Coherent Control of the Photodissociation of Triiodide in Solution Reveals New Pathways

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Abstract: We demonstrate control of the photodissociation of triiodide, solvated in ethanol, via phase-shaped UV pulses. The second-order chirp dependence of the diiodide yield hints at additional pathways involving higher-lying potential energy surfaces.
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1. Introduction

Photodissociation in the solution phase is complicated by the involvement of solvent cages, leading to altered reaction and energy disposal pathways compared with equivalent gas phase experiments [1]. In the case of triiodide (I_3^-) in ethanol, certain gas phase dissociation products are not seen in the solution phase and doubts remain on the number of pathways involved in dissociation via excitation to the high-lying absorption band (peaks at 290nm) [2,3]. Here we perform coherent control and pump-probe experiments to examine the influence of the second-order chirp and the energy of excitation on the diiodide (I_2^-) yield. Our observations point to additional mechanisms involved in the photodissociation that haven't so far been discussed [2,3].

2. Experimental methods

The sample tetra-*n*-butylammonium triiodide (TBAT, Sigma-Aldrich) was dissolved in UV-grade ethanol (Uvasol, Merck Millipore) and carried through a home-built liquid delivery system involving a 100 µm-path length flow cell (Starna), a sample reservoir, and a peristaltic pump with Teflon tubing (Cole Parmer). The reservoir maintains concentration of the sample (OD~1 at 290 nm) during the course of an experiment due to the partial reversibility of dissociation. A commercial Ti:sapphire ultrafast laser system (Coherent Elite USP) provides ~35 fs-long light pulses at 800 nm used for monitoring the photoproduct I_2^- (with an absorption band around 750 nm) and as a pump for a home-built two-stage NOPA, whose output is frequency-doubled to generate transform-limited pulses at 290 nm (~60 fs) for excitation of triiodide. For closed-loop coherent control experiments and controlling of the second-order chirp rate we used a home-built pulse shaper, based on an AOM in the 4f-geometry [4] and designed for mid-UV operation with a technical efficiency of ~50% around 290 nm. In open-loop control experiments the chirp was varied from -10000 fs^2 to 10000 fs^2, and the excitation energy from 100 nJ to 425 nJ.
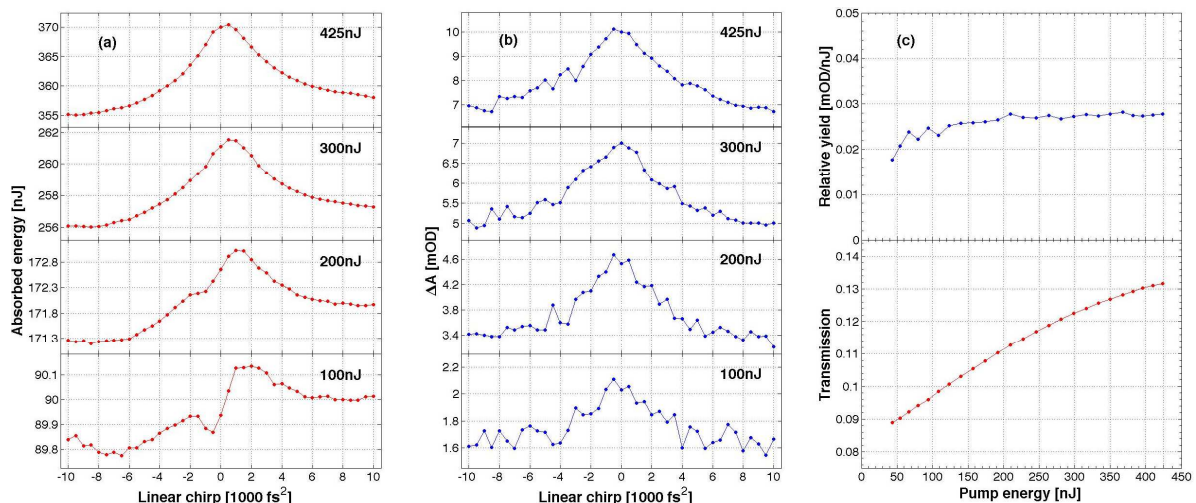

Fig. 1. (a) Chirp-dependence of sample absorption and (b) ΔA. The chirp-ΔA plots were all taken with a constant pump-probe delay of 100 ps. The excitation energies used in (a) and (b) are marked on the corner of each subplot and as ticks in (c). (c) Excitation energy-dependence of the relative I_2^- yield, ΔA/excitation energy (upper) and the sample transmission (lower).

3. Results and discussion

Optimization of the diiodide yield using a closed-loop coherent control protocol at 450 nJ excitation energy ($\sim 1.24 \times 10^{16}$ photons/cm^2) results in an optimal pulse with a shape very close to transform-limited (TL) pulse. Chirp scan shows asymmetry in the absorbed energy whereas the diiodide yield (proportional to the differential absorption ΔA monitored at 800 nm) is symmetric with respect to the sign of the chirp and is maximal for TL-pulse at all excitation energies applied (Fig. 1a,b). The relative diiodide yield, $\Delta A/E_{exc}$, grows slightly with increasing excitation energy (Fig. 1c; note that deviations at low excitations is from contribution of scattering to measured signals), indicating that the whole range lies mostly within the linear regime of dissociation, and excluding the possibility of two-or-more-photon absorption in the sample. The transmission of the sample (at 290 nm) starts to saturate at high excitation levels (> 250 nJ; see in Fig. 1c, lower panel), and fitting to 2-level system ([5], Eq.3) shows more discrepancies towards high excitation level. These signatures suggest the opening-up of additional pathways involving excited state absorption of triiodide.
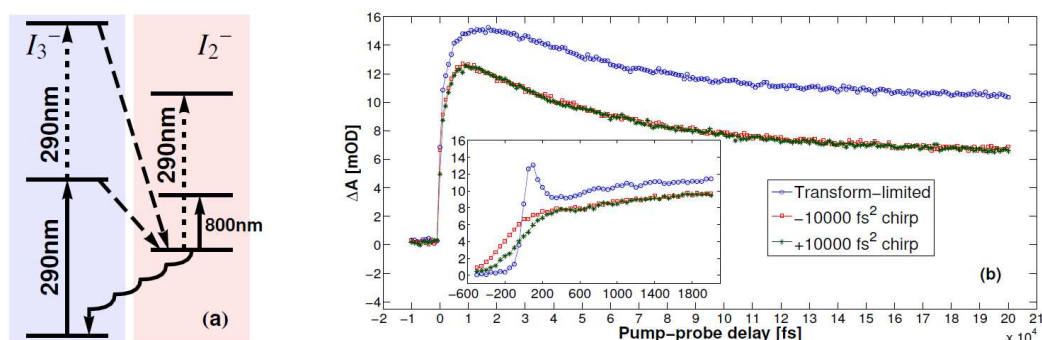

Fig. 2. (a) The energy diagram of the I_3^--I_2^- system. The solid arrows represent the pump (290 nm) and probe (800 nm), the dashed ones dissociation from the upper surfaces, the dotted ones reabsorption of the pump pulse, and the wavy one recombination. (b) Pump-probe traces measured with different chirp rates with 450 nJ excitation (1 ps and 50 fs time step in the main plot and the inset, respectively).

The pump-probe traces in Fig. 2b exhibit an initial fast rise up to ~10 ps, dominated by photoproduct formation, then followed by a slow delay when recombination processes (geminate or non-geminate) outrun dissociation, which lasts until hundreds of picoseconds and further. It is demonstrated here that the TL pulse is more favorable to photoproduct formation than chirped pulses at all probed time delays and photoproduct formation is insensitive to the sign of the chirp, which reaffirms the chirp scan results. In Fig. 2a we present a diagram including viable additional excited states in the photodissociation process. The two-photon cascaded-absorption of the reactant could be more effective for short pulses, and in the case of additional dissociation from higher excited state(s) the overall I_2^- yield will be higher. Absorption of excitation photons by I_2^- during a long excitation pulse can be a parasitic effect that suppresses its absorption of the probe photon. The interplay between the two dissociation channels of I_3^- can eventually lead to the observed behavior of the I_2^- yield in our coherent control and chirp scan experiments.

Taking into account the chirp dependence of the absorption, our work shows that the photodissociation of triiodide can be controlled even in the regime where the relative yield is nominally excitation-independent. In this regard, the excitation energy-dependent features depicted in Fig. 1a (the shift of the maximal absorbed energy towards the positive chirp side and the appearance of a dip on the negative chirp side) deserve further investigation. Spectrally-resolved studies are in progress to investigate if other unknown species formed at high excitations influence pump-probe signal in the same spectral region, or a spectral shift of the I_2^- absorption band due to, e.g., dissociation of the solvent [5].

4. References

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