Towards Controlling Photochemical Reactivity in Small Polyatomic Molecules in Solution: Difluorodiiodomethane

P. Z. El-Khoury[1], S. K. Pal[2], A. S. Mereshchenko[3], A. N. Tarnovsky[3]

[1]Department of Chemistry, University of California, Irvine, California 92697, USA
[2]School of Basic Sciences, Indian Institute of Technology, Mandi, Himachal Pradesh 175 001, India
[3]Department of Chemistry, Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH, USA

Abstract. Ultrafast transient absorption and tools of computational photochemistry monitor the efficient formation of molecular iodine from difluorodiiodomethane promoted to the lowest excited state in inert solvents: this requires significantly larger photon energies in the gas-phase.

One of the main challenges in the field of photochemical reaction dynamics is to understand the effect of initial conditions on the outcome of ultrafast molecular transformations. In solution or condensed phases, the bath plays an intimate, time-dependent role in the entire reaction process. This adds further complexity to the reaction dynamics which involve multiple potential energy surfaces. A topic of significant interest is two- *vs* three-body photodissociation in which the excited state species yields two or three products, [1,2]. The latter decay may occur simultaneously, in a concerted fashion, or sequentially, as a result of vibration energy redistribution in hot radicals. CF_2I_2 follows several dissociation channels in the gas-phase, [3-5], this complexity constituting the major driving force behind selecting this molecule as a target system for condense-phase ultrafast transient absorption studies.

In the gas phase, excitation of CF_2I_2 in the 351-337 nm range exclusively causes direct two-body decay: $CF_2I_2 \rightarrow CF_2I\cdot + I\cdot$, ref. [3]. Excitation at $\lambda < 266$ nm leads to a concerted decay: $CF_2I_2 \rightarrow :CF_2 + I\cdot + H\cdot$. In the intermediate range, two-body decay is followed by C–I bond dissociation in vibrationally hot radicals, [4,5]. Only upon 193-nm (6.5 eV) excitation of CF_2I_2 is molecular iodine elimination observed, [6].

Following 350-nm excitation of CF_2I_2 in *n*-hexane, a 75-fs decay of ΔA signals in short-time visible/near-IR transient absorption spectra is assigned to the lowest excited-state depopulation due to dissociation. At 10 ps, the evolution of visible/near-IR transient absorption ΔA is dominated by vibrationally excited I_2, which terminates at ~200 ps in *n*-C_6H_{14} and ~500 ps in CCl_4, with the formation of a ~520-nm band characteristic of cold I_2, Fig. 1.
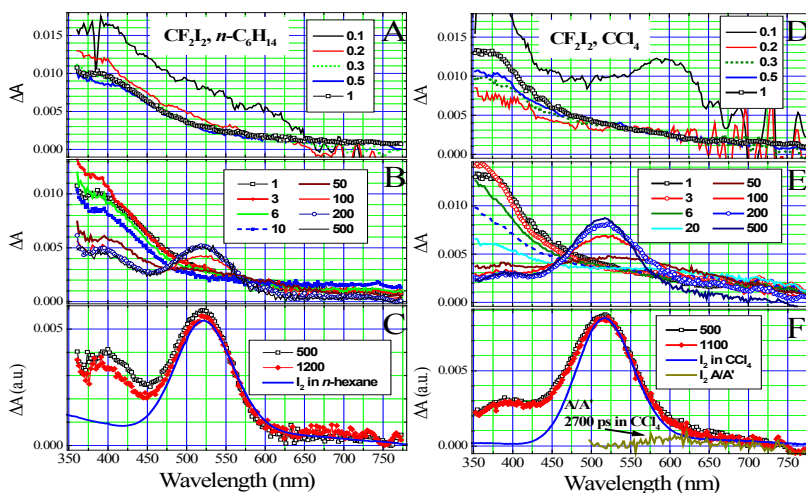
Fig. 1. The transient absorption spectra (symbols) for CF_2I_2 in n-C_6H_{14} (A-B) and CCl_4 (D-F) after 350-nm, 100-fs excitation. Time delays (ps) are given in the insets. In CCl_4, a small fraction (6%) of the formed I_2 molecules is trapped in the long-lived A/A' excited states. Steady-state absorption spectra of I_2 are shown for comparison.

One I_2 molecule is produced per electronically excited CF_2I_2* on the basis of the absence of the time-dependence of ΔA signals on CF_2I_2 concentration, the linear dependence of I_2 concentration on the pump energy, and the time scale observed for I_2 formation. By means of benzophenone triplet state actinometry, we obtained a 32% (500 ps) and 66% (1 ns) quantum yield for I_2 formation in n-C_6H_{14}, [2] and CCl_4, respectively. This is in contradiction to the gas-phase findings where the lowest excited state of CF_2I_2 accessed at about 350 nm dissociates to produce $CF_2I\cdot$ and $I\cdot(^2P_{3/2})$ photofragments. The electronically excited states of CF_2I_2 in the Franck-Condon (FC) region are unaltered as evidenced by identical UV absorption spectra in the gas-phase and solution, but the resonance Raman spectra of CF_2I_2 are strongly solvent-dependent, [6]. As we observed the formation of I_2 from CF_2I_2 in all CH_3OH, alkanes and chlorinated alkanes, we conclude that the solvent affects the dynamics after $CF_2I_2^*$ leaves the FC region. Two possible mechanisms can be thought of: (i) a consecutive three body-decay, in which hot CF_2I rapidly dissociates, and the nascent I-atoms collapse into I_2, (ii) the involvement of possible precursors of I_2, namely, an CF_2I–I intermediate, analogous to the CH_2I–I isomer of CH_2I_2, [2].

To distinguish between these two reaction mechanisms, we first conducted an *ab initio* investigation of ground-state pathways leading to I_2 elimination from CF_2I_2, [7]. Direct formation of I_2 from CF_2I_2 is found to be highly endothermic, proceeding through a cyclic-skewed transition state at 2.71 eV above CF_2I_2. However, a minimum corresponding to CF_2I–I is found to be at 1.08 eV above CF_2I_2. 350-nm excitation populates the lowest excited state of B_1 symmetry, which does not correlate to I_2, [5,6], $CF_2I\cdot$ and $I\cdot$ being the sole photoproducts in the gas phase. In solution, the solvent cage arrests the separation of nascent photofragments, which renders the formation of the CF_2I–I isomer possible following excitation of CF_2I_2. The computed minimum energy path from $CF_2I\cdot+I\cdot$ to CF_2I–I is nearly barrierless, [7]. Vibrationally hot CF_2I–I can dissociate into $:CF_2$ and I_2 because the formation of $:CF_2+I_2$ from cold CF_2I–I is only uphill by 0.82 eV *vs.* 1.10 eV requiring for the production of the $CF_2I\cdot+I\cdot$ species. The light $:CF_2$ fragment is thought to escape the solvent cage before the backward orientation-specific insertion reaction takes place. Second, the photochemical reaction path was modeled using CASSCF calculations following the promotion of CF_2I_2 into its lowest-lying excited singlet state, [8]. It was found that conical intersection drives the electronically excited CF_2I_2 species to the $CF_2I\cdot+I\cdot$ radical pair. Third, the formation of a CF_2I–I intermediate was monitored through its intense CF_2 stretching by means ultrafast IR absorption following 350-nm excitation of CF_2I_2 in CCl_4, [9]. A delayed rise of the CF_2 fundamental absorption

places an upper limit of 400 fs for C–I bond dissociation and primary geminate recombination, Fig. 2. The CF_2 absorption weakens at about 5 ps, concurrently with the formation of I_2 monitored in the visible region. According to our normal mode analysis, the isomer has a built-in vibrational energy dissipation pathway which efficiently channels one quantum deposited on the CF_2 moiety into two quanta of the v_7 mode, which is best described by CF_2 scissoring coupled to the "reactive" C–I stretching.
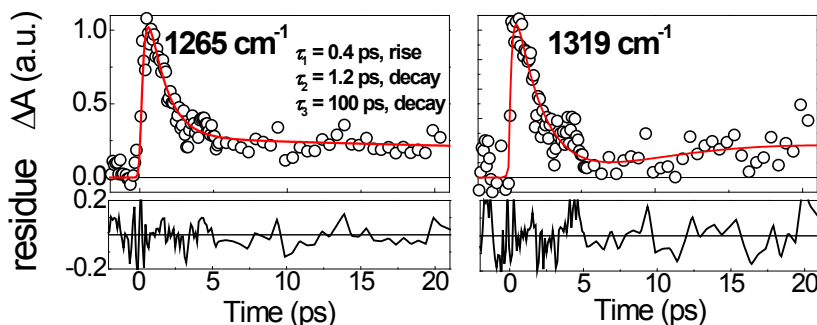

Fig. 2. CF_2I_2 in CCl_4 excited at 350 nm. The 1265 and 1319 cm^{-1} kinetic ΔA traces (symbols) measured at the high-energy wing of the CF_2 stretching absorption band ($v_9 = 1252$ cm^{-1}, MP2/Sadlej-pVTZ) in the CF$_2$I–I isomer. The best three-exponential fits convoluted with an instrument response function of 235 fs (fwhm) and fit residuals are shown as lines.

In summary, the ultrafast formation of I_2 from CF_2I_2* in solution is a result of switching dissociation into molecular iodine elimination through the intermediacy of the short-lived CF$_2$I–I isomer. This reaction proceeds through a series of distinct symmetry-allowed steps rather than the symmetry-forbidden, high-energy molecular elimination reaction path which retains C_{2v} symmetry.

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