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First Experimental Observation of Gas-Phase Nitrosyl Thiocyanate

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The unstable nitrosyl thiocyanate molecule has been generated in the gas phase for the first time from an in situ heterogeneous reaction at low temperature. The product was detected and characterized by a photoelectron spectrometer-photoionization mass spectrometer (PES-PIMS). The electronic and geometric structures of the molecule were investigated with the help of quantum chemical calculations at the B3LYP, CBS-QB3, and CCSD(T) levels. The joint spectroscopic and theoretical studies provided evidence for the formation of nitrosyl thiocyanate, and indicated that the molecule adopts an open-chain, bent structure with the NO and SCN groups bonding by a relatively strong interaction.

Introduction

The generation and spectroscopy of sulfur–nitrogen compounds, which are known to be extremely unstable and highly reactive, is one of the very active areas of chemistry.[1,2] The thiocyanate group, SCN, is ambidentate and has the potential to bond through sulfur or nitrogen forming RSCN or RNCS type molecules. In vivo thiocyanate originates from smoking cigarettes and dietary items that contain or generate nitriles. It forms during detoxification of cyanide and normally occurs in blood at a concentration less than 2 mg per 100 mL.[3] Given the biochemical significance of NO/NO^+, nitrosyl thiocyanate, ONSCN, (**1**) is a species of potential biochemical interest.

ONSCN is a highly unstable blood-red compound known only in solution, which is formed by mixing a very acidic solution of sodium nitrite with a solution of potassium thiocyanate.[4] At room temperature ONSCN decomposes into NO and $(SCN)_2$ and shows the typical nitrosyl and thiocyanate group reactions [see Equation (1) and (2)].

$$H^+ + HNO_2 + SCN^- \rightleftharpoons ONSCN + H_2O \tag{1}$$

$$2\ ONSCN \rightleftharpoons 2\ NO + (SCN)_2 \tag{2}$$

Despite the instability, it is widely used as a nitrosating agent in organic chemistry and biochemistry.[5,6] However, its structure is unknown since it is very unstable at high concentration and room temperature. Westwood et al. pointed out that potential media for generating and investigating **1** are the dilute gas-phase or an inert low-temperature matrix, which would provide important information on its full electronic and geometric characterization.[7]

The calculated results predicted that **1** has planar, bent structures and that isomer ON–SCN (**1a**) is more stable than ON–NCS (**1b**),[7–9] in agreement with the notion that S–nitrosation is more favourable through a soft-soft interaction, characterized by a large charge transfer from the nucleophile to the electrophile.[7,8,10]

On the other hand, there has been interest in simple, often transient, species containing triatomic pseudohalide groups e.g. –SCN, –NCO, –NNN. Recently several of these have been detected and spectroscopically characterized. Klapötke et al. have successfully isolated nitrosyl azide ON–N_3 at low temperature.[11] They studied the reaction of AgOCN with $ClNO_2$, ClNO, and BrNO by means of gas-phase IR spectroscopy, and proposed a reaction mechanism involving the formation of two neutral intermediates OCN–NO_2 and OCN–NO.[12] Our group recently reported the in situ generation of ONNCO in the gas phase and the subsequent characterization by photoelectron spectroscopy.[13] Thiazyl thiocyanide NS–SCN has been produced by an online process using NSCl passed over heated AgSCN and monitored by gas-phase FTIR spectroscopy.[14] Westwood and colleagues tried to observe the very interesting NS–NCO molecule from the reaction of $NSCl_{(g)}/AgNCO_{(s)}$, but in fact they observed another species, S_2N_2CO, recorded by HeI photoelectron, photoionization mass and mid-infrared spectroscopy.[15] The unexpected result has prompted them

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to carried out an ab initio study of some isomers of CN_2OS,[7] which also includes the ONSCN compound.

In this work we report the first gas phase generation and characterization of the unstable molecule **1** and its investigation by HeI photoelectron spectroscopy−photoionization mass spectroscopy and quantum chemical calculations.

Results and Discussion

Molecular Geometries

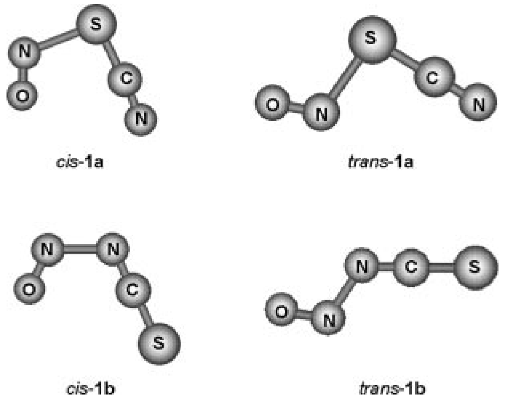
Given that both the thiocyanate and isothiocyanate exist for the CH_3 derivatives, we have performed an identical calculation for the molecules **1a** and **1b**. As shown by ab initio calculations[7–9], **1a** and **1b** both have planar, bent structures. Each molecule has, in principle, two rotational isomers, the *cis* and *trans* isomers. The calculated structural parameters are compiled in Table 1 (Figure 1).

Table 1. Calculated structures of planar nitrosyl thiocyanate.[a]

	cis-**1a**	*trans*-**1a**	*cis*-**1b**	*trans*-**1b**
r(O–N)	1.136	1.142	1.140	1.154
r(N–S) or *r*(N–N)	2.081	2.043	1.686	1.552
r(S–C)	1.667	1.676	1.567	1.561
r(C–N)	1.160	1.158	1.213	1.219
(S–C–N)	174.5	179.6	178.7	176.7
(O–N–S) or (O–N–N)	115.2	114.4	115.3	112.4
(N–S–C) or (N–N–C)	95.35	94.45	116.3	119.6

[a] Bond lengths in Å and angles in degrees at B3LYP/6-311++G(3d) level.

All calculations predict **1a** to be the more stable in the gas phase. According to the CCSD(T)/6-311++G(3d) level of theory, the more stable *cis*-**1a** isomer gives a total energy less than that of *cis*-**1b** by 11.2 kcal mol^{-1}.



cis-**1a** *trans*-**1a**

cis-**1b** *trans*-**1b**

Figure 1. Stable conformers of nitrosyl thiocyanate.

Figure 2 shows a limited 3D plot of the potential energy surface, which indicates that both the *cis* and *trans* conformers of **1a** lie in a deep well with respect to the N–S coordinate and need only rotate around the long N–S bond with a low barrier. At the CBS-QB3 level the energy gap between the *cis* and *trans* conformers is calculated to be 2.0 kcal mol^{-1}, and the transition state resides just 4.5 kcal mol^{-1} above the *trans* conformer.

In several molecules containing triatomic pseudohalide groups e.g. –SCN, –NCO, –NNN, etc., it has been established that the atoms are not colinear. When combining the SCN ligand with NO, the SCN angle shows a deviation of about 5° from linearity, which is similar to those of XSCN (X = CN[16], SCN[17], Cl[18], Br[18]). Comparing the predicted NO bond with experimentally determined bond lengths of similar molecules, we find that the predicted O–N bond of **1** (1.136–1.154 Å) lies between the diatomic NO (1.151 Å)[19] and ClNO (1.139 Å)[20], favoring ClNO slightly. However, on considering the linearity from the

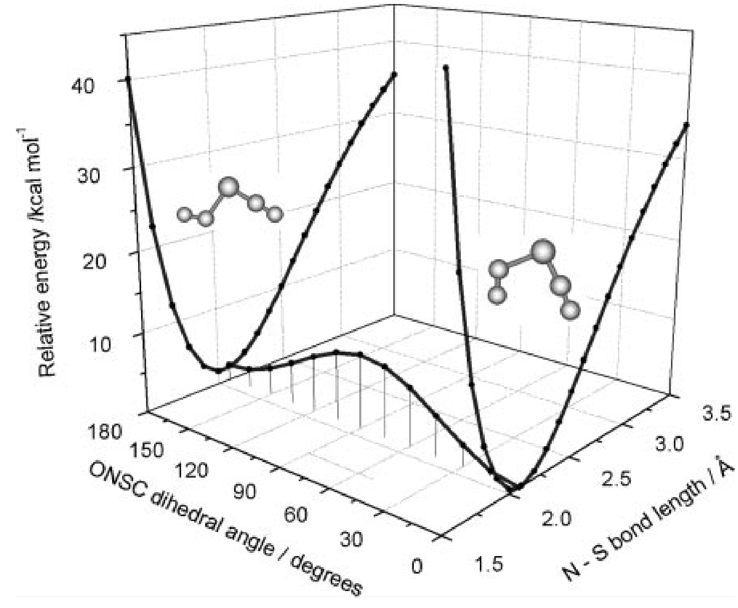


Figure 2. Calculated [B3LYP/6-311++G(3d)] potential-energy surfaces for the *cis* and *trans* conformers along the N–S coordinate together with the interconnecting surface obtained by torsion of the N–S bond in **1a**.

point of the whole molecule **1a** the calculated N–S bond length (2.043–2.081 Å) is much longer than that of S_2N_2 (1.65 Å)[21] and NSCN (1.49 Å)[22], and the NSC angle (95.35–94.45°) is much smaller than the NSC in NSCN[22] (109.3°) and ∠SSC in $(SCN)_2$[17] (108.2°). These data indicate that a strong interaction exists between the NO and SCN groups.

Photoionization Mass Spectroscopy

The HeI photoionization mass spectrum (Figure 3) observed at –60 °C is relatively simple. The main peaks in the spectrum are NO^+, SCN^+, $ON–SCN^+$, and Cl^+, respectively, with the dominant feature being the NO^+ peak. Since there are no NO, SCN, and Cl photoelectron peaks in the PE spectrum (Figure 4), it is suggested that the signals of NO^+, SCN^+, and Cl^+ come from the dissociation of parent ions. For some molecules, HeI photoionization produces a fragmentation ion distribution similar to that of electron-impact ionization.[23] This may be rationalized by a similar energy deposition mechanism for the two methods, as the interaction energies (some tens of electronvolts) are comparable. The dominant fragment ions NO^+ and X^+ (X = SCN) in the HeI photoionization mass spectra are analogous to those of other ONX molecules (X = Cl, CH_3) in the electron impact spectra. They mostly result from the direct dissociation of the parent ions ONX^+. Although there is no parent ion peak for ClNO in the photoionization mass spectra of the products, the PE bands of the ClNO molecule appear in the photoelectron spectrum (Figure 4). This indicates that the signals of Cl^+ and a part of NO^+ originate from the dissociation of $ClNO^+$, which is very unstable and dissociates to Cl^+/NO or NO^+/Cl once it is formed. This also agrees with the electron impact mass spectrum of ClNO, which also shows no $ClNO^+$ peak. In a word, we demonstrated that we generated **1** under our experimental conditions though we could not distinguish **1a** and **1b** isomers from a photoionization mass spectroscopy study.

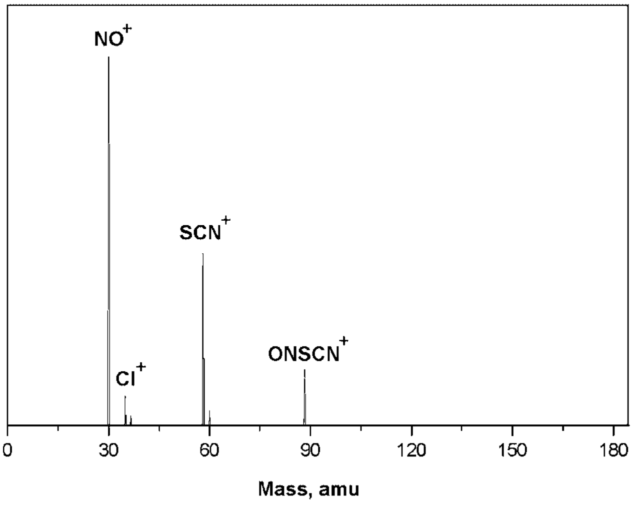


Figure 3. The HeI photoionization mass spectrum of nitrosyl thiocyanate.

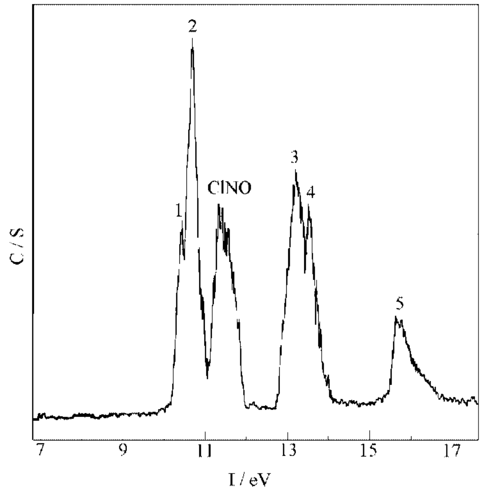


Figure 4. The HeI photoelectron spectrum of nitrosyl thiocyanate.

Photoelectron Spectroscopy

The HeI photoelectron spectrum of **1** recorded at –60 °C is shown in Figure 4. It does not show any of the decomposing products but only the reactant ClNO[20] with an unnumbered band between 11.0 and 12.0 eV. The reaction was also monitored simultaneously by photoionization mass spectroscopy. The PE spectrum clearly shows a group of distinct bands below 11 eV, another group in the 12.5–14 eV range, and one additional band above 15 eV. In previous photoelectron spectroscopy experiments, XSCN (X = Cl, Br), instead of XNCS, was produced by passing gaseous halogen over solid AgSCN.[18] Our photoelectron spectroscopic experimental results also agree better with the ROVGF and CBS-QB3 calculations on **1a** than those on **1b** (see Table 2), though we cannot completely exclude the existence of **1b**. There is no noticeable difference between the orbital energies of the two most stable conformers of *cis*- and *trans*-**1a**. So our discussion is reduced to the analysis of the slightly more stable conformer *cis*-**1a** only. The experimental and calculated ionization energies for the *cis*- and *trans*-**1a** are collected in Table 2. It is noted that the ROVGF results are in good agreement with the experimental data.[13,24]

The unstable nitrosyl thiocyanate (**1**) can be characterized by its three groups of bands, which can be attributed to the lone electron pair of sulfur, the π system, and the S–C bond. Therefore, the study of these bands may reflect the extent and character of the intramolecular interactions. 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 as a two perpendicular four-electron three-centre π system, which suggests four

Table 2. Experimental and computed ionization energies (eV) for the isomers of **1**.

Exp. I_v	Calcd. *cis*-**1a**		*trans*-**1a**		*cis*-**1b**	*trans*-**1b**
10.45	10.338[a]	10.485[b]	10.440[a]	10.407[b]	9.840[a]	10.154[a]
10.65	10.733[a]		10.686[a]		10.195[a]	10.198[a]
13.20	13.423[a]		13.455[a]		12.673[a]	12.389[a]
	13.454[a]		13.485[a]		13.792[a]	14.070[a]
13.46	13.716[a]		13.767[a]		13.868[a]	14.148[a]
15.68	15.604[a]		15.732[a]		15.543[a]	15.733[a]

[a] According to C_s symmetry using the ROVGF/6-311++G(3d) method. [b] According to C_s symmetry using the CBS-QB3 method.

new bands in the spectrum: the high-energy bonding in- and out-of-plane π orbitals [$\pi_b(a')$ and $\pi_b(a'')$] and the low-energy nonbonding in- and out-of-plane π orbitals [$\pi_{nb}(a')$ and $\pi_{nb}(a'')$]. If the molecule is linear, the perpendicular MO pairs are degenerate. In the case of the strongly bent ONSCN, we would expect, using HeI radiation, to observe ionization from the six highest filled molecular orbitals. The appearance of all the π_{SCN} bands is expected on the basis of the calculations. And the S lone pair in the SCN group is a part of the π system. The additional bands of a pσ type orbital (σ_{SCN}, localized mainly on N) and a σ type orbital (S–C bonding) are expected in the photoelectron spectrum.

The shape and intensity of the first group of bands suggest that it should be attributed to two ionization processes. Consistent with analogous molecules XSCN (X = H[25], CH_3[26], Cl[18], Br[18], I[27]), the first two bands are assigned to the nonbonding in- and out-of-plane π orbitals [$\pi_{nb}(a')$ and $\pi_{nb}(a'')$] partially localized on the pseudohalide group. In the molecule ONNCO[13], the first two orbitals $\pi_{nb}(a')$ and $\pi_{nb}(a'')$ are distributed fairly evenly over the whole molecule, whereas for *cis*-**1a** there is a dominant S 3p involvement in the first two π orbitals as indicated by the two relatively low ionization potentials. These are also supported by the quantum chemical calculated results. The first band of ONNCO at 10.71 eV is attributed to an in-plane combination of a strong antibonding π_{NO} and nonbonding π_{NCO} with the same a′ symmetry.[13] Therefore, the first ionization process of ON–SCN can easily be assigned by combining the NO and SCN moieties.

The vertical ionization potential of the first band (10.45 eV) is in good agreement with the calculated ionization energy of *cis*-**1a** (10.338 eV by ROVGF method and 10.485 eV by CBS-QB3). It is a structureless band and can be compared to the first PE band of CH_3NO[28] at 9.70 eV and ONCN[29] at 11.50 eV. The HOMO 18a′ (Figure 5) for this ionization process can be described as an in-plane combination of nonbonding π_{SCN} and antibonding π_{NO}. It also shows that an interaction may exist between both of the moieties. The second band at 10.65 eV is sharp and characteristic of a nonbonding orbital with considerable lone-pair character. It derives from the ionization of the 4a′′ orbital and coincides with the calculation value of 10.733 eV. This band is ascribed to the nonbonding out-of-plane π_{SCN} [$\pi_{nb}(a'')$], mainly localized on the sulfur atom. This orbital can also be regarded as the antisymmetric combination of the out-of-plane sulfur lone-pair and π_{CN} orbital.

An interesting and important feature for PE spectra of compounds containing SCN is that the energetic order of the first two highest occupied orbitals is $\pi_{nb}(a'') < \pi_{nb}(a')$, such as for XSCN (X = H, CH_3, Cl, Br, I).[18,25–27] However, this trend is reversed in ONSCN, as is the case in ONNCO.[13] Because of the extensive incorporation of the π_{NO} antibonding character into the 18a′, with $\pi_{nb}(a')$ character, its ionization becomes less energetic. Compared with analogous molecules XSCN (X = CH_3, Cl, Br, I)[18,26,27] the separation of $\pi_{nb}(a')$ and $\pi_{nb}(a'')$ is also quite narrow. The obvious decrease of the separation of nonbonding π orbitals (π_{nb}) in *cis*-**1a** reflects the direct interaction between the π_{SCN} and π_{NO} moieties. This interaction is so strong that it shifts the $\pi_{nb}(a')$ band causing the exchange in the sequence of the $\pi_{nb}(a')$ and $\pi_{nb}(a'')$ bands.

The two bands between 12.5–14.0 eV come from the ionization of the two bonding π orbitals (a′ and a′′) and a terminal –SCN pσ type orbital, as considerable mixing between orbitals of the same symmetry often occurs for the XSCN molecule.[18,26,27] Combining our calculated ROVGF results and the assignments of the PE spectrum of other XSCN molecules, we assigned the third band as arising from the ionizations of the in-plane bonding π_{CN} orbital 17a′ and out-of-plane bonding π_{SCN} orbital 3a′′, and the fourth band at 13.46 eV as arising from the ionization of the 16a′ pσ type orbital. This is in good agreement with the calculation value 13.716 eV, which is also in good agreement with the corresponding experimental values of the PE band from pσ type orbitals in ClSCN[18] at 13.66 eV and BrSCN[18] at 13.43 eV.

The PE band at 15.68 eV is the ionization of the 15a′ orbital, which is in agreement with the calculated value 15.604 eV. The primary MO character is $\sigma_{(S-C)}$ bonding with considerable s character on all the atoms; similar bands occur in the PE spectrum of HSCN[25] (Figure 5).

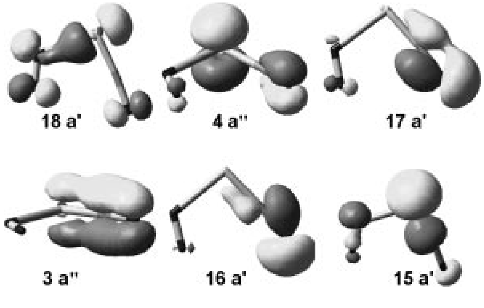


Figure 5. Characters of the first six highest occupied molecular orbitals for *cis*-**1a**.

Based on the above discussion, we consider the photoelectron spectrum shown in Figure 4 to be that of **1** and the assignment of the photoelectron spectroscopic bands is reasonably supported by previous studies on analogous molecules, as well as the ROVGF and CBS-QB3 calculations. From the experimental PE spectra of **1** and some thiocyanate with similar symmetry, a clear correlation of the respective bands can be seen. One important difference is the inversion in the sequence of the $\pi_{nb}(a')$ and $\pi_{nb}(a'')$ bands, which has relations with the interaction between the π_{SCN} and π_{NO} moieties in **1**. However, the isomers **1a** and **1b** cannot be reliably distinguished by our photoelectron spectroscopy experiment. It is hoped that this study could stimulate further experimental work to enable the different isomers of this important unstable species to be distinguished.

Conclusions

The unstable molecule **1** has been generated in the gas phase for the first time by means of an online reaction of gaseous nitrosyl chloride with silver thiocyanate at low temperature. Using the home-made PES-PIMS we have obtained the photoelectron and mass spectra of **1**. With the help of theoretical studies, the electronic and geometric structures of **1** were investigated by photoelectron spectroscopy. The assignment of the photoelectron spectroscopic bands is reasonably supported by previous studies on analogous molecules, as well as by the ROVGF and CBS-QB3 calculations. Both the spectroscopic and theoretical investigations have proved the formation of **1**, and suggest that the molecule adopts an open-chain, bent structure. It is indicated that the NO and SCN moieties bond by means of a relatively strong interaction, which is related to the inversion of the first two π orbitals. This fact proves that our home-made PES-PIMS can be used as a powerful tool for the investigation of transient species in the gas phase.

Experimental Section

Over the past decades, ultraviolet photoelectron spectroscopy (UPS) has established itself as one of the important techniques used to obtain a direct measure of atomic and molecular energy levels. Moreover, some groups using photoelectron spectroscopy have made great progress and extended the application to transient or unstable species. Using photoelectron spectroscopy and infrared matrix isolation spectroscopy, Dyke et al. studied the thermal decomposition of organic azides.[30–32] By combining HeI photoelectron spectroscopy with mid-infrared absorption and mass spectroscopy, Westwood and colleagues investigated ground, excited, and ionic states of various small unstable molecules.[33–35] To improve our ability of studying the transient species, our group has built a photoelectron spectrometer-photoionization mass spectrometer (PES-PIMS) as described elsewhere.[23] A schematic diagram of the PES-PIMS is shown in Figure 6. The modification of the spectrometer was based on the HeI photoelectron spectrometer. An important feature of our experiment is the measurement of both mass and PE spectra. The ions are produced by soft ionization of transient species with HeI (21.2 eV) radiation. The ions formed are transferred by a set of electrostatic lenses. The field-free drift region has a length of 120 cm. A dual MCP is used to detect charged particles. The signal is recorded using a 500 MHz digital oscilloscope (Tektronix, TDS2024) and then transferred to a PC for storage and analysis.

The photoelectron spectrum was recorded on a double chamber UPS machine-II,[36,37] which was built specifically to detect transient species at a resolution of about 30 meV as indicated by the $Ar^+(^2P_{2/3})$ photoelectron band. Experimental vertical ionization energies (Iv in eV) are calibrated by simultaneous addition of a small amount of argon and methyl iodide to the sample.

When the mass spectra are measured, pulsed positive voltages are applied to the repelling and attracting electrodes, and then the cation is extracted into the time-of-flight drift region. Proper pulsed voltages U_1 and U_2 are chosen to meet the requirement of the first spatial focus to pursue the high mass resolution. The optimum mass resolution can reach 410 at $m/z = 254$. When the photoelectrons are collected, both U_1 and U_2 are set to 0. Hence, the photoelectron can fly directly to the energy analyzer through the electron path. Thus, the photoelectron and photoionization mass spectra can be recorded within a few seconds.

In general, we can observe the electronic structure by the photoelectron spectrum and the dissociation of molecular ions by mass spectra with this experimental apparatus. The joint spectrometer is characterized by at least two advantageous features. Firstly, the reaction conditions can be optimized online to improve the yield of the desired species. It can be used to investigate not only general gaseous samples but also transient species produced by gas-solid reactions or microwave discharge etc. Other inlet modifications with high-temperature furnaces or low-temperature cells can also be easily attached to the spectrometer. Secondly, with the advances of fast detection and high sensitivity TOFMS will help us to resolve some problems of photoelectron spectroscopy in complicated systems.

Generation and Detection of ONSCN

The intermediate **1** was generated at –60 °C by passing gaseous ClNO over finely powdered AgSCN, similarly for producing other

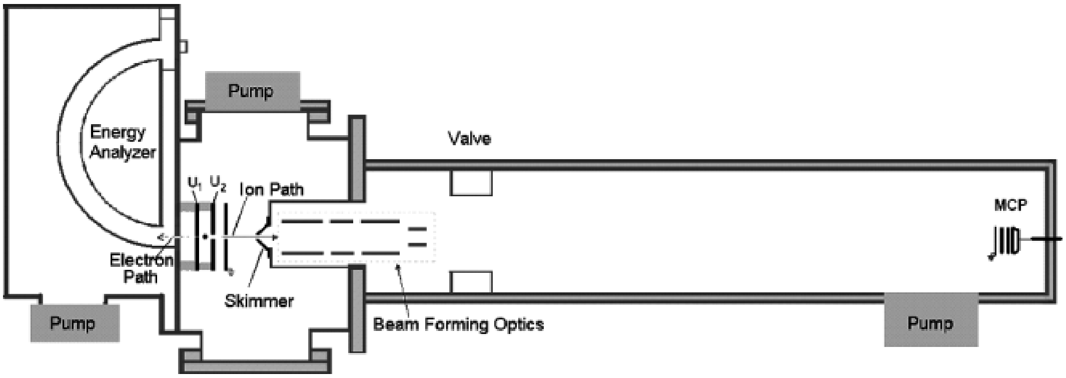


Figure 6. Schematic diagram of the experimental apparatus PES-PIMS. It mainly consists of an ultraviolet photoelectron spectrometer and a home-made time-of-flight mass spectrometer (TOFMS). The photo source (HeI) in the ionization region is marked with a dot.

unstable species like ONNCO[13] and NSSCN[14]. The reaction was monitored simultaneously in situ by photoelectron and photoionization mass spectra. The reaction is be represented by Equation (3).

$$\mathrm{ClNO\ (g) + AgSCN(s)} \xrightarrow{-60\ ^{\circ}\mathrm{C}} \mathrm{ONSCN\ (g) + AgCl\ (s)} \qquad (3)$$

AgSCN (ACROS) was dried in vacuo (10^{-4} Torr) for 2 h at 60 °C before the experiment was performed. ClNO was prepared as reported[38] and identified by photoelectron[20] and photoionization mass spectroscopy.

Quantum Chemical Calculations

On the basis of the previous theoretical discussions on the isomers of CN_2OS[7], we have only considered the four most stable isomers, *cis*- and *trans*-**1a**, *cis*- and *trans*-**1b**, which are related to our experiment. The geometries were optimized at the B3LYP/6-311++G(3d) level, which is a hybrid functional method based on the Becke's three-parameter nonlocal exchange functional[39], with the nonlocal correlation due to Lee, Yang, and Parr.[40] To determine the barrier between the *cis* and *trans* rotamers, the potential energy surface scans for internal rotation around the N–S bond were carried out at the B3LYP/6-311++G(3d) level before the appropriate transition states were optimized at the CBS-QB3 level.[41] The ionization energies for *cis* and *trans* isomers were calculated at the ab initio level according to Cederbaum's outer valence Green's function (OVGF) [42] method at the 6-311++G(3d) basis set, and by taking the difference between the energy of the neutral atom and the ion (CBS-QB3 calculation). All the calculations were performed using the Gaussian 03 program package.[43]

Supporting Information (see footnote on the first page of this article): HeI photoionization mass spectra of ClNO, and reaction products of $NOCl_{(g)}/AgSCN_{(s)}$ at room temperature are included.

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