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Population of triplet states in acetophenone: A quantum dynamics perspective

Miquel Huix-Rotllant [a, b, **], Irene Burghardt [a], Nicolas Ferré [b, *]

[a] *Institut für Physikalische und Theoretische Chemie, Göethe-Universität Frankfurt, D-60439 Frankfurt am Main, Germany*
[b] *Aix-Marseille Université, CNRS, Institut de Chimie Radicalaire, 13397 Marseille Cedex 20, France*

A B S T R A C T

When initially excited to its first singlet excited state, acetophenone, a prototypical aromatic ketone, is characterized by a singlet to triplet conversion quantum yield close to 100%. In this work, the time evolution of photo-excited acetophenone is theoretically investigated using quantum dynamics simulations based on the Multi Configuration Time Dependent Hartree (MCTDH) method. A model Hamiltonian, comprising both electronic and vibronic terms, is defined and its parameters are fitted to available data obtained by high-level quantum chemical calculations. An exploratory MCTDH dynamics shows a sequential mechanism $S_1 \rightarrow T_2 \rightarrow T_1$. The population in the triplet manifold is distributed evenly among the two states, explaining the origin of acetophenone rich photochemistry.

Initialement excité vers son premier état excité singulet, l'acétophénone, une cétone aromatique typique, est caractérisée par une conversion singulet vers triplet proche de 100%. Dans ce travail, l'évolution temporelle de l'acétophénone photo-excitée est étudiée de faҫon théorique par dynamique quantique basée sur la méthode Multi Configuration Time Dependent Hartree (MCTDH). Un Hamiltonien modèle, comprenant des termes électroniques et vibroniques, est défini et ses paramètres sont déterminés à partir de données obtenues par des calculs de chimie quantique de haut niveau. La dynamique MCTDH exploratoire montre un mécanisme séquentiel $S_1 \rightarrow T_2 \rightarrow T_1$. La population est distribuée également dans les deux états triplet, expliquant l'origine de la photochimie riche de l'acétophénone.

1. Introduction

Acetophenone, like many other aromatic ketones, features energetically close excited singlet and triplet states, even in the Franck–Condon region [1–3]. The relatively fast triplet state population makes photo-excited aromatic ketones very efficient molecular systems for hydrogen abstraction, double bond addition or bond cleavage. More specifically, acetophenone is characterized by a lowest singlet state (of $n \rightarrow \pi^*$ character) experimentally estimated

at 3.38 eV above the electronic ground state and calculated (adiabatically) at 3.44 eV [3]. It is noteworthy that two (lowest) triplet states of $n \to \pi^*$ and $\pi \to \pi^*$ characters are quasi-degenerate with the singlet excited state. This peculiarity opens the possibility to efficiently populate both triplet states immediately upon light absorption. This efficient singlet to triplet decay is further enhanced by the existence of an extended region of near-degeneracy which culminates with the presence of the so-called 3-state crossing.

While static mechanistic details have been reported elsewhere [1,3], the photochemical path is summarized in Fig. 1. Examination of this picture shows that the two triplet states have phosphorescence light emission at similar wavelengths, such that it is experimentally difficult to assess which state(s) is(are) photoactive. However this knowledge is of tremendous importance to understand, for instance, the photoreduction properties of acetophenone, which can in turn be modulated by external factors like the presence of chemical substituents or polar solvents. As a matter of fact, recent near infra-red spectroscopy studies have shown that triplet states of substituted acetophenones are in "thermal" equilibrium, finding that their respective populations remain unaffected by the above-mentioned factors [4]. Moreover, the same work concludes that the $^3\pi\pi^*$ photoreduction activity is zero. However, the ordering of the triplet states in these molecular systems appears to be sometimes inverted with respect to bare acetophenone.

The kinetics of the intersystem crossing of acetophenone have not been reported to the best of our knowledge, but there are reports on the closely related benzaldehyde molecule [5, 6]. Ultrafast electron diffraction experiments by Zewail and co-workers showed a lifetime of the first singlet excited state of 42 ps [5], whereas theoretical Marcus theory estimates by Ou and Subotnik predicted a four times faster process [6]. Accordingly, the dynamical mechanism of the acetophenone populated triplet states remains an open question and the central aim of the present contribution.

The computational investigation of excited state populations and, by extension, the calculation of quantum yields, is still in its infancy for at least two main reasons [7]. First, the selected theoretical model must be flexible enough to describe with the same accuracy some (or many) electronic states, their couplings and crossings. Second, the statistical nature of the property under consideration imposes to sample a large portion of the phase space, including the possibility to jump (hop) from one state to another. While direct quantum dynamics simulations propagating a wavepacket with the time-dependent Schrödinger equation would be an ideal method of choice (the so-called standard method) [8], its computational cost remains prohibitive for most systems of interest. On the other hand, cost efficient semi-classical molecular dynamics simulations (Ehrenfest, surface-hopping, etc.) are cost-effective approaches which do not require the a priori knowledge of the (electronic) potential energy surface [9–11]. Nevertheless, the classical propagation of the nuclear degrees of freedom implies to perform a statistical sampling over several trajectories, which turns out to be difficult to converge when several branchings and crossings are implied in the photochemical process.

Here, we have chosen to perform full quantum dynamics simulations employing the multi-configuration time-dependent Hartree (MCTDH) method [12–14]. This approach has proven to be very accurate, especially when strong non-adiabatic effects are present [15–18]. In MCTDH, the vibronic wavepacket is represented by the time-dependent wavefunction

$$\Psi(\{Q_i\}, t) = \sum_{j_1}^{N_1} \cdots \sum_{j_n}^{N_n} A_{j_1 \cdots j_n}(t) \prod_{k=1}^{f} \phi_{j_k}^{(k)}(Q_k, t), \qquad (1)$$

in which Q_k are combined nuclear coordinates and $A_{j_1 \cdots j_k}(t)$ are the multi-configuration expansion coefficients of the Hartree-products, $\phi_{j_k}^{(k)}(Q_k, t)$ are the time-dependent single particle functions. The Ansatz is inserted into the Dirac-Frenkel variational principle, $\langle \delta\Psi(t) | \widehat{H} - i\hbar \frac{\partial}{\partial t} | \Psi(t) \rangle = 0$, from which a set of equations of motion for the propagation of the time-dependent expansion coefficients and single-particle-functions is derived. The variational principle implies that one gets a systematic better description of the wavepacket with additional single particle functions, and thus the wavepacket can be systematically converged. In practice, efficient implementations of the real-time
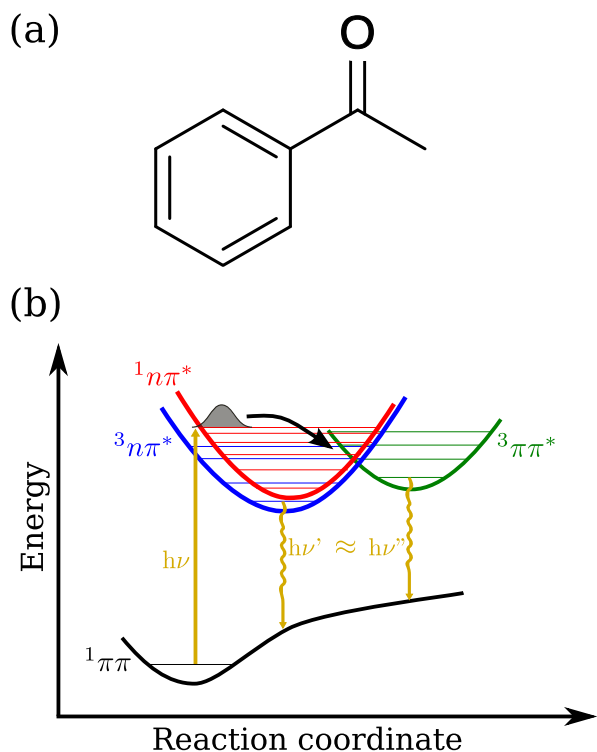

Fig. 1. (a) Acetophenone chemical structure; (b) Schematic representation of the $^1n\pi^*$-based photochemistry of acetophenone, including $^3n\pi^*$ and $^3\pi\pi^*$ triplet populations and eventually phosphorescence.