

out CI over the complete set of 10 π orbitals, using up to doubly (SD-CI) or quadruply (SDTQ-CI) excited configurations from the ground state.¹⁷ Table I shows the results. Of particular interest is that the SD-CI $^3B_{1u}$ state has a lower energy at the ROHF geometry by 32 kcal/mol, while the 1A_g state is lower at the triplet UHF geometry by 4 kcal/mol. Using the geometries that correspond to the lowest SD-CI energies calculated for each state, we find that **4** has a singlet ground state at the SDTQ-CI/STO-3G level, with the $^3B_{1u}$ and 5A_g states 7 and 56 kcal/mol, respectively, higher in energy. The 1A_g ground state is a biradical, as shown by the major terms in its CI wave function (eq 1) and

$$\psi_{CI} = 0.697(b_{2u})^2 - 0.529(b_{3g})^2 \quad (1)$$

by the natural orbital occupancies of the frontier MO's, 1.078 and 0.922, respectively.

We then carried out SDTQ-CI/[4s,2p] calculations over the first 12 π orbitals obtained using the Dunning-Huzinaga (9s,5p)/[4s,2p] contracted Gaussian basis set,¹⁸ with the geometries that gave the lowest SDTQ-CI/STO-3G energies for the 1A_g and $^3B_{1u}$ states. At this level, the 1A_g state remains the ground state by 15 kcal/mol below the $^3B_{1u}$ state.¹⁹

Since use of proper MCSCF wave functions is not yet practically possible for so large a system as **4**, the geometries obtained from UHF and ROHF wave functions for the states are uncertain, especially for the singlet and triplet states. As a result, there is uncertainty in the singlet-triplet gap. Although the geometry for the triplet state is not optimal because of spin contamination by a higher quintet state, and consequently the energy values of the individual states might change in a calculation based on a spin-pure triplet geometry, it seems unlikely that this would result in a drastic selective stabilization of the triplet. Therefore, the calculations suggest that a singlet is either the ground state or a very low-lying excited state of **4**, in confirmation of qualitative prediction based on disjoint HMOs and in accord with the INDO/CI result.¹² This species now becomes an attractive synthetic target as an experimental test of theory.

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Supplementary Material Available: Diagram of optimized geometries for 1,2,4,5-tetramethylenebenzene (3 pages). Ordering information is given on any current masthead page.

(17) The CI calculations were carried out using the MELD package of routines developed by Professor E. R. Davidson's group.

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Observation of an Unusually Low CO Stretching Frequency on Fe(100)

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We report here our observation with high-resolution electron energy loss spectroscopy (HREELS) of an unusually low CO

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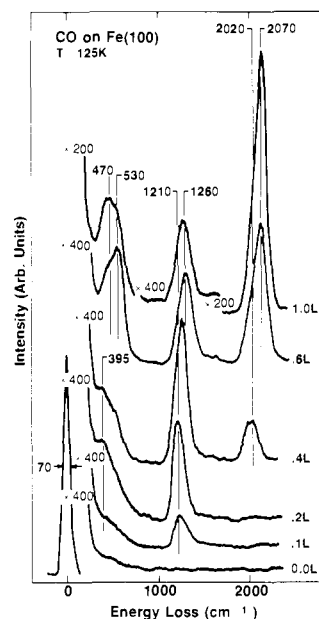


Figure 1. Vibrational spectra for CO chemisorbed on Fe(100) at 125 K for various exposures. Primary beam energy, 5.0 eV.

stretching frequency (1210 cm^{-1}) for a chemisorbed CO molecular state (α_3) on Fe(100). This chemisorbed state is the precursor state for CO dissociation. Our recent studies of CO adsorption on Fe(100) using X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD)¹ showed that CO adsorbs molecularly in three sequentially filled states ($\text{CO}(\alpha_1)$, $\text{CO}(\alpha_2)$, and $\text{CO}(\alpha_3)$), and that CO dissociation is correlated with the most tightly bound molecular state, $\text{CO}(\alpha_3)$. The stretching frequency for this $\text{CO}(\alpha_3)$ state is 1210 cm^{-1} indicating a substantially weakened C-O bond relative to the gas-phase molecule, which has a stretching frequency of 2143 cm^{-1} . Along with the very recently reported observation for CO on Cr(110)² ($1150\text{--}1330\text{ cm}^{-1}$), it is the lowest CO stretching frequency reported to date for CO adsorbed on any single-crystal metal surface.^{3,4} Since all the previously observed CO molecular states on iron surfaces have substantially higher vibrational frequencies ($1530\text{--}2070\text{ cm}^{-1}$),^{5,6} this report demonstrates a striking example of the geometric effect of the adsorption site on the CO bond weakening upon chemisorption.

The experiments reported here were performed in a stainless steel UHV system with a base pressure of 3×10^{-10} torr equipped with a 127° cylindrical sector HREELS and TPD. The same Fe(100) crystal and cleaning procedures used for our previous XPS and TPD studies¹ were used. CO TPD spectra were identical with those observed previously for the clean Fe(100) surface. HREELS spectra as a function of CO exposure are shown in Figure 1. For CO exposure up to 0.2 langmuir at 125 K, one loss peak clearly dominates at 1210 cm^{-1} . There is also a weak peak at 395 cm^{-1} . Above 0.3 langmuir CO exposure, a loss peak appears at 2020 cm^{-1} which increases in intensity with CO exposure. This second peak shifts to 2070 cm^{-1} at 1.0 langmuir CO exposure. With the appearance of the second peak at 2020 cm^{-1} , the loss peak at 1210 cm^{-1} shifts to 1260 cm^{-1} . Initially the intensity of the loss peak at 1210 cm^{-1} increases with CO exposure. However, with increasing CO exposure above 0.4 langmuir, the 1210-cm^{-1} loss peak intensity decreases as the loss peak at 2020 cm^{-1} increases in

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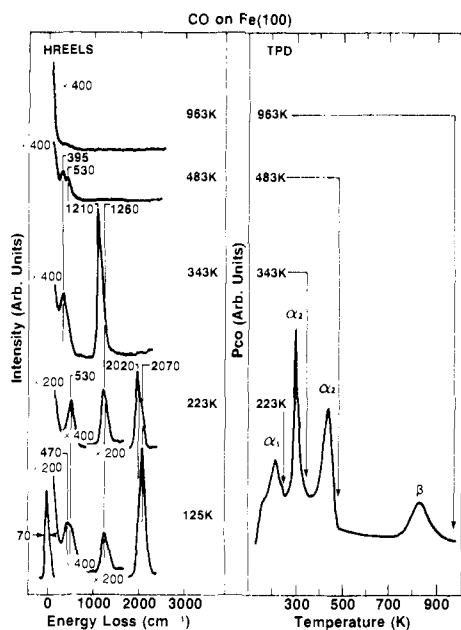


Figure 2. Set of vibrational spectra for the CO remaining adsorbed on a Fe(100) surface after partial CO desorption at the temperature indicated on the reference desorption spectrum.

intensity. With the emergence of the loss peak at 2020–2070 cm^{-1} , two loss peaks develop at 530 and 470 cm^{-1} .

The HREELS spectrum following 1.0 langmuir CO exposure at 125 K is shown in Figure 2. The HREELS spectrum taken following desorption of the $\text{CO}(\alpha_1)$ state at 223 K clearly shows a shift of the loss peak at 2070 cm^{-1} back to 2020 cm^{-1} , coupled with a decrease in the peak intensity. Following desorption of $\text{CO}(\alpha_1)$ the intensity of the loss peak at 1260 cm^{-1} increases slightly without any shift in the frequency and the 470- cm^{-1} loss peak disappears completely. Upon heating to 343 K to desorb $\text{CO}(\alpha_2)$, the 2020- and 530- cm^{-1} peaks disappear completely and the 1260- cm^{-1} peak shifts back to 1210 cm^{-1} always with a substantial increase in the intensity. After heating to 483 K, the 1210- cm^{-1} loss peak disappears and a new peak appears at 530 cm^{-1} . Flashing to 963 K removes the two loss peaks at 530 and 530 cm^{-1} .

From the above observations, it can be clearly seen that three molecular states, $\text{CO}(\alpha_3)$, $\text{CO}(\alpha_2)$, and $\text{CO}(\alpha_1)$, are filled and desorb sequentially. The CO stretching frequencies of $\text{CO}(\alpha_3)$, $\text{CO}(\alpha_2)$, and $\text{CO}(\alpha_1)$ can be assigned to be 1210, 2020, and 2070 cm^{-1} , respectively. The Fe–CO stretching frequencies can be also assigned to be 395, 530, and 470 cm^{-1} for $\text{CO}(\alpha_3)$, $\text{CO}(\alpha_2)$, and $\text{CO}(\alpha_1)$, respectively. The new loss peak at 530 cm^{-1} which appears after heating to 483 K (Figure 2) is believed to be due to the Fe–O stretching vibrations for the dissociated oxygen atoms.

In agreement with our recent XPS and TPD study,¹ adsorbed $\text{CO}(\alpha_3)$ molecules are the precursor for dissociation on Fe(100) upon heating. The unusually low CO stretching frequency of $\text{CO}(\alpha_3)$ (1210 cm^{-1}) indicates substantial C–O bond weakening and is consistent with $\text{CO}(\alpha_3)$ dissociation upon heating.

From the general correlation between the C–O stretching frequencies and adsorption sites for CO coordinated with metal surfaces and in carbonyl complexes,⁷ the 1210- cm^{-1} C–O stretching frequency must be correlated with the highest coordination site, the 4-fold site on Fe(100). This 4-fold site is the highest coordination site present on any of the low-index iron surface planes. The lowest CO stretching frequency so far observed on iron crystal surfaces is 1530 cm^{-1} on the Fe(111) surface.⁵ This frequency has been attributed to the “deep hollow” sites on Fe(111) with three coordinating surface iron atoms. Both the 3- and 4-coordinate adsorption sites are quite open, which may result in greater back-donation from the iron d orbitals into the CO $2\pi^*$ antibonding orbitals. From this point of view, the low CO stretching frequency for the $\text{CO}(\alpha_3)$ state on the 4-fold sites on Fe(100) is due to the large number of coordinated iron surface atoms available for $2\pi^*$ back-bonding. CO bond weakening may also be facilitated by the 4-fold symmetry of the Fe(100) adsorption site for $\text{CO}(\alpha_3)$. Due to the 4-fold symmetry, the overlap between the two perpendicular CO $2\pi^*$ antibonding orbitals and the d_{xz}, d_{yz} orbitals of the 4-coordinated iron atoms⁸ can be maximized. On adsorption sites with other symmetries, the overlap cannot be maximized for all the coordinated iron atoms. At this point we cannot exclude the possibility of a “tilted configuration” that would increase the overlap of the CO $2\pi^*$ orbitals and the iron d orbitals. A low 1330- cm^{-1} C–O frequency was found for a Nb cluster compound where Nb atoms were directly interacting with the π -electron system of the CO ligands.⁹ The decrease of the intensity of the $\text{CO}(\alpha_3)$ loss peak with the increase in the $\text{CO}(\alpha_2)$ and $\text{CO}(\alpha_1)$ intensity might be partly related to the reorientation of $\text{CO}(\alpha_3)$ molecules.

In conclusion, the precursor state for CO dissociation on Fe(100) has an unusually low CO stretching frequency (1210 cm^{-1}). The geometry of the precursor adsorption site, i.e., the 4-fold site on Fe(100), is suggested to be the major factor determining the unusual CO bond weakening of $\text{CO}(\alpha_3)$ on this surface through the enhanced iron–CO $2\pi^*$ back-bonding.

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