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Internal Conversion vs. Intersystem Crossing – What Drives the Dynamics of Cyclic α,β -Enones?

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Abstract. The origin of ultrafast intersystem crossing and its competitiveness with singlet pathways was studied in cyclic α,β -enones by transient absorption, time-resolved photoelectron spectroscopy and *ab initio* calculations.

1 The role of triplet state dynamics

Intersystem crossing (ISC) in photoexcited organic molecules is often thought of as an inherently slow process. Especially in molecules with fast singlet channels as those governed by conical intersection (CoIns), triplet state formation is rarely seen. For example, the dynamics in butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) takes place within 100 fs after light absorption [1]. However, there exist examples where this is not the case as, e.g., for α,β -enones [2,3]. In acrolein ($\text{CH}_2=\text{CH}-\text{CH}=\text{O}$) a CH_2 -group of butadiene is replaced by an oxygen and triplet state formation can be observed although both butadiene and acrolein dynamics are governed by ethylene-type CoIns which are localized only at one side of the molecule [2]. So the question arises as to why such a small change in the molecular structure causes completely different dynamics. To address this issue, we used time-resolved photoelectron spectroscopy (TRPES) and transient absorption (TA) in cyclohexane, acetonitrile and methanol as solvent to discern the initial dynamics of cyclic α,β -enones. Here, we focus on our results on 2,3,4,5-tetramethyl-2-cyclopentenone (TMCPO) and compare them with the less methylated derivatives 2-cyclopentenone (CPO) and 3-methyl-2-cyclopentenone (3MeCPO).

2 Absorption Spectrum and Potential Energy Surfaces

The absorption spectrum of TMCPO is typical for many α,β -enones. It has a bright $^1\pi\pi^*$ -state around 220 nm and a weakly absorbing $^1n\pi^*$ -state on its red flank (see Fig. 1a). The significant spectral shifts correlate with the dipole moments of the states which increases for the $^1\pi\pi^*$ -state and decreases for the $^1n\pi^*$ -state with respect to the ground state. The shape of the $^1n\pi^*$ -band shows that the lifetime of this state might be significantly reduced in methanol as a solvent.

A sketch of the relevant potential energy surfaces is shown in Fig. 1b. Upon excitation to the bright $^1\pi\pi^*$ -state, the molecules relax to the lower lying $^1n\pi^*$ -state from where they can return to the ground state by one of multiple CoIns (see examples for CPO in Fig. 1c) or progress to the triplet manifold where various pathways are possible [3]. Our calculations show that direct access to the CoIns is hindered by a large energy gap to the energetic minimum of S_1 (more than 1 eV at the

3s2p1d ANO/MR-SOCI level) but that the $^3\pi\pi^*$ -state is energetically close favoring ISC through a spin-orbit coupling of 30-50 cm^{-1} on the whole $^1n\pi^*$ -manifold.

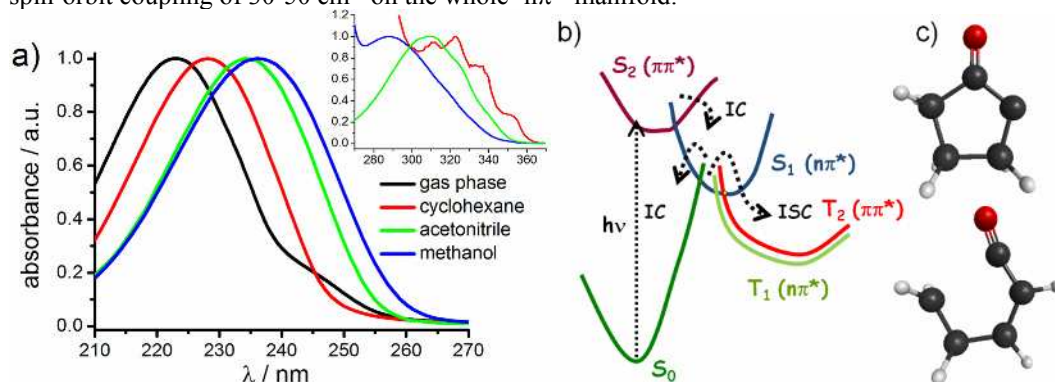


Fig. 1. a) Absorption spectrum of TMCPO b) Sketch of the potential energy surfaces c) Lowest lying conical intersections between S_1 and S_0 at 3s2p1d ANO/MR-SOCI for 2-cyclopentenone (CPO).

3 Experimental results

The photoelectron spectrum of TMCPO excited to the $^1\pi\pi^*$ -state at 216 nm and probed at 267 nm is shown in Figure 2. The $^1\pi\pi^*$ -state is seen by the band at low photoelectron kinetic energy and relaxes to the $^1n\pi^*$ -state within roughly 150 fs. It is shifted in time toward lower photoelectron kinetic energy due to large amplitude motions caused by the CoIn between the $^1\pi\pi^*$ - and the $^1n\pi^*$ -state being strongly deformed out-of-plane (a similar motion has been observed before in TRPES [3]). The $^1n\pi^*$ -state is seen in the two photon probe region at higher photoelectron kinetic energy and decays itself within 2.8 ps. These decay times are much shorter in CPO

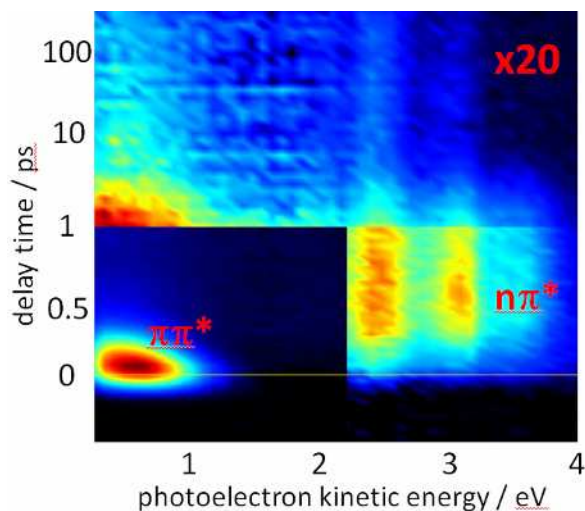


Fig. 2. a) Photoelectron spectrum of TMCPO excited at 216 nm and probed at 267 nm.

and 3-methyl-CPO (ca. 100 fs for $^1\pi\pi^*$ -state and 1.15 and 1.4 ps for the $^1n\pi^*$ -state, respectively). A residual spectrum which is similar for all investigated molecules stays constant for at least 250 ps.

The TA spectrum following excitation of TMCPO in acetonitrile at 228 nm is depicted in Figure 3. Besides the coherent artifact around time zero, one sees three processes, one on the 200 fs timescale originating from the $^1\pi\pi^*$ -state relaxation, one on the ps timescale ($^1n\pi^*$ -state) and a residual spectrum peaking around 280 nm which can be assigned to the triplet states in agreement with [4]. When comparing the time constants for the $^1n\pi^*$ -decay, one sees no big changes between the solvents and the gas phase (between 3 and 4 ps). This is different for CPO and 3MeCPO where the gas phase dynamics are more than a factor of 3 faster than those in the liquid phase. Between 230 and 240 nm, we see a strong ground state bleach. On the timescale of the experiment, we do not observe a change in optical density which means that no population has returned to the ground state and hence, intersystem crossing seems to be the predominant relaxation channel.

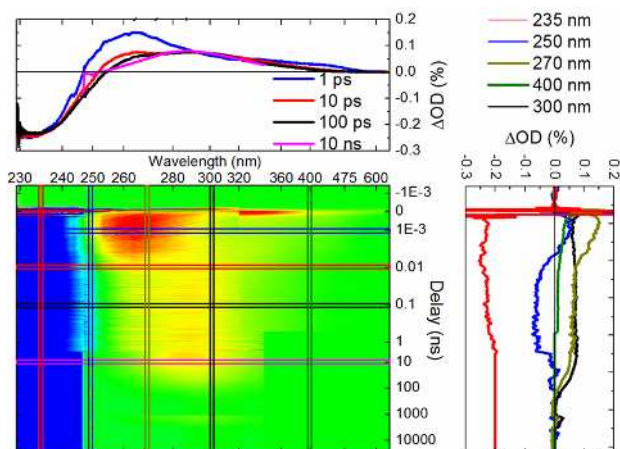


Fig. 3. Transient absorption spectrum of TMCPO in acetonitrile excited at 227 nm measured with different white light continua and pump sources (see [5]).

large 1 eV barrier between the CoIn with the ground state and the $^1n\pi^*$ -state minimum. The CoIn can be accessed after conversion to the $^1n\pi^*$ -state. However, as time progresses, the $^1n\pi^*$ -state minimum is reached and the CoIn lies energetically too high to play a significant role. Therefore, IC might play a role in the gas phase where a faster time constant for the $n\pi^*$ -state is observed and where vibrational motions are less dampened than in liquid phase. In solvent, however, we almost exclusively observe ISC.

5 Outlook

Exact calculations of the solvent dependent energetic position of the states as well as *ab initio* dynamics calculation will reveal more information about these systems. In addition, further experiments on differently substituted molecules and wavelength dependent pump pulses will allow deciphering the role of specific motions on the dynamics. The final goal is to understand the conditions for ISC in molecules which, in principle, would also allow fast IC-processes and to predict when a molecule can be supposed to predominantly react via its singlet or its triplet manifold.

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4 Discussion

Considering the similarity of the transient spectra of the investigated molecules (both TRPES and TA), we conclude that the main reaction pathway is via ISC which is governed by the presence of a $^1n\pi^*$ -state and the energetically close lying $^3\pi\pi^*$ acceptor state. If internal conversion (IC) were dominant, we would expect the ground state bleach to recover on a ps time scale. Similar time constants in the different solvents indicate that ISC does not depend on polarity and that the relative energetic position of the states only plays a minor role, although relative shifts of the $^1n\pi^*$ -band indicate that the singlet dynamics might differ.

This behavior can be explained with the