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NOTE

Ultraviolet Photoelectron Spectroscopic Study of the Reaction of Cyanogen and Hydrogen on a Pt(100) Surface

Catalytic reactions on solid surfaces are usually investigated by monitoring the products of the reaction in a suitable detector once they have left the surface. From the kinetic information obtained by varying the various reaction parameters the reaction mechanism can then be deduced. However, it is often difficult to decide whether a given reaction product is formed during associative desorption of the reactants from the surface or whether it is already present on the surface, unless the direct observation of adsorbed species can be realized. Ultraviolet photoelectron spectroscopy (UPS) is currently being used as a very successful tool for the direct observation of adsorbed particles. Although the interpretation of UPS spectra in terms of the electronic structure of the surface complex formed is by no means straightforward, UPS spectra can be used as "fingerprints" for the characterization of adsorbed species even if the details of the electronic interactions are not yet fully understood (*1*). It is therefore possible to follow a reaction by the changes in the UPS spectra as compared with those of the individual adsorbed reactants. In this note observations of a new feature in the UPS spectrum of C_2N_2 adsorbed on Pt(100) introduced by the reaction with hydrogen are reported and discussed in terms of a molecular orbital formed by the interaction of hydrogen with adsorbed C_2N_2. The occurrence of new features in UPS spectra arising due to coadsorption is considered worthy of discussion here because it is very unusual for new features to be observed in coadsorption of other systems [e.g., Ref. (*2*)].

The experimental setup and procedure have been given elsewhere in detail (*3–5*). Briefly, experiments were performed in a combined LEED/UPS apparatus equipped with the usual facilities for crystal cleaning and manipulation. Cyanogen was generated in a glass cell attached to the ultrahigh vacuum (UHV) system by thermal decomposition of AgCN. UPS spectra of the clean and C_2N_2-saturated (15 L of exposure) Pt(100) surface excited with He II resonance radiation (40.8 eV) are shown in Fig. 1, together with the corresponding difference spectrum (Figs. 1a–c). Apart from the overall decrease in the *d*-band emission intensity three features due to adsorbed C_2N_2 are recognized at 3, 6, and about 16 eV, respectively (Fig. 1c). Adsorbed hydrogen shows very little effect on the UPS spectrum of the clean Pt(100) surface. This is illustrated in the difference spectrum shown in Fig. 1d. The adsorption of cyanogen on Pt(100) has been investigated previously (*4*, *6*, *7*) by other surface-sensitive techniques, and two main, energetically well-separated adsorption states were detected by flash-desorption mass spectrometry. It is thought that C_2N_2 in the lower binding energy state (α) is nondissociatively adsorbed (*6*, *8*), whereas the more strongly bound β states consist

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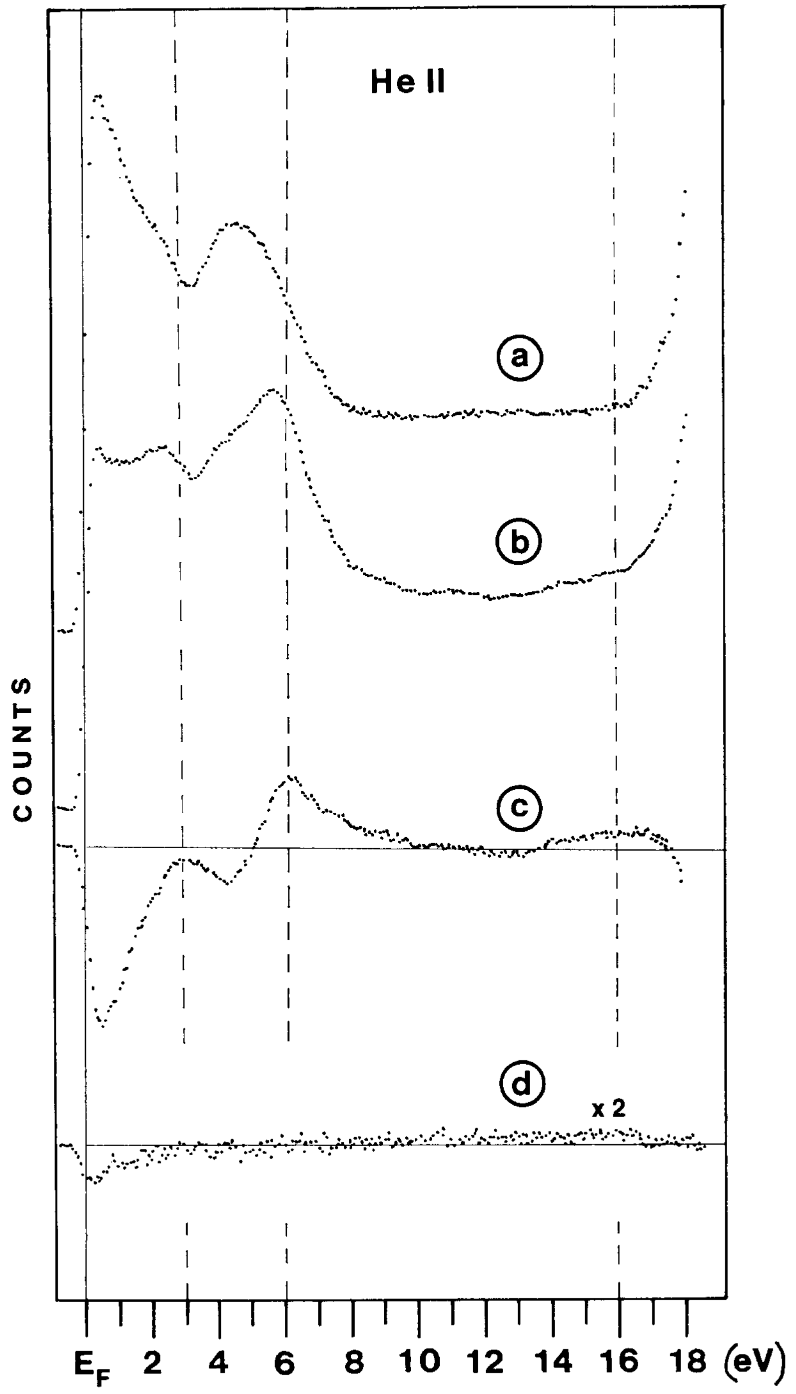

FIG. 1. UPS spectra excited with He II resonance radiation (40.8 eV): (a) clean Pt(100); (b) saturated with C_2N_2 (15 L); (c) difference spectrum, $b - a$; (d) difference spectrum of a hydrogen-saturated "minus" a clean Pt(100) surface.

essentially of a more complex adsorbate layer of CN units associated by attractive lateral interactions into some sort of a polymeric species (*6*, *7*). As discussed in Ref. (*5*), the C_2N_2-induced UPS features were then interpreted by comparison with known gas-phase data, keeping in mind the relatively strong changes expected in the adsorbed state. The prominent peak 6 eV below the Fermi level was ascribed to the overlapping π and nitrogen lone-pair orbitals; the weak feature around 16 eV was assigned to C–C σ bonds present in the adsorbate layer; and the feature within the Pt *d*-band region at 3 eV was associated with the "back bonding" from filled metal *d*-band states into empty $2\pi^*$ states of the adsorbate.

If the C_2N_2-saturated surface is exposed to H_2, a new feature at 13.8 eV can be recognized in the corresponding UPS spectra, which cannot be accounted for in terms of the UPS spectra of the individual adsorbates. Figure 2 shows He II spectra of the C_2N_2-saturated (15 L) Pt(100) surface before and after exposure to 5×10^{-7} Torr of stationary pressure of hydrogen and corresponding difference spectra. Apart from the feature at 13.8 eV mentioned above and some small changes in the Pt *d*-band region we note also some depletion in the 6-eV peak (Fig. 2d) as a result of H_2 exposure. For comparison a schematic gas spectrum of the likely reaction product, HCN, is displayed in Fig. 2c. The work function of the C_2N_2-saturated Pt(100) surface (6.2 eV) was subtracted from the gas-phase levels and the spectrum was aligned to give maximum overlap of the 1π, 5σ levels with the 6-eV region. Accordingly, a chemical shift of 1.8 eV with respect to the gas phase has been applied. The relative contributions of bonding and relaxation to this chemical shift will not be discussed here. The alternative procedure, i.e., matching the 4σ level of gaseous HCN to the 13.8-eV feature, would result in a negative chemical shift (shift toward higher ionization energies as compared with the gas phase) of this level and was disregarded for this reason, the more so because this level should be essentially nonbonding with respect to the surface.

Before proceeding to discuss the experimental results reported above, some complementary experimental observations should be mentioned. (i) Upon heating the crystal after the reaction, desorption of H_2, HCN, and C_2N_2 was observed in the mass spectrometer. The same desorption products were found by Bridge and Lambert (*9*) after the same reaction on a Pt(110) surface. (ii) The reaction was performed with β-C_2N_2 only present on the surface. This was achieved by heating the C_2N_2-saturated surface to 270°C, i.e., above the desorption temperature of α-C_2N_2, before exposure to H_2. After exposure to $\sim$100 L of H_2 identical UPS spectra as shown in Fig. 2 were obtained, suggesting that the β states are predominantly involved in the reaction. (iii) The surface was saturated with H_2 and then exposed to C_2N_2. In this case, no new feature was observed by UPS, and C_2N_2-like spectra as in Fig. 1 were obtained. Therefore, preadsorbed C_2N_2 is necessary to react with gaseous H_2 to show the observed UPS features as in Fig. 2.

As evident from Fig. 2 it is difficult to associate the 13.8 feature with the 4σ level (C–H σ bond) of gaseous HCN. It therefore seems unlikely that the surface complex thus formed by the reaction is simply HCN adsorbed at the surface. As already mentioned, there is strong suggestion from UPS and other techniques that adsorbed C_2N_2 in the β states might be in some sort of a polymeric configuration. It is possible that, due to the C–C bonds present in the surface layer, the formation of C–H bonds is inhibited in the adsorbed state. Another possibility would be the formation of N–H bonds. In order to obtain an idea of the

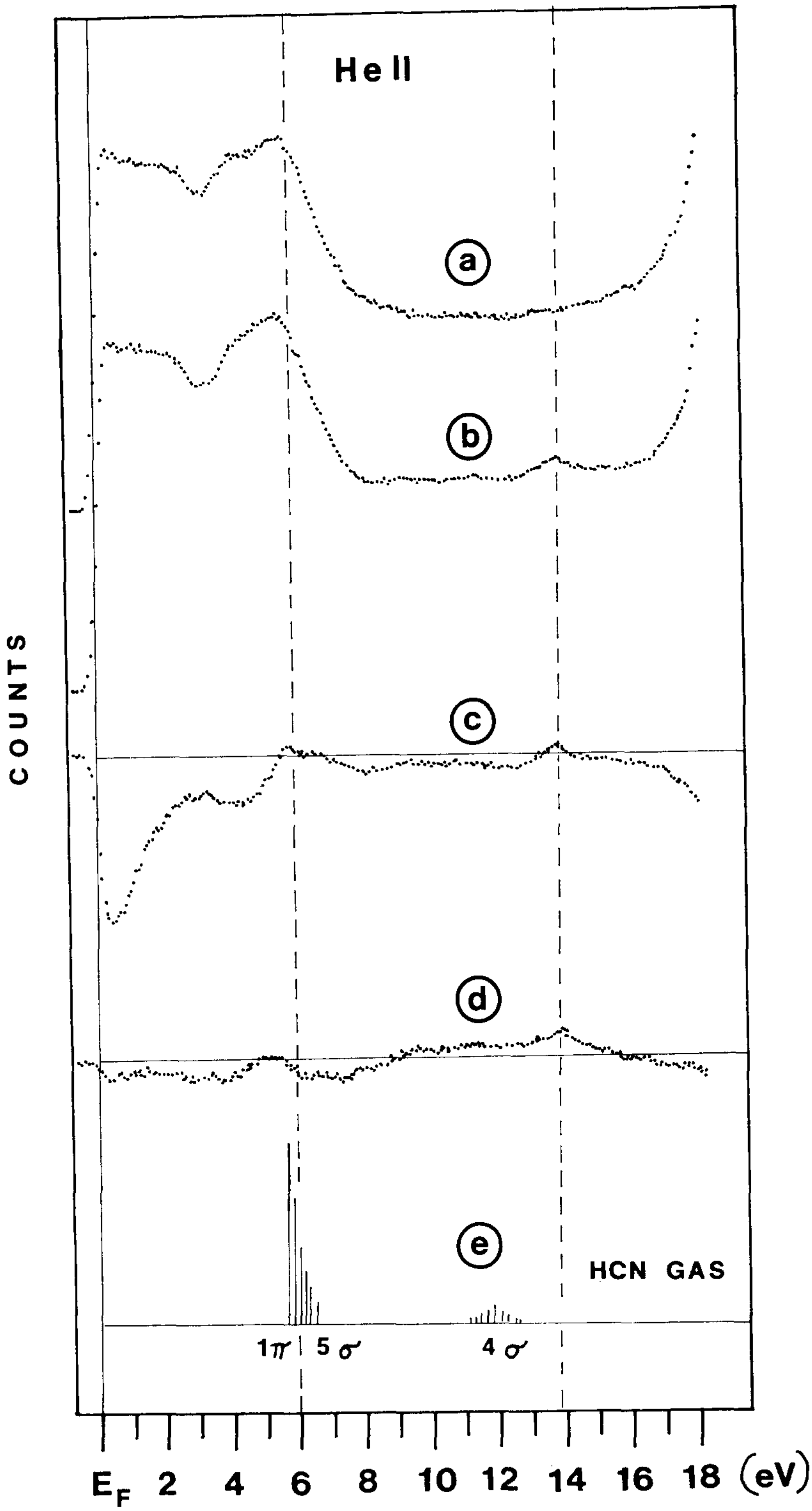

FIG. 2. He II spectra: (a) Pt(100) saturated with C_2N_2 (15 L); (b) Pt(100) saturated with $C_2N_2 + 5 \times 10^{-7}$ Torr of stationary-pressure H_2; (c) difference spectrum *b* – "clean"; (d) difference spectrum, *b* – *a*; (e) schematic gas-phase spectrum of HCN (*11*).

expected, relative position of an N–H level under present conditions with respect to the C–H level, the eigenvalue corresponding to the N–H level in HNCO as determined by *ab initio* calculation (*10*) is compared with the eigenvalue of the C–H level of HCN in the same calculation. The eigenvalues of both levels, however, are almost identical. Thus, there is no evidence that the molecular orbital corresponding to a simple N–H bond should be expected at higher binding energy than that of a C–H bond. However, from the depletion in the 6-eV region (Fig. 2d) a decrease in the emission intensity of the π and N lone-pair orbitals, which are both likely to be involved in the bonding to the metal (*5*), may be inferred. It seems plausible that this decreased emission intensity is associated with the redistribution of electrons into a new molecular orbital involving both π and N lone-pair orbitals together with the H 1s orbital for the bonding of hydrogen to the adsorbate complex. We would like to suggest, therefore, that the observed feature at 13.8 eV below the Fermi level may correspond to an intermediate reaction complex at the surface, from which the final reaction product, HCN, is formed during the desorption process. The fact that preadsorbed C_2N_2 is necessary for the observation of the extra feature in UPS supports the idea of an intermediate surface complex formed by association of H_2 from the gas phase with adsorbed C_2N_2.

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H. Conrad
J. Küppers
F. Nitschke

Institut für Physikalische Chemie
der Universität München
München, Germany

F. P. Netzer

Institut für Physikalische Chemie
der Universität Innsbruck
Innsbruck, Austria

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