Adsorption sites and microstructures of CO_2 on Fe(111) derived from specular and off-specular HREELS

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The dependence on surface temperature and adsorbate pressure of static and time-dependent HREEL (high-resolution electron-energy-loss) spectra provides direct experimental evidence for molecular adsorption of CO_2 on Fe(111) at 100 K in one linear state and two bent states. The data demonstrate that these adsorption states can be distinguished unambiguously by their binding energies and their thermal stabilities. Comparison of HREELS data taken under specular geometry with those taken at off-specular angles allows a complete determination of the individual symmetries and microstructures of CO_2 in these states.

INTRODUCTION

The understanding of surface reactions on an atomic or molecular scale is one of the central themes in surface science. It requires, even for the reaction of a simple adsorbate system, detailed information, preferably obtained experimentally. It needs the identification of all the involved species, their stable adsorption states, their transient intermediates, and their geometric and electronic microstructures, as well as an investigation of the reaction paths between these and the determination of sticking-, desorption-, and transition-rate constants. Note that the transition between different adsorption states means a change of the chemical and electronic configuration with or without moving to different adsorption sites (i.e., on top or bridge positions). A complete picture requires, furthermore, the detection of a possible adsorbate-induced surface reconstruction, and a knowledge of the respective binding and activation energies as well as the vibrational frequencies of the involved species.

In basic research it is therefore important for an experimentalist to look for a suitable system, and for methods that provide as much as possible of the information described above with data accurately enough to derive valid adsorption models, which in turn can be used as input into corresponding theoretical considerations. These conditions are excellently matched by the system CO_2/Fe(111), as first demonstrated by the pioneering work on the interaction of CO_2 with solid state surfaces carried out by Behner and co-workers.[1,2] Moreover, the Fe(111) surface is the most reactive of the low-index iron surfaces, and therefore the most interesting surface for an understanding of the fundamental reactions that occur in catalytic processes such as, per example, Fischer-Tropsch-synthesis.[3]

Different from a previous paper on CO_2,[4] in this paper we present a determination and identification of the different adsorption states of CO_2 on Fe(111), together with an analysis of their geometries as second part of a project including kinetic aspects. Further results on different topics like binding energies and desorption-adsorption kinetics will be published in forthcoming papers.

EXPERIMENT

A. System

The experimental setup is schematically shown in Fig. 1. It was developed by our group[5,6] on account of the fact that charged particle spectrometers cannot be used under partial pressures of reactive gases above 10^{-8} mbar for more than about 20 min without a degeneration of their specifications. The system can roughly be described as a combination of a regular high-resolution electron-energy-loss spectrometer with a synchronized molecular beam source that produces adsorbate pulses (rise time $<10^{-2}$ s) or a continuous adsorbate flux with an almost rectangular intensity distribution between the sharp beam edges. At the sample, the flux can be increased to about 0.3 L/s as measured by means of a Pitot tube. This corresponds to an effective adsorbate pressure of about 3×10^{-7} mbar ($1 L \cong 10^{-6}$ mbar s) at the surface. In the continuous beam mode this flux produces a stationary background pressure below 5×10^{-10} mbar.

A specially designed sample holder allows programmable sample heating to temperatures between 100 and 800 K dur-
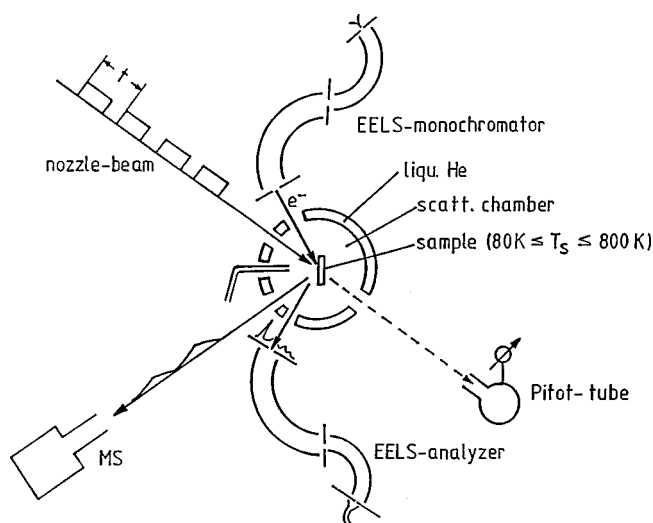

FIG. 1. Schematic diagram of the experimental setup.

ing the (high-resolution electron-energy-loss spectroscopy) (HREELS) measurements without affecting the specifications of the spectrometer by electromagnetic noise for instance. In addition, desorbing species can be measured simultaneously and in phase with the HREELS signals, with a mass spectrometer mounted in specular geometry with respect to the beam source. For the investigation of heterogeneous catalytic reactions, a second gas can be applied by means of a directed capillary doser.

B. Sample preparation

The main contaminants of the commercially available polished α-Fe(111) crystals are S, C, P, and O. Prior to UHV cleaning, the sample was therefore annealed for four weeks at 970–1120 K at 1 bar of hydrogen, ensuring that these contaminants were below our Auger detectability (0.02 ML). Subsequently, the sample was sputtered and annealed, reducing the segregation of bulk sulfur, until the sample could be heated for 30 min to 1000 K without showing contaminants in the Auger spectrum. Prior to each measurement the following cleaning procedure was applied: first, the sample was argon bombarded (150 μA s, 5 keV) and annealed to 1050 K for 10 min at 2×10^{-8} mbar of hydrogen. Subsequently the surface was saturated with ethylene at 100 K, and heated to 800 K in order to produce hydrocarbons and CO as reaction products, which desorb at this temperature. Such a complete cycle was generally sufficient to prepare the sample for a new measurement.

RESULTS AND DISCUSSION

A. Thermal stability

Figure 2 shows a series of HREEL spectra taken from a Fe(111) surface saturated with CO_2 at 100 K. Each spectrum was recorded at 100 K after annealing the sample for 3 min at the indicated temperature. Please note that all relevant losses observed in the present study are listed in Table I for reference.

Considering only the relevant peaks for the moment, we start with the discussion of the loss at 290 meV in Fig. 2(a). Since there is an almost quantitative agreement between the frequency of this loss and the stretching mode of linear CO_2 observable in gas-phase infrared spectra,[7] it is reasonable to interpret this loss also as an excitation of the stretching mode of CO_2 of a linear molecule that is almost unperturbed by the adsorption to the Fe(111) surface.

Inspection of Fig. 2(b) taken after heating to 150 K, clearly shows that the 290-meV loss and the one at about 80 meV have vanished completely, suggesting that these two losses characterize the same CO_2 state. This state will be denoted in the following as α-CO_2 or the α state.

The loss appearing in spectrum 2(b) at about 225 meV is interpreted as the excitation of a stretching mode of CO,[8] and indicates a catalytic dissociation of CO_2 into O and CO already below 150 K. At 300 K the surface is free of CO_2 and contains only CO and probably O and C.

The disappearance of the CO loss at 225 meV, and the strong increase of the loss around 50 meV in Fig. 2(e) taken
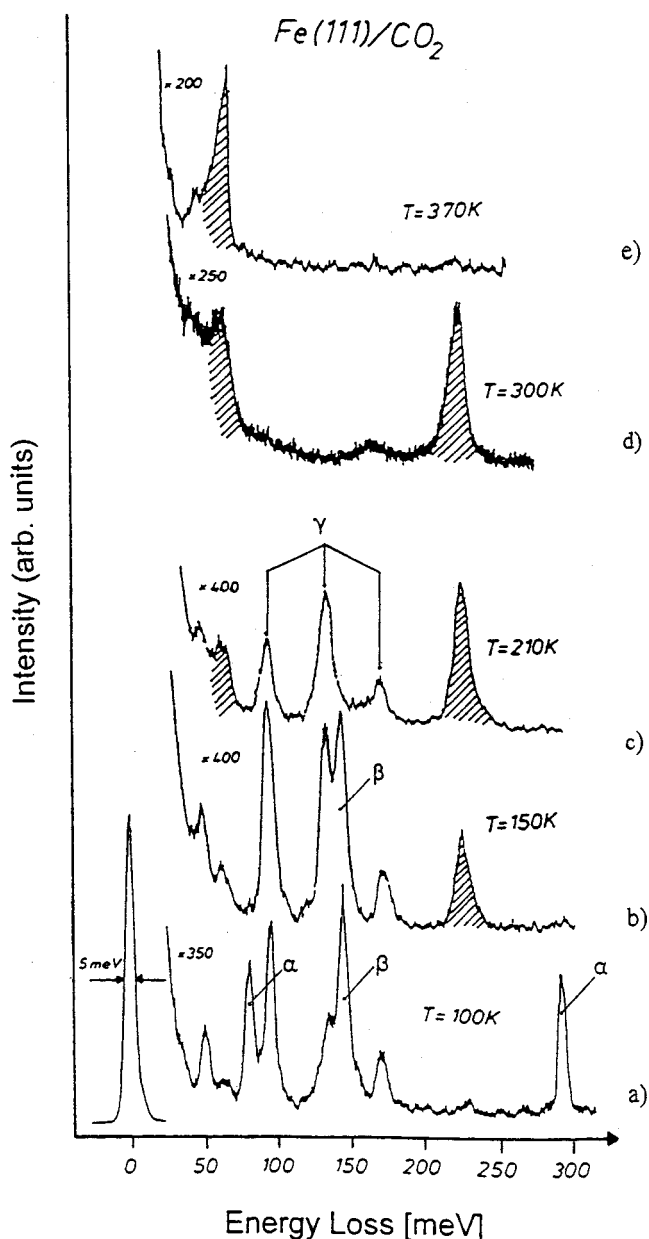

FIG. 2. Series of HREEL spectra taken at 100 K after annealing the sample at the indicated temperature for 3 min. The dashed peaks indicate the presence of CO and/or O on the surface.

at 370 K, indicates that at this temperature also CO is dissociated completely, so that finally the surface contains only iron oxide and iron carbide species. The validity of this interpretation will be demonstrated below by spectra taken after exposing the clean surface directly to CO and O_2.

A comparison of Fig. 2(b) (150 K) with Fig. 2(c) (210 K) leads to the following conclusions: since the loss at 145 meV disappears upon annealing to 210 K, it is characteristic of a further CO_2 state, which will be called the β state. It is obviously more stable than the one associated with the 290-meV loss, but not as stable as a third state, the γ state, characterized by the three losses at 170, 133, and 95 meV, which are visible up to 210 K.

Additional information on the dissociation process is provided in Fig. 3. It shows the characteristic relative loss in-

TABLE I. Listing of all energy losses observed and assigned in this study.

	Frequency $\hbar\omega$ (meV)	Remarks
α state		
sym. stretch	155/170 Fermi resonance	weakly bond, linear, oriented perpendicular to surface, dipole active, desorbs upon heating [Fig. 8(a)]
asym. stretch	290	
bent	80	
β state		
sym. stretch	145 dipole active	symmetricly bent; converts to a γ state and probably dissociates upon heating [Figs. 8(b) and 8(c)]
asym. stretch	198 not dipole active	
bent	95	
γ state		
sym. stretch	133 dipole active	asymmetricly bent, dissociates upon heating [Fig. 8(d)]
asym. stretch	170 dipole active	
CO		
stretch	225 dipole active	observed as dissociation product (Fig. 2) and after adsorption of pure CO (Fig. 4) the 190 and the 250-meV losses were only observed after exposure to CO (Fig. 2)
stretch	190 dipole active	
stretch	250 dipole active	
oxygen, carbon	30–65 dipole active	final state after heating to 370 K [Fig. 2(e)], the oxygen signal is verified by exposure to oxygen (Fig. 4)

tensities of all three adsorption states of CO_2 as functions of surface temperature during a temperature-programmed HREELS experiment (ramp rate 0.2 K/s). It should be noted here that the cross section for the excitation of a loss is determined by the generally weakly coverage-dependent dynamic dipole moment associated with the corresponding vibrational mode; therefore, the relative loss intensities are not an absolute measure, but only proportional or at least monotonous to the corresponding population.

In order to quantify the contribution of desorption on the disappearance of the losses with increasing temperature, the desorbing CO_2 was monitored using the mass spectrometer (MS) simultaneously with HREELS.
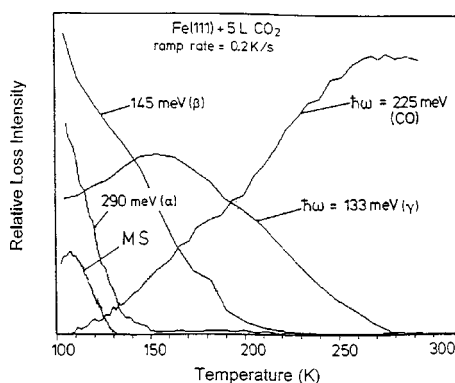

FIG. 3. Comparison of the population of the different adsorption states as a function of the linearly increased surface temperature. The surface was saturated with CO_2 at 100 K.

It is obvious that the MS CO_2 signal ($m/e = 44$), which appears only during the sudden decrease of the 290-meV intensity, clearly indicates that only the α state is substantially emptied by desorption. Below it will be shown that the dissociation of CO_2 from this state can be neglected completely.

Another interesting feature exhibited in Fig. 3 is the maximum of the population of the γ state at 160 K. Its appearance may be interpreted by the assumption that the CO_2 molecules in the γ state occupy the same sites as in the less stable β state, so that they block each other, and that there is not sufficient thermal energy for fast conversion from the β state to the γ state at 100 K. Thus, at this temperature, both states will be populated competitively mainly according to the individual sticking probabilities into these states, causing the β state to become overpopulated while the population of the γ state stays below the amount given by thermal equilibrium, which is mainly determined by the difference of the binding energies of the two states. This distribution stays frozen at 100 K. Thus increasing the temperature or thermal energy causes the surplus of the CO_2 molecules in the β state (145 meV) to decrease either by dissociation or more probably by thermally activated conversion to the γ state, in order to approach thermal equilibrium. The conversion increases the population of the γ state until, at about 160 K, dissociation dominates the process, causing the appearance of a maximum.

The maximum of the population of the γ state in Fig. 2 seems to occur at a temperature well above 150 K. This may be due to the nonsteady heating procedure in the experiment
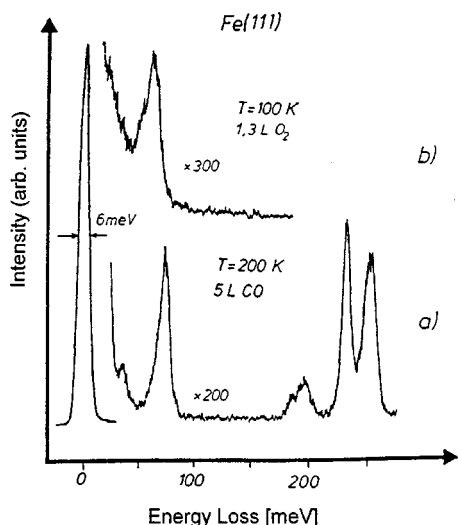
FIG. 4. HREEL spectra taken after exposure to 1.3-L O_2 at 100 K (upper spectrum), and to 5-L CO at 200 K in comparison.

of which the data are shown in Fig. 2, but it is important to see that the Figs. 2(b) and 2(c) both exhibit a larger γ-state intensity than Fig. 2(a).

As mentioned above, a special measurement was carried out to interpret the loss at 225 meV that appears after heating to 150 K, as well as the loss at about 65 meV that appears in all the spectra of Fig. 2. For this reason, the clean samples were exposed to 5 L CO at 200 K (the lower spectrum of Fig. 4) and to 1.3 L O_2 at 100 K (the upper spectrum or Fig. 4). The fact that in the oxygen spectrum only one single loss appears at about 65 meV clearly indicates that losses appearing at this energy are characteristic of atomic oxygen. Note that the small intensity at 65 meV in Fig. 2(a) is rather due to contamination than to dissociation of CO_2 at 100 K, as will be shown below.

Different from oxygen, CO obviously adsorbs into three molecular states indicated by three stretching modes in Fig. 4. in agreement with findings of Seip *et al.*[8] It should be noted that, in contrast to exposure to pure CO, dissociation of CO_2 results in atomic oxygen and CO. This may explain why only one CO state at 225 meV is observed in Fig. 2 in contrast to Fig. 4, which exhibits three losses at 194, 232, and 252 meV.

Conclusively, Figs. 2 and 3 provide clear evidence of at least three molecular adsorption states of CO_2 on Fe(111), which can be unambiguously distinguished by different thermal stabilities.

B. Desorption energies

Figure 5 exhibits a comparison of two loss spectra both taken at a surface temperature of 100 K but under different permanent pressures of CO_2. The CO_2 flux is about 0.1 L/s in upper spectrum [Fig. 5(a)], and less than 10^{-4} L/s in the lower spectrum [Fig. 5(b)]. Note that the low flux spectrum is magnified by a factor of 3. At first glance it can be seen that there is no difference in the intensities of the losses at 50, 95, 133, and 145 meV in contrast to the losses at 290, 170, 155, and 80 meV. The latter are increased by a factor of
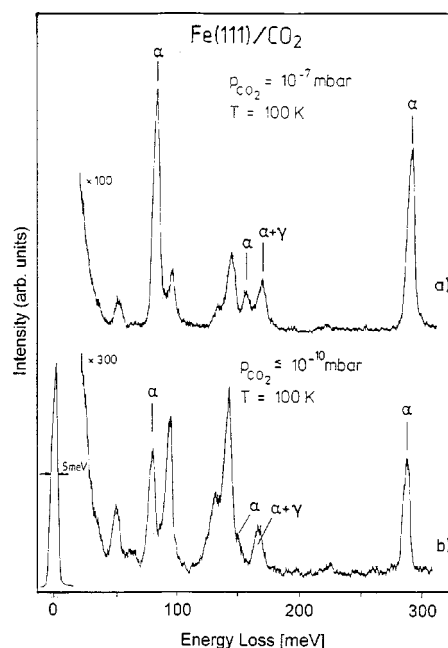

FIG. 5. HREEL spectra both taken at 100 K under a permanent CO_2 pressure of 10^{-7} mbar (upper spectrum), and less than 10^{-10} mbar (lower spectrum).

5 at high flux. This indicates that the loss at 170 meV, assigned to the γ state [Fig. 2(c)], obviously also comprises intensity, which can be associated with the weakly bond α state. Thus, besides the 290-meV loss, we also associate the losses at 80, 155, and 170 meV with the linear α state.

The response of the system to pressure jumps is reversible. This means that switching between the two fluxes will reproduce both spectra within our experimental accuracy, indicating that at 100-K catalytic dissociation of CO_2 can be neglected completely. Therefore, the change of the intensities of the losses related with the α state has to be explained by fast desorption from this state due to the small binding energy of the molecules to the surface.

The binding energy of the two bent states is so strong that the CO_2 molecules adsorbed in these states dissociate rather than desorb. It is obvious that this much stronger chemical bond to the surface causes a deformation (bending) of the CO_2 molecule.[9–11]

A more complete picture of the Fe-CO_2 system may be developed with the help of the following concept. Generally, a linear three-atomic molecule has asymmetric and symmetric stretching modes and two degenerated bending modes. Thus its infrared spectrum should comprise only three distinguishable modes similar to the infrared spectrum of a bent three-atomic molecule with only one bending mode.[12] Actually, gas-phase infrared data of molecular (linear) CO_2 exhibit four modes at 80, 155, 168, and 290 meV, with the symmetric stretching mode being split into 155 and 168 meV, due to a Fermi resonance with the second harmonic of the bending mode.[13] This suggests identifying the 155- and 170-meV losses with the split-symmetric stretching mode, and the prominent peaks at 80 and 290 meV with the excitation of the bending mode and the asymmetric stretching mode of the linear state.

Obviously, the other losses at 50, 95, 133, and 145 meV, and also part of the 170-meV loss, are characteristic of a second and third adsorption state of CO_2. Their assignment might be possible if one assumes that the CO_2 molecules in the stable adsorption states behave similarly to bent free molecules. A brief analysis shows that the frequencies of their asymmetric stretching modes are always higher than those of their symmetric stretching modes.[12] This enables us to interpret the three remaining losses of the γ state in Fig. 2(c) as follows. The 133-meV loss can be assigned as the symmetric stretching mode, the 170-meV loss as the asymmetric stretching mode, and the 95-meV loss as the bending mode of a bent CO_2 species that exists at the Fe(111) surface up to 210 K. Since the intensity of the loss at 95 meV decreases disproportionally compared to the losses at 133 and 170 meV (Fig. 2), it can be concluded that this loss comprises the intensities of the bending modes of both species, which cannot be resolved within our experimental resolution.

The only remaining loss, which has not yet been assigned, is the 145-meV loss. Since it can be assumed that the frequencies of a stretching mode decrease with increasing binding energy to the surface,[14] we assign this loss as the symmetric stretching mode of the β state. The missing asymmetric mode will be identified below.

C. Symmetry

In addition to the identification of the different adsorption states in regard to their thermal stabilities and their binding energies as a first step in the characterization of an adsorption system with vibrational spectroscopy, it is also desirable to clarify their symmetries in order to derive microstructures, which describe the geometric configurations of the different CO_2 states on the surface. These data are essential basic inputs, for instance, into inelastic low-energy electron-diffraction and other more general theoretical investigations. This kind of information may be obtained by angle-resolved HREELS.[15] For a first orientation, Fig. 6 shows a comparison of an in-specular spectrum with an off-specular spectrum. Both measurements were taken at 100 K after heating to 110 K for 3 min. The heating was done to obtain some amount of CO on the surface, which in turn ensures an intensity at 225 meV that represents the dipole-active CO stretching mode. During the whole measurement the Fe(111) surface was permanently exposed to a CO_2 flux of 0.1 L/s that corresponds to about 10^{-7} mbar. The impact energy of the scattering electrons was 5 eV in both spectra, and the off-specular angle was 20°, as indicated. As can clearly be seen, there are substantial differences in regard to the intensities as well as to the number of losses. Since in HREELS the background is mainly produced by dipole scattering, these differences are partially due to a strong reduction of the unstructured background in the off-specular case, and by the excitation of modes with dipole moments oriented parallel to the surface, which is only possible via impact scattering.[15] Most important in this respect is the appearance of a loss at 198 meV in the off-specular measurement. We interpret this loss as the excitation of the missing asymmetric stretching mode of the β-CO_2 state by the symmetric stretching mode at 145 meV.
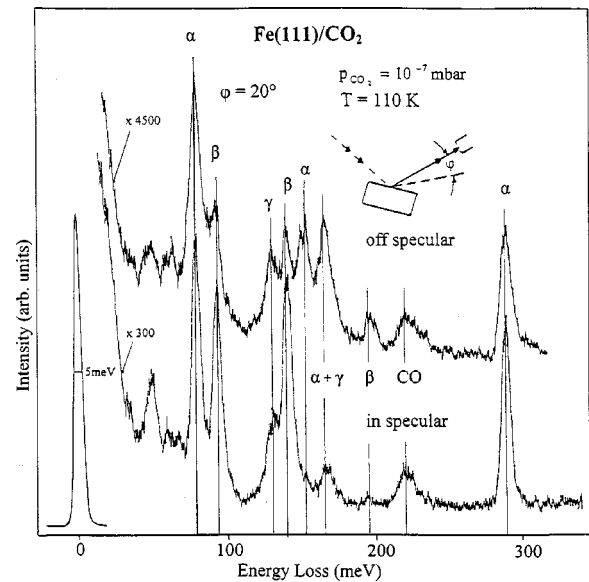

FIG. 6. Selected off- and in-specular spectra in comparison. In order to obtain a CO signal (225 meV), both measurements were taken at 100 K after heating to 110 K for a short time. The impact energy of the scattering electrons was 5 eV, in both spectra and the off-specular angle φ was 20°, as indicated.

A quantitative data reduction of a series of off-specular data is exhibited in Fig. 7. This shows the ratios of the off- and in-specular intensities of characteristic losses versus the off-specular angle φ. Such a plot allows to distinguish between modes that are excited via dipole or impact scattering. Since the stretching mode of CO will be excited only by dipole scattering, even if the molecule is oriented parallel to the surface,[14] its intensity is used as a reference for the be-
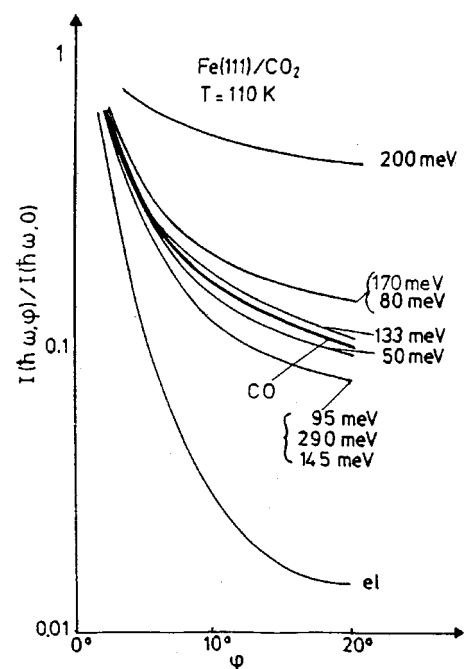

FIG. 7. Ratios between the off- and in-specular intensities of characteristic losses vs the off-specular angle φ.
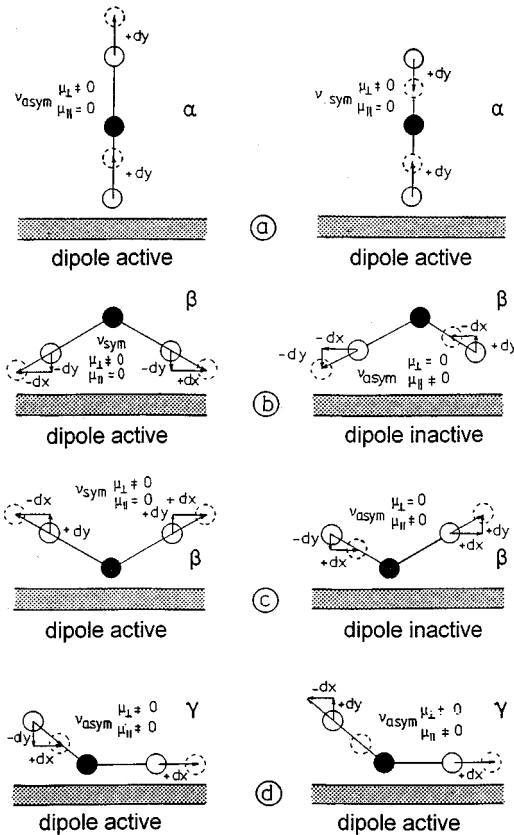
FIG. 8. Schematics of the microstructures of the three adsorption states derived from their different spectroscopic behavior in angle-resolved HREELS.

havior of a mode that is excited by dipole scattering only. In order to be sure to find some CO intensity, the surface temperature was increased to 110 K for a few minutes, as mentioned above. It is easy to see that all losses behave as dipole-excited modes except the one at 198 meV. Its intensity is almost independent of the off-specular scattering angle, and may therefore be excited by pure impact scattering, indicating that the corresponding vibration is associated with a dynamic dipole moment oriented parallel to the surface. This is in contrast to all other modes, which show vibrational amplitudes oriented almost perpendicular to the surface.

D. Structures

In the following the mode assignment and this off-specular information will be used to derive the microstructures of the three different adsorption states populated with CO_2 on the Fe(111) surface at 100 K. The almost quantitative agreement between the two losses at 290 and 170 meV and asymmetric and symmetric stretching modes of the free linear CO_2 molecule, strongly suggest associating the weakly bonded state of CO_2 with a linear configuration. Also since these two modes are excited by dipole scattering, it seems reasonable to relate this state to a linear molecule oriented perpendicular to the surface. This is schematically shown in Fig. 8(a).

Next we have to look for a configuration that explains the appearance of a loss at 198 meV in the off-specular measurements, which we assigned as the asymmetric stretching mode of the β state, together with a loss at 145 meV, interpreted as the symmetric stretching mode of this state. The only configurations of a CO_2 molecule with a dipole-active symmetric stretching mode and a dipole-inactive asymmetric stretching mode are the symmetrically bent ones shown in Figs. 8(b) and 8(c).

The configuration of the γ state may be derived from the fact that its two corresponding stretching modes at 170 and 133 meV are both dipole active. A simple configuration, in which both stretching modes have perpendicular dynamic dipole moments, is shown in Fig. 8(d), with the molecule asymmetrically bound to the surface.

Conclusively, this yields spectroscopic evidence of the existence of two bent CO_2 configurations, in agreement with our thermal stability measurements. The maximum in Fig. 3 is now easy to explain by a thermally activated conversion from the symmetric configuration [Fig. 8(c)] to the asymmetric configuration [Fig. 8(d)]. Under this concern the configuration of Fig. 8(b) is not very probable in agreement with simple molecular-orbital theory[16] which shows that the existence of a bond between CO_2 and the surface via the two oxygen atoms is not very likely.

SUMMARY

An analysis of the differences between loss spectra observed in in- and off-specular geometries (an example is shown in Fig. 6) allowed us to derive a complete picture of the microstructures of CO_2 adsorption states on Fe(111) surfaces. According to this analysis, CO_2 occupies one linear state (α state) with characteristic losses at 80, 155, 168, and 290 meV, and at least two bent states with different local symmetries. It was also possible to observe the complete sets of eigenmodes for each state with HREELS, and to assign all energy losses. The asymmetrical bent γ state is related to losses at 95, 133, and 170 meV, while losses at 95, 145, and 198 meV characterize the symmetrical bent β state. Temperature programmed HREELS measurements reveal experimental evidence of desorption from the CO_2 linear state only, while molecules adsorbed in the bent β and γ states dissociate into CO and O. This observation suggests a lower activation barrier for dissociation than for desorption for both states. The appearance of an intensity maximum in the TP-HREELS data (Fig. 3), characteristic of the occupation of the most stable γ state, led to the conclusion that conversion processes take place between the two bent states.

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