Ultrafast internal conversion without energy crossing

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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.

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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 having also a 0.47 eV mean value and 0.22 eV standard deviation.

These results are counterintuitive as we might expect that such ultrashort lifetimes would require hoppings occurring near conical intersections. However, as we showed in that work, the lowest energy S\(_3\)/S\(_2\) conical intersection was too high for both molecules. In 6-AIH\(^+\), the intersection is 1.3 eV above the S\(_1\) minimum, while in 7-AIH\(^+\), it is 1.5 eV above it.

We rationalized those results by noticing that the mean S\(_3\)/S\(_2\) energy gap during the S\(_1\) 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 (Figure 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.\(^4\) 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 (Figure 1-right). These two regimes can also be respectively identified as the strong and weak coupling limits of Engels and Jortner.\(^5\)

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 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).\(^8\) 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 constant hopping probability \( p \) within \( \Delta t \). Let us also assume that the 0→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 \( \tau \) given by

\[
\tau = \frac{\Delta t}{\ln(1 - p)}.
\]

Figure 2 plots \( \tau \) as a function of \( p \) for \( \Delta t = 0.025 \) fs. (There is nothing special about this particular value of \( \Delta t \) beyond that it is the default value adopted in the Newton-X program.) The internal conversion will be ultrafast (sub-picosecond) for \( p > 2.5 \times 10^{-8} \).

We can now return to the \( n \)-AIH\(^+ \) case. The decoherence-corrected (DC) FSSH equations in Ref.\(^3\) were integrated with \( \Delta t = 0.025 \) fs. The mean instantaneous \( S_3 \rightarrow S_2 \) probability was \( 2.4 \times 10^{-4} \) for 6-AIH\(^+ \) and \( 1.5 \times 10^{-4} \) for 7-AIH\(^+ \). These mean values consider all points from all trajectories until the first hopping to \( S_2 \) including those with null probabilities. With Eq. (1), 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.

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Figure 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.

Figure 2. Plot of the upper state lifetime (\( \tau \)) as a function of the instantaneous probability within \( \Delta t = 0.025 \) fs (\( p \)), according to Eq. (1).

Demonstration of equation (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 \( N \):

\[
p_N = (1 - p)^{N-1} p.
\]

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 \( K = t / \Delta t \),

\[
P_0(t) = \sum_{N=1}^{K} p_N = \sum_{N=1}^{K} (1 - p)^{N-1} p.
\]

To evaluate the summation, we use the geometric series identity...
\[ \sum_{i=1}^{n} a_i a^{-1} = \frac{1 - a^r}{1 - a} \] (4)

to get
\[ \sum_{i=1}^{n} \left(1 - p^{y_i} \right) = 1 - \left(1 - p^y \right)^{n}. \] (5)

Thus, the probability that the system is in state 0 at time \( t \) is
\[ P_0(t) = 1 - \left(1 - p^y \right)^{r/t}. \] (6)

while the probability it is in state 1 is
\[ P_1(t) = \left(1 - p^y \right)^{1/r}. \] (7)

We can rewrite \( P_1(t) \) as
\[ P_1(t) = e^{-t/t}. \] (8)

from where Eq. (1) follows.

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