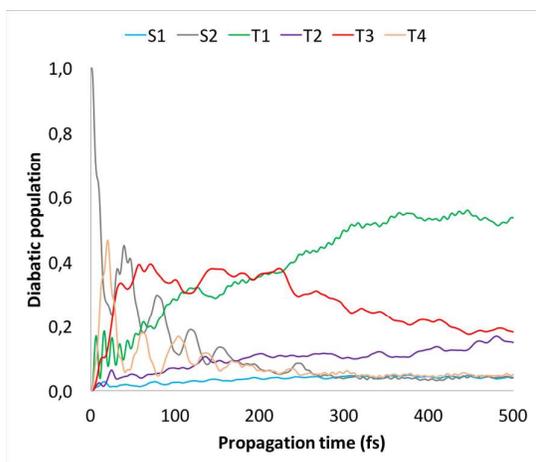
1243 cm^{-1}



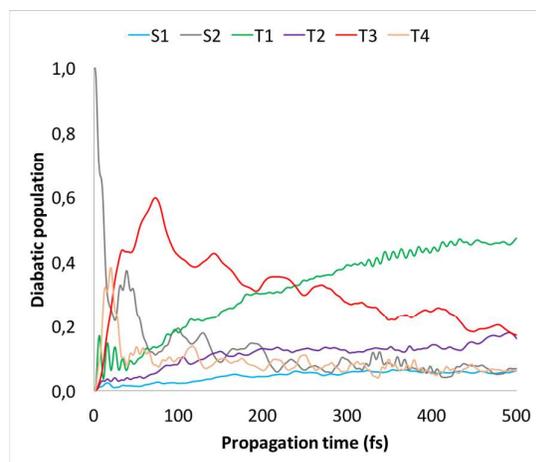
1336 cm^{-1}



1444 cm^{-1}



1482 cm^{-1}



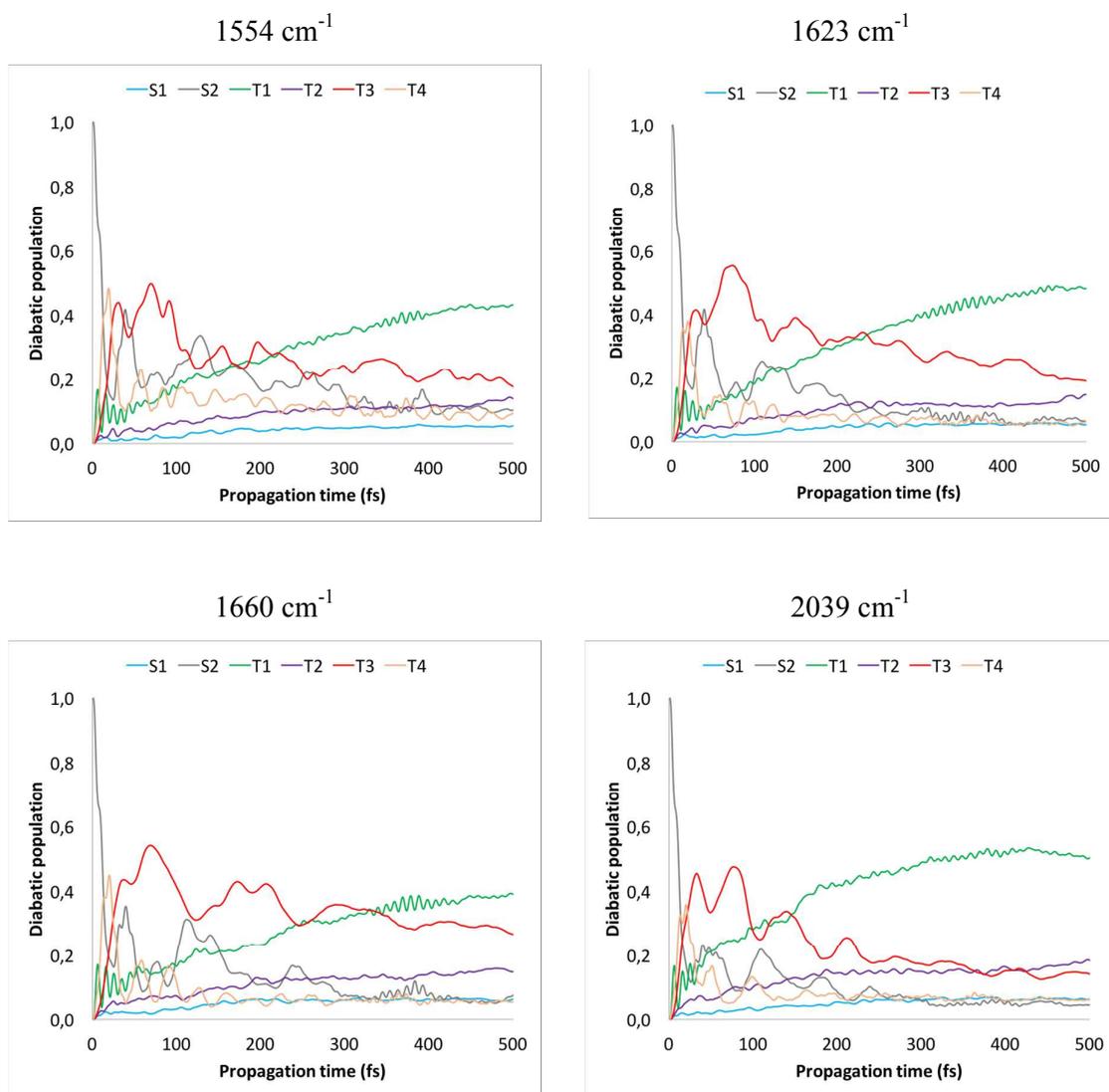


Figure S4. Diatomic electronic populations as a function of time, for different models considering the a'' normal modes at 90 and 475 cm⁻¹, the a' normal modes at 93, 439, 498 and 637 cm⁻¹, and an extra a' normal mode. The triplet contributions are summed up.

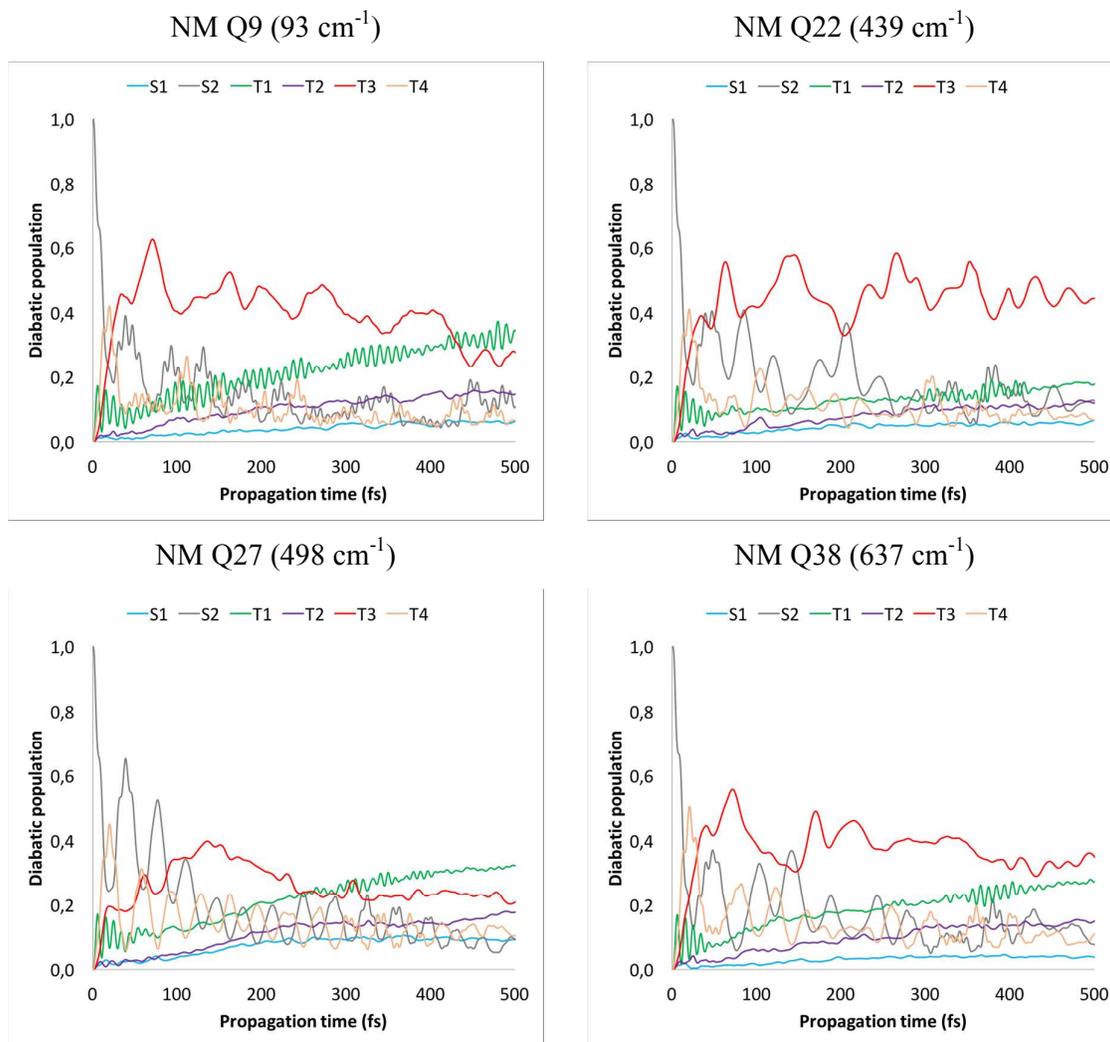


Figure S5. Diabatic electronic populations as a function of time for different 5-modes models arising from the 6-modes Model-1 and excluding the normal mode indicated. The triplet contributions are summed up.

(a) $[\text{Re}(\text{CO})_3(\text{phen})(\text{im})]^+$			(b) $[\text{Re}(\text{CO})_3(\text{bpy})(\text{im})]^+$		
LUMO+1			LUMO		
46a'' -0.0850			79a' -0.0956		
HOMO	HOMO-1	HOMO-2	HOMO	HOMO-1	HOMO-2
45a'' -0.2377	78a' -0.2449	77a' -0.2517	43a'' -0.2373	74a' -0.2468	73a' -0.2512
HOMO-3			HOMO-3		
44a'' -0.2582			42a'' -0.2581		
HOMO-4	HOMO-5		HOMO-4	HOMO-5	
76a' -0.2665	43a'' -0.2761		41a'' -0.2691	40a'' -0.3149	

Figure S6. Kohn-Sham frontier orbitals of (a) $[\text{Re}(\text{CO})_3(\text{phen})(\text{im})]^+$ and (b) $[\text{Re}(\text{CO})_3(\text{bpy})(\text{im})]^+$ in water (energies are in hartrees).

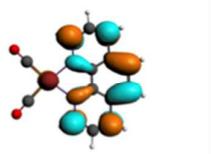
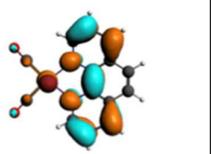
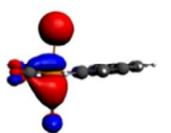
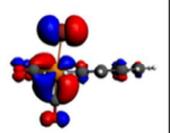
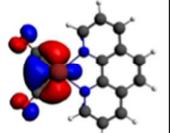
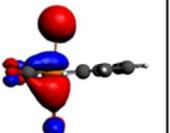
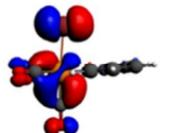
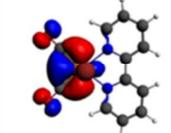
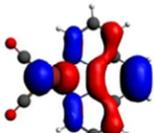
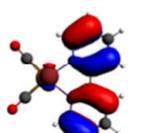
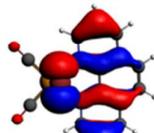
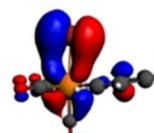
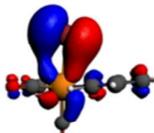
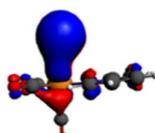
(c) $[\text{Re}(\text{CO})_3(\text{phen})(\text{Br})]$			(d) $[\text{Re}(\text{CO})_3(\text{bpy})(\text{Br})]$		
					
LUMO+1			LUMO		
48a'' -0.0806			77a' -0.0905		
					
HOMO	HOMO-1	HOMO-2	HOMO	HOMO-1	HOMO-2
47a'' -0.2311	76a' -0.2325	75a' -0.2480	45a'' -0.2306	72a' -0.2336	71a' -0.2473
					
HOMO-3			HOMO-3		
74a' -0.2574			44a'' -0.2634		
					
HOMO-4	HOMO-5		HOMO-4	HOMO-5	
46a'' -0.2678	73a' -0.2751		70a' -0.2710	43a' -0.2724	

Figure S7. Kohn-Sham frontier orbitals of (c) $[\text{Re}(\text{CO})_3(\text{phen})(\text{Br})]$ and (d) $[\text{Re}(\text{CO})_3(\text{bpy})(\text{Br})]$ in water (energies are in hartrees).