AECL–5937
Volume 53, number 3 CHEMICAL PHYSICS LETTERS 1 February 1978

HIGH RESOLUTION PHOTOEMISSION STUDY OF CONDENSED LAYERS OF NITROGEN AND CARBON MONOXIDE

P.R. NORTON, R.L. TAPPING*
Atomic Energy of Canada Limited, Chalk River Nuclear Laboratories, Physical Chemistry Branch, Chalk River, Ontario, Canada K0J 1J0

and

H.P. BROIDA**, J.W. GADZUK and B.J. WACLAWSKI
National Bureau of Standards, Washington, D.C. 20234, USA

Received 5 October 1977

High resolution (0.09 eV) UPS spectra have been obtained of condensed films of N_2 and CO. All spectral features are broadened by $\gtrsim$0.6 eV upon condensation. The origin of this broadening is discussed. The difference in linewidths for all equivalent levels, $\Delta\epsilon_{CO-N_2} \approx 0.1$ to 0.2 eV can be understood in terms of a hole–dipole multiphonon excitation mechanism. Photoemission from what is believed to be the $a\,^3\Pi$ excited neutral state of CO has been detected in the solid phase for the first time.

1. Introduction

In this letter we report the first high resolution study of condensed layers of CO and N_2. A theoretical study [1] has indicated that in condensed molecular multilayers, contributions to the linewidth due to interatomic Auger transitions and electron–hole pair shake-up [2] should be reduced to such an extent that linewidths of $<$0.1 to 0.2 eV should be observed. Secondly, residual broadening, due to a hole–dipole multiphonon excitation mechanism, should depend upon the magnitude of the permanent dipole moment of the molecule.

Much has been learned [3] from ultraviolet photoemission spectroscopy (UPS) studies on adsorbed atoms and molecules, but as pointed out recently [2], no vibrational structure has been resolved in these studies even in those cases where the adsorbed species is believed to retain its molecular identity [4]. By contrast, in the gas phase, vibrational structure is easily resolvable using photoelectron spectroscopy (PES) at photon energies of 20–40 eV, and has demonstrated its utility in molecular orbital assignments. It is clearly of considerable interest to deduce the origin of the broadening observed in photoemission from the adsorbed phase, both from the point of view of understanding the physics of the photoemission process and to determine whether PES techniques can resolve vibrational structure in adsorbed molecules. Resolution of vibrational structure would be extremely valuable in determining the mode of bonding to a surface and as a fingerprint technique in assigning molecular orbitals in adsorbed species. Himpsel et al. [5] reported results of a synchrotron radiation study of solid N_2 and O_2, but it was not clear whether the resolution was sufficient to resolve vibrational structure if it were present. The purpose of the present work is thus to test under well-established, high-resolution conditions the theoretical ideas in ref. [1]. In a subsequent paper [6] we shall report results of a study of physisorption and chemi-

* Present address: Alcan International Limited, Research Centre, Kingston, Ontario, Canada.
** Visiting scientist; permanent address: Department of Physics, University of California, Santa Barbara, California 93106, USA.

sorption of these gases on a copper substrate.

2. Experimental methods

The spectrometer and available surface preparation techniques have been discussed previously [7]. Gas phase spectra were obtained by admitting the gas to the spectrometer chamber to pressures of (1–3) × 10^{-3} Pa. Under these conditions good signal to noise (S/N) could be obtained only with HeI excitation (21.2 eV). All solid phase spectra shown here, were obtained with HeII excitation (40.8 eV) to reduce the secondary emission background. The spectrometer resolution, ΔE, is identical at different kinetic energies since electrons are retarded before analysis at a constant pass energy. Relative intensities of the lines in a spectrum will, however, change with $h\nu$ because of effects of changing photoexcitation cross-section and spectrometer sensitivity.

The gases were condensed on an elliptical copper surface that was produced by cutting a high purity copper rod, 1 cm diameter, at 45° to the cylinder axis. This rod was hard soldered to a re-entrant stainless steel well of suitable length. The stainless steel well was attached to a flange that also had a feed-through arrangement to permit the measurement of the EMF of a gold–0.07% iron versus chromel thermocouple. Temperatures are estimated to be accurate to ±2 K. The entire re-entrant well assembly, to within ≈2 cm from the probe face, was wrapped with aluminized Mylar film to reduce radiation heating. The spectrometer vacuum system was pre-baked and after mounting of the sample probe the preparation chamber [7] was outgassed for 12 hours at 325–335 K by means of heating tapes. The main residual gas was H_2O from the Mylar film. Pressures of the order of 1×10^{-7} Pa were attained after a further 24 hours pumping and the pressure was further reduced to $< 7 \times 10^{-8}$ Pa by cooling a re-entrant cold finger to 77 K. Ultra high vacuum conditions were essential to prevent the build up of impurities on top of the condensed layers.

The copper end piece was cooled by flowing cold ^{4}He gas from a liquid He dewar through a syphon. The delivery (horizontal) end of the syphon was fitted with an uninsulated thin-walled stainless steel tube which just reached the end of the re-entrant well. The ultimate temperature of ≈18 K was limited largely by the energy exchange between the inflowing and outflowing He. In these experiments no attempt was made to recover the He and the flow rates were such that 15 ℓ lasted ≈$2\frac{1}{2}$ hours.

The copper surface as cleaned by Ar^+ ion sputtering (2 kV, 20 μA cm^{-2}, 30 min) at 295 K before the condensation experiments. X-ray photoelectron spectroscopy (XPS) showed that the total oxygen plus carbon impurity level was less than 0.1 monolayers. The surface was not then annealed. Condensation was effected by precooling the probe to ≈20 K and then admitting CO or N_2 at low pressure (in the range 10^{-6} to 10^{-4} Pa) until a layer of suitable thickness had built up. The gas always passed over the 77 K cold finger before flowing into the spectrometer chamber [7] where condensation occurred (the Mylar film prevented rapid condensation on the rest of the stainless steel well). The purity of the gases was measured in situ with a quadrupole mass spectrometer, confirming that the total impurity levels were <0.01%. After the film had attained a suitable thickness, judged by the attenuation of the Cu d-band emission (see below), the flow was stopped and a HeII excited spectrum was obtained. This procedure was followed for a series of film thicknesses. The estimated thickness of the films depends upon the value assigned to the mean free path of the ≈35 eV electrons photoemitted from Cu d-band edge. We have used a value of 1 nm. This is a reasonable assumption [8] and is consistent with the 15% attenuation of the platinum d-band at $E_f - 5$ eV observed at a CO coverage of 0.4 to 0.5 monolayers [3]. On this basis the thickness of the films studies in this work ranged from <0.3 nm (submonolayer) to ≈10 nm. We illustrate no data on films of thickness greater than ≈2.5 nm because of the lack of significant changes in the range 2.5 to 10 nm and the appearance of charging effects (binding energies increase slightly and lines broaden) at thicknesses much greater than 10 nm.

3. Experimental results

Fig. 1 shows both the HeI-excited gas phase N_2 spectrum and the HeII-excited spectrum of condensed N_2 at the same resolution. The resolution is estimated from the gas phase spectrum to be ≈0.09 eV and is determined almost entirely by the settings of slit width etc. on the analyser. The spectra are shifted by the dif-

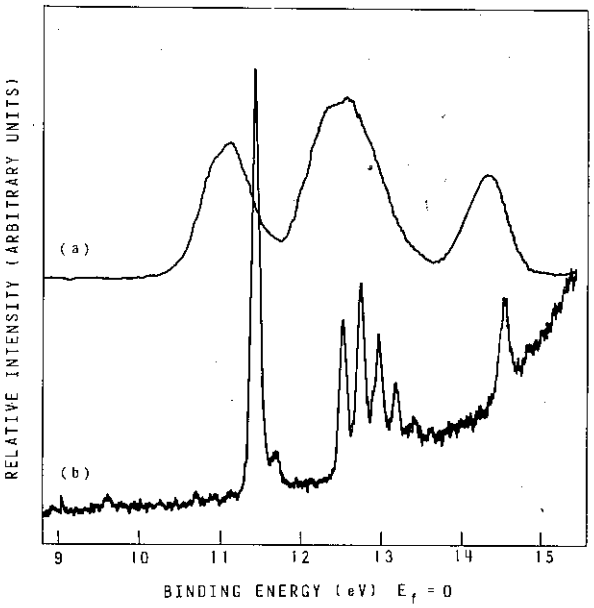


Fig. 1. (a) Photoelectron spectrum of condensed film of N_2 of thickness 2.4 nm. $h\nu$ = 40.8 eV. Same resolution as (b). (b) Photoelectron spectrum of gaseous N_2 at a pressure of $\approx 10^{-3}$ Pa. $h\nu$ = 21.2 eV, resolution $\approx$0.09 eV.

ference in the photon energies to bring them onto a common binding energy (BE) scale referred to the Fermi level of the copper substrate. The 30-fold attenuation of the Cu d-band (not shown in fig. 1) gives an estimated thickness (allowing for the 45° take-off angle) of $\approx$2.4 nm. No N_2-derived structure was observed in the range 0–10 eV. The three bands observed in condensed N_2 had BE's of 11.1, 12.5 and 14.3 eV compared to the gas phase vertical ionization potentials (IP's) of 11.40, 12.75 and 14.60 eV (determined in our experiment, Fermi level energy reference), showing that there is no change in relative splittings upon condensation. These latter values compare very well with previously reported gas phase data [9] (vertical IP's of 15.58, 16.91 and 18.75 eV) if allowance is made for the 4.2 eV work function of copper. Also immediately evident is the broadening of the lines upon condensation from $\approx$0.09 eV (our experimental resolution) to 0.5 eV. The data are collected in table 1.

Fig. 2 shows the spectra of CO condensed on a clean copper substrate with the copper Fermi level as the reference energy. Spectrum (a) is the HeI excited gas phase spectrum of CO, (b) is the HeII-excited spectrum of the clean copper d-band and (c) through (e)

Table 1
Photoemission from condensed N_2. Copper Fermi level = 0 eV; resolution $\approx$0.09 eV

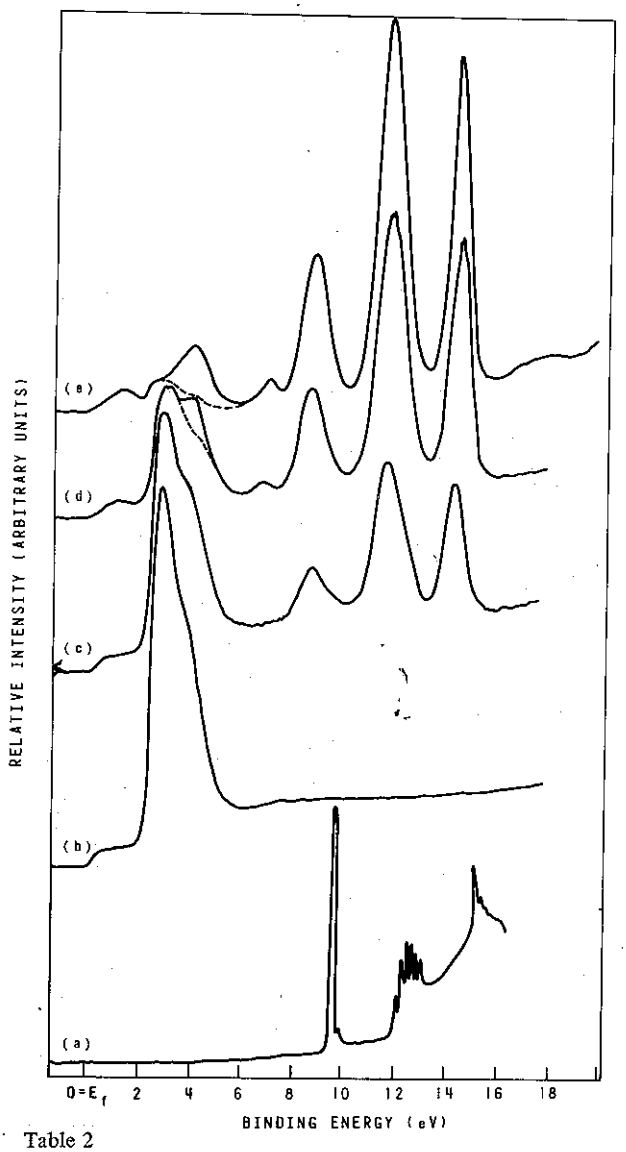
Level	Gas phase vertical IP's (eV)[a]	Solid phase BE (eV)	Solid phase fwhm (eV)	Layer thickness (nm)
$X^2\Sigma_g^+$	11.40	11.1	0.7_1	2.4
$A^2\Pi_u$	12.75	12.5	1.0_8	2.4
$B^2\Sigma_u$	14.60	14.3	0.5_7	2.4

[a] Measured in this work.

the same surface with three different film thicknesses of condensed CO.

Broadening of CO bands upon adsorption or condensation again is evident as in the case of N_2 (see tables 1 and 2). The BE's of the 3 bands present in physisorbed (condensed) multilayers of CO are 8.7 (8.8), 11.7 (11.7) and 14.5 (14.5) eV respectively compared to our measured vertical IP's in the gas phase of 9.86, 12.56 and 15.51 eV referred to the copper Fermi level (cf. 14.01, 16.67 and 19.67 eV for gas phase vertical IP's [9]).

Also evident in figs. 2d and 2e is the growth of three additional levels at 1.3, 4.2 and 7.1 eV. The feature at 4.2 eV deserves further comment. As the thickness of the CO layer increased, the Cu s- and d-bands attenuated uniformly until layers in excess of $\approx$2 CO molecules thick were formed. This layer thickness was judged from the total UPS emission intensity of the CO-derived features compared to that observed in CO chemisorbed on the same substrate at temperatures that allowed use of XPS to determine the coverage. As the layer thickness increased from $\approx$0.5 to 2 nm, three new features appeared and the emission in the region 2–5 eV could be fitted by assuming simultaneous attenuation of the Cu d-band and growth of a single level of width $\approx$1 eV at 4.2 eV. For this reason an estimate of the residual contribution of the Cu d-band is shown as a dashed line in figs. 2d and 2e. The intensities of both sets of CO-derived levels remained constant for layer thickness $\geqslant$3 nm. Close examination of the 7–8 eV region at coverages $<$ 1 monolayer revealed no sign of the 7.1 eV feature. CO purity was checked again in situ during the condensation and was better than 99.99%. The most likely co-condensing impurities would be H_2O and CO_2 but their gas phase concentrations were too low and the positions of the emission features do



not correlate with any bands in either the gas or adsorbed phases [3,10]. It is therefore clear that the 3 bands that appear only in condensed CO multilayers result from CO and not some impurity.

As discussed below, we believe that these levels result from photoemission from an excited state of CO, so the data on this state and the CO ground state are collected in table 2. The ground state levels in tables 1 and 2 are given the designations for the molecular ion and the assignment is determined by the binding energies and splittings, the larger full width at half maximum (fwhm) of the central level and the relative intensities of the levels when compared to HeII-excited gas phase spectra [11].

4. Discussion

Tables 1 and 2 show that the narrowest line observed under our experimental conditions was the $B\,^2\Sigma_u$ level of N_2 (henceforth called, for convenience, the 4σ level). Upon condensation the linewidth increased to 0.57 eV. This is at least a factor of 3 greater than the broadening expected from theory [2]. Since it is not possible, a priori, to calculate the various contributions to the binding energy shift of the 3 observed levels we

Fig. 2. (a) Photoelectron spectrum of gaseous CO at a pressure of $\approx 10^{-3}$ Pa. $h\nu$ = 21.2 eV, resolution ≈ 0.09 eV. Resolution in spectra (b) through (e) same as (a) and $h\nu$ = 40.8 eV. (b) Clean copper valence band. (c) Same surface after adsorption of ≈ 0.5 monolayers CO at 20 K. (d) Same surface after condensation of film ≈ 0.8 nm thick. (e) Same surface after condensation of film ≈ 2.1 nm thick.

Table 2
Photoemission from condensed CO. Binding energies (BE's) and fwhm in eV; copper Fermi level = 0 eV; resolution ≈ 0.09 eV

	Ground state level			Coverage or layer thickness	Gas phase vertical IP's[a]		
	$X\,^2\Sigma^+$	$A\,^2\Pi$	$B\,^2\Sigma$		$X\,^2\Sigma^+$	$A\,^2\Pi$	$B\,^2\Sigma$
BE	8.7	11.6	14.5	$\lesssim$0.5 monolayers	9.86	12.56	15.51
fwhm	1.0_0	1.2_2	0.8_3	($\lesssim 7 \times 10^{14}$ CO cm^{-2})			
BE	8.8	11.7	14.5	2.1 nm			
fwhm	0.9_0	1.1_8	0.7_2	2.1 nm			
	Excited state level #						
	1	2	3				
BE	1.3	4.2	7.1	2.1 nm			

a) Measured in this work.

cannot determine whether the band maxima are shifted by multiphonon excitation (large β; ref. [1]). It is very encouraging however that the differential broadening of all the levels in CO and N_2 (difference in fwhm of the 4σ levels = 0.15 eV for example) is in accord with the phonon theory which suggests that $\Delta\epsilon_{\text{fwhm}} \approx N\epsilon\mu/4R^2$ where N is the number of nearest neighbours, μ is the permanent dipole moment of the molecule ($\mu = 0$ for N_2, ≈ 0.1 D for CO) and R is an effective intermolecular separation in the condensed film [1]. With reasonable assumptions as to the film geometry, $\Delta\epsilon_{CO-N_2} \approx 0.1$ to 0.2 eV which is of the order of the observed differential broadening.

If the differential broadening arises from this mechanism then another mechanism must be sought for the remaining linewidth (0.57 eV in the case of N_2). There are many sources of linewidth that must be considered. The simplest possibility is (differential) charging in the condensed layer. Charging is certainly present for films $\geqslant 10$ nm thick, but the effect seems to be too small to account for the observed broadening at thicknesses of ≈ 2 nm. For example in films of N_2 estimated to be ≈ 30 nm thick, the bands shift to higher BE and broaden by ≈ 0.2 eV. Variation in potential due to site heterogeneity (films were not annealed) would seem to be too small an effect in a molecular solid, but conceivably patch fields from the polycrystalline copper surface could cause variations in the potential at different lattice sites. However, this effect should decrease with film thickness, and very little change was observed in films in the thickness range 1 to 10 nm.

Matthew and Komninos [12] have calculated intra–inter-atomic Auger transition rates and have concluded that, in some circumstances, they should be as rapid as the intra-atomic process involving the same initial hole state. However, for low energy Auger processes of the type considered here, both rates would be low because of the absence of energy conserving final states. This absence of suitable final states is a result of the band gap and thus Auger processes should not contribute significantly to the linewidth. A remaining possibility is that the hole can rapidly migrate to the substrate, or at least to a neighbouring molecule. This seems unlikely since valence band widths (determined by hole hopping times) for weakly bound molecular crystals are usually <0.1 eV.

The width and shape of the $A\,^2\Pi_u(1\pi)$ band in both solid CO and N_2 reflects the original Franck–Condon vibrational envelope of the gas phase spectrum, and in fact can be fitted quite well by summing gaussians of ≈ 0.7 eV fwhm with splittings and relative intensities equal to the gas phase values. It seems very unlikely that the 4σ level width in the solid phase could be explained by excitation of intramolecular vibrations because this level is essentially nonbonding in the gas phase.

Another result to be noted in tables 1 and 2 is the difference in widths of the $X\,^2\Sigma_g^+(5\sigma)$ and $B\,^2\Sigma_u(4\sigma)$ levels in each molecule (0.14 eV and 0.18 eV for N_2 and CO respectively). The 5σ level is essentially nonbonding in the gas phase but has the lowest ionization potential. It is tempting to attribute this small additional width to bonding effects in the solid phase.

The decrease in linewidth between physisorbed and multilayer CO (≈ 0.1 eV) could result from the increased hole lifetime in the multilayers compared to the physisorbed layer. This is perhaps an indication that the linewidths in condensed multilayers do not result from a short hole lifetime. At present it is not possible to pinpoint the major contributor to the ≈ 0.6 eV fwhm in the 4σ level of N_2, but certainly it is possible that the sum total of all the above effects could produce broadening of this magnitude.

Table 2 gives the data on the excited state of CO. This assignment depends upon several observations. These are: (a) experimental elimination of impurity effects, (b) the similarity in splittings, relative intensities and shapes to those observed in photoemission from ground state CO, (c) the similarity (but not equality) in the observed excitation energy to that observed in the gas and condensed phase UV spectroscopy for the $a\,^3\Pi$ state [13,14] and (d) the long lifetime of the $a\,^3\Pi$ state (of the order of several ms in the gas phase) makes detection in the solid phase reasonable [15–17].

The major problem with this reasoning lies in (c) because the gas phase excitation energy is 6.03 eV [13,14] compared to ≈ 7.4 eV observed here (difference in the BE's of the equivalent levels in the ground and excited states). It is necessary to postulate either a change in this excitation energy in the solid phase (due, for example, to intermolecular bonding effects) or an increase in the relaxation energy for photoemission from the excited state, compared to the ground

state molecular ion. This would lead to a lower apparent BE for electrons in the excited state and hence an increase in the measured excitation energy for the production of a $^3\Pi$ state. The latter process would require a differential relaxation at ≈1.4 eV, which seems unlikely. Confirmation of the assignment as the a $^3\Pi$ state requires detection of the phosphorescence from this state under our experimental conditions.

At least two mechanisms could be responsible for the formation of the a $^3\Pi$ state. The most likely are considered to be: (a) capture of an electron by the CO^+ ion leaving CO in an electronically excited metastable state or (b) direct coulombic excitation of neutral CO by secondary electrons. Many energetic secondary electrons are produced in a photoemission experiment and it is worth noting that Netzer et al. [18] have detected a 6 eV energy loss peak in electron energy loss spectra of CO chemisorbed on Pt.

The absence of this excited state in very thin layers (≪2 layers) may indicate that additional fast relaxation processes (vibrational and electronic) are available when the molecule is close to the metal surface. Such processes would reduce the lifetime of the excited state or of the CO^+ ion (needed to form the a $^3\Pi$ state by electron capture) to the point at which the dynamic concentration of the excited state is below our detection limits.

One question that immediately arises is why the equivalent excited state is not observed in solid N_2. There are several possible differences between CO and N_2 which might account for not observing the metastable A $^3\Sigma$ state of N_2; for example (a) N_2^+ dissociative neutralization has a high probability, (b) CO and N_2 metastable states have different electron configurations, and (c) photoionization probabilities are not the same.

5. Conclusions

In this letter we have reported the first photoemission measurements upon solid N_2 and CO under conditions in which vibrational structure should be resolvable. No such structure was resolved. The difference in 4σ-linewidths between N_2 and CO (≈0.15 eV) may be attributable to multi-phonon excitation via a hole–dipole interaction. Several potential sources of the remaining linewidth (≈0.6 eV) are discussed (lifetime broadening, steric inhomogeneities, patch fields, etc.).

Photoemission from what is believed to be the a $^3\Pi$ excited state of CO has been detected in solid CO for the first time. The difference in the excitation energy compared to the gas phase [7.4 eV (solid) versus 6 eV (gas)] is probably due to bonding interactions or charge effects in the solid rather than extra-atomic relaxation effects.

Acknowledgement

The authors wish to thank J.W. Goodale for invaluable technical assistance and R.D. McAlpine for helpful discussions.

References

[1] J.W. Gadzuk, Phys. Rev. B 14 (1976) 5458.
[2] J.W. Gadzuk and M. Šunjić, Phys. Rev. B12 (1975) 524.
[3] J.W. Gadzuk, in: Electronic Structure and Reactivity of Metal Surfaces, NATO Advanced Study Institute Series (Plenum Press, New York, 1976);
E.W. Plummer, in: Interactions on metal surfaces, ed. R. Gomer (Springer, Berlin, 1975).
[4] L.S. Cederbaum, W. Domcke, W. von Niessen and W. Brenig, Z. Physik B 21 (1975) 381;
P.R. Norton and P.J. Richards, Surface Sci. 49 (1975) 567.
[5] F.-J. Himpsel, N. Schwentner and E.E. Koch, Phys. Stat. Sol. 71b (1975) 615.
[6] P.R. Norton and R.L. Tapping, Surface Sci., to be published.
[7] P.R. Norton, Surface Sci. 47 (1975) 98.
[8] C.J. Powell, Surface Sci. 44 (1974) 29.
[9] J.L. Franklin, J.G. Dillard, H.M. Rosenstock, J.T. Herron, K. Draxl and F.H. Field, Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Ions, NSRDS-NBS 26 (US Govt. Printing Office, Washington, 1969).
[10] P.R. Norton and P.J. Richards, Chem. Phys. Letters 38 (1976) 95.
[11] J.W. Rabalais, T.P. Debies, J.L. Berkosky, J.-T.J. Huang and F.O. Ellison, J. Chem. Phys. 61 (1974) 516.
[12] J.A.D. Matthew and Y. Komninos, Surface Sci. 53 (1975) 716.
[13] P.H. Krupenie, The Band Spectrum of Carbon Monoxide, NSRDS-NBS 5 (US Govt. Printing Office, Washington, 1966).
[14] R.M. Hexter, J. Chem. Phys. 46 (1967) 2300.
[15] T.C. James, J. Chem. Phys. 55 (1971) 4118.
[16] G.M. Lawrence, Chem. Phys. Letters 9 (1971) 575.
[17] T.S. Wauchop and H.P. Broida, J. Chem. Phys. 56 (1972) 330.
[18] F.P. Netzer, R.A. Willie and J.A.D. Matthew, Solid State Commun. 21 (1977) 97.