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

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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. CF₂I₂ 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 CF₂I₂ in the 351-337 nm range exclusively causes direct two-body decay: CF₂I₂ → CF₂I+I-, ref. [3]. Excitation at λ< 266 nm leads to a concerted decay: CF₂I₂→:CF₂+I+I-. 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 CF₂I₂ is molecular iodine elimination observed, [6].

Following 350-nm excitation of CF₂I₂ 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 I₂, which terminates at ~200 ps in n-C₆H₁₄ and ~500 ps in CCl₄, with the formation of a ~520-nm band characteristic of cold I₂, Fig. 1.
One I\(_2\) molecule is produced per electronically excited CF\(_2\)I\(_2\)* on the basis of the absence of the time-dependence of \(\Delta A\) signals on CF\(_2\)I\(_2\) 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\(_6\)H\(_{14}\), [2] and CCl\(_4\), respectively. This is in contradiction to the gas-phase findings where the lowest excited state of CF\(_2\)I\(_2\) accessed at about 350 nm dissociates to produce CF\(_2\)-I and I(\(^3P\)) photofragments. The electronically excited states of CF\(_2\)I\(_2\) 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\(_2\)I\(_2\) are strongly solvent-dependent, [6]. As we observed the formation of I\(_2\) from CF\(_2\)I\(_2\) in all CH\(_3\)OH, alkanes and chlorinated alkanes, we conclude that the solvent affects the dynamics after CF\(_2\)I\(_2\)* leaves the FC region. Two possible mechanisms can be thought of: (i) a consecutive three body-decay, in which hot CF\(_2\)-I rapidly dissociates, and the nascent I-atoms collapse into I\(_2\), (ii) the involvement of possible precursors of I\(_2\), namely, an CF\(_2\)-I intermediate, analogous to the CH\(_3\)I–I isomer of CH\(_2\)I\(_2\), [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\(_2\)I\(_2\), [7]. Direct formation of I\(_2\) from CF\(_2\)I\(_2\) is found to be highly endothermic, proceeding through a cyclic-skewed transition state at 2.71 eV above CF\(_2\)I\(_2\). However, a minimum corresponding to CF\(_2\)-I–I is found to be at 1.08 eV above CF\(_2\)I\(_2\). 350-nm excitation populates the lowest excited state of B\(_1\) symmetry, which does not correlate to I\(_2\), [5,6], CF\(_2\)I and I* 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\(_2\)-I–I isomer possible following excitation of CF\(_2\)I\(_2\). The computed minimum energy path from CF\(_2\)-I*–I* to CF\(_2\)-I–I is nearly barrierless, [7]. Vibrationally hot CF\(_2\)-I–I can dissociate into :CF\(_2\) and I\(_2\) because the formation of :CF\(_2\)I from cold CF\(_2\)-I–I is only uphill by 0.82 eV vs. 1.10 eV requiring for the production of the CF\(_2\)-I*–I* 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\(_2\)I\(_2\) into its lowest-lying excited singlet state, [8]. It was found that conical intersection drives the electronically excited CF\(_2\)I\(_2\) species to the CF\(_2\)-I*–I* radical pair. Third, the formation of a CF\(_2\)-I intermediate was monitored through its intense CF\(_2\) stretching by means ultrafast IR absorption following 350-nm excitation of CF\(_2\)I\(_2\) 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 $\nu_7$ mode, which is best described by CF$_2$ scissoring coupled to the “reactive” C–I stretching.

**Fig. 2.** CF$_2$I$_2$ in CCl$_4$ excited at 350 nm. The 1265 and 1319 cm$^{-1}$ kinetic $\Delta A$ traces (symbols) measured at the high-energy wing of the CF$_2$ stretching absorption band ($\nu_9 = 1252$ 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$_2$I$_2^*$ 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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**References**