radical pyrolysis products due to ring closing of allylcarbinyl radical.

Commentary

The results presented here, in conjunction with the results of other investigations, offer a basis for further studies of the structural identities, corresponding heats of formation, and interconversion pathways of the $C_4H_7^+$ species. Appearance potential measurements for $C_4H_7^+$ fragment ions strongly suggest that an upper limit for the heat of formation of the most stable gas-phase $C_4H_7^+$ ion(s) is 206 ± 2 kcal/mol.[4,10] This coincides, within experimental error, with the heat of formation of 1-methylallyl cation determined in that work (204 ± 3) and in the present study (203.1 ± 1.4 kcal/mol). Other structures may be equally stable. The heats of formation of puckered cyclobutyl cation and bicyclobutonium cation are not known, and only a tentative heat of formation for cyclopropylcarbinyl cation (212 kcal/mol[30,31]) has been proposed. Theoretical studies[13] and NMR experiments under stable-ion conditions[2] indicate that these species are all very close in energy. The slightly puckered cyclobutyl cation is a higher energy species; its heat of formation (225.1 ± 1.1 kcal/mol) was determined in this work. A determination of the ionization potential of cyclopropylcarbinyl radical, providing a definitive value for the heat of formation of cyclopropylcarbinyl cation, would greatly further an understanding of the $C_4H_7^+$ system in the gas phase. Producing the radical by pyrolysis is not the method of choice, as was confirmed in this work. Photolysis of an appropriate precursor would allow more control over the ambient temperature and the distance between radical production and the ionization region.

Recently, the first equilibrium between an allyl and a cyclopropylcarbinyl cation was observed under stable-ion conditions.[78] *cis*-1-Methylcyclopropylcarbinyl cation rearranges at −100 °C to 1-ethylallyl cation. However, interconversion between the parent cyclopropylcarbinyl (or bicyclobutonium) cation and 1-methylallyl cation has not been observed in solution. 1-Methylallyl cation[3] and bicyclobutonium cation[2c] are stable up to −20 and −60 °C, respectively, under stable-ion conditions. Continuation of the experiments to higher temperatures resulted in decomposition reactions of the cations. Significant barriers must exist to prevent the interconversion. For comparison, the rearrangement of *sec*-butyl cation to the more stable *tert*-butyl cation has been observed to take place at a significant rate only above ca. −40 °C.[79] The activation energy for this process, assuming a normal log *A*, was estimated to be ~18 kcal/mol. In the gas phase, *sec*-butyl cation can also survive without rearrangement to *tert*-butyl cation.[80] Similarly, the significant barrier to interconversion of bicyclobutonium and 1-methylallyl cations observed under stable conditions suggests that separate preparation of the isomers is possible and their rearrangement pathways may be studied in the gas phase or in matrix-isolation experiments where competing side reactions may be avoided.

Acknowledgment. We thank Peter G. Schultz for his help with the preparation of 2-cyclopropylethanol and *cis*- and *trans*-3-penten-1-ol and Dr. José A. Martinho Simões for his help with the preparation of *trans*-3-penten-1-ol. We also thank Professors D. H. Aue, W. J. Hehre, J. D. Roberts, and W. A. Goddard and Dr. A. F. Voter for helpful discussions. This work was supported in part by the Department of Energy and by the President's Fund of the California Institute of Technology.

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He I Photoelectron Study of Cyanogen Isothiocyanate, NCNCS, Produced by Thermal Isomerization of Sulfur Dicyanide, $S(CN)_2$

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Abstract: A gas-phase synthesis of cyanogen isothiocyanate, NCNCS, first established by microwave spectroscopy during pyrolysis experiments with sulfur dicyanide, $S(CN)_2$, has been investigated with use of He I photoelectron spectroscopy. The photoelectron spectrum of NCNCS has been analyzed by comparison with the spectra of related molecules and with the aid of MO calculations. The first ionization potential is 10.58 eV. The observed separation of the first two photoelectron bands (associated with ionization from a pair of π orbitals) is shown to be consistent with a CNC bond angle of 155 ± 5°, reflecting the molecule's quasilinear character.

Simple compounds containing the SCN group form an interesting class of molecules for spectroscopic and theoretical studies since the SCN moiety shows ambidentate character, bonding via sulfur to give thiocyanates (RSCN) or via nitrogen to give isothiocyanates (RNCS).[1] For example, the parent acid exists as HNCS,[2] whereas both methyl compounds, CH_3SCN and CH_3NCS, are known.[3] The halogen and pseudohalogen derivatives appear to prefer the thiocyanate form XSCN [X = Cl,[4,5] Br,[5],

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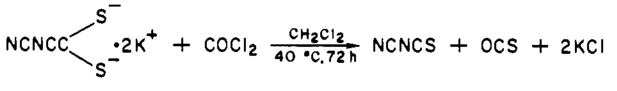
CN,[6] SCN[7]]. This is also the case for the selenium analogues, XSeCN[8] [X = Cl, Br, CN], although it is in contrast with the behavior of the oxygen-containing analogues XNCO [X = Cl,[9] Br,[9] I,[9] CN[10]] in which bonding takes place through nitrogen. To date, the only example of a pseudohalogen isothiocyanate is cyanogen isothiocyanate, NCNCS, first reported by Neidlein and Reuter in 1975.[11] This compound is an isomer of sulfur dicyanide, $S(CN)_2$, which is relatively well-known.[6]

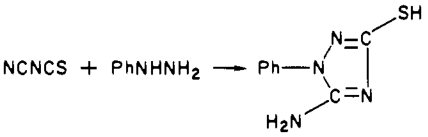
In the original study, NCNCS was prepared by reaction of the potassium salt (I) with phosgene in methylene chloride.[11] The



$$\mathrm{NCNC}\begin{matrix}S^-\\ S^-\end{matrix}\cdot 2K^+ + COCl_2 \xrightarrow[40\ °C,\,72\ h]{CH_2Cl_2} NCNCS + OCS + 2KCl$$

I

solution IR spectrum of the product indicated the presence of both cyano and isothiocyanato groups, and the proposed ordering of the atoms was confirmed by condensing with phenylhydrazine to give the cycloadduct (II).



II

Subsequently it was shown that NCNCS can also be formed by thermal isomerization of $S(CN)_2$ in the gas phase,[12] indicating that the isothiocyanate is thermodynamically the more stable isomer. The new route to NCNCS has enabled its study in the gas phase by both microwave and He I photoelectron spectroscopy. The rotational spectrum is particularly interesting because, in common with other isothiocyanates (RNCS)[13,14] as well as with isocyanates (RNCO)[15,16] and isoselenocyanates (RNCSe),[17] the RNC bond angle is rather flexible and there is a low barrier to linearity. Thus, in terms of structure, NCNCS is intermediate between bent molecules, such as NCN_3,[18] and linear molecules, such as HC_5N.[19] In this case the molecule is quasilinear and analysis of its spectrum requires that the large-amplitude motion be dealt with explicitly.[20]

In this paper, an analysis of the NCNCS photoelectron spectrum is reported as well as a study of the $S(CN)_2$ pyrolysis system using the photoelectron technique to monitor conditions. The NCNCS data provide useful electronic information which can be correlated with the geometric structure of this molecule. When an off-axis substituent is attached to the linear –NCS group, its local $C_{\infty v}$ symmetry is removed and the degeneracy of its π orbitals is lifted. The splitting of associated photoelectron bands can be related to the RNC bond angle via theoretical calculations. Finally, the photoelectron spectra provide a valuable *chemical* diagnostic of the $S(CN)_2$ pyrolysis system and, in particular, allow the optimum conditions for NCNCS production to be determined.

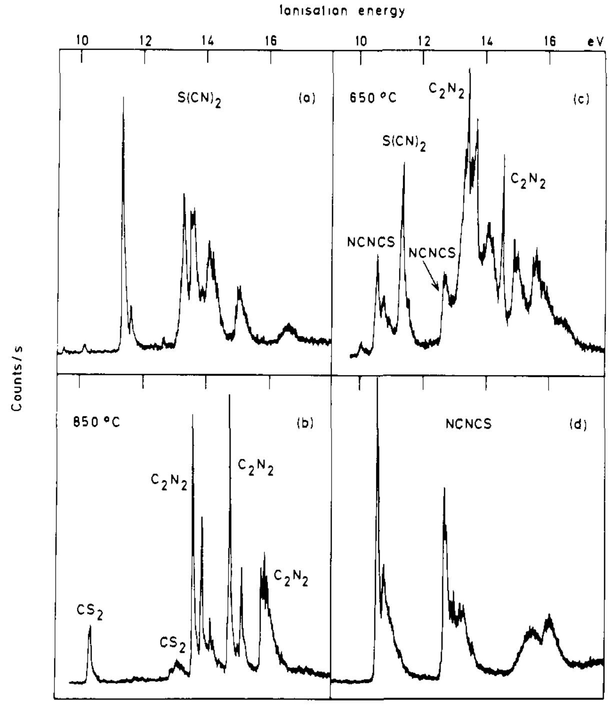


Figure 1. He I photoelectron study of the $S(CN)_2$ pyrolysis system: (a) the photoelectron spectrum of $S(CN)_2$; (b) the photoelectron spectrum obtained when $S(CN)_2$ is pyrolyzed at 850 °C; (c) the photoelectron spectrum obtained when $S(CN)_2$ is pyrolyzed at 650 °C; (d) the photoelectron spectrum obtained by revaporizing NCNCS from a sample produced under the conditions of part c and trapped.

Experimental and Computational Details

Sulfur dicyanide, $S(CN)_2$, was prepared by the reaction of sulfur dichloride, SCl_2, with silver cyanide[21] and purified by vacuum sublimation. The simple experimental setup used for the pyrolysis experiments was similar to that described previously.[12,22] $S(CN)_2$ vapor (50–100 mtorr) was passed through a heated quartz tube (i.d. 8 mm, length 150 mm), via a Pyrex U-tube, into the inlet system of the photoelectron spectrometer. The temperature dependence of the isomerization reaction and conditions for isolating NCNCS from the pyrolysis mixture were determined as described in the next section.

He I photoelectron spectra were obtained by using a modified Perkin-Elmer PS16 instrument fitted with a "Helectros" high-intensity He I/He II discharge lamp. Spectra were calibrated against the known ionization potentials (IPs) of CH_3I, Ar, and $S(CN)_2$. The resolution as measured for the $Ar^{+2}P_{3/2}$ line was 25 meV.

In order to assist in the interpretation of the photoelectron results, MO calculations were performed for NCNCS and the isovalent molecule NCNCO with use of the GAUSSIAN 76 set of programs.[23] For NCNCS, the geometry estimated in the microwave study[12] was used initially (i.e., ∠CNC = 150°) and further calculations were carried out with CNC bond angles between 100 and 180°. Analogous angle variation calculations were performed for NCNCO with use of the published microwave bond lengths.[24] The computed eigenvalues were obtained by using 4-31G basis sets, and MO coefficients referred to are those from STO-3G calculations. Unless otherwise stated, eigenvalues and coefficients refer to ∠CNC = 150° for NCNCS and ∠CNC = 140° for NCNCO.

Isomerization Conditions

The photoelectron spectrum of $S(CN)_2$, previously analyzed by Rosmus et al.,[6] is shown in Figure 1a. At a temperature of 850 °C (the conditions under which the rearrangement was originally discovered by microwave spectroscopy) the parent $S(CN)_2$ spectrum was absent and the new bands were found to be due to

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Table I. Ionization Potential (IP) Data for NCNCS[a]

	IP			
	obsd	calcd[b]	vib freq[c]	assign[d]
(1)	10.58	10.70	1690	(4a″)
(2)	10.85[e]	10.91	400	(17a′)
(3)	12.67	15.87	1940, 645	(15a′)
(4)	12.91	13.83		(3a″)
(5)	13.25[e]	13.77		(16a′)
(6)	15.47[e]	18.19		(2a″)
(7)		18.24		(13a′)
(8)	16.00[e]	17.37		(14a′)

[a] Vertical IP in eV. All IPs ±0.02 eV unless otherwise stated. [b] Calculated by assuming Koopmans' theorem applies. [c] In cm^{-1}, ±60 cm^{-1}. [d] Numbering of orbitals from *calculated* eigenvalues. [e] ±0.05 eV.

CS_2 and $(CN)_2$ (Figure 1b). These molecules do not possess permanent dipole moments and therefore were not detected in the initial study.[12] The apparent absence of features assignable to NCNCS was perhaps surprising but clearly demonstrates the high sensitivity of microwave absorption techniques toward polar molecules of this type.

When the pyrolysis temperature was reduced to 650 °C, the $S(CN)_2$ photoelectron spectrum reappeared together with new bands which were attributed to NCNCS (Figure 1c). Particularly characteristic of the latter is the sharp feature close to 10.6 eV, which is analogous to the first band of $S(CN)_2$.

In both species the first band is assigned to ionization from a non-bonding orbital localized mainly on sulfur. It was not found possible to significantly increase the relative yield of NCNCS above that indicated in Figure 1c. At lower temperatures, the relative amount of $S(CN)_2$ was increased, while at higher temperatures, the yileds of both $S(CN)_2$ and NCNCS were reduced, with increasing amounts of CS_2 and $(CN)_2$ being formed. The conditions used to obtain this spectrum in Figure 1c (ca. 100 mtorr and 650 °C) probably represent the best compromise between the isomerization and decomposition pathways using this simple experimental setup.

By carrying out various vacuum line manipulations, it was found possible to isolate NCNCS from the pyrolysis mixture and thus obtain excellent photoelectron spectra of this species. The best results were obtained when the pyrolysis products were passed through a −95 °C (toluene slush) cold trap, to condense out $S(CN)_2$ and NCNCS, followed by warming to −45 °C (chlorobenzene slush), at which temperature NCNCS can be selectively pumped off. Typically, trapping experiments were carried out for ca. 2 h in order to accumulate enough material for the recording of good spectra. When this method was used, the clean spectrum shown in Figure 1d was obtained. Parallel experiments with a small quadrupole mass spectrometer confirmed that the species had a mass corresponding to that of C_2N_2S.

As well as allowing photoelectron data to be obtained for NCNCS, this study has provided useful information about the $S(CN)_2$ pyrolysis system which was not available from the original microwave work. The new experimental information has enabled high-quality microwave spectra to be obtained which has facilitated an investigation of their unusually complex rotation–vibration patterns.[20]

Photoelectron Spectrum of NCNCS

The He I photoelectron spectrum of NCNCS is shown in Figure 2a and compared with the spectrum of the related molecule NCNCO[10] in Figure 2b. Experimental IPs, ionic vibrational frequencies, and assignments are listed in Table I together with the results of the MO calculations.

In the spectrum of NCNCS, three ionization regions are distinguishable between 10 and 18 eV. The first two regions are shown in more detail in Figure 3 with the assignments indicated [1 to 5 and table].

Assignments of the first two bands in the region 10.5–11.5 eV present no problems since they correlate directly with the analogous bands of HNCS,[25] and NCNCO, Figure 2b. Calculations

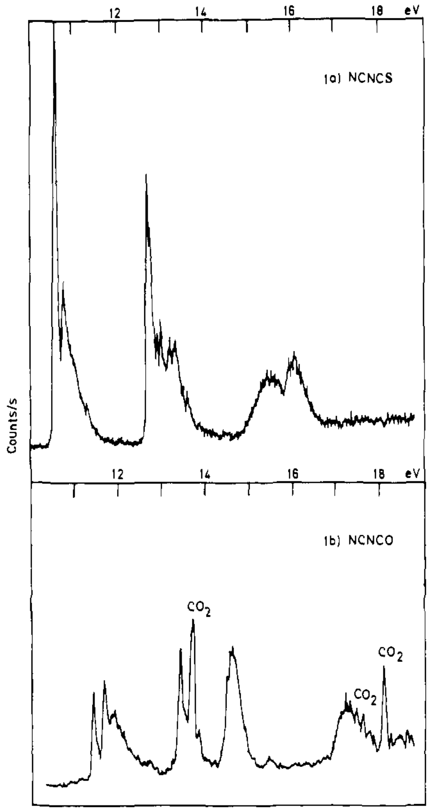

Figure 2. (a) He I photoelectron spectrum of NCNCS. (b) He I photoelectron spectrum of NCNCO (as in Figure 1b of ref 10).

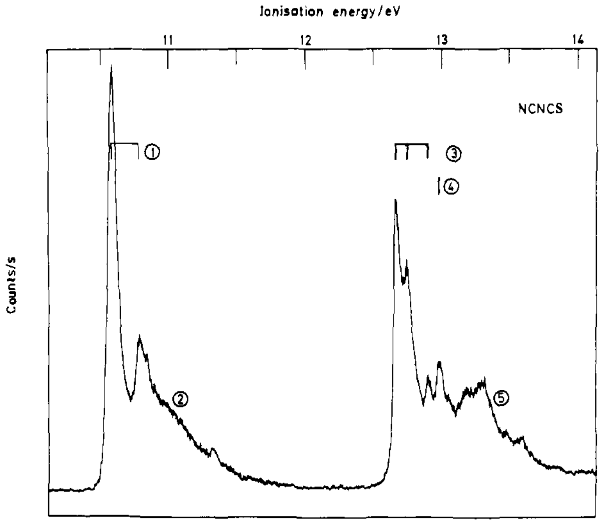

Figure 3. Expansion of the 10–14 eV region of the photoelectron spectrum of NCNCS. Assignments of the first five IPs are indicated (1–5).

indicate that these are associated with ionization from a pair of non-bonding orbitals (4a″) and (17a′) which are localized mainly on the sulfur atom. The STO-3G coefficients for these and the next three highest occupied MOs of NCNCS are illustrated diagramatically in Figure 4. Data for NCNCO are included for comparison. Ionization from the out-of-plane (4a″) orbital gives rise to a sharp band 1 with an intense 0–0 transition at 10.58 eV. The first member of a weak vibrational progression with a spacing of 1690 cm^{-1} can be identified. This frequency probably belongs to the antisymmetric NCS stretching mode ν_2 [1970 cm^{-1} in the neutral molecule[11]].

Band 2, which adjoins the first, has a rather broad profile and is assigned to ionization from the in-plane (17a′) orbital. The

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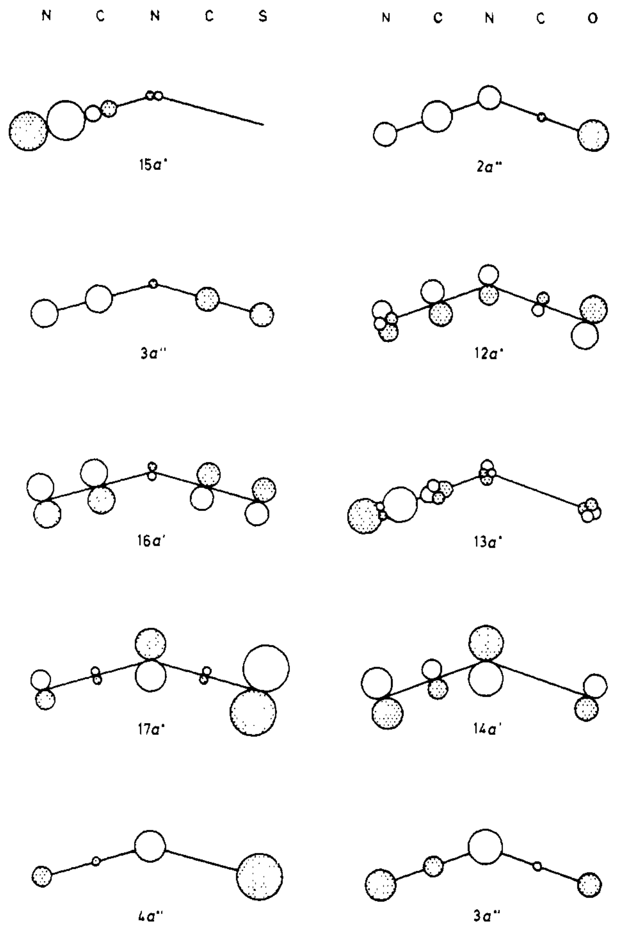

Figure 4. Schematic representation of the five highest occupied molecular orbitals of NCNCM (M = S and O) as obtained from STO-3G calculations. Only the valence-shell p orbitals are presented. The diameters of the circles are proportional to the orbital coefficients. Negative lobes are shaded.

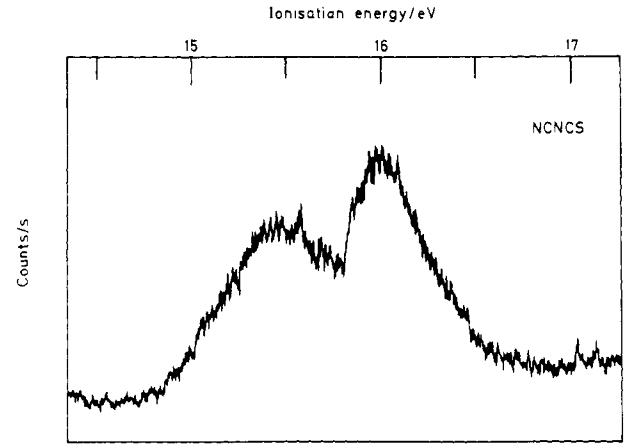

Figure 5. Expansion of the 14.4–17.2 eV region of the photoelectron spectrum of NCNCS.

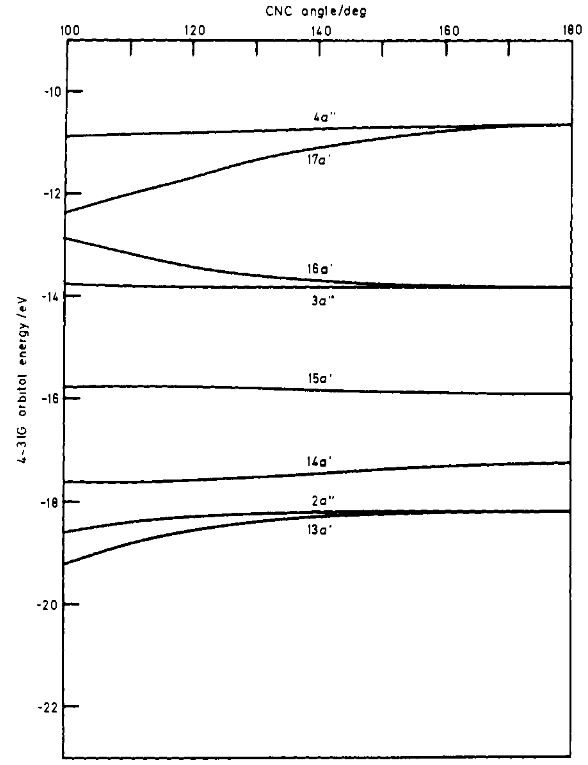

Figure 6. Walsh-type diagram for NCNCS constructed from the results of 4-31G calculations.

vertical IP is estimated as 10.85 eV which indicates a (4a″)–(17a′) splitting of va. 0.27 eV. This may be compared with the calculated splitting of 0.21 eV. The broad structure is due to the excitation of bending vibrations, a process which is formally forbidden when ionization takes place from out-of-plane orbitals. The analogous second IP of HNCS[25] and NCNCO[10] are also broad. A vibrational progression with an interval of 400 cm^{-1} is discernable which is probably associated with an NCN or NCS deformation. It is rather too high for the low-frequency CNC bending vibration which is expected to be ca. 100 cm^{-1}.[20]

The assignment of the features in the region 12.5–14.0 eV presents more of a problem because theory suggests that the observed rather complex pattern probably results from the overlap of three bands. A comparison with the NCNCO data indicates that these are associated with ionization from a pair of π bonding orbitals, (3a″) and (16a′), and from a σ non-bonding orbital (15a′) which is localized mainly on the terminal nitrogen atom, Figure 4. In the case of NCNCO the corresponding π and σ IPs do not overlap and an unambiguous assignment has been possible.[10] The sharp feature at 13.5 eV in the NCNCO spectrum, Figure 2b, was assigned to ionization from a σ orbital and the broader but structured band centered at 14.7 eV to the two π electron ionizations. A similarly satisfying and unambiguous assignment has not proven possible for the analogous IPs of NCNCS. Direct comparison with NCNCO indicates that the sharp peak at 12.67 eV can be reliably identified with the non-bonding σ(N) orbital (15a′). The feature on the side of this peak at 12.75 eV yields an interval of 645 cm^{-1}, of the order expected for a bending vibration of the NCS group and similar in magnitude to intervals observed on several bands in NCNCO and NCN$_3$.[10] Thus it seems likely that this peak is the second member of a short progression (the 12.67-eV peak being the first). It is possible that it is the first member of a progression associated with the fourth IP, but this does not seem likely as the disposition of other adjacent features does not lend any support to this alternative.

The next peak at 12.91 is probably the second member of a progression in 1940 cm^{-1} belonging to an NCS stretching mode which in the neutral molecule is 2016 cm^{-1}.[26] The next peak at 12.98 eV yields an interval of 2580 cm^{-1} which is much too high for a vibrational mode of a molecule such as this. A reasonable assignment for this peak would be that it belongs to the fourth IP. As it is the strongest feature in the vicinity it is assigned as the vertical IP of the less stable component of the π-type orbital degenerate in the linear configuration but split by bending of the chain. The theoretical calculation (Table I) indicates that on bending the (16a′) component is destabilized relative to the (3a″) component by less than 0.1 eV though this is somewhat angle dependent. The fourth IP is thus assigned to the (16a′) orbital, and the broad feature which has a maximum at 13.25 eV is assigned to the (3a″) orbital, the fifth IP. The vibrational structure

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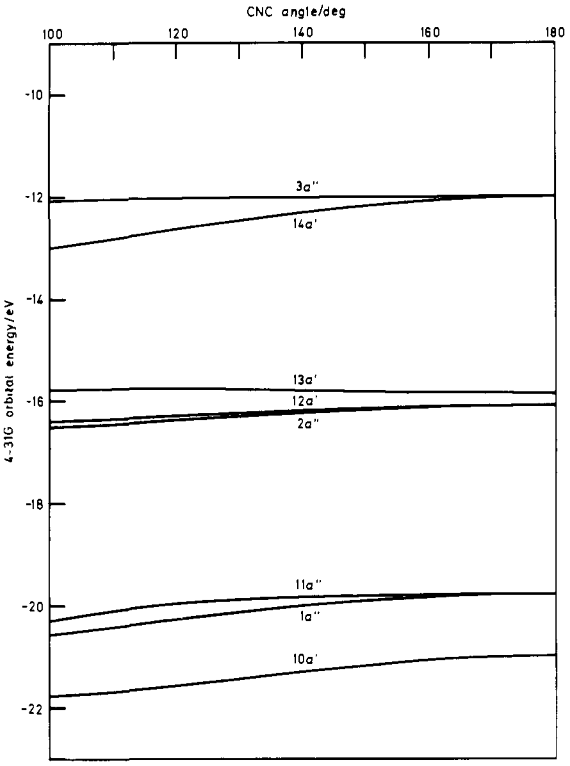

Figure 7. Walsh-type diagram for NCNCO constructed from the results of 4-31G calculations.

is not readily explainable, but the overall pattern seems to be satisfactorily explained by the overlap of three IPs as expected. The assignment of the 15a′ IP at 12.67 eV which is empirically the most secure is at variance with theory (Table I) though this is to be expected as discussed in the next section.

Beyond 14 eV there is a third ionization region, shown in detail in Figure 5. The structure is extended over approximately 3 eV and consists of two broad overlapping bands. The calculations indicate that we may expect a further three IPs in the region up to 20 eV, which are associated with ionization from a pair of π bonding orbitals, (2a″) and (13a′), and from a σ orbital (14a′), which is mainly localized on the CS moiety. The splitting of the π orbitals is predicted to be only 0.05 eV, and they are thus expected to give rise to overlapping bands. The bands between 14 and 17 eV show no well-defined structure, and it is therefore impossible to make an unambiguous assignment. However, on the grounds of intensity, the band with a maximum at 15.47 eV is assigned to the removal of π electrons and that at 16.00 eV to the removal of a σ electron. This assignment implies a reversal of the orbital ordering predicted by the calculations.

Discussion

The He photoelectron spectrum of NCNCS has been analyzed and assigned with the aid of MO calculations and by comparison with the spectra of NCNCO and HNCS. For the first two IPs the agreement between the experimental values and those calculated by using Koopmans' theorem is particularly good. The observed splitting of these bands is to be expected if the system is nonlinear. This result is consistent with microwave measurements on the neutral molecule.[20]

Walsh-type diagrams for NCNCS and NCNCO, calculated by using 4-31G basis sets, are shown in Figures 6 and 7, respectively. In both cases there are three pairs of π orbitals and two σ orbitals in the energy range −10 to −22 eV. As the CNC bond angle is reduced from 180°, the π-degeneracy is lifted, giving rise to in-plane (a′) and out-of-plane (a″) components. The magnitude of the splitting of the highest occupied π orbitals is particularly sensitive to changes in bond angle. Thus the separation of the first two adiabatic IPs should provide a reasonable estimate of this parameter within the limits of Koopmans' theorem. For NCNCO, the microwave data give CNC = 140°, which, from Figure 7, would imply a (3a″)–(14a′) splitting of ca. 0.3 eV. The estimated value from the photoelectron spectrum [Figure 3a of ref 10] is 0.3–0.2 eV, which is consistent with an angle of 145 ± 5°. For NCNCS (Figure 3), the analogous separation is smaller (0.2–0.15 eV), and comparison with Figure 6 implies a bond angle of 155 ± 5° in accord with microwave results.[12]

The NCNCS photoelectron data suggest a reversal of the energy ordering predicted for the (16a′), (3a″), and (15a′) orbitals. The discrepancy between theory and experiment is particularly serious for the band associated with the (15a′) non-bonding orbital, which is predicted to lie 3.2 eV above the assigned value. Similar problems have been encountered in the calculation of nitrogen lone pair IPs for other molecules containing the cyano group, including HCN[26] and $S(CN)_2$.[6] For NCNCO, the discrepancy between observed and calculated (4-31G) IPs for the corresponding band is 2.3 eV. These errors are probably mainly due to the neglect of electron correlation effects[6] which are neglected in Koopmans' approximation. The spectrum of NCNCS may also be complicated by possible mixing between the (15a′) and (16a′) orbitals which may cause the (16a′) orbital to be lower in energy than the (3a″) orbital (cf. Figure 6).

Acknowledgment. We are grateful to the SERC for the award of a research studentship to M.A.K.

Registry No. NCNCS, 56023-03-1.

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