

Exploring the Ultrafast Excited-State Intramolecular Proton Transfer (ESIPT) of β -Diketones in the deep-UV

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Abstract: The photodynamics in symmetric and unsymmetric β -diketones are studied with transient absorption in the deep-UV. Excitation leads to ultrafast ESIPT while further relaxation and isomerization processes depend on the molecular symmetry and solvent environment.

OCIS codes: (320.7150) Ultrafast spectroscopy; (300.6540) Spectroscopy, ultraviolet; (190.7110) Ultrafast nonlinear optics

1. Introduction

Excited-state intramolecular proton transfer (ESIPT) is a prominent model for the description of complex proton transfer dynamics in molecules. Since ESIPT occurs on an ultrafast time scale, we utilize transient absorption (TA) to disclose the underlying mechanism and follow-up processes in various β -diketones. Molecules of this class are applied in commercial sunscreen agents due to high absorption in the UV and fast relaxation to the ground state [1]. After $S_0 \rightarrow S_2$ excitation (the $S_0 \rightarrow S_1$ transition is optically forbidden), the ultrafast ESIPT leads to vibrationally hot tautomeric species [2]. The subsequent relaxation strongly depends on the solvent and the actual symmetry of the molecule under investigation. We address both issues by comparing symmetric and unsymmetric β -diketones in various solvents. Depending on the molecule, photoisomerization reactions and even ground-state intramolecular proton transfer could be observed. Our results lead to a conclusive picture of the photochemistry of β -diketones.

2. Experimental Setup of the TA Spectrometer with Deep-UV Probing Capability

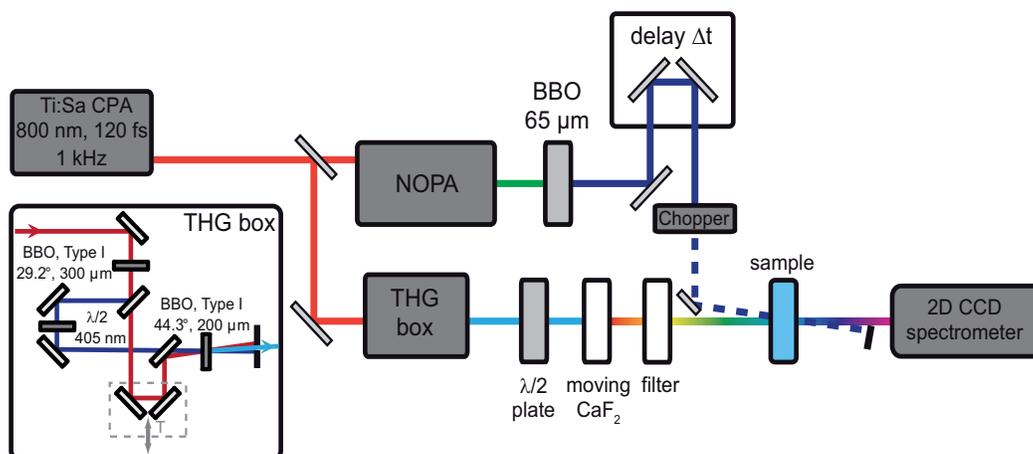


Fig. 1: Experimental setup. The UV excitation pulses are generated via frequency-doubling of the visible output from a NOPA. For deep-UV probing, the third harmonic of the 800 nm fundamental is generated (see inset, THG box) and focused into a CaF_2 plate. A custom-designed filter removes the remainder of the 267 nm pulse. For visible probing, the fundamental is focused into the CaF_2 plate. Data acquisition is performed on a shot-to-shot basis via a chopper and a 2D CCD spectrometer.

Since all electronic transitions of the studied β -diketones are located in the UV, we employ TA with detection capabilities in the deep-UV (see Fig. 1) [3]. Part of the output of a commercial Ti:Sa CPA system (120 fs pulse duration, 1 kHz repetition rate) generates pump pulses in the UV (250–375 nm) by frequency-doubling the visible output of a noncollinear optical parametric amplifier (NOPA, TOPAS white, Light Conversion). Another fraction of the fundamental is used to generate the third harmonic centered at 267 nm (confer inset in Fig. 1). By focusing this beam weakly into a linearly moving CaF_2 plate, a UV white-light supercontinuum ranging from 220 to 330 nm can be generated. We use a custom-designed spectral filter to suppress the high power of the 267 nm beam. By removing both β -barium borate (BBO) crystals in the THG box (see Fig. 1, inset) and exchanging the filter, the fundamental is focused into the CaF_2 plate and it is hence possible to probe in the visible (350–750 nm) with the same setup. Pump

and probe pulses are overlapped in noncollinear geometry under magic-angle configuration. With the help of a mechanical chopper and a 2D CCD camera, the TA signal is detected on a shot-to-shot basis.

3. Results and Discussion

We investigate three symmetric and one unsymmetric β -diketone of the form $R_1-C(O)-CH_2-C(O)-R_2$ (compare structures in Fig. 2, left), showing pronounced keto-enol tautomerism, with TA in the deep-UV and the visible spectral regime. Malonaldehyde (MA) is the simplest symmetric β -diketone, where both residual groups are just protons ($R_1=R_2=H$). In the case of the two other symmetric systems acetylacetone (AA) and dibenzoylmethane (DBM) they residual groups are methyl groups ($R_1=R_2=CH_3$) or phenyl rings ($R_1=R_2=Ph$), respectively. The unsymmetrical β -diketone under investigation is benzoylacetone, ($R_1=CH_3$, $R_2=Ph$). Typically, molecules of this type occur in the chelated enol (CE, confer Fig. 2) form which is the most stable one. However, at cryogenic temperatures several non-chelated enol (NCE, confer Fig. 2) rotamers have been identified which lack an intramolecular H-bond [4]. Possible relaxation pathways are depicted in the energy diagram in Fig. 2. While the initial ESIPT process and the conversion from the NCE to the CE form in the ground state are already known in the literature [4,5] a conclusive picture of the intermediate photochemistry is still under debate. Hence, we performed TA spectroscopy for all four molecules whose linear absorption spectra are presented on the right in Fig. 2.

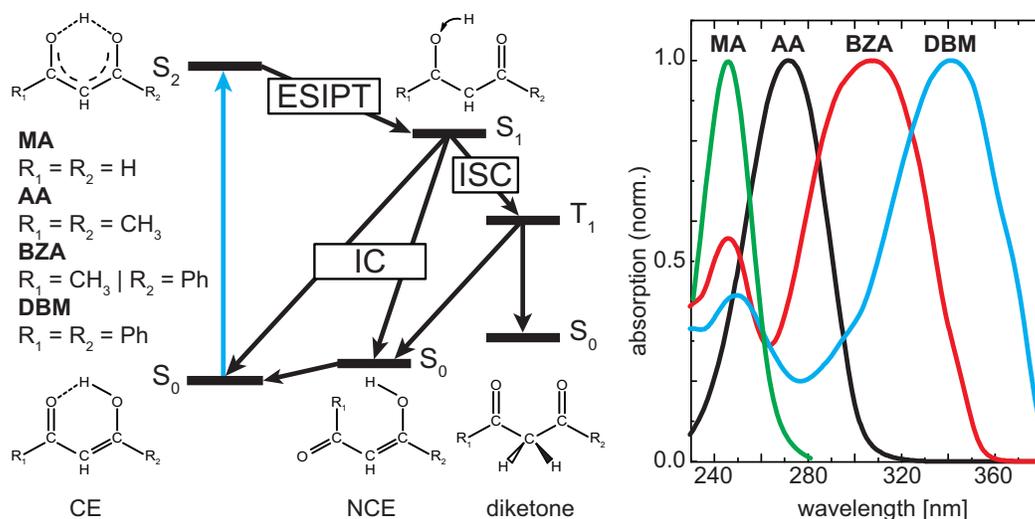


Fig. 2: Left: Possible relaxation pathways for β -diketones after electronic excitation in solution. The non-chelated enol (NCE) is derived from the initial chelated enol (CE) form via a rotation around the C-C or C=C bond. Depending on the substitution (R_1 and R_2), various NCE isomers can be formed. Right: Normalized absorption spectra.

3.1 Symmetric β -Diketones

In all three symmetric molecules (AA, MA, and DBM) we find an initial ultrafast relaxation associated with ESIPT. While it occurs with a time constant $\tau_1 \approx 150$ fs in DBM, in AA and MA $\tau_1 \approx 50$ fs is on the order of our experimental time resolution. In the following, we focus on the exemplary data set of AA dissolved in dioxane (Fig. 3, left). Besides the ground-state bleach (GSB, blue, negative) a decaying positive feature around 240 nm which we attribute to an excited-state absorption (ESA) is visible. This ESA decays with $\tau_2 \approx 2$ ps and can be identified as S_2 lifetime after the ESIPT process. The GSB at 280 nm can however only be described properly with two further time scales, namely $\tau_3 \approx 10$ ps and $\tau_4 \approx 800$ ps. Hence, at least a fraction of the excited-state population repopulates the CE ground state within τ_3 . However, after about 1 ns a positive feature at about 250 nm (see Fig. 3, left) is present. By comparing with results in the literature, this new positive absorption can be identified as the NCE form of AA [5]. In this case the molecule must rearrange in the S_1 state, for which we ascribe also the τ_3 time constant. Hence, in the S_1 state a branching occurs. This rotamer structure then finally relaxes to the NCE ground state within τ_4 . As indicated in the energy diagram in Fig. 2, also a triplet state following the rotamerization might be involved. Hence, we probed also in the visible for a triplet relaxation pathway, e.g. via triplet-triplet absorption, which could not be confirmed. A target analysis revealed that roughly 30 % of the excited-state population leads to the NCE photoproduct. Interestingly, this value cannot be influenced by varying the excess energy. However, if one changes the solvent to *n*-hexane, which has a lower H-bond accepting value [6] ($HBA = 0.00$) compared to dioxane ($HBA = 0.37$), the NCE formation is decreased significantly. This is reasonable since less H-bonds can be formed and the rotamerization process mediated by solute-solvent interaction is decreased. The dynamics in MA resemble those in AA, but no ESA is detectable. NCE formation (≈ 15 %) and the absence of ISC could be confirmed for MA

as well. This is different for DBM where a triplet contribution is identified via an ESA in the visible. However, we find similar time scales and NCE formation yields for DBM as for AA. The population of the triplet state (see Fig. 2, left) in DBM leads to the formation of the keto form and possibly to a partial irreversible photodegradation.

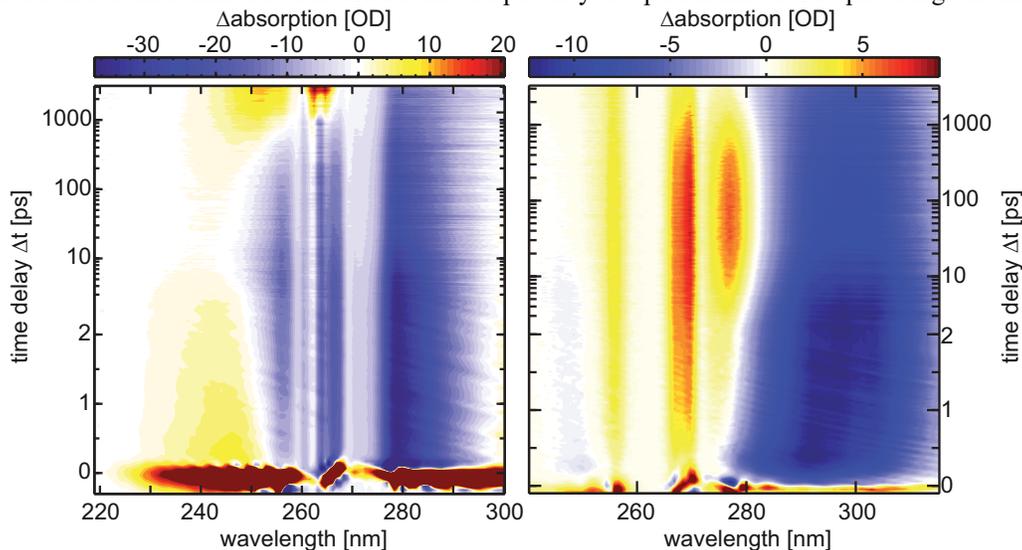


Fig. 3: TA signal of AA in dioxane after 265 nm excitation (left) and BZA in acetonitrile after 335 nm excitation (right). The distorted signal around 267 nm is due to the spectral filter. The time delay is plotted on a linear scale up to 2 ps and logarithmic afterwards. Negative signals (blue) correspond to GSB while positive ones comprise ESA and photoproduct absorption.

2.2. Unsymmetric β -Diketone

The relaxation dynamics of the investigated unsymmetric β -diketone, BZA, are similar to the ones discussed above. Again, three major relaxation pathways were identified: direct internal conversion (IC) from the relaxed S_1 state and after rotamerization either NCE formation or ISC to a triplet state which leads finally to the diketone form. However, as directly deducible from the TA map in Fig. 3 (right) a new positive signal around 250–280 nm which is growing in over a time of 10–100 ps can be observed. The origin of this signal can be explained via the symmetry of the molecule. Since the two residual groups (R_1 and R_2 , see Fig. 2) are different in BZA, the two enolic forms of BZA can be distinguished. These two tautomers presumably exhibit different energies in the excited state and thus lead to different excited-state potential energy surfaces for the rotamerization, giving rise to the new positive signal. To corroborate this assignment we collected TA data in various solvents with increasing HBA values [5,6]. Indeed, in hexane (HBA = 0.00) no such signal can be observed while in ethanol (HBA = 0.75) it is even stronger than for acetonitrile (HBA = 0.40, confer Fig. 3, right). Moreover, by analyzing the red and blue edge of the GSB region (280–320 nm) one can deduce that also ground-state intramolecular transfer occurs. Upon electronic excitation the initial ground-state equilibrium between the two enolic forms of BZA is perturbed. Hence, the molecules which remain in the ground state re-equilibrate on a sub-picosecond time scale.

4. Summary and Outlook

We performed TA spectroscopy with deep-UV probing to elucidate the photochemistry of β -diketones. The symmetric and unsymmetric compounds comprise a common ESIPT but differing subsequent relaxation processes. The latter significantly depend on the solvent environment. In the unsymmetric β -diketone even ground-state intramolecular proton transfer could be identified. Yet, in all cases the same relaxation model could be applied. Recently, we could apply this scheme also to 2-acetylindan-1,3-dione, a biologically relevant β -diketone [7].

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