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Title
STRUCTURAL DETERMINATION OF MOLECULAR OVERLAYER SYSTEMS WITH NORMAL PHOTOELECTRON DIFFRACTION: c(2x2)CO-Ni(001) AND (/3 x /3)R30| Co-Ni(111)

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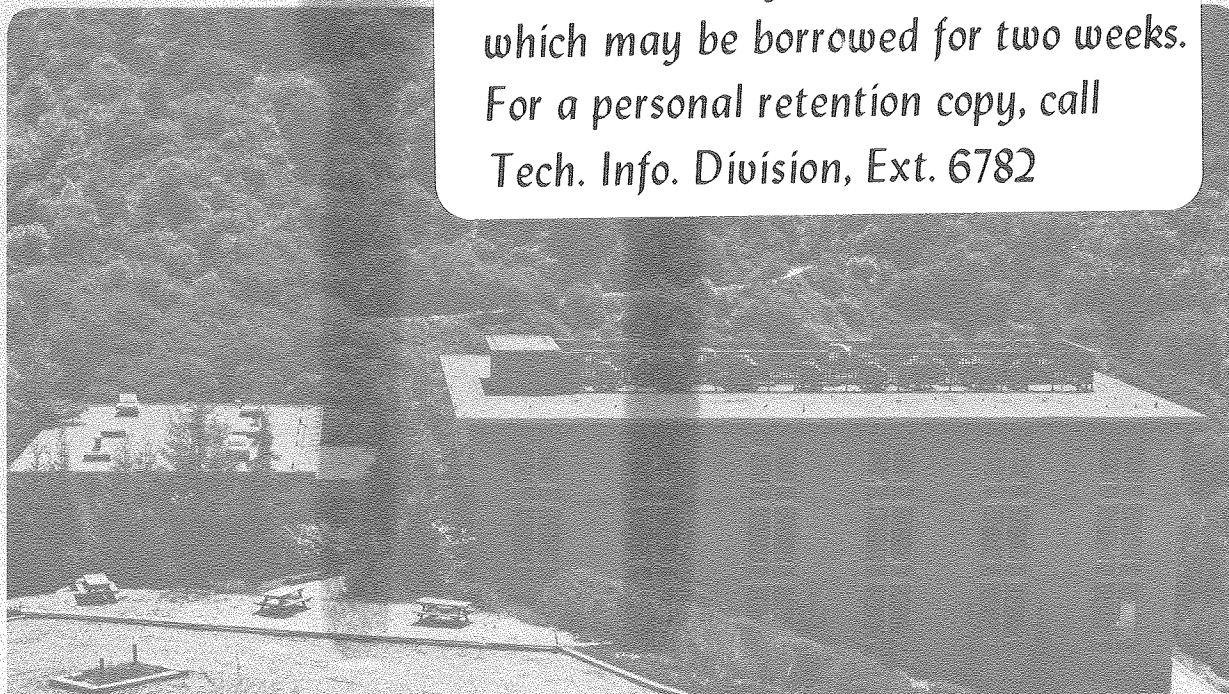## UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

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c(2x2)CO-Ni(001) and ($\sqrt{3}$ x $\sqrt{3}$)R30° CO-Ni(111)

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ABSTRACT

Experimental and theoretical normal photoelectron diffraction

(NPD) studies of CO adsorbed on Ni are presented. It is shown for the

first time that NPD can yield definitive structure determinations in

molecular adsorbate systems. The linear-bonded atop geometry of

c(2x2)CO-Ni(001) is confirmed, while CO is found to occupy the twofold

bridge site in ($\sqrt{3}$ x $\sqrt{3}$)R30° CO-Ni(111).

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The determination of molecular adsorbate bonding geometry is of major importance in surface science, but few structures are known to date. One popular experimental strategy combines photoemission, to establish the molecular species and orientation, with low energy electron diffraction (LEED), for subsequent, quantitative structure studies. Recently it has been shown that normal photoelectron diffraction (NPD) alone is sufficient for structure determination in atomic overlayer systems.[1,2] In this Letter we report the first experimental evidence, for CO on two faces of nickel, that NPD can be used to determine molecular adsorbate structure. We chose to study c(2x2)CO-Ni(001) because it has become a model molecular adsorption system and because LEED structure analysis has been difficult and the subject of controversy prior to the recent establishment of a generally accepted result.[3] In addition, we report the first accurate structure determination for the $(\sqrt{3} \times \sqrt{3})$R30° CO-Ni(111) system, for which no LEED data presently exist. An NPD structural study has certain advantages relative to LEED. Radiation damage is minimal, long-range order is unnecessary, and the localized nature and phase coherence of NPD permits an independent structural determination for each atomic species in the molecule.

Experiments were performed on Beam Line I-1 at the Stanford Synchrotron Radiation Laboratory (SSRL) with an apparatus described elsewhere.[4] By using a grazing-incidence "grasshopper" monochromator equipped with a 1200 ℓ/mm holographic grating during dedicated operation, we obtained photon flux and resolution sufficient to perform

NPD experiments on both the C(1s) and O(1s) adsorbate core levels in the photon energy range $300 \leqslant h\nu \leqslant 650$ eV. These experiments, together with our recent C(1s) shape resonance measurements,[5] are the first systematic ARP studies of these light-element core levels with intermediate energy x-rays.

Clean and CO-covered nickel crystals were prepared and characterized using standard procedures.[5] LEED was not performed on the overlayer systems prior to NPD measurements, to avoid the usual primary beam damage.[3] No time-dependent degradation of the overlayers (as determined by photoemission) was apparent over several hours of NPD experimentation. In addition, LEED measurements after the NPD studies confirmed the surface phases. This is a significant advantage of NPD in the study of molecular overlayers. Our $(\sqrt{3} \times \sqrt{3})R30°$ CO-Ni(111) sample yielded the very faint and diffuse LEED superstructure spots reported in the past for this system,[6] which have discouraged accurate LEED structure studies. However, NPD has been shown to be relatively insensitive to the degree of overlayer lateral order,[1] thus motivating its application to CO-Ni(111).

The NPD calculations were performed using a multiple scattering algorithm detailed elsewhere.[7,8] All orders of multiple scattering were included. Carbon and oxygen phase shifts were generated using the Xα scattered-wave technique,[7] while those of nickel were derived from the Wakoh self-consistent band structure potential.[9] The inner potentials (V_0) used were 11.2 and 10.5 eV for Ni(001) and Ni(111), respectively. The calculations were done for CO with the generally accepted orientation[5] (bond axis normal to the surface, with the carbon

end down), in the top, bridge, and hollow sites, allowing the C-Ni inter-

planar distance ($d_{CNi}^{\perp}$) and the CO bond distance ($d_{CO}^{\perp}$) to vary in steps

of 0.1 Å in a systematic search for the best fit to the experimental curves.

From the systematics of these calculations for the C(1s) level in

the CO-Ni(001) prototype system, we can draw important conclusions

about the NPD process in molecular adsorbates. The theoretical results

indicate[8] that if $d_{CO}^{\perp}$ is held constant and $d_{CNi}^{\perp}$ varied in successive

calculations, the characteristic C(1s) NPD modulation peak energy positions

are shifted to higher kinetic energy as $d_{CNi}^{\perp}$ is decreased, in agreement

with the trend observed in earlier NPD studies of atomic overlayer

systems.[1] In contrast, the peak positions do not disperse with $d_{CO}^{\perp}$

in calculations where $d_{CNi}^{\perp}$ is held constant. These observations imply

that the C(1s) experimental NPD curve should be extremely sensitive to

$d_{CNi}^{\perp}$, but not to $d_{CO}^{\perp}$. This may be understood in terms of the localized

nature of the NPD process. For the C(1s) NPD curve to yield structural

sensitivity to $d_{CO}^{\perp}$, the electron would have to undergo at least one

scattering event off the oxygen atom. But the dominant scattering from

oxygen is a small angle forward scattering, and the phase difference

between the scattered wave and the direct wave is essentially independent

of the position of the oxygen atom, yielding little sensitivity to $d_{CO}^{\perp}$.[8]

The situation is manifestly different for large-angle backscattering off

nickel, which provides the sensitivity to $d_{CNi}^{\perp}$. Here, the backscattered

wave accumulates phase in twice traversing the distance between absorbing

and scattering atoms, so that substantial structural sensitivity is

expected and observed.

The experimental NPD curve for the C(1s) level, shown in the inset in Fig. 1 illustrates the above expectations. It represents the combined results of several experiments on different overlayer preparations and nickel crystals. Individually, peak positions were reproducible to $\pm$ 1-2 eV from one experimental curve to another. As shown in the inset, the match between experimental and theoretical peak positions for $d_{CNi}^{\perp}$ = 1.8 Å and $d_{CO}^{\perp}$ = 1.13 Å in the atop geometry is excellent; peaks (1,2,3,4) fall at energies (85,105,126,154) and (88,106,127,154) eV kinetic energy in theory and experiment, respectively. The quality of the experiment-theory fit can be examined quantitatively by observing the trend in $\Delta E = E$ (theo) $- E$ (expt) for each of the four NPD peaks, as $d_{CNi}^{\perp}$ is varied. These trends are summarized in Fig. 1. The criterion for a perfect match between theory and experiment, $\Delta E = 0$ for each NPD peak, is most nearly met by the $d_{CNi}^{\perp}$ = 1.8 Å calculation. The systematic behavior shown in Fig. 1 simplifies the assessment of error limits for $d_{CNi}^{\perp}$. On the low side, which is more important for this case, the 1.7 Å curve is far outside the acceptable range. We adopt a very conservative lower limit of $d_{CNi}^{\perp}$ = 1.76 Å. On the high side, the longer distances shown are not credible for a C-Ni bond, on chemical grounds. However, even the 1.9 Å curve is off by several standard deviations. To raise it would require shifting the inner potential by $\sim$ 5 eV, from 11.2 eV to $\sim$ 6 eV, which is physically unacceptable. Our final adopted value is $d_{CNi}^{\perp}$ = 1.80 $\pm$ 0.04 Å, with CO in the atop site.

From the above discussion it is clear that the O(1s) NPD curve

must be measured to determine $d_{CO}^\perp$ from NPD alone. Theoretical and experimental results are summarized in Fig. 2. We were able to collect data over only the limited kinetic energy range $0 \le E_k \le 100$ eV because of poor photon flux and resolution above 400 eV. In general, measurement of C(1s) and O(1s) NPD intensities near E_k = 61 eV was hampered by interference from the $Ni(M_{23},V,V)$ Auger peak[1] (see e.g., dashed portion of experimental curve in Fig. 2b). The theoretical curves (Fig. 2a) for fixed $d_{CNi}^\perp$ and various CO illustrate that NPD structural results are less accurate in this lower energy range because modulation peak position dispersion with $d^\perp$ is lower, and additionally, the theoretical NPD curve shape is more model-dependent for $E_k \le 60$ eV.[1,8] In spite of these limitations, a good fit of peak positions for $d_{CNi}^\perp$ = 1.8 Å and $d_{CO}^\perp$ = 1.13 Å is shown in Fig. 2b. It is encouraging that the fit improves at higher energies. The NPD data show an excellent fit for the isolated molecule bond distance $d_{CO}^\perp$ = 1.13 Å, consistent with the LEED result of $d_{CO}^\perp$ = 1.1 Å,[3] but an O(1s) study over a wider kinetic energy range is desirable.

Fig. 3 summarizes the extension of these CO-Ni studies to $(\sqrt{3} \times \sqrt{3})R30°$ CO-Ni(111). The C(1s) NPD results shown in Fig. 3 confirm previous indications[6] that the CO adsorbate molecule is bonded in the two-fold bridge position on Ni(111). Aside from the region near E_k = 90 eV, an excellent fit is obtained for $d_{CNi}^\perp$ = 1.27 ± 0.05 Å in the bridge-bonded site, while poor fits are obtained for other values of $d_{CNi}^\perp$ and other sites. Limited-energy-range O(1s) results are also shown in Fig. 3. As with CO-Ni(001), the isolated molecule value of $d_{CO}^\perp$ = 1.13 Å gives the best agreement with theory. Again, because of the poor quality of the superstructure spots, a precise LEED analysis would have been impossible.

In conclusion, using normal photoelectron diffraction, the top-bonded

CO structure for c(2x2)CO-Ni(001) has been found, confirming recent detailed LEED investigations,[3] while the adsorbate is determined to occupy the two-fold bridge site in $(\sqrt{3} \times \sqrt{3})$R30° CO-Ni(111). Based on these observations and considerations discussed above, NPD shows promise for determining bonding geometries of molecular adsorbates, as a complementary or alternative method to LEED.
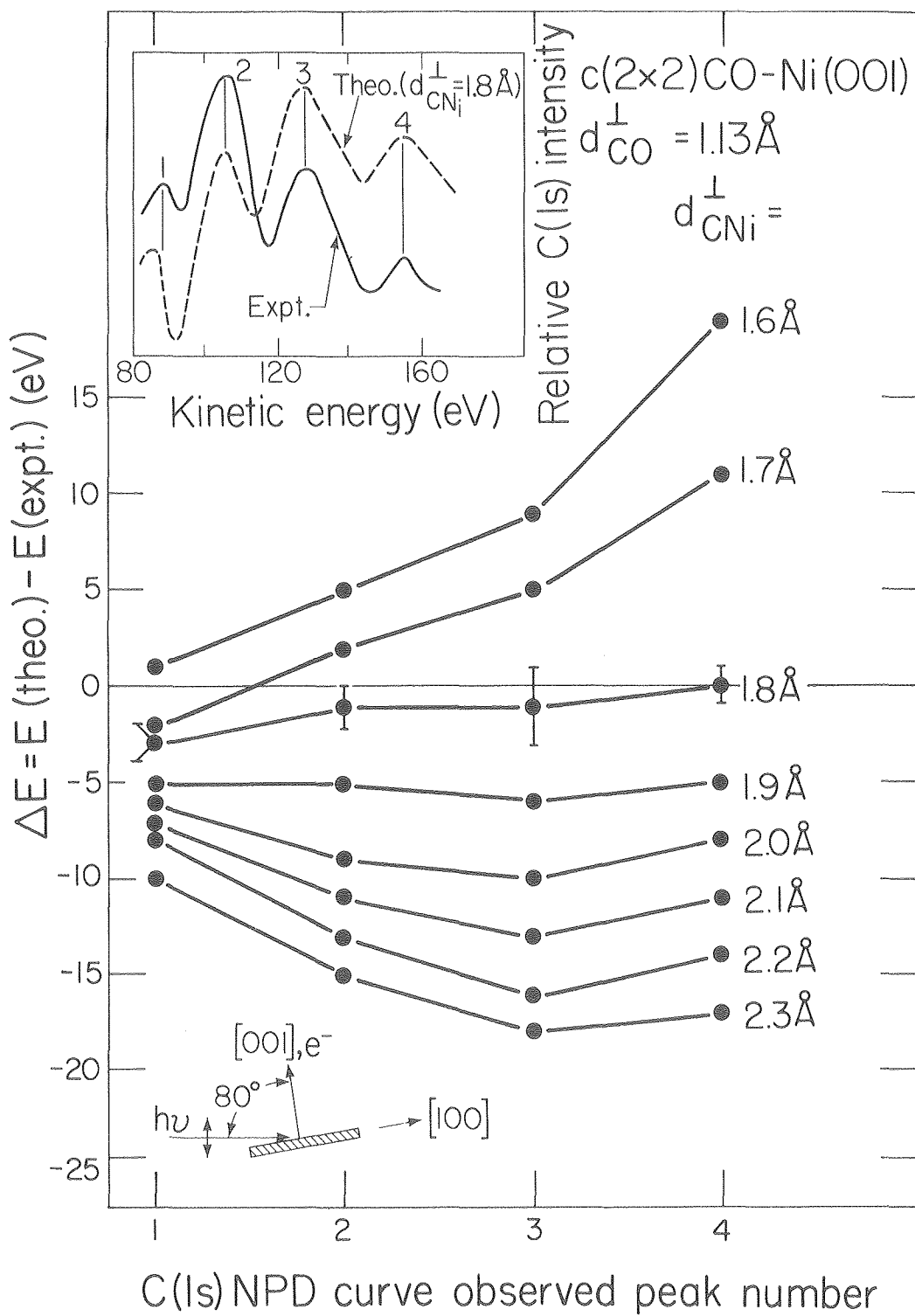
Acknowledgements

References

1. D.H. Rosenblatt, J.G. Tobin, M.G. Mason, R.F. Davis, S.D. Kevan, D.A. Shirley, C.H. Li, and S.Y. Tong, Phys. Rev. B $\underline{23}$, (in press); and references therein.

2. C.H. Li and S.Y. Tong, Phys. Rev. Lett. $\underline{42}$, 901 (1979).

3. S. Andersson and J.B. Pendry, Surf. Sci. $\underline{71}$, 75 (1978); Phys. Rev. Lett. $\underline{43}$, 363 (1979); and M. Passler, A. Ignatiev, F. Jona, D.W. Jepsen, and P.M. Marcus, Phys. Rev. Lett. $\underline{43}$, 360 (1979).

4. S.D. Kevan and D.A. Shirley, Phys. Rev. B $\underline{22}$, 542 (1980).

5. R.F. Davis, S.D. Kevan, D.H. Rosenblatt, M.G. Mason, J.G. Tobin, and D.A. Shirley, Phys. Rev. Lett. $\underline{45}$, 1877 (1980); and references therein.

6. J.C. Compuzano and R.G. Greenler, J. Vac. Sci. Technol. $\underline{16}$, 445 (1979); W. Erley, H. Wagner, and H. Ibach, Surf. Sci. $\underline{80}$, 612 (1979); and references therein.

7. C.H. Li, A.R. Lubinsky, and S.Y. Tong, Phys. Rev. B $\underline{17}$, 3128 (1978).

8. C.H. Li and S.Y. Tong, Phys. Rev. Lett. $\underline{43}$, 526 (1979).

9. S. Wakoh, J. Phys. Soc. Jpn. $\underline{20}$, 1896 (1965).

Figure Captions

Figure 1.   Plot of $\Delta E = E(\text{theory}) - E(\text{experiment})$ versus NPD curve peak

number for the C(1s) level in c(2x2) CO-Ni(001) with fixed

CO bond length and various carbon-nickel spacings, with CO

in the atop site. A comparison of calculated ($d^{\perp}_{CNi}$ = 1.8 Å,

$d^{\perp}_{CO}$ = 1.13 Å) and experimental NPD curves is shown in the

inset.

Figure 2.   a) Calculated NPD curves for the 0(1s) level in c(2x2)

CO-Ni(001) for fixed carbon-nickel spacing and various CO

bond lengths.

b) Comparison of the experimental result to the best-fit

calculation from (a). The dashed portion of the experimental

curve suffers from $Ni(M_{23},V,V)$ Auger interference.

Figure 3.   Comparison of the best-fit calculation to experiment for both

C(1s) and 0(1s) levels in ($\sqrt{3}$ x $\sqrt{3}$)R30° CO-Ni(111). The

calculations are for CO in the two-fold bridge site.
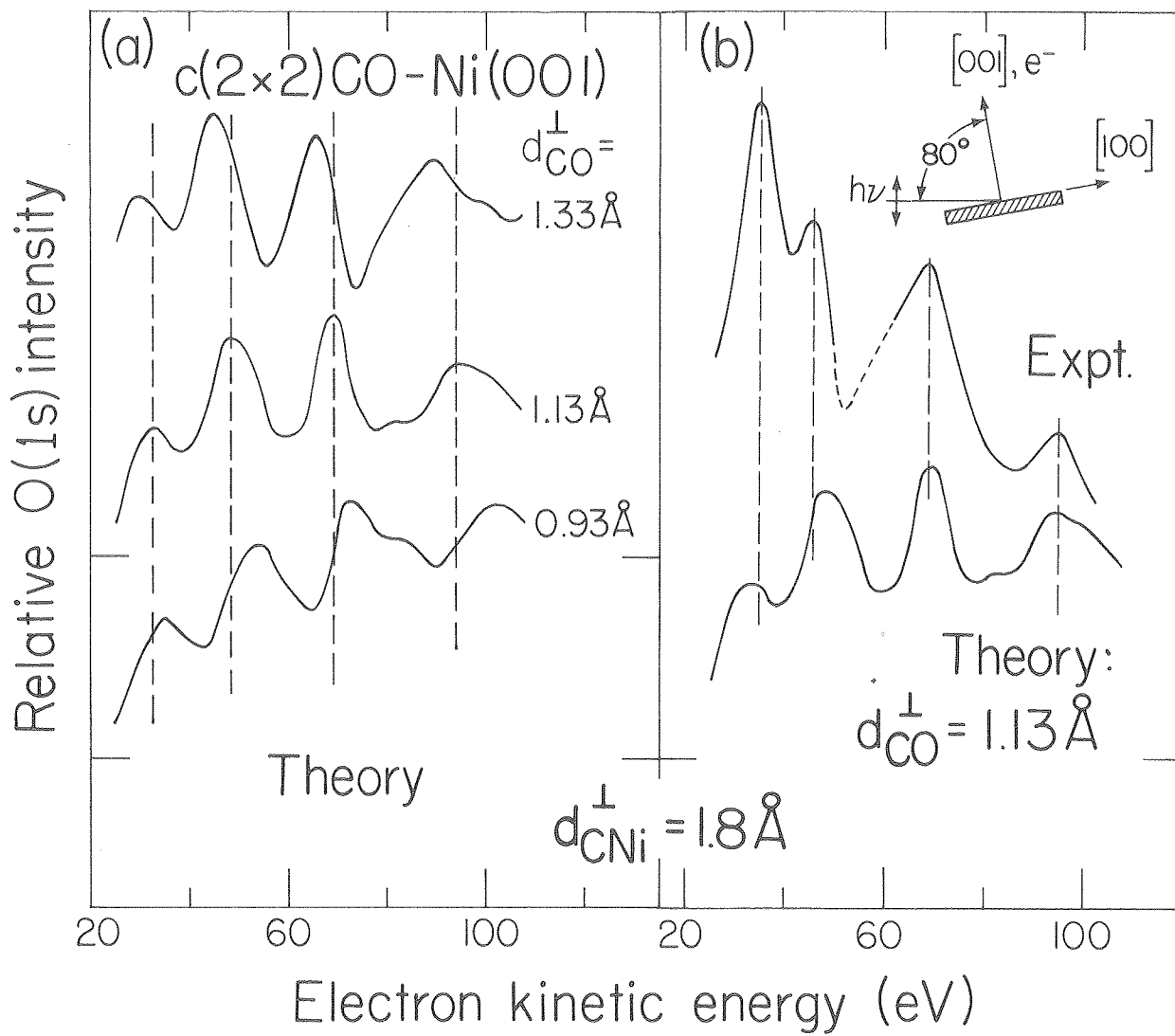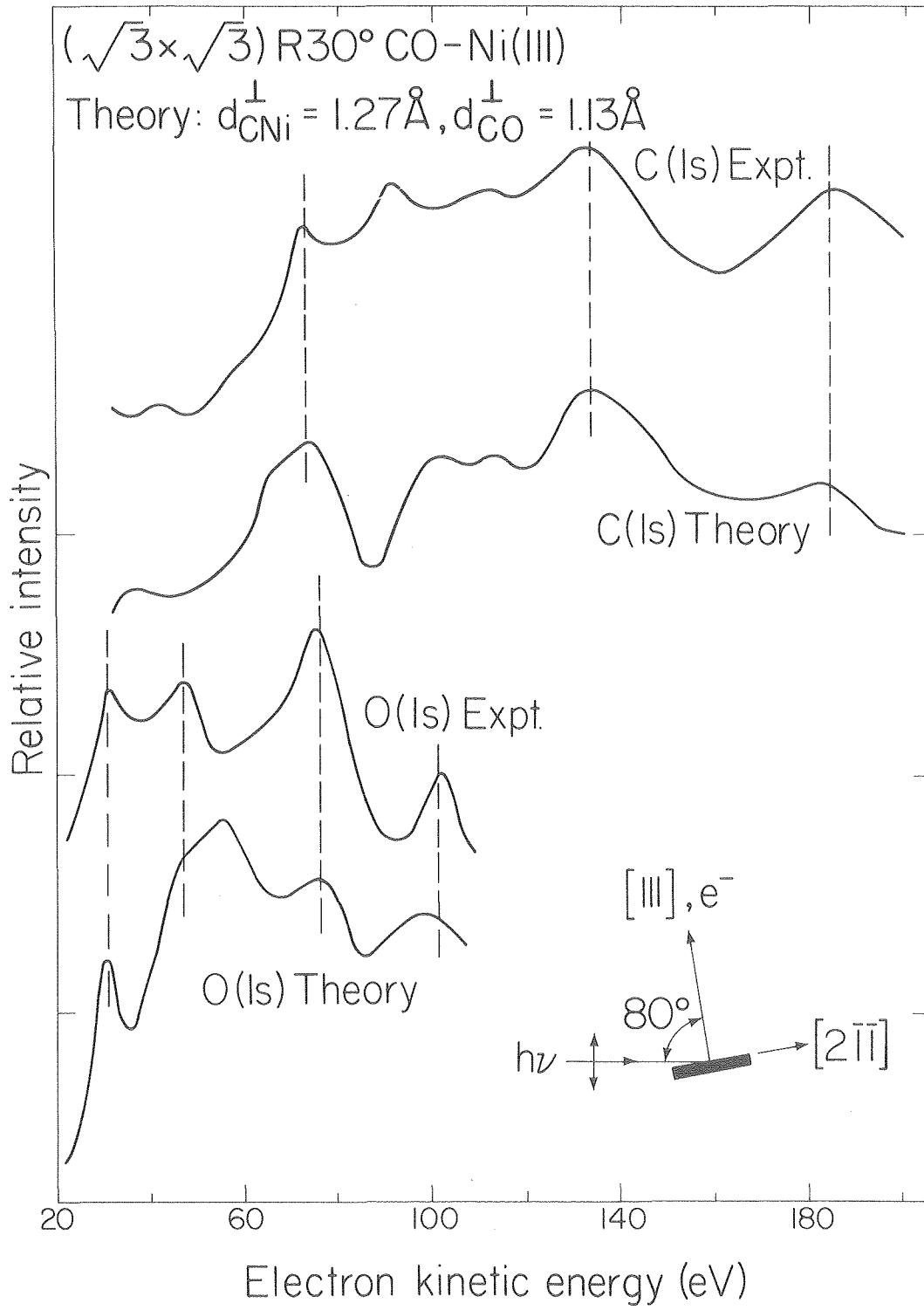
Figure 1.

XBL 8012-2435

Figure 2.

XBL 8012-2436

$(\sqrt{3} \times \sqrt{3})\,R30°\,CO\text{--}Ni(III)$

Theory: $d^{\perp}_{CNi} = 1.27\text{Å}, d^{\perp}_{CO} = 1.13\text{Å}$

C(Is) Expt.

C(Is) Theory

O(Is) Expt.

O(Is) Theory

Relative intensity

$[III],e^-$

$80°$

$h\nu$

$[2\bar{1}\bar{1}]$

20   60   100   140   180

Electron kinetic energy (eV)

XBL 8012–2437

Figure 3.