Photoexcitation, Photoionization, and Photofragmentantion of CF₃CF₂CF₂C(O)CI Using Synchrotron Radiation between 13 and 720 eV

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Supporting Information

ABSTRACT: The main inner shell ionization edges of gaseous $CF_3CF_2CF_2C(O)Cl$, including Cl 2p, C 1s, O 1s, and F 1s, have been measured in Total Ion Yield (TIY) mode by using tunable synchrotron radiation, and several resonance transitions have been assigned with the help of quantum chemical calculations. Interestingly, resonance transitions observed in the C 1s region can be assigned to different carbon atoms in the molecule according to the degree of fluorine substitution. Ionic photofragmentation processes have been studied by time-of-flight mass spectrometry in the Photoelectron-Photoion-Coincidence (PEPICO) and Photo-



electron-Photoion-Photoion-Coincidence (PEPIPICO) modes. These techniques revealed a "memory-lost" effect especially around the C 1s region, since the fragmentation events are independent of the energy range considered. Moreover, different fragmentation mechanisms were inferred from these spectra in the valence (13.0-21.0 eV) as well as in the inner (180.0-750.0 eV) electronic energy regions. The vibrational spectral features of CF₃CF₂CF₂C(O)Cl have been interpreted in terms of a conformational equilibrium between two conformations (*gauche* and *anti* of the CC single bond with respect to the CCl one) at room temperature, as determined from quantum chemical calculations and the detailed analysis of the infrared spectrum.

INTRODUCTION

Over the last few decades fluorinated compounds have been widely used and subsequently distributed in the atmosphere, especially as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs).¹ The degradation of HCFCs in the troposphere results in the emission of different chlorinated compounds such as the simplest perfluoroacyl chloride, $CF_3C(O)Cl.^{2,3}$ Moreover, the degradation of CFCs takes place in the stratosphere, where the loss of chlorine atoms is followed by its reaction with ozone generating atomic and molecular oxygen.¹ The generation of fluoroacyl chlorides in the troposphere and its subsequent degradation in the stratosphere introduced the imminent need for deep knowledge of the photochemical behavior of these compounds. Thus, perfluoroacyl chlorides with short carbon chains, including perfluoropropanoyl chloride, CF₃CF₂C(O)Cl, and trifluoroacetyl chloride, CF₃C(O)Cl, have been deeply studied photochemically.4,5

Perfluorobutanoyl chloride, $CF_3CF_2CF_2C(O)Cl$, has also been the object of different studies, including structural microwave spectroscopy⁶ and photochemical reactions using ultraviolet (UV) light.⁷The photolysis of $CF_3CF_2CF_2C(O)Cl$ was studied in the liquid phase by J. F. Harrys⁷ by irradiating the sample with UV light for several days. A free radical mechanism for the generation of $n-C_3F_7Cl$, $n-C_6F_{14}$, and CO photoproducts was rationalized.

In the present work we present the spectroscopic signatures of gaseous $CF_3CF_2CF_2C(O)Cl$ in the X-ray and VUV region. Synchrotron radiation and time-of-flight mass spectrometry in the PEPICO and PEPIPICO coincidence modes allow determination of the photofragmentation dynamics of the ion generation as a consequence of the photon absorption in the inner shell electronic region, including transitions at the Cl 2p, C 1s, O 1s, and F 1s edges. From the wide range of photon energies applied, a "memory-loss" effect has been clearly determined, as deduced from the close similarity among the several PEPICO spectra recorded at different energies, where no manifestation of site-specific fragmentations could be detected.

Received:December 10, 2014Revised:February 13, 2015Published:February 13, 2015

EXPERIMENTAL SECTION

Synchrotron Measurements. Photoionization measurements using synchrotron radiation were carried out in three campaigns at the Laboratório Nacional de Luz Síncrotron (LNLS) facilities.^{8–10} Specifically, the TGM and the SGM beamlines were used, which allow work in the 7–300 eV and 200–1000 eV energy ranges, respectively.

The resolving power value of the TGM beamline ($\Delta E/E <$ 400) duplicates the one of the SGM beamline. At both beamlines, the intensity of the emergent beam was recorded with a light-sensitive diode. After the linear polarized synchrotron radiation impacts the Toroidal Grating Monochromator or the Spheric Grating Monochromator placed along the TGM or SGM beamlines, respectively, it intersects the molecular beam inside of a high-vacuum chamber (base pressure $\approx 1 \times 10^{-8}$ mbar, working pressure $\approx 1 \times 10^{-6}$ mbar). Both the electrons and the positive ionic fragments generated through the photofragmentation processes are consequently directed to the corresponding detectors, which are located parallel to the plane of the storage ring and perpendicular to the direction of the incident synchrotron radiation and to the sample molecular beam. The ionic detector consists of a Time-Of-Flight (TOF) mass spectrometer of the Wiley–McLaren type.^{11,12}

In the low energy range, the absorption through the gas harmonic filter stage provides an easy and fast way for photon energy calibration. Using neon as the filtering gas, its first ionization potential, at 21.56 eV, can be easily observed on a simple photodiode as well as the stronger Rydberg transitions close to 17 eV. The measurements taken ensure us that the photon energy calibration accuracy is down to the beamline energy resolution.

At high photon energies, the TGM and SGM beamlines are often calibrated by the LNLS staff by using the absorption edges of well-known molecules, like SF₆ and CO. During our experiments, at each electron storage ring injection the zero order of the beamline grating was checked, which assures the photon energy accuracy to be on the same order as the beamline resolution.¹³

The time-of-flight of a particular ion in the PEPICO and PEPIPICO spectra is given by the TOF ion measurement started by the arrival of the first electron involved in the process. Specifically, the first electron released in a given photoionization process starts possible fragmentation channels originating the ions to be detected. Electrons were accelerated to a multichannel plate (MCP) and recorded without further energy analysis. A more detailed description of the performance of the multicoincidence device can be found in the literature.¹⁴

Synthesis. The title compound was synthesized by reaction of perfluorobutanoic acid with phosphorus pentachloride according to the usual method.¹⁵ Thus, 6 mL (49 mmol) of perfluorobutanoic acid, $CF_3CF_2CF_2C(O)OH$, was slowly added using a dropping funnel attached to a twin-neck round-bottom flask containing 12.50 g (60 mmol) of PCl₅. Two "U"-shaped traps immersed in cool baths (-50 and -80 °C, respectively) were connected to the condenser and a CaCl₂ trap was added to the end of the experimental setup. The mixture of $CF_3CF_2CF_2C(O)OH$ and PCl_5 was then heated to 70 °C for 2 h while the produced hydrogen chloride, HCl, and perfluorobutanoyl chloride, $CF_3CF_2CF_2C(O)Cl$, were mainly collected in the -80 and -50 °C traps, respectively. When the reaction finished, the remaining HCl was removed from the -50 °C "U" trap by several trap-to-trap distillations, using a conventional vacuum line and two more "U" traps (immersed in -80 and -196 °C cooled baths). Finally, pure CF₃CF₂CF₂C(O)Cl was obtained in the -80 °C trap. Its purity was checked through a gas-phase FT-IR spectrum using a FT-IR Bruker Equinox 55.

Computational Calculations. Quantum chemical calculations were performed using DFT¹⁶ and MP2¹⁷ methods with the Gaussian 03 package.¹⁸ Three approximation levels (B3LYP/6-311+g(d), B3LYP/cc-pVTZ, and MP2/cc-pVTZ) were used to compute the geometries and the vibrational frequencies of the less energetic conformations of $CF_3CF_2CF_2C(O)Cl$. The NBO BP86/6-311+g(d) approximation was also used in order to compute the energy of the corresponding natural bonding orbitals.

RESULTS AND DISCUSSION

Molecular Structure of CF₂CF₂CF₂C(O)Cl in the Fundamental Electronic State. Grubbs II et al.⁶ reported the molecular structure of perfluorobutanoyl chloride by using microwave spectroscopy and quantum chemical calculations. They concluded that the title compound shows the existence of only one conformation at room temperature corresponding to a planar structure with a dihedral angle τ (CC-CCl) equal to 180° (anti orientation of the C-Cl single bond with respect to the C-C single bond). However, based on previous results obtained for related species, the presence of a second conformation with gauche orientation of the -C(O)Cl group cannot be discarded (C-Cl and C-C single bonds adopting a mutual gauche orientation). Moreover, our computed B3LYP/ 6-311+g(d) values for the dipole moments (0.8635 and 0.8919 D, respectively) are similar for the *anti* and *gauche* conformers, a fact that seems to indicate the experimental feasibility of the observation of both forms through microwave spectroscopy. Thus, the potential energy curve around the τ (CC-CCl) dihedral angle has been computed with the MP2/cc-pVTZ, B3LYP/cc-pVTZ, and B3LYP/6-311+g(d) level of approximations (Figure 1).

Two minima are observed in Figure 1, corresponding to the *anti* and *gauche* conformations, with τ (CC–CCl) dihedral angles close to 80 and 180 deg, respectively. In both cases, the CCCC chain presents an *anti* structure. The optimized



Figure 1. Potential energy curves for the rotation of the τ (CC–CCl) dihedral angle of CF₃CF₂CF₂C(O)Cl calculated with different theoretical approximations.

structures are calculated with the B3LYP/6-311+g(d), B3LYP/cc-pVTZ, and MP2/cc-pVTZ approximations are shown in Figure 2. Both minima were then fully optimized and their



Figure 2. Anti (left) and gauche (right) conformers of $CF_3CF_2CF_2C$ -(O)Cl calculated with the MP2/cc-pVTZ approximation.

vibrational frequencies were calculated using the same approximations. With the double degeneration of the *gauche* conformer taken into account, the Boltzmann distribution was used to calculate the population (X) of both conformations. Table 1 compares the relative total energy, relative free energy,

Table 1. Relative Total Energy (ΔE), Free Gibbs Energy (ΔG°), Populations, and τ (CC-CCl) Dihedral Angle Computed for the *Gauche* Conformer

level of approximation	ΔE^a (kcal.mol ⁻¹)	$\Delta G^{\circ b}$ (kcal.mol ⁻¹)	X^{c}	$\tau CC - CCl^d$
B3LYP/6-311+g(d)	0.04	0.12	62	81.47°
B3LYP/cc-pVTZ	0.21	-0.30	77	88.49°
MP2/cc-pVTZ	0.06	0.08	64	77.85°

 ${}^{a}\Delta E = E_{gauche} - E_{anti}$. ${}^{b}\Delta G^{\circ} = G^{\circ}_{gauche} - G^{\circ}_{anti}$. Calative abundance of the *gauche* form calculated from the Boltzmann distribution at 25 °C. ^dComputed value for the *gauche* conformer.

 τ (CC–CCl) dihedral angle, and percentage in the population of the *gauche* conformation obtained with the three different approximation levels. As can be inferred from Table 1, according to the computed values the *gauche* conformer represents the most abundant form expected for the vapor of CF₃CF₂CF₂C(O)Cl at room temperature.

Gas-Phase Infrared Spectrum. The gas-phase infrared spectrum of $CF_3CF_2CF_2C(O)Cl$ taken with a resolution of 0.5 cm⁻¹ and a pressure of 4 mbar is shown in Figure 3. It is well-known that the $\nu(C=O)$ normal mode of vibration is very sensitive regarding the conformational properties.^{19,20} As



Figure 3. Gas-phase FT-IR spectrum of $CF_3CF_2CF_2C(O)Cl$. The inset shows the carbonyl stretching band.

shown for the title species in the inset of Figure 3, the carbonylic absorption is broad, with a maximum of the signal at 1806 cm^{-1} and a shoulder at 1824 cm^{-1} . The quantum chemical calculations allow assignment of these modes to the *gauche* and *anti* conformers, respectively (see Table S1 and Figure S1 in the Supporting Information).

Total Ion Yield. The Total Ion Yield (TIY) spectra were acquired by recording the count rates of the total ions while the photon energy was scanned. Four TIY spectra of the title compound were measured around the Cl 2p, C 1s, O 1s, and F 1s ionization edges, respectively. The C 1s TIY spectrum shown in Figure 4 is an average of three spectra collected with an energy step of 0.1 eV, between 284.0 and 345.0 eV. The other three TIY spectra presented in Figure 4, Cl 2p, O 1s, and F 1s, are a consequence of averaging two corresponding spectra. The recorded energy step in these cases was 0.05, 0.1, and 0.5 eV, respectively. During the acquisition of all the spectra, every energy step took 3 s.

Below the ionization edges, which were identified by direct inspection of the TIY spectra, several resonance transitions can be observed. It can be noted that the TIY spectrum taken below the C 1s edge presents the largest amount of resonance transition peaks, which might be related to a better overlap between the initial (C 1s) and the final orbitals. In order to assign the resonance transition peaks, the molecular orbital diagram was estimated using the NBO BP86/6-311+g(d) level of approximation (Table S2) for both conformations. Bibliographic data was also used to compare and assign these spectra.^{21,22}

Ionization energies are known to be strongly dependent upon the molecular structure and conformation, as demonstrated by Deleuze and co-workers for the case of molecules having extended carbon chains.^{23–25} Nevertheless, for $CF_3CF_2CF_2C(O)Cl$ no differences in the inner ionization potentials were found within both conformers. Moreover, no significant differences were detected between calculated resonant transition energies as both conformers were compared.

Cl 2p TIY. The Cl 2p ionization potential edge of $CF_3CF_2CF_2C(O)Cl$ is located in the region of 211 eV. This value agrees with reported ones for molecules containing chlorine atoms bonded to carbonyl groups.²⁶ Three broad bands (201.2, 204.2, and 206.0 eV) can also be observed in this spectrum below the chlorine 2p ionization edge. After baseline correction and deconvolution of the peaks (Figure S2), the 201.2 eV band was resolved into two different peaks, located at 201.2 and 202.4 eV. These peaks, with an energy difference of 1.2 eV and an intensity ratio close to 2:1, might be assigned to the transition from the Cl 2p to the final σ^* (C-Cl) state involving a spin-orbital splitting according to similar reported values for chlorinated species (1.6 eV).^{27,28} The energy difference between both peaks and their intensity ratio are related to errors in the baseline correction and the subsequent deconvolution. The remaining peaks might originate from different transitions involving Cl Rydberg orbitals.

C 1s TIY. The TIY spectrum in the C 1s region can be divided into three different regions (285–291 eV, 291–305 eV, and 305–340 eV). The correction of the baseline and the corresponding deconvolution allowed us to distinguish different peaks (Figure S3). Subsequently, the assignment of those peaks was performed with the assistance of quantum chemical calculations and by comparison with some reported values. The assignment of the most relevant peaks is discussed below.



Figure 4. Total ion yield spectra of $CF_3CF_2CF_2C(O)Cl$ around the Cl 2p, C 1s, O 1s, and F 1s ionization edges. Selected assignments corresponding to resonant transitions, the ionization potential (IP), and some molecular orbitals are also depicted.

In order to make the description of the assignment clearer, the carbon atoms of the title compound were numbered in the following way: $C(4)F_3C(3)F_2C(2)F_2C(1)(O)Cl$. The 287.4 and 290.6 eV peaks are originated by the transitions C(1) Is $\rightarrow \pi^* C=O$ and C(1) Is $\rightarrow \sigma^* C-Cl$, respectively. While a C(1) Is $\rightarrow \pi^* C=O$ transition was already reported, ^{22,26} the C(1) Is $\rightarrow \sigma^* C-Cl$ transition to the best of our knowledge has not yet been reported.

The second region (from 291.0 to 305.0 eV) was deconvoluted into several peaks. At 293.8 eV a broad signal which might arise from superimposed transitions from the C(2)/C(3) 1s inner orbital to the antibonding σ^* (C2–F7), σ^* (C2–F8), σ^* (C3–F9), and σ^* (C3–F10) orbitals is observed. An important strong peak observed at 295.6 eV is assigned to the C(1)/C(2)/C(3) 1s $\rightarrow \sigma^*$ (C1–C2)/ σ^* (C2–C3)/ σ^* (C3–C4) transitions. Moreover, the C(4) 1s $\rightarrow \sigma^*$ (C4–F11)/ σ^* (C4–F12)/ σ^* (C4–F13) transitions are evidenced as a unique band at 297.4 eV, while the C(4) 1s $\rightarrow \sigma^*$ (C3–C4) can be detected at 298.4 eV. Finally, the 310.2 eV peak (third region) was assigned to the transition from the C(1) 1s to different C Rydberg orbitals.

The higher amount of fluorine atoms surrounding and bonding the carbon atoms implies a higher nuclear effective charge on the C 1s electrons, originating more energetic transitions. This observation is in total agreement with the chemical shift described by Habenicht et al.²⁹ It is important to emphasize that the approximation used (NBO BP86/6-311+g(d)) predicts the same trend for the different C 1s orbitals. Figure S4 shows the linear correlation between the experimental transition energies and those predicted by the approximation NBO BP86/6-311+g(d) for the TIY C 1s region.

According to the literature, the ionization edge of the C 1s electrons depends on its substituents. Moreover, a C 1s orbital ionization potential chemical shift of ca. 2.2 eV has been determined when an F atom formally replaces an H atom attached to a C atom.^{29–31} In particular, perfluorobutanoyl chloride shows four different types of carbon atoms (C==O, two different CF₂ groups, and CF₃). For these carbon atoms, comparable ionization edges have been reported to be 297.3 eV for the CF₂ group and at 296.55 eV for the C==O group in CF₃C(O)OH.²² The envelope of the TIY spectrum presented in this work is in good agreement with those values reported in the literature.

O 1s TIY. An intense peak located at 530.1 eV dominates the TIY spectrum measured in the O 1s region. It resembles those absorptions reported in different inner-shell excitation studies

of several carbonyl compounds assigned to the O 1s $\rightarrow \pi^*$ (C=O) transition.^{32,33} Moreover, many transitions can initiate the broad band centered at 540.0 eV, in particular, processes involving excitations from the O 1s core orbital to different unoccupied molecular orbitals along different RY(O) and mainly σ^* (C-O) according to the performed calculations.

According to Figure 4, the O 1s ionization potentials corresponding to the carbonyl oxygen of $CF_3CF_2CF_2C(O)Cl$ appears in the region of 543 eV, in good agreement with reported values at 539.6, 535.7, and 535.3 eV for $CF_3C(O)OH$, $CIC(O)SCH_3$, and CIC(O)SCI, respectively.^{22,34,35}

F 1s TIY. $CF_3CF_2CF_2C(O)Cl$ TIY spectrum recorded near the F 1s ionization edge presents a broad peak (685.0–700.0 eV) centered at 695.0 eV. According to the literature²² and to the MO calculated energies, transitions from the F 1s orbital to the unoccupied σ^* (C–F) molecular orbitals are expected to take place at these energies.

The detection of the F 1s ionization edge is even more complicated than in the cases described before; nevertheless, it is expected in the region of 700 eV in comparison with the 695.1 eV reported value for both CF₃ and CF₂ groups in trifluoroacetic acid and in octafluorocyclopentene, respectively.²² Recently, the F 1s ionization threshold of 2,2,2-trifluoroethanol was reported at 695.2 eV.³⁶ Ibuki et al. determined the nonselective ionization of the nonequivalent fluorine atoms in CF₃SF₅, which supports the lack of distinction of different F 1s ionization potentials in the TIY CF₃CF₂CF₂C-(O)Cl spectrum.³⁷

Study of the Photoionization Processes. Valence Region. Photoelectron-Photoion-Coincidence spectra were taken at different energies in the valence region (7.0-21.0 eV) in the TGM beamline (Figure 5). No peaks were observed for energies lower than 12 eV evidencing that the first ionization energy is over 12.0 eV. Despite the low energies used the molecular ion cannot be detected. The heaviest fragment



Figure 5. PEPICO spectra of $CF_3CF_2CF_2C(O)Cl$ taken from 13.0 to 21.0 eV in the LNLS TGM beamline.

detected is formed by the loss of a chlorine atom from the molecule (m/z = 197). Below 17.0 eV the isotopomers of the C(O)Cl⁺ ion (m/z = 63/65) predominate in the spectra, while above this energy the ion with m/z = 69 (CF₃⁺) prevails. CF₃CF₂CF₂⁺, CF₂Cl⁺, CF₃CF₂CF₂Cl⁺, Cl⁺, CF₃⁺, and CF₂CF₂⁺ fragments can also be observed in the spectra. In special CF₃CF₂CF₂Cl⁺, and also CF₂Cl⁺, need of special rearrangement processes to be formed. At 21.0 eV the fragment C₃F₃O⁺ can also be detected.

Energy Profile. The dissociation processes due to the cleavage of only one covalent bond of the molecular ion were also computed. Both the possible fragments and the molecular ion were fully optimized (B3LYP/6-311+g(d), B3LYP/cc-pVTZ), and MP2/cc-pVTZ) and their energies were used to compute the respective dissociation energies and the pathways of the different fragmentation processes (Table 2).

According to Table 2, the generation of the C(O)Cl⁺ ion is energetically preferred in comparison with the formation of the radical C(O)Cl[•]. Even though both ions (C(O)Cl⁺ and CF₃CF₂CF₂⁺) are generated at 13.0 eV and at higher energies, C(O)Cl⁺ prevails over CF₃CF₂CF₂⁺, in agreement with the computed values. Probably, an α rupture described in Scheme 1 originates these fragments:

As mentioned above, the $CF_3CF_2CF_2CO^+$ ion is the heaviest fragment observed in the low energy PEPICO spectra. This fact, together with the detection of Cl^+ ion only at energies higher than 19.0 eV, is well reproduced by the quantum chemical calculations listed in Table 2. This RC(O)-Clcleavage can be explained in terms of another α rupture.

It can be seen from Figure 6 that the trifluoromethyl ion becomes one of the most abundant fragments at energies higher than 17.0 eV. It can be observed, as well, that the formation of the $CF_2CF_2C(O)Cl^+$ ion cannot be detected at any of the mentioned energies (13.0-21.0 eV). The formation of CF_3^+ and the lack of evidence for the formation of $CF_2CF_2C(O)Cl^+$ is not consistent with the theoretical data (Table 2), which does propose the formation of CF_2CF_2C -(O)Cl⁺ favored with respect to the formation of CF_3^+ . A plausible explanation for this phenomenon is that the CF_3^+ ion might be generated from a second dissociation process involving, for instance, the species $CF_3CF_2CF_2C(O)^+$. A similar fact has been observed by Yao Li et al. in the case of the photofragmentation of CF₃OC(O)OOC(O)OCF₃.³⁸ Moreover, another origin of the trifluoromethyl ion could also be caused by the dissociation of $CF_2CF_2C(O)Cl^+$ followed by the corresponding rearrangement, similarly to the reported generation of the HCl⁺ ion in the case of $ClC(O)SCH_{3}^{3}$

lonization in the Inner Shell Regions. The TGM beamline was also used in the 100.0–300.0 eV energy range. PEPICO spectra were measured in the regions near 180.0, 190.0, 201.0, 204.0, 206.0, 211.0, 237.0, and 287.0 eV. At 180.0, 190.0, and 237.0 eV no particular process is expected to take place, while at 201.0, 204.0, and 206.0 eV, different resonance transitions from the Cl 2p might occur (see TIY section). Moreover, at 211.0 eV the Cl 2p ionization takes place. Finally, at 295.0 eV resonance transitions involving C orbitals can be assigned. In addition, in the SGM beamline further PEPICO spectra were measured, specifically at 310.0 eV (energy related to transitions from C 1s); 528.5, 530.0, 532.0, and 547 eV (O 1s); 697.0, 705.0, 725.0, and 750.0 eV (F 1s). Both double- and single-charged positive fragments are expected to be detected at these energies since the system with the hole in the inner electron

		ΔE (eV)	
fragmentation	B3LYP/6-311+g(d)	B3LYP/cc-pVTZ	MP2/cc-pVTZ
$CF_3CF_2CF_2C(O)Cl^{\bullet+} \rightarrow CF_3CF_2CF_2^{\bullet} + C(O)Cl^+$	-0.11	0.11	-0.28
$CF_3CF_2CF_2C(O)Cl^{\bullet_+} \rightarrow CF_3CF_2CF_2^+ + C(O)Cl^{\bullet}$	0.57	0.51	0.55
$CF_3CF_2CF_2C(O)Cl^{\bullet+} \rightarrow CF_3CF_2CF_2C(O)^{\bullet} + Cl^+$	6.78	7.17	7.01
$CF_3CF_2CF_2C(O)Cl^{\bullet+} \rightarrow CF_3CF_2CF_2C(O)^+ + Cl^{\bullet}$	0.39	0.53	0.09
$CF_3CF_2CF_2C(O)Cl^{\bullet+} \rightarrow CF_3^{\bullet} + CF_2CF_2C(O)Cl^+$	0.43	0.53	0.44
$CF_3CF_2CF_2C(O)Cl^{\bullet+} \rightarrow CF_3^+ + CF_2CF_2C(O)Cl^{\bullet}$	0.99	1.08	1.02

Scheme 1. Proposed Formation Mechanism of C(O)Cl⁺



Scheme 2. Proposed Formation Mechanism of CF₃CF₂CF₂CO⁺



shell can evolve and relax by Auger electrons emission, leading to double-charged species.

Figure 6 exhibits the PEPICO spectra taken at both the TGM (inner shell electronic region) and SGM beamlines at the

LNLS facilities. Table 3 lists the branching ratios (%) for fragment ions detected in the PEPICO spectra from 180.0 to 750.0 eV. As can be seen, the atomization process (generation of C^+ , O^+ , F^+ , and Cl^+) becomes predominant over other fragmentations at energies higher than 310 eV. Small fragments, as CF⁺ and CO⁺, also become important at these energies. As expected, the intensity of all ionic fragments with $m/z \ge 60$ $CF_3CF_2CF_2^+$, $CF_2CF_2CI^+$, among others) decrease with increasing energies favoring atomization processes. Derived relative intensities corresponding to different processes involving the formation of C_2F^+ , C_3F^+ , C_2F^+ , C_4F^+ , $C_3F_2^+$, and $C_3F_3^+$ are variable due to the origin of these fragments: all these ions may be generated and added from different fragmentation mechanisms. The natural isotopic contribution of both ³⁵Cl and ³⁷Cl are helpful over the entire energy range to detect not only the atomic ionic fragments, but also the fragments containing a Cl atom as $C(O)Cl^+$, CF_2Cl^+ , $CF_2CF_2CF_2Cl^+$, and $CF_2CF_2CF_2C(O)Cl^+$.



Figure 6. PEPICO spectra of CF₃CF₂CF₂C(O)Cl taken at the TGM (left) and at the SGM beamline (right).

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ion	ш	ы	180.0 eV	190.0 eV	201.0 eV	204.0 eV	206.0 eV	211.0 eV	237.0 eV	297.0 eV	310.0 eV	528.5 eV	532.0 eV	547.0 eV	697.0 eV	705.0 eV	725.0 eV	750.0 eV
C ⁺	12	г	1.7	1.4	1.5	1.5	1.6	1.6	1.7	2.0	4.3	6.6	8.5	7.1	10.5	6.7	8.2	8.8
O ⁺	16	г	1.2	1.0	0.9	1.1	1.1	1.3	1.5	1.1	2.5	3.3	4.7	3.2	4.6	3.1	3.7	4.3
Cl ²⁺	17.5	7						0.5	0.5	0.5	0.0	0.5	0.6	0.9	0.5	0.5	0.4	0.5
\mathbf{F}^+	19	г	1.5	2.2	3.0	2.6	1.8	1.6	1.9	2.0	5.7	9.0	12.8	9.8	16.8	10.6	11.9	14.0
COCl ³⁺	21	б	2.2	0.9	0.7	0.9	1.5	2.4	2.1	2.8	3.3	0.9	3.5	1.6	1.4	1.7	2.1	3.1
C_2^+	24	-	0.6	1.4	1.3	1.6	1.0	0.7	1.4	1.0	2.0	2.7	1.9	2.3	2.5	2.4	1.9	2.4
$\operatorname{CF}_2^{2^+}$	25	7						0.8	0.3	0.7	0.0	0.0	2.7	2.0	1.7	1.3	2.4	2.3
CO ⁺	28	г	1.7	1.6	1.7	2.1	1.6	2.0	2.2	2.3	4.3	4.2	5.3	4.8	4.8	4.5	4.6	4.3
CF^+	31	1	13.5	13.7	13.4	13.9	14.8	13.9	14.8	15.9	22.3	21.6	19.8	22.1	24.4	24.7	24.0	21.5
CI ⁺	35/37	-	8.6	8.6	9.7	10.2	9.7	12.3	13.7	12.7	16.3	14.6	17.4	16.1	12.6	14.7	15.6	15.9
CFC^+	43	-	1.1	0.9	0.7	1.2	0.7	1.2	1.2	0.8	2.2	1.5	1.2	1.3	1.3	1.8	1.6	2.0
FCO ⁺ /CCl ⁺	47	-	1.3	1.3	0.8	1.1	0.8	1.2	1.3	1.1	2.3	1.6	1.2	1.6	1.2	1.5	1.4	2.1
$\operatorname{CF}_{2}^{+}$	50	г	7.3	7.2	7.3	7.4	7.7	8.2	8.3	8.6	9.6	8.5	7.2	8.6	6.3	8.4	8.2	6.8
C_3F^+	55	Г	0.9	0.7	0.5	0.6	0.2	0.4	0.4	0.5	1.6	1.1	0.9	1.0	1.0	1.4	1.2	1.1
$C_2F_2^+$	62	Г	1.3	1.3	1.3	1.2	0.8	1.2	0.8	0.7	1.4	1.3	0.8	1.2	1.1	1.7	1.5	1.2
COCI ⁺	63/65	-	11.2	10.9	9.8	6.6	10.1	7.2	6.6	6.7	3.8	3.0	1.6	2.4	1.9	2.6	2.7	1.5
C_4F^+	67	-	0.4	0.4	0.3	0.3	0.2	0.2										
CF_{3}^{+}	69	г	17.4	19.2	19.9	19.9	21.1	17.4	20.1	19.8	11.4	11.1	6.7	8.8	4.8	7.5	5.7	5.8
CIC_3^+/FC_3O^+	71	-	1.0	1.1	0.8	0.3	1.0	0.2	0.3	0.6	1.8	0.5	0.2	0.9	0.6	0.9	0.1	1.0
$C_3F_2^+$	74	1	1.5	1.0	0.9	0.9	0.3	0.5	0.8	0.8	0.5	0.5	0.2	0.3	0.4	0.4	0.2	0.2
$\rm CF_2 CF_2 CF_2^{2+}$	7S	7	0.1	0.3	0.2	0.3	1.0	1.1	0.7	0.5	0.3	0.4	0.3	0.5	0.1	0.3	0.3	0.1
CF_2CO^+	78	-	0.9	0.7	0.8	0.6	0.3	1.1	0.5	0.5	0.5	0.7	0.2	0.3	0.2	0.7	0.3	0.3
$C_2F_3^+$	81	1	1.3	1.0	1.1	0.9	0.9	1.1	1.1	0.9	0.9	0.9	0.5	0.6	0.5	0.9	0.8	0.5
CF_2CI^+	85/87	1	3.9	3.7	3.2	3.0	3.0	2.2	1.5	1.6								
$C_3F_3^+$	93	1	1.2	0.8	0.9	0.7	0.8	0.6	0.4	0.5	0.8	0.7	0.2	0.4	0.5	0.8		
CF_2CCI^+	66/26	1	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.1								
$CF_2CF_2^+$	100	1	6.3	6.2	7.4	6.7	6.8	8.0	6.7	7.0	3.2	3.5	1.4	2.1	0.8	1.8	1.4	1.3
$\rm C_3F_3O^+$	109	1	1.3	1.0	1.2	0.9	1.0	0.8	0.5	0.6								
$CF_3CF_2^+$	119	1	2.7	2.6	2.6	2.5	2.4	2.2	1.6	1.6	0.5	1.0	0.2	0.5				
$C_3F_5^+$	131	г	0.3	0.2	0.3	0.2	0.5	0.3	0.1	0.1								
$CF_2CF_2CI^+$	135/137	1	0.2	0.1	0.1													
$CF_3CF_2CF_2^+$	169	1	2.6	2.8	2.7	2.9	2.6	4.6	4.1	3.5	0.4	0.9	0.1	0.2				
$CF_2CF_2CF_2CI^+$	185/187	1	3.4	4.0	3.3	3.3	3.1	2.2	1.8	1.9								
$CF_2CF_2CF_2CO^+$	197	1	1.2	1.5	1.3	1.2	1.2	0.9	0.8	0.6								
$CF_2CF_2CF_2CO)$ CI^+	213/215	1	0.2	0.2	0.2	0.1												

matrix matrix<	Kinetic Ent	ırgy R	eales	e (eV) o	of the Mo	st Releva	nt Ionic]	Fragment	is in the	PEPICO	Spectra	of CF ₃ CF	¹ ₂ CF ₂ C(C)CI					
Mot 1 800 eV 900 eV 2010 eV 20										kir	netic energy	release (eV	(
38 1 119 121 107 113 033		ш	ы	180.0 eV	190.0 eV	201.0 eV	204.0 eV	206.0 eV	211.0 eV	237.0 eV	297.0 eV	310.0 eV	528.5 eV	532.0 eV	547.0 eV	697.0 eV	705.0 eV	725.0 eV	750.0 eV
31 1 0.46 0.43 0.43 0.43 0.43 0.43 0.43 0.55 0.66 0.71 0.76 0.86 0.71 0.80 0.73		28	-	1.19	1.21	1.07	1.15	0.82	1.75	1.86	2.06	1.50	1.48	1.37	1.51	1.07	1.43	1.36	1.38
43 1 0.59 0.60 0.62 0.51 0.59 0.79 0.71 0.83 0.79 0.77 0.83 0.79 0.77 0.83 0.73		31	1	0.46	0.45	0.43	0.43	0.43	0.55	0.65	0.66	0.71	0.76	0.86	0.82	0.71	0.80	0.79	0.88
30 1 0.41 0.40 0.39 0.39 0.33 0.32 0.83 0.84 0.73 0.84 0.73 0.85		43	1	0.59	09.0	0.62	0.51	0.59	0.79	0.91	0.72	0.69	0.78	0.70	0.82	0.53	0.79	0.57	0.85
55 1 145 0.53 0.58 0.37 0.23 0.23 0.23 0.23 0.23 0.23 0.34 0.33 0.37 0.35 <th0.35< th=""> 0.35 0.35<!--</td--><td></td><td>50</td><td>1</td><td>0.41</td><td>0.40</td><td>0.39</td><td>0.39</td><td>0.38</td><td>0.72</td><td>0.92</td><td>0.83</td><td>0.83</td><td>0.80</td><td>0.82</td><td>0.84</td><td>0.72</td><td>0.85</td><td>0.85</td><td>06.0</td></th0.35<>		50	1	0.41	0.40	0.39	0.39	0.38	0.72	0.92	0.83	0.83	0.80	0.82	0.84	0.72	0.85	0.85	06.0
62 1 0.44 0.55 0.63 0.37 0.27 0.27 0.23 0.23 0.54 0.73 0.83 0.79 0.65		55	П	1.45	0.53	0.58	0.38	0.28	0.73	0.65	0.52	1.29	1.30	1.44	1.20	0.86	1.35	1.37	1.32
		62	П	0.44	0.55	0.63	0.37	0.27	0.49	0.25	0.28	0.73	0.54	0.73	0.83	0.79	0.65	0.65	0.89
		63	п	0.09	0.08	0.08	0.08	0.10	0.10	0.10	0.10	0.30	0.28	0.45	0.49	0.59	0.56	0.63	0.55
		65	п	0.08	0.08	0.08	0.07	0.08	0.10	0.09	0.08	0.43	0.51	0.87	06.0	1.05	0.94	0.93	1.51
		67	1	0.11	0.10	0.12	0.08	0.06	0.12										
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		69	П	0.10	0.11	0.12	0.12	0.12	0.16	0.25	0.20	0.63	0.50	0.68	0.72	0.63	0.76	0.67	0.79
81 1 042 047 047 047 043 033 072 081 057 064 0.55 063 0.58 0.63 0.65 0.58 0.63 0.65 0.58 0.64 0.55 0.58 0.63 0.55 0.58 0.56 0.55 0.58 0.56 0.55 0.58 0.56 0.55 0.58 0.50 0.55 0.58 0.50 0.55 0.58 0.50 0.55 0.58 0.50 0.55 0.59 0.5 0.51 0.12 0.13 0.10 0.13 0.10 0.13 0.10 0.13 0.12 0.13 0.10 0.13 0.12 0.13 0.10 0.13 0.12 0.13 0.15 0.13 0.15 0.13 0.16 0.17 0.16 0.17 0.16 0.17 0.16 0.17 0.16 0.13 0.11 0.13 0.12 0.13 0.10 0.13 0.10 0.13 0.10 0.13 0.16 0.17 0.16 0.14 0.12 0.13 0.15 0.16 0.16 0.17 0.16 0.14 0.12 0.13 0.15 0.16 0.16 0.17 0.16 0.14 0.12 0.12 0.16 0.16 0.14 0.12 0.13 0.15 0.10 0.15 0.16 0.16 0.16 0.17 0.16 0.16 0.15 0.16 0.16 0.16 0.16 0.16 0.16 0.16 0.16		74	П	0.92	0.31	0.44	0.33	0.18	0.36	0.47	0.54	0.23	0.31	0.30	0.27	0.45	0.48	0.43	0.53
87 1 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0		81	1	0.42	0.47	0.47	0.45	0.33	0.72	0.81	0.57	0.64	0.55	0.63	0.65	0.58	09.0	0.65	0.49
		85	1	0.10	0.10	0.10	0.11	0.08	0.11	0.11	0.09								
		87	1	0.17	0.12	0.13	0.13	0.10	0.13	0.10	0.13								
		93	1	0.41	0.27	0.28	0.23	0.36	0.33	0.35	0.27	0.71	0.45	0.21	1.01	2.38	0.52		
$ \begin{array}{{ccccccccccccccccccccccccccccccccccc$		109	1	0.13	0.14	0.13	0.12	0.13	0.16	0.17	0.16								
		119	П	0.07	0.07	0.07	0.07	0.07	0.09	0.10	0.08	0.18	0.39	0.17	1.05				
		131	п	0.10	0.18	0.17	0.05	0.40	0.21	0.27	0.16								
		135	п	0.07	0.05	0.07													
$ \begin{tabular}{cccccccccccccccccccccccccccccccccccc$		169	1	0.05			0.05	0.05	0.13	0.15	0.10	0.15	0.22	0.16	0.16				
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	+ .	185	1	0.07	0.07	0.07	0.06	0.07	0.07	0.08	0.07								
$ \begin{tabular}{cccccccccccccccccccccccccccccccccccc$	+	187	1	0.10	0.10	0.11	0.11	0.08	0.10	0.13	0.08								
$)^{35}$ Cl ⁺ 213 1 0.06 0.06 0.06 0.06		197	1	0.05	0.04	0.04	0.05	0.05	0.05	0.05	0.05								
) ³⁵ Cl ⁺	213	1	0.06	0.06	0.06													

Due to the similarity between all PEPICO spectra (taking into account all but the logical differences expected from the atomization processes) no specific fragmentation could be identified as was reported by Habenicht and co-workers,²⁹ who described bond selective fragmentation processes in CF_3CH_3 , where the formation of CF_3^+ , C^+ , and CFH_2^+ presents a clear dependence on the excitation site.

The average Kinetic Energy Release (KER) by each of the most relevant ionic fragments was calculated from the (180.0 to 750.0 eV) PEPICO spectra (Table 4). Kinetic energy releases in unimolecular fragmentations provide information concerning reaction energetics and dynamics of single- and multiple-charged ions.⁴⁰ As can be seen from Table 4 the contribution from the heaviest fragments is close to the thermal energy values (0.05 eV).⁴¹

According to relevant data reported in the literature the generation of an ionic fragment with KER values ≤ 0.20 eV implies photofragmentation processes from single-charged ions and, thus, the existence of other nondetected neutral fragments.⁴² Thus, the expected mechanisms for the generation of the two heaviest ionic fragments detected in the spectra are detailed below (Scheme 3). It should be observed that, in

Scheme 3. Formation Mechanisms of Ionic Fragment with KER Values Close to Thermal Values

$CF_3CF_2CF_2C(O)Cl^+ \rightarrow F + CF_2CF_2CF_2COCl^+$	$\text{KER} \approx 0.05 \text{ eV}$
$CF_3CF_2CF_2C(O)Cl^+ \rightarrow F + Cl + CF_2CF_2CF_2CO^+$	$KER \approx 0.05 \text{ eV}$

general trends, the KER values lower than 0.20 eV (m/z > 85) remain constant over the entire incident photon energy for the cationic fragments; thus, the corresponding pathways might be independent of the incident energy.

The two proposed mechanisms agree with the fact that the fragments detected in the PEPICO spectra are the lightest ions generated in the event. Thus, the detection of these fragments $(CF_2CF_2CF_2C(O)Cl^+ \text{ and } CF_2CF_2CF_2C(O)^+)$ in the spectra exclude the generation of other lightest ion(s), as F^+ and/or Cl^+ .

The KER measurements are indicative of the fate of the processes involving CF_3^+ ion. This species presents a signal with a progressive widening as a function of the synchrotron incident energy. Fragments with KER values close to the thermal energy can be observed only in the PEPICO spectra collected below 297.0 eV. More energetic processes imply an appreciable signal widening and a concomitant higher KER value originated by Coulombic explosions caused by double-charged species.

Scheme 4. Formation Mechanism of CF₃⁺ at Energies below 297.0 eV

 $CF_3CF_2CF_2C(O)Cl^+ \rightarrow CF_3^+ + CF_2CF_2COCl KER \le 0.20 \text{ eV}$

On the other hand, from 310.0 eV the increment of the KER values denotes photofragmentation processes implying the generation of different energetic ions in coincidence with CF_3^+ . This topic will be also discussed in the PEPIPICO section.

PEPIPICO Spectra. Three Photoelectron-Photoion-Photoion-Coincidence spectra have been measured at different incident photon energies (528.5, 705.0, and 750.0 eV). Due to a remarkable similarity observed among them, only the 705.0 eV spectrum will be described in detail, and when applicable, discrepancies will be marked.

Eland⁴³ and Simon et al.⁴⁴ studied the relationship between the shape and slope of the double coincidence islands which originate the PEPIPICO spectra and the fragmentation mechanisms. Following these relationships, we were able to elucidate the corresponding mechanisms originating each PEPIPICO island. The experimental slopes and the mechanisms whose theoretical slopes best fit the experimental values are listed in Table 5.

Table 5. Experimental Slopes Found in the PEPIPICO of $CF_3CF_2CF_2C(O)Cl$ Spectrum Taken at 705.0 eV Corresponding to Different Coincidences^{*a*}

coincidences	experimental slope	theoretical slope	proposed mechanism
C^+/CF^+	-1.23	-1.09	SDC
O^+/CF^+	-0.68	-0.72	SDC
E^{+}/C^{+}	0.27	-0.24	SDADCS
F/C_2	-0.27	-0.29	SDADCS
F^+/CF^+	-0.62	-0.62	SDADCS
$\rm CO^+/\rm CF^+$	-0.67	-0.72	SDADCS
CF^+/Cl^+	-2.11	-1.90	SDADCS
CF^+/CF_2^+	-1.61	-1.69	SDC
$CF^+/COCl^+$	-1.82	-1.61	SDADCS
CF^+/CF_3^+	-2.13	-2.11	SDC
$\mathrm{Cl}^{+}/\mathrm{CF}_{2}^{+}$	-0.56	-0.53	SDC
Cl^+/CF_3^+	-2.01	-1.87	SDC

^{*a*}The proposed mechanisms deduced from the agreement of the theoretical slopes with the experimental values are also listed. SDC: Secondary decay in competition. SDADCS: Secondary decay after a deferred charge separation.

The coincidences between atomic ions $(C^+/O^+/F^+/Cl^+)$ and the light CF^+ fragment reflect the importance of the atomization processes. Several dissociation events might be responsible for those coincidences; thus, the interpretation of the corresponding experimental slope is useful but not unique. Therefore, different mechanisms have been proposed for those fragmentations.

Figure 7 illustrates two coincidence islands originated by the two types of fragmentation mechanisms that have been found along this work. For the first coincidence (CF^+/Cl^+) a secondary decay after a deferred charge separation mechanism has been proposed; in this case, both $^{35}Cl^+$ and $^{37}Cl^+$ isotopic contribution islands can be clearly observed. A deferred charge separation mechanism is deduced from the information on the second island $(CF^+/CF_3^+$ coincidence). The PEPIPICO islands corresponding to the rest of the coincidences described in Table 5 are depicted in Figure S5.

As can be inferred from Table 5, two different islands present contributions from the CF_3^+ ion at this energy (Cl^+/CF_3^+) and CF^+/CF_3^+). Both coincidences are originated from a four-body dissociation mechanism (secondary decay in competition). Scheme 5 illustrates both fragmentation mechanisms. At 528.5 eV, the CF^+/CF_3^+ coincidence presents a different slope value, indicating the energy dependence of the dissociation pathway. In particular, at 705.0 eV a C–C cleavage, where both fragments retain a positive charge, was proposed as a first step, while at 528.5 eV, the C–C cleavage process might be different, resulting in the formation of a double-charged and a neutral fragment (see Scheme 6).

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Figure 7. $CF^{+/35}Cl^{+}$ and $CF^{+/37}Cl^{+}$ (left) and CF^{+}/CF_{3}^{+} (right) coincidence islands in the PEPIPICO spectrum of $CF_{3}CF_{2}CF_{2}C(O)Cl$ taken at 705.0 eV.

Scheme 5. Proposed Fragmentation Mechanism for the Coincidences Cl^+/CF_3^+ and CF^+/CF_3^+ at 705.0 eV

Cl ⁺ /CF ₃ ⁺	$\begin{array}{c} CF_3CF_2CF_2C(O)Cl^{2+} \rightarrow CF_3CF_2^+ + CF_2C(O)Cl^+ \\ CF_3CF_2^+ \rightarrow CF_3^+ + CF_2 \end{array}$
	$CF_2COCl^+ \rightarrow Cl^+ + CF_2C(O)$
CF ⁺ /CF ⁺	$CF_3CF_2CF_2C(O)Cl^2 \rightarrow CF_3CF_2^+ + CF_2C(O)Cl^+$ $CF_2C(O)Cl^+ \rightarrow CF_2^+ + nf_2^+$
CF /CF3	$CF_{3}CF_{2}^{+} \rightarrow CF_{3}^{+} + CF_{2}$

Scheme 6. Proposed Fragmentation Mechanism for the Double Coincidence CF^+/CF_3^+ at 528.5 eV

	$CF_3CF_2CF_2C(O)Cl^{2+} \rightarrow CF_3CF_2^{2+} + CF_2C(O)Cl$
CF^+/CF_3^+	$CF_3CF_2^{2+} \rightarrow CF_3^+ + CF_2^+$
	$CF_2^+ \rightarrow CF^+ + F$

Two other coincidences $(CF^+/C(O)Cl^+ \text{ and } Cl^+/CF_2^+)$ are worth mentioning. The experimental slope of the first coincidence together with the parallel shape of the island denotes a secondary decay after a deferred charge separation mechanism (Scheme 7).

Scheme 7. Proposed Fragmentation Mechanism for the Double Coincidence between CF^+ and $C(O)Cl^+$

CF ⁺ /C(O)Cl ⁺	$\begin{array}{c} CF_3CF_2CF_2C(O)Cl^{2+} \rightarrow CF_3CF_2 + CF_2C(O)Cl^{2+} \\ CF_2C(O)Cl^{2+} \rightarrow CF_2^+ + C(O)Cl^+ \end{array}$
	$CF_2^+ \rightarrow CF^+ + F$

The coincidence between Cl^+ and CF_2^+ can be explained as a secondary decay in competition mechanism as described in Scheme 8.

CONCLUSIONS

The impact of monochromatic variable synchrotron radiation on an effusive molecular beam of $CF_3CF_2CF_2C(O)Cl$ was studied in the 13.0–720.0 eV energy range. Dissociation mechanisms in the outermost energetic range were elucidated

Scheme 8. Proposed Fragmentation Mechanism for the Coincidence between Cl^+ and CF_2^+

Cl ⁺ /CF ₂ ⁺	$\begin{array}{c} CF_3CF_2CF_2C(O)Cl^{2+} \rightarrow CF_3CF_2CF_2^+ + C(O)Cl^+ \\ CF_3CF_2CF_2^+ \rightarrow CF_2^+ + CF_3CF_2 \\ C(O)Cl^+ \rightarrow CO + Cl^+ \end{array}$

by means of PEPICO spectra and quantum chemical calculations.

Resonance transitions which take place below the main ionization potentials (Cl 2p, C 1s, O 1s, and F 1s) were detected by means of TIY spectra. Moreover, each transition was studied computationally, especially at the C 1s transition energy region. PEPICO and PEPIPICO spectra were also measured in these regions; the analysis of the results obtained from both coincidence techniques allowed resolution of the corresponding fragmentation mechanisms. Many of the mechanisms proposed for the evolution of the title species under synchrotron conditions point to the formation of usual radicals and species, like Cl, of relevant importance in the photochemistry of the atmosphere.¹ Thus, the preeminence of one photochemical process or another is dependent on the altitude considered, that is, how the radiation energy originating in the sun impacts the molecule independent of its location.

ASSOCIATED CONTENT

Supporting Information

Tables S1, S2, and S3 present the assignment of the normal modes of vibration of the $CF_3CF_2CF_2C(O)Cl$ molecule, the 69 lowest energy molecular orbitals corresponding to the gauche and anti $CF_3CF_2CF_2C(O)Cl$ conformations calculated with the NBO BP86/6-311+g(d) approximation and their symmetry and the theoretical electronic difference between the initial and final orbital for the gauche conformer of $CF_3CF_2CF_2C(O)Cl$ and the corresponding experimental values, respectively. Figure S1 presents the calculated (MP2/cc-pVTZ) infrared spectra for both $CF_3CF_2CF_2C(O)Cl$ conformers and the sum of those spectra compared with the experimental one. The deconvolution of the TIY spectrum taken around the Cl 2p and C 1s ionization edges are shown in Figures S2 and S3, respectively. Linear correlation between the experimental transition energies and those predicted by the approximation NBO BP86/6-311+g(d) for the TIY C 1s region is depicted in Figure S4. Finally, PEPIPICO islands corresponding to double coincidences described in Table 5 (with exception of CF⁺/Cl⁺ and CF^+/CF_3^+ shown in Figure 7) are illustrated in Figure S5. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The synchrotron measurements described in this work were performed in the Laboratório Nacional de Luz Síncrotron (LNLS) under proposals TGM-12776, TGM-15163, and SGM-15206; thus, we want to express our deep gratitude to this institution, especially to all TGM and SGM beamline stuff for their assistance and collaboration during the measurements. Finally we would like to genuinely thank the Facultad de Ciencias Exactas, Universidad Nacional de La Plata, República Argentina, Consejo Nacional de Investigaciones Científicas Y Técnicas (CONICET) and Agencia Nacional de Promoción Científica y Tecnológica ANPCyT for the financial support. R.L.C.F. is a reaserch fellow of Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brazil.

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