

Photoelectron spectroscopic studies of the adsorption of organic molecules with lone pair orbitals on transition metal surfaces†

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Abstract. Ultraviolet and x-ray photoelectron spectroscopy have been employed to investigate the adsorption of methanol, ethanol, diethylether, acetaldehyde, acetone, methyl acetate and methylamine on surfaces of Fe, Ni and Cu. All these molecules adsorb molecularly at low temperatures (≤ 100 K). Lone pair orbitals of these molecules are stabilized on these metal surfaces (by 0.4–1.0 eV) due to molecular chemisorption. The molecules generally undergo transformations as the temperature is raised to 120 K or above. The new species produced seems to depend on the metal surface. Some of the product species identified are methoxy species, formaldehyde and carbon monoxide in the case of methanol and methyl acetate, ethoxy species in the case of ethanol and 2-propanol in the case of acetone.

Keywords. Photoelectron spectroscopy; adsorption of organic molecules; UVPS and XPS studies of adsorption.

1. Introduction

Adsorption of molecules on metal surfaces is fruitfully studied by techniques of electron spectroscopy (Rao and Hegde 1981; Rao 1981; Thomas 1974). Ultraviolet photoelectron spectroscopy (UVPS) has been found to be specially useful in investigating electron states of adsorbed molecules and in characterizing adsorbed species (Spicer *et al* 1975; Lloyd *et al* 1977). In this laboratory, we have investigated adsorption of CO, N₂ and O₂ on transition metal surfaces by employing UVPS and related techniques (Kamath *et al* 1982a; Rao *et al* 1982; Jagannathan *et al* 1980). We considered it most worthwhile to systematically investigate the adsorption of several organic molecules possessing lone-pair orbitals on the surfaces of a few transition metals by employing UVPS. This is because such molecules would be expected to chemisorb on metals through their lone-pair orbitals and UVPS should directly give information on the nature of bonding (Luth *et al* 1977). The molecules we have examined are methanol,

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ethanol, diethyl-ether, acetaldehyde, acetone, methyl acetate and methylamine and the transition metals employed are Fe, Ni and Cu. It was our purpose to compare the electron states of such a related series of adsorbate molecules on the three metals and to study the thermal transformations of the adsorbate molecules. We have obtained quantitative information on the stabilization of the lone-pair orbitals of the different molecules due to chemisorption on metals by matching the experimental difference UV photoelectron spectra with the gas phase spectra (Rao *et al* 1979 ; Turner *et al* 1970) of the free molecules. We have employed x-ray photoelectron spectra in the C (1s), O (1s) and N (1s) regions to study the nature of the adsorbed species. By means of the changes observed in both UVPS and XPS, we have attempted to characterize the species resulting from the transformations of the adsorbed molecules. It has thus been possible to show that all the molecules studied adsorb molecularly at low temperatures, but undergo transformations at higher temperatures.

2. Experimental

All the spectra were recorded on the ESCA spectrometer of VG Scientific Limited, UK, fitted with a sample preparation chamber and a gas handling manifold. Specpure strips of Fe, Ni and Cu were used. The metals were etched with argon ions under UHV ($\sim 5 \times 10^{-10}$ torr) conditions to obtain atomically clean surfaces (Rao *et al* 1980 ; Jagannathan *et al* 1980). All the organic compounds were purified by fractionation. The metals were exposed to the adsorbate vapours in the sample preparation chamber to the desired extent. Exposures are referred to in Langmuirs, L ($1L = 10^{-6}$ torr sec). The temperature of the sample could be varied by using a special probe designed for the purpose. UV photoelectron spectra were recorded with HeII radiation (40.81 eV).

Difference spectra of adsorbed molecules were plotted with the aid of a DEC-1090 computer system wherein the spectra of the metals were subtracted from the observed spectra after multiplication with an appropriate attenuation factor.

3. Results and discussion

3.1. Methanol

At low temperatures (~ 80 K), methanol is found to adsorb molecularly on Fe, Ni and Cu surfaces. Thus, the HeII UV photoelectron spectra of methanol adsorbed on these metal surfaces (figures 1-3) show features very similar to those of methanol in gas phase. Difference spectra due to the adsorbed species are also compared with the gas phase spectrum in figures 1-3. The binding energy of the $6a'' + 1a'$ band in the gas phase could be matched with the third band in the difference spectra to obtain satisfactory electron states of methanol molecularly adsorbed on the three metals. The energies and assignments are summarized in table 1. We see that there is a shift of the lone-pair orbital towards higher binding energy by about 0.6 eV due to chemisorption. In x-ray photoelectron spectra we see peaks at 286.0 and 533.0 eV respectively due to C (1s) and O (1s) levels of molecularly adsorbed methanol (see figures 4 and 5 for typical spectra).

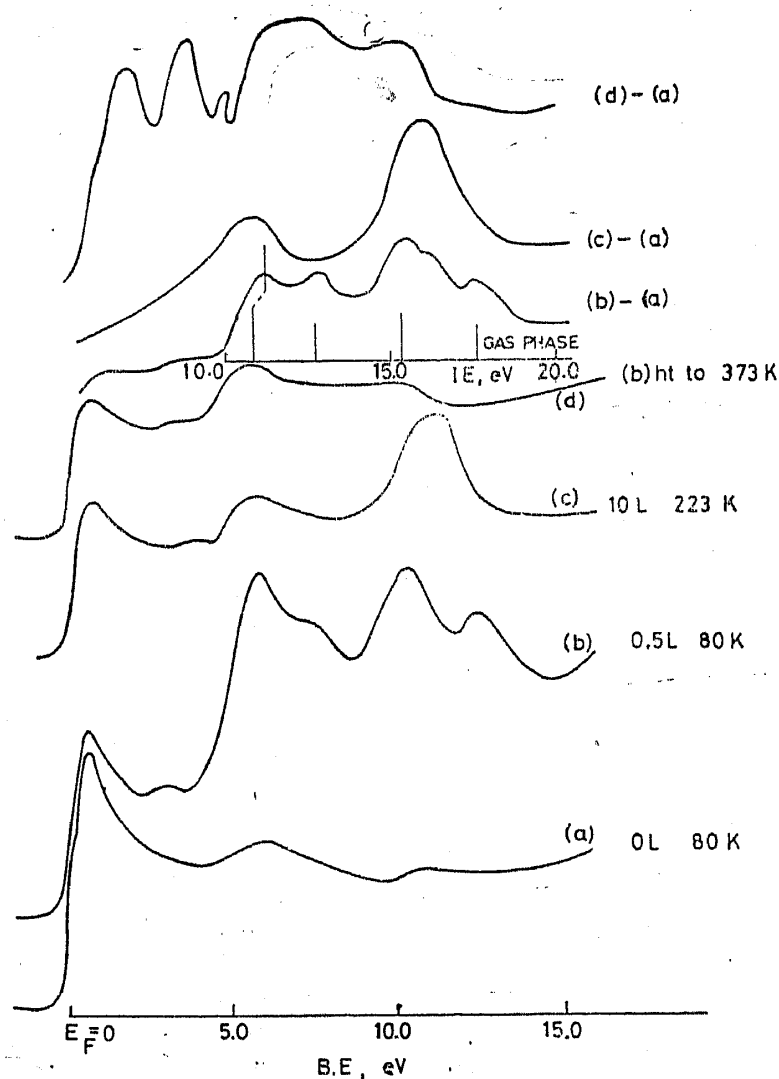


Figure 1. HeII spectra of methanol adsorbed on Fe at different temperatures and exposures. Difference spectra are also shown in the figure along with the positions of bands in the gas phase.

Significant changes occur both in the HeII spectra and the x-ray photoelectron spectra on progressively heating the sample from 80 K to 300 K. The major changes observed on the surfaces of the three metals are as follows :

3.1a. The HeII spectrum of methanol adsorbed on Fe at 223 K (figure 1) shows only two bands corresponding to $2a''$ and $6a'' + 1a'$ orbitals. The bands corresponding to $7a'$ and $5a'$ orbitals of methanol are absent in the spectrum. We attribute this to the formation of the methoxy species, CH_3O . Methoxy species is known to be formed on heating methanol on Ni surface (Kojima *et al* 1981 ; Rubloff and Demuth 1977 ; Demuth and Ibach 1979) and Cu (Bowker and Madix 1980 ; Ryberg 1981 ; Sexton *et al* 1981 ; Steinbach and Spenglet 1981 ; Carlson *et al* 1981). Both the C ($1s$) and O ($1s$) bands in XPS shift towards lower binding energies (figure 4). Such shifts have been observed on Cu surface by Bowker and Madix (1980) when methoxy species is formed.

Table 1. Electron state of molecularly adsorbed organic molecules.

| Gas phase | Fe | Ni | Cu | Assignment |
|-----------------------|-----------|-----------|-----------|---|
| <i>Methanol</i> | | | | |
| 10.8 | 6.1 (0.6) | 5.8 (0.6) | 6.5 (0.5) | 2a'' (n _O) |
| 12.7 | 7.6 | 7.0 | 8.1 | 7a' (n _O) |
| 15.2 | 10.1 | 9.8 | 10.6 | 6a'' + 1a' (σ _{CO} ; π _{CH₃}) |
| 15.6 | 11.1 | | | |
| 17.7 | 12.4 | 12.3 | 12.8 | 5a' |
| <i>Diethylether</i> | | | | |
| 9.61 | 6.2 (0.8) | 4.8 (0.0) | 5.6 (0.0) | n _O |
| 11.08 | .. | .. | .. | |
| .. | 8.1 | 7.5* | 7.7* | |
| .. | 8.8 | | | |
| .. | 9.9 | 10.2 | 10.4 | |
| 16.23 | 12.0 | 11.7 | 12.3 | |
| .. | 14.5 | 15.3 | 15.9 | |
| <i>Acetaldehyde</i> | | | | |
| 10.3 | 5.5 | | | a' (n _O) |
| 13.24 | 8.0* | | | a'' (π _{CO}) |
| 14.15 | | | | a' (σ) |
| 15.34 | | | | a' (σ) |
| 15.6 | 10.5* | | | a'' (π _{CH₃}) |
| 16.47 | | | | a' |
| <i>Acetone</i> | | | | |
| 9.7 | .. | 4.6 (0.5) | 5.5 (0.4) | a' (n _O) |
| 12.6 | .. | 8.5* | 9.1* | a'' (π _{CO}) |
| 14.0 | .. | | | a'' (CH ₃) |
| 15.7 | .. | 10.2 | 11.2 | a'' (π _{CH₃}) |
| 18.15 | .. | 12.65 | 13.7 | a' (π _{CH₃}) |
| <i>Methyl acetate</i> | | | | |
| 10.5 | 6.4 (0.4) | 5.8 (0.3) | 6.5 (0.3) | n _O |
| 11.3 | | | | π _{C=O} |
| 12.9 | 8.4 | 7.7 | 8.5 | |
| 14.05 | 10.1 | 9.4 | 10.3 | |
| 14.9 | | | | |
| 16.3 | 12.0 | 11.35 | 12.2 | |
| | 14.3 | 13.6 | 14.5 | |
| <i>Methylamine</i> | | | | |
| 9.6 | 6.0 (1.0) | .. | 5.8 (0.6) | n _N |
| 13.2 | 8.55 | .. | 8.0 | π _{CH₃} |
| 14.3 | | | | |
| 15.4 | .. | .. | 10.45 | σ _{CN} ; π _{CH₃} |
| 16.8 | | | 12.4 | π _{NH₂} |

* broad

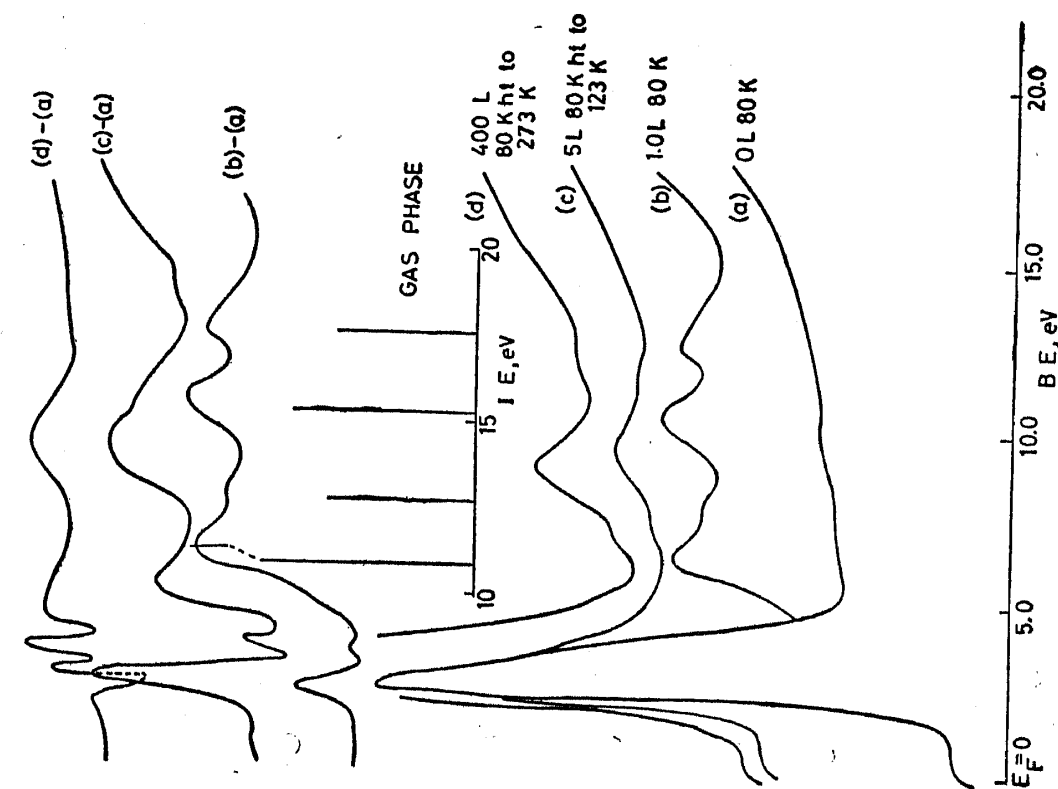


Figure 2. HeII spectra of methanol adsorbed on Ni at different temperatures and exposures. Difference spectra are also shown in the figure along with the position of bands in the gas phase.

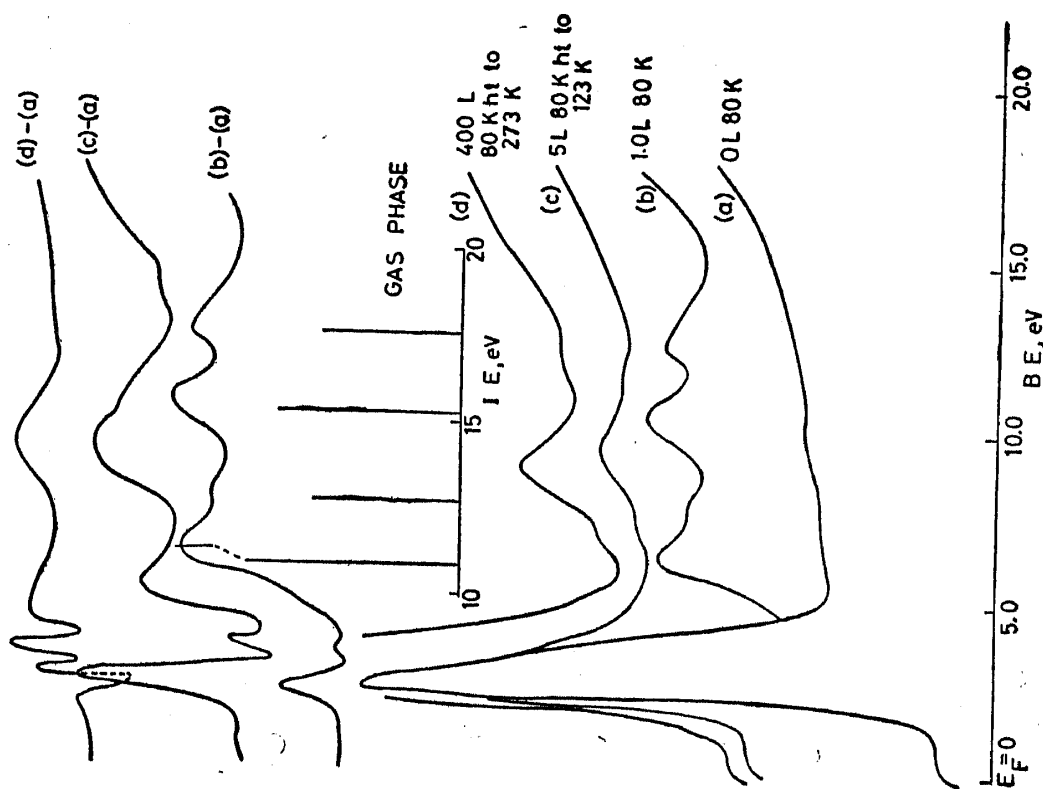


Figure 3. HeII spectra of methanol adsorbed on Cu at different temperatures and exposures. Difference spectra are also shown in the figure along with the positions of bands in the gas phase.

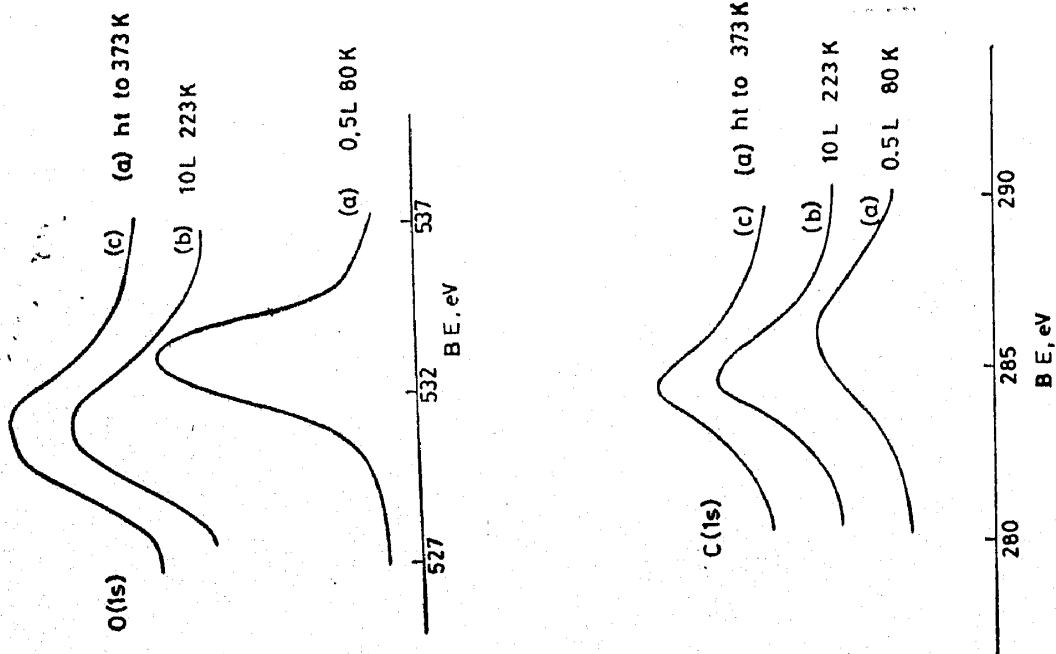


Figure 4. Carbon 1s and oxygen 1s bands in xps of methanol adsorbed on Fe at different temperatures and exposures.

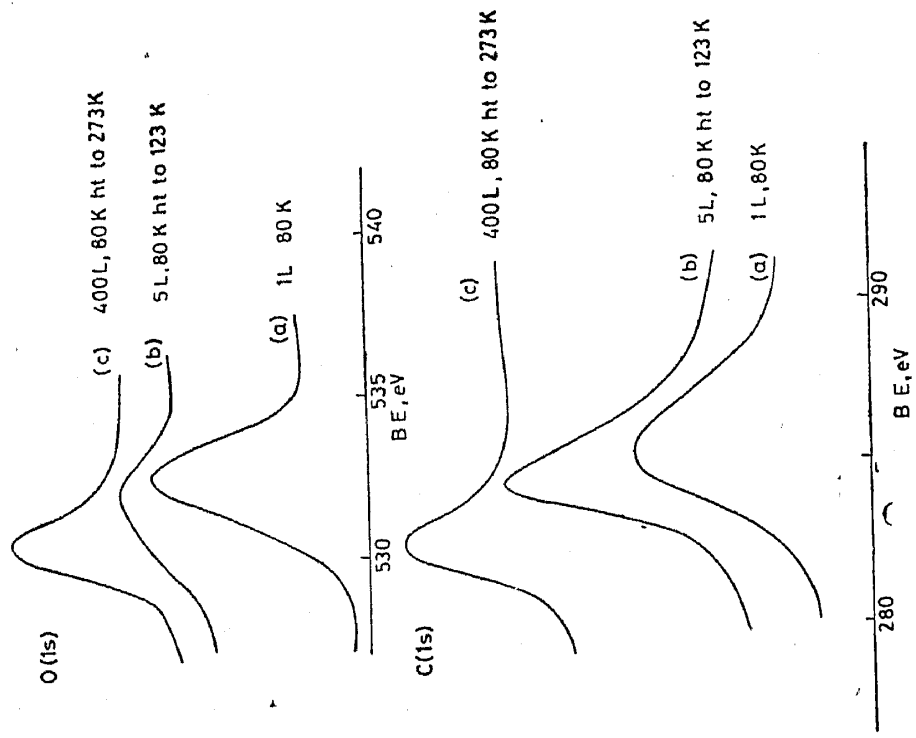


Figure 5. Carbon 1s and oxygen 1s bands in xps of methanol adsorbed on Cu at different temperatures and exposures.

3.1b : In the case of Cu, warming to 123 K results in the appearance of two bands at 5.3 and 9.3 eV in the difference spectrum (figure 3). Formaldehyde adsorbed on Cu gives a UV photoelectron spectrum (Kojima *et al* 1981) very similar to that shown in figure 3 with bands at 5.4 eV and 8.5 eV (weak) as well as a broad band extending between 8.9 and 11.0 eV with the maximum around 10 eV. The C (1s) and O (1s) bands in xps at 123 K are shifted towards lower binding energies suggesting a decomposition of methanol (figure 5). It, therefore, appears that methanol dissociates to give formaldehyde on the Cu surface studied by us at 123 K. This observation differs from that of Bowker and Madix (1980) who found the methoxy species on Cu (110) surface when methanol adsorbed at 140 K was subsequently heated to 270 K ; these workers employed much higher exposures than in the present study.

3.1c : In the case of Ni, warming to 123 K results in drastic changes in the HeII spectrum (figure 2). The C (1s) and O (1s) bands in xps are shifted towards lower binding energies indicating new species due to decomposition of methanol. We attribute the complex HeII spectra to the presence of more than one type of species, probably CH_3O , H_2CO and other products ; such products are known to be formed on Ni surface (Kojima *et al* 1981 ; Demuth and Ibach 1979).

3.1d : On warming to 300 K or higher, we observe considerable changes in the UVPS of the adsorbed species on all the three metal surfaces. The C (1s) and O (1s) bands in xps are also further shifted to lower binding energies (figures 4 and 5) and appear around 284.0 eV (282.7 eV for Cu) and 530.6 eV respectively. These changes suggest the formation of CO and carbide species on the metal surfaces due to the decomposition of the intermediate species observed at 123/223 K.

Our observation of the occurrences of different types of transformations of methanol on the three metal surfaces studied by us is interesting indeed. In table 2 we show the various adsorbed species formed on Fe, Ni and Cu surfaces at different temperatures. We can understand the formation of CH_3O and H_2CO from CH_3OH on metal surfaces in terms of the sequences shown in chart 1. Thus, the formation of methoxy species on Fe surface could occur as shown in sequence (a) of chart 1. Formation of H_2CO can occur either by sequence (b) or (c) in chart 1. Sequence (c) has been noticed on Ag metal by Wachs and Madix (1978). However, in the case of Cu, sequence (b) is more probable since the heat of chemisorption of hydrogen (ΔH_a) is somewhat low. In table 3 we have listed the heats of chemisorption of hydrogen taken from Stevenson (1955). We see that on Cu, ΔH_a is lowest suggesting thereby that adsorption of hydrogen is not as favoured. Formation of H_2CO may therefore not occur by sequence (c) which would require chemisorption of hydrogen on Cu.

3.2. Ethanol

Figure 6 shows the ultraviolet photoelectron spectrum of ethanol adsorbed on Fe at 273 K. The spectrum shows four distinct bands at 5.5, 7.8, 9.2 and 10.5 eV. On comparison with the gas phase spectrum of ethanol, we see that bands due to π (CH_2) and σ (CO) orbitals are missing. It appears that the spectrum in figure 6 is due to ethoxy species similar to that observed on Cu surface by Carlson *et al*

Table 2. Products obtained from methanol, ethanol, diethylether, methyl acetate and methylamine adsorbed on metal surfaces.

| Approximate temperature (K) | Fe | Ni | Cu |
|-----------------------------|---|---|---|
| <i>Methanol</i> | | | |
| 80 | CH ₃ OH | CH ₃ OH | CH ₃ OH |
| 123/223 | CH ₃ O | Transformation products | H ₂ CO |
| 300 | CO | CO | CO |
| <i>Ethanol</i> | | | |
| 273 | C ₂ H ₅ O | .. | .. |
| <i>Diethylether</i> | | | |
| 80 | C ₂ H ₅ OC ₂ H ₅ (chemisorbed) | C ₂ H ₅ OC ₂ H ₅ (physisorbed) | C ₂ H ₅ OC ₂ H ₅ (physisorbed) |
| 223-323 | Transformation products | Transformation products | Transformation products |
| <i>Methyl acetate</i> | | | |
| 80 | CH ₃ COOCH ₃ | CH ₃ COOCH ₃ | CH ₃ COOCH ₃ |
| 123/173 | CH ₃ O | Transformation products | H ₂ CO |
| <i>Methylamine</i> | | | |
| 80 | .. | .. | CH ₃ NH ₂ |
| 123 | .. | .. | Partial decomposition |
| 173 | CH ₃ NH ₂ + decomposed products | .. | .. |
| 300 | Decomposition products | .. | Decomposition products |

(1981). Ethanol is apparently adsorbed molecularly only at low temperatures just as methanol.

3.3. Diethylether

Figures 7-9 show the UVP spectra of diethylether adsorbed at 80 K on Fe, Ni and Cu surfaces. Difference spectra and the gas phase spectrum are also shown in these figures. In table 1 we have shown the positions and assignments of chemisorbed diethylether. On matching the most intense band of the difference spectra with the 17.2 eV gas phase band, we find that the lone-pair orbital shows a shift of about 0.8 eV on Fe due to chemisorption; no such shift is observed on Cu and Ni surfaces. Thus, the spectra in figures 8 and 9 appear to be due to physisorbed diethylether on Ni and Cu surfaces. It is not clear why we are

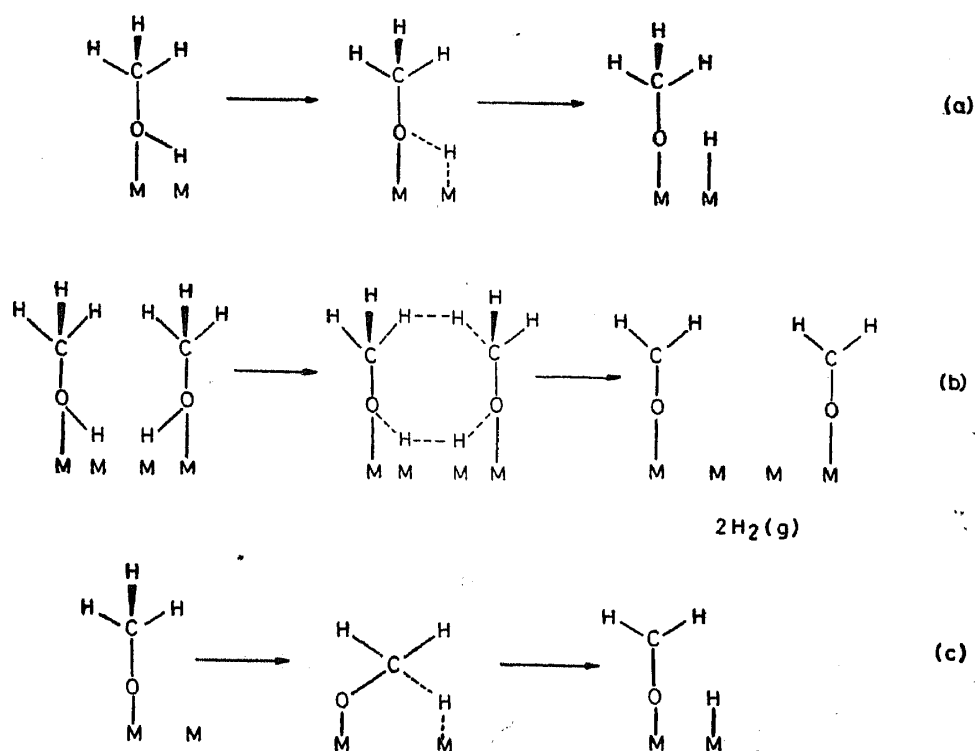


Chart 1. Mechanism of formation of methoxy species and formaldehyde from methanol adsorbed on metals.

Table 3. Heat of chemisorption of hydrogen (ΔH_a) on metals and the products formed by methanol on their surfaces.

| Metal | $-\Delta H_a^*$ kcal/mole | Product on warming to 123/223 K |
|-------|------------------------------|---|
| Fe | 31.6 | CH_3O |
| Ni | 28.9 | $\text{CH}_3\text{O}/\text{H}_2\text{CO}$ |
| Cu | 25.6 | H_2CO |

* From Stevenson (1955).

finding this difference in behaviour amongst the three metals ; errors in matching the gas phase and difference spectra could partly contribute to this difficulty since there are only three bands in the gas phase spectrum. XP spectra in the C (1s) and O (1s) regions of Fe and Ni surfaces are shown in figures 10 and 11. The C (1s) region shows two distinct bands in the case of Fe at 286.5 and 289.6 eV while in the case of Ni (and Cu, not shown in the figure) a single band at 285.9 is observed. The O (1s) band appears around 533.7 eV. XPS and UVPS data suggest that molecular diethylether interacts in a distinctly different way with Fe as compared to Ni and Cu.

On warming, drastic changes are observed in the UVP spectra (figures 7-9). XPS in the C (1s) and O (1s) regions show bands at lower binding energies around 284 eV and 530 eV respectively. These suggest dissociation of diethylether. It

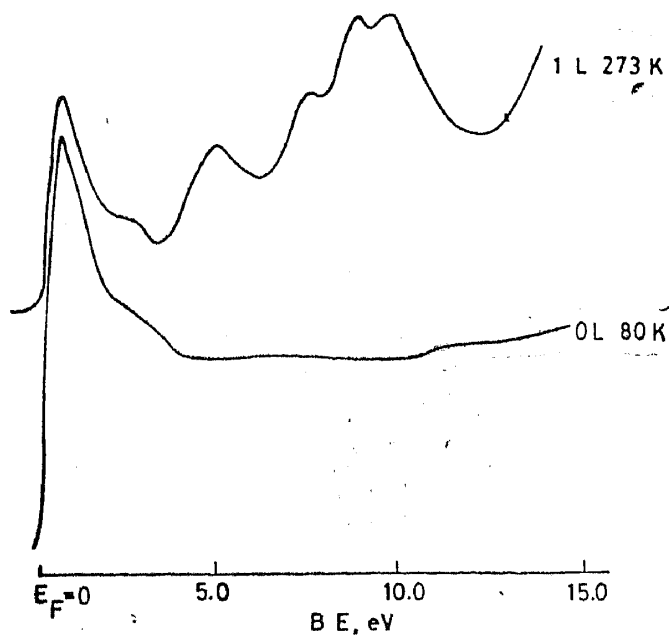


Figure 6. HeII spectra of ethanol adsorbed on Fe at 273 K.

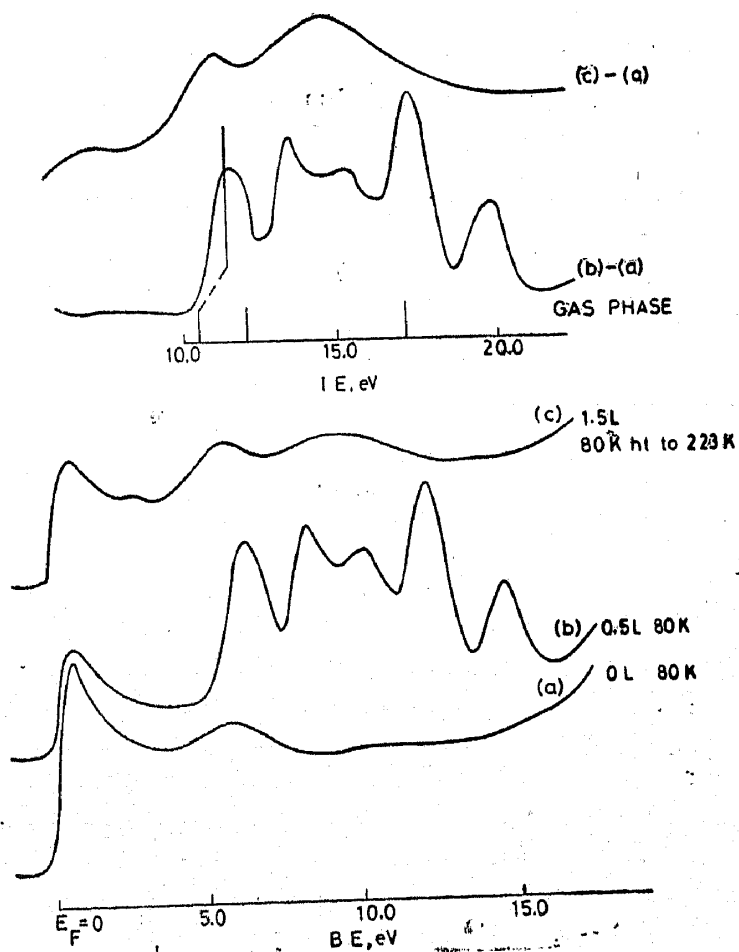


Figure 7. HeII spectra of diethyl ether adsorbed on Fe at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase,

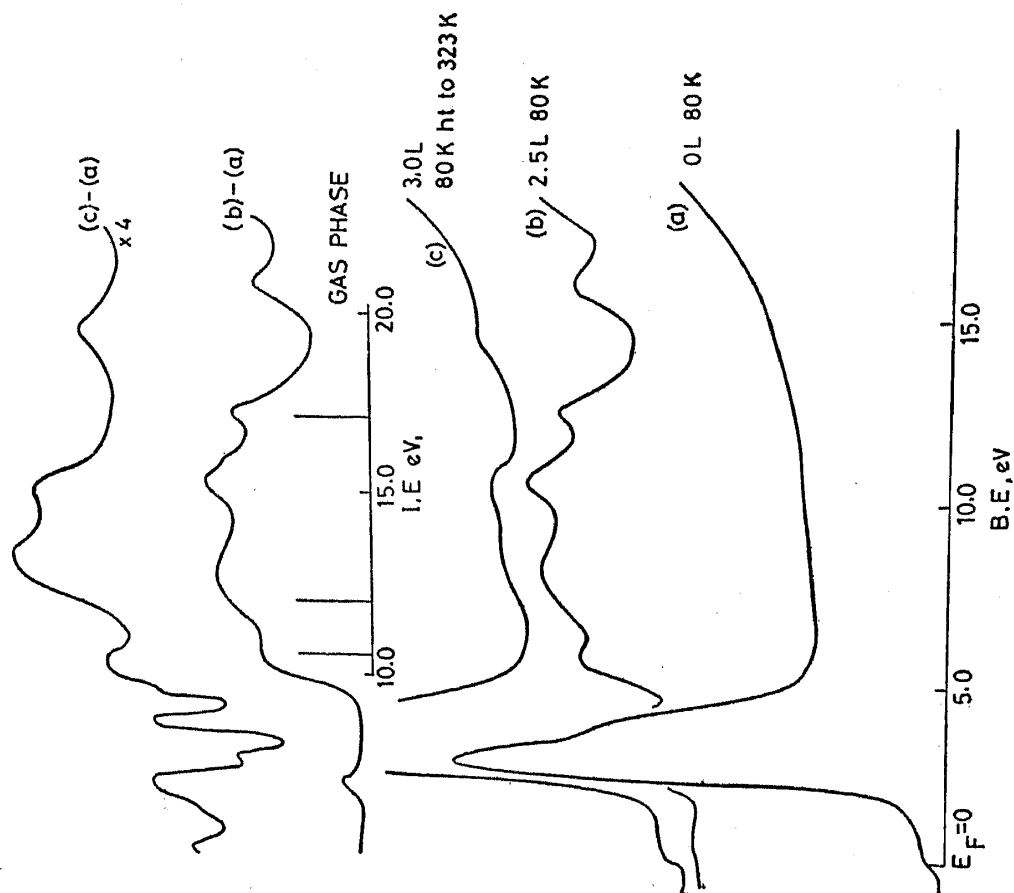


Figure 9. HeII spectra of diethyl ether adsorbed on Cu at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

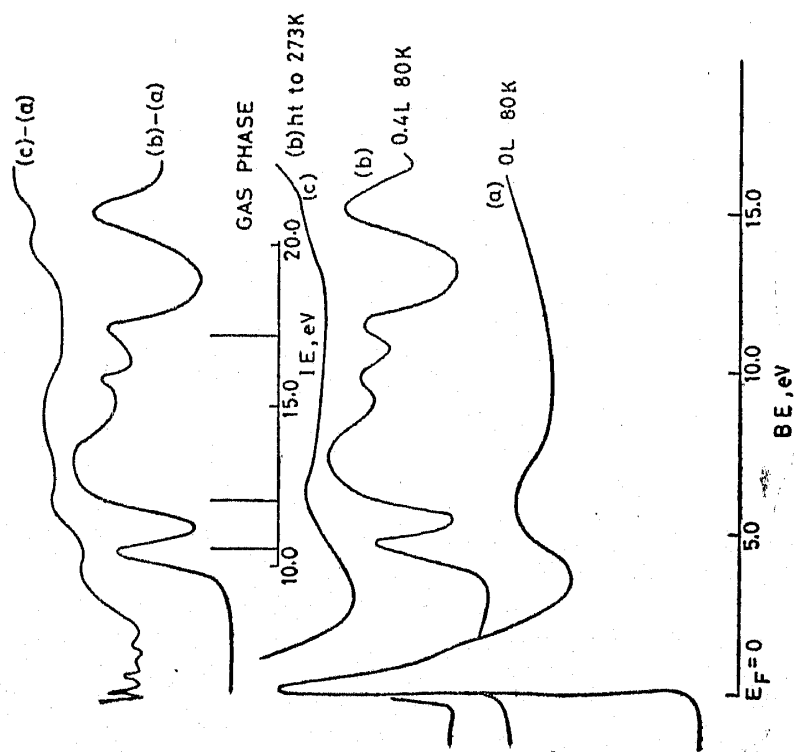


Figure 8. HeII spectra of diethyl ether adsorbed on Ni at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

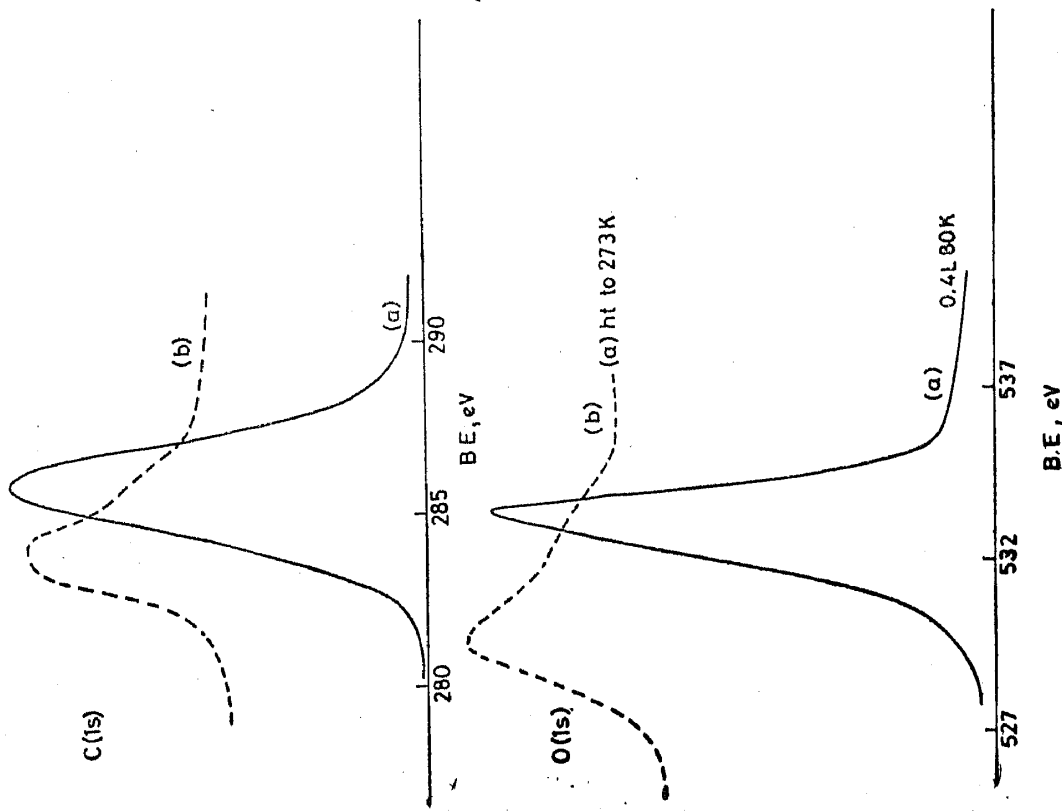


Figure 11. Carbon 1s and oxygen 1s bands in xps of diethyl ether adsorbed on Ni at different temperatures and exposures.

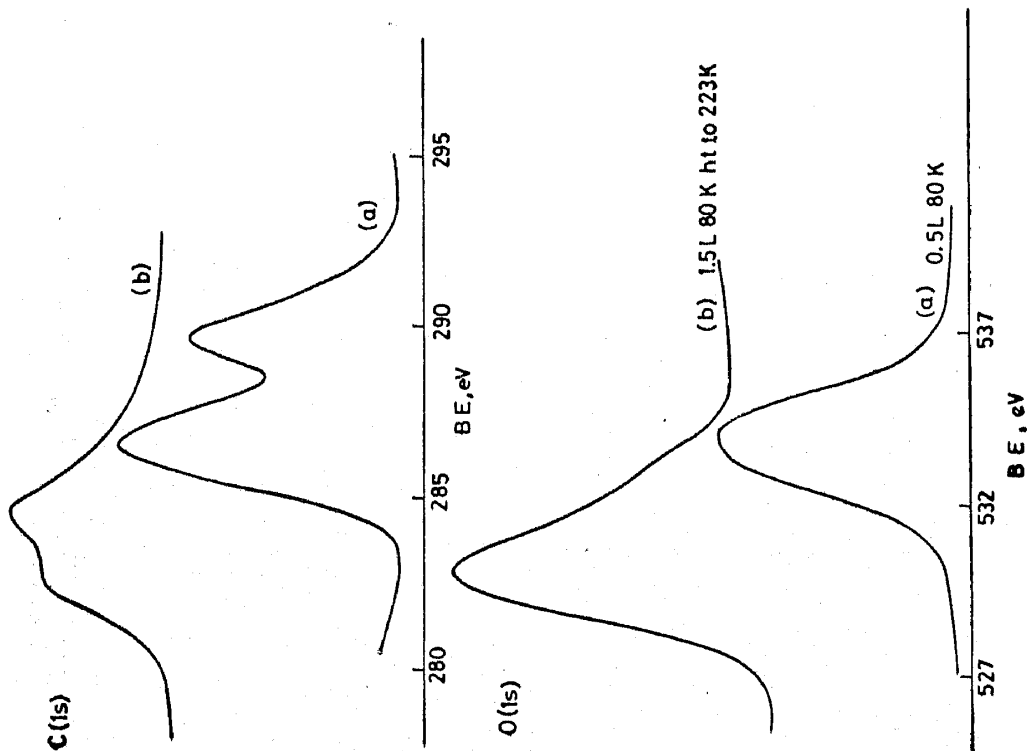


Figure 10. Carbon 1s and oxygen 1s bands in xps of diethyl ether adsorbed on Fe at different temperatures and exposures.

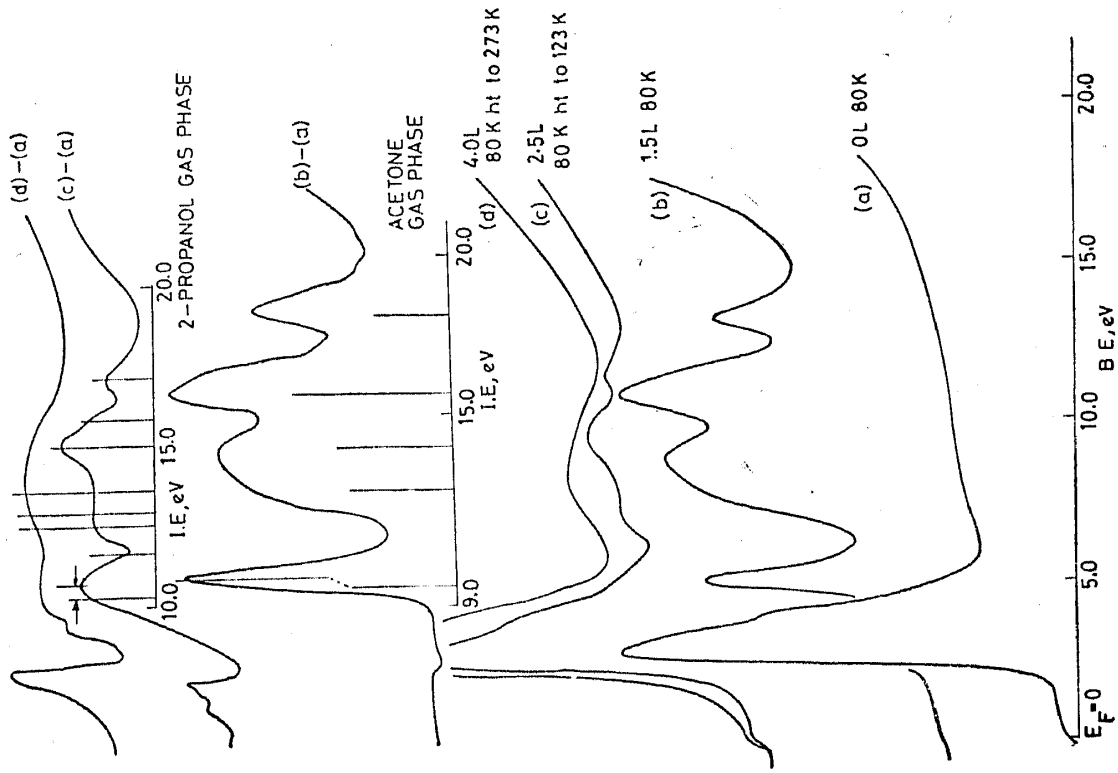


Figure 13. HeII spectra of acetone adsorbed on Cu at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

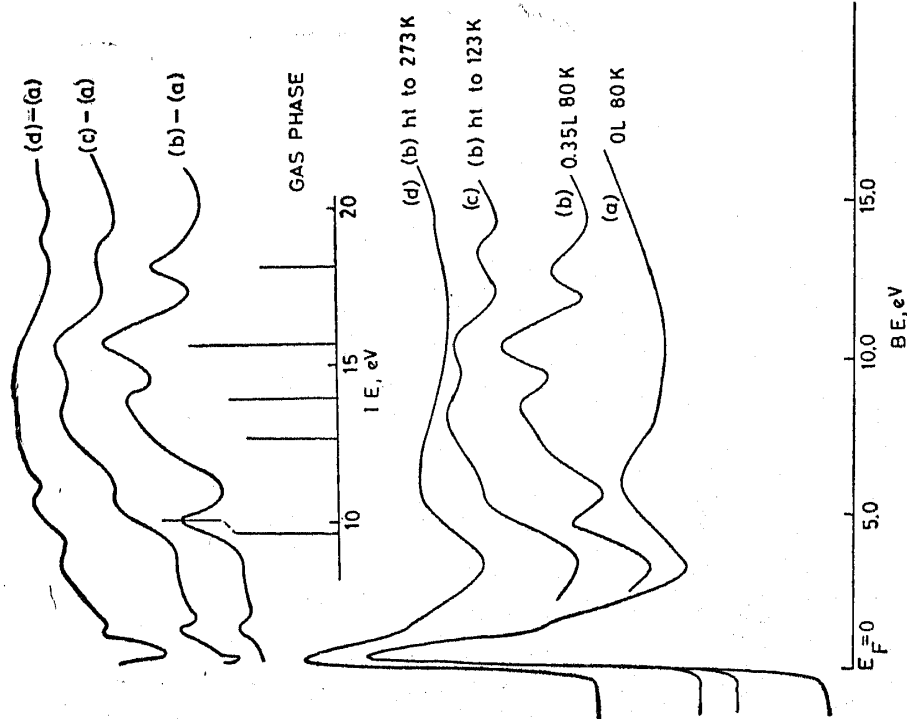


Figure 12. HeII spectra of acetone adsorbed on Ni at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

appears from the difference spectra at these temperatures (223–323 K), that diethylether undergoes different transformations on these metal surfaces. We are not able to assign the spectra to any definite species at this stage.

3.4. Acetone

HeII spectra of acetone adsorbed on Ni and Cu at 80 K are shown in figures 12 and 13. Difference spectra are also compared with the gas phase spectrum in these figures. It is clear that at 80 K acetone is molecularly adsorbed on both Ni and Cu surfaces. The highest lying lone-pair orbital shows a chemisorption shift towards higher binding energy by about 0.5 eV. Electron states of molecularly adsorbed acetone and their assignments are listed in table 1. The O(1s) bands in xps (figures 14 and 15) appear around 532.5 eV in both the metals; the C(1s) spectrum shows two distinct bands on Ni at 285 and 288 eV corresponding to the two types of carbons (methyl and carbonyl respectively). These bands appear at 291.23 and 293.88 eV in the spectrum of acetone in the gas

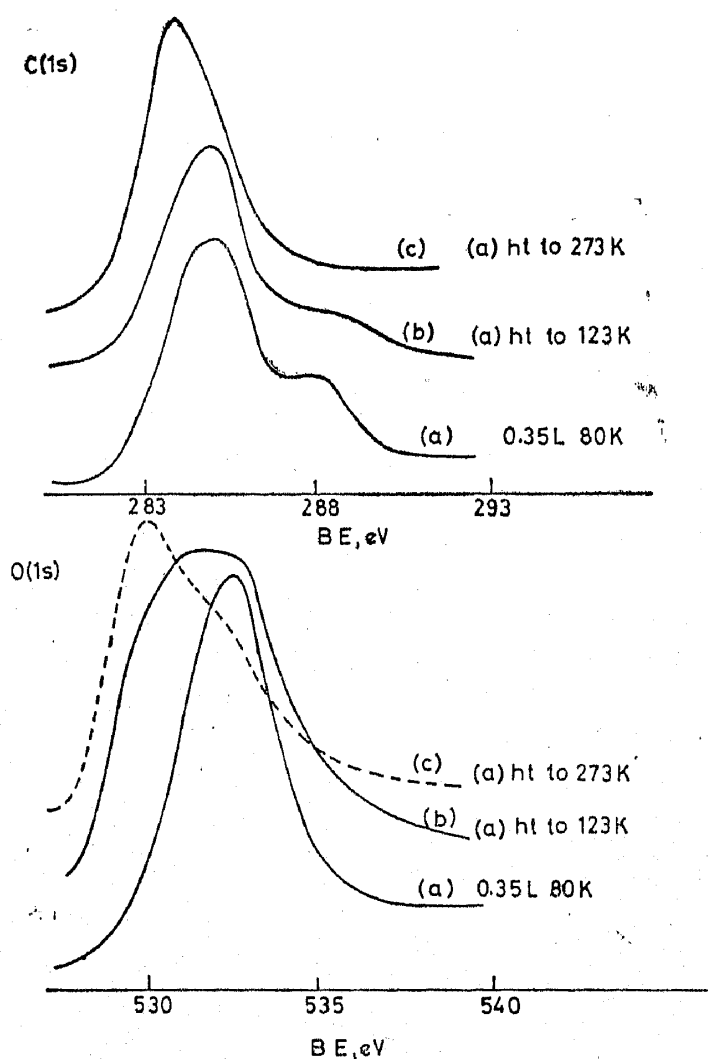


Figure 14. Carbon 1s and oxygen 1s bands in xps of acetone adsorbed on Ni at different temperatures and exposures.

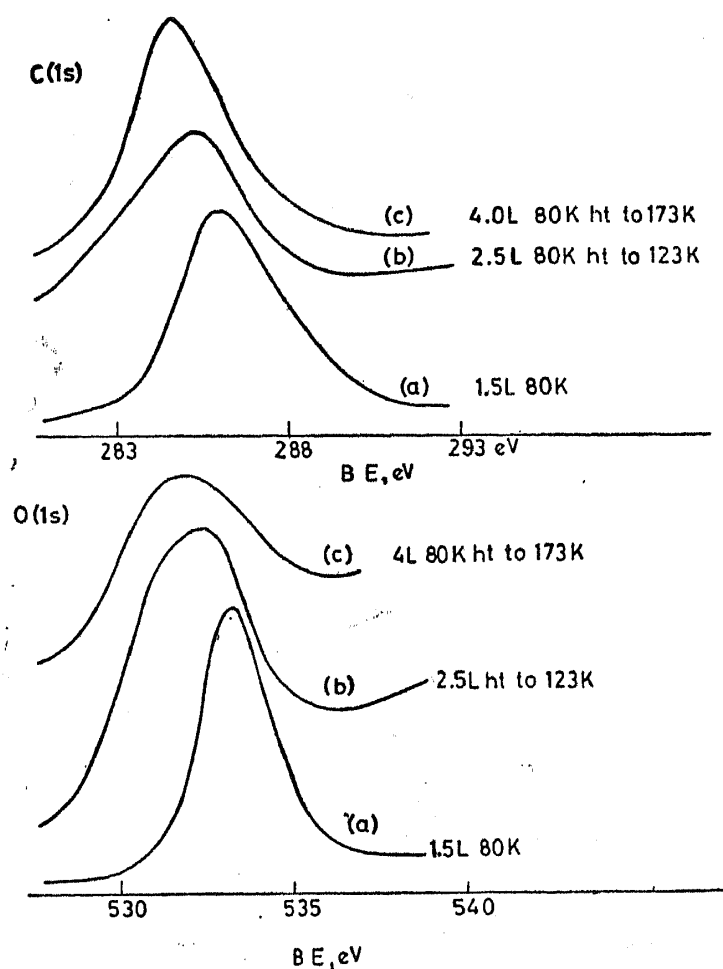


Figure 15. Carbon $1s$ and oxygen $1s$ bands in XPS of acetone adsorbed on Cu at different temperatures and exposures.

phase (Bakke *et al* 1980). On Cu, the two bands in the C($1s$) spectrum are not resolved (figure 15).

We notice several changes in UVPS of adsorbed acetone on warming. The resultant changes are noted below :

3.4a : In the case of Cu, on warming to 123 K, UVPS shows definitive changes as shown in figure 13. The resulting spectrum is similar to the gas phase spectrum of 2-propanol (figure 13) reported by Katsumata *et al* (1973). The formation of 2-propanol implies surface reduction of acetone. The C($1s$) and O($1s$) bands in XPS show a shoulder on the lower binding energy side at 123 K.

3.4b : In the case of Ni, drastic changes are observed in the spectra on warming to 123 K. The appearance of the spectrum is suggestive of the presence of more than one surface species formed due to the dissociation of acetone. The C($1s$) and O($1s$) bands in XPS show shoulders on the lower binding energy side. The probable surface species are 2-propanol and propene beside acetone itself.

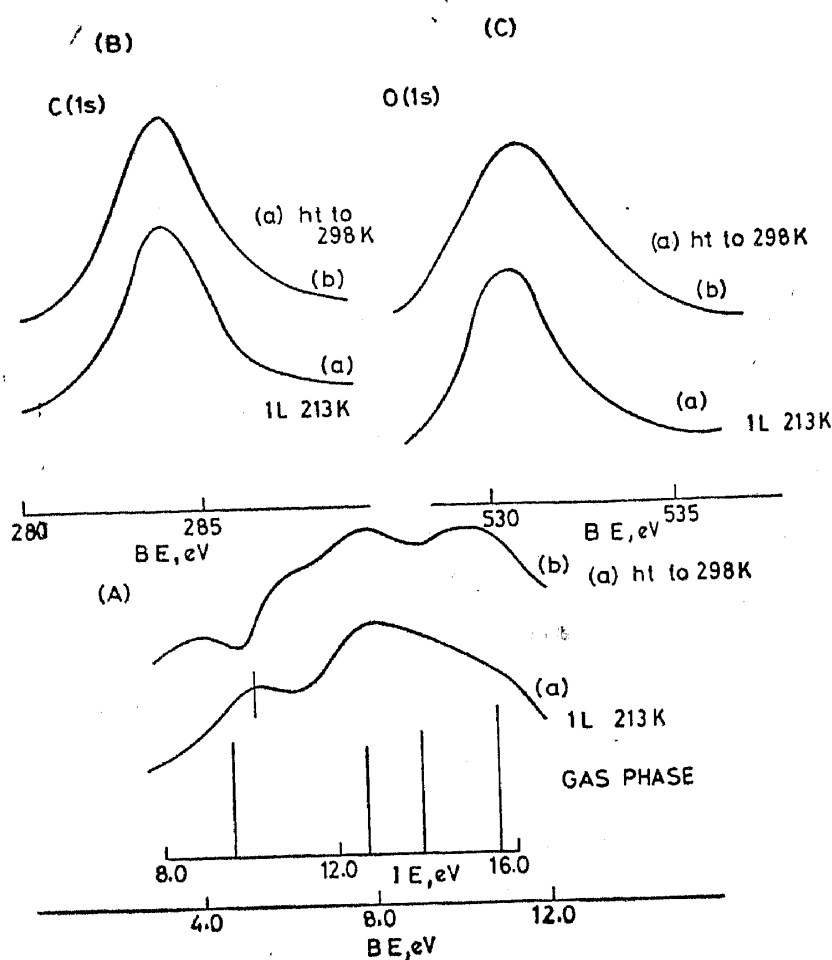


Figure 16. (A) Difference spectra of acetone adsorbed on Fe at different conditions. (B) Carbon 1s bands in xps and (C) Oxygen 1s bands of acetone adsorbed on Fe.

On further warming to 300 K, we notice considerable changes in UVPS; the C(1s) and O(1s) bands are shifted to lower binding energies and suggest the presence of adsorbed CO.

3.4c : Adsorption of acetone on Fe at 213 K shows broad features quite unlike the gas phase acetone spectrum (figure 16). This and the appearance of C(1s) and O(1s) bands in xps at lower binding energies (figure 16) indicate dissociative adsorption of acetone at this temperature. Molecular adsorption occurs only at low temperatures (~100 K). Further heating to 300 K results in the appearance of C(1s) and O(1s) at still lower binding energies; these along with the changes observed in UVPS are indicative of the formation of CO species.

3.5. Acetaldehyde

UV photoelectron difference spectra of acetaldehyde adsorbed on Fe are shown in figure 17 along with the gas phase spectrum. Although we could match the observed bands in the difference spectrum against the gas phase spectrum of acetaldehyde, we find that the bands in the difference spectra are much too broad

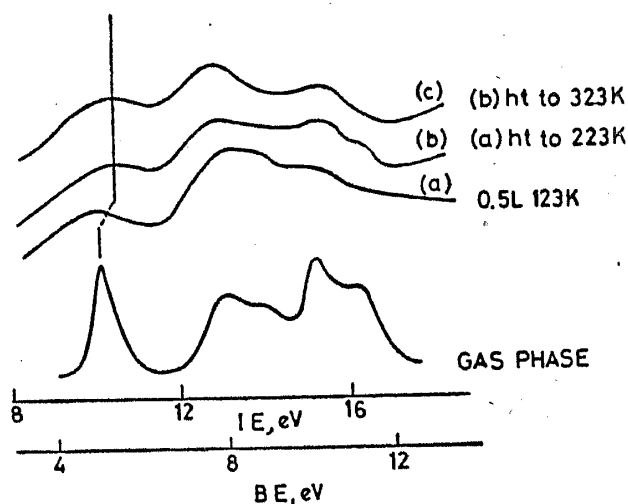


Figure 17. Difference HeII spectra of acetaldehyde adsorbed on Fe at different temperatures and exposures; gas phase spectrum is also shown.

to be due to molecularly chemisorbed species alone. It is possible that there is some decomposition over the entire range 123 K–323 K. However, if we decide to match the 13.2 eV gas phase band with the second band in the difference spectra, we find a lone-pair shift of 0.4 eV due to the molecularly chemisorbed species.

3.6. Methyl acetate

HeII photoelectron spectra of methyl acetate adsorbed on Fe, Ni and Cu at 80 K are shown in figures 18–20. Difference spectra are also compared with the gas phase spectrum (Sweigart and Turner 1972) in these figures. The 12.9 eV band in the gas phase spectrum could be matched with the second band in the difference spectra. The difference spectra show a single band corresponding to the 10.5 eV (n_o) and 11.3 eV (π_{CO}) bands in the gas phase. The highest energy band in the region 13.5–14.5 eV that we see in the spectra of the adsorbed species is not found in the gas phase spectrum, since the latter was obtained with HeI excitation. The lone-pair orbital (n_o) shows a chemisorption shift towards higher binding energy of ~ 0.3 eV on all the three metal surfaces. In table 1 we have listed the energies and some of the assignments of UVPS bands of chemisorbed methyl acetate. We see that the lone-pair shift is much lower in methyl acetate than in methanol or acetone.

XPS spectra (figures 21–23) in the C(1s) region show two bands around 285.7 eV and 289.7 eV (290.0 eV for Ni); the band at 285.7 eV is due to methyl carbons while the carbonyl carbon is responsible for the band near 289.0 eV. The band near 285.7 eV is about twice as intense as the 289.7 eV band as expected. This is similar to the two bands observed in the C(1s) and O(1s) regions by Bowker and Madix (1981) and Edwards (1976) in their studies on acetic acid. The O(1s) band appears around 533.1 eV on all the three metals; this is a composite band arising from the overlap of the two bands due to the two different kinds of oxygen (C=O and C–O). This is evident from the large value of the fwhm (3.8–4.4 eV) compared to that found in methanol or acetone (2.4–3.0 eV). Both the UVPS

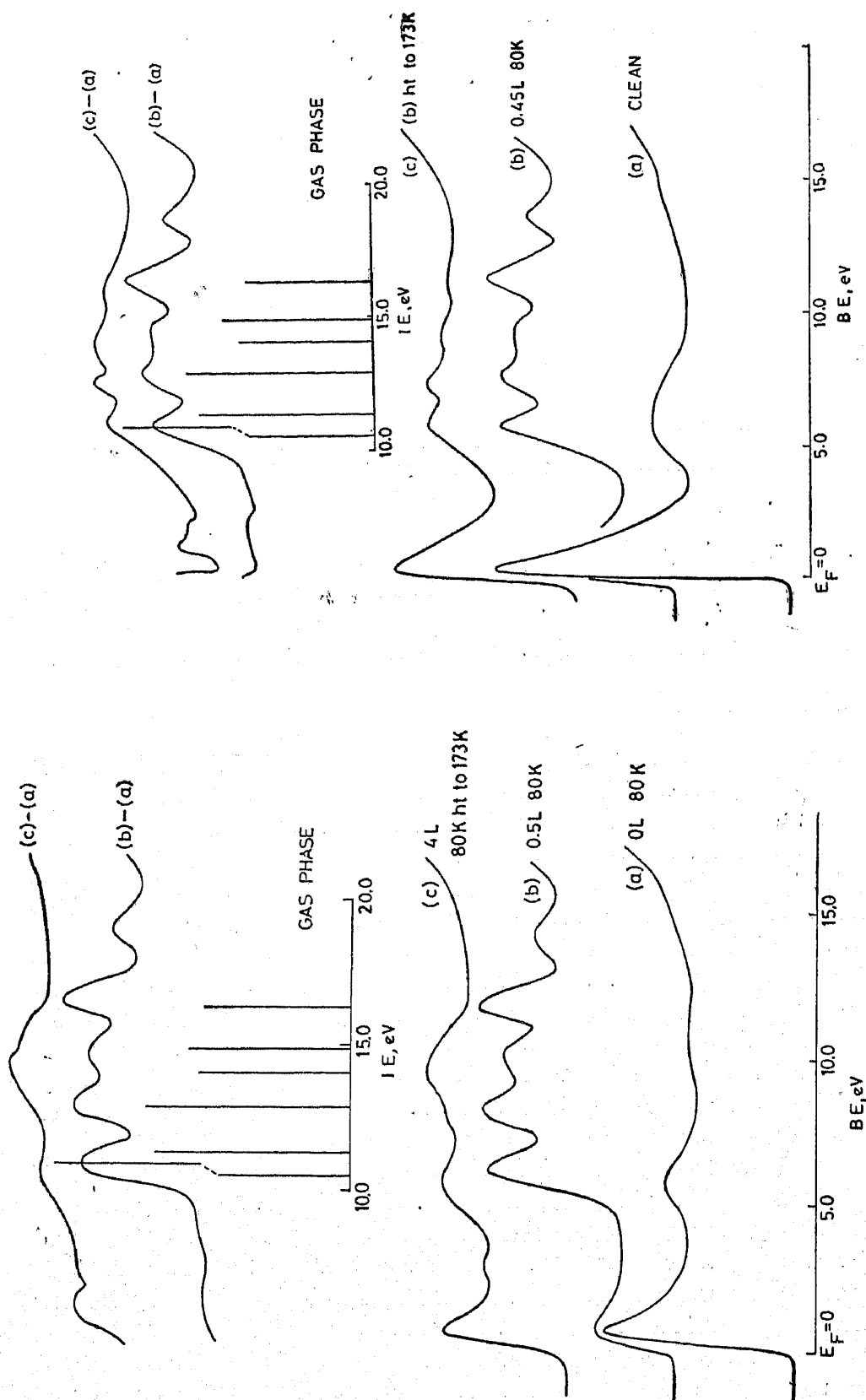


Figure 18. He I spectra of methyl acetate adsorbed on Fe at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

Figure 19. He I spectra of methyl acetate adsorbed on Ni at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

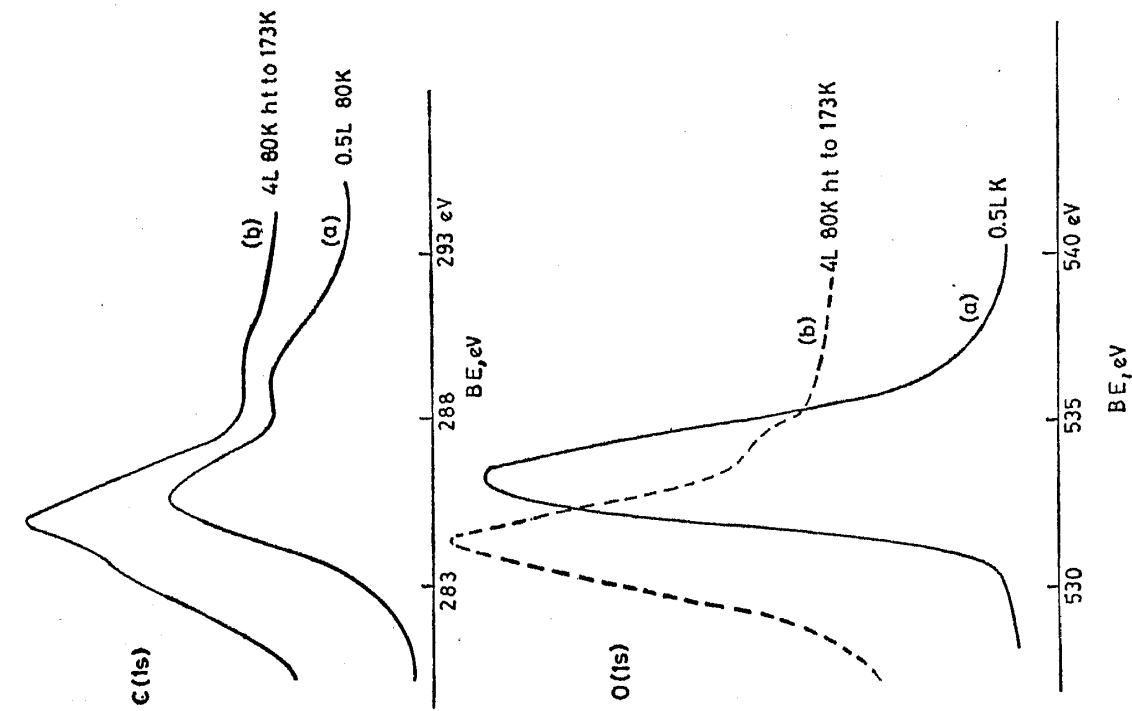


Figure 21. Carbon 1s and oxygen 1s bands in XPS of methyl acetate adsorbed on Fe at different temperatures and exposures.

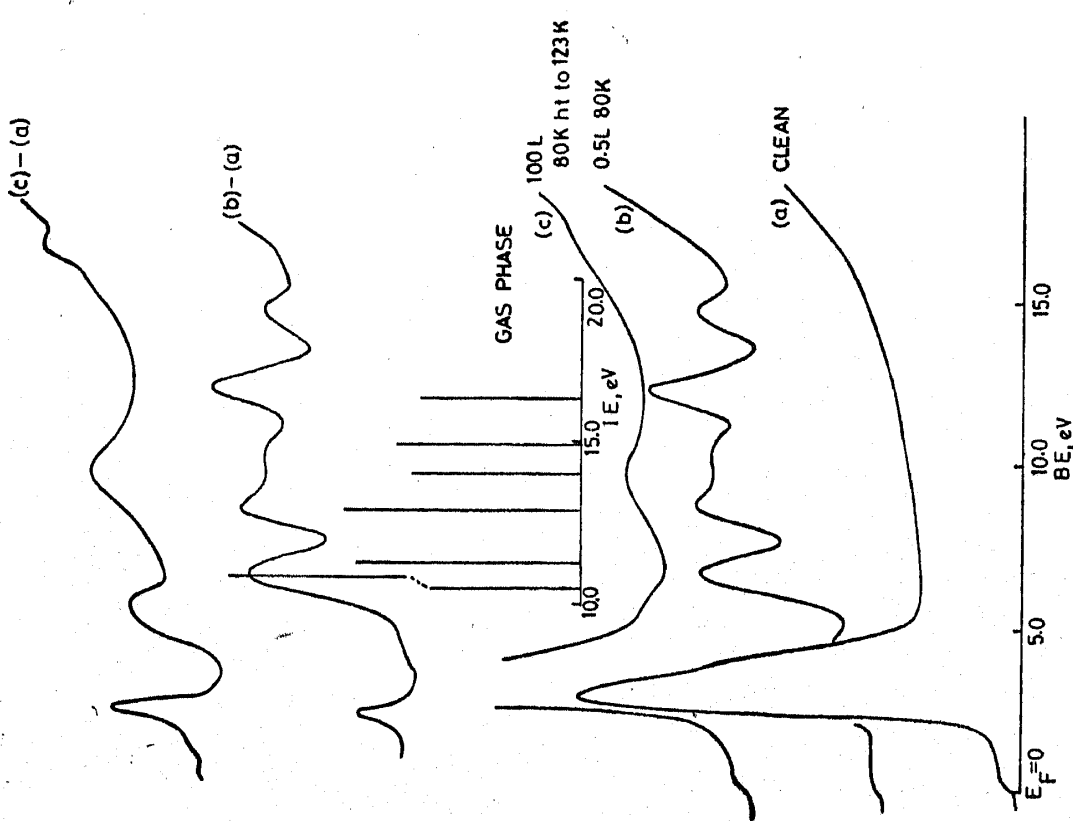


Figure 20. HeII spectra of methyl acetate adsorbed on Cu at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

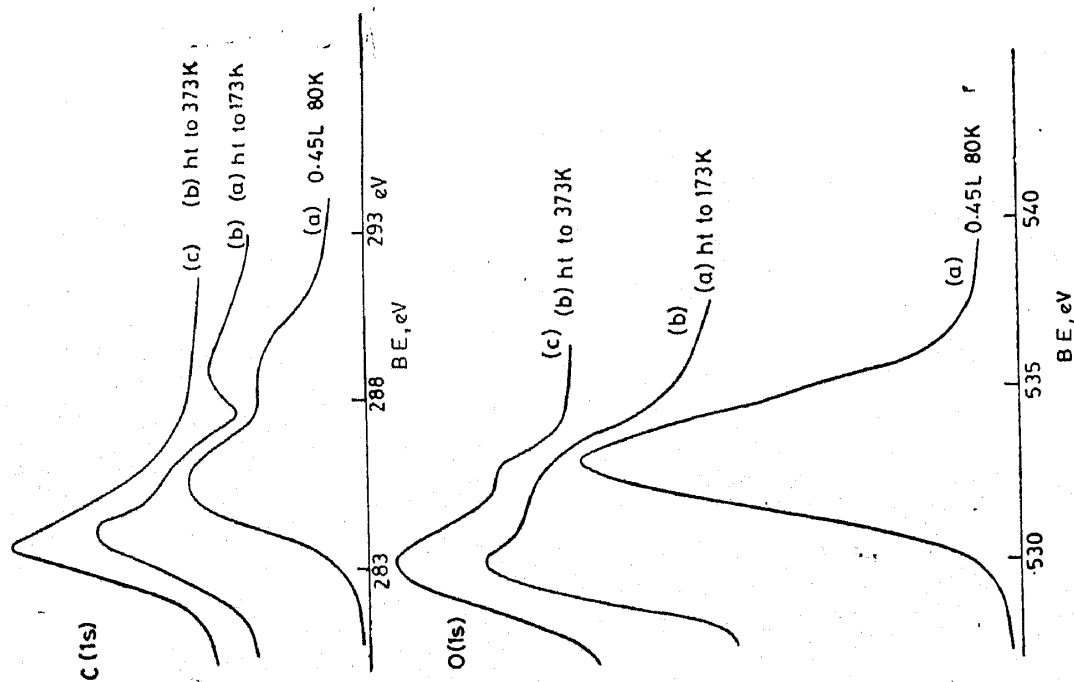


Figure 22. Carbon 1s and oxygen 1s bands in xps of methyl acetate adsorbed on Ni at different temperatures and exposures.

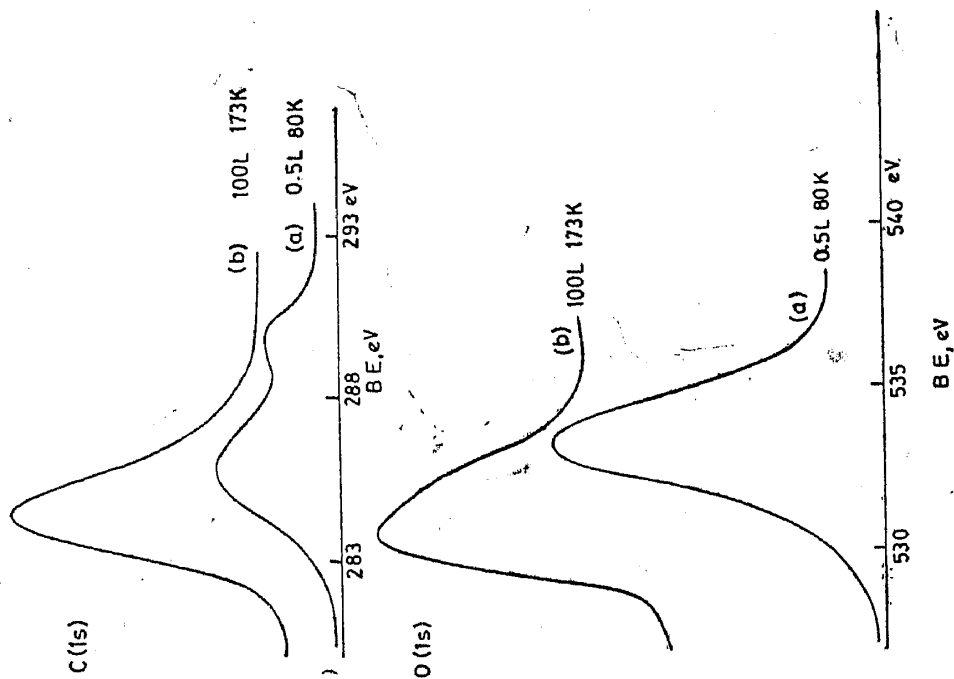


Figure 23. Carbon 1s and oxygen 1s bands in xps of methyl acetate adsorbed on Cu at different temperatures and exposures.

and XPS studies at 80 K clearly establish the presence of molecularly adsorbed methyl acetate on the three metals. We, however, notice significant changes in the spectra on warming the samples.

The main results of thermal effects are as follows :

3.6a : On the Fe surface, heating to 173 K causes drastic changes in the UVPS (figure 18). The resulting spectrum is identical to that of the methoxy species obtained on adsorbing methanol at 223 K. The C (1s) region in XPS shows a band at 284.8 eV while in the O (1s) region we see a band at 531.3 eV. In the case of methanol, we found the C (1s) and O (1s) bands at 284.7 and 531.1 eV respectively. It therefore appears that methyl acetate decomposes to give methoxy species on Fe when warmed to 173 K.

3.6b : On the Ni surface, warming to 173 K results in diffuse bands with features similar to the 80 K spectra in the UVPS (figure 19). In the C (1s) region, we see bands at 285.7 and 289.0 eV and a new band on the low energy side at 284.0 eV. The O (1s) region shows bands at 530.5 and 532.6 eV. These suggest that part of the adsorbed methyl acetate has undergone decomposition.

3.6c : On warming to 123 K, the UVPS of methyl acetate adsorbed on Cu shows drastic changes (figure 20). We see only two bands in the difference spectrum. The difference spectrum is similar to that obtained on warming methanol adsorbed on Cu from 80 K to 123 K wherein we found formation of formaldehyde on the surface. The C (1s) band in XPS appears at 284.6 eV at this temperature and the O (1s) band is broad with the maximum at 530.6 eV and a shoulder at 532.4 eV. At 123 K, methanol adsorbed on Cu shows the C (1s) band at 284.5 eV ; the O (1s) band is broad with a maximum at 532.3 eV and a distinct shoulder at 530.6 eV. The C (1s) and O (1s) bands are as expected of methyl acetate adsorbed at 123 K except that in the latter case the 530.6 eV band is more intense indicating decomposition of methyl acetate. Based on these XPS and UVPS results, we suggest that formaldehyde is formed on warming methyl acetate adsorbed on Cu just as in the case of methanol. It is interesting that adsorption of methyl formate (HCOOCH_3) on Cu at 295 K also yields formaldehyde (Kojima *et al* 1981).

In the adsorption of methyl acetate, only the lone-pair orbital, n_o , shows a relatively small chemisorption shift, but the orbital, π_{co} is unaffected. Methyl acetate, therefore, seems to interact with the metal through the lone-pair orbital of the ether-type oxygen rather than the carbonyl oxygen as shown in chart 2. The sequence of reactions taking place on metal surfaces is also shown in this chart. Formaldehyde could be formed as per sequence (a) on Cu, while methoxy species could be produced as per sequence (b) on Fe. It is interesting that the transformations found in methyl acetate are exactly the same as those found with methanol. In view of this observation (and also because of the small shift of the carbonyl lone-pair orbital energy), we seem to be justified in suggesting bonding through the ether-type oxygen of the ester to the metal in chart 2.

3.7. Ammonia

Ammonia adsorbed on Fe at 80 K shows a broad band around 7 eV and another around 12 eV at 80 K in the HeII spectra (figure 24). These two peaks corres-

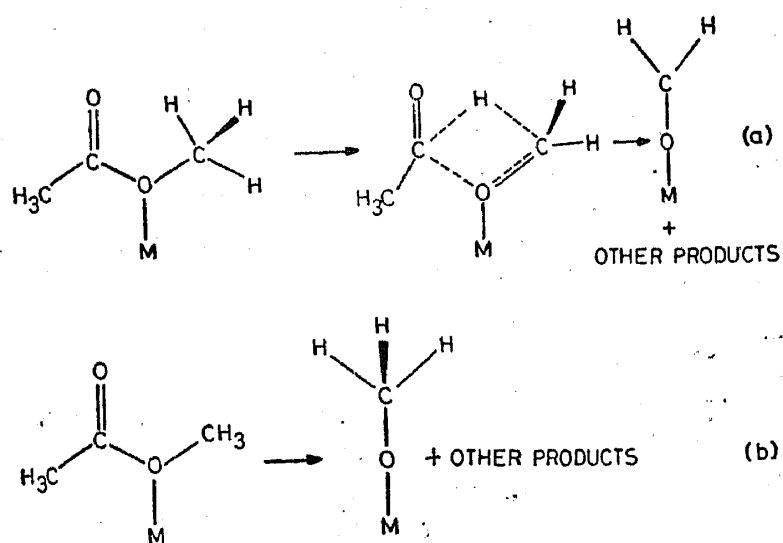


Chart 2. Mechanism of formation of methoxy species and formaldehyde from methyl acetate adsorbed on metals.

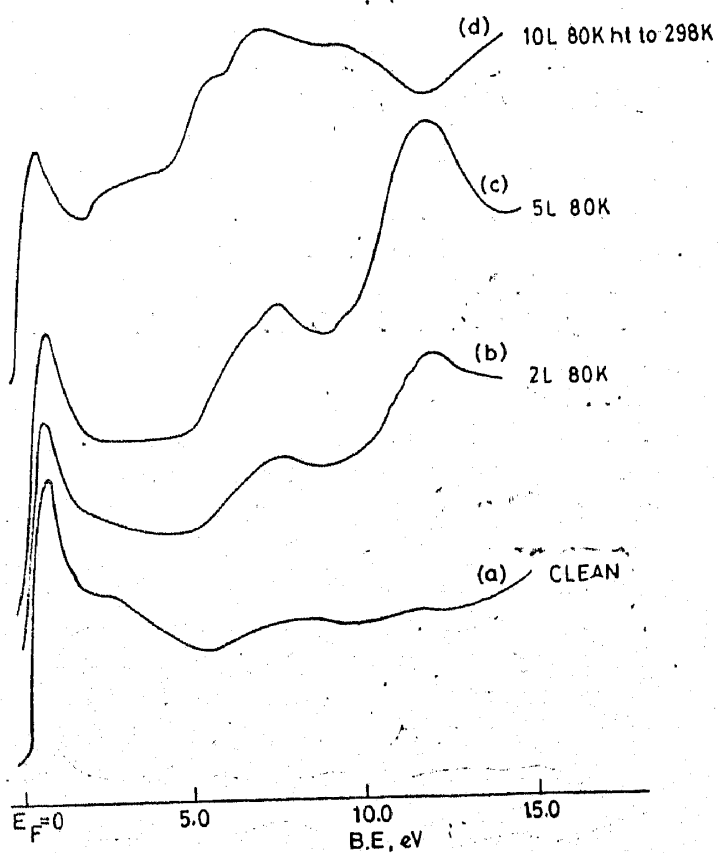


Figure 24. HeII spectra of ammonia adsorbed on Fe at different temperatures and exposures.

pond to the two bands at 10.2 and 14.9 eV in the gas phase spectrum of ammonia. On warming to 298 K, we notice significant changes in the spectrum similar to those reported by Kishi and Roberts (1977) suggesting dissociation of ammonia. The N(1s) signal of molecularly adsorbed species appears around 400 eV (figure 25). On warming this to 298 K, we see a weak band around 397 eV corresponding to a nitrogen species (N or NH) formed due to dissociation of ammonia.

3.8. Methylamine

HeII spectra of methylamine adsorbed on Cu at 80 K and Fe at 173 K are shown in figures 26 and 27. The difference spectra are compared with the HeI gas phase spectrum in these figures. The gas phase spectrum was shifted by ~ 4.4 eV (for Cu) and ~ 4.6 eV (for Fe) so as to obtain the best matching of all the bands between the gas phase and the difference spectra. The highest occupied orbital (lone-pair orbital of nitrogen) on methylamine is shifted towards higher binding energy by 1.0 eV on adsorption on Fe surface and by 0.6 eV on Cu surface. Electron states of adsorbed CH_3NH_2 are tabulated in table 1. XP spectra in the C(1s) region at low temperatures show bands at 286.0 eV (for Cu) and 285.0 eV (for Fe); in the N(1s) region, bands are found at 399.6 eV (for Cu), 399.1 eV (for Fe) as shown in figures 28 and 29. The relatively lower binding energy of the C(1s) peak on Fe could be due to partial decomposition of methylamine at 173 K on this surface. Such decomposition is also indicated by the broad maxima in the UVP difference spectra.

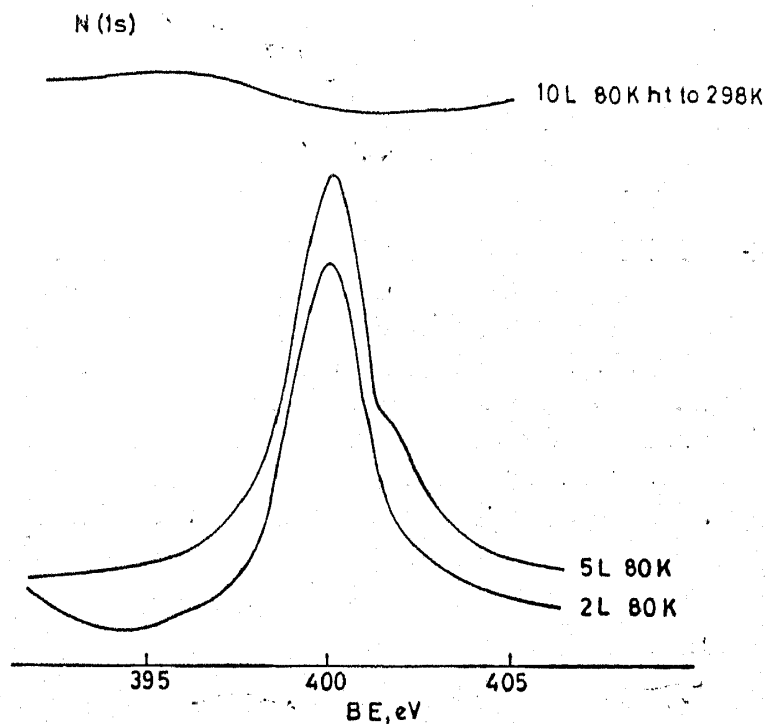


Figure 25. Nitrogen 1s spectra of ammonia adsorbed on Fe at different temperatures and exposures,

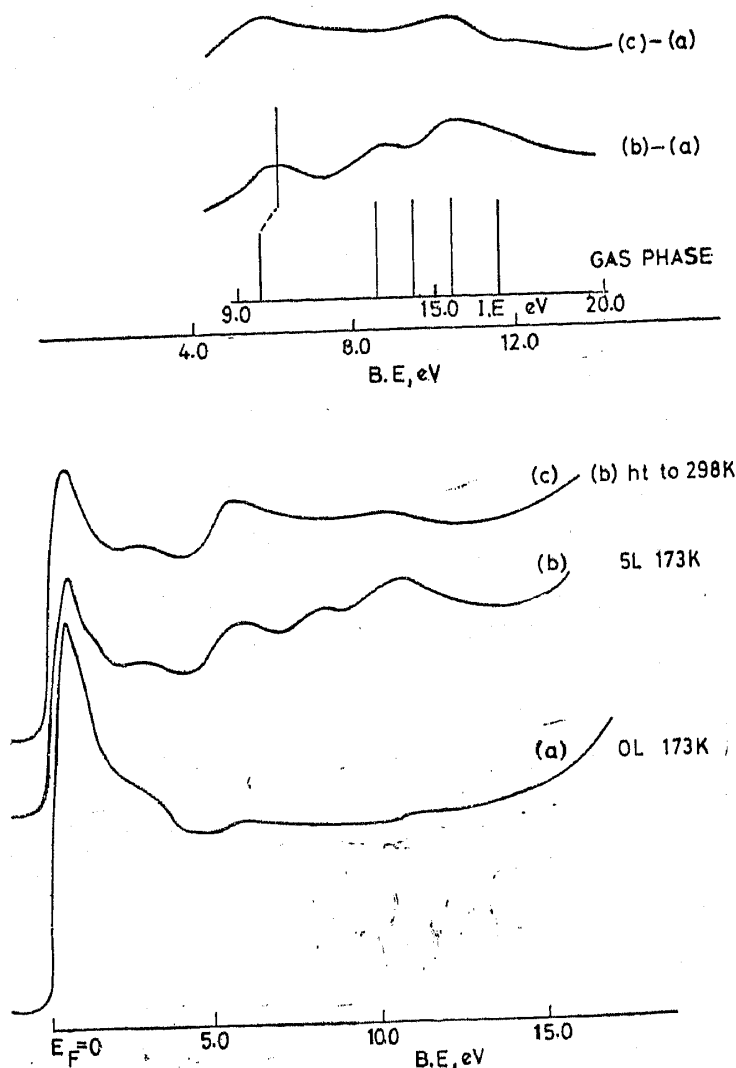


Figure 26. HeII spectra of methylamine adsorbed on Fe at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

UVPS of Cu + CH_3NH_2 show considerable changes on warming to 123 K and C(1s) and N(1s) bands in xps are shifted towards lower binding energies appearing at 285.0 eV and 399.1 eV. These observations suggest occurrence of decomposition of CH_3NH_2 to a nitrogenous species on the metal surface (just as in the case of NH_3). On warming to 300 K, drastic changes are seen in the UVPS on both Cu and Fe surfaces with almost complete disappearance of the bands due to molecular methylamine. The C(1s) band in xps is shifted to 284.0 eV and the N(1s) band shows little or no shift, but the intensity is appreciably lowered.

4. Concluding remarks

(a) All the organic molecules containing lone-pair orbitals that we have examined in the present study adsorb molecularly (associatively) on Fe, Ni and Cu surfaces at low temperatures (≤ 100 K).

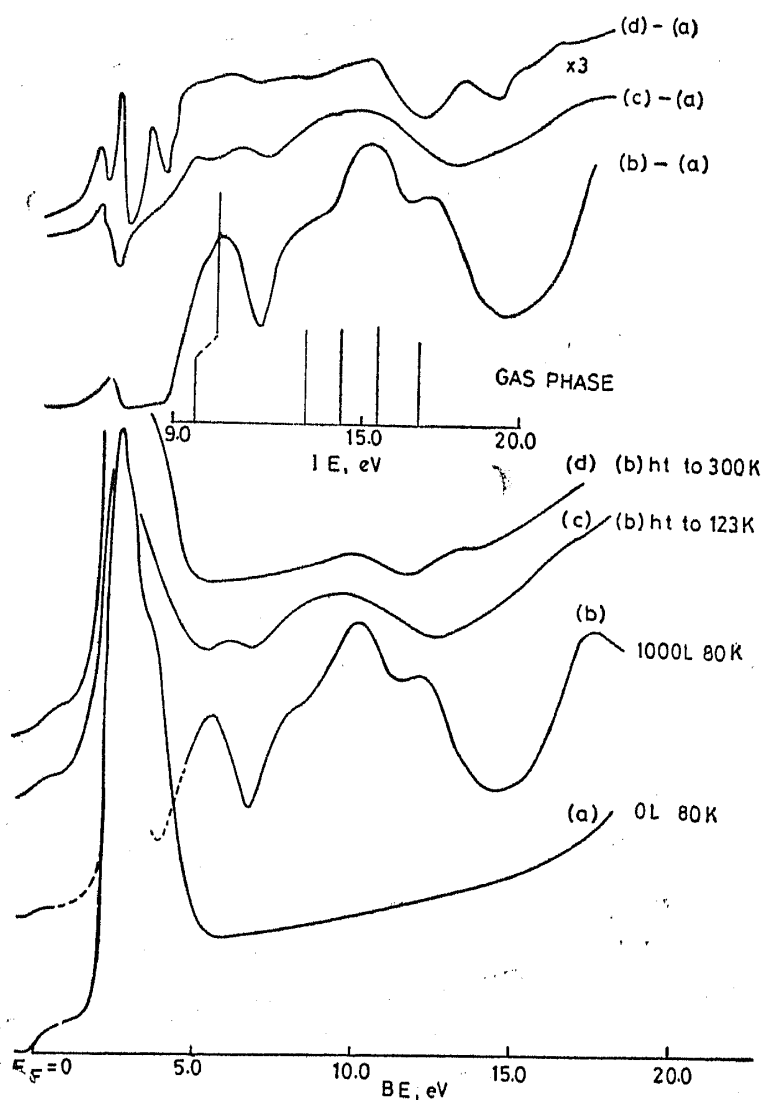


Figure 27. HeII spectra of methylamine adsorbed on Cu at different temperatures and exposures. Difference spectra are also shown along with the positions of bands in the gas phase.

(b) We are able to estimate the stabilization of the lone-pair orbitals due to chemisorption in terms of the increase in its binding energy. These data are presented in table 4 where we have listed the molecules in the order of increasing ionization energy of the lone-pair orbital. The data suggest that the shift generally shows an increasing trend with the decreasing first ionization energy as expected. Furthermore, the stabilization of the lone pair seems to vary as $\text{Fe} > \text{Ni} > \text{Cu}$, decreasing with increasing number of d -electrons, a trend that is not readily understandable.

(c) Chemisorption of molecules gives rise to variation in the core level binding energy of the atom containing the lone pair ($1s$ binding energy of oxygen or nitrogen in the present study would be expected to vary just as in coordination compounds). After accounting for extramolecular relaxation/polarization shifts

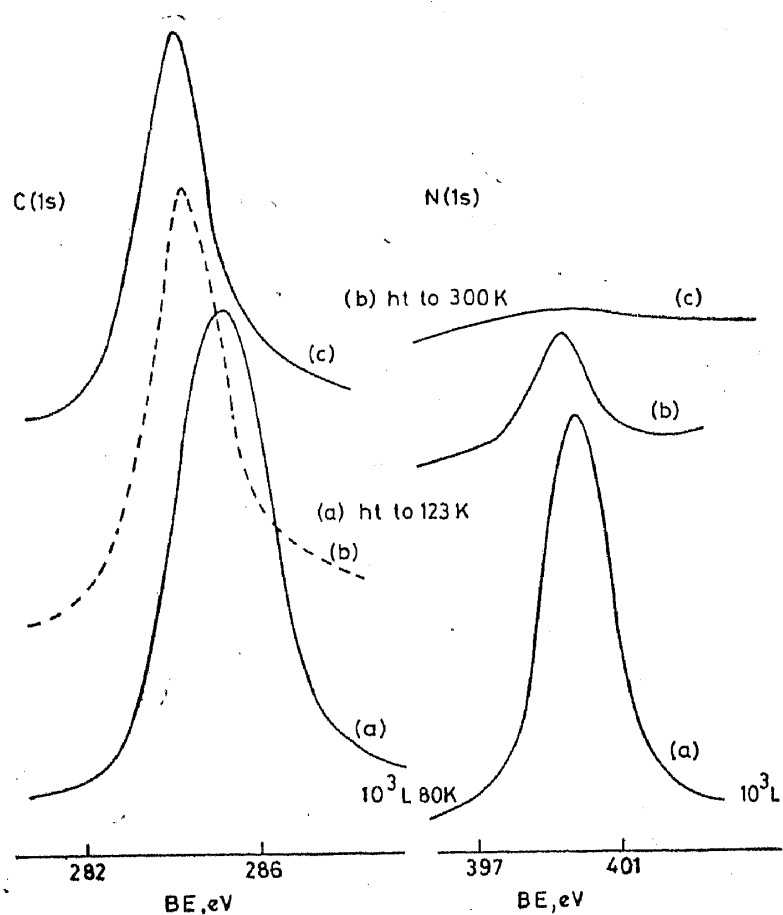


Figure 28. Carbon 1s and nitrogen 1s bands in xps of methylamine adsorbed on Cu at different temperatures and exposures.

Table 4. Stabilization of the lone-pair orbitals (in eV) on molecular chemisorption.

| Molecule | Lone-pair IE | Lone-pair shifts on | | |
|----------------|--------------|---------------------|-----|-----|
| | | Fe | Ni | Cu |
| Methanol | 10.8 | 0.6 | 0.6 | 0.5 |
| Methyl acetate | 10.5* | 0.4 | 0.3 | 0.3 |
| Acetone | 9.6 | .. | 0.5 | 0.4 |
| Diethylether | 9.6 | 0.8 | .. | .. |
| Methylamine | 9.6 | 1.0 | .. | 0.6 |

* The shifts are of the ether type oxygen which is involved in chemisorption bonding.

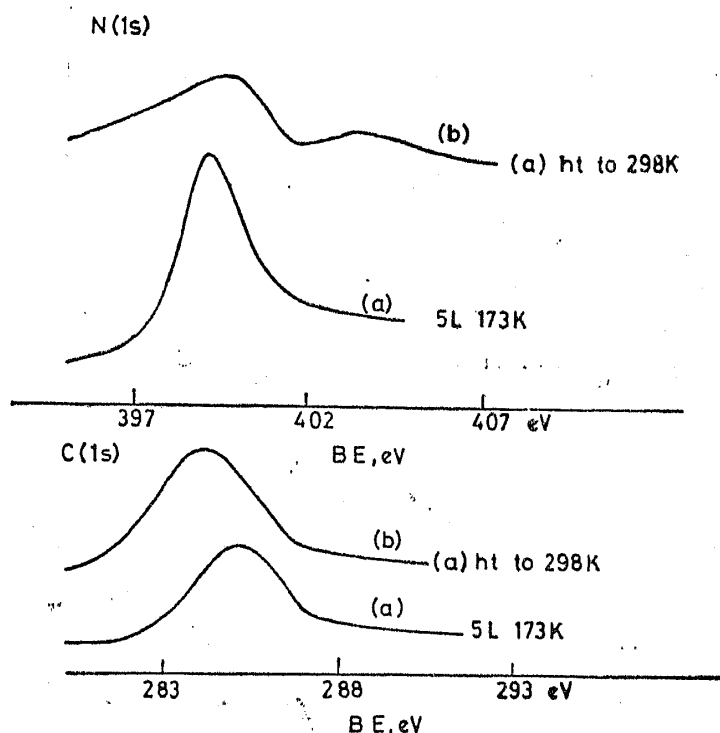


Figure 29. Carbon 1s and nitrogen 1s bands in XPS of methylamine adsorbed on Fe at different temperatures and exposures.

(by matching C (1s) binding energies of adsorbates with those of free molecules), we find the O (1s) binding energy increases by about 0.6 ± 0.2 eV in the case of methanol and acetone adsorbed on the three metal surfaces studied.

(d) Warming the substrate to temperatures above 120 K generally results in the transformation of the adsorbate molecules in all the cases. The nature of the species produced appears to depend on the metal surface and temperature as can be seen from table 2. Methanol gives methoxy species or formaldehyde depending on metal. These transformations are not only reflected in changes in the valence band region (in UVPS) but also in the C (1s) and O (1s) binding energies in XPS. It is interesting that methyl acetate gives the same transformation products on metal surfaces as methanol (table 2). In the case of methylamine we find formation of a nitrogenous species as in ammonia.

(e) The results of our studies on the adsorption of organic molecules find support from Auger studies carried out for the first time in this laboratory (Kamath *et al* 1982b). Thus, Auger spectra also show the transformation of methanol to formaldehyde on Cu surface.

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