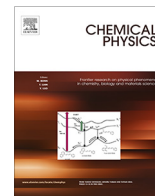




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## Ultrafast internal conversion in 4-aminobenzonitrile occurs sequentially along the seam

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### ABSTRACT

Upon UV light absorption, 4-aminobenzonitrile undergoes an ultrafast radiationless decay process from a charge-transfer state to a locally-excited state. This pathway proceeds through an extended seam of conical intersections between the second- and first-excited singlet electronic states. Quantum dynamics simulations show that planar geometries dominate the earlier times (<20 fs), after which the whole seam becomes explored, as the wavepacket spreads and breathes along both sides of the unstable ridge with respect to the amino-bending coordinate.

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### 1. Introduction

4-aminobenzonitrile (ABN), and its *N*-dimethyl derivative, DMABN [1] are well-known prototype systems for studying intramolecular charge transfer (ICT) in electron donor/acceptor molecules. Despite their chemical similarity, their luminescent patterns are quite different according to the environment: ABN shows single fluorescence in any solvent (normal band), whereas DMABN exhibits normal fluorescence in non-polar solvents but dual fluorescence in polar ones (normal and anomalous bands) [2,3]. The sensitivity of ABN derivatives to their environment makes them good candidates as fluorescent probes, chemical sensors, molecular switches, or electro-optical switches [4–8].

It is well-established that the normal band is originated from a locally-excited (LE) state, while the anomalous band is due to a charge-transfer (CT) state, with a large dipole moment that is stabilized in polar solvent environments. The exact structure of the species responsible for the anomalous band and the mechanism that populates them are still controversial due to contradictory arguments, based on both experimental observations and theoretical calculations, which support different models and hypotheses [1,3,9,10,11].

Three received models have been proposed regarding the structure of the luminescent CT species: the planar ICT model (PICT) [12], the twisted one (TICT) [10,13], and the partially twisted or pretwisted one (pTICT) [14]. It seems sufficiently proven that the PICT and TICT species actually correspond to two minimum-energy

points in the potential-energy surface (PES) of the excited CT state in both ABN and DMABN, but their respective roles in the fluorescent spectra remain to be clarified. A fourth model, the rehybridized ICT (RICT) [15], is thought to be a stable species corresponding to a  $\pi\sigma^*$  excited state but is nowadays discarded as a luminescent species [16–19].

The ICT mechanism is triggered upon UV light absorption, which populates first the  $S_2$  state of CT character [20]. The subsequent sequence of steps leading to the  $S_1$  PES (with both LE and CT regions) until the luminescent species are formed is still under discussion. Gómez et al. proposed the following mechanism in 2005 [20]. After excitation to the  $S_2$  state, the system relaxes to the PICT minimum. The system follows then a barrierless pathway along the amino-bending coordinate to the optimized  $S_2/S_1$  conical intersection (denoted CI- $C_2$ ). Because of the extended conical intersection seam, ultrafast radiationless decay from  $S_2$  to  $S_1$  can take place at various torsion angles of the amino group leading either to the LE or the TICT geometries on  $S_1$ . Experimental works suggest initial production of the LE species on  $S_1$  through internal conversion from  $S_2$  and later equilibration with a CT species on  $S_1$  [9].

Park et al. reported recently an experimental study based on highly time-resolved fluorescence spectra (TRFS) over the whole emission domain of DMABN in acetonitrile [18]. Such accurate measurements provide valuable information about the dynamics of the ICT process free from the interferences of the solvent reorganization and vibrational relaxation dynamics that occur on the same time scale. The experimental techniques used in that work also give access to an analysis of the ultrafast events that occur within the first few femtoseconds. From their observations it is concluded that, after photoexcitation to the  $S_2$  state (CT), there is

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significant internal conversion to the  $S_1$  state in less than 30 fs for geometries that are still quasiplanar, thus in the LE region. A similar ultrafast mechanism was also proposed in a previous work by the McCamant group [21,22].

Computational studies carried out on ABN and DMABN have shown that the topographies of the  $S_2$  and  $S_1$  PESs of both systems are similar, but small energetic changes are suspected to induce a different interplay between the LE and CT species and lead to either normal or dual fluorescence [3,20]. The initial steps of the deactivation mechanism, though, are expected to be analogous in both systems, so the experimental conclusions, derived by Park et al. [18] for DMABN, should hold in a qualitative way for ABN as well.

In a previous work [23] on ABN, we have shown that ultrafast production of the LE species in  $S_1$  can occur efficiently via  $S_2/S_1$  internal conversion involving a newly-investigated planar conical intersection (denoted  $CI-C_{2v}$ ), both in the gas phase and a polar solvent. Although this conical intersection is not the lowest-energy one within the  $S_2/S_1$  intersection seam, it is easily accessible from the Franck-Condon point both geometrically and energetically. In other words, the system is able to deactivate first upon involving coordinates associated to such in-plane skeletal deformations in a first stage, while bending and twisting motions may occur on longer time scales once vibrational energy is redistributed. Curchod et al. did recently a study on DMABN [24] using time-dependent DFT combined with Multiple-Spawning dynamics. While their molecular system (DMABN) is slightly different from ours (ABN), they have reached similar conclusions: ultrafast transfer from  $S_2$  to  $S_1$  can occur without torsion of the amino group.

In the present work, we investigate in more detail the competition between the deactivation pathways through a planar conical intersection,  $CI-C_{2v}$ , and through the low-lying  $C_s$  one,  $CI-C_s$ , so as to provide further information about the ultrafast process that populates the LE state almost immediately after the initial photoexcitation of the CT state. Our objective is to determine whether deactivation occurs specifically around  $CI-C_{2v}$ , if the system rather bifurcates early on towards  $CI-C_s$ , as suggested by Gómez et al. [20], or if the situation is intermediate, with significant delocalization along the amino-bending coordinate so that the wavepacket will reach the whole portion of the  $S_1/S_2$  seam connecting the bent conical intersection to the planar one at similar times.

## 2. Computational details

The topographies of both coupled PESs involved in the initial steps of the process was first determined from a CASSCF(12,11)/cc-pVDZ study using the Gaussian 09 package [25]. Energies in these regions were further refined at the CASPT2 level with the Molcas 7 package [26] so as to include the effect of dynamic correlation in the calculations. In our previous study, we showed that the effect of a polar solvent on ABN only enhances the efficiency of the radiationless decay but does not change the mechanism of the ultrafast process under study (less than 30 fs) [3,23]. This was not accounted for in the present study, as calculations *in vacuo* seem sufficient to provide reliable mechanistic information.

In order to run quantum dynamics calculation with the multi-layer version [27] of the multiconfiguration time-dependent Hartree (ML-MCTDH) method implemented in the Heidelberg MCTDH package [28,29], analytical expressions of quasidiabatic coupled PESs are required, often in the form of what is called a vibronic-coupling Hamiltonian (VCH) model [30–32]. Its entries are expressed usually as linear (linear vibronic-coupling model – LVC) or quadratic (quadratic vibronic-coupling model – QVC) functions of normal Cartesian coordinates originated from the ground-state equilibrium geometry (Franck-Condon point). This is the type of approach that we used in the present work. However, the main

originality of our strategy is that we explicitly used analytical relationships between adiabatic data and diabatic parameters so as to obtain the latter automatically. Consistently with our previous study [23], three diabatic states are involved (corresponding diagonal entries of the electronic-energy matrix:  $H_{11}(\mathbf{Q})$ ,  $H_{22}(\mathbf{Q})$ , and  $H_{33}(\mathbf{Q})$ ). In addition, along some directions or coordinates, the model was adjusted to obtain a better description of the conical intersections. We thus circumvent numerical fitting procedures that, in some cases, can occur to be time consuming and tedious tasks from a technical perspective. Our full-dimensional models of coupled PESs (39D in the present study) are based on CASSCF energies and geometries and further refined to match CASPT2 data in the gas phase.

The choice of an adequate coordinate system depends on the process under study. In particular, for molecular systems with large-amplitude motions, normal-mode coordinates are not adequate to describe motions leading far from the equilibrium position [33]. Thus, it is often beneficial to describe the molecular system with curvilinear coordinates, *i.e.*, distances and angles, since they describe large-amplitude motions such as for example torsions in a more natural way; in other words, they will provide a simpler expression of the PES. Unfortunately, the use of curvilinear coordinates can lead to very complicated expressions of the kinetic-energy operator (KEO) [34,35], which can be expressed numerically (but exactly) [36–40] or analytically [41–45]. An analytical approach is more practical, as there is no need to compute the numerical the KEO on a grid and then fit the results or make further approximations (for example upon considering Taylor expansions). However, an analytical expression of the KEO is not always compatible with an “MCTDH format” (see below), where operators must be written as sums of products of low-dimensional functions. Some specific types of coordinates allow this condition to be fulfilled, in particular so-called polyspherical coordinates, denoted  $\mathbf{Q}_{\text{poly}}$  [41,43,44], which were indirectly used in this study. However, the actual coordinates,  $\mathbf{Q}$ , used here to define the model and to run the dynamics were obtained after several transformations of the polyspherical coordinates.

### 2.1. Sets of coordinates

Fig. 1 depicts the polyspherical vectors and subsystems used to define relative frames (red:  $S_1$ ; green:  $S_{1,1}$ ; blue:  $S_{2,1}$ ; pink:  $S_{1,2,1}$ ). Subsystems are defined so as to avoid numerical issues related to poles due to collinear vectors (such as  $\mathbf{R}_1^{(1)}$  and  $\mathbf{R}_2^{(1,1)}$ ) around the reference geometry [45].

Each vector is expressed in terms of spherical coordinates. These coordinates,  $\mathbf{Q}_{\text{poly}}$ , were carefully selected so as to

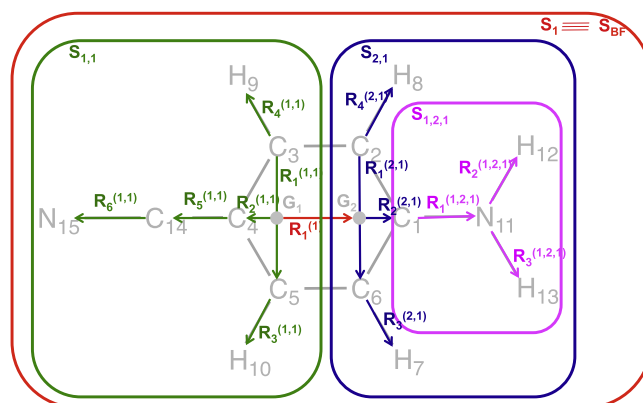


Fig. 1. Polyspherical vectors and subsystems.

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