

AN OVERVIEW ON THE ELECTRONIC AND VIBRATIONAL PROPERTIES OF ADSORBED CO

Shin-ichi ISHI, Yuichi OHNO and B. VISWANATHAN

Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan

Received 20 July 1984; accepted for publication 26 March 1985

This paper addresses itself to the question of the inadequacy of the donation–backdonation model for treating CO adsorption (both strong and weak) especially in the light of recent measurements by ARUPS, I-UPS, HREELS and NEXAFS to identify the 2π level with or without occupancy. The variation, including the sign (decrease or increase) of the work function as a result of CO adsorption, is identified to be due to the reversal or change in magnitude of the polarity of the molecule in the adsorbed state. The reversal of the ordering of the valence states according to this model becomes a natural consequence of the relaxation of the equilibrium internuclear distance. The systematics in the adsorption super-structures and the variation of other adsorption parameters especially that of adsorption energy are considered for both group VIII and Ib metals. The characteristics of the vibrational properties of adsorbed CO on group VIII and Ib metals are considered in terms of the electronic properties with a view to obtain possible correlations in the future. The need for more accurate measurements to evaluate the $\widetilde{5\sigma}$ – $\widetilde{1\pi}$ separation in the adsorbed state is indicated, which will enable, it is hoped, a synthesis to be made of a unified correlation between internuclear distance, $\nu(\text{C-O})$ and $\Delta(\widetilde{5\sigma}$ – $\widetilde{1\pi})$ within a single framework model. The characteristics of nitrogen (isoelectronic with CO) adsorption on group VIII metals are also considered for comparison.

1. Introduction

Considerable attention has been focussed on the correlation between electronic and vibrational properties of CO adsorbed on metals on the basis of the donation and backdonation model which was originally proposed by Blyholder [1]: CO–metal bonding is normally considered to arise from electron transfer from the 5σ orbital of CO to unoccupied metal orbitals accompanied with backdonation of electrons from occupied $d\pi$ orbitals with $sp\pi$ orbital mixing to the unoccupied 2π orbitals of CO. The 2π orbital couples with metal orbitals of π -symmetry to form a bonding and an anti-bonding level whose orbital characteristics are mostly $d\pi$ and 2π respectively. Schematic representation of the CO levels is given on the basis of perturbation theory with a two state model in fig. 1a[2–4], which represents the simplified molecular orbital (MO) picture. This picture seems to consolidate its foundation now from different theoretical approaches as follows: (1) in the more elaborate MO

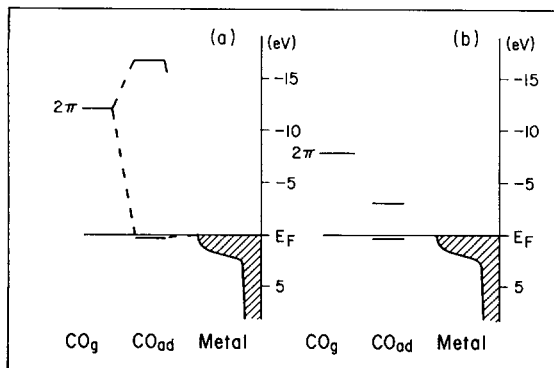


Fig. 1. Schematic representation of the CO levels by means of a simplified MO method [2–4] (a) and by various measurements [20,21] (b).

calculation procedures in comparison with that described, like *ab initio* [5] and $X\alpha$ [6] methods, the extent of donation and backdonation is deduced from the values of the coefficients of the composite MO. The net charge due to donation and backdonation is estimated in terms of a population analysis which is unduly approximate for hetero-atomic systems. (2) On the other hand, the extent of donation and backdonation according to the resonance theory, which is similar to Mulliken's donor–acceptor theory[7], is estimated on the basis of the coefficients of the configuration state functions assumed. There may be inadequacy in the extent of valence configurations that are plugged into these functions because of calculational problems, or due to the choice being limited for want of proper representations for the various possibilities. (3) The third approach is by means of the Anderson model Hamiltonian method including overlap by Doyen and Ertl[8], who treat only coupling of the 5σ and 2π orbitals to the metallic d-states. The absolute magnitude of donation and backdonation is deduced from the average occupation number of the eigenstate of the ad-molecular orbitals within the Hartree–Fock approximation.

Brodén et al.[9] argued in the early stages that the difference ($\Delta(\widetilde{4\sigma} - \widetilde{1\pi})$) in the binding energy of $\widetilde{4\sigma}$ and $\widetilde{1\pi}$ orbitals is correlated with the carbon–oxygen stretching frequency ($\nu(\text{C–O})$), where a tilde over the orbital notation indicates a level in the adsorbed state. Nieuwenhuys [10] has analysed all the available experimental data for a possible correlation between the UPS data and $\nu(\text{C–O})$ on group VIII metals on the basis of work function changes ($\Delta\phi$). According to him, the magnitude of $\Delta\phi$ depends on the extent of donation of electrons to the metal and results in a decrease of work function while backdonation leads to an increase. Heskett et al. [11] have recently investigated a similar correlation with due consideration given to satellite structure observed in the region of the valence levels. Their analysis encompasses group Ib metals. They state that the metal–CO bond is formed in the conventional

donation and backdonation manner in the strong adsorption (CO/transition metal) systems, so that the $\widetilde{2\pi}$ level is partially occupied in the neutral ground state of the adsorbed system, while the $\widetilde{2\pi}$ is unoccupied in the neutral ground state for weak adsorption (CO/noble metal) systems, where the bond results from 5σ -metal charge transfer. In addition, both have dealt with N_2 adsorption in a similar manner. However, there appears to be some difficulty in the assignment of partially occupied or unoccupied molecular levels, especially that of $\widetilde{2\pi}$ of CO in the adsorbed state. Because of its relevance for the donation and backdonation model, the studies relating to its identification are briefly considered.

A variety of electron emission measurements such as Field Emission Energy Distribution (FEED) Spectroscopy, Ultraviolet Photoelectron Spectroscopy (UPS), and Surface Penning Ionization Electron Spectroscopy (SPIES) from CO covered surfaces show a broad peak in the range of 0–3 eV below the Fermi level (E_F). FEED measurements on CO/W(100) [12] and CO/Ir(100) [2] showed peaks at 7–7.5 eV below the vacuum level (E_V) and at 0.6 and 1.25 eV below E_F respectively. The UPS spectra by means of angle-resolved UPS (ARUPS) and polarization-dependent ARUPS (PARUPS) exhibited broad and weak induced structures at 0–2 eV below E_F on Ni(111), Ni(100) and Ni(110) [13], Ni(100) [14], Cu(111) [15] and Cu(100) [16]. The studies of SPIES on Ni(111) [17], Pd(111) [18] and Mo(110) [19] located an analogous peak at 0–2.0 eV below E_F . On this basis, these authors claimed to have identified the $\widetilde{2\pi}$ orbital which participates in backdonation of an electron from the metal. However, recently Miranda et al. [20] showed by means of a detailed ARUPS study of CO/Pd(111) that the reported emission around 2 eV with respect to E_F cannot be ascribed to the $\widetilde{2\pi}$ orbital, but to a shifted Pd surface state. According to the simplified MO picture depicted in fig. 1a, the antibonding level whose component consists mostly of 2π character would have to be observed at a location above the position of the unoccupied 2π level of gas phase CO. A peak at ~ 3 eV above E_F as illustrated in fig. 1b has been observed by Bremsstrahlung Spectroscopy or Inverse UPS (I-UPS) [21] which can detect the unoccupied states without disturbing the occupied orbitals. Besides, for the weak interaction system of CO/Ag [22] the unoccupied $\widetilde{2\pi}$ level has been shown to be reduced by nearly 1 eV from that of gaseous CO. The position of the unoccupied $\widetilde{2\pi}$ level appears to be different from that shown in figs. 1a and 1b. However, this is not surprising, because the simplified MO picture neglects the presence of continuous levels in the metal for the treatment of the CO-metal interaction. It is therefore clear that the simplified MO picture such as that shown in fig. 1a is inadequate to assign the exact positions of the electronic levels of CO in the adsorbed state.

In recent years, it has been realized that electronically excited states of adsorbates play an important role in a variety of surface processes. Energy levels in the excited states can be probed by High Resolution Electron Energy

Loss Spectroscopy (HREELS) [23] or Near-Edge X-ray Absorption Fine Structure (NEXAFS) [24]. These studies, in recent times, have shown a correspondence of the excitation energies for the molecularly adsorbed state of CO with that of gaseous CO. For example, EELS [23,25] identifies an excitation energy value of 6–8 eV on both Ni and Cu surfaces, which is assigned to the $\widetilde{5\sigma}$ (or $\widetilde{1\pi}$) \rightarrow $\widetilde{2\pi}$ excitation, while the excitations observed by NEXAFS [24] studies at ~ 287 and ~ 534 eV attributable to $\widetilde{2\sigma}$ or $\widetilde{1\sigma}$ to $\widetilde{2\pi}$ are similar to the observations in the gaseous state. Thus these results show that CO retains its molecular characteristics in the adsorbed state. The only anomalous observation as considered in the literature is the reversal of $\widetilde{5\sigma}$ and $\widetilde{1\pi}$ levels in the adsorbed state on transition metals. However, it is shown subsequently in this paper that it is no longer anomalous as the ordering of the levels is in complete accordance with the possible elongation of the internuclear distance of gaseous CO. The picture that emerges from recent experiments by ARUPS [20], I-UPS [21], HREELS [23], and NEXAFS [24] is that the $\widetilde{2\pi}$ orbital is unoccupied (virtual orbital in Hartree–Fock theory in quantum chemistry) in the neutral ground state in both strong and weak adsorption systems.

Thus, no clear view seems to have emerged for CO–metal bonding in terms of the donation and backdonation model. The purpose of the present paper is to discuss a correlation between the electronic and vibrational properties of both weak and strong CO adsorption systems in general terms without restricting oneself only to the donation and backdonation model. A similar attempt has been made by Davenport [26] who argued that the frequency and intensity of the CO stretching modes in metal carbonyls are explainable without recourse to the usual donation and backdonation.

The composition of the present paper is as follows: In section 2 the characteristics of gaseous CO, especially the variation of dipole moment with internuclear distance and the electronic structure, will be presented. Section 3 deals with the review of the available literature data on the characteristics of adsorbed states. The correlation between electronic and vibrational properties and work function changes which form the central theme of the present paper will be discussed in section 4. Finally the characteristics of molecular adsorption of nitrogen (N_2) (an isoelectronic molecule with CO) will be compared with that of adsorbed CO in section 5.

2. Electronic structure of gaseous CO

The electronic configuration of the ground state of CO is given by

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2, \quad (2.1)$$

in terms of a single-configuration [27]. The ground state configuration is a singlet state $^1\Sigma^+$. The molecular orbitals of 1σ and 2σ are mainly the $1s$

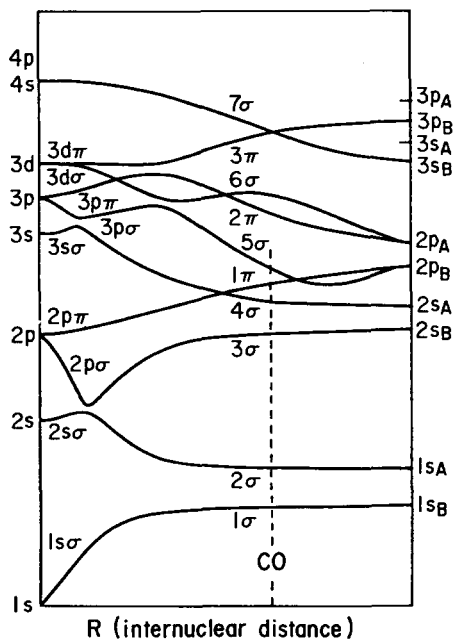


Fig. 2. Molecular orbital correlation diagram of AB hetero-molecule [27].

orbitals of oxygen and carbon respectively. The bonding orbitals are the 3σ and doubly degenerate 1π , so the conventional chemical bond for CO is described as the triple bond ($C\equiv O$). The non-bonding orbitals are 4σ and 5σ , which are mostly concentrated on oxygen and carbon respectively. The unoccupied levels in CO are 6σ , 7σ , ... of σ -symmetry and 2π , 3π , ... of π character. The highest occupied molecular orbital (HOMO) is 5σ and the lowest unoccupied MO (LUMO) is 2π . A simplified MO correlation diagram (orbital energies as a function of the internuclear distance, R , of an AB hetero-diatom molecule) is shown in fig. 2 in which $R = 0$ and $R = \infty$ denote the situations of a united atom and separated atoms respectively. At the equilibrium distance (R_e) of CO, represented by the dashed line in fig. 2, the value of the 5σ ionization energy is lower than that of 1π . However, the correlation diagram shows a change in the ordering of 5σ and 1π levels when the internuclear distance is greater than the equilibrium value. This trend is also confirmed by ab initio calculations [28].

In table 1, the data concerning the electronic configuration, state symbols, equilibrium bond distance, C–O stretching frequency, dissociation energy, dipole moment and first ionization energy are assembled for some typical configurations of CO, namely neutral CO, CO^+ , CO^- and CO^* (neutral excited state) [29].

Table 1
Summary of molecular characteristics of CO in neutral, ionic and excited states

CO	CO ⁺	CO ⁻	CO*		CO*		
Configuration	$---(1\pi)^4(5\sigma)^2$	$---(1\pi)^4(5\sigma)^1$	$---(1\pi)^4(5\sigma)^2(2\pi)^1$	$---(1\pi)^4(5\sigma)^1(2\pi)^1$	$---(1\pi)^3(5\sigma)^2(2\pi)^1$	$---(1\pi)^3(5\sigma)^2(2\pi)^1$	
State	$1\Sigma^+$	$2\Sigma^+$	2Π	$(\uparrow\uparrow)$ $a^3\Pi$	$(\uparrow\downarrow)$ $A^1\Pi$	$(\uparrow\uparrow)$ $a'^3\Sigma^+$	$(\uparrow\downarrow)$ $I^1\Sigma^-$
Re (Å)	1.13	1.12	1.17	1.21	1.24	1.35	1.39
$\nu(\text{CO})$ (cm ⁻¹)	2143	2214	~1850	1743	1518	1229	1092
D (eV)	11.2	8.4	8.1	5.21	3.17	4.32	3.17
μ (debye)	0.1			1.38		1.06	
	(⁻ CO ⁺)			(⁺ CO ⁻)		(⁻ CO ⁺)	
I (eV)	14.01	26.8	-1.5				

The polarity of the neutral ground state molecule is denoted as ⁻CO⁺ which is contrary to the normal electronegativity values of carbon and oxygen. However, this situation arises from the fact that the center of the 5σ orbital lies along the molecular axis but outside the internuclear distance. In fig. 3, the variation of the dipole moment is shown as a function of the internuclear distance together with the values calculated by the Hartree-Fock (HF) method

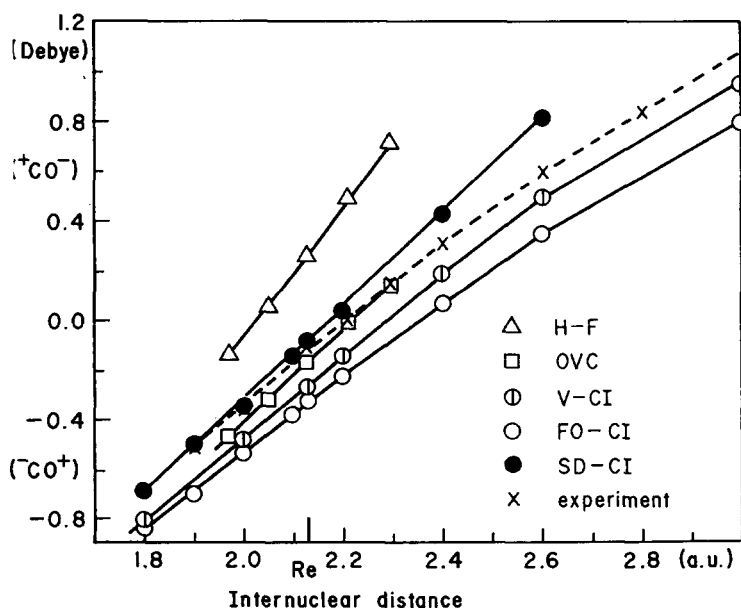


Fig. 3. Experimental and calculated values of dipole moment variation with internuclear distance for CO ($X^1\Sigma^+$) [30,31].

and other higher order approximations (OVC (Optimized Valence Configuration) [30], V-CI (Valence Configuration Interaction), FO-CI (First Order CI) and SD-CI (Single and Double excitations CI) [31]) which include to a certain extent electron correlation effects. It is seen that the values obtained by HF calculations are not in agreement with the experimental values, while values obtained by higher order approximations are in agreement with experimental values, which may be due to CI correction caused almost entirely by polarization of the 1π . The polarity of CO in the ground state as stated above is denoted as ${}^{-}\text{CO}^{+}$ but the polarity changes when the internuclear distance lengthens (see fig. 3) or when the 5σ molecular orbital of CO is perturbed upon excitation from 5σ to 2π (see table 1).

In essence it is seen that the polarity of CO and the ordering of 5σ and 1π energy levels in a neutral molecule can easily change as a result of the elongation of C–O internuclear distance.

3. Properties of adsorbed CO on group VIII and Ib metals

All available information on these systems are summarised in table 2. The main deductions from the values given in this table include:

- (1) LEED results show that CO overlayers form ordered structures with increasing coverage except for Ag and Au.
- (2) Adsorption energy (E) is in the range of ~ 30 – 40 kcal/mol for group VIII and 6 – 15 kcal/mol for group Ib metals. The variation of E with coverage for many group VIII metals is given in fig. 4.
- (3) Normally the work function increases due to CO adsorption (except Pt(111), Pt(100)-(5 \times 1) on group VIII and Ib metals). Fig. 5 shows that $\Delta\phi$ is dependent on CO exposure on several VIII metals and copper.
- (4) Fig. 6 shows the variation of $\nu(\text{C-O})$ with coverage for a number of group VIII metals. The absolute values of ν at initial coverages and its shift with coverage are different for different metals even though the adsorption energy is almost the same. The different sites of ad-CO species: the spectral regions 2130 – 2000 , 2000 – 1880 , 1880 – 1800 and less than 1800 cm^{-1} correspond to on-top (head-on or terminal) CO, two fold bridge, three fold bridge and four fold bridge adsorbed-CO respectively [85].

The valence level peak positions of adsorbed CO are given in table 3. Brodén et al. [9] once proposed that the larger the $\Delta(4\sigma-1\pi)$ separation, the greater the CO bond weakening and so the dissociation becomes easier. However, the results in table 3 do not support this hypothesis, the validity of which has already been questioned [108].

Valence photoelectron spectra of CO adsorbed on Ag(110) [83] and Ag(111) [109] as well as that on Al(111) [110] at low temperatures are similar to the spectrum of gaseous CO, which contains due to the 5σ , 1π and 4σ levels, an

Table 2
Summary of adsorption parameter CO on group VIII and Ib metals

Surface	Adsorbate structure	θ	E (kcal/mol)	$\Delta\phi$ (eV)	$\nu(\text{C-O})$		$\nu(\text{M-CO})$		References			
					$\theta \sim 0$	$\theta \geq 0.5$	$\theta \sim 0$	$\theta \geq 0.5$	LEED	E	$\Delta\phi$	ν
Fe (110)	$\alpha(4 \times 2)$	1/4	35	1.2	1890	1985	456	$\begin{cases} 360 \\ 440 \end{cases}$	[32]	[33]	[32]	[32]
	Distorted $p(1 \times 2)$	1/2		0.86						[34]	[33]	
	$\alpha(2 \times 2)$	1/2										
Ru (0001)	Diffuse (1×1)			1.6	1800	$\begin{cases} 1850 \\ 2000 \end{cases}$	550	515	[35]	[36]	[36]	[36]
	$(\sqrt{3} \times \sqrt{3})R30^\circ$	1/3	29	~ 0.65	1984	2060	445	445	[37]	[38]	[38]	[39]
	$(2\sqrt{3} \times 2\sqrt{3})R30^\circ$	7/12			1980	2080			[38]			[40]
Os (0001)	$(5\sqrt{3} \times 5\sqrt{3})R30^\circ$	49/75										
	$(\sqrt{3} \times \sqrt{3})R30^\circ$	1/3	~ 33						[41]	[41]		
	$(2\sqrt{3} \times 2\sqrt{3})R30^\circ$	7/12										
Co (0001)	$(3\sqrt{3} \times 3\sqrt{3})R30^\circ$	16/27										
	$(\sqrt{3} \times \sqrt{3})R30^\circ$	1/3	30	1.0					[42]	[42]	[42]	
	$(2\sqrt{3} \times 2\sqrt{3})R30^\circ$	7/12										
Rh (111)	$p(2 \times 2)$	1/4	32		1990	$\begin{cases} 2070 \\ 1870 \end{cases}$	480	420	[43]	[43]	[43]	[45]
	$(\sqrt{3} \times \sqrt{3})R30^\circ$	1/3							[44]			
	(2×2)	3/4										
(100)	$\alpha(2 \times 2)$	1/2	32	1.28					[44]	[46]	[46]	
	Split (2×1)	4/5										
	$\alpha(2 \times 2)$	1/2	31	0.97					[47]	[47]	[47]	
Ir (111)	$(2 \times 1) \text{ p}1\text{gl}$	1										
	$(\sqrt{3} \times \sqrt{3})R30^\circ$	1/3	34	0.18					[48]	[48]	[48]	
	$(2\sqrt{3} \times 2\sqrt{3})R30^\circ$	7/12										
Ir (100)- (1×1)	(2×2)	1/2	35						[50]	[49]		

Ir	(100)-	$\alpha(2 \times 2)$								[50]	
	(5 \times 1)	(1 \times 1)								[51]	
(110)	p(2 \times 2)	1/4	37	0.23					[51]	[51]	
	(4 \times 2)	3/4								[51]	
	(2 \times 1)plg1	1								[51]	
Ni	(111)	$(\sqrt{3} \times \sqrt{3})R30^\circ$	1/3	27	1.1	1817	{1915 2045}	380	[52]	[52]	[53]
		$\alpha(4 \times 2)$	1/2			1815	1910	380	[53]	[53]	[54]
		$(\sqrt{7}/2 \times \sqrt{7}/2)R19^\circ$	1/2	30	1.1	1820	1910	400	[55]	[55]	[54]
	(100)	$\alpha(2 \times 2)$	1/2	30	1.1	{2000 1900}	{2015 1935}	{460 365}	[56]	[56]	[54]
(110)		$\alpha(2 \times 2)$	1/2	30	1.3	{1990 1880}	{2015 1935}	{450 345}	[57]	[57]	[58]
		(4 \times 2)				{1960 1855}	{2015 1930}	{444 436}	[59]	[59]	[60]
	(111)	$(\sqrt{3} \times \sqrt{3})R30^\circ$	1/3	34	1.0	1813	{1936 2092}		[61]	[61]	[63]
(100)		$\alpha(4 \times 2)$	1/2	40	0.93	1985	{1950 2096}	315	[65]	[65]	[64]
		Hexagonal	1/2	40	1.25	1880	1960	347	[66]	[66]	[68]
		$\alpha(2 \times 2)$	1/2	40					[66]	[66]	[68]
		(4 \times 2)	3/4						[66]	[66]	[68]
(111)		(2 \times 1)	1	33	-0.15	2065	{2100 1872}	468	[66]	[66]	[67]
		$(\sqrt{3} \times \sqrt{3})R30^\circ$	1/3	33		2081	{2110 1870}	{468 365}	[70]	[72]	[71]
(100)-		$\alpha(4 \times 2)$	1/2	37	0.4	2080	2096		[70]	[72]	[71]
		Hexagonal	1/2	37					[70]	[72]	[71]
	(100)-	$\alpha(2 \times 2)$	1/2	37	0.4	2080	2096		[70]	[72]	[71]

Table 2 (continued)

Surface	Adsorbate structure	θ	E (kcal/mol)	$\Delta\phi$ (eV)	$\nu(\text{C-O})$		$\nu(\text{M-CO})$		References		
					$\theta < 0$	$\theta \geq 0.5$	$\theta < 0$	$\theta \geq 0.5$	LEED	E	$\Delta\phi$
(1×1)	$(\sqrt{2} \times 3\sqrt{2})R45^\circ$	2/3			$\begin{cases} 1950 \\ 2000 \end{cases}$	$\begin{cases} 1950 \\ 2030 \end{cases}$		[71]			
(100)-	(4×2)	3/4	28	-0.1	2000	$\begin{cases} 1950 \\ 2030 \end{cases}$		[71]	[72]	[71]	[71]
(5×1)											
(110)	(2×1)p1g1	1	31	0.15		2097	476	[73]	[73]	[73]	[74]
(111)	$(\sqrt{3} \times \sqrt{5})R30^\circ$	1/3	12	-0.47	2078	2070		[75]	[76]	[76]	[76]
(100)	$(\sqrt{7}/3 \times \sqrt{7}/3)R49^\circ$	4/7									
	$\alpha(2 \times 2)$	1/2	14	-0.23	2079	$\begin{cases} 2088 \\ 2100 \end{cases}$		[77]	[77]	[77]	[78]
	Hexagonal						350				[79]
(110)	(2×1)		13	-0.29	$\begin{cases} 2088 \\ 2104 \end{cases}$	$\begin{cases} 2094 \\ 2082 \end{cases}$		[80]	[80]	[80]	[80]
(111)	Disordered		6.5	-0.3			685				[81]
(110)	Disordered			-0.8						[82]	[82]
(110)	Disordered		14	-0.85						[83]	[83]
										[84]	[84]

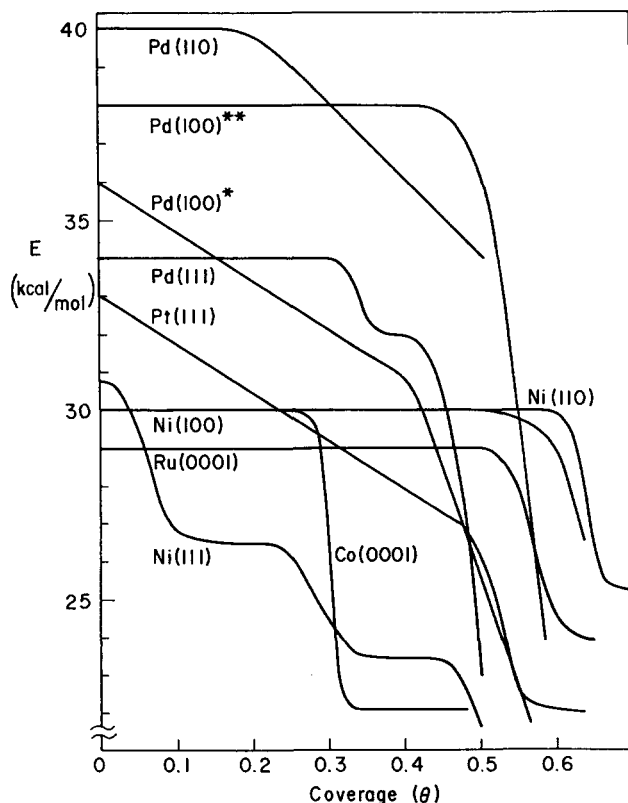


Fig. 4. Variation of adsorption energy with coverage for CO on a variety of metals (Pd(110) [65], Pd(100)** [62], Pd(100)* [61], Pd(111) [59], Pt(111) [66], Ni(100) [55], Ni(110) [57], Ru(0001) [38], Co(0001) [42] and Ni(111) [52]).

order of increasing ionization energies. The ordering of the levels in the adsorbed systems is the same as that in the gas phase.

It is essential to comment on a recent work by Heskett et al.[11]. They have explained the assignment of satellite structures in terms of the so-called "screening and unscreening" model [111,112]. However, the validity of this model has been questioned [113]. At least this model may lead to a misunderstanding on the assignment of satellite peaks in core level regions, though Heskett et al. have not considered this aspect at all. The position of the $\bar{2}\pi$ level should be observed below E_F if this screening model is applicable. However, experimental observations do not support the postulate that the $\bar{2}\pi$ level is below E_F [24].

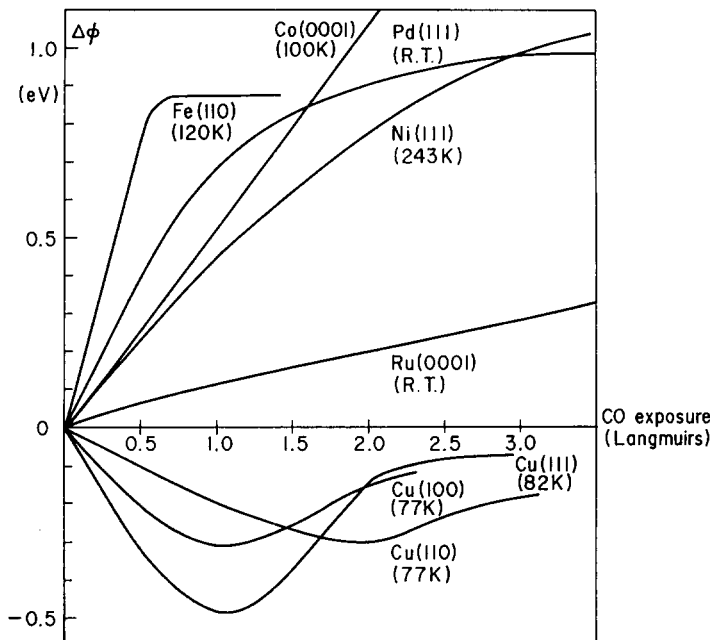


Fig. 5. Work function changes as a function of CO exposure on a variety of metals (Fe(110) [32], Co(0001) [42], Pd(111) [59], Ni(111) [52], Ru(0001) [38], Cu(111) [76], Cu(100) [77] and Cu(110) [80]).

4. Correlation between electronic and vibrational properties of adsorbed CO

The viewpoint for a correlation between electronic and vibrational properties for CO adsorption will be presented first. The $\nu(\text{C-O})$ observed by IRAS and EELS for adsorbed CO is generally less than that of gaseous CO (see table 2). This observation at least indicates that the equilibrium C-O bond distance is greater than that of gas phase CO. Depending on the order of magnitude of the C-O bond distance the polarity of CO in the adsorbed state can also change as can be seen from fig. 3, wherein the data for gaseous CO are given. The positions of the 5σ and 1π levels are originally close to each other at or near the equilibrium distance in multi-bond species of diatomic molecules. However, they either overlap or reverse the ordering as a result of the elongation of the bond distance. Therefore, it is not surprising that the ordering of the levels observed by UPS for CO adsorption systems reverses in comparison with that of gas phase. This statement about the reversal of $\widetilde{5\sigma}$ and $\widetilde{1\pi}$ levels has been substantiated by a number of experimental studies (see table 3).

It is interesting to note that Brodén et al. [114] have already tried to correlate the variation of bond length on adsorption with the $\widetilde{1\pi}-\widetilde{4\sigma}$ separation

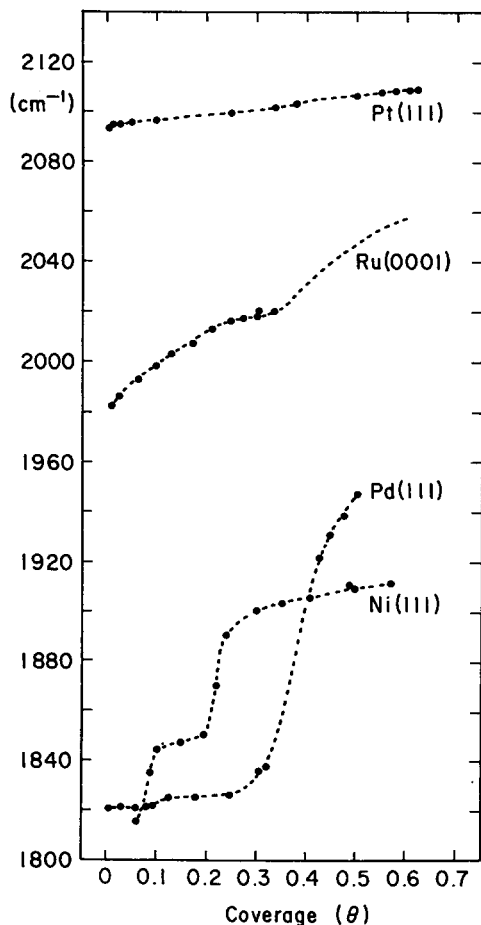


Fig. 6. Variation of CO stretching frequency with coverage for CO adsorption on some hexagonal close packed surfaces (Pt(111) [68], Ru(0001) [39], Pd(111) [60] and Ni(111) [53]).

for both on top and bridge bonded CO. However, they have used the values of bond lengths of CO in various configurations and its elongation, i.e., 0.02 Å for on top and 0.07 Å for bridge mode as deduced from metal carbonyls. In addition, their analysis is mainly concerned with CO/Ni system.

A point which is not yet well understood concerns the adsorption energy and the change of work function on group VIII and Ib metals. The work function increases due to CO adsorption on group VIII metals except for Pt(111) and Pt(100)-(5 × 1), but the work function decreases for Ib metals. Although the work function of Pt(111), Pt(100)-(5 × 1) and group Ib metals decreases as a function of coverage, the trend of variation appears to be

Table 3

Peak positions of valence levels with respect to E_F and energy separation for $\widetilde{4\sigma}$ and $\widetilde{1\pi}$ level ($\Delta(\widetilde{4\sigma}-\widetilde{1\pi})$) for CO adsorption on group VIII metals

Substrates	Peak positions			$\Delta(\widetilde{4\sigma}-\widetilde{1\pi})$	References	
	$\widetilde{5\sigma}$	$\widetilde{1\pi}$	$\widetilde{4\sigma}$			
Fe	(110)	7.5	10.4	2.9	[86]	
		8.1	6.9	11.0	4.1	[87]
	(100)	7.0	10.5	3.5	[88]	
	(111)	7.6	10.8	3.2	[89]	
Ru	(0001)	7.6	10.7	3.1	[90]	
Co	(0001)	7.5	11.0	3.5	[42]	
		7.9	7.7	10.7	3.0	[91]
Rh	(111)	8.3	7.8	11.2	3.4	[92]
	(100)		7.6	10.8	3.2	[93]
	(110)	7.6	8.7	10.6	1.9	[94]
		7.6	10.6	3.3	[95]	
Ir	(111)	9.2	8.6	11.7	3.1	[96]
			8.9	11.5	2.6	[49]
	(100)	9.2	8.6	11.7	3.1	[96]
	(110)		{7.6 8.7}	11.3	(3.7) ^{a)}	[97]
Ni	(111)	8.1	7.1	11.2	4.1	[98]
			6.5			
		8.3	7.9	10.9	4.0	[99]
	(100)	8.3	7.8	10.8	3.0	[100]
		8.0	7.5	10.6	3.1	[99]
	(110)	8.4	6.5	11.7	5.2	[101]
			8.0	11.0	3.0	[102]
Pd	(111)	8.2	7.5	11.2	3.7	[103]
		7.8	7.3	10.7	3.4	[20]
	(100)		7.9	10.8	2.9	[71]
	(110)		7.9	10.8	2.9	[104]
Pt	(111)	9.2	8.4	11.9	3.5	[67]
		9.6	8.6	12.0	3.4	[105]
	(100)		8.8	11.4	2.6	[70]
	(110)	9.2	8.2	11.7	3.5	[106]
		9.1	7.9	11.7	3.8	[102]
CO	(gas)	14.0	16.9	19.7	2.8	[107]

^{a)} The data obtained under precovered CO conditions for hydrogen adsorption.

different for Pt(111), Pt(100)-(5 × 1) and Cu from that observed for Ag and Au. In the former case a minimum is observed as a function of coverage (fig. 5) while a continuous decrease has been recorded in the case of Ag and Au [116,118]. The adsorption energy varies by a factor of 3 or more between group VIII and Ib metals. Besides, the occupied valence levels observed by UPS are almost similar for CO adsorption systems on both group VIII and Cu metals.

Especially, the behaviour of CO adsorption on Pt(111) seems to be quite different from that on other group VIII metals [3], i.e., the work function decreases and the value of $\nu(\text{C-O})$ in the case of Pt(111) are close to those of CO in the gas phase. A probable explanation for this observation from the viewpoint of the donation and backdonation is that the extent of backdonation to CO from Pt(111) is less than that of other group VIII metals [10]. However, this causes serious difficulties in extending the adsorption systems to group Ib metals, i.e., the work function change and the $\nu(\text{C-O})$ are almost similar for the CO/Pt(111) and CO/Cu systems, but the value of the adsorption energy for CO/Pt is greater by 3 times than that for CO/Cu.

We now consider the Nieuwenhuys standpoint [10]. According to him, $\Delta\phi$ and $\nu(\text{C-O})$ depend on the absolute magnitude of backdonation. One of the main results obtained from this postulate is that the contribution of backdonation on open surfaces, e.g. fcc (110), is larger than that on fcc (100) and (111). The expected variation of $\nu(\text{C-O})$ among the various planes of the metals according to this postulate should be $\nu(110) \ll \nu(100)$ and $\nu(110) \ll \nu(111)$. However, the experimental data presented in table 2 seem not to support such a postulate. Secondly, the expected trend for the work function change is $\Delta\phi(110) > \Delta\phi(100)$ and $\Delta\phi(110) > \Delta\phi(111)$ at saturation coverage. It should be remarked that at saturation the total number of adsorbed molecules (N_a) varies for the different planes of the metals and the variation is as follows ($N_a(110) > N_a(100) > N_a(111)$) [3,52]. It is, therefore, apparent that such a correlation cannot be postulated without taking into account the number density of adsorbate molecules.

Krause et al. [83] consider CO adsorption on Ag(110) as "physisorption" and compare the work function changes (decrease) observed with that for rare gas adsorption. Even in "physisorption", especially for the Xe/transition metal systems, it is expected to consider in addition to Van der Waals forces the charge transfer forces which may contribute mainly to the observed work function changes [115]. It should also be remembered that CO is adsorbed parallel to the surface on Ag(110) [83] as well as on Al(111) [110], while the adsorption bond is parallel to the surface normal for other metals.

The absolute magnitudes of the change in work function in the case of Ir and Pt are comparable, although the work function decreases on Pt(111) and the reconstructed surface of Pt(100) as a result of CO adsorption. On the basis of the magnitude of the work function change, one can expect that the values of the C-O stretching frequency on Ir, which has not yet been recorded on single crystal surfaces [116], will be of the same magnitude or less as has been observed on Pt surfaces. On the contrary, the $\nu(\text{C-O})$ on Os surfaces may be near that of Ru if it will be observed.

Although the variation of the adsorption energy with coverage seems to be reflected in the change of the C-O stretching frequency, this correlation can by no means be established at present. For example, the trend of variations

$\nu(\text{C-O})$ as well as the adsorption energy as a function of coverage for Pd(100) [61] as reported by Hoffmann and Bradshaw [60] are similar. However, the trend obtained by Behm et al. [62] for the same Pd(100) seems to be different (see fig. 4). Although it might be expected that the $\nu(\text{C-O})$ could be used as a criterion for determining the strength of the metal-CO bond, this correspondence is indirect. A more direct relationship would be the variation of stretching of the metal center of gravity of CO ($\nu(\text{M-CO})$), which reflects the metal-CO interaction with the CO molecular axis parallel to the surface normal and carbon atom closest to the surface with adsorption energy. The variation of the $\nu(\text{M-CO})$ stretching on Pd(100) with coverage [64] has been observed to be similar to the change of the adsorption energy as observed by Behm et al. [62].

The bridge site adsorption is usually denoted by a configuration >C=O which is similar to the situation existing in carbonyl compounds. However, the carbonyl compounds exhibit large dipole moment values (~ 2.0 debye) and the C-O internuclear distance is also fairly large (≥ 1.2 Å). Although the observed stretching frequency for "bridge site" adsorption (~ 1900 cm^{-1}) is comparable to that in carbonyl compounds (~ 1600 – 1900 cm^{-1}), it is unlikely that the bonding situation, especially that between C and O, can be compared with that existing in carbonyls. In the bridge site adsorption, if it occurs, CO should have a different bonding character from what is perceptible from the notation >C=O [62,117]. For example, one can visualize one possibility that as a result of bridge site adsorption, the degeneracy of the $\widetilde{1\pi}$ orbitals is lifted and the resulting scheme accounts for the shifting of the stretching frequency to lower values [99]. Similar lifting of the degeneracy of $\widetilde{1\pi}$ levels has also been predicted by CNDO calculations for a particular geometry of bridge site adsorption [118].

In summary of this section, the overlapping or reversal of $\widetilde{5\sigma}$ and $\widetilde{1\pi}$ levels in UP spectra on group VIII and Cu metals means the elongation of C-O bond length and a consequent decrease of C-O stretching frequency from that of gaseous CO. The extent of separation between $\widetilde{1\pi}$ and $\widetilde{4\sigma}$ is determined mainly by the location of the $\widetilde{1\pi}$ level because the position of $\widetilde{4\sigma}$ is nearly constant for the variation near the equilibrium internuclear distance due to the non-bonding character of the $\widetilde{4\sigma}$ orbital. The attempt to establish an empirical law between electronic and vibrational properties for CO adsorption systems may require the exact C-O bond distance in the adsorbed state. The order of elongation of the C-O bond distance may in magnitude be at most 0.1 Å or less. It is not surprising for CO adsorption systems to show an increase or a decrease of work function due to CO adsorption. This only indicates that the polarity of adsorbed CO changes as a result of the elongation of the C-O bond distance. In order to understand the mechanism of metal-CO bonding, the determination of metal-carbon bond distances is essential. This is a remaining problem for future studies.

5. Nitrogen adsorption

The ground state for gaseous nitrogen is a ${}^1\Sigma_g^+$ state in the $D_{\infty h}$ symmetry notation with electronic configuration

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2. \quad (5.1)$$

Here and hereafter we use the $C_{\infty v}$ symmetry notation as the same notation has been used for gas phase CO. Then, one can also write instead of (5.1)

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2. \quad (5.2)$$

The orbital characters of nitrogen are almost similar to those of CO. The molecular properties of nitrogen are summarized in table 4 [29].

Molecular nitrogen adsorption on metal surfaces has been observed at ~ 200 K or lower in UHV systems. The orientation of the adsorbed nitrogen molecule has been deduced by the application of surface selection rules for IRAS [119] and EELS [120] measurements and the observation of two (for molecular axis parallel to surface normal) or three (for molecular orientation parallel to the surface) peaks in UPS measurements [101]. It has been shown that the orientation is parallel to the surface normal similar to CO adsorption except for $N_2/Pd(111)$ at 45 K [101] and $N_2/Cu(111)$ at 50 K [121]. Indirect experimental evidence for this observation is given by XPS measurements [122–124]. Since on end-on adsorption the 1s levels of the two nitrogen atoms will be perturbed to different extents and appear as two peaks, on side-on adsorption only one peak due to 1s levels of nitrogen atoms will be observed.

Table 5 lists the available literature data for N_2 adsorption on metals, namely, adsorbate superstructure (LEED) pattern, adsorption energy (E) at initial coverages, work function changes ($\Delta\phi$) and the N–N stretching vibration ($\nu(N-N)$) at higher coverages. We will briefly state the general features of these quantities given in table 5. Adsorption energies are ~ 10 kcal/mol or less. Work function changes ($\Delta\phi$) are different for different metals and even for different planes of the same metal, but the absolute values of ($\Delta\phi$) are small except for $N_2/Ir(100)$ and $N_2/Rh(100)$ [10]. The $\nu(N-N)$ of adsorbed N_2 , with the limited data available, is less by ~ 100 cm^{-1} than that of the gas phase. This means at least that the N–N bond distance has lengthened a bit compared to that of gaseous N_2 . When one compares these quantities for N_2 adsorption with those for CO adsorption given in table 2, one finds that the order of magnitude of E and $\Delta\phi$ is similar to that for CO/noble metals, but the ratio for $\nu(N-N)$ of adsorbed N_2 to $\nu(N-N)$ of gaseous N_2 ($\sim 2200/2358$) is slightly less than the ratio of that of CO ($\sim 2100/2143$).

The main feature of the UPS studies on nitrogen adsorption on group VIII metals is that the separation between $\widetilde{1\pi}$ and $\widetilde{4\sigma}$ levels ($\Delta(\widetilde{4\sigma}-\widetilde{1\pi})$) is larger than that of CO adsorption even though the value of the separation in the gas

Table 4
 Summary of molecular characteristics of N_2 in neutral, ionic and excited states [29]

	N_2	N_2^+	N_2^-	N_2^*
Configuration	$---(1\pi_u)^4(3\sigma_g)^2$	$---(1\pi_u)^4(3\sigma_g)^1$	$---(1\pi_u)^4(3\sigma_g)^2(1\pi_g)^1$	$---(1\pi_u)^4(3\sigma_g)^1(1\pi_g)^1$
State	$1\Sigma^+$	$2\Sigma^+$	$2\Pi_g$	$(\uparrow\uparrow)$
$R_c(\text{\AA})$	1.09	1.12	1.19	$a^1\Pi_g$
$r(\text{NN})(\text{cm}^{-1})$	2358	2207	1968	$B^3\Pi_g$
$D(\text{eV})$	9.8	8.7	7.9	1.21
$I(\text{eV})$	15.6	27.1	-1.9	1.22
				1733
				$(\uparrow\downarrow)$
				$A^3\Sigma_u^+$
				$a'^1\Sigma_u^-$
				$---(1\pi_u)^3(3\sigma_g)^2(1\pi_g)^1$
				1.28
				1461
				1530

Table 5
Summary of adsorption parameter for N₂ on group VIII metals

Surface	Adsorbate structure	E (kcal/mol)	$\Delta\phi$ (eV)	$\nu(\text{N-N})$	References			
					LEED	E	$\Delta\phi$	ν
Fe	(100)	≤ 7.5				[125]		
	(111)	7.5	0.14			[126]	[126]	
Ru	(0001)	$(\sqrt{3} \times \sqrt{3})R30^\circ$	8	2220	[127]	[127]		[127]
Rh	(111)	8	-0.15			[10]	[10]	
	(100)	9	-0.5			[10]	[10]	
	(110)	10	0.2			[10]	[10]	
Ir	(111)		-0.2				[10]	
	(100)	8	-0.7			[10]	[10]	
	(110)	10	0.1			[10]	[10]	
Ni	(100)	p1g1 (2×2)	8.5	2200	[124]	[124]		[128]
	(110)	Diffuse c(2×2)	8.5	2194	[119]	[119]	[119]	[119]
Pt	(111)		9.2	2238		[129]		[129]
			9	-0.3		[10]	[10]	
	(100)		9	-0.3		[10]	[10]	

phase is smaller than that of gaseous CO. This statement is substantiated by the data given in fig. 7 (and table 6), wherein the $\widetilde{4\sigma}$ - $\widetilde{1\pi}$ separation for both CO and N₂ in the gas phase as well as in the adsorbed state are compared with different reference situations like with respect to Fermi level (panel a in fig. 7), aligning $\widetilde{4\sigma}$ (panel b) or $\widetilde{1\pi}$ (panel c) levels or with respect to vacuum level (panel d). However, this observation is not peculiar. The orbital characteristics (contours), especially that of 4σ , which is mostly non-bonding orbital in both molecules, in the case of nitrogen has higher charge density on the two atoms while it is mainly concentrated on one side of the molecule along the molecular axis in the case of CO. This reflects strongly in the variation of the energy of the 4σ level as a function of internuclear distance for N₂ and CO, where for N₂ this level is stabilized for internuclear distance elongation [133] while in the case of CO, the variation is of lower gradient [28]. In table 6, the data on the peak positions of valence levels observed for nitrogen adsorption on group VIII metals are given. The data of W(110) [122] and Al(111) [131] are also included for comparison.

Nieuwenhuys [10] has treated the N₂ adsorption also in terms of a donation and backdonation model while Heskett et al. [11] have concluded that the $\widetilde{2\pi}$ ($\widetilde{1\pi_g}$) is unoccupied in the neutral ground state for weak adsorption systems in contrast to MO cluster model calculations [134], which support the backdonation of the metal electron to N₂ for bonding. It is usually considered that both $\widetilde{5\sigma}$ and $\widetilde{4\sigma}$ levels are involved in bonding with the surface in the case of nitrogen [101,11]. This contention probably arises from the similarity of the

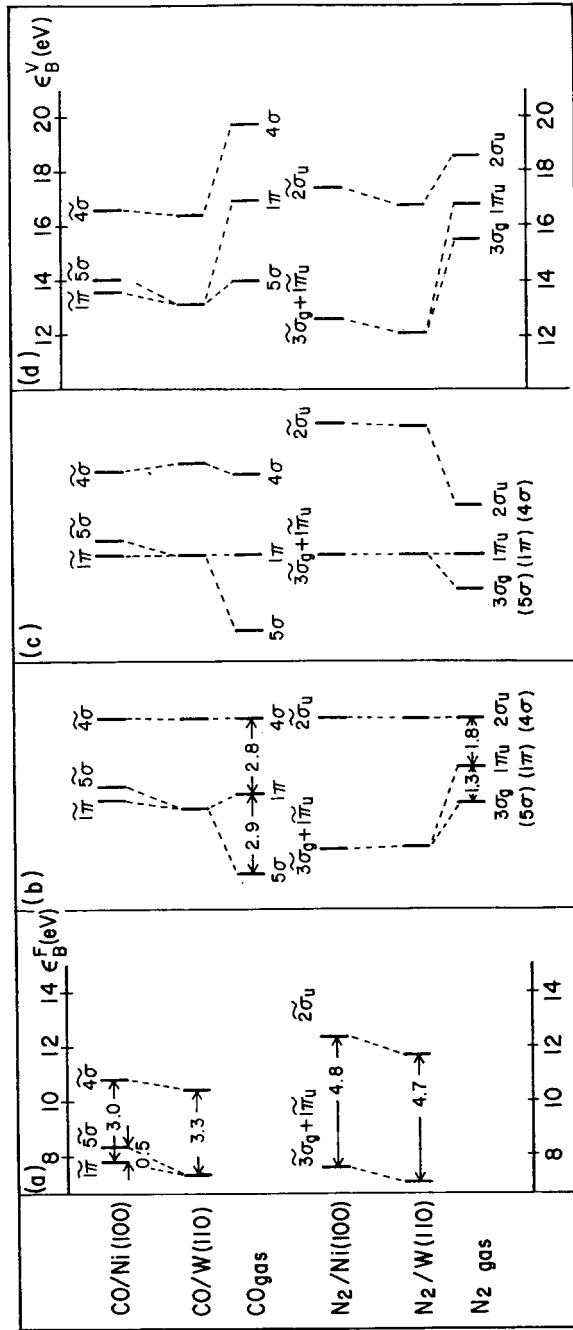


Fig. 7. Peak positions of valence levels on adsorbed state (Ni(100) [112] and W(110) [122]) and in the gas phase for CO and N₂ with respect to different references. (a) Fermi level, (b) 4σ, (c) 1π and (d) vacuum level.

Table 6

Peak positions of valence levels with respect to E_F and energy separation for $\widetilde{4\sigma}(2\widetilde{\sigma}_u)$ and $\widetilde{1\pi}(1\widetilde{\pi}_u)$ level ($\Delta(|\widetilde{4\sigma}-\widetilde{1\pi}|)$) for N_2 adsorption on metals

Surface	Peak positions			$\Delta(\widetilde{4\sigma}-\widetilde{1\pi})$	References	
	$\widetilde{5\sigma}$	$\widetilde{1\pi}$	$\widetilde{4\sigma}$			
Ni (100)		7.6	12.4	4.8	[112]	
Ni (110)	8.1		7.8	11.8	4.0	[101]
Fe (111)		8.0	11.7	3.7	[130]	
Ir (110)		8.0	11.8	3.8	[124]	
W (110)		7.0	11.7	4.7	[122]	
Pd (111)	8.7		10.3	11.9	1.6	[101]
Al (111)	10.5		11.9	13.7	1.8	[131]
condensed phase		11.1	12.5	14.3	1.8	[132]
N_2 (gas)	15.5		16.8	18.6	1.8	[107]

orbital contours of the two levels. However, the energy position of the $\widetilde{4\sigma}$ level in the case of nitrogen appears to be unfavourable for any bonding and hence the bonding can result mainly from the $\widetilde{5\sigma}$ level.

The preferred orientation of N_2 adsorption at extremely low temperatures is the molecular axis being parallel to the surface on some metals [135]. The UPS spectra for these systems exhibit three peaks in the valence region as well as that of gaseous CO, typical examples of which have been given in table 6. The adsorption energy for side-on adsorption of N_2 has been found to be lower than that observed for end-on adsorption. The work function may remain constant or decrease because of the closed-shell electronic configuration of the adsorbate or due to side-on adsorption state being similar to rare gas adsorption as described in section 4.

References

- [1] G. Blyholder, J. Phys. Chem., 68 (1964) 2772.
- [2] K. Klapper, H.F. Kempin and G. Ertl, Phys. Rev. Letters 41 (1978) 333.
- [3] T. Engel and G. Ertl, Advan. Catalysis 28 (1979) 1.
- [4] T.B. Grimley, in: Molecular Processes in Solid Surfaces, Eds. E. Drauglis et al. (McGraw-Hill, New York, 1969) p. 299.
- [5] P.S. Bagus, K. Hermann and M. Seel, J. Vacuum Sci. Technol. 18 (1981) 435.
- [6] D.E. Ellis, E.J. Baerends, H. Adachi and F.W. Averill, Surface Sci. 64 (1977) 649.
- [7] R.S. Mulliken, J. Am. Chem. Soc. 74 (1952) 811.
- [8] G. Doyen and G. Ertl, Surface Sci. 43 (1974) 197.
- [9] G. Brodén, T.N. Rhodin, C. Brucker, R. Benbow and Z. Hurych, Surface Sci. 59 (1976) 593.
- [10] B.E. Nieuwenhuys, Surface Sci. 105 (1981) 505.
- [11] D. Heskett, E.W. Plummer and R.P. Messmer, Surface Sci. 139 (1984) 558.

- [12] P.L. Young and R. Gomer, *J. Chem. Phys.* 61 (1974) 4955.
- [13] P.J. Page and P.M. Williams, *Disc. Faraday Soc.* 58 (1974) 80.
- [14] R.J. Smith, J. Anderson and G.J. Lapeyre, *Phys. Rev.* B15 (1980) 632.
- [15] S.Å. Lindgren, J. Paul and L. Wallden, *Chem. Phys. Letters* 84 (1981) 487.
- [16] C.F. McConville, C. Somerton and D.P. Woodruff, *Surface Sci.* 139 (1984) 75.
- [17] F. Bozso, J. Arias, J.T. Yates, Jr., R.M. Martin and H. Metiu, *Chem. Phys. Letters* 94 (1983) 243.
- [18] H. Conrad, G. Ertl, J. Küppers, S.W. Wang, K. Gérard and H. Haberland, *Phys. Rev. Letters* 42 (1979) 1082.
- [19] F. Mucchielli, C. Boiziau, R. Nuvolone and J. Roussel, *J. Phys.* C13 (1980) 2441.
- [20] R. Miranda, K. Wandelt, D. Rieger and R.D. Schnell, *Surface Sci.* 139 (1984) 430.
- [21] Th. Fauster and F.J. Himpsel, *Phys. Rev.* B27 (1983) 1390.
- [22] J.E. Demuth, D. Schmeisser and Ph. Avouris, *Phys. Rev. Letters* 47 (1981) 1166.
- [23] Ph. Avouris, N.J. DiNardo and J.E. Demuth, *J. Chem. Phys.* 80 (1984) 491.
- [24] J. Stöhr and R. Jaeger, *Phys. Rev.* B26 (1982) 4111.
- [25] S. Ishi and Y. Ohno, *Surface Sci.* 139 (1984) L219.
- [26] J.W. Davenport, *Chem. Phys. Letters* 77 (1981) 45.
- [27] S. Huzinaga, *Molecular Orbital Theory* (Iwanami Shoten, Tokyo, 1980) p. 241 (in Japanese).
- [28] A.D. McLean and M. Yoshimine, *Table of Linear Molecule Wave Functions* (IBM, San Jose, CA, 1967).
- [29] K.P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand-Reinhold, New York, 1979).
- [30] F.P. Billingsley II and M. Krauss, *J. Chem. Phys.* 60 (1974) 4130.
- [31] K. Kirby-Docken and B. Liu, *J. Chem. Phys.* 66 (1977) 4309.
- [32] W. Erley, *J. Vacuum Sci. Technol.* 18 (1981) 472.
- [33] G. Wedler and H. Ruhmann, *Surface Sci.* 121 (1982) 464.
- [34] J. Benziger and R.J. Madix, *Surface Sci.* 94 (1980) 119.
- [35] K. Yoshida, *Japan J. Appl. Phys.* 20 (1981) 823.
- [36] U. Seip, M.-C. Tsai, K. Christmann, J. Küppers and G. Ertl, *Surface Sci.* 139 (1984) 29.
- [37] E.D. Williams and W.H. Weinberg, *Surface Sci.* 82 (1979) 93.
- [38] T.E. Madey and D. Menzel, *Japan. J. Appl. Phys. Suppl. 2, Part 2* (1974) 229.
- [39] H. Pfnür, D. Menzel, F.M. Hoffmann, A. Ortera and A.M. Bradshaw, *Surface Sci.* 93 (1980) 431.
- [40] G.E. Thomas and W.H. Weinberg, *J. Chem. Phys.* 70 (1979) 1437.
- [41] N. Vennemann, E.W. Schwarz and M. Neumann, *Surface Sci.* 126 (1983) 273.
- [42] H. Papp, in: *Proc. IVC-8, ICSS-4, ECOSS-3, Cannes, 1980*, p. 245.
- [43] P.A. Thiel, E.D. Williams, J.T. Yates Jr. and W.H. Weinberg, *Surface Sci.* 84 (1979) 54; T. Matsushima, T. Matsui and M. Hashimoto, *J. Chem. Phys.* 81 (1984) 5151.
- [44] D.G. Castner, B.A. Sexton and G.A. Somorjai, *Surface Sci.* 71 (1978) 519.
- [45] L.H. Dubois and G.A. Somorjai, *Surface Sci.* 91 (1980) 514.
- [46] Y. Kim, H.C. Peebles and J.M. White, *Surface Sci.* 114 (1980) 363.
- [47] R.A. Marbrow and R.M. Lambert, *Surface Sci.* 67 (1977) 489.
- [48] J. Küppers and A. Plagge, *J. Vacuum Sci. Technol.* 13 (1976) 259; C.M. Comrie and W.H. Weinberg, *J. Vacuum Sci. Technol.* 13 (1976) 264.
- [49] J. Küppers and H. Michel, cited in ref. [3], p. 15.
- [50] J.A. Grant, *Surface Sci.* 18 (1969) 228.
- [51] J.L. Taylor, D.E. Ibbotson and W.H. Weinberg, *J. Chem. Phys.* 69 (1978) 4298.
- [52] K. Christmann, O. Schober and G. Ertl, *J. Chem. Phys.* 60 (1974) 4719.
- [53] J.C. Campuzano and R.G. Greenler, *Surface Sci.* 83 (1979) 301; J.C. Campuzano, R. Dus and R.G. Greenler, *Surface Sci.* 102 (1981) 172.
- [54] J.C. Bertolini and B. Tardy, *Surface Sci.* 102 (1981) 131.

- [55] J.C. Tracy, *J. Chem. Phys.* 56 (1972) 2736;
K. Akimoto, Y. Sakisaka, M. Nishijima and M. Onchi, *Surface Sci.* 88 (1979) 109.
- [56] T.N. Taylor and P.J. Estrup, *J. Vacuum Sci. Technol.* 10 (1973) 26.
- [57] H.H. Madden, J. Küppers and G. Ertl, *J. Chem. Phys.* 58 (1973) 3401.
- [58] M. Nishijima, S. Masuda, Y. Sakisaka and M. Onchi, *Surface Sci.* 107 (1981) 31.
- [59] G. Ertl and J. Koch, *Z. Naturforsch.* 25a (1970) 1906.
- [60] A.M. Bradshaw and F.M. Hoffmann, *Surface Sci.* 72 (1978) 513.
- [61] J.C. Tracy and P.W. Palmberg, *J. Chem. Phys.* 51 (1969) 4852.
- [62] R.J. Behm, K. Christmann, G. Ertl and M.A. Van Hove, *J. Chem. Phys.* 73 (1980) 2984.
- [63] R.J. Behm, K. Christmann, G. Ertl, M.A. Van Hove, P.A. Thiel and W.H. Weinberg, *Surface Sci.* 88 (1979) L59.
- [64] A. Ortega, A. Garbout, F.M. Hoffmann, W. Stenzel, R. Unwin, K. Horn and A.M. Bradshaw, in: *Proc. IVC-8, ICSS-4, ECOS-3, Cannes, 1980*, p. 335.
- [65] H. Conrad, G. Ertl, J. Koch and E.E. Latta, *Surface Sci.* 43 (1974) 462.
- [66] G. Ertl, M. Neumann and K.M. Streit, *Surface Sci.* 64 (1977) 393.
- [67] P.R. Norton, J.W. Goodale and E.B. Selkirk, *Surface Sci.* 83 (1979) 189.
- [68] B.E. Hayden and A.M. Bradshaw, *Surface Sci.* 125 (1983) 787.
- [69] H. Steiniger, S. Lehwald and H. Ibach, *Surface Sci.* 123 (1982) 264.
- [70] H.P. Bonzel and T.E. Fischer, *Surface Sci.* 51 (1975) 213;
G. Brodén, G. Pirug and H.P. Bonzel, *Surface Sci.* 72 (1978) 45.
- [71] R.J. Behm, P.A. Thiel, P.R. Norton and G. Ertl, *J. Chem. Phys.* 78 (1983) 7437.
- [72] P.A. Thiel, R.J. Behm, P.R. Norton and G. Ertl, *J. Chem. Phys.* 78 (1983) 7448.
- [73] C.M. Comrie and R.M. Lambert, *J.C.S. Faraday Trans. I*, 72 (1976) 1659;
R.M. Lambert, *Surface Sci.* 49 (1975) 325.
- [74] P. Hofmann, S.R. Bare and D.A. King, *Surface Sci.* 117 (1982) 245.
- [75] J. Kessler and F. Thieme, *Surface Sci.* 67 (1977) 405.
- [76] P. Hollins and J. Pritchard, *Surface Sci.* 89 (1979) 486.
- [77] J.C. Tracy, *J. Chem. Phys.* 56 (1972) 2748.
- [78] K. Horn and J. Pritchard, *Surface Sci.* 55 (1976) 701.
- [79] S. Andersson, *Surface Sci.* 89 (1979) 477.
- [80] K. Horn, M. Hussain and J. Pritchard, *Surface Sci.* 63 (1979) 244.
- [81] J.F. Wendelken and M.V.K. Ulehla, *J. Vacuum Sci. Technol.* 16 (1979) 441.
- [82] G. McElhiney, H. Papp and J. Pritchard, *Surface Sci.* 54 (1976) 617.
- [83] S. Krause, C. Mariani, K.C. Prince and K. Horn, *Surface Sci.* 138 (1984) 305.
- [84] G.M. McElhiney and J. Pritchard, *Surface Sci.* 60 (1976) 397.
- [85] H. Ibach and D.L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibration* (Academic Press, New York, 1982) p. 284.
- [86] G. Ertl, J. Küppers, F. Nitschké and M. Weiss, *Chem. Phys. Letters* 52 (1977) 309.
- [87] E.S. Jensen and T.N. Rhodin, *Phys. Rev.* B27 (1983) 3338.
- [88] T.N. Rhodin and C.F. Brucker, *Solid State Commun.* 23 (1977) 275.
- [89] M. Textor, I.D. Gay and R. Mason, *Proc. Roy. Soc. (London)* A356 (1977) 37.
- [90] J.C. Fuggle, T.E. Madey, M. Steinkilberg and D. Menzel, *Phys. Letters* 51A (1975) 163;
J.C. Fuggle, M. Steinkilberg and D. Menzel, *Chem. Phys.* 11 (1975) 307.
- [91] F. Greuter, D. Heskett, E.W. Plummer and F.-J. Freund, *Phys. Rev.* B27 (1983) 7117.
- [92] W. Braum, M. Neumann, M. Iwan and E.E. Koch, *Phys. Status Solidi (b)* 90 (1978) 525.
- [93] D.E. Peebles, H.C. Peebles and J.M. White, *Surface Sci.* 136 (1984) 463.
- [94] R.J. Baird, *J. Electron Spectrosc. Related Phenom.* 24 (1981) 55.
- [95] R.J. Baird, R.C. Ku and P. Wynblatt, *Surface Sci.* 97 (1980) 346.
- [96] C.W. Seabury, T.N. Rhodin, M.M. Traum, B. Benbow and Z. Hurych, *Surface Sci.* 97 (1980) 363.
- [97] D.E. Ibbotson, T.S. Wittrig and W.H. Weinberg, *Surface Sci.* 97 (1980) 297.
- [98] P.M. Williams, P. Butcher, J. Wood and K. Jacobi, *Phys. Rev.* B14 (1976) 3215.

- [99] C. Guillot, Y. Jugnet, Y. Lassailly, D. Chanderaris, J. Lecante and J.C. Vedrine, in: Proc. IVC-8, ISCC-4, ECOSS-3, Cannes, 1980, p. 1158.
- [100] C.L. Allyn, T. Gustafsson and E.W. Plummer, *Chem. Phys. Letters* 47 (1977) 127; *Solid State Commun.* 28 (1978) 85.
- [101] K. Horn, J. DiNardo, W. Eberhardt, H.-J. Freund and E.W. Plummer, *Surface Sci.* 118 (1982) 465.
- [102] D. Rieger, R.D. Schnell and W. Steinmann, *Surface Sci.* 143 (1984) 157.
- [103] D.R. Lloyd, C.M. Quinn and N.V. Richardson, *Solid State Commun.* 20 (1976) 409.
- [104] H. Conrad, G. Ertl, J. Küppers and E.E. Latta, *Disc. Faraday Soc.* 58 (1974) 116.
- [105] M. Trenary, S.L. Tang, R.J. Simonson and F.R. McFeely, *Surface Sci.* 124 (1983) 555.
- [106] S.R. Bare, P. Hofmann and D.A. King, *Vacuum* 31 (1981) 463.
- [107] D.W. Turner, G. Baker, A.D. Baker and C.R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley, New York, 1970).
- [108] H.P. Bonzel and H.J. Krebs, *Surface Sci.* 117 (1982) 639.
- [109] D. Schmeisser, A. Gutman and K. Jacobi, 6th European Conf. on Surface Science (ECOSS-6), York, 1984.
- [110] T.-C. Chiang, G. Kaindl and D.E. Eastman, *Solid State Commun.* 36 (1980) 25.
- [111] O. Gunnarsson and K. Schönhammer, *Phys. Rev. Letters* 41 (1978) 1608; R.P. Messmer, S.H. Lamson and D.R. Salahub, *Phys. Rev.* B25 (1982) 3576.
- [112] C.R. Brundle, P.S. Bagus, D. Menzel and K. Hermann, *Phys. Rev.* B24 (1981) 7041.
- [113] S. Ishi and Y. Ohno, *Surface Sci.* 143 (1984) L408.
- [114] G. Brodén, G. Pirug and H.P. Bonzel, *Chem. Phys. Letters* 51 (1977) 250.
- [115] For example, B.E. Nieuwenhuys, O.G. van Aardenne and W.M.H. Sachtler, *Chem. Phys.* 5 (1974) 418;
J. Küppers, F. Nitschke, K. Wandelt and G. Ertl, *Surface Sci.* 87 (1979) 295;
S. Ishi and T. Matsui, in: *Catalytic Reaction on Solid Surfaces, II*, Eds. T. Toya and K. Azuma (Kyoritsu Shuppan, 1983) section 4. Rare-gas adsorption on metals (in Japanese).
- [116] The $\nu(\text{C}-\text{O})$ has been observed on Ir films: D. Reinalda and V. Ponoc, *Surface Sci.* 91 (1979) 113.
- [117] A. Ortega, F.M. Hoffmann and A.M. Bradshaw, *Surface Sci.* 119 (1982) 79.
- [118] G. Blyholder, *J. Vacuum Sci. Technol.* 11 (1974) 197.
- [119] M. Grunze, R.K. Driscoll, G.N. Burlund, J.C.L. Corrish and J. Pritchard, *Surface Sci.* 89 (1979) 381.
- [120] W. Ho, R.F. Willis and E.W. Plummer, *Surface Sci.* 95 (1980) 171.
- [121] M. Copel, cited in ref. [11].
- [122] J.C. Fuggle and D. Menzel, *Surface Sci.* 79 (1979) 1.
- [123] M. Golze, M. Grunze, R.K. Driscoll and W. Hirsch, *Appl. Surface Sci.* 6 (1981) 464.
- [124] D.E. Ibbotson, T.S. Wittig and W.H. Weinberg, *Surface Sci.* 110 (1981) 313.
- [125] G. Ertl, S.B. Lee and M. Weiss, *Surface Sci.* 114 (1982) 527.
- [126] G. Ertl, S.B. Lee and M. Weiss, *Surface Sci.* 114 (1982) 515.
- [127] A.B. Anton, N.R. Avery, B.H. Toby and W.H. Weinberg, *J. Electron Spectrosc. Related Phenomena* 29 (1983) 181.
- [128] P. Dowben, cited in ref. [11].
- [129] P.A. Shigeishi and D.A. King, *Surface Sci.* 62 (1977) 379.
- [130] M. Grunze, M. Golze, J. Fuhler, M. Neumann and E. Schwarz, in: *Proc. Intern. Congr. on Catalysis*, 1984, Vol. IV, p. 133.
- [131] Ph. Avouris, D. Schmeisser and J.E. Demuth, *J. Chem. Phys.* 79 (1983) 488.
- [132] P.R. Norton, R.L. Tapping, H.P. Broida, J.W. Gadzuk and B.J. Wacławski, *Chem. Phys. Letters* 53 (1978) 465.
- [133] P.E. Cade, K.D. Salsms and A.C. Wahl, *J. Chem. Phys.* 44 (1966) 1973.
- [134] H. Itoh, G. Ertl and A.B. Kunz, *Chem. Phys.* 59 (1981) 149;
K. Hermann, P.S. Bagus, C.R. Brundle and D. Menzel, *Phys. Rev.* B24 (1981) 7025.
- [135] D. Schmeisser, K. Jacobi and P.M. Kolb, *Vacuum* 31 (1981) 439.