

## **FLUORESCENCE YIELD NEAR EDGE SPECTROSCOPY OF $\pi$ -BONDED CO ON Fe(100)**

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Received 28 March 1989; accepted for publication 30 June 1989

Near edge X-ray absorption fine structure (NEXAFS) spectra of CO adsorbed on the Fe(100) surface are reported. Spectra, obtained by fluorescence yield (FYNES), are presented for each of the four individual CO adsorption configurations observed on this surface. The  $\pi$ -bonded state exhibits an unusual FYNES spectrum and polarization dependence which indicates that the molecule is either extensively rehybridized or tilted with respect to the surface normal. The FYNES spectra of each of the adsorption states directly reflect the perturbation of the carbon–oxygen bond by the surface and track systematically with the heat of adsorption.

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## 1. Introduction

The adsorption and dissociation of CO on Fe(100) is of particular interest due to the isolation of a precursor state to CO dissociation [1]. A rich history of experimental work has resulted in a gradual evolution of our understanding of the adsorption/dissociation process on this surface. Early photoemission studies focused on the issue of whether CO adsorption was molecular or dissociative [2–4]. Later studies showed that the adsorption process is complex with at least three different molecular adsorption states coexisting on the surface at cryogenic temperatures. Dissociation occurs from a single molecular state at approximately 440 K [5,6]. This precursor state to dissociation is the first to fill and saturate, at adsorption temperatures below 300 K, with the other two molecular states filling sequentially. A surface which contains only the precursor state can be prepared by carefully controlling the CO dose or by annealing a CO saturated surface at 350 K. One engaging aspect of this precursor state is its unusually low carbon–oxygen stretching frequency ( $1200\text{ cm}^{-1}$ ) as determined by EELS [7,8] and the large apparent tilt of the molecular axis with respect to the surface normal as determined NEXAFS [9]. These results coupled with subsequent UPS measurements [6,10] has lead to the speculation that the CO molecule is  $\pi$ -bonded to the surface in a fashion similar to various organometallic carbonyl clusters [11].

A detailed orbital description of the  $\pi$ -bonded state is not available but there has been theoretical justification for parallel bonding of CO to the Fe(100) surface [12]. However, there is not good agreement between the orbital energies predicted by the theoretical study and the binding energies of bonding orbitals as measured by UPS.

In this study we continue to examine the chemical nature of the  $\pi$ -bonded state (we use the labels  $\pi$ -bonded, precursor and  $\alpha_3$ -CO interchangeably in this paper to describe CO bound to the surface in the pre-dissociated form) and report near-edge X-ray absorption spectra obtained via fluorescence yield measurements (fluorescence yield near-edge spectroscopy FYNES). These data were collected to complement previously collected NEXAFS data obtained by electron yield [9]. The earlier NEXAFS data were limited to only the CO saturated surface (mixed molecular adsorption states) and the  $\pi$ -bonded state. Here we present FYNES spectra for the CO/Fe(100) system as a function of various thermal treatments which allow us to extract the near-edge spectra of each of the individual adsorption states on the surface. We were able to extract these data, in part, due to the superior signal to background of the fluorescence yield technique [13].

## 2. Experimental

Tunable radiation in the 275–350 eV range was supplied by the extended range grasshopper monochromator (ERG) on the U1 beamline at the National

Synchrotron Light Source, Brookhaven National Laboratory. The data were collected in a specialized UHV system designed to perform in-situ FYNES measurements in gaseous environments relevant to heterogeneous catalysis. This UHV system and the method of fluorescence detection has been described in detail elsewhere [14,15]. The Fe(100) crystal was mounted such that the electric field vector of the light could be rotated in the plane defined by the surface normal and the [110] direction. Unfortunately, the manipulator was not capable of azimuthal rotation.

The sample was cooled by LN<sub>2</sub>, heated resistively and the temperature monitored by a type K thermocouple spot-welded to the back edge of the crystal. The temperature was accurately controlled by a programmer in the range 100–1000 K. Sample cleaning procedures were the standard heating and sputtering cycles used to clean iron [1]. Sample cleanliness was verified by AES and temperature programmed CO desorption (CO TPD is extremely sensitive to surface impurities).

Since the collection of the FYNES data required an average of 20 min of data acquisition for each spectrum and since each experiment consisted of five such spectra, concern was raised as to the stability of the surface under the prolonged exposure to the synchrotron radiation. However, we were able to verify the stability of the surface by periodically performing a TPD experiment on an irradiated surface. There was no evidence of radiation damage (such as premature dissociation) observed in these experiments. We are confident that the prolonged data acquisition time did not influence the results of this study.

### 3. Results

The temperature programmed desorption of CO from the Fe(100) surface is shown in fig. 1. Four major desorption features are evident. The three features labeled  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  are due to desorption of CO bound in molecular adsorption states, i.e. the carbon–oxygen bonds remain intact upon adsorption. The  $\beta$  peak (800 K) is due to the second-order recombination of adsorbed atomic carbon and oxygen (dissociated CO). These assignments have been verified by XPS, UPS [6], and EELS investigations [1]. The peak labeled  $\alpha_3$  is the desorption feature associated with the  $\pi$ -bonded CO state.

The three molecular states are sequentially filled in the order of decreasing heat of adsorption and coexist on the surface at temperatures below 240 K [1,6]. The molecular states are sequentially desorbed in the reverse order during the TPD experiment. Heating the CO saturated surface to 240 K removes the  $\alpha_1$  and heating to 350 K removes the  $\alpha_2$  state. Heating the sample above 440 K results in a partial decomposition of the  $\pi$ -bonded  $\alpha_3$  state as well as some desorption. The partitioning of the desorption versus dissociation channel has been discussed elsewhere [6]. A key feature of the desorption

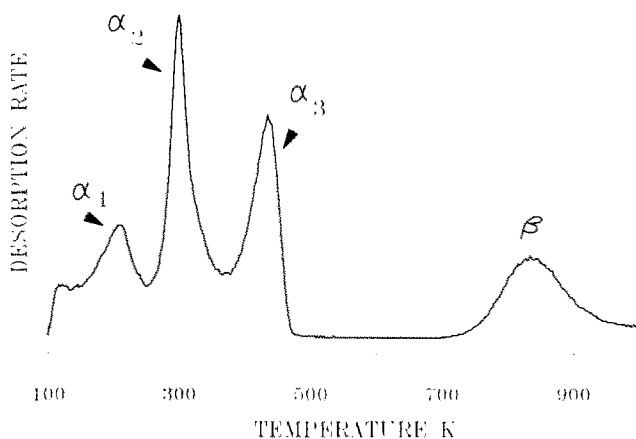


Fig. 1. Temperature programmed desorption spectrum of CO from a CO saturated Fe(100) surface. Heating ramp was 10 K/s and the adsorption temperature was 83 K.

experiment is that no  $\beta$ -CO exits on the surface prior to the CO  $\alpha_3$  desorption event. It is possible, to produce surfaces of mixed or pure CO adsorption states from the saturated surface by annealing at the correct temperature. For example, annealing a CO saturated surface at 350 K leads to a surface that contains only molecules bound in the  $\pi$ -bonded state.

The issue of surface coverage should be mentioned at this time. The CO saturated surface coverage is  $1.2 \times 10^{15}$  molecules/cm<sup>2</sup>, one molecule per surface site ( $\theta_{\text{CO}} = 1$ ). The sum of the  $\alpha_1$  and  $\alpha_2$  states is half a monolayer and the  $\alpha_3$  state also occupies half a monolayer. The partitioning that occurs during the decomposition of the  $\alpha_3$  state results in a quarter of a monolayer of  $\beta$ -CO ( $\theta_{\beta} = 0.25$ ,  $\theta_{\alpha_3} = 0.25$ ). Both the  $\alpha_3$  and  $\beta$ -CO states form well defined  $c(2 \times 2)$  surface structures. The partitioning of the desorption versus decomposition channel appears to be the result of competition for the four-fold hollow sites on the surface [6].

Carbon edge FYNES data were obtained for CO adsorbed on the Fe(100) surface as a function of decreasing surface coverage in a set of annealing experiments. The results are shown for one angle of incidence ( $30^\circ$ ) in fig. 2. The FYNES spectrum of the CO saturated surface, labeled 83 K in fig. 2, exhibits the characteristic  $\pi$  (288.5 eV) and  $\sigma$  (306 eV) resonances of Co adsorbed on transition metals [14]. Heating the surface to 240 K to desorb the  $\alpha_1$  adsorption state results in the spectrum labeled 240 K in fig. 2. The desorption of the  $\alpha_1$  state results in a small negative shift ( $-0.3$  eV) in the  $\pi$  resonance and a somewhat larger shift ( $-3.0$  eV) in the  $\sigma$  resonance. Heating the surface to 350 K desorbs the remaining  $\alpha_2$  state and leaves only the  $\alpha_3$  state ( $\pi$ -bonded CO) on the surface. It can be seen in fig. 2 that the FYNES

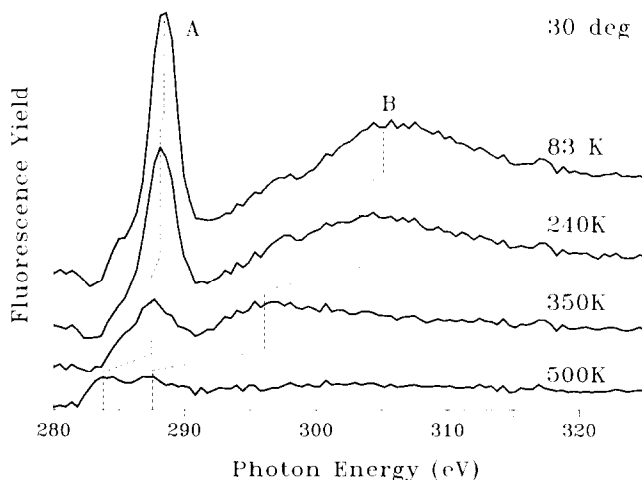


Fig. 2. FYNES spectra of the CO saturated Fe(100) surface as a function of annealing temperature. The temperature to the right of each spectrum indicates the annealing temperature. The angle of the electric field vector with respect to the surface normal was  $30^\circ$ . The A feature is the  $\pi$  resonance and the B feature is the  $\sigma$  resonance.

spectrum of  $\alpha_3$  state (labeled 350 K) is remarkably different from that of the other two molecular CO adsorption states. The  $\pi$  resonance is weak and both the  $\pi$  and  $\sigma$  resonances exhibit a negative energy shift with respect to the  $\alpha_2$  state. Heating the surface above the dissociation temperature ( $T > 440$  K) results in the FYNES spectrum labeled 500 K in fig. 2. This spectrum is basically that of adsorbed atomic carbon on the Fe(100) surface. The  $\pi$  resonance is replaced by an edge jump which appears at lower energy consistent with the large chemical shift in the C1s binding energy that is observed when CO dissociates [6].

The spectrum labeled 83 K in fig. 2 is that of a mixture of CO adsorption states. It contains signals from the  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  states whereas the spectrum labeled 240 K contains only the  $\alpha_2$  and  $\alpha_3$  states. Subtraction of the 240 K spectrum from the 83 K spectrum yields the FYNES spectrum of the  $\alpha_1$ -state and subtraction of the 350 K spectrum from the 240 K spectrum yields the spectrum of the  $\alpha_2$  state. The difference spectra obtained in this manner along the spectra of the  $\alpha_3$  and  $\beta$  (dissociated) CO states are compared in fig. 3. The general trend in the spectra is a gradual shift in the position of the  $\pi$  resonance to lower energy with a much more pronounced shift to lower energy in the position of the  $\sigma$  resonance as the heat of adsorption increases. These shifts are a direct manifestation of the magnitude of the perturbation of the carbon-oxygen bond by the surface and will be discussed in more detail later.

A major application of NEXAFS is the determination of molecular orientation of adsorbed molecules. This approach has been particularly successful in

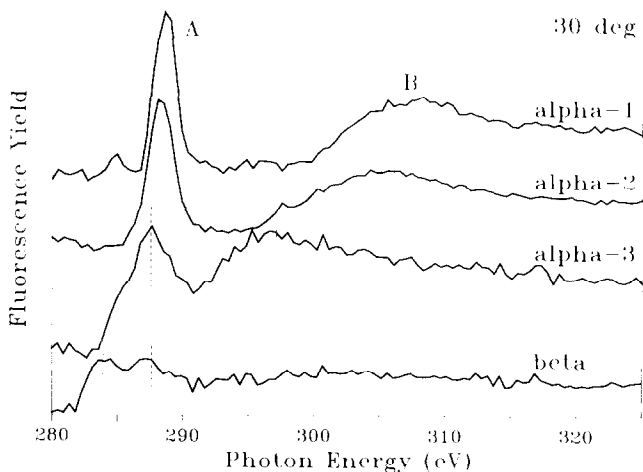


Fig. 3. FYNES spectra for the individual CO adsorption states taken with the electric field vector at  $30^\circ$  from the surface normal. The  $\alpha_1$  and  $\alpha_2$  spectra were obtained by the difference technique.

the case of CO on transition metal surfaces due to the strong polarization dependence of the X-ray absorption features. The two X-ray absorption features of adsorbed CO arise from a transition of the carbon 1s level ( $\sigma$ -symmetry) to the partially occupied  $2\pi$  and the unoccupied  $6\sigma$  orbitals of adsorbed CO [16]. The dipole selection rule predicts that the  $\alpha$  resonance will exhibit a maximum intensity when the electric field vector is perpendicular to the molecular axis, whereas the  $\sigma$ -resonance exhibits maximum intensity when the electric field vector is along the molecular axis. The experimental arrangement in the present study was such that the angle of incidence  $\theta_i$  was also the angle of the electric field vector  $\theta_E$  with respect to the surface normal. That is to say, where  $\theta_i = \theta_E = 90^\circ$ , the electric field vector is in the surface plane of the sample. In the case of CO bonded vertically with respect to the surface plane (the case for most transition metals) a maximum  $\pi$  intensity and a minimum  $\sigma$  intensity are observed at  $\theta_E = 90^\circ$ . In the opposite polarization ( $\theta_E \approx 0^\circ$ ) the  $\sigma$ -resonance should reach a maximum and the  $\pi$ -resonance should vanish.

To probe the polarization dependence of each of the adsorbed CO states on this surface, FYNES spectra were collected at two additional angles of incident radiation. The data, after normalization by the incident X-ray flux, are presented in figs. 4–7 for each of the adsorption states.

The  $\alpha_1$  and  $\alpha_2$  states, shown in figs. 4 and 5 respectively, exhibit the classic response of CO adsorbed on transition metal surfaces. The  $\pi$  resonance dominates at high angles of incidence ( $\theta_E = 90^\circ$ ) but decreases rapidly as the electric field vector moves out of the surface plane towards the surface normal.

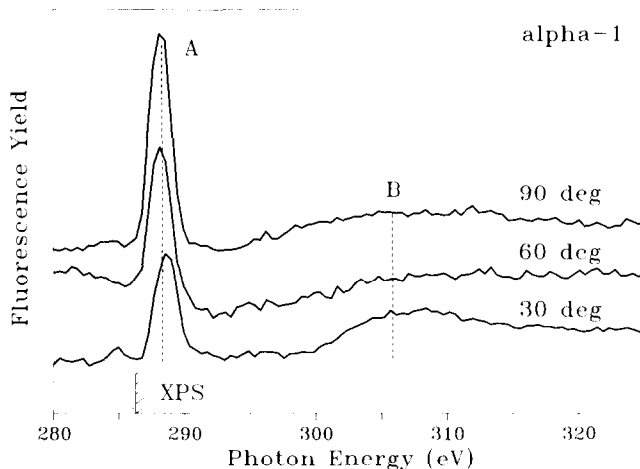


Fig. 4. FYNES spectra of the  $\alpha_1$  state as a function of the angle of the electric field vector with respect to the surface normal.

In all likelihood, this is evidence for CO adsorbed with the carbon oxygen bond basically perpendicular to the surface plane. However, data at larger number of polarization angles are necessary to quantitatively determine any small differences in tilt angle that might exist between the two states. The  $\alpha_3$  state, shown in fig. 6, exhibits virtually no polarization dependence at the angles measured. These data are consistent with earlier data [9] which were rationalized by a molecular tilt angle close to the “magic angle” ( $54.7^\circ$ ) where

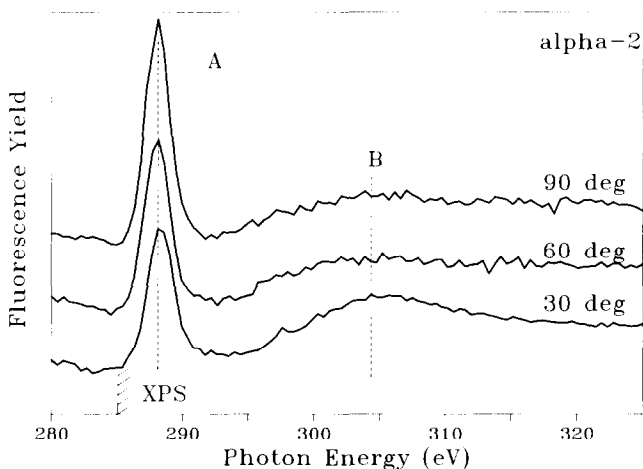


Fig. 5. FYNES spectra of the  $\alpha_2$  CO adsorption state as a function of the angle to the electric field vector with respect to the surface normal.

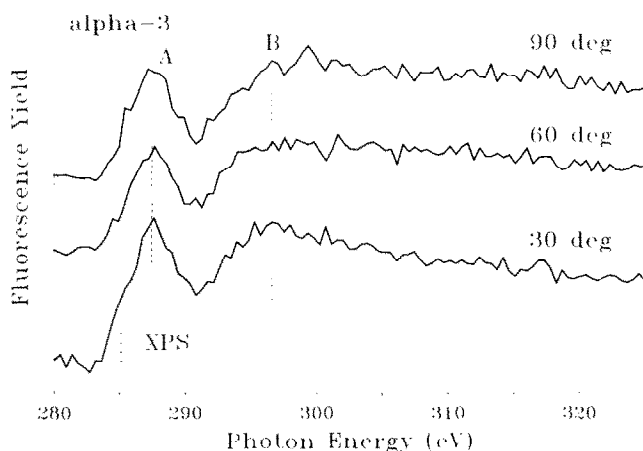


Fig. 6. FYNES spectra of the  $\alpha_3$  CO adsorption state as a function of the angle of the electric field vector with respect to the surface normal.

a lack of polarization is anticipated. However, this interpretation ignores possible rehybridization and a potential lowering of the symmetry of the parent molecular orbitals in this strongly perturbed CO adsorption state. The FYNES data obtained for the  $\beta$  state (atomic carbon) were of low intensity and consequently poorer signal to noise as shown in fig. 7. Although the signals are poor, there is a polarization dependence in the  $\beta$ -CO signal which

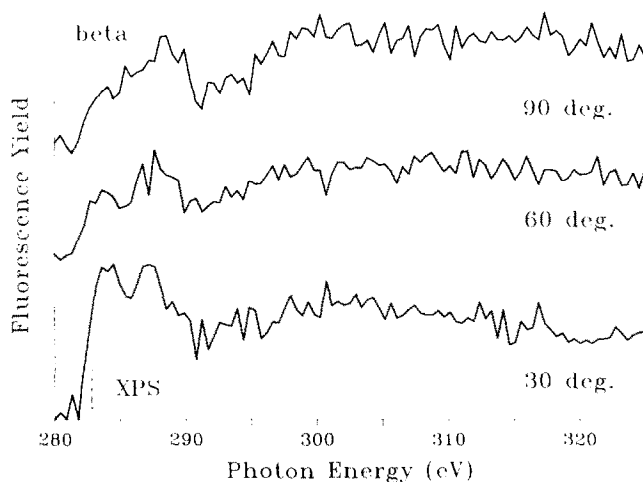


Fig. 7. FYNES spectra of the  $\beta$  adsorption state (atomic carbon) as a function of the angle of the electric field vector with respect to the surface normal.



is especially pronounced at edge. The origin of this effect is not clear but may be associated with local symmetry of the individual metal–carbon bonds in this system.

#### 4. Discussion

In this manuscript we have presented near edge X-ray absorption spectra (obtained in the FYNES mode) for each of the three adsorption states of CO on Fe(100). The two adsorption states which are occupied at temperatures below 300 K, the  $\alpha_1$  and  $\alpha_2$  states, exhibit near-edge spectra which are typical of CO chemisorbed on transition metal surfaces. A strong  $\pi$  resonance is observed when the  $E$  vector is in the surface plane which decrease in intensity as the  $E$  vector moves towards the surface normal. The  $\sigma$  resonance displays the opposite behavior with a maximum intensity observed with the  $E$  vector perpendicular to the surface plane. This type of polarization response signifies CO bound with molecular axis perpendicular to the macroscopic surface plane. These FYNES data are congruous with the normal carbon–oxygen vibrational frequencies (1950–2100  $\text{cm}^{-1}$ ) and orbital energies (UPS data) associated with these adsorption states [7,8]. However, important differences exist in the FYNES spectra of these two adsorption states which reflect the degree to which the surface perturbs carbon–oxygen bond. For example, it can be seen in fig. 3 that the  $\sigma$  resonance in the  $\alpha_2$  spectrum is 2.9 eV closer to the adsorption threshold than the  $\sigma$ -resonance in the  $\alpha_1$  state. The variation in the  $\alpha$  resonance position is known to be approximately linear with the C–O bond length [17]. Using the relationship of Sette et al.,  $\Delta\sigma = a\Delta R$ , where  $a = 32$  eV/Å,  $\Delta\sigma$  is the  $\sigma$  resonance shift and  $\Delta R$  is the bond length change. The  $\sigma$  resonance shift between the  $\alpha_1$  and  $\alpha_2$  states indicates that the C–O bonds of molecules bound in the  $\alpha_2$  state are 0.09 Å longer than those bound in the  $\alpha_1$  state. UPS spectra of these two states also exhibit different orbital energies for the  $5\sigma$  and  $1\pi$  molecular orbitals [6]. These UPS data were interpreted in terms of weakly bound, almost physisorbed,  $\alpha_1$  state with the  $\alpha_2$  state being a more conventional chemisorbed configuration. The present data supports that interpretation. A shorter C–O bond, approaching the gas phase value, is expected in the physisorbed state whereas back-bonding will weaken the C–O bond in the chemisorbed state [18].

The FYNES spectrum of the  $\alpha_3$  state is distinct from near-edge spectra of conventionally bound CO. The  $\pi$  resonance is shifted down in energy very close to the absorption threshold (fig. 3) and the  $\sigma$  intensity is extremely weak and broad in all polarizations (fig. 6). Analyzing these spectra within the framework of the unoccupied orbitals of the parent molecule yields a C–O bond length of 1.43 Å and a molecular tilt of approximately  $54.7^\circ$  (so-called “magic angle”). In this scheme, the weak  $\pi$  resonance is interpreted in terms

of extensive occupation of  $2\pi^*$  which lowers the transition probability for the X-ray absorption process. The unusually large width of  $\pi$  resonance is associated with a lifting of the degeneracy of the  $\pi$  orbitals via a direct interaction with the surface. This type of line broadening has been observed in the case of CN parallel bonded to Pd(111) [19]. In fact, a splitting of the  $\pi$  resonance of into two distinct peaks due to the interaction of the  $\pi$  orbitals with the surface (one set of  $\pi$  orbitals interacting, one set non-interacting) is reported for that case.

Although it is possible to generate this self-consistent model for the near-edge spectrum of the  $\alpha_3$  state in terms of unmodified molecular orbitals of CO, a note of caution must be raised. The UPS spectra of  $\pi$ -bonded CO on both the Fe(100) and Cr(111) surfaces clearly show that the occupied molecular orbitals of the  $\pi$ -bonded CO are extensively rehybridized with respect to conventionally bound CO. The extensive reorganization of the carbon–oxygen bond in the  $\alpha_3$  state brings into question the assignment of the “ $\pi$ ” and “ $\sigma$ ” resonances in the spectra of the  $\alpha_3$  state. The unusual position and polarization response of these features in the near-edge spectrum of the  $\alpha_3$  state may reflect a lowering of the carbon–oxygen bond order. In this case, it would not be appropriate to interpret the spectral feature in terms of  $\pi$  and  $\sigma$  resonances of CO. It is interesting in this respect that the near-edge spectrum of the  $\alpha_3$  state is reminiscent of the spectra of adsorbed methoxy [20] which contains a carbon–oxygen single bond. A lowering of the CO bond order from three to one would also explain the exceptionally low stretching frequency of the carbon–oxygen bond as well as the UPS data. Theoretical input in the form of orbital energies and symmetry assignments are required to differentiate between this two possible interpretations of the near-edge spectrum of the  $\alpha_3$  state. The exact orientation of the carbon–oxygen bond with respect to the surface, therefore, remains uncertain.

## Acknowledgements

The authors would like to thank the members of the Exxon PRT team for the use of the beamline and their help in setting up the experiment. One of us D.D. would like to acknowledge the support of the NSLS/HFBR Faculty and Student Support Program. We would also like to thank the Rolling Stones for supplying the sound track for this experiment.

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