Population of triplet states in acetophenone: a quantum dynamics perspective
Population des états triplets de l'acétophénone: un point de vue dynamique quantique

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Abstract

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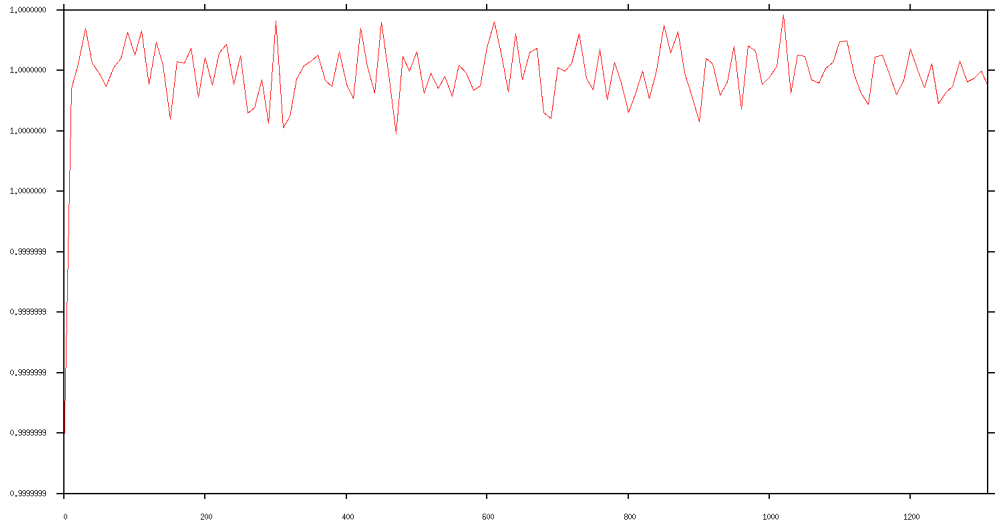
1. Time-evolution of the wavefunction norm

Figure 1: Evolution of the norm of the wavefunction for the MCTDH dynamics presented in the main text.



2. Long time dynamics

In this section, we explore a long time quantum dynamics without initial impulsion of the wavepacket. The conditions of this calculation are summarized in Table 1. In this dynamics, the norm of the wavefunction is only converged with an error of 0.01, and the highest single particle functions have a population of 0.1. Therefore, the conclusions of this dynamics are only approximate.

Table 1: Summary of the mode combination and single particle function scheme used in MCTDH for acetophenone. The frequencies represent the normal mode vibrational frequency in cm^{-1}.

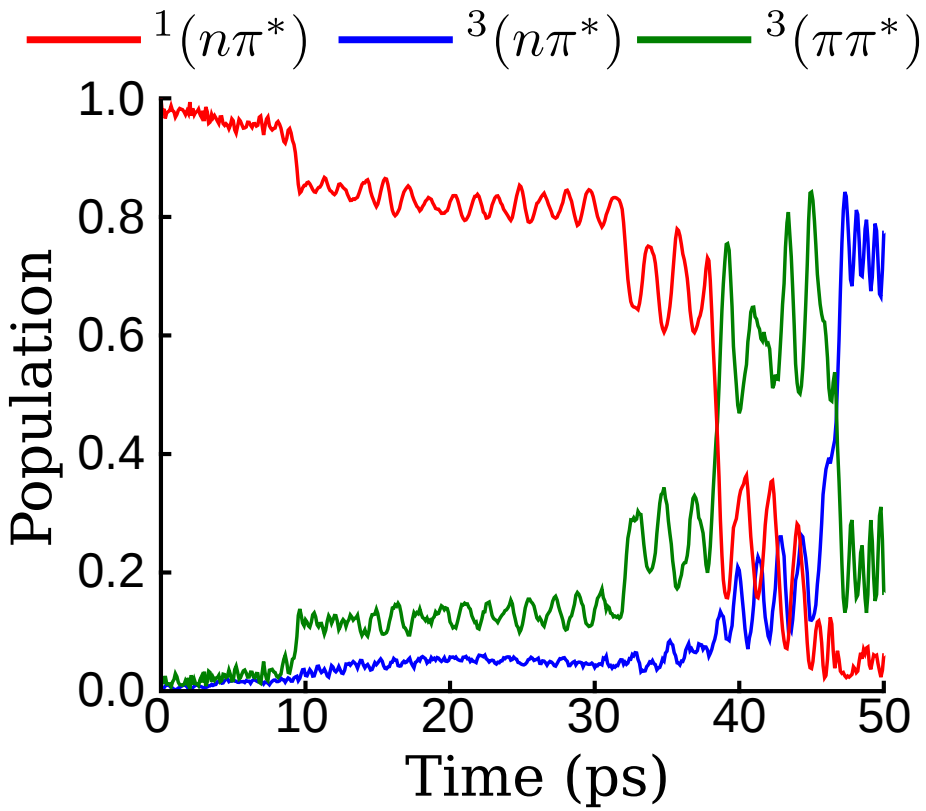
Mode	Frequencies	SPF[a]		
		$^3n\pi^*$	$^3\pi\pi^*$	$^1n\pi^*$
1	87 , 150 , 188	2	2	2
3	193 , 351 , 551	2	2	2
3	227 , 482 , 531	2	2	2
4	493, 652 , 767	2	2	2
5	702 , 748 , 836	2	2	2
6	891 , 938 , 975	2	2	2
7	985 , 1050 , 1067	2	2	2
8	1092 , 1138 , 1162	2	2	2
9	1212 , 1262 , 1299	2	2	2
10	1361 , 1452 , 1463	2	2	2
11	1552 , 1567 , 1616	2	2	2
12	1625 , 1637	2	2	2
13	1665 , 1686	2	2	2

[a] Single particle functions

In Figure 2, the evolution of populations is shown. The full quantum trajectory can be divided into 4 different timescales: (i) the first 9 ps are characterized by a relatively slow transfer towards $^3\pi\pi^*$ and no significant population on $^3n\pi^*$; (ii) From 9 ps to 30 ps, a sudden transfer occurs, lowering the $^1n\pi^*$ population from 95% to 85% in half a picosecond, with a concomitant increase of the $^3\pi\pi^*$ population, while the $^3n\pi^*$ population remains close to 1–2%; (iii) From 30 ps to 45 ps, a first population inversion occurs, the singlet state population drops to less than 20% in a few ps, and the triplet $^3\pi\pi^*$ state becomes the dominant state, while the $^3n\pi^*$ slowly acquires population; and (iv) From 45 ps on, a second population inversion takes place, this time between the triplet states, eventually reaching the final ratio: 5% in $^1n\pi^*$, 15–20% in $^3\pi\pi^*$, 75–80% in $^3n\pi^*$.

From this results, we can easily interpret that the nuclear wavepacket evolves initially by means of an internal conversion process on the singlet surface. This process is slow due to the small vibronic couplings in acetophenone. At around 9 ps, the wavepacket reaches a region of strong non-adiabatic coupling, and thus, a coherent coupling between the $^1n\pi^*$ and $^3\pi\pi^*$ starts. The transfer of population remains essentially constant from 9 ps and 32 ps, with an average value of 80% of the population in the $^1n\pi^*$ state. The evolution of the $^3\pi\pi^*$ population is concomitant with the singlet population, due to the direct coupling between these

Figure 2: Evolution of diabatic populations of the lowest singlet and triplets of acetophenone.



two states. The $^3n\pi^*$ population, which is not directly coupled to the singlet state, remains in an average value of about 5-10%. Accordingly, the ISC mechanism dominates during more than 20 ps. After 30 ps, population oscillations dramatically increase. There, most of the wavepacket arrives to the non-adiabatic coupling region, culminating in a population inversion between $^1n\pi^*$ and $^3\pi\pi^*$ states. At the same time, the $^3n\pi^*$ population exceeds 10% and starts to oscillate coherently with other state populations for a few ps. Here, several mechanisms co-exist: a very strong ISC able to populate efficiently the $^3\pi\pi^*$ state and a relatively efficient conical intersection between the two triplet states. The fast $^3\pi\pi^*$ population is a clear indication that non-adiabatic couplings are fully active through out-of-plane nuclear displacements, which in turn activate the coupling between the triplet states. As a matter of fact, the $^3\pi\pi^*$ state dominates only for 10 ps before to be overpassed by the $^3n\pi^*$ one.