A TRIR, TREPR and Computational Study on the Reactivity and Structure of the 2,2,2-Trifluoroethoxycarbonyl Radical§

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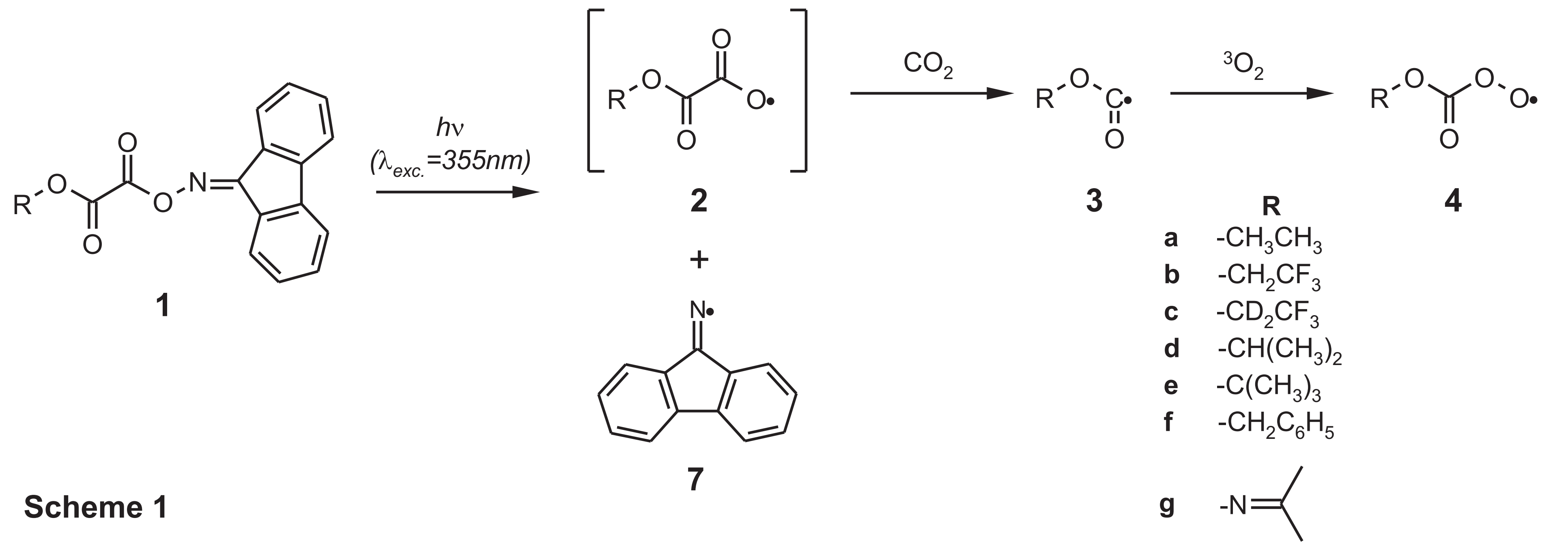
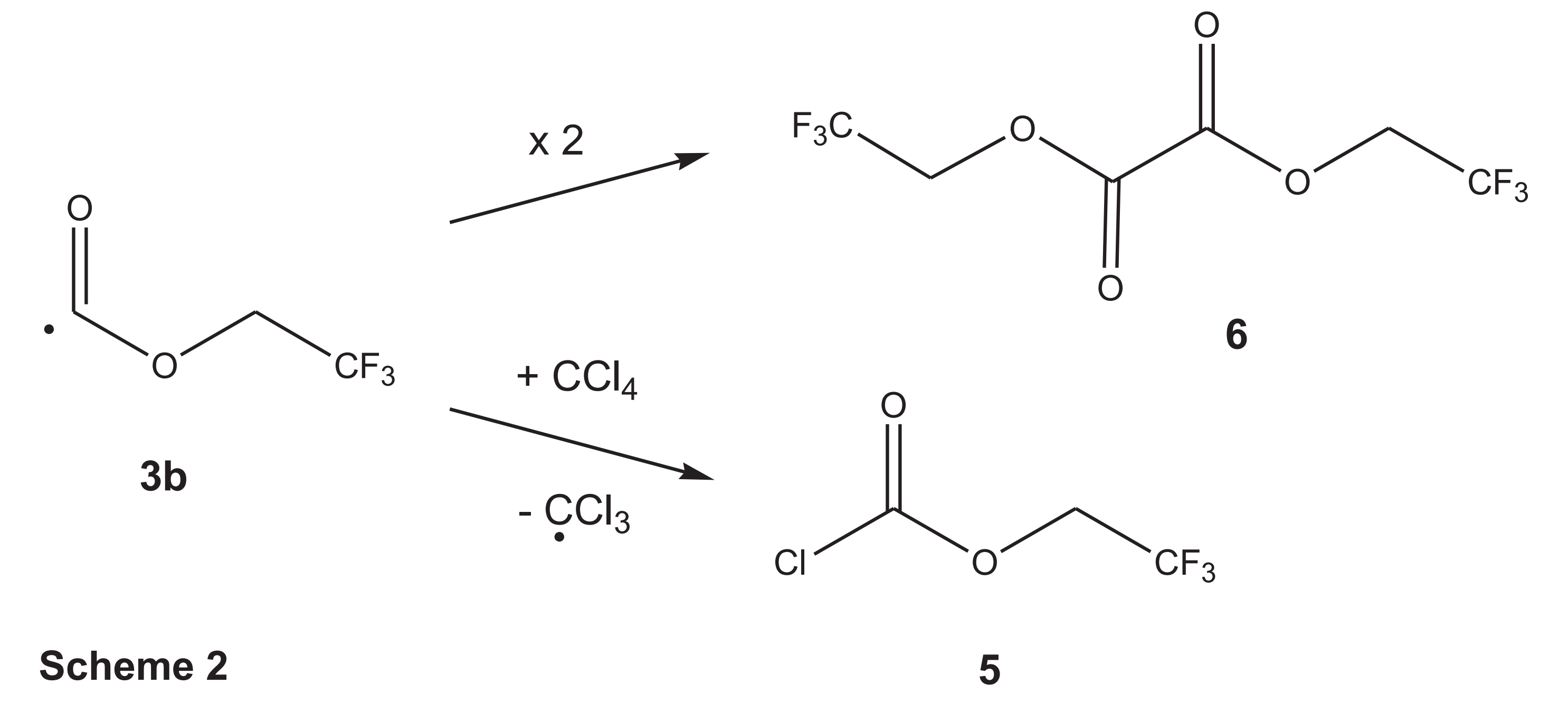
Laser flash photolysis ("LFP") of **1b** in tetrachloromethane (4.0 mM, Ar purge) at $\lambda_{exc.}$ = 355 nm resulted in bleaching of the precursor bands at 1802 and 1770 cm^{-1} and the formation of a transient at 1823 cm^{-1}. Additionally, the strong ν_{as} of CO_2 at 2335 cm^{-1} was observed. Both the 1823 cm^{-1} transient and ν_{as} (CO_2) built up during the rise-time (25 ns) of the STEP/SCAN setup. Furthermore, IR bands growing in at 1781 and 1741 cm^{-1} were detected (Figure 1). When the solution was purged with oxygen prior to LFP, again the disappearance of two precursor bands and the immediate formation of the CO_2 absorption at 2337 cm^{-1} was noted. A transient species was observed at 1852 cm^{-1}, decaying with a lifetime of 4.3+0.5 μs. Quenching of the 2,2,2-trifluorethoxycarbonyl radical (3b) with $^3O_2$ leads to the formation of the 2,2,2-trifluorethoxycarbonylperoxy radical (4b), which has a characteristic absorption at 1852 cm^{-1}, decaying with a measured lifetime of τ = 4.3+0.5 μs (Figure 2). Decarboxylation of the intermediary alkoxycarbonylcarbonyloxy radical causes the intense initial absorption at 2335 cm^{-1}. The alkoxycarbonylcarbonyloxy radical (2) itself has such a short lifetime, that it cannot be monitored with our setup. Concomitant with the decay of the 2,2,2-trifluorethoxycarbonyl radical (3b), we observe the formation of two products A and B containing a carbonyl moiety as indicated by the growing IR bands at 1781 and 1741 cm^{-1}(Scheme 2). It appears possible, that one of these two bands belongs to 2,2,2-trifluoroethylchloroformate (5), formed by chlorine atom abstraction by **3b** from the solvent CCl_4. 2,2,2-Trifluoroethylchloroformate has been twice described before. Unfortunately, the IR data published in the literature are inconsistent. Our data would be in agreement with the 1780 cm^{-1} band reported by *Gilligan and Stafford*. Another possible product would be the formal radical dimer bis(2,2,2-trifluoroethyl)oxalate (6). According to calculations (B3LYP/6-31G(d)) this compound should show two carbonyl bands around 1770 cm^{-1}. A plot of the integral values versus the time yields the lifetime of **3b** in CCl_4. The measured lifetime of τ = 3.6+0.5 μs is in good agreement with data on other alkoxycarbonyl radicals that have previously been published.[1] The data is summarized in table 1.



Scheme 1



Scheme 2

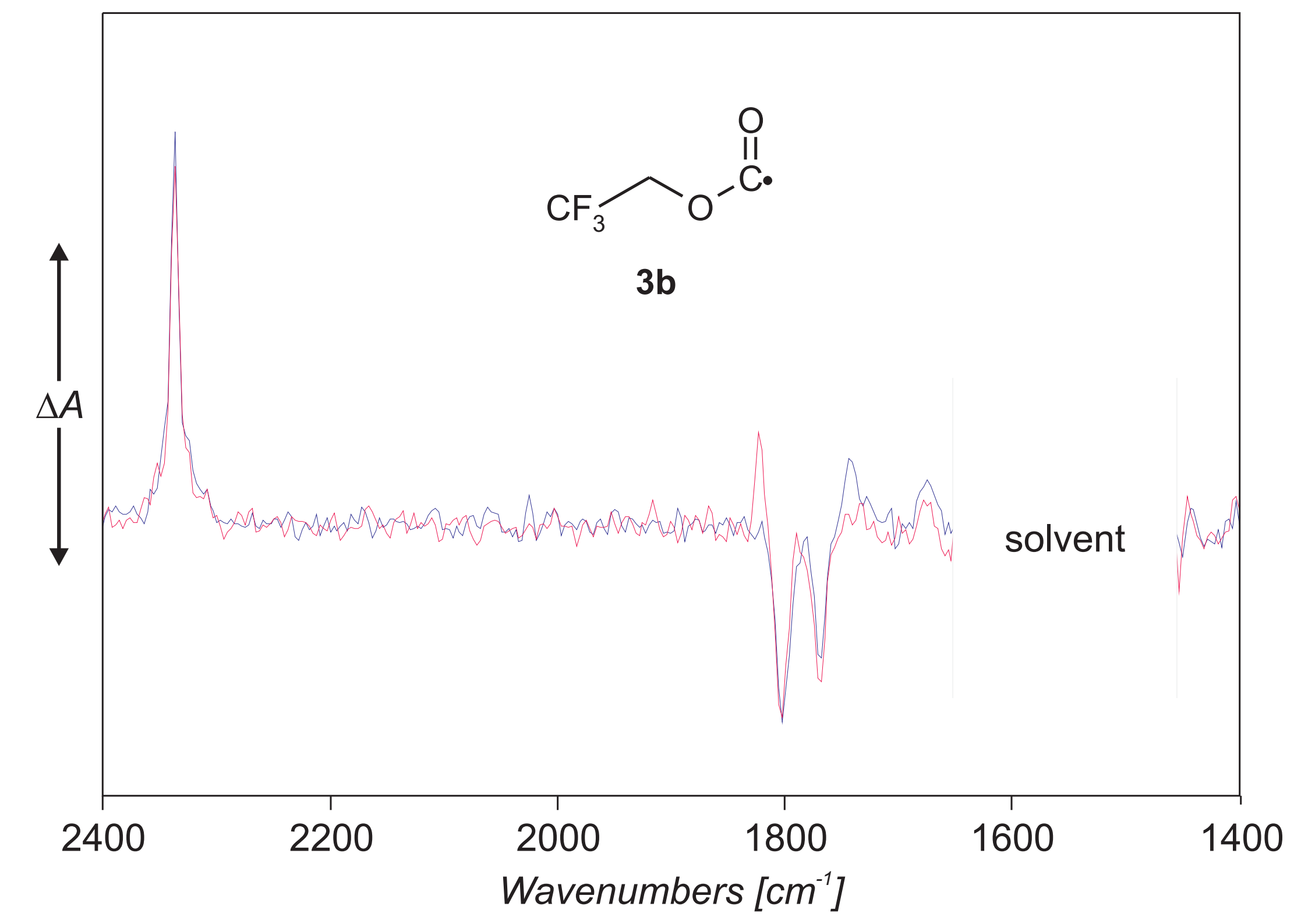


Figure 1. Time-resolved IR difference spectra (time resolution 500 ns, spectral resolution 6 cm^{-1}) showing the photochemistry of **1** in CCl_4 purged with argon. Bands appearing on irradiation ($\lambda_{exc.}$=355 nm) are pointing upwards; bands disappearing are pointing downwards. Red line, spectrum 500 ns after irradiation; blue line, spectrum after 20 μs.

radical	lifetime τ [μs]	$\nu_{C=O}$ exp. [cm^{-1}]	$\nu_{C=O}$ calcd. [cm^{-1}]
3a	2.4[d]	1802[d]	1781[d]
3b	3.6[a]	1823[a]	trans: 1883[c] cis: 1853[c]
3c	3.5[b]	1814[b]	trans: 1883[c] cis: 1851[c]
3d	4.4[d]	1799[d]	1803[d]
3e	2.0[d]	1790[d]	1800[d]
3f	-	-	1784[d]
4a	4.9[d]	1845[d]	1854[d]
4b	4.3[a]	1852[a]	1895[e]
4c	2.8[b]	1857[b]	1894[e]
4d	10.9[d]	1842[d]	1846[d]
4e	10.6[d]	1846[d]	1845[d]
4f	-	-	1850[d]

[a]: in CCl_4, ambient temperature. [b]: in CH_3CN, ambient temperature.
[c]: UMP2/cc-pVTZ, unscaled. [d]: Ref. 1 [e]: UB3LYP/6-311++g(d,p), unscaled.

Table 1. Lifetime, experimental and calculated C=O stretching vibrations of transient species.

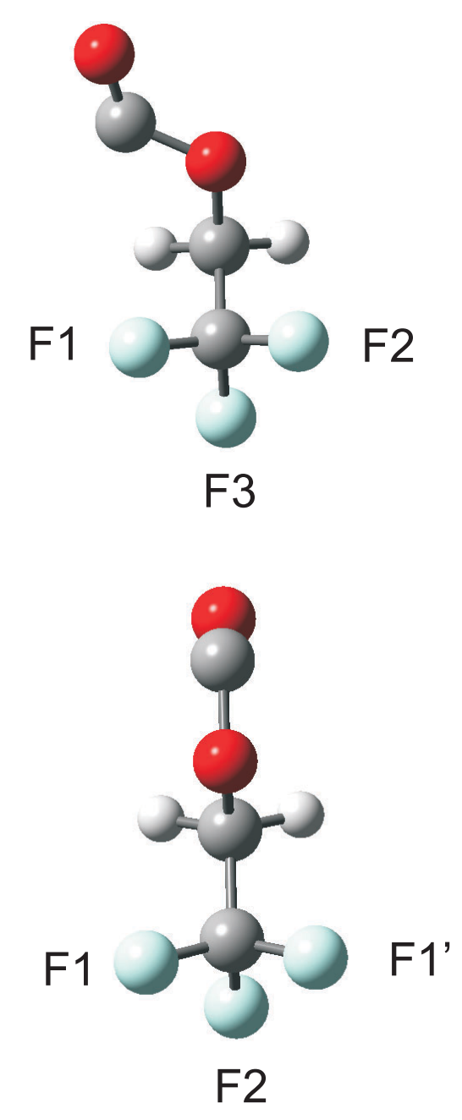


Figure 5. Optimized geometries (UMP2/cc-pVTZ) of *trans*-3b (top) and *cis*-**3b** (bottom).

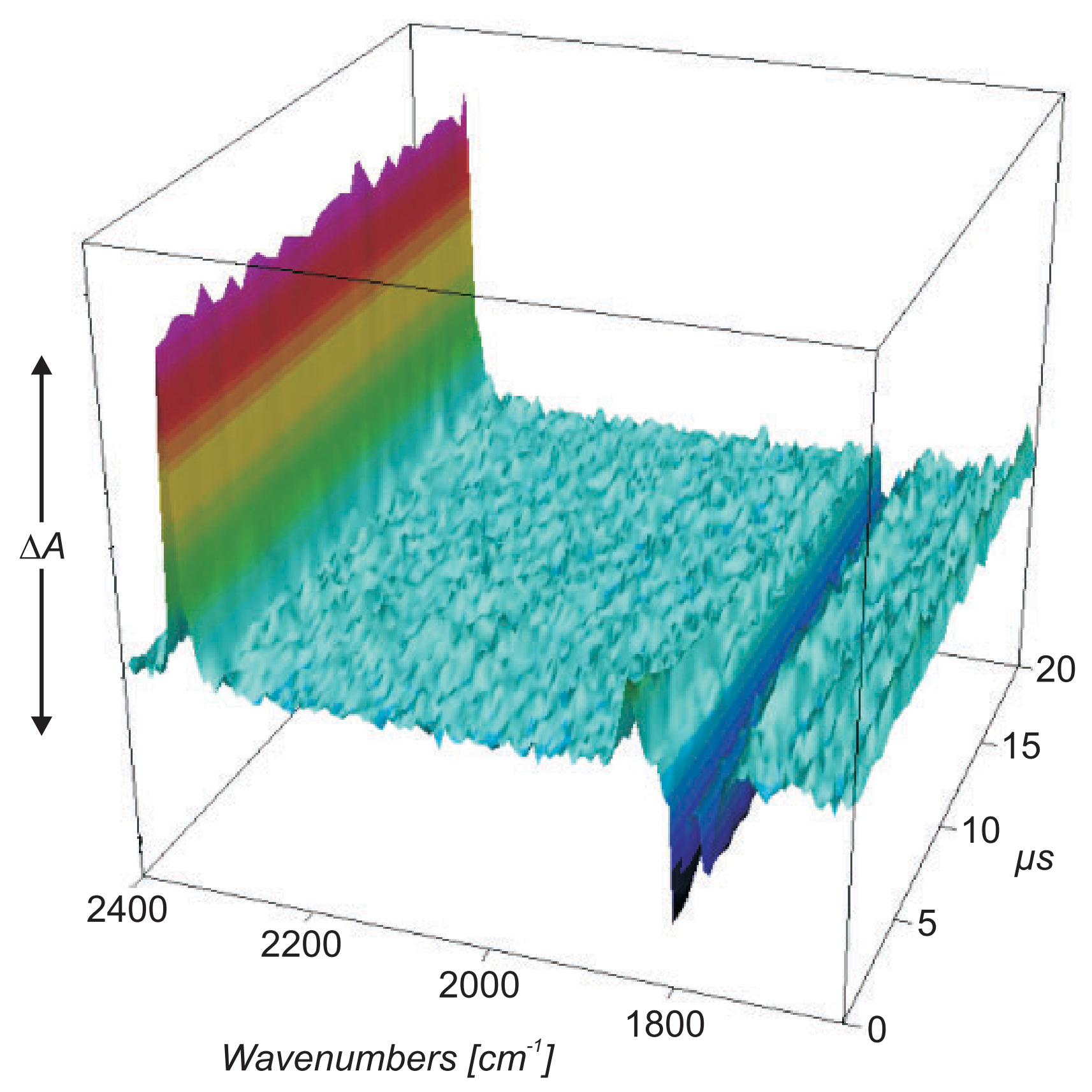


Figure 2. A 3-dimensional representation of the time-resolved difference STEP/SCAN FTIR spectrum of **1b** in oxygen-saturated CCl_4. The transient absorption is observed at 1852 cm^{-1}. Carbon dioxide is observed at 2337 cm^{-1}, whereas the two disappearing bands at 1802 and 1770 cm^{-1} belong to the starting material.

The photochemistry of **1** was also investigated by time-resolved EPR spectroscopy. LFP ($\lambda_{exc.}$ = 308 nm) of **1b** in CCl_4 (1 atm. Ar) led to the detection of the 1:1:1 triplet of the 9-fluorenoneiminyl radical (7), centered at g = 2.0032, with a coupling constant α_N = 9.6 G. In addition, we observed a signal that at first glance looks like a doublet of doublets at g = 2.001 (α_1 = 2.1 G; α_2 = 0.70 G) (Figure 3), but on close inspection can be identified as 1:3:3:1 quartet with additional HFS, partially superimposed on the iminyl triplet (Figure 4). Using TRIR spectroscopy, we could unequivocally identify the primary reaction intermediate in the LFP of **1b** as the trifluoroethoxycarbonyl radical, **3b**. This structure is consistent with the TREPR spectrum observed, as coupling of the unpaired electron spin with the nuclear spins of a freely rotating trifluoromethyl group would indeed result in quartet HFS. The additional HFS observed for **3b**, but not for **3c**, possibly is due to coupling with the proton (but not deuteron) nuclear spins. In addition to our experimental work, we performed calculations on the structure of **3b**. We discovered, that **3b** should occur as two different rotamers, *cis*-**3b** (C_s) and *trans*-**3b** (C_1)(Figure 5). On the (UMP2/cc-pVTZ + ZPE) level of theory, *trans*-**3b** was calculated to be lower in energy than *cis*-**3b** by 0.71 kcal/mol. At the same level of theory, both radical conformers were predicted to show a barrier of about 4 kcal/mol (*cis*-**3b**: 4.2 kcal/mol, *trans*-**3b**: 3.9 kcal/mol) for rotation around the CF_3-CH_2 bond. This value is consistent with experimental data on the barrier for CF_3-CH_2 bond rotation in 2,2,2-trifluoroethanol, which has been reported as $\Delta H^{\#}$=3.7 kcal / mol. Assuming a value of log (A/s^{-1}) = 13, this translates into a lifetime for bond rotation of ca. 1 ns. Hence, the trifluoromethyl group must be freely rotating on the much longer experimental time-scale. We also calculated the hyperfine splitting constants of both conformers using DFT. For the more stable *trans*-**3b**, the largest coupling predicted is $|J_{1,5}|$ = 4.1 G with the fluorine atom positioned closest to the radical center (F1, c.f. Figure 5), with coupling (calc.: $|J_{1,5}|$ = 2.08 G) also present to F2. Coupling to F3 is small (calc.: $|J_{1,5}|$ = 0.49 G). Averaged, the three individual fluorine couplings yield a value for $|J_{1,5}|$ = 2.22 G, which is in agreement with the experimental value of 2.1 G. Coupling to the hydrogen atoms is calculated to be very small ($|J_{1,4}|$ = 0.24 and 0.28 G). It is therefore unlikely to be the reason for the additional HFS (J = 0.7 G) observed. Figure 6 shows a simulated EPR spectrum of *trans*-**3b** based on averaged fluorine and proton coupling constants (blue). Apart from the 0.7 G coupling missing, the agreement with the experimental spectrum (Figure 4) is excellent. The simulated spectrum of conformationally frozen *cis*-**3b** reveals a significantly different coupling pattern, with a large coupling (calc.: $|J_{1,5}|$ = 7.44 G) to F2, practically no coupling with F1 and F1' (calc.: $|J_{1,5}|$ = 0.22 G) and significant coupling (calc.: $|J_{1,4}|$ = 1.81 G) with the two equivalent hydrogen atoms. Averaged, the fluorine couplings amount to 2.6 G, which is somewhat larger than the averaged fluorine coupling observed for *trans*-**3b**. Figure 6 shows the simulated spectrum of *cis*-**3b**, based on the averaged fluorine and proton couplings (red). The 0.7 kcal / mol calculated difference in energy in favor of *trans*-**3b** would translate into a 70:30 mixture of *trans*-**3b** and *cis*-**3b** present under equilibrium conditions. It is thus conceivable that the additional transitions in the experimental spectrum of **3b** stem from a contribution of the *cis*-isomer predicted to be slightly less stable. Figure 7 shows the experimental TREPR spectrum obtained upon LFP of **1c** in CCl_4. The quartet observed partially overlaps with the middle band of the iminyl triplet. The agreement is good with the simulated spectra of both *trans*- and *cis*-**3c**. The calculated HFS constants for both isomers are similar to those obtained for **3b**, with the exception of the deuteron coupling, which is predicted to be negligible. Figure 8 shows the simulated EPR spectra of both conformers of **3c**.

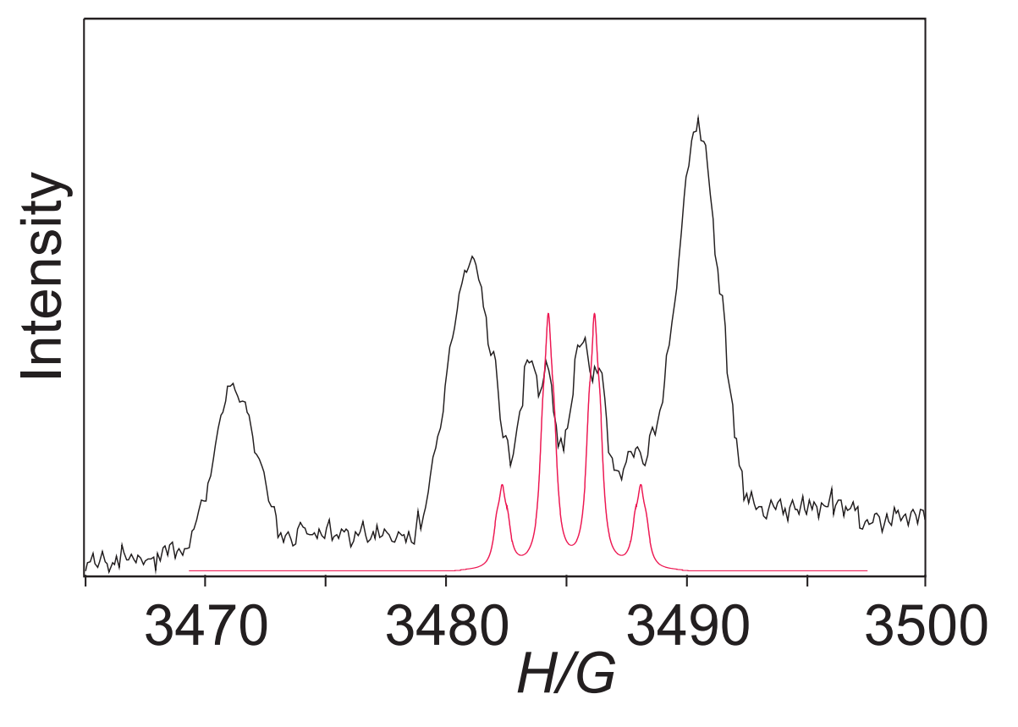


Figure 4. Black: Experimental TREPR spectrum measured 420 ns after LFP (308 nm) of **1b** in CCl_4. Red: Simulated EPR spectrum for *trans*-**3b**, based on the averaged fluorine and proton HFS constants obtained at the ub3lyp/epr-II level of theory.

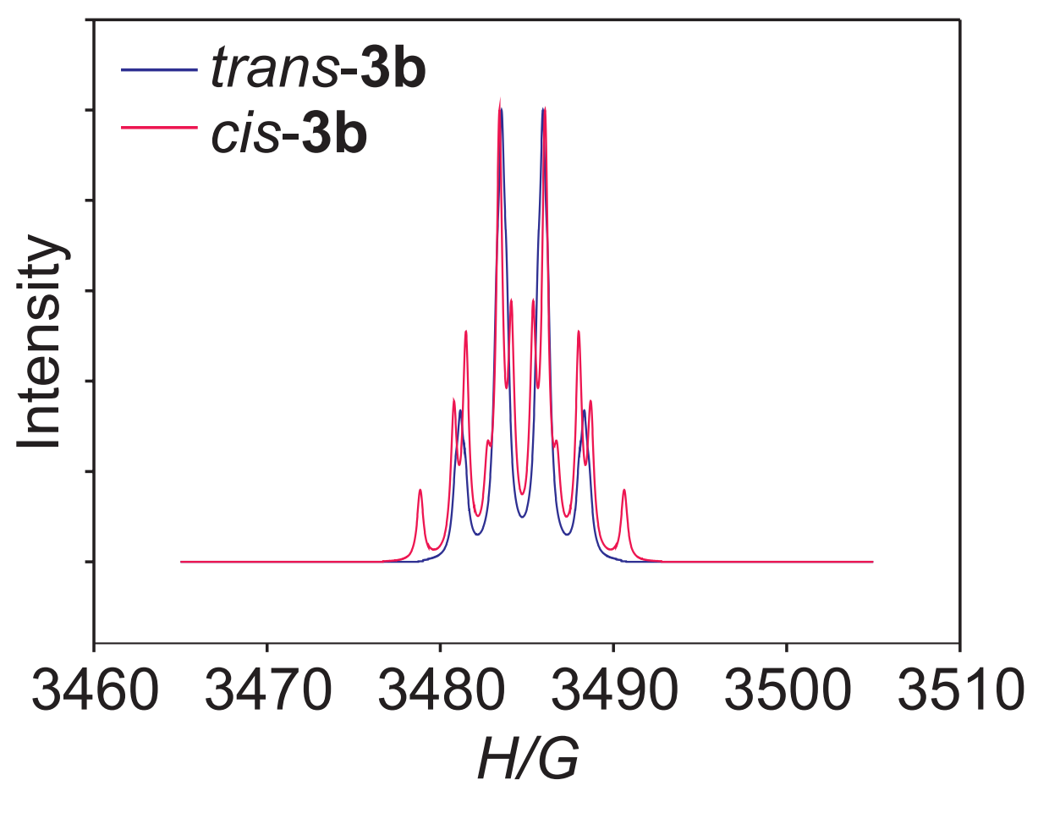


Figure 6. Simulated EPR spectra of both *trans*-**3b** (blue) and *cis*-**3b** (red), based on the averaged fluorine and proton HFS constants obtained at the ub3lyp/epr-II level of theory.

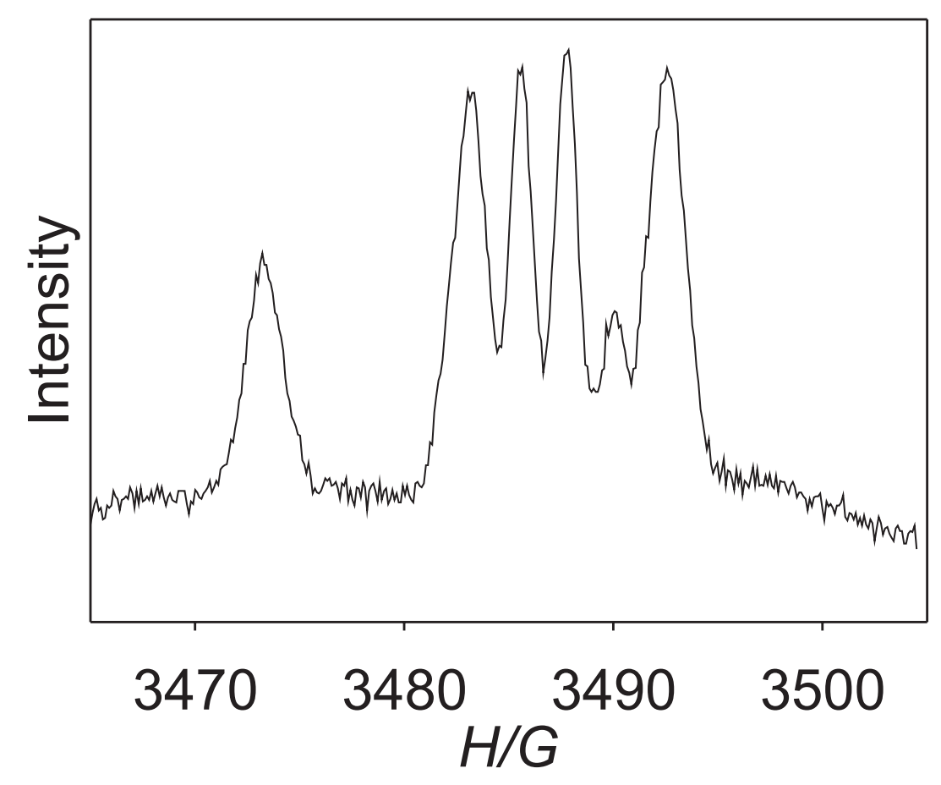


Figure 7. Experimental TREPR spectrum measured 420 ns after LFP (308 nm) of **1c** in CCl_4.

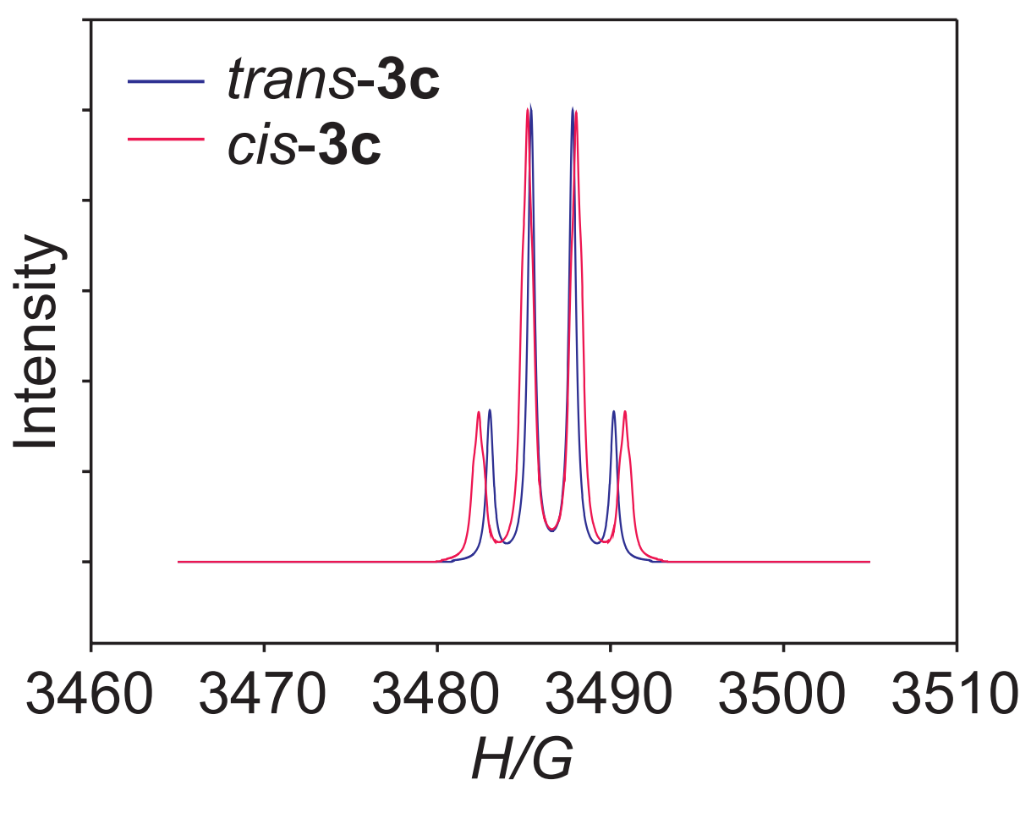


Figure 8. Simulated EPR spectra of both *trans*-**3c** (blue) and *cis*-**3c** (red), based on the averaged fluorine and deuteron coupling constants obtained at the ub3lyp/epr-II level of theory.

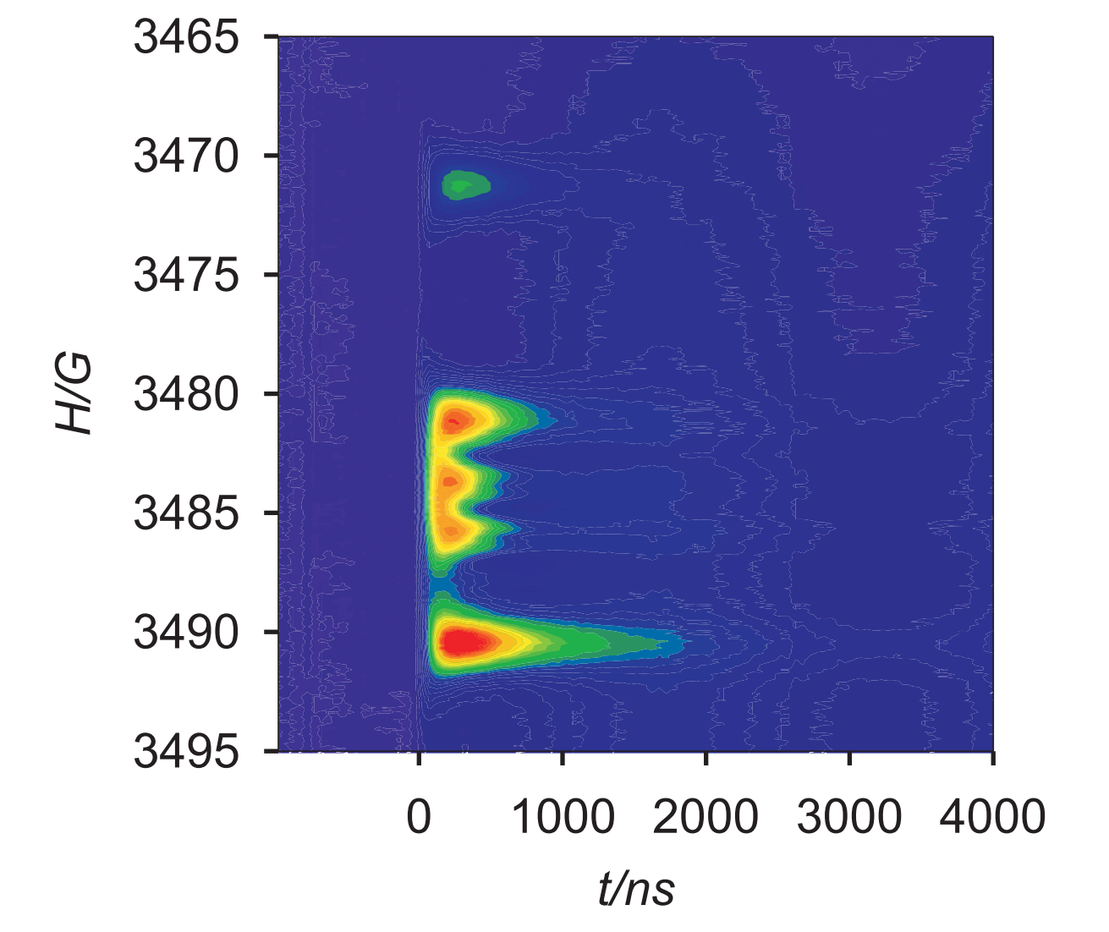


Figure 3. Time-resolved EPR spectrum, observed upon LFP (308 nm) of **1b** in CCl_4. The x-axis gives the time dependence of the signal, the y-axis the dependence on the magnetic field. Signal intensities are indicated by color encoding (red: high intensity, blue: low intensity).

The results described above can be analyzed in two directions, referring to the two halves of the oxalate precursors. Concerning the fluorenone oxime subunit of **1a**-**g**, this study presents no surprises. Formation of the 9-fluorenone iminyl radical (**7**) is clearly evident from the TREPR spectra, which can be compared with previously published data.[1] This finding is consistent with the results of earlier studies on the photochemistry of fluorenone oxime esters and carbamates.[1,3-4] As far as it relates to the chemistry, spectroscopy and structure of the oxalate-derived fragments, our present study presents novel findings that introduce new aspects to alkoxycarbonyl radical chemistry. Our data, both experimental and computational, indicate the possible existence of two conformers of alkoxycarbonyl radicals, which differ with respect to the dihedral angle around the R-O-C(O) bond. In case of the trifluoroethoxycarbonyl radical **3b**, both the s-*cis*- and the s-*trans*-isomer are likely formed and observed experimentally, the *trans*-isomer being slightly lower in energy. In contrast to this, the s-*trans* isomer is predicted to be formed almost exclusively in case of the ethoxycarbonyl radical **3a**, and very likely also in case of other alkyl-substituted alkoxycarbonyl radicals. While this preference likely does not play a large role as far as the reactivity of simple alkoxycarbonyl radicals is concerned, it may have a profound influence on the stereoselectivity of intramolecular addition reactions of alkene-functionalized alkoxycarbonyl radicals, where small differences in activation energies may lead to large differences in product yields.

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