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Gas-Phase Generation and Electronic Structure Investigation of Chlorosulfanyl Thiocyanate, ClSSCN

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The chlorosulfanyl thiocyanate molecule, ClSSCN, was generated in the gas phase through heterogeneous reaction of SCl_2 on the surface of finely powdered AgSCN for the first time. The reaction products were detected and characterized in situ by ultraviolet photoelectron and photoionization mass spectrometry. The molecular geometry and electronic structures of ClSSCN were investigated by a combination of PES experiment and theoretical calculations with the density functional theory and ab initio methods. It was found that the outermost electrons of ClSSCN reside in the Cl–S antibonding π orbital, predominantly localized on the sulfur atom, and the experimental first vertical ionization potential of ClSSCN is 10.20 eV. The dominant fragment $SSCN^+$ in the mass spectrum indicates that the ClSSCN cation prefers the dissociation of the Cl–S bond.

1. Introduction

The sulfur−sulfur bond is a structural feature of widespread occurrence in both organic and inorganic sulfur chemistry. Because of the frequency of disulfide bridges in the structure of many proteins, enzymes, and antibiotics, it plays an important role in stabilizing the structure and in determining the biological activity of the molecules.[1−3] Recently, considerable attention has been paid to the structure and conformational preferences of simple disulfides. Geometric gas-phase structures of noncyclic disulfides XSSX are characterized by a gauche conformation around the S−S bond. Structural studies of nonsymmetrically substituted disulfides of the type XSSY are less common. Recently, experimental studies on the structure of $FC(O)SSCF_3$, $FC(O)SSCH_3$, and $FC(O)SSC(O)CF_3$ have been performed in the gas phase.[4]

Thiocyanates with a SCN group attached directly to sulfur, XSSCN, which possess a sulfur−sulfur bond, have long been known. The first unstable thiocyanate containing a single S−S bond, NCSSCN, was synthesized by Söderbäck in 1918.[5] Various polysulfides NCS_nCN ($n < 9$) have been studied by Raman spectroscopy.[6] Thiazyl thiocyanide NSSCN was generated by an on-line process using NSCl passed over heated AgSCN and studied by gas-phase FTIR spectroscopy.[7]

We have a long-standing interest in the generation, spectroscopy, and electronic structure of small stable and unstable species. In this work, we present the generation of chlorosulfanyl thiocyanate ClSSCN and its subsequent detection and characterization by ultraviolet photoelectron and photoionization mass spectrometry with the help of density functional theory (DFT) and ab initio calculations. The joint spectroscopic and theoretical study provided useful information about the molecular structures, stability, ionization, reaction, and dissociation properties of the interesting unstable ClSSCN molecule.

2. Experimental Section

2.1. Generation. Silver thiocyanate was found to be an ideal precursor for the preparation of thiocyanates.[8,9] In this work,

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ClSSCN was generated by passing SCl_2 vapor over finely powdered AgSCN at 40 °C, and in situ photoelectron and mass spectra were recorded. The precursor SCl_2 was prepared according to a previous report,[10] and its PE spectrum is identical to that recorded previously.[11] AgSCN was purchased from the ACROS Company, and its purity was better than 99%. Before reaction, silver thiocyanate was dried in a vacuum (1×10^{-4} Torr) for 2 h at 60 °C.

2.2. Instrumentation. The experimental apparatus used in this work has been described previously.[12,13] Briefly, the photoelectron and photoionization mass spectrometer consists of two parts; one part is the double-chamber UPS-II machine,[14] the other is a time-of-flight mass spectrometer. The photoelectron (PE) spectrum was recorded on the double-chamber UPS-II machine[14] which was built specifically to detect transient species at a resolution of about 30 meV as indicated by the $Ar^+(^2P_{3/2})$ photoelectron band. Experimental vertical ionization energies are calibrated by the simultaneous addition of a small amount of argon and methyl iodide to the sample. Mass analysis of ions is achieved with the time-of-flight mass analyzer mounted directly to the photoionization point. The relatively soft ionization is provided by single-wavelength HeI radiation. The PE and PIMS spectra can be recorded within seconds of each other under identical conditions.

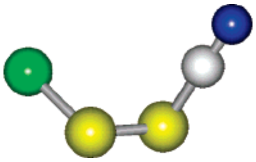
2.3. Computation. Electronic structure calculations were carried out using the Gaussian series of programs.[15] The geometries of the ClSSCN molecule were optimized with B3LYP and MP2 methods at the 6-311+G* and 6-311+G(3df) basis set levels. To assign the PE spectrum of ClSSCN molecule, we applied the outer-valence Green's function (OVGF) calculations with a 6-311+G* basis set, which include sophisticated correlation effects of the self-energy, to the molecules to give accurate results of the vertical ionization energies.[16] The adiabatic ionization energy was calculated by taking the difference between the energy of the neutral molecule and the ion at the CBS-QB3 level of theory.[17] Three-dimensional MO plots were obtained with the GaussView program. Each orbital displayed with the 0.08 isodensity value was oriented in a way that allowed for the best view.

Table 1. Total Molecular Energy (au) and Geometric Constants (Å, deg) for the Equilibrium Structure of ClSSCN at Different Theoretical Levels

	B3LYP/ 6-311+G*	B3LYP/ 6-311+G(3df)	MP2/ 6-311+G*	MP2/ 6-311+G(3df)
E	−1349.498367	−1349.536166	−1347.560489	−1347.777085
Cl−S	2.102	2.062	2.064	2.030
S−S	2.080	2.039	2.056	2.018
S−C	1.709	1.702	1.701	1.697
C−N	1.158	1.155	1.181	1.176
Cl−S−S	106.2	106.4	104.7	104.9
S−S−C	103.1	103.9	101.0	102.1
S−C−N	175.7	176.5	175.2	177.2
Cl−S−S−C	87.37	86.92	85.05	84.60
S−S−C−N	179.7	178.8	176.3	172.7

3. Results and Discussion

3.1. Molecular Structure. Geometry optimizations were performed for ClSSCN using the DFT and ab initio methods.



The structural parameters are depicted in Table 1 (for further geometric constraints, see the Supporting Information). It is well-known that the B3LYP method and the MP2 approximation with small or intermediate basis sets predict S−S, S−Cl, S−F, S−O, etc., bonds longer than they actually are. As demonstrated in test calculations for S_2Cl_2, the values derived with the MP2 method using a large basis set are expected to be close to the experimental values. Comparing the predicted Cl−S bond with the experimentally determined bond length of some similar molecules, we can see that the predicted Cl−S bond length of ClSSCN is close to that of the SCl_2[18] (2.015 ± 0.002 Å) and S_2Cl_2[19] (2.057 ± 0.002 Å) molecules. In several molecules containing triatomic pseudohalide groups, e.g., SCN, NCO, NNN, etc., it has been established that the atoms are not collinear.[20,21] When combining with ClS, the SCN angle shows about 5° deviation from linearity, which is similar to those of XSCN (X = CN,[22] SCN,[8] Cl[23]). The calculated S−C and C−N bond lengths are also close to the previous reported values. Particularly important parameters are the S−S bond length and Cl−S−S−C dihedral angle as the joint between the ClS and SCN moieties. Comparison of the S−S bond length in S_2X_2 (X = Cl,[24] H,[25] CSN_3[26]) shows that the S−S bond in ClSSCN is a typical $S^{II}-S^{II}$ bond (2.04−2.06 Å). The dihedral angle Cl−S−S−C that determines the molecular symmetry is in

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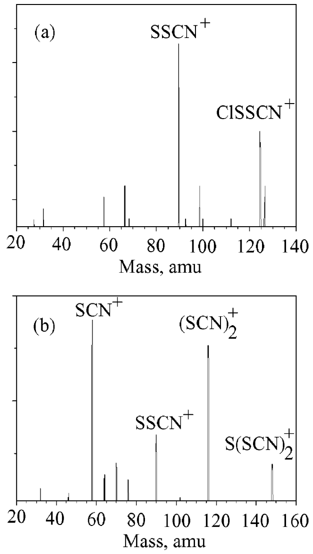
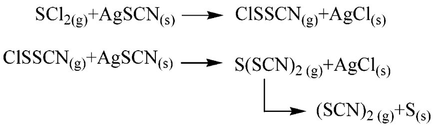


Figure 1. Photoionization mass spectra of (a) ClSSCN and (b) the gaseous products of the reaction at 70 °C.

close agreement with the experimental values of 84.8−85.2°, 83.5 ± 1.1°, 90.6 ± 0.5° found for S_2Cl_2,[19] S_2Br_2,[27] and S_2H_2, respectively.[28]

3.2. Photoionization Mass Spectrometry. The reaction process for generating ClSSCN was monitored by photoionization mass spectrometry. The ultraviolet photoionization mass spectra of the reaction products of gaseous SCl_2 and AgSCN at different temperatures are shown in Figure 1. Figure 1a depicts the mass spectrum of the reaction at 40 °C, which shows a typical fragmentation distribution of ClSSCN cation. The peaks in the spectrum are SCN^+, SCl^+, $SSCN^+$, S_2Cl^+, and $ClSSCN^+$, respectively, with the dominant features being the $SSCN^+$ and parent $ClSSCN^+$ peaks. The appearance of the ClSSCN molecular ion confirms its generation and identification. Normally, HeI photoionization produces a fragmentation distribution that is very similar to the distribution observed using electron-impact ionization. This may be rationalized by a similar energy deposition mechanism for the two methods, because the interaction energies (approximately tens of electronvolts) are comparable. As the strongest peak in the HeI PIMS of ClSSCN, the SX^+ (X = SCN) fragment is analogous to that of the electron-impact spectra of other ClSX molecules (X = Cl, SCl, and CH_2CH_3),[29] which mostly result from the direct dissociation of the Cl−S bond in the $ClSX^+$ parent ions.

Figure 1b illustrates the photoionization mass spectrum of the gaseous products of the reaction at 70 °C, which reveals features for SCN^+, $SSCN^+$, $(SCN)_2{}^+$, and $S(SCN)_2{}^+$, respectively. Other fragments came from the dissociation of molecular ions $(SCN)_2{}^+$ and $S(SCN)_2{}^+$. Several attempts were made to maximize the intensities of $S(SCN)_2{}^+$ by raising the reaction temperature, but they all failed until CS_2 appeared, the product of pyrolysis for AgSCN. A possible reaction route is illustrated by the following sequence



In a word, by analyzing the results of ultraviolet photoionization mass spectrometry, we confirmed the generation of ClSSCN under our experimental conditions. And the dominant fragment $SSCN^+$ found in the mass spectrum indicates that the ClSSCN cation prefers the dissociation of Cl−S bond.

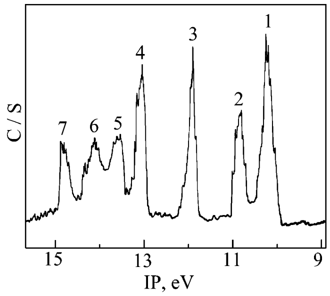


Figure 2. HeI photoelectron spectrum of ClSSCN.

Table 2. Experimental and Calculated Ionization Energies[a] and MO Characters for ClSSCN[a]

band	exp[b]		calcd		MO	character
1	10.20(V)	9.86(A)[c]	10.19(V)[d]	10.24(V)[e]	31	$\pi_{nb(ClS)}$
2	10.83		10.84	10.86	30	$\pi_{nb(SCN)}$
3	11.91		11.93	11.88	29	$\pi_{nb(ClS)} + \pi_{nb(SCN)}$
4	13.01		12.92	12.97	28	n_{Cl}, $\pi_{b\,(CN)}$
			13.07	12.99	27	n_{Cl}, $\pi_{b\,(CN)}$
5	13.65		13.66	13.68	26	$\pi_{b(ClS)}$
6	14.07		14.05	14.03	25	$\pi_{b(ClS)} + \pi_{b\,(SCN)}$
7	14.76		14.60	14.56	24	σ_{CN}

[a] All energies are in eV units; (V) = vertical ionization energy; (A) = adiabatic ionization energy; if no symbol is listed the vertical ionization energy is implied. [b] ±0.01 eV. [c] CBS-QB3. [d] ROVGF from the geometries of MP2/6-311+G*. [e] ROVGF from the geometries of B3LYP/6-311+G*.

3.3. Photoelectron Spectroscopy. The HeI photoelectron spectrum of ClSSCN is shown in Figure 2 (for that of the gaseous products of the reaction between SCl_2 and AgSCN, see the Supporting Information). It exhibits seven ionization bands in the low-energy region. We attempted to obtain the PE spectrum of $S(SCN)_2$, of which the crystal structure has been determined by X-ray methods,[30] but found that gaseous $S(SCN)_2$ is highly unstable and very easily decomposes into $(SCN)_2$ and S. The PE spectrum of the gaseous products of the reaction at 70 °C, corresponding to the mass spectrum in Figure 1b, shows the typical bands of $(SCN)_2$.[8]

The experimental and calculated ionization energies as well as the molecular orbital character of ClSSCN are listed in Table 2. It is noted that the ROVGF results are in good

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agreement with the experimental data.[31,32] Considering the PE spectra of S_2Cl_2[33] and $(SCN)_2$,[8] we can characterize the chlorosulfanyl thiocyanate by its bands that are attributed to the π systems of the ClS and SCN moieties, the nonbonding orbitals of chlorine atom, and the C−N bond. Therefore, the study of these bands may reflect the extent and character of the intramolecular interactions. The MO calculation predicts that the first three transitions for ClSSCN belong to an antibonding electron from the ClS and SCN π systems.

The first band, at 10.20 eV with an ionization onset of 9.88 eV, corresponds to the ionization process of ClSSCN (X^1A) → $ClSSCN^+$ (X^2A). The experimental result is in good agreement with the calculated vertical IPs. The first band is due to ionization of an electron from the π type of Cl−S antibonding orbital, predominantly localized on the sulfur atom. It is similar to the first ionization band of the analogous molecule SCl_2, ClSCN.[23,33] Because there is more S 3p involvement in the first orbital of ClSSCN, its first IP is lower than that of ClSCN (10.52 eV).

The second band is localized at 10.83 eV, which is in agreement with the ROVGF results. It can be described as a π_{SCN} antibonding orbital primarily residing on the sulfur atom. This orbital can also be regarded as being the antisymmetric combination of the sulfur lone-pair and π_{CN} orbital. In most cases, the spectra of pseudohalides are somewhat more complicated. The electronic structure of the SCN group can be explained in two ways. One can assume a single S−C bond and a triple C≡N bond. In this case, the appearance of two new bands resulting from the C≡N π bonds is expected in the low-energy region of the spectrum. Another interpretation is that the SCN unit is considered to be two perpendicular four-electron, three-center π systems. Consistent with analogous XSCN (X = CN,[23] SCN[8]) molecules, there are ionization events from two π_{CN} orbitals following the first band in ClSSCN (Figure 3). Corresponding to the second π_{CN} orbitals, the third PE band at 11.91 eV is the ionization result of the combination of π_{ClS} and π_{SCN} antibonding character.

The 3p nonbonding orbitals of the chlorine atoms are expected to locate in the energy range 11−14 eV. The first ionization potential (IP) of the Cl atom is 12.97 eV,[34] and that of chlorine-containing molecules exhibits an IP very close to this value (e.g., Cl_2 = 11.59,[35] HCl = 12.75,[35] ClF = 12.77 eV[36]). On this basis, the fourth and fifth bands at 13.01 and 13.65 eV are expected to be the results of electron ejection from orbitals containing considerable amounts of chlorine 3p character. The ionization of nonbonding electrons should raise a typical sharp intense band. However, the unusually large width of the fourth band suggests the possibility that this band is actually a composite of two overlapping transitions. And the calculated IPs of orbitals 28 and 27 indicate that both transitions are too close to being resolved. Because of the extensive incorporation of the SCN group, both have primary MO characters that are a mixture of nonbonding orbitals of the chlorine atom and bonding π_{CN}. The remaining chlorine orbitals form MO 26, which is strongly S−Cl bonding. It raises a typical band at 13.65 eV for ionization of electrons from bonding orbitals.

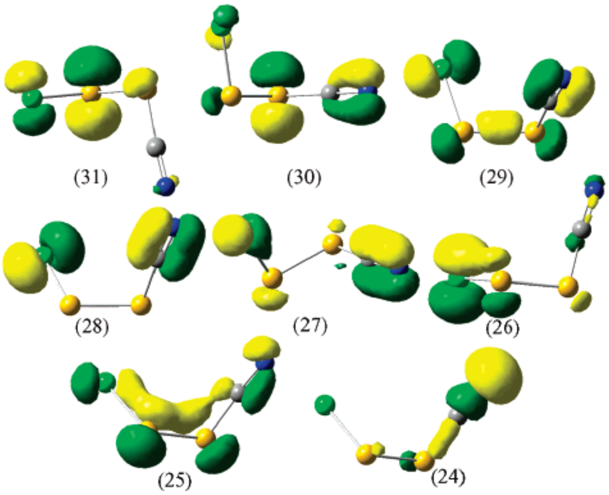

Figure 3. Characters of the first eight highest occupied molecular orbitals for ClSSCN.

The bands at higher energy 14.07 and 14.76 eV are due to the ionization of bonding orbitals, corresponding to a combination of π_{SCl} and π_{SCN} bonding and a σ_{CN} bonding, respectively (Figure 3).

In a word, the outer molecular orbital structure of ClSSCN was studied through photoelectron spectroscopy and quantum chemical calculations for the first time. The outermost electrons reside in the Cl−S antibonding π orbital, predominantly localized on the sulfur atom. The halogen nonbonding electrons are more tightly bound than the antibonding electrons from the ClS and SCN π systems.

4. Conclusions

The novel transient species ClSSCN was generated in the gas phase for the first time through in situ heterogeneous reaction of gaseous SCl_2 with AgSCN. The gaseous reaction products were detected and characterized by ultraviolet photoelectron and photoionization mass spectrometry. The geometric and electronic structures of ClSSCN were investigated by a combination of PES experimental and theoretical studies with the help of DFT and ab initio calculations. The assignment of the PES bands is reasonably supported by previous studies on analogous molecules, as well as the ROVGF and CBS-QB3 calculations. Both the spectroscopic and theoretical investigations have proved the formation of the chlorosulfanyl thiocyanate molecule and suggest that the outermost electrons reside in the Cl−S antibonding π orbital,

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predominantly localized on the sulfur atom. The halogen nonbonding electrons are more tightly bound than the antibonding electrons from the ClS and SCN π systems. The dominant fragment $SSCN^+$ in the mass spectrum indicates that the ClSSCN cation prefers the dissociation of the Cl−S bond.

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Supporting Information Available: HeI photoelectron spectrum of the gaseous products $(SCN)_2$ of the reaction between gaseous SCl_2 and AgSCN at 70 °C; calculated geometric constants for the equilibrium structure of the neutral molecule and cation; orbital energies with the first eight highest occupied molecular orbitals; and energies of the dissociated fragment of $ClSSCN^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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