ELECTRON ENERGY LOSS STUDY OF THE ELECTRONICALLY EXCITED STATES OF ADSORBED CO_2: CASE STUDY CO_2/Fe

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Electron energy loss (EEL) spectra of CO_2 adsorbed and condensed on Fe(111), Fe(110) and stepped Fe(110) are presented. Linear adsorbed or condensed CO_2 shows losses at 6, 8.5, 12, 13.3 and 15.3 eV. These spectra are compared with electronic excitations of gaseous CO_2.

1. Introduction

The adsorption of CO_2 on iron surfaces has recently been studied applying UPS, XPS, thermal desorption, adsorption calorimetry, and the vibrating capacitor method [1–4]. The results revealed a strong face specificity of CO_2 adsorption and the formation of various adsorbed species depending on the adsorption temperature [1,2,4]. At 77 K both, only slightly distorted linear CO_2 and a bent, anionic CO_2^- species, are observed [3]. The latter moiety is stable up to 160–180 K. Above this temperature adsorbed carbon monoxide and oxygen are found on the surface, and above room temperature complete decomposition into C and O takes place [1,3]. There is clear evidence that adsorption and reaction activity increase in the sequence Fe(110) → stepped Fe(110) → Fe(111) → evaporated Fe films.

Recently, a consistent assignment of the electronic excitations in the electron energy loss spectra (EELS) of free and chemisorbed CO has been presented [5]. It was shown that for a variety of molecular environments (i.e. free, physisorbed or chemisorbed) the electronic excitation energies change only slightly.

It is the aim of this paper to present EEL spectra of CO_2 adsorbed or condensed on various iron surfaces and to compare these with experimental and calculated valence excitation energies of free CO_2 reported in the literature [6].

2. Experimental

The experiments were performed in a commercial, ion-getter-pumped UHV system (VG Instruments) equipped with a four-grid LEED optics, which also served as analyzer for AES, He(I)-UPS and EELS [7], a Kr^+-ion gun, a quadrupole mass spectrometer, a sample holder with a combined heating and cooling system, which allowed the choice of any constant temperature between 77 and 500 K, and a vibrating capacitor. The residual gas pressure was smaller than 1×10^{-8} Pa.

The iron single crystals were cleaned in the usual way applying heat treatment and ion bombardment (concerning stepped Fe(110) see ref. [8]). The
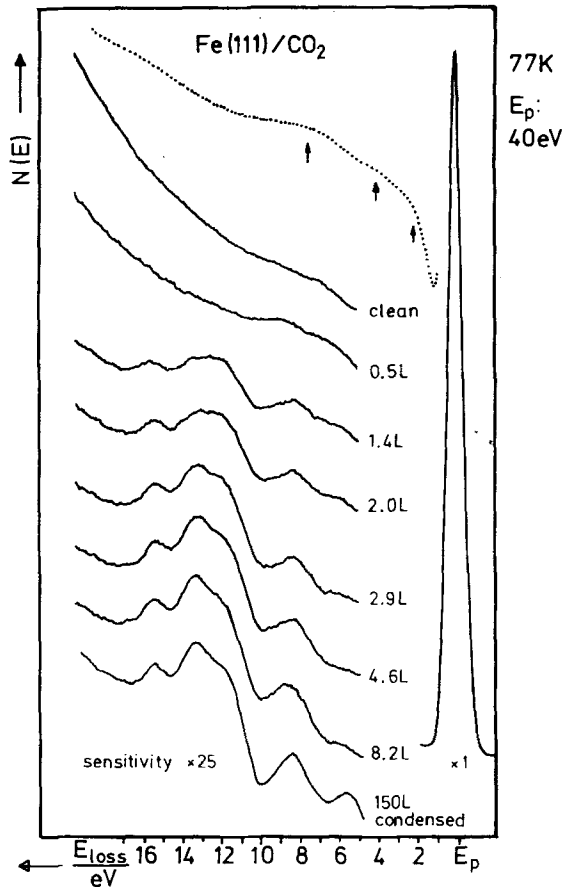

Fig. 1. EEL spectra of CO_2 adsorbed and condensed on Fe(111) at 77 K as a function of exposure. Primary energy 40 eV.

Auger electron spectra of the clean iron surfaces did not indicate any impurities, the LEED patterns consisted of sharp spots on a low background.

Carbon dioxide (Linde AG, purity 99.999%) was admitted from a glass cylinder via a leak valve. The EEL spectra were taken from adsorbates, the state of which was checked by means of He(I)-UPS, and changes in work function [2]. The primary energy was varied from 30 to 100 eV.

3. Results

When a Fe(111) surface is exposed to CO_2 at 77 K various energy loss peaks are observed in the energy range between 4 and 18 eV. The spectra shown in fig. 1 were obtained with a primary energy of 40 eV. At small exposures a peak at 9 eV is built up. With increasing coverage adsorbate induced losses at 8.5, 12 (shoulder), 13.3 and 15.3 eV are enhanced. By
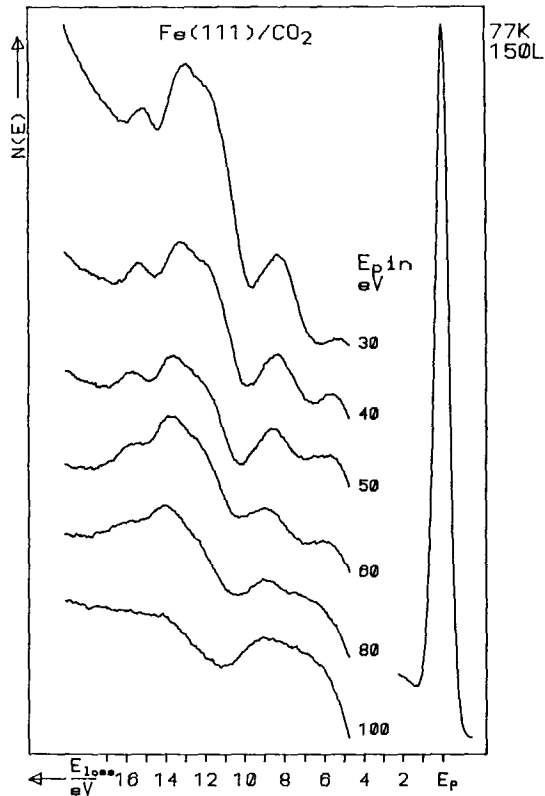

Fig. 2. EEL spectra of CO_2 condensed on Fe(111) at 77 K as a function of primary energy.

increasing the CO_2 pressure to more than 2×10^{-6} Pa it is possible to condense CO_2 on the iron surface [2]. As the curve at the bottom of fig. 1 shows (150 L), the EEL spectrum of the condensate is nearly identical to that of the adsorbate. The peaks in these spectra are much more pronounced than those observed for the clean iron surface which are shown at the top of fig. 1. In addition, an EEL spectrum of the clean iron surface is plotted as a dotted line which was obtained with 35 eV primary energy and enhanced sensitivity. Three losses are detectable, at 2, 4 and 7.5 eV.

With increasing primary energy the losses of the clean iron surface become more blurred. This is also valid for the adsorbed and condensate induced peaks as fig. 2 shows. It cannot be excluded at this point, however, that the effect shown in fig. 2 is to some degree caused by electron induced damage of the sample since longer exposure of the adsorbate to the electron beam induces some spectral changes. At first, the shoulder at 12 eV vanishes, and the maxima of the losses at 13.3 and 15.3 eV shift to higher loss energies. This
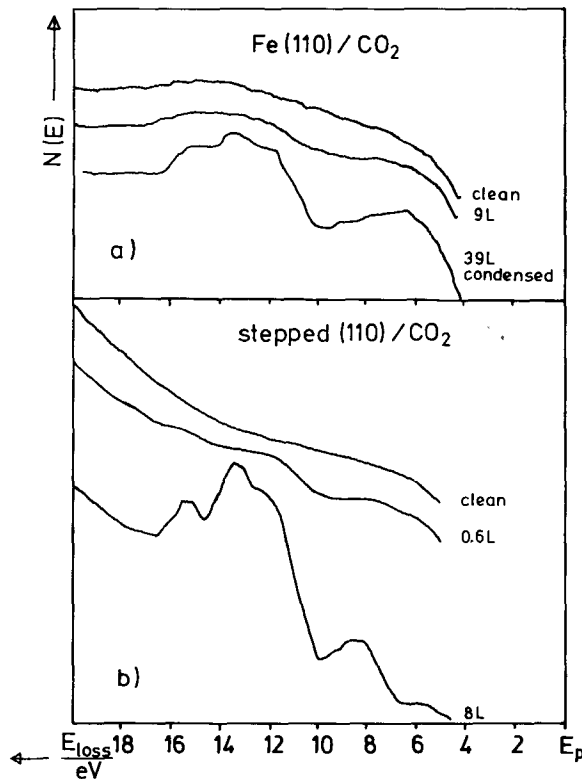

Fig. 3. EEL spectra of CO_2 adsorbed and condensed at 77 K (a) on Fe(110) and (b) on stepped Fe(110). Primary energy 80 eV (a), 40 eV (b).

also holds for the 8.5 eV peak. A further signal at 6 eV is visible between 30 and 60 eV primary energy. At higher primary energies it is no more observable, perhaps due to the formation of a broad signal between 6 and 10 eV.

UPS reveals, as already mentioned, a face specificity of CO_2 adsorption on iron. This also follows from EELS. The comparison of figs. 1 and 3 shows that, in the case of Fe(111) and stepped Fe(110), after an exposure to about 1 L CO_2, the CO_2 signals are detectable, whereas with Fe(110) only after an exposure to 9 L a signal begins to grow up. At such an exposure the CO_2 induced losses on Fe(111) and stepped Fe(110) have already reached maximum intensity. Only when condensation takes place (fig. 3a, 39 L), the CO_2 induced losses on Fe(110) agree with those observed with Fe(111) (fig. 2, $E_p = 80$ eV). The difference in the EEL spectrum of clean Fe(110) and stepped Fe(110) (figs. 3a and 3b) is not due to a face specificity. It is caused by the change in primary energy. A similar effect is observed with Fe(111).
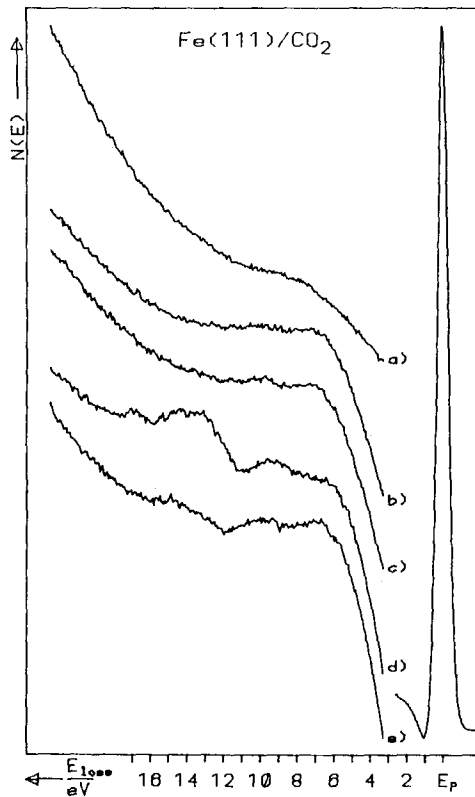

Fig. 4. Temperature dependence of EEL spectra of CO_2 adsorbed on Fe(111). Primary energy 40 eV. (a) 140 K, clean; (b) 140 K, 1.2 L; (c) 140 K, 2.4 L; (d) cooled to 77 K + 2.4 L; (e) heated to 140 K + 60 L.

By means of UPS [2,3] and measurements of changes in work function [2] we were able to prove that adsorption of linear CO_2 and condensation of CO_2 at 77 K are completely reversible [2]. Heating to 140 K leads to desorption of these species, whereas cooling from 140 to 77 K and exposure to CO_2 results in readsorption of CO_2. At 140 K only the bent, anionic CO_2^- species is adsorbed. EELS exhibits that adsorption of this moiety causes a maximum increase of the primary peak by a factor of 2.5 and enhanced intensity at about 7 and 10 eV (fig. 4, curves b and c). When the crystal is cooled to 77 K an exposure to 2.4 L CO_2 leads to a spectrum which agrees with those known from fig. 1. The losses at 8.5, 12, 13.3 and 15.3 eV vanish again after heating to 140 K.

4. Discussion

With the presently used spectrometer it was not possible to infer more detailed information on the electronically excited states of the bent, anionic CO_2^- species [9]. The two losses at 7 and 10 eV are too weak and broad to draw further conclusions.

However, the EEL spectra of linear CO_2 in the adsorbed and condensed state allow a comparison with the known electronic excitation of gaseous CO_2. Fridh, Åsbrink and Lindholm [6] have put together excitations of CO_2 observed with various methods in order to find a definitive assignment based on their own HAM/3 calculations of excitation energies. Fig. 5a represents their diagram, fig. 5b the EEL spectrum of the condensate, obtained with 40 eV primary energy (fig. 2), however, redrawn in order to adjust the energy scales to fig. 5a. In spite of the fact that optical selection rules should only be applied to electron impact induced electronic transitions in the range of higher energies ($E_p > 50$ eV), the 40 eV spectrum has been used. This has been done since this spectrum is well-structured, is representative for both adsorbate and condensate (fig. 1), and is in principle not changed with increasing primary energy.

Fridh et al. [6] assign the observed excitations of gaseous CO_2 in the following way:

(1) $1\pi_g \rightarrow 2\pi_u$: transition with final states $^3\Sigma_u^+$, $^3\Delta_u$, Σ_u^-, $^3\Sigma_u^-$, and Δ_u around 9 eV. They are all dipole forbidden and exhibit therefore only very small intensity.

(2) $1\pi_g \rightarrow 2\pi_u$: transition with final state Σ_u^+ in the region between 11 and 13 eV (Rathenau progression).

(3) $1\pi_g \rightarrow np\sigma_u$, $1\pi_g \rightarrow np\pi_u$: Rydberg transitions with intense bands starting at ~ 11 eV converging to the ionization energy of the $1\pi_g$ ion state at 13.7 eV.

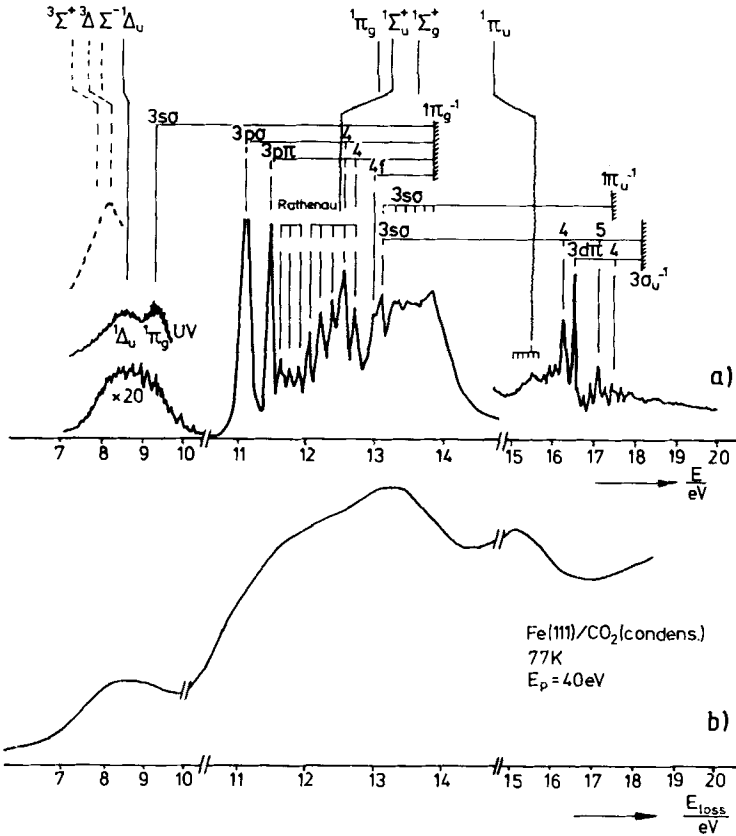(4) $4\sigma_g \rightarrow 2\pi_u$: transition with vibrational structure and final state $^1\pi_u$ at 15.5 eV.

Fig. 5. (a) Electronic excitation of CO_2 in the gas phase after Fridh et al. [6]. (b) EEL spectrum of CO_2 condensed on Fe(111) at 77 K (primary energy 40 eV).

(5) $1\pi_u \rightarrow 3s\sigma_g$: Rydberg transitions with intense bands starting at ~ 13 eV converging to the ionization energy of the $1\pi_u$ ion state at 17.3 eV.

(6) $3\sigma_u \rightarrow ns\sigma_g$, $3\sigma_u \rightarrow nd\pi_g$: Rydberg transitions with intense bands starting at ~ 16.5 eV converging to the ionization energy of the $3\sigma_u$ ion state at 18.0 eV.

$4\sigma_g$, $3\sigma_u$, $1\pi_u$ and $1\pi_g$ denote occupied valence orbitals of CO_2, $2\pi_u$ the lowest unoccupied valence orbital. To illustrate the nature of the orbitals involved in the valence excitations, we show in fig. 6 quasi-three-dimensional plots of the active orbitals. Clearly, electronically excited states cannot be assigned one-electron transitions. For example, the $1\pi_g \rightarrow 2\pi_u$ one-electron transition leads to six final electronically excited states, i.e. $^1(\Sigma_u^+, \Sigma_u^-, \Delta_u)$ and $^3(\Sigma_u^+, \Sigma_u^-, \Delta_u)$. Therefore, the $^1\Sigma_u^+$ state, causing the Rathenau progression can be thought to originate from the above mentioned transition. The Rydberg character of the Rathenau series is indicated by the main quantum number n,
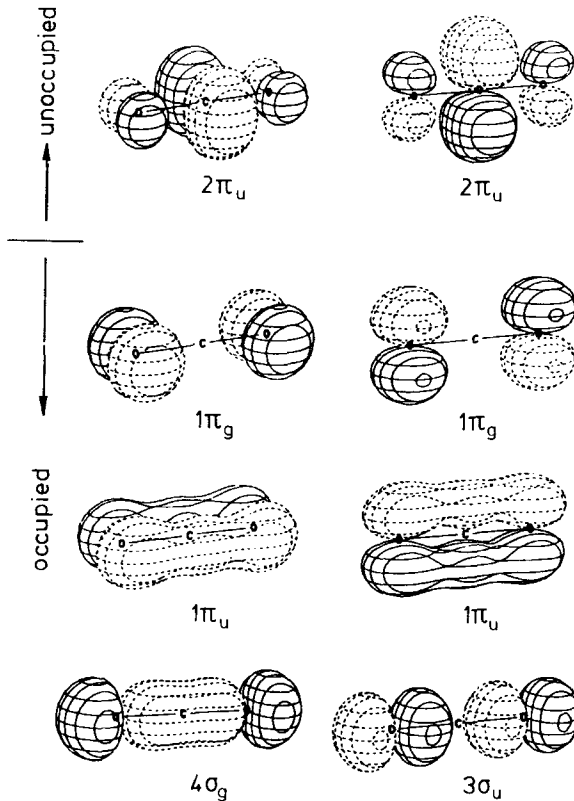
Fig. 6. Valence one-electron orbitals of CO_2 as taken from the literature [11].

the angular momentum s, p, and d, and the molecular symmetry σ_u, σ_g, π_u, and π_g.

At this point some comments concerning dipole selection rules seem appropriate. We recall that the intensity of an optical transition is determined by the matrix element $\langle \psi_f \mid p \mid \psi_i \rangle$, where ψ_f and ψ_i are the final, and initial state wavefunctions, respectively, and p is the dipole operator. Since the ground state of CO_2 is $^1\Sigma_g^+$, the axial component of p (p_z, where z points along the CO_2 internuclear axis) can excite $^1\Sigma_u^+$, the components (p_x, p_y) perpendicular to the axis $^1\Sigma_u^+$ final states. Therefore, dipole selection rules allow excitation, e.g. into the $^1\Sigma_u^+$ state resulting from the $^1\pi_g \rightarrow {}^2\pi_u$ one-electron excitations but not into the other five resulting states, which therefore show very weak intensities in the gas phase (fig. 5a). However, it is interesting to note that the EEL spectrum of adsorbed and condensed CO_2 (fig. 5b) shows losses around 8.5 eV, the intensity of which is comparable to those observed

above 10 eV. They can only be assigned to the superposition of the dipole forbidden $^1\pi_g \rightarrow {}^2\pi_u$ transitions [1]. Arguments for the enhanced intensity are:
(i) In the case of EELS dipole scattering only plays a part when the measurement occurs in transmission or specularly. The used four-grid optics, however, integrates over a large solid angle and registers electrons for which the selection rules are not strongly valid.
(ii) The low energy of the primary electrons allows for spin-flip.

The broad intensity distribution in the region between 11 and 14 eV in fig. 5b should be assigned to the Rathenau progression. The Rydberg transitions which have high intensity in the gas phase spectrum should be suppressed in the solid state. The marked maximum at 13.5 eV can be explained by the intense $1\pi_u \rightarrow 3s\sigma_g$ transition (13.2 eV in gas phase), which has, after Fridh et al. [6], more valence character. Due to the arguments given above (i and ii), the forbidden transitions $3\sigma_u \rightarrow 2\pi_u$ (final state $^1\pi_g$) and $1\pi_u \rightarrow 2\pi_u$ (final state $^1\Sigma_g^+$) may enhance the intensity around 13 eV, also. The loss at 15.5 eV in fig. 5b corresponds to a $4\sigma_g \rightarrow 2\pi_u$ excitation in the gas phase.

The first ionization potential of CO_2 lies at 13.7 V. There are, however, no features in the spectrum of the condensate that point to ionization.

As discussed in connection with fig. 2, there is a shift of the maxima of the EEL spectrum when the primary energy is changed. This observation shows that more than one loss contributes to each signal and that the cross sections of the contributing excitations differ in their dependence on the primary energy.

There is an indication of a further loss in the condensate induced EEL spectrum at 6 eV (fig. 2). The gas spectrum, however, does not exhibit a corresponding peak. At present, we cannot assign the signal definitely.

Solymosi and Kiss [10] use EEL spectra in a differentiated form as a finger print technique to look for the presence of undissociated CO_2 in the adsorbate on rhodium. Due to big differences in resolution and the techniques applied, it is not possible to compare their spectra with the spectra in this paper directly.

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