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Study by static SIMS, XPS and UPS of the adsorption of cyanogen on (100) Ni surfaces

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Abstract

The interaction of cyanogen with (100) Ni surfaces at room temperature was studied using secondary ion mass spectrometry in a static mode, and photoemission spectroscopies (XPS and UPS).

It has been shown that cyanogen is adsorbed on this nickel surface in a dissociative mode: atomic carbon and nitrogen are present on the surface as well as CN fragments. These adsorbed species have been characterized by XPS and UPS.

Increasing the temperature in the 400 K range increases the rate of the dissociation reaction of CN into atomic carbon and nitrogen. Moreover carbon is found to dissolved into the bulk for temperatures as low as 475 K. No evidence has been found of a polymerized form of cyanogen molecules on this nickel surface, when the temperature is increased unlike the results obtained for the (111) Ni surface.

Keywords: Chemisorption; Cyanogen; Nickel; Secondary ion mass spectroscopy; Visible and ultraviolet photoelectron spectroscopy; X-ray photoelectron spectroscopy

1. Introduction

The surface chemistry of small molecules on transition and noble metal surfaces is the subject of much investigation because of its relevance to catalytic reactions. $(CN)_2$ is with HCN the least complicated molecule containing the carbon–nitrogen triple bond. However, there are only few studies of the adsorption of cyanogen on nickel surfaces.

For exposures at temperatures lower than 250 K of a (110) Ni surface a c(2×2) structure is obtained by LEED for a cyanogen coverage of about one monolayer [1]. TDS and ARUPS experiments indicate the presence of intact C_2N_2 molecules in this monolayer phase. By ARUPS five spectral bands are seen in the valence band region of adsorbed C_2N_2 due to emission from $4\sigma_u$, $5\sigma_g$, $1\pi_u$ and $1\pi_g$. This is the result of the lowering of symmetry of the adsorbed C_2N_2 and a lifting of the degeneracy of the π states. Molecules are oriented with their molecular axes along [001] that is perpendicular to the troughs.

Above 250 K dissociation of $(CN)_2$ into CN occurs upon adsorption. On a (111) Ni surface, adsorption of $(CN)_2$ at 300 K [2] produces a disordered surface structure. A dissociative chemisorption occurs, the CN group being more or less

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parallel to the surface with both carbon and nitrogen atoms bonded to the surface. However, in a theoretical study using a cluster model and the atom superposition and electron delocalization molecular orbital (ASED-MO) method [3], it is found that for CN adsorption on (111) Ni, the end-on (through the carbon) configuration is more favoured than the lying-down or other configurations. On this surface, upon heating the cyanogen monolayer to 400 K [2], a (6 × 6) surface structure is formed. This kind of ordering might result from a polymerization of the cyanide groups to form $(C_2N_2)_3$.

Above 800 K all the CN are dissociated into carbon and nitrogen atoms. Nitrogen atoms desorbed from the surface as N_2 molecules and carbon atoms are dissolved into the bulk of the sample.

In a previous study the adsorption of cyanogen on a polycrystalline silver surface has been studied by static secondary ion mass spectrometry (SIMS) [4] and a reaction of polymerisation of cyanogen has been demonstrated upon heating treatment at 500 K.

In this work the adsorption of cyanogen on nickel surfaces has also been studied by SIMS in order to determine the adsorption mode of cyanogen on the (100) Ni surface and to check the results concerning the CN polymerization on nickel near 400 K [2]. SIMS, when used in a static, low damage mode, can provide information on the species present on the surface, with a particularly high sensitivity. Moreover, by means of the observed molecular ions, information on the adsorption mode can be obtained [5–8]. XPS and UPS experiments were also performed in order to identify the chemical nature of the adsorbate and to determine its adsorption geometry on the surface.

2. Experimental

2.1. Methods

2.1.1. Static SIMS experimental set-up

The experimental ultrahigh vacuum apparatus has been described in detail elsewhere [9]. SIMS experiments were carried out with a Riber Q 156 quadrupolar mass spectrometer in a static mode: low energy (1 keV) and low density (6×10^{10} ions cm^{-2} s^{-1}) primary argon ions were used in order to work in static SIMS conditions [4]. Furthermore the total energy bandpass of the selection–detection system was selected in order to promote the superficial ions [10].

2.1.2. XPS and UPS experimental set-up

The experimental set-up used for XPS and UPS experiments consisted of a preparation chamber and an analysis chamber, the base pressure in the chambers being in the 10^{-10} mbar range during the experiments. In the preparation chamber the sample can be dosed with different gases by mean of a thin stainless steel tube with the out-gas being positioned just in front of the sample surface. With a tungsten filament mounted on a translational motion the sample can be heated by the rear face near 600 K.

For XPS experiments the primary photon beam was produced with a dual-anode X-ray tube (Al Kα (1486.6 eV) and Mg Kα (1253.6 eV) radiation). To obtain lower energy photons and thus to work in the UPS mode an ultraviolet helium lamp was used. In these two spectroscopic techniques emerging photoelectrons were analysed with detection normal to the surface using a Riber Mac2 semi-imaging spectrometer having an angular acceptance of about 22°. XPS spectra were calibrated to the Au $4f_{7/2}$ peak at a binding energy of 84.0 eV. In XPS experiments, the working conditions were chosen in order to have a total resolution of the system equal to about 1.2 eV. In this value both the broadness of the source radiation and the analyser resolution were taken into account. For UPS experiments the chosen total energy resolution was about 150 meV as determined from the Fermi edge. During UPS experiments the sample was polarized with a low negative voltage of -15 V in order to increase the kinetic energy of photoelectrons because of the poor sensitivity of this spectrometer for electrons having a kinetic energy lower than 10 eV.

2.2. Sample preparation

Samples used were monocrystalline nickel sheets 10 mm × 10 mm × 2 mm prepared ex situ by electrochemical polishing. These nickel samples have (100) orientation. In the experimental set-up the samples were submitted to classical preparation consisting of repetitive cycles of Ar ion sputtering (500 eV, 1 μA cm^{-2}) and heating (1000 or 600 K depending on the experimental vessel). The purity of the surface was checked by AES, SIMS or XPS.

The exposures of the surfaces to $(CN)_2$ were performed at room temperature unless otherwise specified. Cyanogen was prepared in situ by thermal decomposition at 630 K of AgCN [11,12]. The maximum pressure of the reacting species was 10^{-6} mbar as measured with ionization gauges located near the pumping units. It should be noted that this pressure value was underestimated by about one order of magnitude owing to the introduction of the gas just in front of the sample by means of a capillary [4]. This fact has two consequences: the exposure values, expressed in Langmuir, are underestimated and cyanogen doses are not directly comparable for the two experimental apparatuses (SIMS and XPS, UPS) because the geometries are not the same.

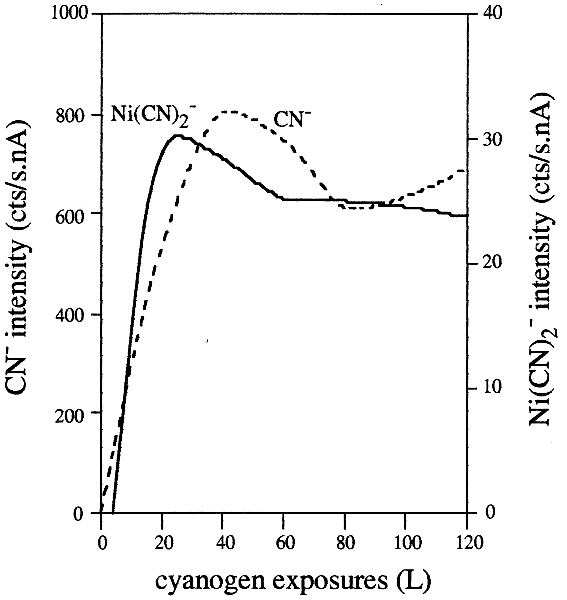

Fig. 1. Evolutions of the negative secondary ionic intensities as functions of the exposure to cyanogen.

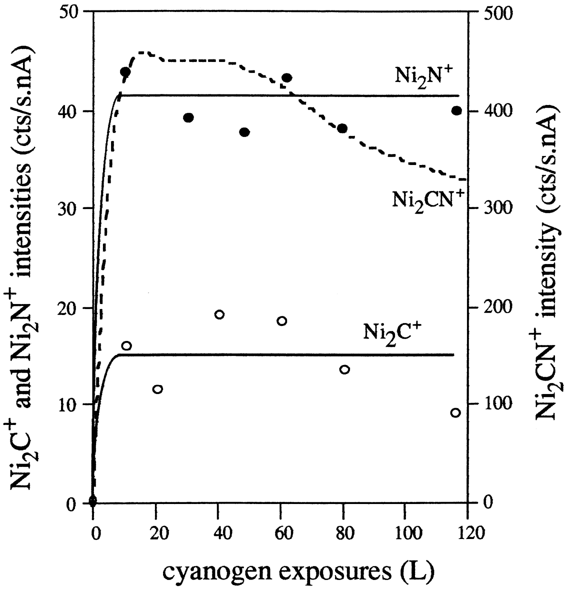

Fig. 2. Evolutions of the positive secondary ionic intensities as functions of the exposure to cyanogen (○, Ni_2C^+; ●, Ni_2N^+; dashed line, Ni_2CN^+).

3. C_2N_2 exposures studied by static SIMS

3.1. *Results and discussion*

A nickel sample is dosed with cyanogen at room temperature between 0 and 120 L (experimental conditions: $(CN)_2$ pressure $= 10^{-8}$ mbar, exposure time $t = 1000$ s). After each 10 L exposure the surface is analysed by static SIMS. Positive and negative secondary ions such as Ni_2CN^+, Ni_2N^+, Ni_2C^+ and $Ni(CN)_2^-$, CN^- are detected in addition to ions involving only nickel. The evolutions of the intensities of negative secondary ions as function of the cyanogen exposure are presented in Fig. 1 and those of positive ions in Fig. 2. It can be observed in Fig. 1 that saturation of the surface in cyanide species occurs for cyanogen exposures of 20 L. Moreover, secondary ions such as Ni_2CN^+, Ni_2N^+ and Ni_2C^+ are attributed to the presence on the nickel surface of CN(a), N(a) and C(a) ((a) stands for adsorbed species). Their detection at cyanogen exposures as low as 10 L (Fig. 2) reveals that a dissociative adsorption of $(CN)_2$ into CN(a), N(a) and C(a) takes place on the (100) Ni surface upon cyanogen dosing at room temperature. These static SIMS results are in agreement with previous results obtained for cyanogen adsorption on Ni (111) [2].

After saturation of the Ni (100) surface with cyanogen at room temperature (total exposure higher than 20 L), the temperature of the sample is increased gradually in steps of 50 K up to 800 K in order to study the evolution of cyanide species adsorbed on the surface sample as a function of its temperature. After each temperature increase, the surface is analysed by static SIMS and the SIMS spectra are characteristic of compounds still adsorbed on the nickel surface at a given temperature. This kind of experiment can be compared with a 'negative' TPD study.

CN(a), C(a) and N(a) are observed to be adsorbed on the surface because of the detection of the same secondary ions as previously. The intensity of CN^- and $Ni(CN)_2^-$ and the yields, Ni_2CN^+/Ni_2^+, Ni_2N^+/Ni_2^+ and Ni_2C^+/Ni_2^+ are plotted versus temperature in order to study the evolutions of the quantity of CN(a), N(a) and C(a) species adsorbed on the surface with temperature (these yields can be related to the amount of adsorbed species [6]).

These evolutions are presented in Figs. 3 and 4, respectively. Between 300 and 375K, no important variations of the secondary ionic intensities, either negative or positive is observed. Only a small evolution is observed for the positive ions ratios (Fig. 4): Ni_2CN^+/Ni_2^+ decreases when Ni_2N^+/Ni_2^+ and Ni_2C^+/Ni_2^+ increase. This can be accounted for by a dissociation reaction of CN(a) into C(a) and N(a). Moreover, between 375 and 475 K, $Ni(CN)_2^-$ and CN^- intensities decrease rapidly as well as the Ni_2CN^+/Ni_2^+ ratio as can be seen in Figs. 3 and 4. The kinetics of the last dissociation reaction increases. In the same temperature range, Ni_2N^+/Ni_2^+ is multiplied by a factor of 3 and Ni_2C^+/Ni_2^+ goes to zero (Fig. 4). This last point can be accounted for by carbon dissolution into the bulk of the sample. Above 475 K, all the cyanide species are desorbed from the nickel surface and at 575 K the SIMS spectrum is characteristic of a clean nickel surface.

Thus, the desorption of the cyanide species from the nickel surface occurs through the cracking of adsorbed CN species to C(a) and N(a). Moreover, during this heating treatment of the sample there is no evidence of the appearance of new secondary ions which would be the expression of the presence on the surface of a polymerized compound of cyanogen.

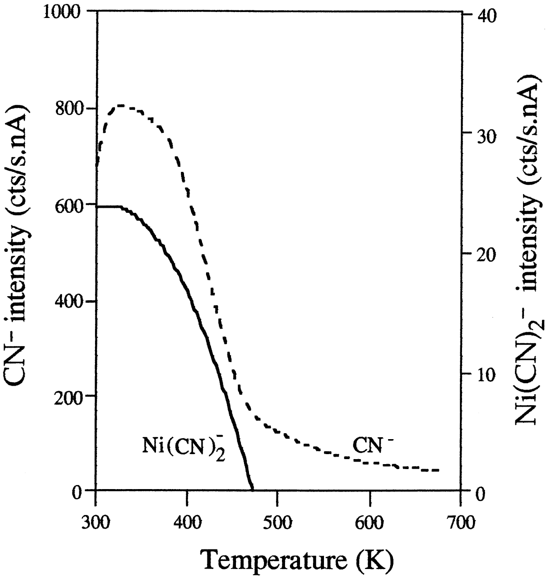

Fig. 3. Evolution of the negative secondary ionic intensities as a function of the temperature.

4. C_2N_2 exposures studied by XPS and UPS

4.1. Results and discussion

In order to confirm the SIMS results and to determine the adsorption geometry of CN fragments on the nickel surface, studies by XPS and UPS of the cyanogen/Ni (100) system have been performed.

4.1.1. XPS results

After obtaining a nickel surface free of contaminants, the surface is exposed two times to 10^{-7} mbar of cyanogen during 30 s (3 and 6 L of cyanogen). On XPS spectra these exposures are characterized by the appearance of a C 1s and a

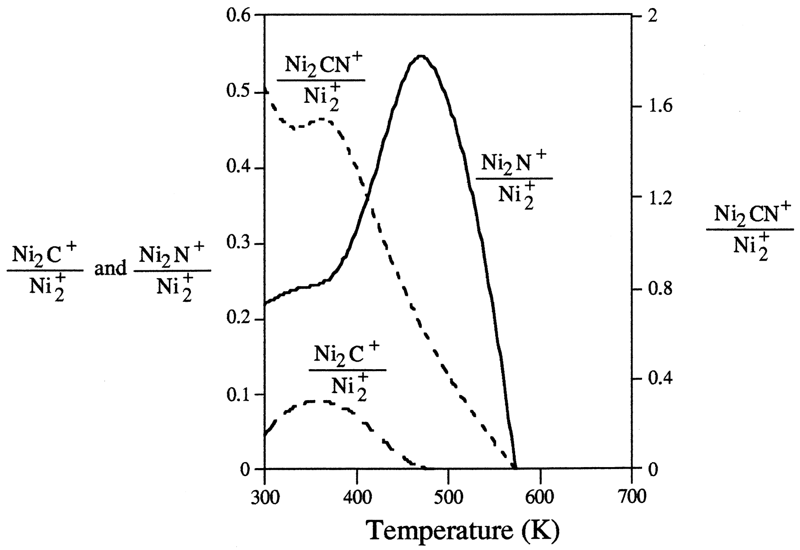

Fig. 4. Evolution of positive secondary ionic ratios as a function of the temperature.

N 1s peak positioned respectively at binding energies equal to 284.1 and 397.3 eV (Fig. 5).

C 1s and N 1s peak areas ($I_{\mathrm{C\ 1s(N\ 1s)}}$) are proportional to the number of atoms on the surface ($N_{\mathrm{C(N)}}$) multiplied by the ionization cross-section corresponding to the 1s level of these elements ($\sigma_{\mathrm{C\ 1s(N\ 1s)}}$) and by the transmission function of the spectrometer which is proportional to E^{-1} under our experimental conditions:

$$I_{\mathrm{C\ 1s(N\ 1s)}} \propto N_{\mathrm{C(N)}} \sigma_{\mathrm{C\ 1s(N\ 1s)}} E^{-1}.$$

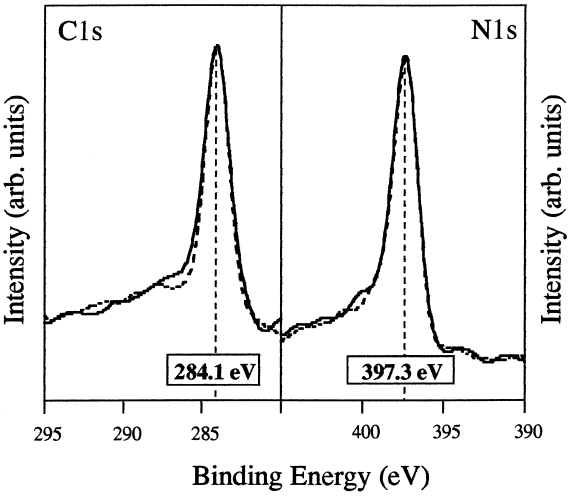

Fig. 5. C 1s and N 1s XPS spectra for 3 L (dashed line) and 6 L (solid line) cyanogen exposures.

In this formula the mean free paths of the C 1s and N 1s photoelectrons were not taken into account because C and N atoms are located on the sample surface. This formula has been applied to our experimental results obtained after 3 and 6 L of cyanogen exposure (Table 1). C/N values which are obtained (close to unity) confirm the presence of cyanide species adsorbed on the nickel surface. In these molecules all carbon atoms and nitrogen atoms are equivalent because only one C 1s peak and one N 1s peak are observed. Moreover, under our experimental conditions a cyanogen dose of 3 L is enough to saturate the Ni (100) surface with cyanogen because no differences

Table 1
Atomic ratios between carbon and nitrogen obtained from XPS experiments

$(CN)_2$ exposure (L)	$I_{\mathrm{C\ 1s}}$ (counts s^{-1} eV^{-1})	$I_{\mathrm{N\ 1s}}$ (counts s^{-1} eV^{-1})	C/N with $\sigma_{\mathrm{C\ 1s}}=1$, $\sigma_{\mathrm{N\ 1s}}=1.8$ [13]
3	1040	2000	0.98
6	1085	1912	1.07

are observed in the spectra between 3 and 6 L cyanogen exposures.

When an Ru (100) surface is exposed to cyanogen [14] at 100 K the presence of molecular cyanogen is characterized by an N 1s peak at a binding energy of 401.3 eV. This peak shifts to 397.6 eV when the temperature is increased to 250 K. This shift can be attributed to the dissociation of $(CN)_2$ into CN on the Ru (100) surface. Moreover, an XPS study of the cyanogen/Si (100) and Si (111) systems [15] has shown that at low temperature (100 K), a multilayer of molecular cyanogen is present on these surfaces and is characterized by photoelectrons peaks C 1s and N 1s positioned at binding energies equal to 287.6 and 399.8 eV, respectively. At about 250 K, this multilayer is desorbed and a monolayer of molecular cyanogen is adsorbed on the silicon surface. These cyanogen molecules interact more strongly with the substrate, this interaction inducing a 1.8 eV shift of the C 1s and N 1s peaks towards the lower binding energies: C 1s at 285.8 eV and N 1s at 398 eV. At 650 K, the dissociation of $(CN)_2$ into 2(CN) is evidenced by a shift of C 1s to a binding energy equal to 285.4 eV. The total dissociation of cyanogen into atomic carbon and nitrogen on Si(100) and (111) surfaces which occurs at 800 K corresponds to the appearance of a C 1s peak at 283.5 eV and of a N 1s peak at 397.6 eV.

When comparing the results of this work on the cyanogen/Ni (100) system with results in the literature, the C 1s and N 1s spectra obtained here are characteristic of the presence on the surface of carbon and nitrogen atoms and/or of CN fragments in which the triple bond would be weakened because of an interaction of C and N atoms with the substrate. However, it should be noted that cyanogen adsorption on Ni (100) induces no energy shift and no shape modification of the Ni $2p_{3/2}$ peak. This peak remains positioned at a binding energy of 852.6 eV which is characteristic of metallic nickel [16] and its FWHM remains equal to 1.62 eV. Although the sensitivity to surface nickel atoms is not so good in this experiment because of the detection of the photoelectrons in a direction normal to the surface, no direct evidence can be found in these XPS results concerning the Ni 2p line, of a significant charge transfer from nickel atoms to CN fragments.

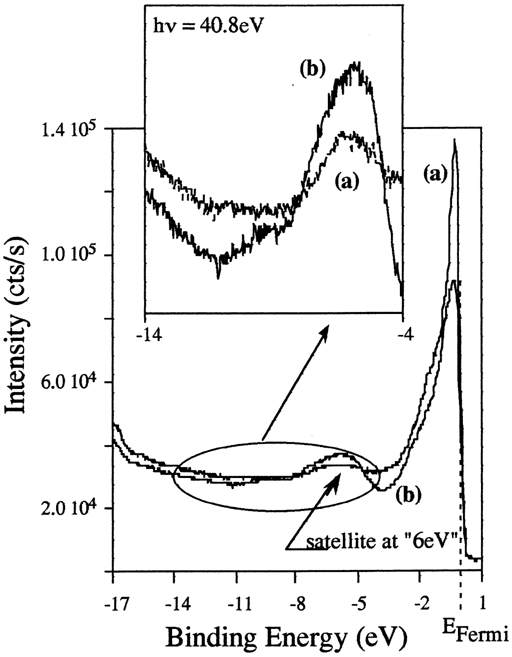

Fig. 6. UPS spectra using He II radiation of a clean Ni (100) surface (a) and after dosing of the surface to 3 L of cyanogen (b). A zoom of the zone corresponding to binding energies between −4 and −14 eV is also shown.

4.1.2. UPS results

UPS experiments using He I and He II radiation are performed in parallel to XPS analysis. A UPS spectrum characteristic of a clean Ni (100) surface is presented in Fig. 6a using He II primary radiation. It is composed mainly of a thin structure at −0.2 eV which can be attributed to a surface emission phenomena [17] and of the satellite peak at 6 eV below the Fermi level.

When this surface is dosed with 3 L of cyanogen (Fig. 6b) a large decrease in the intensity of the band at −0.2 eV is observed as well as a new structure between −5 eV and −14 eV characteristic of the adsorbate. In order to identify more precisely this new structure a difference spectrum between these two spectra has to be done. In doing this difference a problem arises from the presence of the nickel satellite peak at −6 eV that is to say in the same energy range as the photoemission

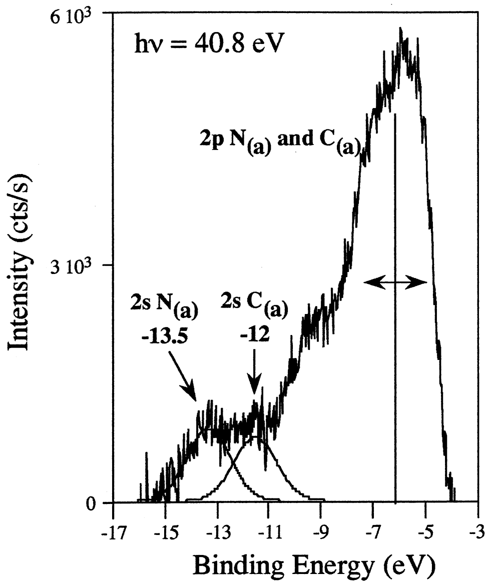

Fig. 7. Difference spectrum between the UPS spectrum of a nickel surface saturated with cyanogen and the UPS spectrum of a clean Ni (100) surface.

bands of adsorbates. This problem was solved by suppressing the contribution of this satellite signal in the two UPS spectra before subtraction. The result of this mathematical treatment between 'initial spectrum: clean Ni (100)' and 'final spectrum: Ni (100) saturated with 3 L of cyanogen' is presented in Fig. 7.

Referring to SIMS results described previously where the presence of C and N atoms has been demonstrated on the nickel surface and using UPS results obtained in different studies on transition metal carbides and nitrides, the peaks at −13.5 eV and at −12 eV can be ascribed respectively to the 2s bands of atomic nitrogen and atomic carbon adsorbed on the sample surface. Because of the detection of these 2s bands the 2p bands characteristic of carbon and nitrogen atoms have to be present in the difference spectrum and be positioned at binding energies 5–6 eV lower than the corresponding 2s bands. That is why in the structure characteristic of the adsorbate molecular orbitals presented in Fig. 7, it is possible to locate these 2p bands around −7 eV, the contribution of the N 2p band being greater than that of the C 2p band as regards the ionization cross-sections presented in Table 2 [18]. However, the energy width of the structure in the difference spectrum is too large to be attributed only to the atomic 2p bands of carbon and nitrogen. For this reason photoemission bands characteristic of molecular orbitals 4σ, 1π and 5σ of CN fragments should also be present between −11 and −5 eV [19–21]. However, it is impossible to go further and to attribute exactly to each molecular orbital of CN fragments a binding energy in the difference spectrum.

Table 2
Ionization cross-sections for carbon and nitrogen [18]

	He I	He II
$\sigma_{C\ 2s}$	1.230	1.170
$\sigma_{N\ 2s}$		1.086
$\sigma_{C\ 2p}$	6.128	1.875
$\sigma_{N\ 2p}$	9.588	4.351

5. Conclusion

The results of this study by SIMS, XPS and UPS of the cyanogen/Ni (100) system have shown that at room temperature cyanogen is adsorbed on a Ni(100) surface in a dissociative mode and that reactions (1) and (2) take place on the nickel surface.

$$(CN)_{2(g)} \rightarrow 2CN(a), \quad (1)$$

$$CN(a) \rightarrow C(a) + N(a). \quad (2)$$

This dissociative adsorption is characterized with SIMS by the presence of secondary ions such as Ni_2CN^+, Ni_2C^+, Ni_2N^+, CN^- and $Ni(CN)_2^-$.

The appearance on the surface of C(a), N(a) and of CN fragments in which carbon and nitrogen atoms interact strongly with the substrate atoms is characterized by the presence in the XPS spectra of a C 1s peak at a binding energy of 284.1 eV and of a N 1s peak at 397.3 eV with a ratio C/N equal to unity after correction of the peak areas by the corresponding relative sensitivity factors.

UPS results confirm the dissociative adsorption reaction of cyanogen on Ni(100) surface and the presence on the surface of C(a), N(a) and CN(a). The atomic 2s bands of carbon and nitrogen are positioned at binding energies of −12 eV and −13.5 eV respectively, the corresponding 2p bands around −7 eV and the bands characteristic of molecular orbitals of CN between −11 and −5 eV. These last UPS results concerning the adsorbed CN fragments can be related to that obtained in the case of cyanogen adsorption on a palladium surface [19] where it was deduced that the CN fragments are adsorbed parallel to the metal surface.

Increasing the temperature in the 400 K range increases the rate of the dissociation reaction of CN into atomic carbon and nitrogen. Carbon is found to be dissolved into the bulk for temperatures as low as 475 K. Moreover, no polymerization reaction of cyanogen on this nickel surface is detected upon heating treatments unlike the results obtained for the cyanogen adsorption on (111) Ni [2] or on silver [4].

References

[1] N. Rösch, T. Fox, F.P. Netzer, M.G. Ramsey, D. Steinmüller, J. Chem. Phys. 94 (1991) 3276.

[2] J.C. Hemminger, E.L. Muetterties, G.A. Somorjai, J. Am. Chem. Soc. 101 (1979) 62.

[3] Z. Xu-Yan, S. Dan Hua, C. Pei Lin, Surf. Sci. 223 (1989) 393.

[4] S. Bourgeois, R. Gouttebaron, M. Perdereau, Surf. Sci. 395 (1997) 356.

[5] C.M. Greenlief, P.L. Radloff, S.A. Akhter, J.M. White, Surf. Sci. 186 (1987) 563.

[6] A. Brown, J.C. Vickerman, Surf. Sci. 124 (1983) 267.

[7] V. Matolin, E. Gillet, Surf. Sci. 238 (1990) 75.

[8] M. Barber, J.C. Vickerman, Surf. Sci. 68 (1977) 130.

[9] S. Bourgeois, M. Perdereau, J. Spectrosc. Electron. 6 (1981) 335.

[10] S. Bourgeois, M. Perdereau, Le Vide, Les Couches Minces 38 (1983) 183.

[11] F.P. Netzer, Surf. Sci. 61 (1976) 343.

[12] R. Gouttebaron, Ph.D. Thesis, University of Bourgogne, 1996.

[13] J.H. Scofield, J. Electron Spectrosc. Relat. Phenom. 8 (1976) 129.

[14] N.J. Gudde, R.M. Lambert, Surf. Sci. 124 (1983) 372.

[15] Y. Bu, L. Ma, M.C. Lin, J. Phys. Chem. 99 (1995) 1046.

[16] Auger and X-ray Photoelectron Spectroscopy, D. Briggs, M.P. Seah (Eds.), Practical Surface Analysis, second ed., Vol. 1 Wiley, New York, 1990.

[17] T.T.A. Nguyen, R. Cinti, J. Micros. Spectrosc. Electron. 1 (1976) 157.

[18] J.J. Yeh, I. Lindau, At. Data Nucl. Data Tables 32 (1) (1985).

[19] M.G. Ramsey, G. Rosina, F.P. Netzer, Surf. Sci. 218 (1989) 317.

[20] M.G. Ramsey, G. Rosina, F.P. Netzer, Surf. Sci. 217 (1989) 140.

[21] D.W. Turner, C. Backer, A.D. Backer, C.R. Brundle, Molecular Photoelectron Spectroscopy, Wiley, New York, 1970.