

UV-light induced vibrational coherences explain Kasha rule violation in *trans*-azobenzene

Artur Nenov^{1,*}, Rocío Borrego-Varillas², Aurelio Oriana², Lucia Ganzer², Francesco Segatta¹, Irene Conti¹, Cristian Manzoni², Giulio Cerullo², and Marco Garavelli¹

¹Università degli Studi di Bologna, Dipartimento di Chimica Industriale, I-40136 Bologna, Italy

²Politecnico di Milano, Dipartimento di Fisica, I-20133 Milano, Italy

Abstract. Sub-20-fs transient absorption spectroscopy and simulations show that CNN-bendings dominate the sub-ps dynamics of $\pi\pi^*$ -excited *trans*-azobenzene, thereby driving the system to the ground state through a non-productive decay channel in violation of the Kasha rule.

1 Introduction

Azobenzene (AB) based compounds are prominent photoswitches which undergo an ultrafast (picosecond) *trans-cis* photoisomerization. The desire to enhance their performance has spawned a considerable amount of experimental and theoretical works aimed at scrutinizing the photoactivity of AB [1]. However, there is still a controversy over two key aspects of the photoisomerization of *trans*-AB initiated by deep-UV light resonant with the lowest bright $\pi\pi^*$ transition: the isomerization mechanism itself and the wavelength dependence of the quantum yield (QY) [2]. Experimental findings suggest that a significant part of the population is involved in an ultrafast relaxation dynamics (~0.45 ps) [3]. It is still unclear what is the nature of the associated molecular motion, whether this relaxation channel is reactive (i.e. leading to *cis*-AB) or not and if is responsible for the QY decrease. In this work we address these questions by combining time-resolved transient absorption (TA) spectroscopy utilizing sub-20-fs pump pulses peaking at 320 nm [4] and broadband probe pulses (360-700 nm) [5], nonlinear spectroscopy simulations in the perturbative regime (i.e. applying weak external optical electric fields) and mixed quantum-classical dynamics simulations within the multi-configurational wavefunction framework (i.e. CASPT2).

2 Results and discussion

Figure 1(b) shows the TA spectra in the visible between 360-700 nm for the first 500 fs. In agreement with previous studies, at early times (< 100 fs) we observe two photoinduced absorption (PA) bands: a broad intense band ranging from 550 nm to 700 nm (PA1) and a narrower band between 450 nm and 500 nm (PA2), fingerprints of the $\pi\pi^*$ state. A global fit of the data reveals that PA1 and PA2 decay with a lifetime of ~50 fs (Figure 1(d)),

* Corresponding author: artur.nenov@unibo.it

giving rise to a new PA band (PA3) peaking around 400 nm, a fingerprint of the $n\pi^*$ state. It shows oscillatory behavior with a period of 170 fs (195 cm^{-1}). Measurements on longer timescale show a PA3 decay described by the sum of three exponentials with time constants 0.45 ps, 2.5 ps and ~ 9 ps.

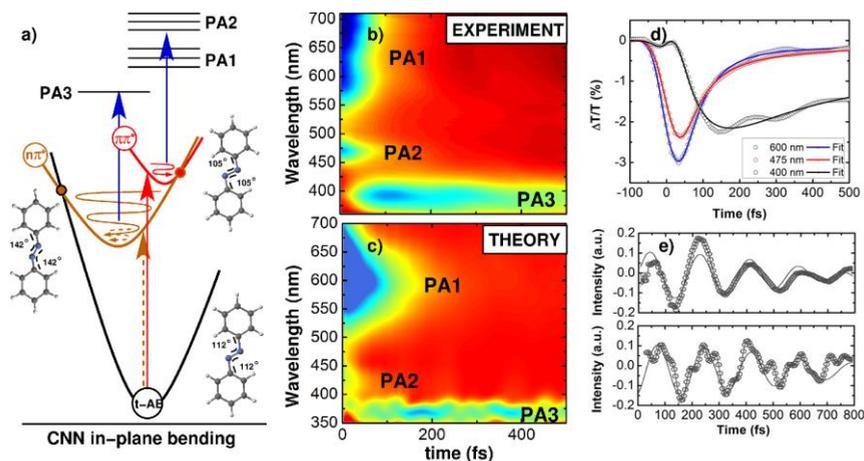


Fig. 1. a) Scheme of the sub-ps photophysics of *trans*-AB. b) Experimental (ethanol) and c) theoretical (gas-phase) TA maps of *trans*-AB with (d) extracted dynamics at 400, 475 and 600 nm. (e) Intensity beats of the residuals extracted from PA3 signal: experimental at 400 nm (top) and computed at 370 nm (bottom). Open dots represent the data and solid lines the fits.

Figure 1(c) depicts the simulated TA map in the same temporal and spectral windows. The remarkable agreement allows us to identify the nature of the individual PA signals [6]. The simulations reproduce the observed oscillatory dynamics, showing that the intensity beats with a 195 cm^{-1} frequency are the result of vibrational dynamics along the 660 cm^{-1} and 852 cm^{-1} modes, both having strong CNN bending contribution. These modes have been reported to be particularly intense in time-resolved Raman studies [3] and in photoionization spectroscopy experiments [7]. Together with the 205 cm^{-1} CNN bending and the 300 cm^{-1} CCN bending modes, they constitute a quartet of hot modes that accumulate almost 10000 cm^{-1} reorganization energy upon $\pi\pi^* \rightarrow n\pi^*$ decay due to the large out-of-equilibrium displacement along the bending coordinate at the conical intersection (CI) connecting both surfaces (Figure 1(a)).

In order to explain the molecular motions governing the ultrafast (sub-ps) dynamics, we performed adiabatic molecular dynamics simulations utilizing quantum mechanical gradients at the CASPT2 level of theory (Figure 2) [8]. A single trajectory was initiated in the Franck Condon point (C_{2h} symmetry) of the bright $\pi\pi^*$ state (red dotted line in Figure 2(a)) without initial kinetic energy and the energies of the close lying electronic states were monitored for the first 100 fs. It is apparent that the $\pi\pi^*$ state crosses several times with the $n\pi^*$ state, which exhibits a pronounced destabilization correlated with the CNN bending, in intervals of ca. 40 fs (gray-shaded areas in Figure 2(a)). Through CI optimization techniques we show the existence of an extended non-planar $\pi\pi^*/n\pi^*$ CI seam.

Starting from a non-planar CI geometry we followed the molecular dynamics in the $n\pi^*$ state through a fully unconstrained simulation for 200 fs (Figure 2(b)) allowing us to address the potential activation of either the (asymmetric) inversion or the torsion mechanism at early times. As noted earlier, upon relaxing to the $n\pi^*$ state the wavepacket accumulates nearly 10000 cm^{-1} potential energy in the CNN bending modes. As a consequence, we observe only in-plane dynamics (bending + stretching) during the first 200 fs. Fourier transformation of the energy gap dynamics allows to extract the frequencies

of the leading modes: 200 cm^{-1} , 300 cm^{-1} , 650 cm^{-1} , 850 cm^{-1} (bendings), 1650 cm^{-1} (CC stretching), the 650 cm^{-1} , 850 cm^{-1} modes giving rise to the intensity beats observed for the ESA signal PA3 (Figure 1(e)). The reorganization energy accumulated in the bending deformations drives AB within 20 fs far beyond the $n\pi^*$ equilibrium towards a CI with the ground state situated $\sim 5000 \text{ cm}^{-1}$ above the $n\pi^*$ minimum. The CI region is revisited every 40 fs. It is this energetically high lying segment of the CI seam with nearly planar geometries, which remains inaccessible after direct $n\pi^*$ excitation, that effectively funnels half of the $n\pi^*$ population back to the ground state within the first 500 fs after $\pi\pi^*$ excitation (Figure 1(a)). This also accounts for the drop in photoisomerization efficiency when exciting $\pi\pi^*$ as compared to $n\pi^*$ excitation.

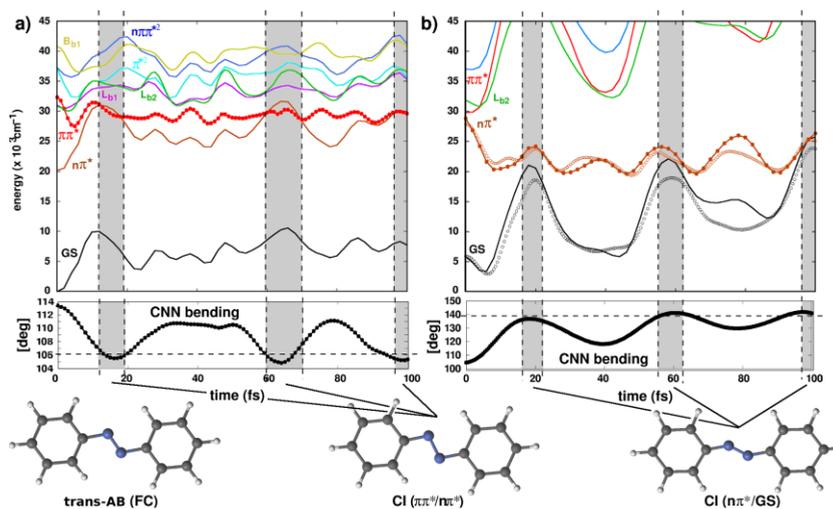


Fig. 2. Structure of the excited state manifold up to 45 kcm^{-1} along the molecular dynamics in the $\pi\pi^*$ state (red) initiated at the FC point (a) and along the $n\pi^*$ state (brown) initiated at the CI ($\pi\pi^*/n\pi^*$) (b).

References

1. H.M.D. Bandara, S.C. Burdette, *Chem. Soc. Rev.* **41**, 1809 (2012)
2. H. Rau, E. J. Lueddecke, *J. Am. Chem. Soc.* **104**, 1616 (1982)
3. M. Quick, A.L. Dobrykov, M. Gerecke, C. Richter, F. Berndt, I.N. Ioffe, A.A. Granovsky, R. Mahrwald, N.P. Ernsting, S.A. Kovalenko, *J. Phys. Chem. B*, **118**, 8756 (2014)
4. R. Borrego-Varillas, A. Candeo, D. Viola, M. Garavelli, S. De Silvestri, G. Cerullo and C. Manzoni, *Opt. Lett.* **39**, 3849 (2014).
5. R. Borrego-Varillas, L. Ganzer, G. Cerullo and C. Manzoni, *Appl. Sci.* **8**, 2076 (2018).
6. A. Nenov, R. Borrego-Varillas, A. Oriana, L. Ganzer, F. Segatta, I. Conti, J. Segarra-Martí, J. Omachi, M. Dapor, S. Taioli, C. Manzoni, S. Mukamel, G. Cerullo and M. Garavelli, *J. Phys. Chem. Lett.* **9**, 1534 (2018).
7. E.M.M. Tan, S. Amirjalayer, S. Smolarek, A. Vdovin, F. Zerbetto, W.J. Buma, *Nat. Commun.* **6**, 5860 (2015)
8. O. Weingart, A. Nenov, P. Altoé, I. Rivalta, J. Segarra-Martí, I. Dokukina, M. Garavelli, *J. Mol. Model.*, in press (2018), DOI:10.1007/s00894-018-3769-6