The Photoelectron Spectra of Isocyanic Acid and Related Compounds

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The photoelectron spectra of isocyanic acid and related compounds

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Photoelectron spectra of isocyanic acid, isothiocyanic acid and hydrazoic acid excited by helium resonance radiation are presented. A complete identification of the orbitals from which electrons are ejected has been obtained by comparison with the photoelectron spectra of carbon dioxide, carbon oxysulphide and nitrous oxide, by consideration of the vibrational structure and intensities of the bands and by comparison with the photoelectron spectra of methyl isocyanate and methyl isothiocyanate. A clear relation is found between the photoelectron spectra and the bond angles in the neutral molecules.

1. Introduction

The molecular structures of isocyanic acid (HNCO), isothiocyanic acid (HNCS) and hydrazoic acid (HN_3) present an interesting problem for the theory of valence, in that the angle between the N—H bond and the linear parts of the molecules is 114° in HN_3 (Winnewisser & Cooke 1964) 128° in HNCO (Jones, Shoolery & Schulman 1950) and 135° in HNCS (Kewley, Sastry & Winnewisser 1963). There is also a regular variation in the N—H bond length, which is greatest for HNCS and least for HN_3. The electronic structures of these molecules are expected to be similar to those of the linear molecules carbon dioxide, carbon oxysulphide and nitrous oxide, with which they are isoelectronic. The electronic structure of CO_2, for instance, can be written: $s\sigma_g^2\ s\sigma_u^2\ s\sigma_g^2\ p\sigma_u^2\ p\pi_u^4\ p\pi_g^4$, of which the last four orbitals are accessible to ionization by 21 eV photons. The photoelectron spectrum of CO_2 (Eland & Danby 1968*a*) contains evidence for strong bonding power in the electrons of the bonding π orbital $p\pi_u$ only. This is in accordance with the bond lengths, which are more nearly appropriate for C—O double bonds than for the triple bonds suggested by the molecular orbital model in which the $p\sigma_u$ orbital provides a framework of σ bonds to which the π bonds are added. The photoelectron spectra of COS and N_2O (Turner & May 1967) are similar to that of CO_2, but in the spectrum of N_2O the energy order of $p\sigma_u$ and $p\pi_u$ is reversed and the band corresponding to ionization from $p\pi_u$ is peculiarly weak and extended.

HNCO, HNCS and HN_3 have six normal modes of vibration (Orville Thomas 1953), namely: ν_1, principally N—H stretching; ν_2, antisymmetric stretching similar to ν_3 of CO_2; ν_3, symmetric stretching corresponding to ν_1 of CO_2; ν_4 an in plane bending mode, mainly an N—H bend; ν_5 and ν_6, in and out of plane bending modes corresponding to ν_2 of CO_2. Apart from ν_6 all of these modes are of symmetry a′, and their excitation is allowed on ionization. The analysis of bands in the photoelectron spectra is based on the principle that only modes which are closely related to the change in equilibrium molecular structure brought about by ionization are strongly excited. This principle has been found to hold in many cases and seems to be of general validity.

2. Experimental

Photoelectron spectra were obtained using an apparatus which has been described (Eland & Danby 1968*b*), and energy scales were established by reference to the spectroscopic ionization potentials of standard gases. HNCS was prepared in the spectrometer inlet system by heating a mixture of solid potassium thiocyanate and potassium bisulphate, previously finely ground and dried over phosphorus pentoxide *in vacuo* for several days. The composition of the gas produced by this reaction varies as the reaction proceeds; the main impurities, which could be clearly identified by their photoelectron spectra, are water and carbon disulphide. A sample of gas prepared in the same way and analysed by mass spectrometry was found to contain smaller amounts of hydrogen sulphide and sulphur dioxide also. The presence of these impurities did not impede observation of the photoelectron spectrum of HNCS except in the first band, with which the strong first ionization bands of CS_2 and H_2S overlap.

HN_3 was obtained by heating a mixture of sodium azide and stearic acid to 70 °C in the inlet system of the photoelectron spectrometer. No impurities could be detected in the gas produced, either in the photoelectron spectrum or by mass spectrometry. Samples of HNCO made by the reaction between potassium cyanate and phosphoric acid were kindly supplied by I. C. Vinall. The only significant impurity in these samples was cyanogen, amounting to 10 % in the worst sample and only 1 % in the best one. The presence of cyanogen did not interfere with the photoelectron spectrum of HNCO because the ionization bands of the two molecules do not overlap. Methyl isocyanate and methyl isothiocyanate were commercial products; both of these compounds were examined by mass spectrometry and no significant quantities of impurity could be detected in either of them.

3. Results and discussion

3.1. *Comparison with the linear molecules*

If the N—H groups were collinear with the rest of the molecule the molecular orbitals of HNCO would be of the same character as those of CO_2, and the π orbitals would remain degenerate. The lower electronegativity of nitrogen as compared with oxygen should tend to

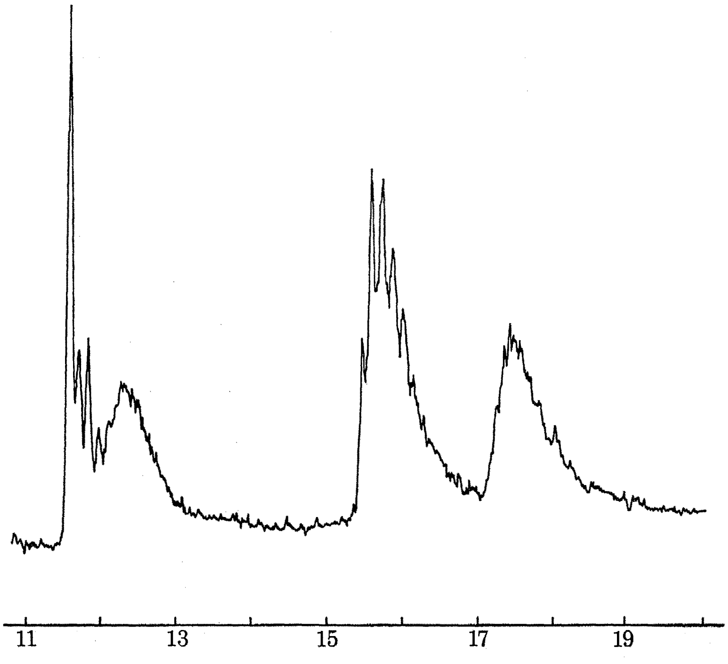

Figure 1. Photoelectron spectrum of HNCO.

increase all the orbital energies, but bonding to the hydrogen atom should stabilize one or both of the σ orbitals. The presence of a hydrogen atom off axis in the real molecules must lift the degeneracy of both the bonding and non-bonding π orbitals to produce two pairs of orbitals of symmetry a″ and a′ out of and in the plane of the molecules respectively. In the simplest model the orbital a′ (πnb) derived from the non-bonding π orbital becomes a lone pair on the nitrogen atom and the orbital a′(πb) derived from the bonding π orbital becomes a pure C—O π bond. The out of plane orbitals a″(πnb) and a″(πb) retain their original π character. The photoelectron spectra of HNCO, HNCS and HN_3 might each be expected, therefore to contain six ionization bands; only four bands are found in each spectrum (figures 1, 2, 3).

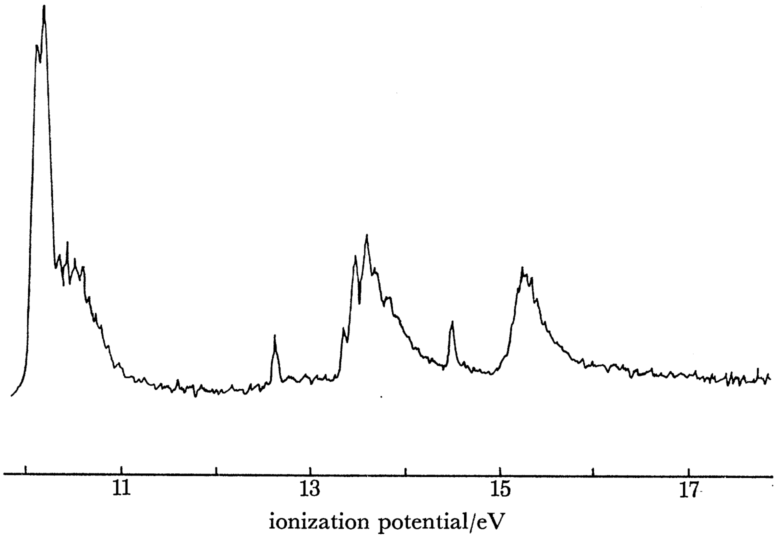

Figure 2. Photoelectron spectrum of HNCS.

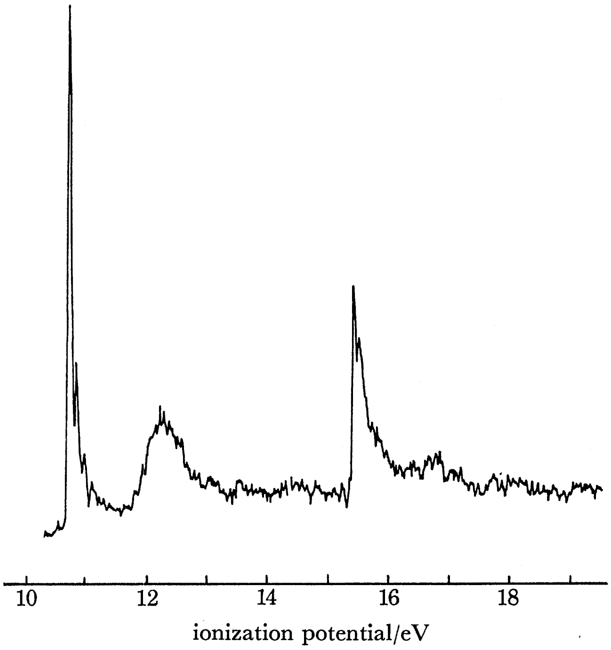

Figure 3. Photoelectron spectrum of HN_3.

This dilemma can be partially resolved by examination of the areas of the bands, which give a measure of their total intensities and thus, since the degeneracies of all the ionic states are the same, of the occupancy of the orbitals which give rise to them (Price 1969). The relative areas of the four bands in the photoelectron spectrum of HNCO starting from the lowest ionization potential are 6:7:12:4.5; in the spectrum of HNCS, (35):(20):36:18. The first three bands in the spectrum of HN_3 have relative areas of 4.5:4.6:3.5; the fourth band is too extended for a meaningful area to be measured. The figures for HNCO and HNCS indicate that in both cases the third bands represent ionization from two nearly degenerate orbitals. The spectra of these molecules contain evidence, therefore, for ionization from five occupied orbitals; the sixth ionization expected on the basis of comparison with CO_2 and COS must either be so weak as to escape detection or occur at too high an ionization potential to be observed with 21 eV He excitation.

3.2. *The first bands*

In the spectra of HNCO and HN_3 the first ionization bands consist of sharp single peaks followed by weak vibrational satellites. For HNCO there are three satellite peaks with irregular intensities and spacing; the sizes of the intervals between the main peak and the satellites are appropriate for vibrational excitation. The three peaks must correspond to the three stretching modes of HNCO; the frequencies in the ion (ν') compared with those in the molecule (ν'') are as follows: $\nu_3'(\nu_3'') = 1050\ (1327)\ \mathrm{cm^{-1}}$, $\nu_2'(\nu_2'') = 2020\ (2274)\ \mathrm{cm^{-1}}$, $\nu_1'(\nu_1'') = 3222\ (3531)\ \mathrm{cm^{-1}}$. In the spectrum of HN_3 the first band contains a single progression in 1073 $\mathrm{cm^{-1}}$. The vibration excited is probably the symmetric stretching mode ν_3', which has a frequency of 1270 $\mathrm{cm^{-1}}$ in the molecule. The proportional reduction in frequency of this mode upon ionization is then approximately the same in HNCO and HN_3; in both cases the reduction is greater than occurs on ionization of CO_2 or N_2O.

The first band in the photoelectron spectrum of HNCS is obscured by the presence of impurities mentioned in §2, but it is nevertheless quite sharp. In the spectra of all three compounds, therefore, the shapes of the first bands indicate ionization from non-bonding orbitals whose occupancy does not affect the bond angle. This description is appropriate only for the out of plane non-bonding π orbital a″ (πnb). The first ionization potentials are 11.60 ± 0.01 eV for HNCO, 10.05 ± 0.1 eV for HNCS and 10.740 ± 0.005 eV for HN_3.

3.3. *The second bands*

Figures 4 and 5 show details of the second bands, which in the spectra of HNCO and HNCS adjoin the first. In each case a long progression of closely spaced peaks can be seen with maximum intensity occurring for excitation of several vibrational quanta in the ionic state. The mean frequencies are 565 $\mathrm{cm^{-1}}$, 655 $\mathrm{cm^{-1}}$ and 445 $\mathrm{cm^{-1}}$ for HNCO, HNCS and HN_3 respectively, frequencies appropriate for bending vibrations. There is a distinct increase in spacing towards higher vibration quantum numbers (positive anharmonicity) in the second bands of HNCO and HN_3. Excitation of the bending vibrations of the linear molecules CO_2, N_2O is strictly forbidden on ionization and has not been observed, and it seems unlikely that the corresponding modes ν_5 and ν_6 of HNCO should be strongly excited. The remaining bending mode is ν_4, and strong excitation of this N—H bending is to be expected when an electron is removed from a lone pair on the nitrogen atom. The first band in the photoelectron spectrum of ammonia and the second band in that of water provide examples of strong excitation of bending modes following lone pair ionizations, and in both of these cases also the anharmonicity is positive. The second bands in the spectra of HNCO, HNCS and HN_3 can therefore be attributed to ionization from the in plane non-bonding π orbital a′ (πnb). The vertical ionization potentials to this first excited state of the ion are 12.39 ± 0.1 eV for HNCO, 10.35 ± 0.1 eV for HNCS and 12.2 ± 0.1 eV for HN_3.

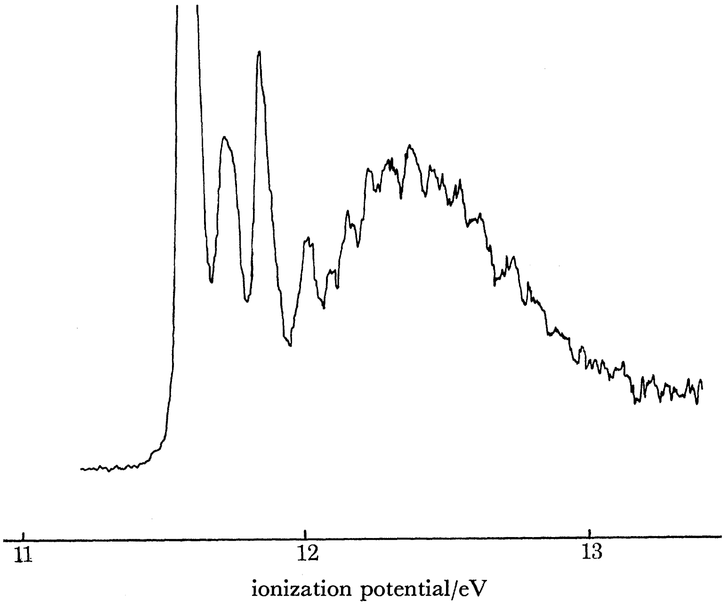

FIGURE 4. Detail of the first and second bands of HNCO.

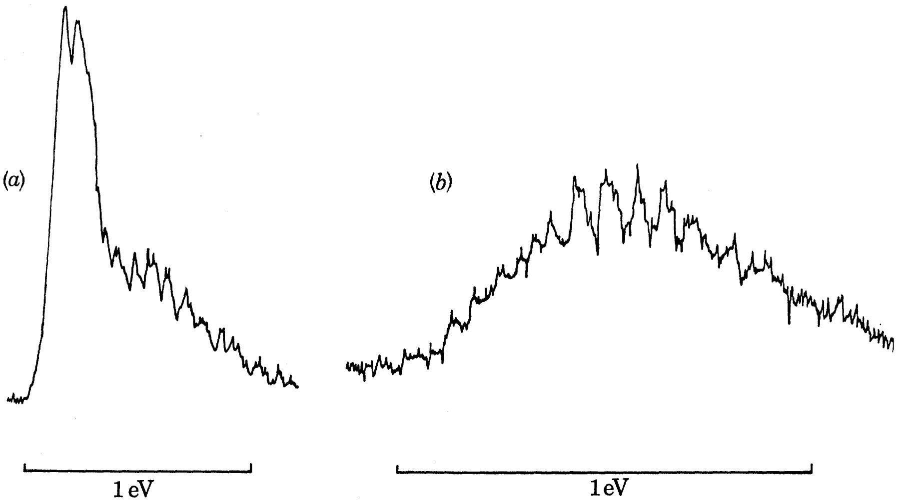

FIGURE 5. Detail of the first and second bands of (a) HNCS and (b) the second band of HN_3.

3.4. *The third bands*, HNCO *and* HNCS

In figure 6 the third bands in the spectra of HNCO and HNCS are shown on an expanded scale. Each contains a progression of well-spaced peaks which are nevertheless not resolved down to the baseline. The mean frequencies are 1113 cm^{-1} for HNCO and 856 cm^{-1} for HNCS, both of which are close to the symmetric stretching frequencies, ν_3'', of the neutral molecules. The vibrational intensities in the third bands of both HNCO and HNCS show that the electron removed is strongly bonding, and the excitation of ν_3' means that the bonding power must be concentrated in the linear parts of the molecules. The photoelectron spectrum of CO_2 shows that such bonding power is a characteristic of the bonding π orbital π_u only. The proportional reduction in ν_3 in the third band of HNCO is very close to the corresponding reduction in ν_1 of CO_2 when a bonding π electron is removed. This close correspondence shows that the structured part of the third ionization bands of HNCO and HNCS is due to ionization of an a″ (πb) electron.

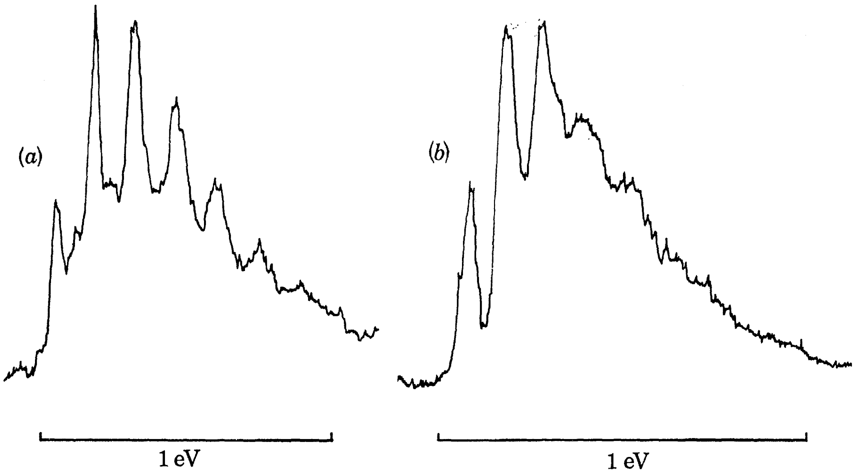

Figure 6. Detail of the third bands of (*a*) HNCO and (*b*) HNCS.

It has already been suggested that the third bands of HNCO and HNCS represent ionizations from two nearly degenerate orbitals. If this is so the second components of the bands must be continua underlying the structured parts, which could explain the apparent lack of resolution. Such continuous or nearly continuous bands can be produced by excitation of low-frequency bending vibrations, such as is expected to occur on ionization from either the remaining π orbital a′ (πb) or from the pσ orbital. The third bands of HNCO and HNCS can be explained by accidental near degeneracy between the a″ (πb) and pσ orbitals, or by small splitting between the components of the bonding π orbital a″ (πb) and a′ (πb). Of these explanations the latter is more likely to apply to both molecules and is to be preferred. The adiabatic ionization potentials for ionization from the a″ (πb) orbitals are 15.54 ± 0.05 eV for HNCO and 13.33 ± 0.03 eV for HNCS.

3.5. *The fourth bands*, HNCO *and* HNCS

The fourth band in the photoelectron spectrum of HNCO is almost continuous, but part of a long progression in 450 cm^{-1} can be distinguished at high resolution. The fourth band in the spectrum of HNCS is similar, and part of a progression in 445 cm^{-1} can be made out. These frequencies are too low to represent any but bending vibrations, and again excitation of the N—H bending mode ν_4' is most probable. Of the orbitals in HNCO and HNCS to which bands in the photoelectron spectra have not yet been assigned occupancy of the pσ orbital only is expected to affect the N—H bond angle. The absence of excitation of the stretching modes is in accordance with the non-bonding character of the pσ orbital of CO_2 found in its photoelectron spectrum. The vertical ionization potentials for the fourth bands are 12.39 ± 0.1 eV for HNCO and 10.35 ± 0.1 eV for HNCS.

3.6. *The third and fourth bands in the spectrum of* HN_3

The ionization potentials of the bonding π orbitals and the pσ orbitals are reduced by conversion from CO_2 to HNCO and from COS to HNCS. For the same to be true of conversion from N_2O to HN_3 it is necessary for the third band in the photoelectron spectrum of HN_3 to represent ionization from the pσ orbital, in agreement with the band areas (see §3.1). The fourth band must then represent ionization from the bonding π orbitals, and the low intensity and diffuseness of this band are in keeping with the characteristics of the corresponding band in the spectrum of N_2O. The vibrational structure of the third band is weak and complex, and the modes involved have not been identified; no vibrational structure has been seen in the fourth band. The ionization potential for the third band of HN_3 is 15.47 ± 0.01 eV, and for the fourth band the vertical ionization potential is approximately 16.8 eV.

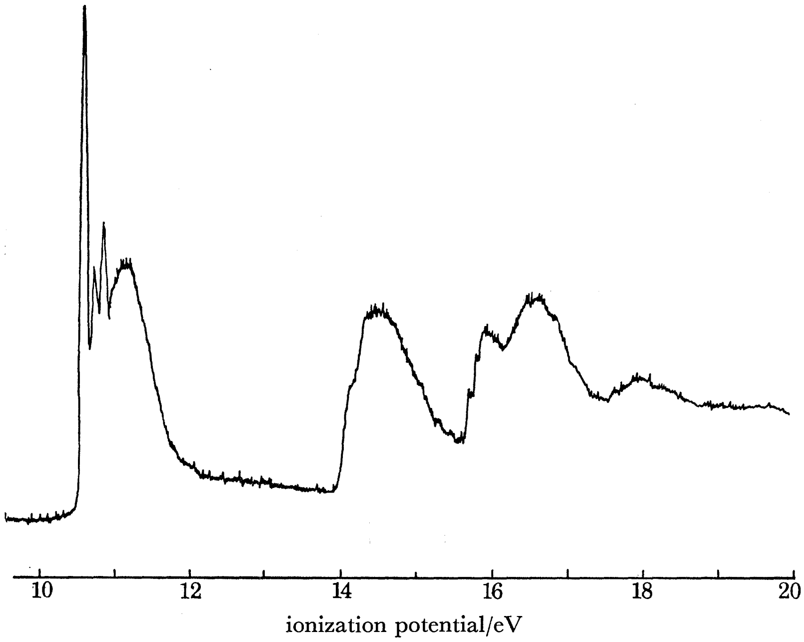

FIGURE 7. Photoelectron spectrum of CH_3NCO.

3.7. *Methylated compounds*

The effect on the photoelectron spectra of some small molecules of replacing a hydrogen atom by a methyl group is illustrated by a bar diagram in figure 9. In every case the spectrum of the methylated compound contains just one more band than that of the parent compound, and one of the bands always lies between 14 and 16 eV. In the spectra of methyl iodide, methyl bromide, methyl cyanide, methanol and methyl mercaptan the bands near 15 eV can be identified with ionization from the e orbitals of the methyl group by their relative intensity and characteristic humped structure, which has been shown to be caused by a Jahn-Teller effect (Baker, Baker, Brundle & Turner 1968). Correspondences between the other bands in the spectra of the methyl compounds and bands in the spectra of the parent compounds can also be discovered on the basis of relative intensities and vibrational structure. All the bands of the parent compounds are shifted towards lower ionization potential by methylation.

The photoelectron spectra of methyl isocyanate and methyl isothiocyanate are shown in figures 7 and 8, and their relation to the spectra of the free acids is illustrated in figure 10. In both cases two new bands are found instead of the one new band expected. The weak new bands which appear at high ionization potential in the spectra of both methyl compounds cannot be related to any bands in the spectra of the free acids: these bands must correspond to

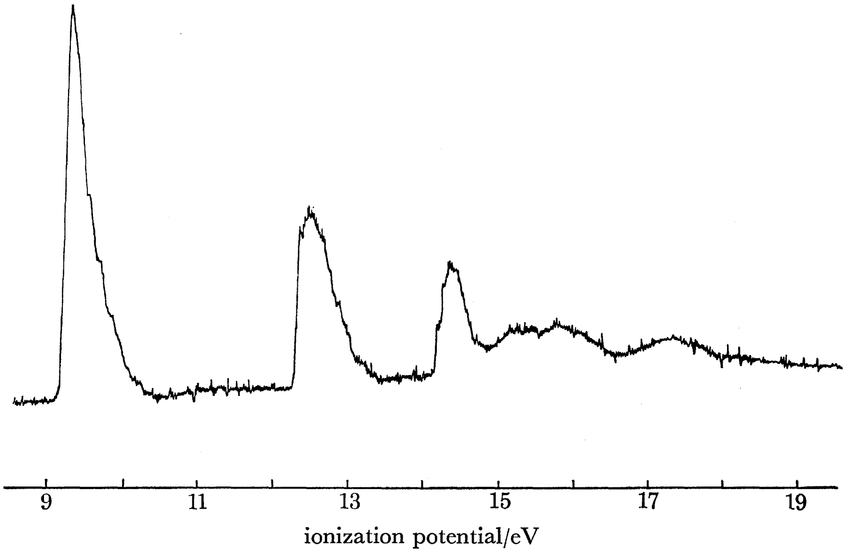

FIGURE 8. Photoelectron spectrum of CH_3NCS.

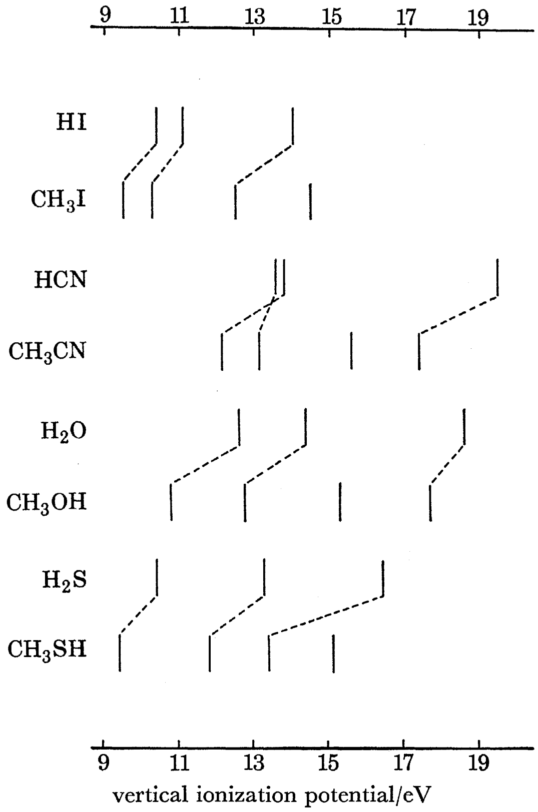

FIGURE 9. Vertical ionization potentials of some simple hydrogen and methyl-compounds. The dashed lines connect ionizations from orbitals of similar character.

ionization from the CH_3—N sσ orbitals. Since methylation reduces the ionization potential of such orbitals the H—N sσ bonding orbitals in the free acids must have even higher ionization potentials, and are not observed in the spectra for this reason. It follows that the N—H bonding in HNCO and HNCS is brought about chiefly by overlap between the hydrogen 1s orbitals and the sσ orbitals of the linear parts of the molecules.

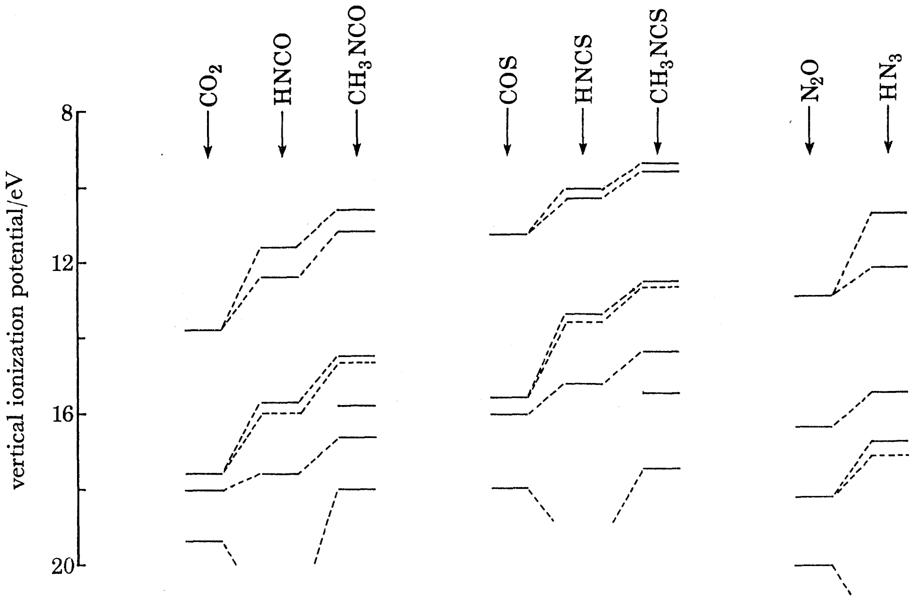

FIGURE 10. Orbital correlations deduced from the photoelectron spectra. The correct symmetry designations of the orbitals of HNCO and HNCS starting from the lowest ionization potential are a″a′a″a′a′a′. For HN_3 the order is a″a′a′a″a′.

3.8. *Molecular structure and photoelectron spectra*

The final identifications of bands in the photoelectron spectra with ionizations from the various orbitals are illustrated in figure 10. Several consequences of the differences in bond angle between HN_3, HNCO and HNCS are now apparent:

(*a*) The splitting between the two components of the non-bonding orbital increases in the order of diminishing bond angle.

(*b*) The proportional reduction in the N—H bending frequency following ionization from the orbital a′ (πn) increases in the same order. The frequencies in the ion (ν_4') and in the molecule (ν_4'') are as follows: $\nu_4'(\nu_4'')$ for HN_3 = 445 (1152) cm^{-1}, for HNCO 565 (797) cm^{-1} and for HNCS 655 (816) cm^{-1}.

(*c*) The band corresponding to ionization from the pσ orbital is sharpest for HN_3 and the proportional reduction in the N—H bending frequency in this band is greatest for HNCS.

Both (*a*) and (*b*) show that the smaller the bond angle the more effective is the in plane p orbital of nitrogen in determining it, while (*c*) illustrates the converse, that the larger the angle the more strongly is the p orbital in the molecular axis involved. These observations are entirely in accordance with the molecular structures and with the orbital assignments, which they confirm.

The photoelectron spectra show that the energies of the out of plane π orbitals are hardly affected by bond angle, and also that the splitting between in plane and out of plane π orbitals is less for the bonding than for the non-bonding ones. The two orbitals whose energy is most strongly affected by bond angle are therefore the pσ orbital and the in plane non-bonding π orbital a′ (πnb). The energy of pσ rises as the bond angle decreases, whereas the energy of a′ (πnb) falls. The equilibrium configuration of the molecules will be a position of minimum energy determined mainly by the competing energy requirements of these two orbitals.

I should like to thank Dr J. C. Danby for his encouragement throughout this work and also thank C. G. Rowland for several helpful discussions.

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