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Formation of XNCO species (X = F, Cl) through matrix-isolation photochemistry of XSO_2NCO molecules

Norma L. Robles[a,b], Andrea Flores Antognini[a], Rosana M. Romano[b,*]

[a] INQUINOA (CONICET-UNT) Instituto de Química Física, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, San Lorenzo 456, (4000) Tucumán, Argentina
[b] CEQUINOR (UNLP-CONICET), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 y 115, (1900) La Plata, Argentina

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ABSTRACT

The photochemistries of the molecules $ClSO_2NCO$ and FSO_2NCO isolated in solid argon matrices at ~10 K have been investigated. After photolysis of the matrices with broad-band UV–visible radiation ($200 \leq \lambda \leq 800$ nm) the products were identified by their IR spectra. $ClSO_2NCO$ decomposes in two steps. In the first place, the photolysis gives a 1:1 molecular complex between SO_2 and ClNCO. In the second step, ClNCO decomposes in different parallel photochemical channels to give ClNO, NO, CO and the ClCO· radical, while SO_2, transformed from a complexed to an uncomplexed form, remains stable on photolysis. The SO_2:ClNCO molecular complex was theoretically investigated by *ab initio* and DFT methods. Based on the comparison with the experimental findings, a structure in which the lone pair of one of the oxygen atoms of the SO_2 unit interacts with the unoccupied σ^*Cl–N orbital of ClNCO was proposed. On the other hand, FSO_2NCO remains almost photostable when exposed to similar conditions, with the only formation of FNCO and CO in very small proportions.

1. Introduction

Chlorosulfonyl isocyanate and, in minor extent, fluorosulfonyl isocyanate are extensively used as reactants in the synthesis of pharmaceutical products, herbicides and pesticides [1–3], what may result in the emission of these compounds into the atmosphere. In this context, the understanding of the photochemical processes that occur under the action of light results of fundamental importance from an environmental point of view. However, to the best of our knowledge, no studies involving the photochemistry of $ClSO_2NCO$ and FSO_2NCO exist so far.

The photochemical study of species isolated in noble gases matrixes is a powerful tool for understanding photoevolutive processes in single molecules [4,5]. The inert environment reduces the possibility of molecular interactions, and the vibro-rotational transitions are negligible due to the low temperatures. In addition, the photochemistry of matrix isolated species can be assumed as a suitable model for understanding photodegradation of compounds in the atmosphere, since the dilution mimic very well the conditions to which the substances are exposed when reached by solar irradiation [6].

The structural, conformational and vibrational properties of $ClSO_2NCO$ [7–9] and FSO_2NCO [10–12] have been reported previously. The UV spectrum of gaseous $ClSO_2NCO$ presents two absorptions at 196 and 288 nm, assigned to the $n \rightarrow \pi^*$ transition of the SO_2 group and to the $\pi \rightarrow \pi^*$ transition localized in the NCO group [8]. The UV spectrum of FSO_2NCO in gas phase is very similar to that of its chlorine congener, with the maxima occurring at 196 and 300 nm [8]. Recently, the photoelectronic spectrum of $ClSO_2NCO$ was analysed [13]. The purpose of the present work is the understanding of the photochemical behaviours of these compounds when isolated in solid inert matrixes at cryogenic temperatures.

2. Materials and methods

A commercial sample of $ClSO_2NCO$ (Aldrich) was purified by repeated trap-to-trap condensation *in vacuo*. FSO_2NCO was obtained through the reaction of $ClSO_2NCO$ with SbF_3, and subsequently purified by repeated trap-to-trap distillations [10]. The purity of the compounds was checked by means of the gas-phase FTIR spectra. The Ar gas (AGA) was passed through a trap cooled to −90 °C to retain possible traces of impurities. A gas mixture of each sulfonyl isocyanate compound with argon, in an approximately 1:1000 proportion, was prepared by standard manometric methods. The mixture was then deposited on a CsI window cooled to ca. 10 K by means of a Displex closed-cycle refrigerator (SHI-APD Cryogenics, model DE-202), using the pulse deposition technique [14–16]. FTIR spectra of each matrix sample were recorded at resolutions of 0.5 and 0.125 cm^{-1}, with 256 scans, using a Nexus Nicolet instrument equipped with either an MCTB or a DTGS detector (for

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* Corresponding author.
E-mail address: romano@quimica.unlp.edu.ar (R.M. Romano).

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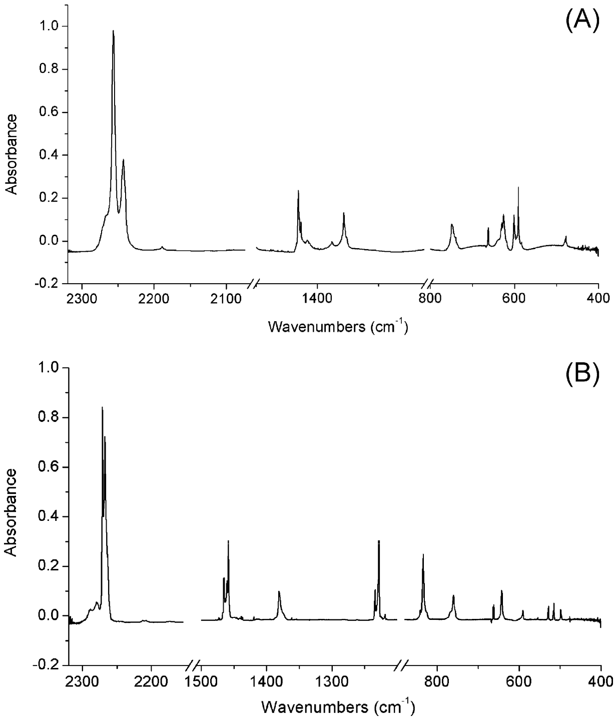


Fig. 1. FTIR spectra of $ClSO_2NCO$ (A) and FSO_2NCO (B) isolated in solid Ar in an approximately proportion 1:1000 taken immediately after deposition.

the ranges 4000–400 or 600–180 cm^{-1}, respectively). Following deposition and IR analysis of the resulting matrix, the sample was exposed to broad-band UV–visible radiation ($200 \leq \lambda \leq 800$ nm) from a Spectra-Physics Hg-Xe arc lamp operating at 800 W. The output from this lamp was limited by a water filter to absorb IR radiation and so minimize any heating effects. The FTIR spectra of the matrices were recorded at different irradiation times in order to monitor closely any change in the spectra.

All the quantum chemical calculations were performed using the Gaussian 03 program package [17]. Methods derived from Density Functional Theory (DFT) and *ab initio* calculations (MP2) were used in combination with 6-311+G(2df) and aug-cc-pVDZ basis set. Geometry optimizations were sought using standard gradient techniques by simultaneous relaxation of all the geometrical parameters. The calculated vibrational properties correspond in all cases to potential energy minima for which no imaginary frequency was found.

3. Results and discussion

3.1. Matrix-isolated spectra of $ClSO_2NCO$ and FSO_2NCO

To the best of our knowledge, no studies on the isolation of $ClSO_2NCO$ or FSO_2NCO in solid argon matrices exist so far. As a starting point for the analysis of the matrix photochemical products of these compounds, the study and interpretation of the IR spectra of the isolated species becomes necessary.

Fig. 1 shows the FTIR spectra of $ClSO_2NCO$ and FSO_2NCO isolated in solid Ar in an approximately proportion 1:1000 and Table 1 lists the wavenumbers of the IR absorptions, together with a tentative assignment. All the observed absorptions in the IR spectra of the matrices are in accordance with the gas-phase reported values, included in Table 1 for comparison purposes, with the exception of the ν_{as} $N^{13}CO$ that were not reported previously.

Many of the features in the matrix-isolated spectra of both molecules present a complicated pattern (see for example the spectral region corresponding to the ν_{as} NCO vibrational mode of $ClSO_2NCO$ in Fig. 2). Gas phase electron diffraction [7], microwave [18] and also vibrational [8,9] studies for $ClSO_2NCO$ have revealed that this molecule possesses only one conformation at ambient temperature. Similar results were found for FSO_2NCO from gas electron diffraction [12] and vibrational [10,11] methods. Taking into consideration the reported structures, the splitting of the IR absorptions were then attributed to different matrix sites. After irradiation of the matrix (see Sections 3.2 and 3.3) all the bands have presented the same behaviour with photolysis, which reinforces this interpretation. Under annealing experiments some of the absorptions increase their intensities at expense of the others, given additional evidences for the presence of different sites in the solid matrix.

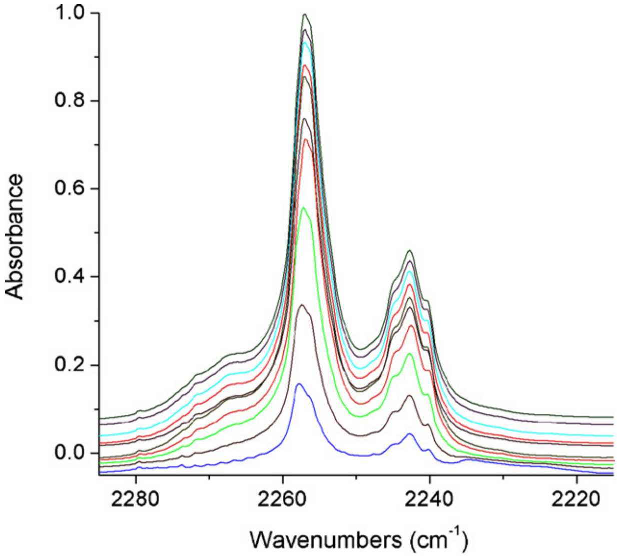


Fig. 2. FTIR spectrum in the region of the ν_{as} NCO vibrational mode (2215–2285 cm^{-1}) of an Ar matrix initially containing $ClSO_2NCO$ at different irradiation times (from top to bottom: t = 0, 15, 30, 60, 120, 240, 480, 960, 1920 and 3840 s).

3.2. Photolysis of $ClSO_2NCO$ isolated in solid Ar

The matrix isolated $ClSO_2NCO$ was exposed to broad-band UV–visible radiation ($200 \leq \lambda \leq 800$ nm) and IR spectra of the matrix were taken after different irradiation times. Several changes were observed to occur, even at very short photolysis times as 15 s. All the absorptions developed on photolysis, together with a tentative assignment, were summarized in Table 2.

The intensity of all the absorptions previously assigned to $ClSO_2NCO$ decreases following the same kinetic behaviour, which is in complete agreement with the presence of only one conformation. As observed in Fig. 3, that shows the decay of the IR bands of the compound against the irradiation time, $ClSO_2NCO$ is almost completely consumed after the exposition for 1 h to the photolyzing radiation.

For the assignment of the several signals developed on photolysis of the matrix, we first analysed the behaviour they present against the irradiation time, which allow as to group them according to this criteria. There is a set of absorptions, appearing at 2204.5/2201.0, 1348.1/1347.2/1346.1, 1148.0, 700.3, 555.9 and 520.5 cm^{-1}, that first grow, up to approximately 15 min of irradiation, and then suffer a slightly decay (see Fig. 4). Considering the possible fragments arising from unimolecular photofragmentation of the starting molecule, and comparing the developed absorptions with reported values, we can conclude that the observed IR signals could correspond to ClNCO and SO_2 molecules.

Table 1
Ar-matrix and gas-phase IR wavenumbers (in cm^{-1}) of $ClSO_2NCO$ and FSO_2NCO.

$ClSO_2NCO$		FSO_2NCO		Assignment
Ar-Matrix	Gas-Phase[a]	Ar-Matrix	Gas-Phase[b]	
2255.7 2256.1 2244.9 2242.6 2240.2	2262 2257 2253	2271.0 2268.9 2267.2 2263.4	2280 2274 2269	ν_{as} NCO
2189.0 2184.6		2212.8 2211.0 2207.7 2204.8		ν_{as} $N^{13}CO$
1434.4 1431.9 1430.9 1429.4 1427.0	1443 1440	1465.3 1460.6 1458.1	1475 1470 1463	ν_{as} SO_2
1376.1 1359.7 1356.8 1351.8	1373 1361 1353	1381.1	1389 1380 1372	ν_s NCO
1200.0 1178.8	1202	1234.3 1228.2	1241 1236 1231	ν_s SO_2
		841.4 834.5	839 836	ν FS
749.2 740.0	749	768.7 760.6	766	ν SN
631.9 629.6 626.0	643 638 633	642.9	658 654 651	$\delta_{in\text{-}plane}$ NCO
601.2 591.0 589.9	598 595 593	591.0	605	δ_s SO_2
479.8 478.1	484 479 474	530.6 528.6	530	$\delta_{out\text{-}of\text{-}plane}$ NCO
431.7	535 530	517.2 515.3	523 517 511	ρ SO_2
		498.9 496.7	506 499	δ FSO_2

[a] Ref. [9].
[b] Ref. [11].

Claimed to be present in the interstellar space [19], ClNCO was firstly obtained in the gaseous phase through vacuum thermolysis of trichloroisocyanuric acid [20]. Subsequent investigations had proposed its synthesis by passing a flow of Cl_2 diluted in N_2 over solid AgNCO suspended on glass wool [21]. Additionally, evidence of its presence, again in the gas phase, was reported as a consequence of the photoisomerization of ClCNO irradiated with 254 nm UV light [22]. Although the matrix isolated IR spectrum of ClNCO is hitherto unknown, the wavenumbers observed in this work are consistent with the IR reported values for the compound in the gaseous phase [23]. The 2204.5/2201.0 cm^{-1} features, depicted in Fig. 5, are in agreement with the most intense IR absorption of

Table 2
Wavenumbers and assignment of the IR absorptions appearing after broad-band UV–vis photolysis of an Ar matrix containing $ClSO_2NCO$ at ~10 K.

Experimental wavenumbers [cm^{-1}]	Molecule	Assignment	Wavenumbers reported previously [cm^{-1}]
2204.5 2201.0	$SO_2\cdots ClNCO$	ν_{as} NCO	-
2138.3	free CO	ν CO	2138.2 [a]
2136.5	complexed CO	ν CO	-
1877.1	ClCO·	ν CO	1877.1 [b]
1874.2 1872.8 1871.8 1870.4	NO	ν NO	1875 [c] 1871.8 [d]
1804.8 1803.4	ClNO	ν NO	1805.9 [e] 1804.8 [f]
1351.1	SO_2	ν_{as} SO_2	1355.0 1351.3 [g]
1348.1 1347.2 1346.1	$SO_2\cdots ClNCO$	ν_{as} SO_2	-
1148.0	$SO_2\cdots ClNCO$	ν_s SO_2	-
700.3	$SO_2\cdots ClNCO$	$\delta_{i.p.}$ NCO	-
610	$SO_2\cdots ClNCO$	ν ClN	-
570.6	ClNO	ν ClN	585.2 [f]
555.9	$SO_2\cdots ClNCO$	$\delta_{o.o.p.}$ NCO	
520.5	$SO_2\cdots ClNCO$	δ SO_2	
517.5	SO_2	δ SO_2	519.9 517.3 [g]

[a] Ref. [26].
[b] Ref. [27].
[c] Ref. [28].
[d] Ref. [29].
[e] Ref. [30].
[f] Ref. [31].
[g] Ref. [24].

a gaseous sample reported at 2212.2 cm^{-1} and assigned to the ν_{as} NCO of ClNCO. Bands at 700.3 and 555.9 cm^{-1} are also discernable in the spectra of the irradiated matrices and attributed to the $\delta_{i.p}$ NCO and $\delta_{o.o.p}$ NCO of ClNCO, by comparison with the reported values for the gaseous sample at 707.7 and 559.0 cm^{-1}, respectively. An extremely weak absorption at 610 cm^{-1} may be assigned to the ν ClN of ClNCO, considering the 607.7 cm^{-1} reported value and also its very low intensity in gas phase.

In contrast with the ClNCO molecule, for which no Ar-matrix IR spectrum was reported, SO_2 has been extensively studied in matrix conditions [24,25]. All the fundamentals were observed as doublets assigned to SO_2 molecules trapped in two different matrix sites known as stable (S) and metastable (M) sites (ν_{as} SO_2: 1355.0 (S) and 1351.3 (M) cm^{-1}; ν_s SO_2: 1152.3 (S) and 1147.2 (M) cm^{-1}; δ SO_2: 519.9 (S) and 517.3 (M) cm^{-1}) [24]. These results were also reproduced in our laboratory from samples of SO_2 diluted in Ar. The absorptions developed as a consequence of the photolysis of $ClSO_2NCO$ isolated in Ar matrix depicted in Fig. 4, observed at 1347.2, 1148.0, and 520.5 cm^{-1}, appear shifted with respect to the signal of free SO_2. These differences give us reasons to believe that the photodecomposition of $ClSO_2NCO$ leads to a loose complex between the two photoproducts, ClNCO and SO_2, which are necessarily confined at the site of their formation by the rigidity of the Ar matrix. A theoretical study of the SO_2:ClNCO molecular complex, together with the comparison with the experimental vibrational data, is presented below (Section 3.4).

As clearly observed in Fig. 4, the absorptions assigned to the SO_2:ClNCO molecular complex, that start to developed at the very first stage of irradiation, decrease at longer times of photolysis, turning the complex into an intermediate product, that also decomposes upon irradiation. According to the literature, the UV absorption spectrum of ClNCO in gas phase presents a band at

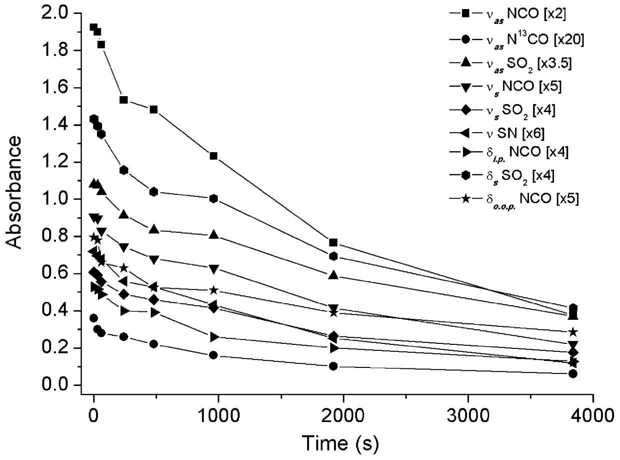


Fig. 3. Plot of the intensities of the absorptions of $ClSO_2NCO$ isolated in solid Ar in an approximately 1:1000 proportion against the irradiation time.

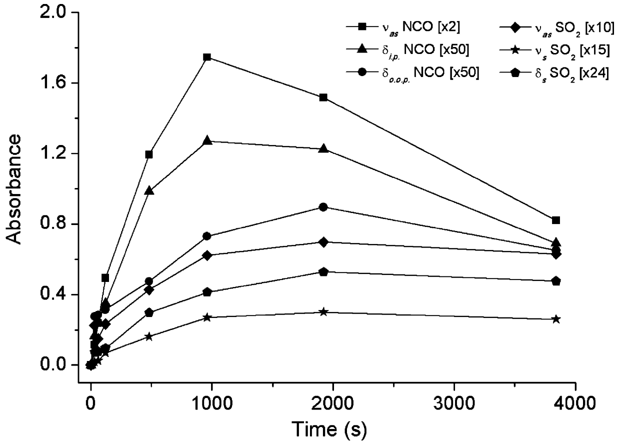


Fig. 4. Plot of the intensities of the absorptions assigned to $ClNCO\cdots SO_2$ formed in an Ar matrix containing $ClSO_2NCO$ in an approximately 1:1000 proportion against the irradiation time.

250 nm, and the compound decomposes upon exposition to 249 nm UV light generating Cl, $N(^2D)$ and CO [22].

Different features appear in the FTIR spectra of the matrices, that can be interpreted as arising from the decomposition of the SO_2:ClNCO, according to their kinetic behaviour (see Fig. 6). Two bands, at 2138.3 and 2136.5 cm^{-1}, are assigned to the CO molecule. Free CO isolated in Ar matrix originates an absorption reported at 2138.2 cm^{-1}, while red-shifted features were observed for adducts in which the CO molecule bonds through the oxygen atom [26]. A characteristic sharp band at 1877.1 cm^{-1} was readily assigned to the ClCO· radical, by comparison with the same value reported previously in similar conditions [27]. The multiplet at 1874.2/1872.8/1871.8/1870.4 cm^{-1} may be attributed to the NO molecule, being 1875 cm^{-1} the Ar-matrix reported value [28] and 1871.8 cm^{-1} the wavenumber observed by our group during the photolysis of NO_2 isolated in an Ar matrix [29]. A broad doublet at 1804.8/1803.4 cm^{-1} can be assigned to the νNO fundamental of ClNO, previously observed at 1805.9 [30] and 1804.8 [31] in argon matrices. Small absorptions notable at longer irradiation times at 1351.1 and 517.5 cm^{-1} are consistent with the formation of uncomplexed SO_2 [24,25].

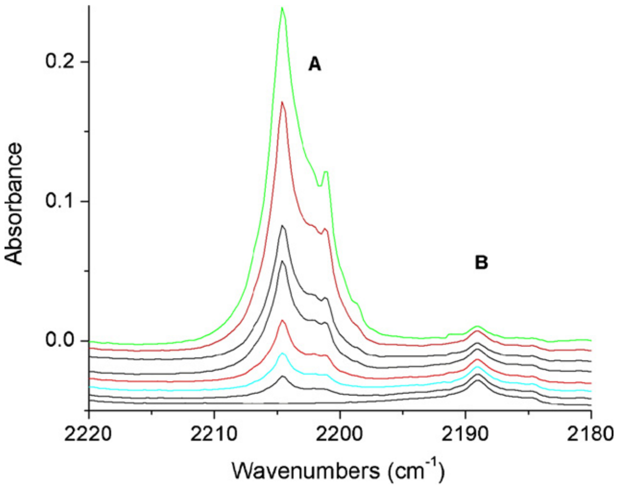


Fig. 5. FTIR spectrum of an Ar matrix initially containing $ClSO_2NCO$ at different irradiation times in the region of the (A) ν_{as} NCO of ClNCO and (B) ν_{as} $N^{13}CO$ of $ClSO_2NCO$ (from bottom to top: t = 0, 15, 30, 60, 120, 240, 480 and 960 s).

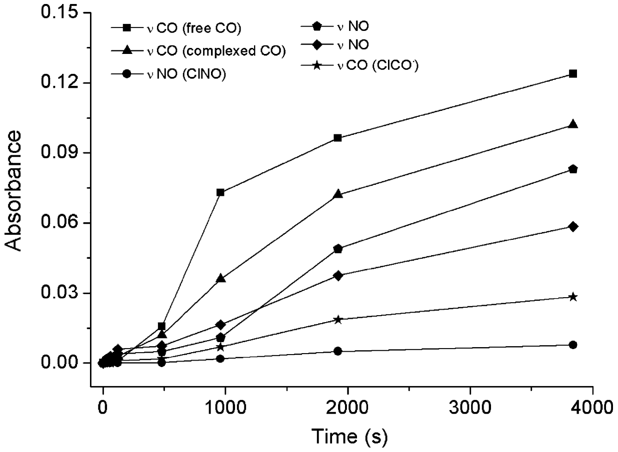


Fig. 6. Plot of the intensities of the absorptions assigned to CO, NO. ClNO and ClCO· formed in an Ar matrix containing $ClSO_2NCO$ in an approximately 1:1000 proportion against the irradiation time.

3.3. Photolysis of FSO_2NCO isolated in solid Ar

Unlike the rich photochemistry observed for $ClSO_2NCO$ isolated in Ar matrix, the fluorinated congener FSO_2NCO displays a higher photostability against broad-band UV–visible radiation ($200 \leq \lambda \leq 800$ nm). A low-intensity signal at 2234.5 cm^{-1}, appearing at long irradiation times (see Figs. 7 and 8), was interpreted in terms of the formation of FNCO. Reported wavenumbers for this species in neon matrix [32] confirm such assignment. The presence of a monomeric CO signal, which increases upon irradiation, was attributed to photodecomposition of FNCO.

Although the UV spectra of FSO_2NCO and $ClSO_2NCO$ are very similar [8], the rate of the photodecomposition in matrix conditions is considerable slower for the former compound. This finding is comparable with the behaviour observed for matrix isolated $XC(O)SCH_3$, with X = F, Cl. The photolysis of $ClC(O)SCH_3$ with light in the $200 \leq \lambda \leq 800$ nm region occurs with the total consumption of the starting compound in two steps, the first consisting of fragmentation in CO and $ClSCH_3$, and the second entailing detachment of a hydrogen atom from the methyl group of $ClSCH_3$ with the formation of the molecular complex $H_2C{=}S\cdots HCl$ [33]. On the other hand, exposition of $FC(O)SCH_3$ to the same photolyzing radiation results, mainly, in photoisomerization of the *syn* into the *anti* form of the

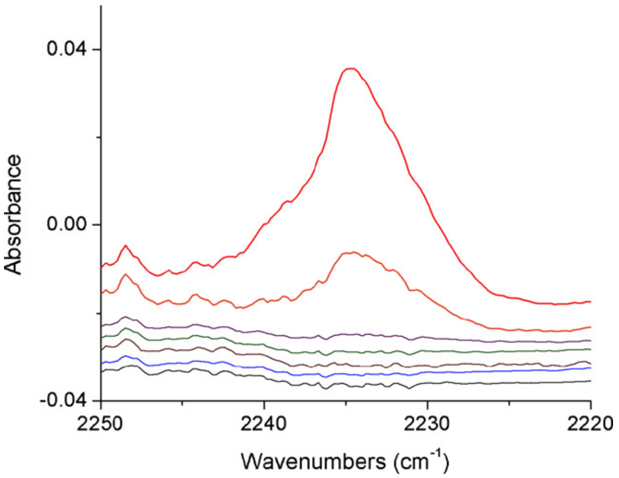


Fig. 7. FTIR spectrum in the region of the ν_{as} NCO vibrational mode of FNCO (2250–2220 cm^{-1}) of an Ar matrix initially containing FSO_2NCO at different irradiation times (from bottom to top: $t = 0$, 45, 300, 600, 900 and 5400 s).

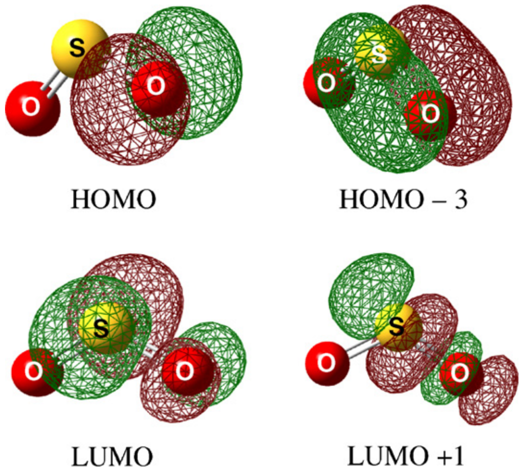


Fig. 9. Schematic representation of the donor and acceptor possibilities of the SO_2 molecule used as starting points for the geometry optimization of the SO_2:ClNCO complexes.

molecule. The elimination of CO, with the concomitant formation of CH_3SF, was clearly observed when the sample was irradiated with a more energetic light [34].

3.4. Theoretical study of the SO_2:ClNCO molecular complexes

The FTIR spectra of the irradiated matrices containing $ClSO_2NCO$ were tentatively interpreted in terms of the formation of a SO_2:ClNCO complex, favoured by the matrix cage effect. To help in the interpretation of the spectra, and also to understand the origin of the interactions between the two subunits, a theoretical investigation of this system was performed. The structure of van der Waals complexes could be usually explained by donor–acceptor interactions between the monomers (see, for example, Refs. [35–38] and references cited therein), since the geometry of the complex depends on the orbital overlap that favour the electron interaction.

As a starting point for the structure search of the SO_2:ClNCO complexes, the donor and acceptor characteristics of the two subunits were analysed. Both molecules, SO_2 and ClNCO, can act as electron donor or acceptor. In the NBO framework [39], the occupied molecular orbitals of SO_2 with high energy correspond to a lone electron pair localized on each of the oxygen atoms and πS=O orbitals. The LUMO (π^*S=O) and LUMO + 1 (σ^*S=O) orbitals, can act as electron acceptor in the complex. Fig. 9 shows a schematic representation of the interaction possibilities of the SO_2 that were taken into account for the optimization of the complexes. Similarly, the NBO analysis for ClNCO, depicted schematically in Fig. 10, reveals different interaction sites for this species, acting either as electron donor or acceptor in the complex.

Taking into account the analysis presented above, 12 possible 1:1 complexes were explored, since the dilution of the matrix make a complexation of a higher order difficult. First, bidimensional potential energy scans were performed, in which the corresponding intermolecular distance were varied between 2.0 and 4.0 Å in steps of 0.1 Å, while the intermolecular angle were scanned in 10° steps. Each of the energy minima was subsequently fully optimized by simultaneous relaxation of all the geometrical parameters of

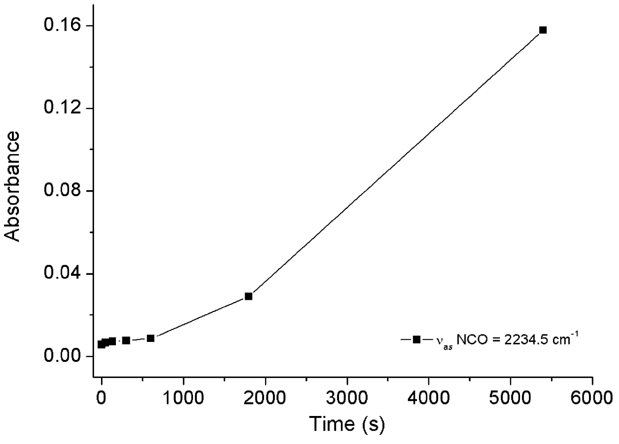


Fig. 8. Plot of the intensity of the absorption assigned to FNCO formed in an Ar matrix containing FSO_2NCO in an approximately 1:1000 proportion against the irradiation time.

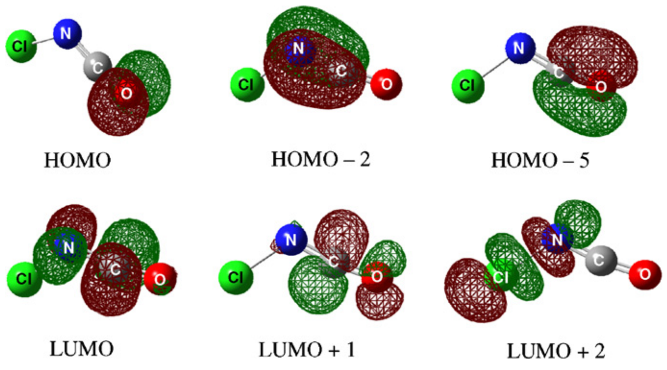


Fig. 10. Schematic representation of the donor and acceptor possibilities of the ClNCO molecule used as starting points for the geometry optimization of the SO_2:ClNCO complexes.

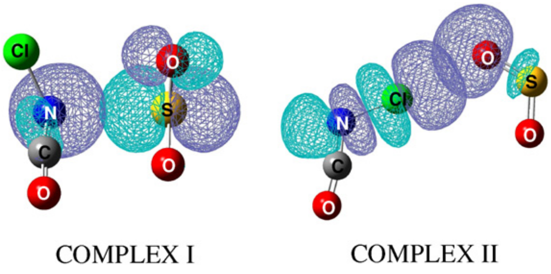
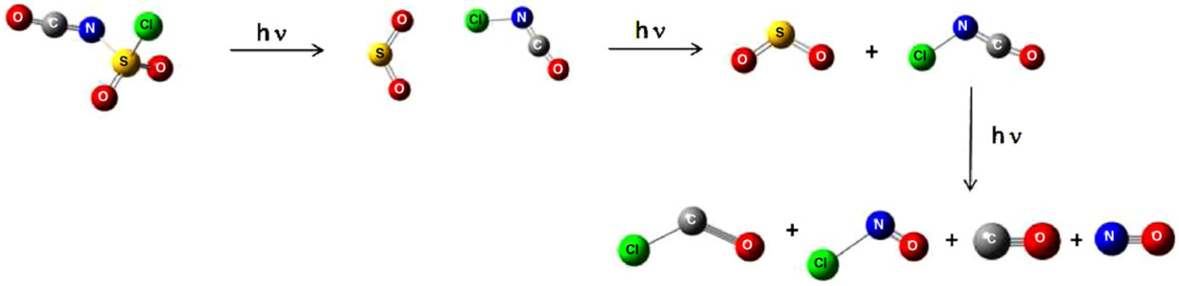


Fig. 11. Optimized structures of the SO_2:ClNCO complexes using the MP2/cc-aug-pVDZ approximation and schematic representation of the donor-acceptor orbital interactions.

Table 3
Calculated wavenumbers for the SO_2:ClNCO complexes and wavenumber shifts with respect to the monomers using the MP2/aug-cc-pVDZ and comparison with the experimental results obtained through the Ar-matrix photochemistry of $ClSO_2NCO$.

Calculated wavenumbers (cm^{-1}) MP2/aug-cc-p VDZ				Experimental wavenumbers (cm^{-1})		Assignment
Complex I	$\Delta\nu$ (cm^{-1})	Complex II	$\Delta\nu$ (cm^{-1})	Ar-matrix	$\Delta\nu$ (cm^{-1})	
2234.6 (100)	+1.2	2234.5 (100)	+1.1	2204.4	–	ν_{as} NCO
1281.8 (2)	−7.0	1292.5 (1)	+3.4	–	–	ν_s NCO
1211.8 (16)	+5.9	1203.3 (13)	−2.6	1347.2	−8.2	ν_{as} SO_2
1030.8 (2)	+9.5	1021.2 (2)	−0.1	1148.1	−4.1	ν_s SO_2
715.4 (3)	+8.3	703.7 (2)	−3.4	700.3	−7.4	ν ClN
603.1 (<1)	−2.0	600.3 (<1)	−4.8	635.1	–	$\delta_{in\text{-}plane}$ NCO
546.6 (2)	+2.3	545.0 (2)	+0.7	555.9	−3.3	$\delta_{out\text{-}of\text{-}plane}$ NCO
467.2 (3)	+4.2	466.2 (4)	+3.2	519.5	+0.6	δ_s, SO_2



Scheme 1. Outline of the mechanisms occurring on broad-band UV–visible photolysis of matrix-isolated $ClSO_2NCO$.

the complex, followed by a vibrational calculation to characterize the energy minima as stable structures, for which no imaginary frequencies occur.

Only two structures, depicted in Fig. 11, have remained as minima after the optimizations, while some of the other have presented imaginary frequencies or have converged to one of these two structures. The simulated IR spectra of these two complexes were then compared with the experimental IR absorptions assigned to the SO_2:ClNCO adduct formed through the matrix photochemistry of $ClSO_2NCO$. The comparison, presented in Table 3, allow us to conclude that the structure of the photochemically induced complex may correspond, most plausible, to complex II. As can be observed in Fig. 11, the two subunits in complex II are held together by the interaction of the lone pair of one of the oxygen atom of the SO_2 molecule, acting as the electron donor, with the unoccupied σ*Cl–N orbital of ClNCO, that corresponds to the acceptor species.

4. Conclusions

The matrix-isolation photochemistry of XSO_2NCO compounds, with X = F, Cl, were investigated. $ClSO_2NCO$ presents a rich photochemistry, with almost a total consumption of the molecule after 1 h of broad-band UV–visible photolysis in matrix conditions. On the other side, FSO_2NCO appears as a very stable product when exposed to the same radiation. Similar results were found in the matrix isolated photochemical study of $ClC(O)SCH_3$ [33] and $FC(O)SCH_3$ [34], being the fluorinated compound much more stable than the chlorinated one when exposed to radiation in the range between 200 and 800 nm.

The photochemically induced decomposition of $ClSO_2NCO$ is outlined in Scheme 1. The photoproducts have been identified by their IR spectra and the observed behaviours of the IR absorptions as a function of irradiation time. In the first place, the compound decomposes to give SO_2 and ClNCO molecules. The IR shifts of the observed signals with respect to the corresponding of the isolated molecules were interpreted in terms of the formation of a molecular complex, with the assistance of theoretical calculations. After a potential energy search for different structures of the complex, and a comparison of the theoretical spectrum with the experimental one, a structure in which the lone pair of one of the oxygen atom of the SO_2 interacts with the σ*Cl–N unoccupied orbital of ClNCO was proposed as the most plausible form to explain the experimental findings. In the second step, ClNCO decomposes in different parallel photochemical channels to give ClNO, NO, CO and the ClCO· radical, while SO_2, transformed from a complexed to an uncomplexed form, remains stable on photolysis.

As it was stated in the literature, the dominating source of inorganic halogen species in the stratosphere is the photochemical degradation of fully halogenated compounds, while in the troposphere, halogen species can only be released from less stable partially halogenated organic compounds [40]. It follows that the photolysis of halogenated species, such us ClNCO in this case, might supply the environment of reactive species capable to suffer chemical reactions.

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