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Conformational Analysis of Trifluoroacetyl Triflate, $CF_3C(O)OSO_2CF_3$: Experimental Vibrational and DFT Investigation

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Abstract: The conformations of trifluoroacetyl triflate, $CF_3C(O)OSO_2CF_3$, were investigated through vibrational experimental methods (gas-phase FTIR, liquid-phase Raman, and Ar-matrix FTIR spectroscopy) and Density Functional Theory (DFT) calculations. A potential energy surface was computed using the B3P86 /6-31+g(d) approximation as a function of the dihedral angles $\tau1$ = CC–OS and $\tau2$ = CO–SC. The surface reveals three minima, which were further optimized using the B3LYP method with various basis sets (6-31++G(d), 6-311++G(d), tzvp and cc-pvtz). The global minimum corresponds to a *syn-anti* conformer (the C=O double bound *syn* with respect the O–S single bond and the C–O single bond *anti* with respect to de S–C single bond). The other two minima represent enantiomeric *syn-gauche* forms. The Ar-matrix FTIR spectrum exhibited clear evidence of the presence of two conformers. Furthermore, the randomization process observed following broad-band UV-visible irradiation facilitated the identification of the IR absorption of each conformer. Based on the Ar-matrix FTIR experiments, the vapour phase of trifluoroacetyl triflate at room temperatures was composed of approximately 60-70% of the *syn-anti* conformer and 30-40% of the *syn-gauche* form.

Keywords: conformations; matrix-FTIR; gas-phase FTIR; Raman; DFT

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1. Introduction

Trifluoroacetyl triflate ($CF_3C(O)OSO_2CF_3$, TFAT) is a convenient reagent for trifluoroacetylation reactions in organic synthesis [1]. Its efficacy in trifluoroacylation reaction with various nucleophilic molecules, including alcohols [2], amines [2], aromatic activated substrates [3], covalent fluorides [4] and halides [5], between others, has been reported. However, TFAT's high reactivity imposes limitations on the choice of solvents for these reactions, with benzene, saturated hydrocarbons, and common halogenates solvents being among the few compatible options [1]. Despite its widespread use as a reagent and its availability from commercial sources, the structural and vibrational properties of trifluoroacetyl triflate remain unexplored, to the best of our knowledge.

Our group has successfully prepared molecules with the general formula $XC(O)OSO_2CF_3$, where X = F [6] or Cl [7,8], by reacting halocarbonylsulphenyl chloride, XC(O)SCl, with silver triflate salt, $AgSO_3CF_3$. These molecules exhibit interesting conformational equilibrium. In the gas phase, $FC(O)OSO_2CF_3$ exists as a mixture of *anti* (the C–O single bond *anti* with respect to the S–C single bond) and *gauche* (the C–O doble bond *gauche* with respect to the S–C single bond) forms. In both conformers the C=O doble bond is *synperiplanar* with respect to the O-S single bond. Gas Electron Diffraction (GED) measurements revealed that the *syn-anti* rotamer predominates at ambient temperature, comprising 67(8)% of the gas-phase composition, whereas matrix-FTIR estimated its presence at 59(5)% [6]. Similar results were obtained for $ClC(O)OSO_2CF_3$, with the *syn-anti* conformer constituting 66(8)% according to matrix-FTIR measurements [7] and 67(11) % based on GED experiments [8]. Notably, $FC(O)OSO_2CF_3$ and $ClC(O)OSO_2CF_3$ are unique in exhibiting prevailing *anti* conformation around the S–O single bond, unlike other $XOSO_2CF_3$ species, which typically adopt a *gauche* conformation (see Ref. 6 and 8 and references cited therein). In this sense, a close and well-known example is the $ClC(O)OSO_2Cl$ molecule, where the *gauche* conformation predominates over the anti [9].

Matrix IR spectroscopy emerged as a valuable technique for investigated conformational equilibrium. Under such conditions, IR absorptions are narrowed compared to those observed in gas and condensed phases. This phenomenon primarily arises from the inhibition of rotation and intermolecular interactions in the isolated environment. Consequently, this method enables the discernment of bands with small wavenumber differences, particularly useful in distinguishing spectral features between conformers.

The experimental setup employed in matrix formation ensures the preservation of the conformational composition existing at the temperature of the mixture prior to deposition. However, irradiating a compound isolated within a matrix can induce interconversion between conformers, leading to a randomization process. This results in a final state where the proportion of each conformer approximates 50%. This phenomenon was observed in FC(O)SBr isolated in matrices [10]. It was explained by a transition to an excited state, wherein the minimum in the potential curve as a function of the torsion angle coincides with the maximum of the energy surface in the ground state. Consequently, this leads to a decay with equal probability to the two conformers. This process has been observed for several other molecules (see, for example, Ref. 11–13, and references cited therein). This behaviour constitutes a very important tool for a clear assignment of the IR absorptions to each conformer.

In this work, we explored two distinct routes for synthesizing trifluoroacetyl triflate. The first route involved the reaction of trifluoroacetyl chloride with silver triflate, while the second route by the reaction between trifluoroacetic and triflic acid. For the latter method, which has been reported in several works in the literature [2,14–16]. we sought to optimize the conditions to yield a highly pure sample. We conducted a comprehensive analysis using various spectroscopic techniques. Specifically, we measured the FTIR spectra of the vapor phase, the Raman spectrum of the liquid phase, and the FTIR spectra of the sample isolated in solid argon immediately after deposition and at different intervals following broad-band UV-visible irradiation. To provide theoretical insights, we employed Density Functional Theory (DFT) methods to calculate a potential energy surface. Subsequently, we optimized the minima over this surface. The assignment of vibrational spectra and the experimental estimation of the proportion of conformers in the vapour phase at ambient temperature were carried out based on the Ar-matrix FTIR spectra before and after irradiation, aided by predictions from theoretical calculations.

2. Materials and Methods

Chemicals. Trifluoroacetic acid ($CF_3C(O)OH$, Carlo Erba), phosphorus pentachloride (PCl_5, Sigma Aldrich), silver triflate ($AgSO_3CF_3$, Fluka), and triflic acid ($HOSO_2CF_3$, Sigma Aldrich) were utilised without further purification. Ar (AGA) was purified by passing it through two U-traps. The first trap contained thermally activated Molecular Sieve and the second was cooled to approximately –90 °C with an acetone-bath to retain potential traces of impurities, primarily H_2O and CO_2.

The FTIR spectra were acquired using a Nexus Nicolet instrument, equipped with either a cryogenic MCTB (for the range 4000–400 cm^{-1}) or a DTGS detector (for the range 600–180 cm^{-1}). For vapour-phase IR studies at ambient temperature, a 10 cm gas cell fitted with CsI windows was employed.

Raman spectra were obtained using a Horiba-Jobin-Yvon T64000 Raman spectrometer equipped with a confocal microscope and CCD detection system. Excitation was achieved using a 514.5 nm excitation wavelength from an Ar multiline laser. Wavenumbers were calibrated using the 459 cm^{-1} band of CCl_4. The net liquid sample was contained within a sealed capillary for ambient temperature measurements.

A 1 L vacuum flask was filled with TFAT and Ar in a proportion 1:1000 using standard manometric techniques. The gas mixture was deposited onto a CsI window, cooled to approximately 15 K using a Displex closed-cycle refrigerator (SHI-APD Cryogenics, model DE-202) employing the pulse deposition technique. Matrix-isolated FTIR spectra were recorded in the 4000–400 cm^{-1} range using a Thermo Nicolet 6700 instrument equipped with a DTGS detector. The matrices were exposed to broad-band UV-visible radiation ($200 \leq \lambda \leq 800$ nm) emitted by a Spectra-Physics Hg–Xe arc lamp operating at 1000 W. To mitigate heating effects, the lamp output was restricted by a water filter to absorb infrared radiation.

All of the quantum chemical calculations were conducted using the Gaussian 03 program system [17]. A relaxed potential energy surface was computed using the B3P86 [18] functional in conjunction with the 6-31+G(d) basis set. Geometry optimizations of the energy minima employing the B3LYP [19,20] method and various basis set functions were sought using standard gradient techniques, allowing for simultaneous relaxation of all geometrical parameters. Subsequently these optimised structures were characterised by their vibrational properties. Natural Bond Orbital (NBO) analysis was performed for each structure and the orbital stabilization energies were calculated [21].

3. Results and Discussion

3.1. Synthesis of Trifluoroacetyl Triflate (TFAT)

Trifluoroacetyl triflate was synthetised via the reaction between trifluoroacetic acid and triflic acid, as illustrated in Scheme 1. Phosphorus pentoxide served as the dehydrating agent. These reactions were conducted at ambient temperature under an inert atmosphere, utilising either nitrogen or argon.

$$CF_3C(O)OH + HOSO_2CF_3 \xrightarrow[- H_2O]{P_2O_5} CF_3C(O)OSO_2CF_3$$

Scheme 1. Synthesis of trifluoroacetyl triflate.

The formation reaction of TFAT by this route competes with the dehydration of trifluoroacetic and triflic acids caused by phosphorus pentoxide, according to the reactions described in Scheme 2. Taking into account that the spectroscopic studies carried out in this work, particularly matrix-isolation spectroscopy, require highly pure samples, various stoichiometric ratios of the reagents were explored. This optimization aimed to minimize secondary reactions and ensure optimal conditions for the desired reactions.

$$2\ CF_3C(O)OH \xrightarrow[- H_2O]{P_2O_5} CF_3C(O)OC(O)CF_3$$

$$2\ HOSO_2CF_3 \xrightarrow[- H_2O]{P_2O_5} CF_3SO_2OSO_2CF_3$$

Scheme 2. Secondary reactions in the synthesis of trifluoroacetyl triflate.

TFAT undergoes hydrolysis at room temperature, yielding trifluoroacetic acid and triflic acid [1], as well as the two anhydrides depicted in Scheme 2. Due to its hydrophilicity, purification must be conducted in a moisture-free environment. Initially, the reaction between trifluoroacetic acid and triflic acid was carried out with an equimolar ratio of both acids, following previously reported conditions [1,14]. Under these reaction conditions, a high proportion of the $CF_3C(O)OC(O)CF_3$ anhydride relative to TFAT was obtained. Subsequently, experiments were conducted using a 2:1 ratio between trifluoroacetic and triflic acids, respectively, as described in existing literature [2,15]. However, these tests yielded even poorer results than the previous ones.

To minimise the formation of the $CF_3C(O)OC(O)CF_3$ anhydride, the reaction was conducted with a 1:2 ratio between trifluoroacetic and triflic acids. This ratio was chosen deliberately to favour the formation of the $CF_3SO_2OSO_2CF_3$ anhydride over the $CF_3C(O)OC(O)CF_3$ anhydride, which exhibits lower volatility (approximately 8 mbar at ambient temperature) and facilitates its subsequent separation from TFAT. The synthesis of the TFAT used for the spectroscopic studies presented in this work was carried out under these conditions, using an Ar atmosphere to mitigate potential hydrolysis reactions.

Efforts to synthesise trichloroacetyl triflate by reacting silver triflate with trifluoroacetyl chloride, aiming to eliminate water presence, were unsuccessful. Initially, trifluoroacetic acid ($CF_3C(O)OH$) was reacted with an approximately 50% excess of phosphorus pentachloride (PCl_5) to yield trifluoroacetyl chloride ($CF_3C(O)Cl$) [22]. The reaction was conducted in a flask, with $CF_3C(O)OH$ being added dropwise to PCl_5 at room temperature (25 °C). The apparatus was connected to two traps cooled with refrigerated baths for subsequent distillation, and $CF_3C(O)Cl$ was isolated in the trap at –60°C. Subsequently, trifluoroacetyl chloride was reacted with ~50% excess of silver triflate at –20 °C. Before utilisation, the salt was dried in an oven at 120 °C. The progress of the reaction was monitored using FTIR and Raman spectroscopy. Unfortunately, this reaction failed to yield any favourable results, and after numerous attempts, we decided to abandon this route.

3.2. Quantum Chemical Calculations

To identify different conformational isomers, we computed a potential energy surface as a function of two dihedral angles τ1 = CC–OS and τ2 = CO–SC, as shown in Figure 1. Each torsional angle was varied from 0 to 360° in steps of 10°. The energy at each data point was determined using the B3P86/6-31+g(d) approximation, while all geometric parameters were simultaneously optimized, except for the torsion angles τ1 and τ2.

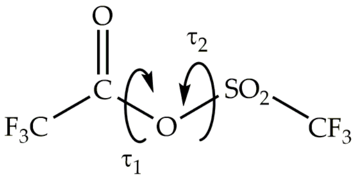
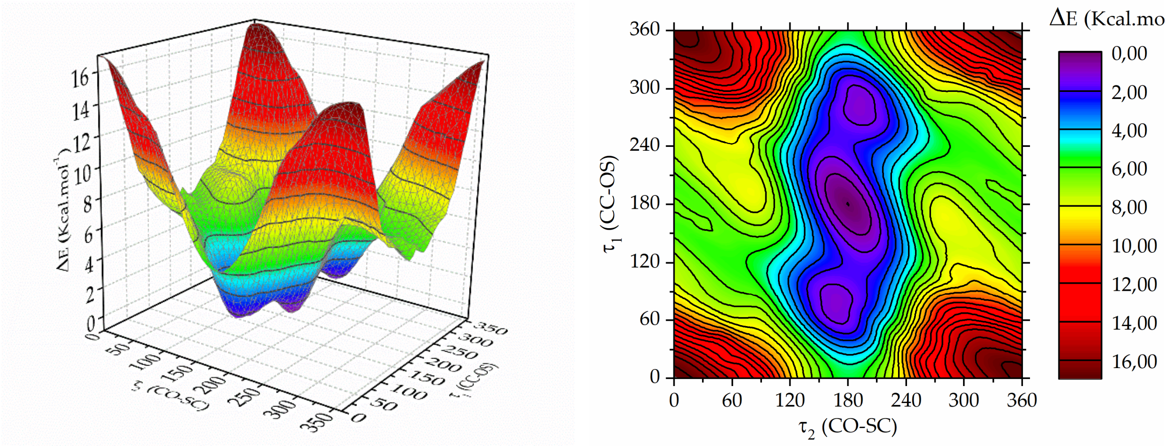


Figure 1. Definition of the dihedral angles τ1 = CC–OS and τ2 = CO–SC of trifluoroacetyl triflate.

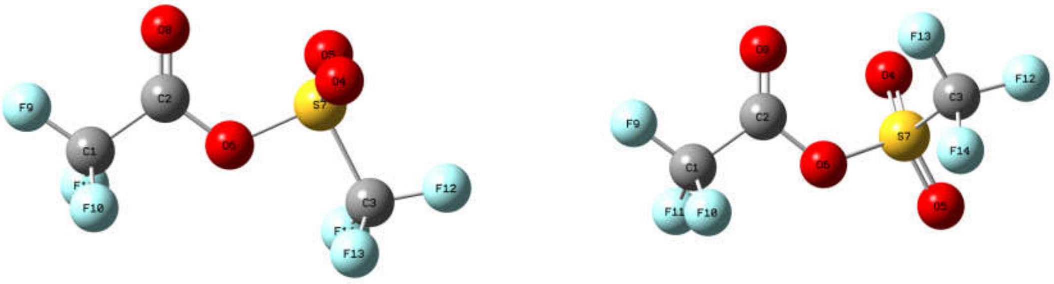
Figure 2 displays the calculated potential energy surface (left panel) and the contour map (right panel). The global minimum is evident, corresponding to τ1 = τ2 = 180°. Moreover, the surface reveals two additional local minima, where τ2 is approximately 180, while τ1 is around 70 and 290°, respectively. Subsequently, each of these minima underwent optimization using the B3LYP method with various basis functions, involving the simultaneous relaxation of all geometric parameters. The global energy minimum is denoted as the *syn-anti* conformer, characterised by the C=O double bound being *syn* with respect the O–S single bond and the C–O single bond *anti* with respect to de S–C single bond. The second is termed as the *syn-gauche*, where the C=O double bound is *syn* with respect the O–S single bond and the C–O single bond *gauche* with respect to de S–C single bond.



(**a**) (**b**)

Figure 2. (**a**) Potential energy surface and (**b**) contour map computed with the B3P86 /6-31+g(d) approximation as a function of the dihedral angles τ1 = CC–OS and τ2 = CO–SC of trifluoroacetyl triflate varied from 0 to 360° in steps of 10°.

Figure 3 exhibits the molecular models of the optimised structures for both rotamers of trifluoroacetyl triflate, computed using the B3LYP/cc-pvtz approximation. The geometrical parameters are detailed in Table S1 of the Supplementary Material, while the Cartesian coordinates for the *syn-anti* and *syn-gauche* conformers are provided in Tables S2 and S3, respectively. In all instances, energy minima devoid of imaginary frequencies were achieved. Furthermore, Table S4 presents a comprehensive compilation of wavenumbers, IR and Raman intensities, along with tentative assignment for each conformer, calculated using the B3LYP/cc-pvtz approximation.



(**a**) *syn-anti* (**b**) *syn-gauche*

Figure 3. Molecular models of the conformers of trifluoroacetyl triflate computed with the B3LYP/cc-pvtz approximation: (**a**) *syn-anti* (the C=O double bond *syn* with respect to the O–S single bond and the C–O single bond *anti* with respect to the S–C bond); (**b**) *syn-gauche* (the C=O double bond *syn* with respect to the O–S single bond and the C–O single bond *gauche* with respect to the S–C bond).

Table 1 presents the energy differences and Gibbs free energy differences between the *syn-gauche* and *syn-anti* conformers, calculated with B3LYP theoretical approximation with various basis sets. Additionally, the relative population of the rotamers at 25 °C was determined using the Boltzmann equation, considering a degeneracy of 2 for the *syn-gauche* form. The table reveals that, across all cases, the *syn-anti* form corresponds to the lowest energy conformer. However, the computed percentage at room temperature fluctuates depending on the basis set utilized, ranging from 96 to 69%. These findings will be discussed further along with the analysis of the experimental results.

Table 1. Energy differences and Gibbs free energy differences between *syn-gauche and syn-anti* conformers of trifluoroacetyl triflate and % of the *syn-anti* rotamer calculated with B3LYP theoretical approximation and different basis sets.

Theoretical approximation	ΔE (Kcal.mol^{-1}) [1]	ΔG° (Kcal.mol^{-1}) [2]	% *syn-anti* [3]
B3LYP/6-31++G(d)	1.26	2.22	96
B3LYP/6-311++G(d)	1.23	2.02	94
B3LYP/tzvp	1.11	1.34	83
B3LYP/cc-pvtz	0.87	0.88	69

[1] ΔE = E(*syn-gauche*) – E(*syn-anti*); [1] ΔG° = G°(*syn-gauche*) – G°(*syn-anti*); [3] Calculated at ambient temperature (25 °C) and considering degeneracy 2 for the *syn-gauche* conformer.

To comprehensively understand the conformational preferences of TFAT, we conducted orbital interaction analyses using Natural Bond Orbital (NBO) formalism. Table 2 summarizes the key NBO stabilization energies computed, encompassing both hyperconjugative and anomeric effects. The hyperconjugative effect involves the interaction between a non-bonding orbital with π character, known as nπ(O), located on the oxygen atom (–O–), and the π antibonding orbital of the C=O double bond, referred to as π*(C=O). On the other hand, the *syn* conformation is stabilized by the anomeric effect corresponding to the lpσO → σ*C=O interaction. The *syn-anti* conformer is additionally stabilised by two lpσO → σ*S=O interactions, while for the *syn-gauche* form the lpσO → σ*S–C interaction emerges as the most significant factor contributing to its stabilization (see Table 2 for details). Figures S1 and S2 depicts a schematic representation of these orbital interactions. Upon

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analysis of the values presented in Table 2, it becomes evident that both hyperconjugative and anomeric effects play significant roles in stabilizing the *syn-anti* over the *syn-gauche* rotamer.

Table 2. Main orbital interaction energies (Kcal.mol^{-1}) involved in the stabilization of the *syn-anti* and *syn-gauche* conformers of trifluoroacetyl triflate, calculated with the NBO formalism using the B3LYP/cc-pvtz approximation.

Orbital interaction [1]	*syn-anti*	*syn-gauche*
lpπO6 → π*C2=O8	39.20	35.65
lpσO6 → σ*C2=O8	7.20	7.48
lpσO6 → σ*S=O4	5.42	–
lpσO6 → σ*S=O5	5.42	–
lpσO6 → σ*S–C3	–	5.93
Total anomeric effect	18.04	13.41
Total hyperconjugative effect	39.20	35.65
Total	57.24	49.06

[1] Atom numbering refers to Figure 3.

The vibrational spectra (IR and Raman) of each TFTA conformer were simulated using the B3LYP theoretical approximation in conjunction with various basis sets. The results will be discussed in the following section, alongside the experimental findings.

3.3. Vibrational Studies

As stated in the introduction, to the best of our knowledge, there have been no prior vibrational studies conducted on trifluoroacetyl triflate reported in the literature. In this study, we conducted measurements and analyses of the FTIR spectra in the gas phase, the Raman spectrum in the liquid phase, and the FTIR spectra of matrix-isolated $CF_3C(O)OSO_2CF_3$. Our focus was particularly on identifying signals that could be attributed to different conformers. Figure 4 illustrates the experimental spectra, while Table 3 presents the experimental wavenumbers alongside the predicted values for the *syn-anti* and *syn-gauche* conformers, calculated using the B3LYP/cc-pvtz approximation, and a tentative assignment. For band assignment, we considered the following criteria: i) theoretical predictions, especially differences in wavenumbers for the vibrational modes of each conformer; ii) the behaviour of IR absorptions of TFAT isolated in an argon matrix following UV-visible irradiation; and iii) comparison with reported values for molecules similar to TFAT.

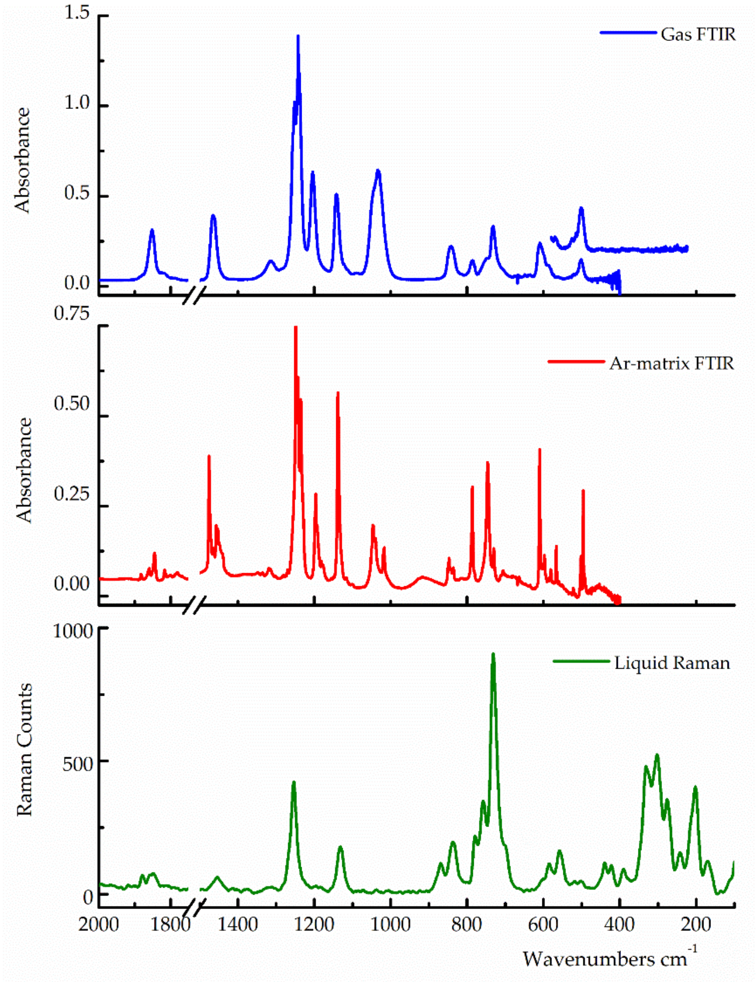

Figure 4. Gas-phase FTIR spectrum (blue-trace, pressure 1.7 mbar, 0.5 cm^{-1} resolution, 64 scans), Ar-matrix FTIR spectrum (red-trace, 1:1000, 0.5 cm^{-1} resolution, 256 scans) and liquid-phase Raman spectrum (green-trace, $\lambda_{exc.}$ 514.5 nm) of trifluoroacetyl triflate.

The expected differences between the IR spectra of both conformers were meticulously scrutinized based on the computationally simulated spectra. As shown in Table 3, certain vibrational modes are expected to exhibit nearly identical wavenumbers for both forms. Conversely, several vibrational modes display significant wavenumber disparities, enabling their distinct detection, particularly in the Ar-matrix FTIR spectra, which feature narrower bands compared to the gas and liquid phase spectra. Figure 5 illustrates the plot of the IR spectra simulated using the B3LYP/cc-pvtz approximation for the *syn-anti* and *syn-gauche* conformers, each multiplied by the relative abundance calculated using the same theoretical approximation, as well as the weighted sum of the individual spectra. This plot highlights selected regions where appreciable wavenumber differences were observed. These simulated spectra were then compared with the experimental spectra, with particular emphasis on the Ar-matrix FTIR spectrum, which served as a valuable tool for assignment purposes.

Table 3. Experimental wavenumber (gas FTIR, Ar-matrix FTIR and liquid Raman) in cm^{-1} of trifluoroacetyl triflate, comparison with the calculated wavenumbers using the B3LYP/cc-pvtz approximation for the *syn-anti* and *syn-gauche* conformers, and tentative assignment.

Experimental			**B3LYP/cc-pvtz**		**Tentative assignment**
Gas-FTIR ν (cm^{-1})	**Ar-matrix FTIR ν (cm^{-1})^a**	**Liquid Raman ν (cm^{-1})**	***syn-anti***	***syn-gauche***	
1852	1860	1880		1892	ν C=O $_{syn\text{-}gauche}$
	1845	1851	1882		ν C=O $_{syn\text{-}anti}$

Experimental			B3LYP/cc-pvtz		Tentative assignment
Gas-FTIR **ν (cm^{-1})**	**Ar-matrix FTIR** **ν (cm^{-1})^a**	**Liquid Raman** **ν (cm^{-1})**	*syn-anti*	*syn-gauche*	
1465	1475	1455		1434	ν_{as} SO_2 ***syn-anti***
	1453		1426		ν_{as} SO_2 ***syn-gauche***
1314	1319	1317	1301		ν C–CF_3 ***syn-anti***
	1315			1293	ν C–CF_3 ***syn-gauche***
1252	1249		1242		ν_{as} CF_3 (–SO_2) ***syn-anti***
	1248			1241	ν_{as} CF_3 (–SO_2) ***syn-gauche***
1241	1243	1266	1236		ν_{as} CF_3 (–C=O) ***syn-anti***
	1241			1234	ν_{as} CF_3 (–C=O) ***syn-gauche***
1234 sh	1236		1231	1231	ν_{as} CF_3 (–SO_2)
	1228	1254	1225	1225	ν_s SO_2 *syn-anti*
1204	1200			1182	ν_{as} CF_3 (–C=O) ***syn-gauche***
	1196		1179		ν_{as} CF_3 (–C=O) ***syn-anti***
1142	1136	1133	1106	1106	ν_s CF_3 (–SO_2)
1040	1047		1061		ν C–O ***syn-anti***
	1018			1043	ν C–O ***syn-gauche***
842	847	840	852		δ OCO ***syn-anti***
	836			843	δ OCO ***syn-gauche***
788	788	780		774	$\delta_{o.o.p.}$ (C=O) ***syn-gauche***
	786		765		$\delta_{o.o.p.}$ (C=O) ***syn-anti***
779 sh	780		770	770	ν_s CF_3 (–SO_2)
751	746	759	741		δ_s CF_3 (–C=O) *syn-anti*
733	730			734	δ_s CF_3 (–C=O) ***syn-gauche***
704 sh	705	733	686	686	ν S–O
611	611			594	ω SO_2 ***syn-gauche***
	609		587		ω SO_2 *syn-anti*
600	601	585		575	ν C–S ***syn-gauche***
	598		566		ν C–S *syn-anti*
585 sh	580		556	554	δ CF_3 (–SO_2)
566	566	559	544	547	δ CF_3 (–SO_2)
522	521		519	517	δ CF_3 (–C=O)
498	496		489		δ SO_2 *syn-anti*
	492			487	δ SO_2 *syn-gauche*
		438	432	428	δ O=S=O
		421	415	381	δ C–C=O
		330	325	335	δ F–C–C
		302	300	284	δ F–C–C
		276	257	277	δ F–C–S
		242	236	243	ω CF_3 (–C=O)
		202	186	200	δ C–O–S
		170	159	149	δ O–S–C

[a] Only the most intense matrix sites are listed.

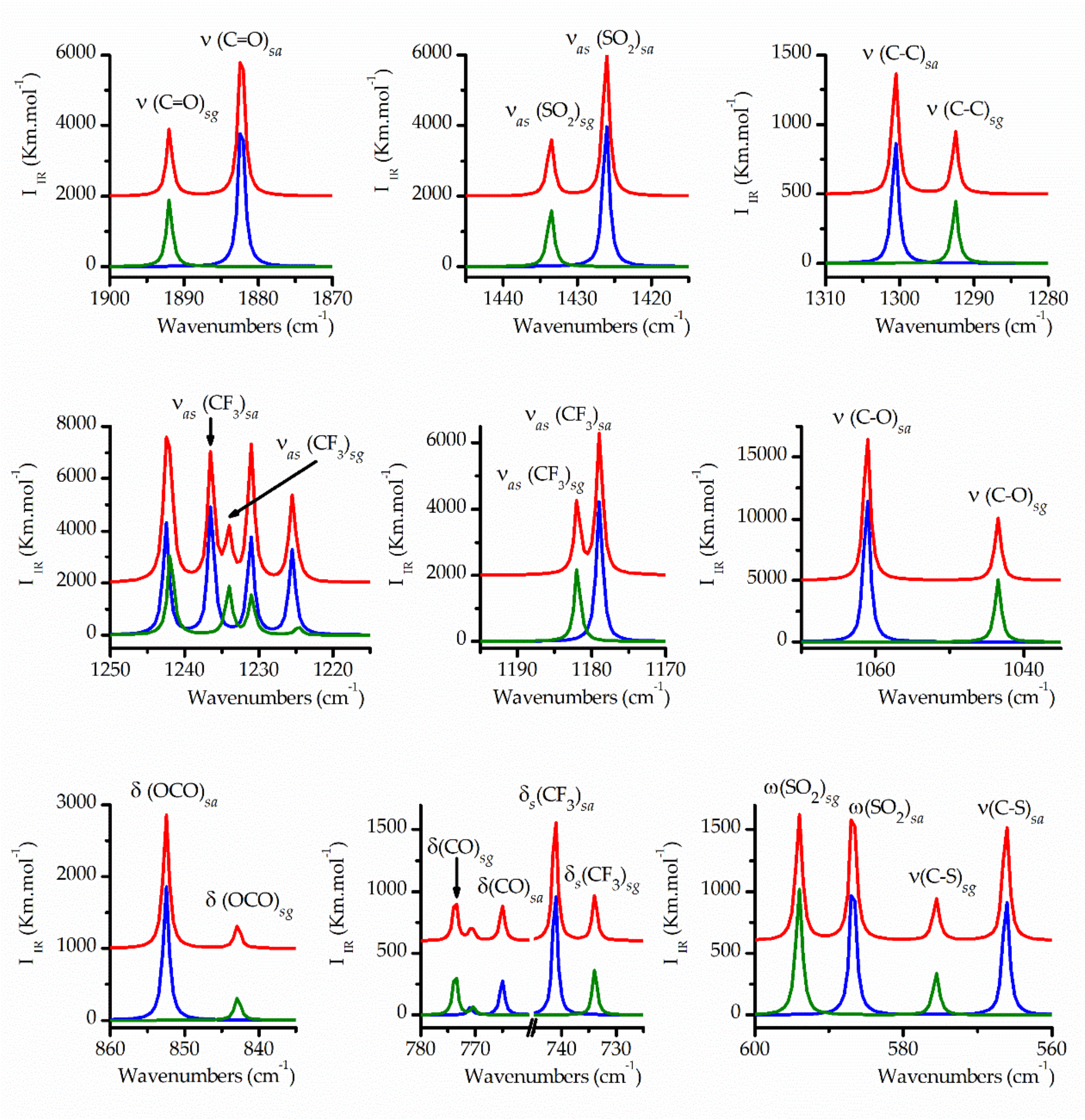

Figure 5. Simulated IR spectra in selected regions for the conformers of TFAT, scaled by their relative abundances at 25 °C, calculated with the B3LYP/cc-pvtz approximation: *syn-anti* conformer, blue spectrum scaled by 0.69 factor; *syn-gauche*, green spectrum scaled by 0.31 factor; weighted sum of the spectra of the two conformers, red spectrum.

Another significant aspect aiding in the interpretation and assignment of the spectra was the analysis of the FTIR spectra following broad-band UV-visible irradiation of TFAT isolated in an Ar matrix. The matrix underwent exposure to UV-visible light for varying durations (15 and 30 s, and 1, 2, 4, 7, 12, 20, 30, 50 and 80 min). Changes occurring after each irradiation period were monitored using FTIR spectroscopy. During photolysis, it was observed that the IR absorptions corresponding to the *syn-gauche* conformer increased, while those of the *syn-anti* form decreased. The final two spectra, taken after 50 and 80 minutes of photolysis, exhibited no further changes, indicating the system had reached a stationary state. Figure 6 illustrates selected regions of the FTIR spectrum of the matrix taken immediately after deposition and after 12 and 50 min of photolysis. These spectral regions were chosen based on clear identification of both conformers, corresponding to the ν(C=O), ν(C–O) and δ(OCO) vibrational modes. For clarity, the spectra were normalized to the bands of the high-energy conformer. The pronounced increase in the relative intensities of the signals from the *syn-gauche* conformer compared to those of the *syn-anti* rotamer is evident in the Figure.

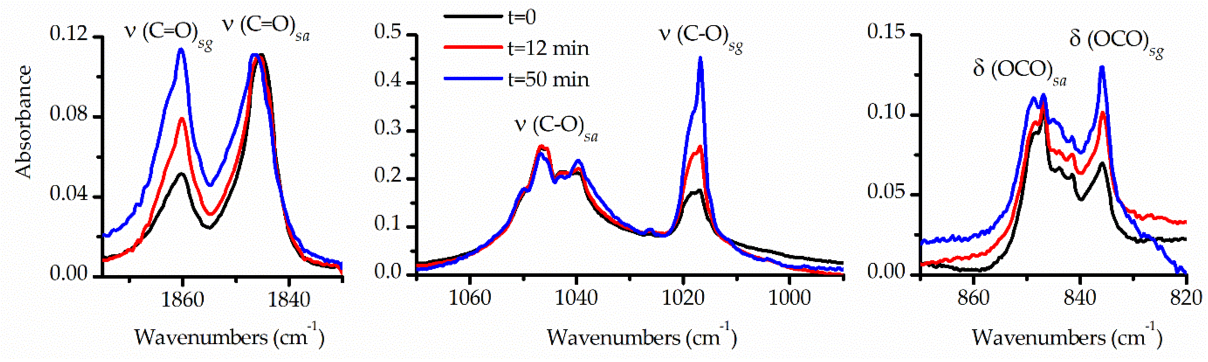

Figure 6. Selected regions of FTIR spectra of an Ar-matrix containing TFAT in 1:1000 proportion: after deposition (black trace) and 12 (red trace) and 50 minutes (blue trace) photolysis with broad-band UV-visible light. The spectra are normalized to the intensities of the absorption assigned to the *syn-anti* conformer.

The abundances of the conformers were estimated from the IR matrix spectra using two different approaches. Firstly, it was assumed that in the last two spectra, taken after 50 and 80 min respectively, where a constant ratio of intensities of the bands assigned to the two conformers was achieved, the proportion of each conformer was approximately 50%, following a process known as conformational randomization. Experimental absorptivity coefficients were then calculated from the area ratio. Utilizing this relationship along with the intensity ratio in the spectrum acquired prior to irradiation, the percentage of each rotamer at room temperature was estimated. In a second method, absorptivity coefficients calculated using the B3LYP/cc-pvtz approximation were employed to correct the relationship of experimental intensities in the IR spectra of the matrix before irradiation. These procedures were performed for each of the normal modes depicted in Figure 6 (ν(C=O), ν(C–O) and δ(OCO)). Estimates between approximately 60-70% were obtained for the *syn-anti* form. The percentage determined for each normal mode using both described methods are presented in Table S5 of the supplementary material. Considering the various factors influencing these measurements, particularly the presence of matrix sites affecting the relative intensity of some bands, whose changes may also be influenced by irradiation, the dispersion of these values can be deemed acceptable. Moreover, they align well with the relative population predictions obtained using the B3LYP/cc-pvtz method.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org, Figure S1: Schematic representation of the hyperconjugative and anomeric interactions in the *syn-anti* conformer of trifluoroacetyl triflate calculated with the NBO formalism using the B3LYP/cc-pvtz approximation: (a) lpπ O → π* C=O; (b) lpσ O → σ* C=O; (c) lpσ O → σ* S=O; Figure S2: Schematic representation of the hyperconjugative and anomeric interactions in the *syn-gauche* conformer of trifluoroacetyl triflate calculated with the NBO formalism using the B3LYP/cc-pvtz approximation: (a) lpπ O → π* C=O; (b) lpσ O → σ* C=O; (c) lpσ O → σ* S–C; Table S1: Geometrical parameters (distances in Å and angles in degrees) for the *syn-anti* and *syn-gauche* conformers of $CF_3C(O)OSO_2CF_3$ calculated with the B3LYP/cc-pvtz approximation; Table S2: Cartesian coordinates (in Å) of the *syn-anti* conformer of $CF_3C(O)OSO_2CF_3$ calculated with the B3LYP/cc-pvtz approximation, Table S3: Cartesian coordinates (in Å) of the *syn-gauche* conformer of $CF_3C(O)OSO_2CF_3$ calculated with the B3LYP/cc-pvtz approximation; Table S4: Wavenumbers, IR and Raman intensities, and tentative assignment, calculated with the B3LYP/cc-pvtz approximation for the *syn-anti* and *syn-gauche* conformers of $CF_3C(O)OSO_2CF_3$; Table S5: Percentage of the *syn-anti* conformer of $CF_3C(O)OSO_2CF_3$ estimated from the relative intensities of selected IR bands of the Ar-matrix FTIR spectrum of TFAT. I, using the relationship of the absorption coefficients of the involved bands when the concentrations of the two rotamers becomes equal after the randomization process (in this case, broad-band UV-visible irradiation of the matrix for 50 min); II) through the use of the absorption coefficients obtained from the B3LYP/cc-pvtz approximation.

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Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

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