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► **To cite this version:**

Saikat Mukherjee, Mario Barbatti. Ultrafast internal conversion without energy crossing. Results in Chemistry, 2022, 4, 10.1016/j.rechem.2022.100521 . hal-03781329

HAL Id: hal-03781329

<https://hal.science/hal-03781329>

Submitted on 20 Sep 2022

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Ultrafast internal conversion without energy crossing

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ARTICLE INFO

Keywords:

Excited states
Nonadiabatic dynamics
Weak coupling
Gap law
Computational photochemistry

ABSTRACT

Ultrafast (sub-picosecond) internal conversion can occur between electronic states without energetically accessible conical intersections. For that, the molecule must remain in a region of at least weak nonadiabatic coupling, multiplying the odds of a transition, each with a small probability. This phenomenon is discussed with a simple analytical model correlating the instantaneous probability to the lifetime.

Introduction

The most accepted picture of molecular events following a photoexcitation dictates that an ultrafast, sub-picosecond internal conversion between electronic states should occur at the proximity of a conical intersection, where the nonadiabatic couplings are large enough to induce the transition [1]. If, however, the molecule rests on regions of considerable energy gaps, the gap law [2] predicts that the internal conversion will be slow, competing with other time-consuming processes such as intersystem crossing and luminescence. Although such a picture tends to be correct, there may be exceptions.

Our team recently found that the S_3 to S_2 internal conversion of n -protonated azaindoles (n -AIH⁺) was ultrafast, despite the absence of energetically accessible conical intersections [3]. For 6-AIH⁺, surface hopping simulations predicted an S_3 lifetime of 156 ± 40 fs, even though the energy gaps at the hopping time had a distribution with a 0.47 eV mean value and 0.13 eV standard deviation. Similarly, for 7-AIH⁺, the predicted S_3 lifetime was 278 ± 36 fs with energy gaps at the hopping times also having a 0.47 eV mean value and 0.22 eV standard deviation. Ultrafast dynamics at large energy gaps has also been observed in quantum wavepacket propagation [4]. Aleotti *et al.* reported that the $S_2 \rightarrow S_1$ pyrene dynamic occurs within 100 fs without the molecule ever coming near a crossing point.

These results are counterintuitive as we might expect that such ultrashort lifetimes would require hoppings occurring near conical intersections. However, as shown in Refs. [3–4], the lowest energy conical intersection was too high for the discussed molecules. In 6-AIH⁺, the S_3 /

S_2 intersection is 1.3 eV above the S_3 minimum, while in 7-AIH⁺, it is 1.5 eV above it [3]. In pyrene, S_2/S_1 intersection is 0.4 eV above the Franck-Condon point [4].

We rationalized our AIH⁺ results by noticing that the mean S_3/S_2 energy gap during the S_3 dynamics was 0.6 and 0.8 eV for 6- and 7-AIH⁺, respectively. Thus, n -AIH⁺ vibrating on S_3 is constantly in a weak coupling region. The small hopping probabilities are compensated by the high number of timesteps where the hopping can occur, causing the ultrafast internal conversion.

Based on this example, we can distinguish two types of ultrafast dynamics. The first is the usual situation where the molecule relaxes on the upper electronic state until it enters the nonadiabatic coupling region with small energy gaps and large hopping probabilities (Fig. 1-left). Ethylene dynamics would be the prototypical example with its twisted-pyramidalized conical intersection funneling the excited-state population within less than 100 fs [5]. The second type—exemplified by S_3 -excited n -AIH⁺—occurs when the molecule remains at moderate gaps, where the hopping probability is small but the hopping opportunities numerous (Fig. 1-right). These two regimes can also be respectively identified as the strong and weak coupling limits of Engels and Jortner [2].

This short paper further develops how ultrafast internal conversion can occur in this second scenario. We work in the frame of instantaneous probabilities, in which the probability of a nonadiabatic transition between electronic states is a function of time, such as in the fewest switches surface hopping (FSSH) [6]. An alternative would be to work with global nonadiabatic frameworks, which evaluate the total

Abbreviations: FSSH, Fewest switches surface hopping; n -AIH⁺, protonated n -azaindole.

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<https://doi.org/10.1016/j.rechem.2022.100521>

Received 21 July 2022; Accepted 10 September 2022

Available online 15 September 2022

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probabilities that the molecule would end in each state, just like in the Landau-Zener model [7]. Another alternative would be to employ Fermi's Golden rule to get probability per unit of time (rate) [2]. Nevertheless, working with instantaneous probabilities can directly connect the discussion to FSSH surface hopping simulations. Let us suppose a molecule is instantaneously prepared in state 1 in a nonadiabatic coupling region, where it can change to state 0 with a constant hopping probability p within Δt . Let us also assume that the $0 \rightarrow 1$ back hopping probability is null. It is a simple exercise [see Section *Demonstration of equation (1)*] to show that the population of state 1 decays exponentially with the time the molecule remains in the nonadiabatic coupling region with a time constant τ given by

$$\tau = -\frac{\Delta t}{\ln(1-p)} \quad (1)$$

Fig. 2 plots τ as a function of p for $\Delta t = 0.025$ fs. (There is nothing special about this particular value of Δt beyond that it is the default value adopted in the *Newton-X* program [8].) The internal conversion will be ultrafast (sub-picosecond) for $p > 2.5 \times 10^{-5}$. In the strong coupling regime (Fig. 1-left), the molecule should immediately hop to the lower state. For a maximum survival time of 10 fs, it means $p > 2.5 \times 10^{-3}$.

We can now return to the n -AIH⁺ case. The decoherence-corrected FSSH equations in Ref. [3] were integrated with $\Delta t = 0.025$ fs. The distribution of $S_3 \rightarrow S_2$ probabilities is shown in Fig. 3-Top. This distribution considers all points from all trajectories until the first hopping to S_2 , including those with null probabilities. It peaks at zero, and the mean probability was 2.4×10^{-4} for 6-AIH⁺ and 1.5×10^{-4} for 7-AIH⁺. Fig. 3-bottom shows the hopping probabilities at the hopping time. As expected, they strongly drop with increasing energy gaps.

With Eqn 1 and p given by the mean instantaneous $S_3 \rightarrow S_2$ probability, the S_3 lifetime is $\tau = 104$ fs for 6-AIH⁺ and 166 fs for 7-AIH⁺, which are 30 to 40 % smaller than the actual lifetimes predicted by the surface hopping simulations. This difference is due to neglecting the back hoppings in the analytical model.

Concluding, we showed that a molecule subject to a continuous weak nonadiabatic coupling regime can still undergo ultrafast internal conversion even without moving near conical intersections.

Demonstration of Eqn 1

To find the lifetime of state 1, we should compute the probability p_N that the system will hop to state 0 at a time t' corresponding to $N = t'/\Delta t$ time steps. Under the assumption that there are no back hoppings, this probability is the product of the probability of not having hopped in any of the previous $N-1$ steps times the probability of hopping at step N :

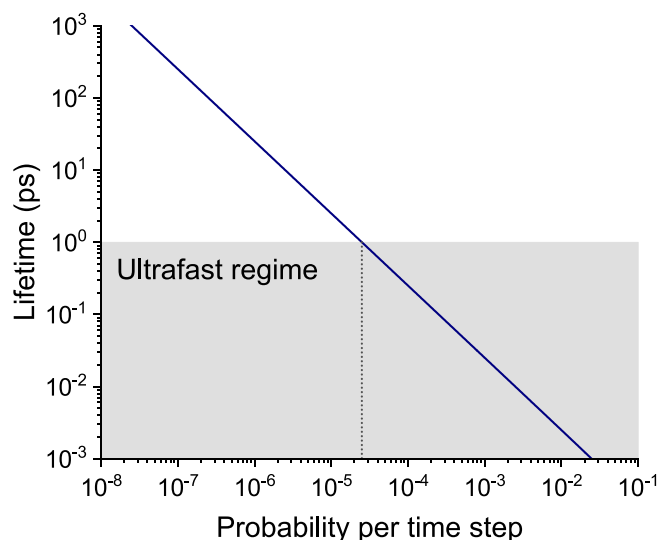


Fig. 2. Plot of the upper state lifetime (τ) as a function of the instantaneous probability within $\Delta t = 0.025$ fs (p), according to Eqn 1.

$$p_N = (1-p)^{N-1}p. \quad (2)$$

The probability $P_0(t)$ that the system is in state 0 at time t is the sum of all p_N probabilities from $N = 1$ to K , where $K = t/\Delta t$,

$$P_0(t) = \sum_{N=1}^K p_N = \sum_{N=1}^K (1-p)^{N-1}p. \quad (3)$$

To evaluate the summation, we use the geometric series identity

$$\sum_{i=1}^n a^{i-1} = \frac{1-a^n}{1-a} \quad (4)$$

to get

$$\sum_{N=1}^K (1-p)^{N-1}p = 1 - (1-p)^K. \quad (5)$$

Thus, the probability that the system is in state 0 at time t is

$$P_0(t) = 1 - (1-p)^{t/\Delta t}, \quad (6)$$

while the probability it is in state 1 is

$$P_1(t) = (1-p)^{t/\Delta t}. \quad (7)$$

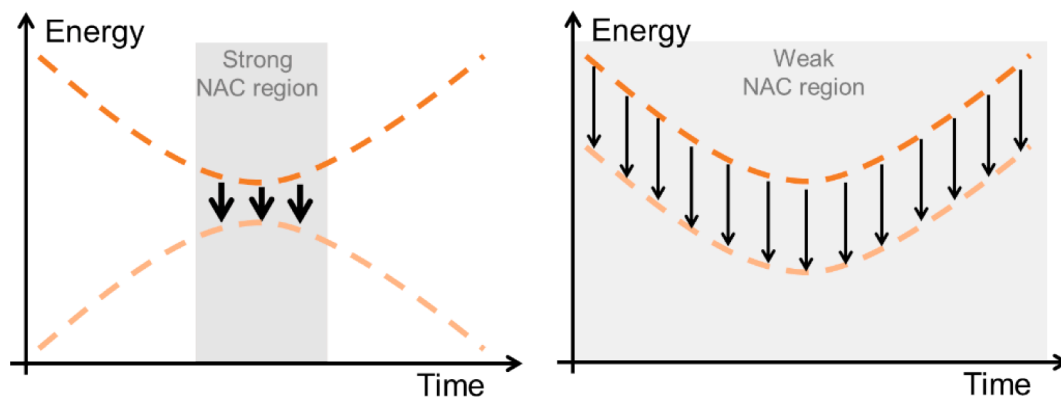


Fig. 1. Two ways of reaching ultrafast internal conversion of a molecule moving in the upper state. Left: the energy gap with the state below is tiny for a short period, increasing the hopping probability for a few timesteps. Right: the energy gap remains small for long periods but never close to an intersection; hopping with small probabilities can happen over many timesteps.

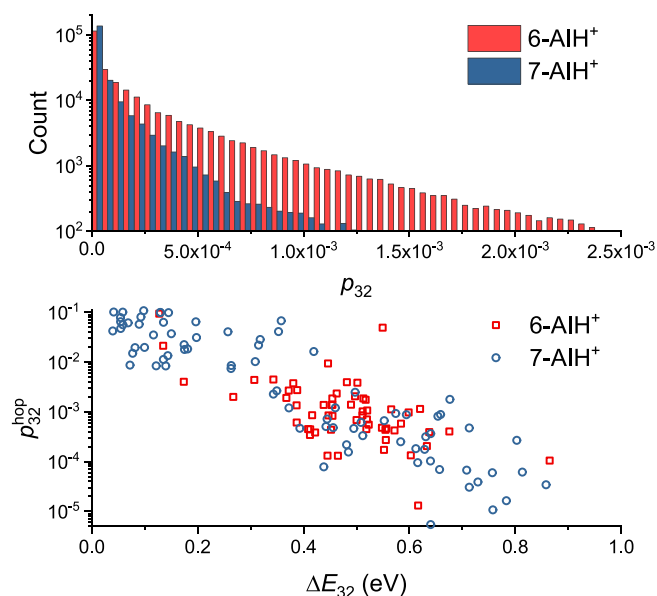


Fig. 3. Top: Histogram of probabilities of $S_3 \rightarrow S_2$ hopping for all time steps in S_3 . Bottom: $S_3 \rightarrow S_2$ hopping probabilities as a function of the energy gap when the hopping occurs. n -AIH⁺ data from Ref. [3].

We can rewrite $P_1(t)$ as

$$P_1(t) = e^{-t/\tau}, \quad (8)$$

from where Eqn 1 follows.

This constant-probability model is meant as proof of principle that ultrafast transitions can occur at large gaps. Nevertheless, it does not imply that ultrafast transitions at large gaps must have constant probabilities.

CRedit authorship contribution statement

Saikat Mukherjee: Conceptualization, Methodology, Writing – review & editing, Funding acquisition. **Mario Barbatti:** Methodology,

Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data used in this research is available at DOI: 10.6084/m9.figshare.19794130.v1

Acknowledgements

The authors thank the funding provided by European Research Council (ERC) Advanced grant SubNano (Grant agreement 832237).

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