



Theory-guided access to efficient photodegradation of the simplest perfluorocarboxylic acid: Trifluoroacetic acid



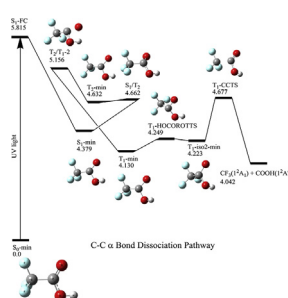
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HIGHLIGHTS

- The multi-reference quantum chemical methods were used.
- The PESs of the low-lying singlet and triplet excited states of TFA were constructed.
- The non-adiabatic processes were discussed in detail for the photodissociation.
- The channel involving ISC is the most possible channel for direct photodegradation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 22 September 2016

Received in revised form

18 March 2017

Accepted 27 March 2017

Available online 30 March 2017

Handling Editor: I. Cousins

Keywords:

Trifluoroacetic acid

Photodegradation

CASPT2

Intersystem crossing

ABSTRACT

The photodegradation approaches of perfluorocarboxylic acids have attracted considerable attention and have been developed extensively. However, the reaction channels along which the perfluorocarboxylic acid molecules dissociate remain to be deciphered by means of the quantum chemical method at the electronically excited state level of theory until now. Here we report the photodissociation mechanism of the simplest perfluorocarboxylic acid, trifluoroacetic acid, using the complete active space self-consistent field (CASSCF) and the multi-configurational second-order perturbation (CASPT2) methods. The C–C and C–O α bond fission channels were both taken into account. Based on the constructed potential energy surfaces, it is concluded that the C–C α bond fission, which would probably account for further degradations and mineralizations, may mainly take place in the triplet manifolds via intersystem crossing from the S_1 state. Thus, taking the computational results of the simple member of perfluorocarboxylic acids as a rational clue, strategies to enhance intersystem crossing process efficiencies of the photodegradation of perfluorocarboxylic acids can be developed.

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1. Introduction

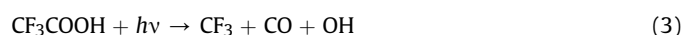
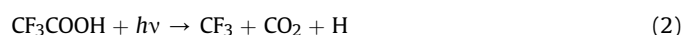
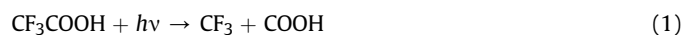
Pollution of perfluorochemicals (PFCs), especially the perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs),

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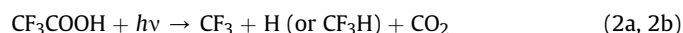
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have become an important environmental issue due to their worldwide distributions, chemical stabilities and potential biological toxicities. Photochemical treatment, as one of the efficient approaches for the degradation of PFCs, draws significant attention, and has been put into extensive experimental practices in recent years (Hori et al., 2004; Chen et al., 2007a, 2007b; Hori et al., 2007; Yamamoto et al., 2007; Wang et al., 2008; Yamada et al., 2008; Cao et al., 2010; Estrellan et al., 2010; Qu et al., 2010; Wang et al., 2010;

Chen et al., 2011; Cho, 2011; Giri et al., 2011; Vaalgamaa et al., 2011; Wang and Zhang, 2011; Giri et al., 2012; Li et al., 2012; Song et al., 2012; Zhao et al., 2012; Hsu et al., 2013; Shao et al., 2013; Song et al., 2013; Taniyasu et al., 2013; Cheng et al., 2014; Giri et al., 2014; Qu et al., 2014; Wang and Shi, 2014; Jin et al., 2015; Lyu et al., 2015a, c, b; Guo et al., 2016; Merino et al., 2016; Yamazaki et al., 2016; Zhang et al., 2016). Trifluoroacetic acid (trifluoroethanoic acid, referred to as TFA) is the simplest member of the perfluorocarboxylic acid family. The mechanical studies on the photodissociation of TFA upon UV–Vis irradiations may provide meaningful manifest enlightenment for understanding the degradations of other perfluorocarboxylic acids consisted of longer carbon chains such as PFOA. On the other hand, TFA is a pivotal product in the photodegradation processes of PFOA and PFOS. Additionally, TFA exists in the atmosphere as a gas phase pollutant with concentration of 20–150 pg/m³ (Frank et al., 1996), which is probably caused by the degradation of HFCs (Bowden et al., 1996). The investigation on the photolysis mechanism of TFA is therefore of realistic importance in environmental protections. In 1963, Mearns and Back (Mearns and Back, 1963) first investigated the photolysis of TFA vapor upon photoexcitations at the wavelength range of 200–220 nm controlling the experimental temperatures between 90 and 190 °C. The major products of photolysis were CO₂ and C₂F₆, while smaller amounts of CO, H₂, and CF₃H were also detected. The primary dissociation processes they suggested are shown as below:



The channel (1) was considered the main primary photolytic process, while the channel (2) and channel (3) were thought to be the minor processes accounting for 27 and 7% of the total, respectively. Miyoshi and Matsui studied the photodissociation of TFA in the gas phase at 193 nm, and by means of the photoionization mass spectrometry they detected the HOCO and CF₃ radicals as the dissociation products (Miyoshi and Matsui, 1994). Osborne et al. (1999) measured the UV photodissociation products of TFA by means of the time-resolved infrared absorption technique. The UV light source they used was a conventional flashlamp, which makes a range of wavelengths. By the transmission of Spectrosil quartz, the short wavelength used in their photolysis was about 165 nm. They found the relative yields of COOH, CO₂ and CO to be 0.28 ± 0.07, 0.61 ± 0.09 and 0.11 ± 0.06, respectively, and proposed at least three channels for these three products, including the channel (1) as illustrated above, and two another channels shown as follows:



Kim et al. (Kwon et al., 2001) investigated the photodissociation dynamics of TFA at a wavelength of 193 nm using an ArF excimer laser. They measured the rotationally resolved laser-induced fluorescence (LIF) spectra of the dissociated OH fragments. By analyzing the distribution among the products of the available energy at 193 nm, they concluded that the TFA molecule dissociates into trifluoroacetyl and hydroxyl radicals in the triplet state by overcoming an energy barrier.

On the other hand, early *ab initio* calculations on the decomposition pathways of TFA in the ground state were reported by

Francisco in 1992 (Francisco, 1992). The structures were optimized at the Hartree–Fock level using the 3–21G and 6–31G* basis sets, and the single point energies were refined by the MP4SDTQ method. On the basis of the calculated results about heats of reaction and dissociation barrier heights, Francisco suggested the C–C fission and 1,2-fluorine shift processes were the two lowest energy pathways, the energy barriers of which were predicted to be 80.5 and 81.6 kcal/mol, respectively (Francisco, 1992).

However, to our best knowledge, no theoretical studies on the dissociation pathways in the excited states have been reported, and the photodegradation mechanism of TFA remains to become unraveled up to now. To this end, we constructed the potential energy surfaces (PESs) of the low-lying singlet and triplet excited states along the C–C α and C–O α fission pathways, which are associated with the pivotally competitive routes in photodegradation processes, and determined the photodissociation mechanism of TFA on the basis of the characters of the calculated PESs.

2. Computational details

The ground state minimum structure was obtained at the B3LYP (Becke, 1988, 1993; Lee et al., 1988)/def2-QZVPPD (Rappoport and Furche, 2010) level using the ORCA 3.0.3 program (Neese, 2012), which was taken as the equilibrium geometry in the succeeding calculations of vertical excitation energies (VEEs) and corresponding oscillator strengths. While the stationary points on the C–C and C–O α dissociation channels in the low-lying singlet and triplet states of TFA were all optimized using the complete active space self-consistent field method (CASSCF) (Roos, 1987) with Dunning correlation consistent triple-zeta (cc-pVTZ) basis sets (Dunning, 1989). To give an adequate description to the excited states with Rydberg characteristics, the Aug-cc-pVTZ basis set (Kendall et al., 1992) containing the diffuse functions was used. The harmonic frequencies were checked at the same level as the geometry optimizations to determine the converged geometries whether minima or transition states. To consider the dynamics correlation fractions of correlation energies, single-point energies were refined at the multi-configurational second-order perturbation theory (CASPT2) (Finley et al., 1998). When more than one CI roots in the CI Davidson procedure were needed to be specified, the state-average (SA) CASSCF and multi-state (MS) CASPT2 methods were applied. In our calculations, only one CI root was used for the investigation on the S₀ and T₁ PESs, while the vertical excitation energies were calculated including five CI root with equal weight, and the S₁ and T₂ PESs as well as the linear interpolations of the internal coordinate (LIIC) calculations were performed using two CI roots with equal weight. For uniformity, they will be all denoted as SA-CASSCF and MS-CASPT2. The intrinsic reaction coordinates (IRC) analyses starting from all the transition state geometries were carried out at the same level as the structural optimization processes to confirm the right connections between transition states and minima (or dissociation fragments). The minimum energy geometries of the surface crossing seams were also obtained for both the conical intersection and intersystem crossing (ISC) points at the SA-CASSCF level. The surface crossing calculations were performed by means of COLUMBUS program package 7.0 (Császár and Pulay, 1984; Shepard, 1987; Fogarasi et al., 1992; Shepard et al., 1992; Shepard, 1995; Helgaker et al., 1997; Lischka et al., 2001, 2002, 2004, 2011, 2015; Dallos et al., 2004), while all the other CASSCF and CASPT2 calculations mentioned above were carried out using the MOL-CAS8.0 program (Karlström et al., 2003; Varyazov et al., 2004; Aquilante et al., 2010).

An active space containing 12 electrons and 9 molecular orbitals was selected for all the CASSCF and CASPT2 calculations. The six

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