20 M/Chrom WAW, 90 °C) showed a 55% yield of methyl ethyl ketone and a 5% yield of a component having a retention time equal to that of 1-buten-3-one.

Reaction of $CpMo(CO)_3(CH_3)$ with C_2H_4 in the Presence of 1-Buten-3-one. A 36-mg (0.138-mmol) sample of $CpMo(CO)_3(CH_3)$ was weighed into an NMR tube fitted with a ground-glass joint and 2.5 μL (ca 0.03 mmol) of 1-buten-3-one introduced with a syringe. The tube was quickly attached to a vacuum line, cooled to 77 K, and evacuated. Ethylene (0.25 mmol) and 0.42 mL of THF-d_8 were condensed in and the tube was sealed. The tube was heated to 100 °C, and NMR spectra were recorded over the next 18 h. In 1 h, 46% of the $CpMo(CO)_3(CH_3)$ (0.36 ppm) was consumed and a 25% yield of 2-butanone (δ 0.96 (3 H, t), 2.37 (4 H, q), 2.02 (3 H, s)) observed. A total of 80% of the 1-butene-3-one had decomposed. In 6 h, the reaction was 95% complete and a 54% yield of 2-butanone was found. After 18 h all $CpMo(CO)_3(CH_3)$ had been consumed and a 58% yield of 2-butanone was measured. The tube was broken open, and the volatile contents were vacuum distilled and analyzed by GC (10 ft × $^1/_4$ in. 20% Carbowax 20M/Chrom WAW, 90 °C). A 55% yield of --butanone was confirmed relative to added internal standard (pentane). Only traces (<5%) of 2-buten-3-one were present.

Acknowledgment. We are grateful to Professor M. Y. Darensbourg for supplying spectral data on chromium hydrides and for helpful discussions. We also thank Professors J. Halpern and J. Norton for several stimulating discussions on metal hydride/metal alkyl reactions, and Professor Halpern for disclosing results on the manganese system prior to publication. We appreciate several insightful comments from the reviewers. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract Number W-7405-ENG-48.

Preparation and HeI Photoelectron Spectra of the Halogen Thiocyanates, XSCN (X = Cl and Br)

D. C. Frost, C. B. MacDonald, C. A. McDowell, and N. P. C. Westwood*

Contribution from the Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Y6. *Received September 10, 1980*

Abstract: The unstable chlorine and bromine thiocyanate molecules have been generated in the gas phase by reaction of AgSCN (solid) or $(SCN)_2$ (gas) with molecular chlorine or bromine, respectively. ISCN does not appear to be formed by this route. The structures are established as nonlinear X—S—C≡N molecules, and the observed HeI photoelectron spectra are assigned on this basis with the assistance of minimal basis ab initio calculations. The electronic structures of these molecules lie between those of SX_2 and $S(CN)_2$; the chemical behavior suggests an analogy with the interhalogen compounds.

Simple thiocyanates are rather intriguing compounds, since the SCN group is ambidentate, bonding at either S or N, and forming R—S—C≡N (thiocyanate) or R—N=C=S (isothiocyanate) type molecules.[1,2] The parent acid exists as HNCS in the gas phase,[3] whereas both methyl derivatives, CH_3NCS and CH_3SCN, can be isolated.[4] The halogen thiocyanates, on the other hand, are known only as unstable intermediates in solution, chemical and spectroscopic studies indicating an XSCN rather than an XNCS structure.[5-8] This is in contrast to the substituted oxygen analogues, XNCO (X = CN, Cl, Br, and I), which bond only through nitrogen, and which we have investigated previously by ultraviolet photoelectron spectroscopy (UPS).[9,10]

In this work we present the preparation, detection, and ultraviolet photoelectron spectra of the XSCN molecules (X = Cl and Br). Since these unstable molecules are quite novel in the gas phase, there are several interesting features relevant to such a study. A priori it is uncertain whether the halogen is bonded through S or N in the gas-phase molecules, and this we shall attempt to establish. Second, we have previously studied the photoelectron spectrum of the archetypal pseudohalogen, $(SCN)_2$.[11] This molecule is the starting point for formation of the halogen thiocyanates, and so we may view all of these molecules as interhalogen compounds with the SCN group possessing an electronegativity somewhere between Br and I. Equilibria between $(SCN)_2$ and X_2 (compare, e.g., BrCl, ICl, IBr, etc.) may thus be anticipated. Third, as found with the halogen azides and isocyanates,[10] it is of some interest to establish the nature of the interaction between the off-axis substituent and the pseudohalide grouping. By analogy with the structures of the XN_3 and XNCO molecules we expect a linear, or quasilinear, SCN group. To this end, we have also conducted some ab initio calculations in order to evaluate the electronic and geometric structures. Finally, the XSCN molecules provide the intermediate stage between the $S(CN)_2$[12] and SX_2 (X = Cl[13,14] and Br[15,16]) molecules previously studied by UPS, and thus an investigation of the XSCN molecules provides an assessment of how the orbital energies change as X is replaced by CN.

---

(1) Bacon, R. G. R. "Organic Sulphur Compounds"; Kharasch, N., Ed.; Pergamon: New York, 1961; pp 306–25.

(2) Guy, R. G. "The Chemistry of Cyanates and their Thio derivatives", Patai, S., Ed.; Wiley: New York, 1977; Part II, pp 819–86.

(3) Beard, C. I.; Dailey, B. P. *J. Chem. Phys.* **1950**, *18*, 1437–41.

(4) Lett, R. G.; Flygare, W. H. *J. Chem. Phys.* **1967**, *47*, 4730–50.

(5) Angus, A. B.; Bacon, R. G. R. *J. Chem. Soc.* **1958**, 774–8.

(6) Bacon, R. G. R.; Irwin, R. S. *J. Chem. Soc.* **1958**, 778–84.

(7) Bacon, R. G. R.; Guy, R. G. *J. Chem. Soc.* **1960**, 318–24.

(8) Nelson, M. J.; Pullin, A. D. E. *J. Chem. Soc.* **1960**, 604–12.

(9) Frost, D. C.; Kroto, H. W.; McDowell, C. A.; Westwood, N. P. C. *J. Electron Spectrosc. Relat. Phenom.* **1977**, *11*, 147–56.

(10) Frost, D. C.; MacDonald, C. B.; McDowell, C. A.; Westwood, N. P. C. *Chem. Phys.* **1980**, *47*, 111–124.

(11) Frost, D. C.; Kirby, C.; Lau, W. M.; MacDonald, C. B.; McDowell, C. A.; Westwood, N. P. C. *Chem. Phys. Lett.* **1980**, *69*, 1–6.

(12) Rosmus, P.; Stafast, H.; Bock, H. *Chem. Phys. Lett.* **1975**, *34*, 275–80.

(13) Colton, R. J.; Rabalais, J. W. *J. Electron Spectrosc. Relat. Phenom.* **1975**, *3*, 345–57.

(14) Solouki, B.; Rosmus, P.; Bock, H. *Chem. Phys. Lett.* **1974**, *26*, 20–4.

(15) De Leeuw, D. M.; Mooyman, R.; De Lange, C. A. *Chem. Phys. Lett.* **1979**, *61*, 191–4.

(16) Nagy-Felsobuki, E.; Peel, J. B. *Chem. Phys.* **1980**, *45*, 189–94.

0002-7863/81/1503-4423$01.25/0

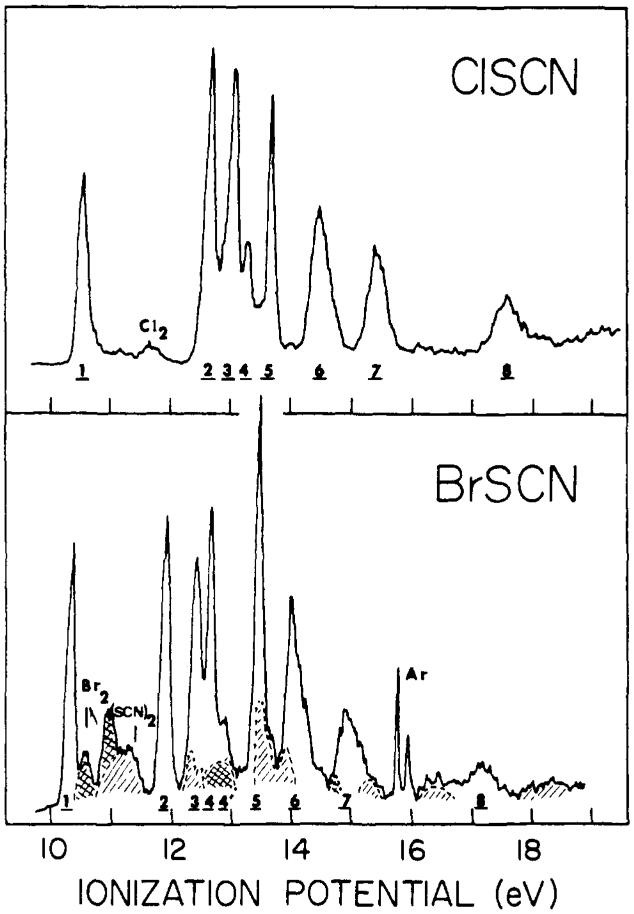


Figure 1. HeI photoelectron spectra of ClSCN and BrSCN. Hatched areas are residual Br_2 and $(SCN)_2$.

Experimental Section

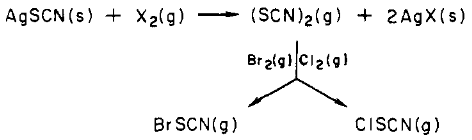
Thiocyanogen, $(SCN)_2$, was generated as previously described[11] by passage of a gaseous halogen (Cl_2 or Br_2) at low pressure over solid AgSCN. The AgSCN, prepared by reaction of aqueous solutions of $AgNO_3$ and KSCN, was filtered, washed, dried under vacuum, and stored in the dark. The reaction occurring at room temperature is represented by

$$2Ag(SCN)(s) + X_2(g) \rightarrow (SCN)_2(g) + 2AgX(s) \qquad X = Cl \text{ or } Br$$

The product from this reaction is then passed directly into the ionization chamber of a photoelectron spectrometer[17] and monitored. If this procedure is continued for a prolonged period the $(SCN)_2$ gradually disappears and a second reaction product dominates. This change of product upon saturation of the AgSCN column with X_2 may be represented thus:

$$Ag(SCN)(s) + X_2(g) \rightarrow XSCN(g) + AgX(s)$$

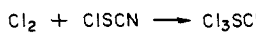
In this instance the resulting photoelectron (PE) spectrum shows either ClSCN or BrSCN depending upon the initial halogen. This procedure can be tedious, since the column must first become exhausted. A superior route is illustrated by the following sequence:



$$AgSCN(s) + X_2(g) \longrightarrow (SCN)_2(g) + 2AgX(s)$$
$$Br_2(g) \swarrow \quad \searrow Cl_2(g)$$
$$BrSCN(g) \qquad ClSCN(g)$$

The initial $(SCN)_2$ is thus simply titrated in the gas phase with the appropriate halogen, leading to rapid formation of the desired XSCN species. We shall see later that X_2 and $(SCN)_2$ exist in equilibrium, but for these species the equilibrium is mainly over to the XSCN side.

In experiments conducted with excess Cl_2, we have found evidence for the formation of ClCN and SCl_2. This concurs with previous solution work which suggests the formation of Cl_3SCN and subsequent decomposition,[18,19]



$$Cl_2 + ClSCN \longrightarrow Cl_3SCN\ (ClSCCl{=}NCl)$$
$$\downarrow\uparrow$$
$$SCl_2 + ClCN$$

A similar scheme has been proposed for the solution reaction of excess Br_2 with BrSCN.[20]

Some additional points are worthy of note. All reactions occur at room temperature; heating the AgSCN column above 150 °C leads to the formation of CS_2 and no enhancement in the yield. In the initial stages some HNCS is occasionally observed, particularly if the AgSCN is not completely dry. In addition, some $S(CN)_2$ is sometimes also observed; the precise mechanism of its formation is not clear. During all of the above reactions, a yellow-red-brown material is deposited on the glass inlet leading into the spectrometer. This material is presumably polymeric pseudohalide.

HeI and NeI photoelectron spectra were recorded for both ClSCN and BrSCN and calibrated with the known ionization potentials (IP's) of CH_3I, Ar, N_2, and H_2O. Resolution was variable, but generally in the 25–35 meV range.

Table I. Experimental and Calculated (STO-3G) Ionization Energies and Assignments for ClSCN

	experimental		calculated[a]	
band	IP,[b] eV	ν^+, cm^{-1}	assignment[c]	orbital energy, eV
	(10.45)	570 ± 50		
1	10.52		3a''	−9.00
2	12.67		8a'	−11.33
3	13.05 }[d]		7a'	−11.68
4	13.28 }		2a''	−12.25
5	13.66		6a'	−13.57
6	14.47		1a''	−14.08
7	15.44		5a'	−14.12
8	17.55		4a'	−17.13
9			3a'	−25.29

[a] Structure, average of SCl_2 and $S(CN)_2$ geometries (see text). Linear SCN group. [b] Vertical IP's (adiabatic IP's in parentheses). All bands ±0.02 eV, except band 8 (±0.05 eV). [c] Valence orbital numbering. [d] Band 4 may be a vibrational component (see text).

Table II. Experimental Ionization Energies and Assignments for BrSCN

	experimental		
band	IP,[a] eV	ν^+, cm^{-1}	assignment[b]
	(10.26)	450 ± 50	
1	10.32		3a''
2	11.89		8a'
3	12.39		7a'
4	12.65	2050 ± 60	2a''
5	13.43	400 ± 60	6a'
6	14.00		1a''
7	14.93		5a'
8	17.18		4a'

[a] Vertical IP's (adiabatic IP's in parentheses). All bands ±0.02 eV except band 8 (±0.05 eV). [b] Valence orbital numbering.

Results

The HeI photoelectron spectra of ClSCN and BrSCN are shown in Figure 1. NeI spectra (not shown) were also recorded, in order to assess variations in photoionization cross-section. As noted in Figure 1, the spectrum of BrSCN shows residual Br_2 and $(SCN)_2$ and so intensity changes between HeI and NeI spectra have to be assessed with caution.

---

(17) Frost, D. C.; Lee, S. T.; McDowell, C. A.; Westwood, N. P. C. *J. Electron Spectrosc. Relat. Phenom.* **1977**, *12*, 95–109.

(18) Feher, F.; Weber, H. *Chem. Ber.* **1958**, *91*, 2523–7.

(19) Bacon, R. G. R.; Irwin, R S.; Pollock, J. McC.; Pullin, A. D. E. *J. Chem. Soc.* **1958**, 764–73.

(20) Feher, F.; Linke, K.-H. *Chem. Ber.* **1964**, *97*, 2413–7.

The numerical values for the IP's and any resolvable vibrational structure are collected in Tables I and II for ClSCN and BrSCN, respectively, together with the proposed assignments which we shall consider later.

Identification and Structure

Chlorine and bromine thiocyanate have not been observed previously in the gas phase, and so their identification and structures must first be established. Earlier work involving solution reactions of a halogen with a metal thiocyanate has shown that the ratio of halogen to metal thiocyanate determines whether $(SCN)_2$ or XSCN is produced.[1,2,5-8] The present results indicate that an analogous situation occurs in the gas phase. With a fresh AgSCN column, both Cl_2 and Br_2 react to produce $(SCN)_2$. As the AgSCN diminishes, XSCN is formed. The alternative route to ClSCN or BrSCN, involving gas-phase titration of $(SCN)_2$ with Cl_2 or Br_2 establishes the similarity with the interhalogen compounds. All the available evidence of the present experiments suggests, therefore, that the solid–gas system behaves in an identical fashion to the solid–solution system.

Additionally, preliminary microwave evidence for chlorine thiocyanate obtained within this department[21] establishes not only the formula ClSCN, but also the fact that Cl is indeed bonded to S and not N. This was previously indicated by solution infrared.[6,8] As will become evident later the PE spectra are entirely consistent with the formula XSCN, and not XNCS (compare our ealier work on XNCO[10]). We may also usefully compare our PE spectra of the XSCN molecules with those of the valence isoelectronic CH_3SCN and CH_3NCS molecules, for which photoelectron spectra have been obtained.[22-25]

Since the BrSCN PE spectrum is directly analogous to the ClSCN spectrum we shall assume that it has a similar geometric and electronic structure. Interestingly, it has been suggested that the iodine analogue has the isothiocyanate structure INCS,[2] since I is more electropositive than the SCN moiety. However, recent solution infrared results support the ISCN structure.[26] We have attempted to obtain photoelectron spectra for this species by gaseous admixture of I_2 and $(SCN)_2$. In this case the equilibrium must lie well to the left, since ISCN is not formed in detectable amounts.

To assess further the geometric and electronic structure of ClSCN we have performed ab initio calculations by using an STO-3G minimal basis set internal to the GAUSSIAN 70 program.[27] The assumed planar structure was a composite of the known structures of $S(CN)_2$[28] and SCl_2,[29,30] viz., S–Cl = 2.014 Å, S–C = 1.701 Å, C–N = 1.157 Å, ∠ClSC = 100.59° and a slightly off-axis C≡N group (5°, trans to Cl). This gives a total energy of −938.86729 au, an improvement of only 26.7 cal mol^{-1} over a structure with a completely linear SCN grouping, suggesting that, as for other pseudohalide containing molecules, quasilinearity may be important. The calculated rotational constants based on such a composite structure give good agreement with the observed values.[21]

Given that both the thiocyanate and isothiocyanate forms exist for the CH_3 derivative, we have also performed an identical calculation for the isothiocyanate isomer, ClNCS, based on an estimated structure derived from the known ClNCO, HNCS, and CH_3NCS structures, viz., N–Cl = 1.71 Å, N–C = 1.20 Å, C–S = 1.56 Å, and ∠ClNC = 126°. This gives a total energy less than that of ClSCN by 46.8 kcal mol^{-1}. This compares, for example, to calculated (STO-3G) energy differences of 7.21 kcal mol^{-1} between the known ClNCO and the unknown ClOCN isomers, and 69.5 kcal mol^{-1} between the known HNCO and HCNO isomers.[31] It is therefore conceivable that the ClNCS isomer could exist, although there is no definite evidence for this species under the conditions of our experiment.

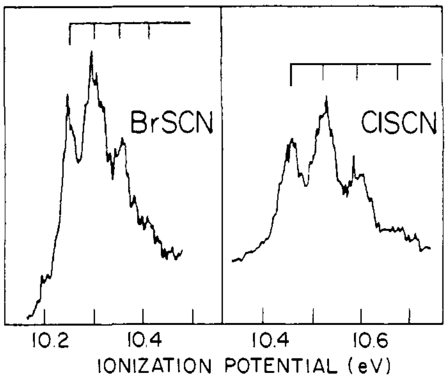


Figure 2. Expansion of the first bands of BrSCN and ClSCN.

The calculated orbital energies for the ClSCN structure with a linear NCS group are included in Table I together with the proposed assignments. The photoelectron spectra of ClSCN and BrSCN will therefore be discussed on the basis of this structure.

Assignments and Discussion

The HeI PE spectra of ClSCN and BrSCN (Figure 1) give a distinct band (no. 1) below 11 eV, followed by several closely spaced bands in the 12–16 eV range, and one additional band above 17 eV, eight in all. Simple molecular orbital arguments predict eight orbitals within the HeI region, the same as observed in the valence isoelectronic halogen isocyanates.[10] By analogy with the XNCO molecules, a similar terminology will be used to describe the molecular orbitals. Thus, if the molecules were linear we would expect a doubly degenerate π nonbonding orbital (π_{nb}), a doubly degenerate halogen p-type π orbital, a pσ type orbital (σ SCN, localized mainly on N), and a doubly degenerate bonding π orbital (π_b) in order of increasing IP. A σ orbital with substantial s character is also expected within the HeI region. In the XSCN molecules with an off-axis halogen atom, each degenerate π orbital splits into an in- and out-of-plane pair (a′ and a″ in C_s symmetry).

The first band (1) in both ClSCN (vertical, 10.52 eV) and BrSCN (vertical, 10.33 eV) is well separated from the rest of the spectrum and shows vibrational intervals of 570 ± 50 and 450 ± 50 cm^{-1}, respectively (Figure 2). The decrease from the chloro to bromo compound suggests an X–S stretching frequency; the proposed molecular ground state values are 520 and 451 cm^{-1}, respectively.[8] The widths of the Franck–Condon envelopes are, as expected, intermediate between those observed for the SX_2[13-16] and $S(CN)_2$[12] molecules. This orbital, the 3a″, which is an out-of-plane π nonbonding orbital involves considerable S 3p character, plus some X antibonding character, in accord with the increased frequency in the ion for ClSCN (compare also SCl_2^+, 530[14] (548 cm^{-1}),[13] and SCl_2, 514[32] (518 cm^{-1})[33]). The measured value for $BrSCN^+$ (450 cm^{-1}) apparently remains unchanged from the neutral molecule (451 cm^{-1}).[8] This latter value appears anomalously high for an S–Br stretching frequency, e.g., SBr_2, 250–350 cm^{-1}; SBr_2^+, 400 cm^{-1};[15] S_2Br_2, 302 cm^{-1};[34] $SSBr_2$, 317 cm^{-1}.[35]

---

[21] Richards, R. J.; Davis, R. W.; Gerry, M. C. L. *J. Chem. Soc., Chem. Commun.*, submitted.

[22] Eland, J. H. D. *Philos. Trans. R. Soc. London, Ser. A* **1970**, *268*, 87–96.

[23] Cradock, S.; Ebsworth, E. A. V.; Murdoch, J. D. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 86–100.

[24] Andreocci, M. V.; Bossa, M.; Furlani, C.; Piancastelli, M. N.; Cauletti, C.; Tarantelli, T. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 105–12.

[25] Neijzen, B. J. M.; De Lange, C. A. *J. Electron. Spectrosc. Relat. Phenom.* **1980**, *18*, 179–88.

[26] Raby, C.; Buxeraud, J.; Claude, J. *Ann. Chim. (Paris)* **1976**, *1*, 65–7.

[27] Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. *QCPE* **1973**, *11*, 236.

[28] Pierce, L.; Nelson, R.; Thomas, C. *J. Chem. Phys.* **1965**, *43*, 3423–31.

[29] Murray, J. T.; Little, W. A.; Williams, Q.; Weatherly, T. L. *J. Chem. Phys.* **1976**, *65*, 985–9.

[30] Davis, R. W.; Gerry, M. C. L. *J. Mol. Spectrosc.* **1977**, *65*, 455–73.

[31] Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 3674–85.

[32] Stammreich, H.; Forneris, R.; Sone, K. *J. Chem. Phys.* **1955**, *23*, 972–3.

[33] Savoie, R.; Tremblay, J. *Can. J. Spectrosc.* **1972**, *17*, 73–8.

[34] Bradley, E. B.; Bennett, C. R.; Jones, E. A. *Spectrochim. Acta* **1965**, *21*, 1505–8.

In the XNCO molecules,[10] the 3a″ orbital is distributed fairly evenly over the whole molecule, whereas for the XSCN molecules there is a dominant S 3p involvement, as indicated by the relatively low value for the first IP, and the enhanced intensity in the NeI spectrum (compare also the C_{2v} analogue, $S(CN)_2$[12]). This is supported by the STO-3G results for ClSCN which indicate approximately 60% S 3p character and 22% Cl 3p antibonding character, with most of the balance supplied by N 2p (11%) and some C 2p (2%). Following the XNCO molecules[10] the first IP becomes sharper from Cl to Br indicating increased X p character in the 3a″ orbital as the halogen becomes heavier.

Between 12 and 14 eV there are four additional orbitals to accommodate—the in-plane analogue of the first orbital (a′), two orbitals (a′ and a″) involving extensive X p character, and a terminal -SCN pσ type orbital (a′). Considerable mixing between orbitals of the same symmetry can occur as we have seen for the XNCO molecules.[10] The -SCN pσ type orbital is easily assigned, since it is essentially the sharpest peak (band 5) in the ClSCN (13.66 eV) and BrSCN (13.43 eV) spectra, incurring only a small shift from Cl to Br, and occurring in a similar position to the sharp pσ type orbitals in $(SCN)_2$ (ca. 13.5 eV)[11] and $S(CN)_2$ (13.2, 14.02 eV).[12] For BrSCN there is some structure resolved on this band (400 ± 60 cm^{-1}) corresponding to either an S–Br stretching frequency or an SCN bend. Sufficient resolution was not achieved for the chlorine analogue. The STO-3G calculation correctly identifies the fifth orbital as -SCN pσ, remarkably within 0.1 eV. We regard this as fortuitous since Koopmans' defects are known to occur for such well-localized orbitals.[12]

The preceding three bands (2–4), spanning less than 0.8 eV in both molecules, present an assignment problem since, for ClSCN (Figure 1), there are two distinct bands at 12.67 (band 2) and 13.05 eV (band 3), and a weak band at 13.28 eV (band 4) which may be associated with band 3, possibly as a vibrational component. The BrSCN spectrum, on the other hand, shows three distinct bands at 11.89 (band 2), 12.39 (band 3), and 12.65 eV (band 4), with a weak component at ca. 12.9 eV (band 4′). The relative intensities of these bands are partly confused by the presence of residual Br_2 and $(SCN)_2$, and thus inspection of the NeI spectrum is not particularly illuminating. Considering BrSCN first, a reasonable assignment is obtained if bands 2, 3, and 4 are assigned to the 8a′ (π_{nb}), 7a′, and 2a″ orbitals. The peak marked 4′ is therefore assigned to a vibrational component of band 4 (2050 ± 60 cm^{-1}, an ionic CN stretching frequency), since it is very weak and becomes sharper in the absence of Br_2 and $(SCN)_2$. In an analogous fashion, band 2 of ClSCN is assigned to the π_{nb} orbital (8a′), and bands 3 and 4 to the 7a′ and 2a″ orbitals. The STO-3G results for ClSCN (Table I), which support this assignment, indicate that substantial mixing occurs among orbitals of the same symmetry, viz. (all numbers are percentages): 8a′, Cl 3p 45, S 3p 16, S 3s 12, C 2p 10, and N 2p 10; 7a′, Cl 3p 58, S 3p 1, C 2p 18.5, and N 2p 18.5; 2a″, Cl 3p 61, S 3p 0, C 2p 16, and N 2p 19. Thus although the 7a′ and 2a″ orbitals have predominant Cl 3p and minimal S 3p character they cannot be described as Cl lone pairs since there is appreciable electron density on the CN group. The 8a′ orbital does however fit the description of an inplane π nonbonding orbital since it possesses S 3s and 3p character and antibonding Cl 3p character.

It is not entirely clear if bands 3 and 4 of ClSCN relate directly to the 7a′ and 2a″ orbitals, or whether both orbitals are in band 3 (as in ClNCO[10]) with band 4 as a vibrational component (ca. 1900 cm^{-1}, as in BrSCN). Nonetheless it is clear that the bands marked no. 3 and 4 in ClSCN correspond to bands 3, 4, and 4′ in BrSCN, and that these correspond to the 7a′ and 2a″ orbitals. Such an assignment follows that for the valence isoelectronic XNCO molecules[10] and gives π_{nb} separations of 2.15 and 1.57 eV for ClSCN and BrSCN, respectively, reasonably large since the molecules are quite bent. In addition to the ab initio calculations this assignment is supported by the NeI intensity changes, where both bands 1 and 2 (particularly the first) increase appreciably in intensity with respect to the other bands due to appreciable S 3p character. The ab initio calculations do however indicate a splitting of 0.57 eV between the 7a′ and 2a″ orbitals in ClSCN, whereas they are almost degenerate in the experimental spectrum. A similar effect was observed for ClNCO:[10] calculated (STO-3G) separation, 0.48 eV; experimental separation, ca. 0 eV.

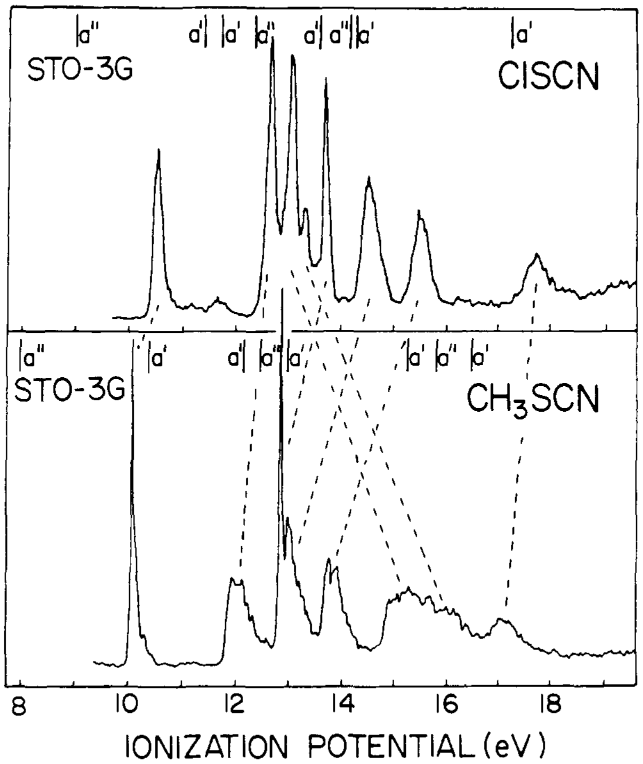


Figure 3. HeI photoelectron spectra of ClSCN and CH_3SCN. Comparison of STO-3G calculated values (vertical lines) and correlation of IP's (dashed lines).

As mentioned above, band 5 in both ClSCN and BrSCN is assigned to the SCN pσ orbital (6a′). The remaining three bands in the spectra of both molecules are therefore assigned to the π_b (1a″), π_b (5a′), and 4a′ orbitals in order of increasing IP. The two π_b levels at 14.47 and 15.44 eV in ClSCN and 14.00 and 14.93 eV in BrSCN exhibit a discrete separation, and are relatively broad in accord with their overall bonding character. The calculation (Table I) indicates virtually no separation of these π_b orbitals. In an analogous ab initio calculation for CH_3SCN (Figure 3) the π_b orbitals are separated by 0.62 eV (experimentally 0.7 eV), whereas in ClNCO the calculations bunch the last three IP's within 0.8 eV, although they experimentally span 2.3 eV.[10] Since a minimal basis set is used for these calculations not too much should be construed from them. In addition, for ClSCN as with ClNCO, lowlying unoccupied orbitals, both π and particularly σ, are expected to cause large shifts to Koopmans' values. As with the corresponding halogen azides and isocyanates,[10] the magnitude of the π_b separation is less than that for the π_{nb} separation.

The position of the last IP (ClSCN 17.55 eV and BrSCN 17.18 eV) is followed by the calculated value for ClSCN (17.13 eV), the eigenvectors indicating a σ orbital (S–C bonding) with considerable s character on all the atoms. The next IP of ClSCN is calculated at 25.3 eV, beyond the HeI range.

The proposed assignments are supported by the sum rule[36] which, for planar molecules, is valid for the individual partial sums of the a′ and a″ orbitals. For ClSCN, an a″ orbital sum may be obtained from the Cl, S, and CN fragments, which takes account of the mutual inductive effects. Taking the a″ values, Cl, 13.0 eV; S, 10.36 eV; and CN, 14.48 eV from molecular chlorine, the sulfur atomic ionization energy, and cyanogen, respectively, the total calculated a″ sum is 37.84 eV. The experimental a″ sum

---

(35) Feuerhahn, M.; Vahl, G. *Chem. Phys. Lett.* **1979**, *65*, 322–3.

(36) Kimura, K.; Katsumata, S.; Achiba, Y.; Matsumoto, H.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 373–80.

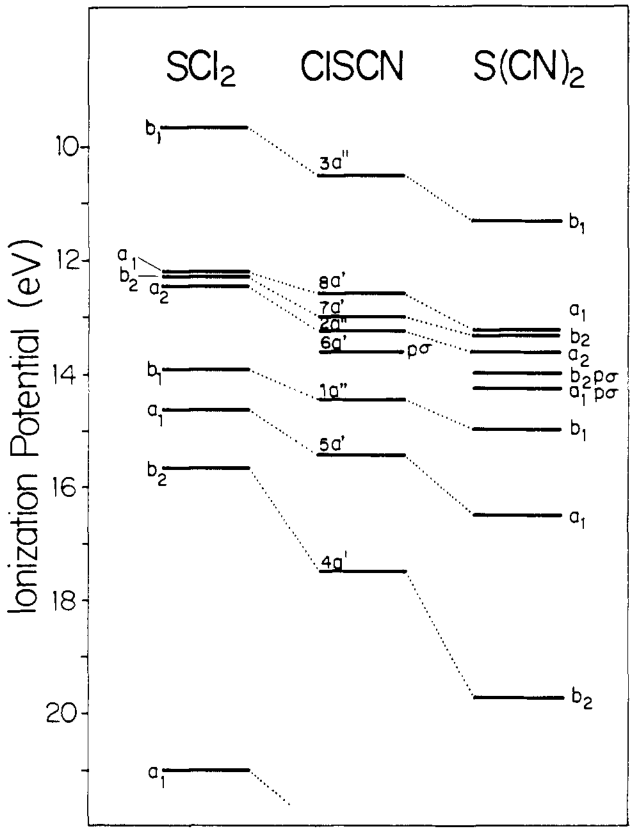


Figure 4. Correlation of the ionization potentials of SCl_2, ClSCN, and $S(CN)_2$.

from the assignments of Table I is 38.27 eV, in good agreement. With the use of a value of 11.67 eV for Br (from Br_2) the calculated a'' sum for BrSCN is 36.51 eV, again in good agreement with the experimental sum, from Table II, of 36.97 eV. We should, however, point out that interchanging the assignments of bands 2, 3, and 4, which are very close in energy, also provides a'' sums in reasonable agreement, and thus for closely spaced orbitals the sum rule is not a definite test.

A further correlation can be provided by comparing the PE spectrum of ClSCN to that of CH_3SCN (Figure 3). This provides two checks, one for a comparison of ClSCN with CH_3SCN, indicating a correspondence not obtainable with CH_3NCS, and the other for the proposed assignment. The assignment is assisted by some minimal basis set (STO-3G) calculations on CH_3SCN (Figure 3), the ordering being the same as that given in a previous assignment of the PE spectrum of this molecule,[25] thereby giving us some confidence in the ClSCN result. The assignments are therefore shown on the figure for CH_3SCN, the dashed lines giving the correlation to ClSCN. We would add that one PE spectrum of CH_3SCN[24] is so poorly resolved that the spectrum is barely recognizable making such a correlation rather difficult.

Figure 4 shows how the orbital energies of ClSCN derive from those of the C_{2v} molecules, SCl_2,[13,14] and $S(CN)_2$,[12] again emphasizing the structure Cl—S—C≡N. The SCl_2 assignment is fairly firm, except for the precise ordering in the 12.4 eV region. Replacement of a Cl atom by a more electronegative CN group increases all IP's and introduces an additional pσ orbital. Replacement with a second CN group gives a further shift to higher binding energy and the introduction of a second pσ orbital. The relative smoothness of the IP changes from SCl_2 through ClSCN to $S(CN)_2$ and the absence of crossing supports the proposed assignments for ClSCN. The largest shift (4a') involves progressive replacement of S and Cl 3p orbitals with C and N 2s orbitals which have an inherently higher binding energy. We note that the next orbital (3a') in ClSCN is predicted at ca. 22 eV since the corresponding a_1 orbitals in SCl_2 and $S(CN)_2$ occur at ca. 21 and ca. 23 eV, respectively. A similar correlation can be constructed by using SBr_2,[15,16] BrSCN, and $S(CN)_2$[12] where similar trends are observed.

Before concluding it is worth commenting on our observations that I_2 and $(SCN)_2$ do not appear to form ISCN. From all the experiments that we have conducted with the $X_2/(SCN)_2$ system it appears that ClSCN is the most stable compound, BrSCN exists in the presence of small amounts of Br_2 and $(SCN)_2$, and ISCN is completely dissociated into I_2 and $(SCN)_2$. This concurs with the early solution work,[8] and is analogous to the equilibria involved with ICl (like ClSCN, not dissociated), IBr (like BrSCN, partially dissociated), and BrCl (like ISCN, extensively dissociated). On electronegatively grounds ISCN should actually be more like I_2 or IBr. The fact that it is unstable may derive from the fact that I and SCN, being close in electronegativity, do not form a particularly polar bond, thereby gaining very little in energy over I_2 and $(SCN)_2$.

Conclusions

ClSCN and BrSCN have been generated virtually quantitatively in the gas phase from the reactions of solid thiocyanate or gaseous $(SCN)_2$ with Cl_2 or Br_2. Since the XSCN molecules behave as interhalogens, equilibria exist between $(SCN)_2$ and X_2. ISCN remains dissociated and cannot be formed by this route. The molecular geometry of these molecules is established as a bent X—S—C≡N structure; the electronic structure is intermediate between that of SX_2 and $S(CN)_2$. Both the geometric structure and the assignment of the HeI photoelectron spectra are supported by minimal basis set ab initio calculations. It is also worth pointing out that the photoelectron spectra of the XSCN molecules can be directly related to those of the recently prepared XSeCN molecules.[37]

Acknowledgment. The financial suppport of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. We also wish to thank M. C. L. Gerry for details of the microwave spectrum of ClSCN and C. A. de Lange for copies of the photoelectron spectra of the XSeCN species and many stimulating discussions.

---

(37) Jonkers, G.; De Lange, C. A., to be published.