

# IR-spectroscopy of CO on iron ultrathin films

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## Abstract

In contrast to the well-known surface enhanced Raman scattering (SERS) the surface enhanced infrared absorption (SEIRA) of molecules adsorbed on metal island films is hardly investigated. The results of our experiments add at least one important fact for a better understanding of the chemical contribution to SEIRA. Under ultrahigh vacuum conditions we measured IR-transmission spectra of in-situ grown iron films on MgO(0 0 1) on which CO was adsorbed. The MgO(0 0 1) surface was prepared by cleavage in UHV. Deposition of iron leads to growth of epitaxial islands. After CO exposure IR-transmission spectra taken at normal incidence show strong absorption lines in the C–O stretch region with number, intensities, positions, and shapes dependent on Fe-film morphology and Fe-film thickness. For each of the films under investigation the strongest C–O line shows an asymmetric (Fano-like) shape which reveals non-adiabatic interaction of vibrations with a continuum of other excitations, i.e. free electron transitions. The dynamic dipole moment is enhanced by about two orders regarding adiabatic values. However, with grazing incidence IR reflection spectroscopy of CO on thick and annealed iron films we observe symmetric lines and intensities without any extra enhancement. Obviously, the Fano-like non-adiabatic interaction is somewhat like the chemical effect in SEIRA. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Infrared spectroscopy; Thin films; Surface enhanced molecular absorption

## 1. Introduction

In contrast to the well-known surface enhanced Raman scattering (SERS) the surface enhanced infrared absorption (SEIRA [1]) of molecules adsorbed on metal island films is hardly investigated. As in the case of SERS two effects should contribute to SEIRA which are field enhancement and a more unclear chemical contribution. SEIRA receives growing interest for its exploitation in laterally and time resolved infrared (IR) investigations.

The results of our experiments add at least one important fact for a better understanding of the

chemical effect [2]. We investigated the infrared (IR) absorption of small molecules (CO) adsorbed on epitaxial Fe films grown on MgO(0 0 1). This metal-film system is of special interest in surface science (e.g. [3]) and is well investigated with respect to structural properties [4–6]. For example, for substrate temperatures  $> 300$  K iron forms three dimensional islands with crystalline facets. The IR transmission spectra of such iron films nicely reveal the growth behavior [7]. The spectra could be fully understood if surface scattering of free charge carriers as well as quantum size effects [8] are taken into account and if island films are described in terms of two-dimensional effective media [9,10].

Although iron is not a noble metal IR absorption by CO adsorbates is indeed enhanced. Additionally, the CO-stretching line has an asymmetric Fano-like

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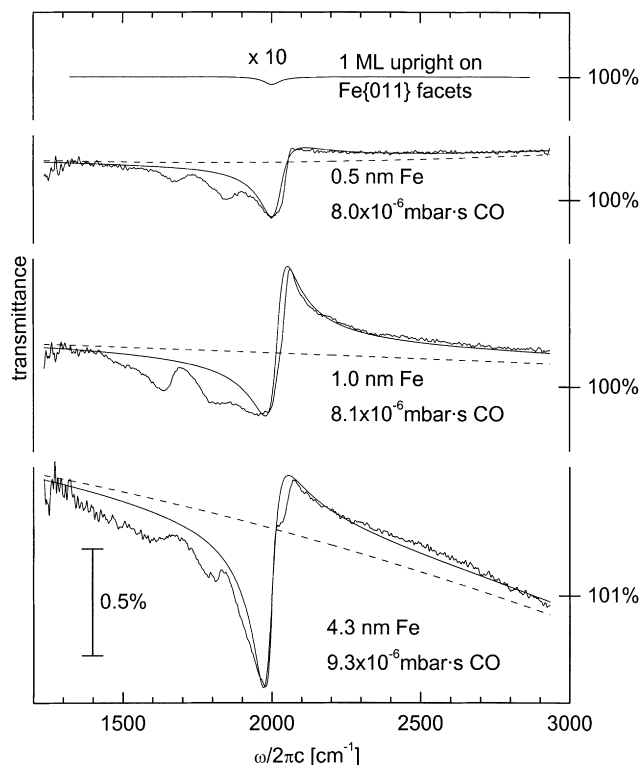


Fig. 1. Relative transmittance of CO on Fe films as measured at 115 K (noisy spectra) and calculations (smooth through lines): Lorentz-oscillator model (on top, parameters see the text) and fits to the strongest absorption line according to the non-adiabatic model [2,11]. Fit parameters:  $\omega_0$  is  $2014 \text{ cm}^{-1}$  for 0.5 nm,  $2023 \text{ cm}^{-1}$  for 1 nm and  $1987 \text{ cm}^{-1}$  for 4.3 nm, respectively.  $\gamma$  is  $103 \text{ cm}^{-1}$  for 0.5 nm,  $87 \text{ cm}^{-1}$  for 1 nm and  $77 \text{ cm}^{-1}$  for 4.3 nm, respectively. The asymmetry  $\omega_0\tau$  is 0.4 for 0.5 nm, 1.14 for 1 nm and 0.61 for 4.3 nm, respectively.  $\Theta\mu^2$  corresponds to the oscillator strength. It is (in  $10^{-9} \text{ A/V}$ ) 220 for 0.5 nm and for 1 nm, but it is 500 for 4.3 nm. The broken line displays the baseline change.

shape. Such a shape was predicated by Langreth [11] for non-adiabatic interaction of vibrations with a continuum of electronic transitions activated by the IR radiation. As the electronic properties of thin metal films strongly depend on thickness and morphology this Fano-like effect should also be determined by those film parameters. Here we will give our results on this subject.

## 2. Experimental

Our experiments are performed with an FTIR-spectrometer (Bruker IFS66v/S with  $\text{LN}_2$ -cooled MCT-detector) that is connected with a UHV chamber (base pressure  $< 2 \times 10^{-10}$  mbar) via Viton-O-ring sealed KBr-windows. The spectrometer and the

optical path of the IR beam outside the chamber are evacuated to 3 mbar. A rotatable optic consisting of gold coated mirrors allows us to measure alternatively in transmission or reflection mode. The UHV-chamber is further equipped with a sample manipulation system, a crystal cleaver, a water cooled electron impact evaporator (Omicron), a quartz microbalance for calibration of the deposition rate and a LEED system. The MgO crystals ( $7 \text{ mm} \times 7 \text{ mm} \times 12 \text{ mm}$ ; purity  $> 99.9\%$ ) were mounted in an OHFC-copper frame to allow transmission measurements. The substrate temperature was measured by a chromel–alumel-thermocouple attached to the sample holder. The crystals were cleaved in UHV. The iron films were deposited on the just cleaved MgO(001) plane ( $7 \times 7 \text{ mm}^2$ ) at a substrate temperature of about 315 K. For all experiments comparable

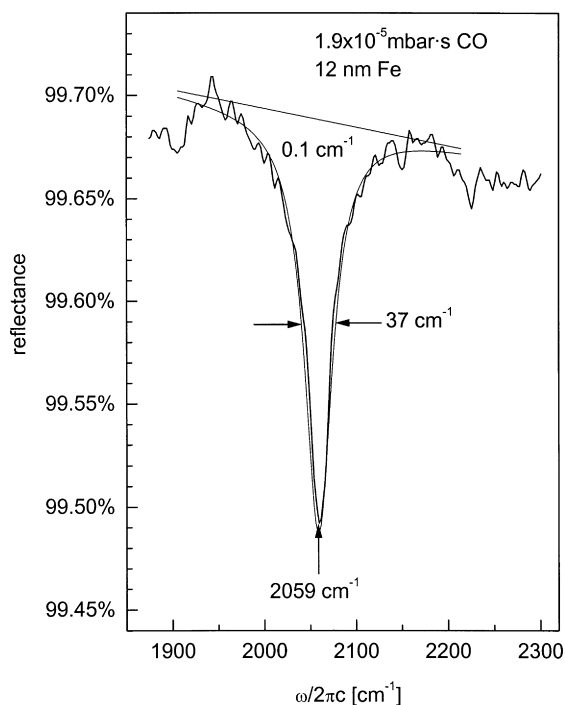


Fig. 2. Normalized IR reflectance (measured without a polarizer) at CO saturation coverage for oblique incidence at  $75^\circ$  (noisy spectrum). The smooth line is based on a Lorentzian oscillator model and is used for an estimate of the peak area (indicated in the figure).

deposition rates around 0.5 nm/min were used. Before and after deposition the rate was calibrated by positioning the microbalance at the sample position during preparation. The thickness of a film was calculated from deposition time and quartz crystal frequency shift resulting from deposited iron assuming the density of the bulk material ( $7.88 \text{ g/cm}^3$ ). The reported iron film thicknesses are accurate within  $\pm 5\%$ . For the reflection experiment an about 12.5 nm thick smooth iron film on MgO(0 0 1) was produced by annealing about 9 nm Fe and a further deposition of about 3 nm Fe. After cooling the samples down to about 115 K they were exposed to CO (purity 99.997 vol.%) at a partial pressure of about  $10^{-8}$  mbar.

Spectra shown in this article were recorded in the frequency range from 1000 to  $7000 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$ . The transmission spectra were measured for normal incidence. Reflection at  $75^\circ$  was measured without a polarizer. Each spectrum is the average of 100 coadded scans sampled during an

accumulation time of 22 s while the film was exposed to CO. Reference spectra were taken at about 115 K immediately before CO exposure.

### 3. Results and discussion

Fig. 1 shows the spectral consequences of CO adsorption for three different Fe-thicknesses for saturation (regarding IR spectra) exposures which are about  $8.5 \times 10^{-6}$  mbar s for the three Fe films of this adsorption experiment. The following happened: The baseline changed towards higher transmittance values and strong absorption bands in the CO-stretching region appeared. At least three well separated CO peaks arose from low exposures up to saturation. All of them showed shifts to higher frequencies with increasing exposure [2]. They can be attributed to different but well defined adsorption sites as will be discussed in another article [2]. Clearly, the strongest line (at about  $1960 \text{ cm}^{-1}$  for 1 nm Fe) is asymmetric and the shape is different for the three samples. The appearance of baseline shift and asymmetry must be correlated to non-adiabatic interaction of CO-vibration with electronic transitions.

After a suitable background conformation [2] (which has to be different from the background function used by Langreth) we applied the Fano-like susceptibility model function of Langreth [11] (which is a Lorentz oscillator with an imaginary contribution to the real part of the transition dipole  $\mu$ , i.e.  $\mu$  becomes  $(1 + i\omega\tau)\mu$ ) to the main absorption line. The relevant fit parameters are  $\Theta\mu^2$  ( $\Theta$  is the CO-coverage), asymmetry  $\tau$ , the Lorentz-damping  $\gamma$ , and the resonance frequency  $\omega_0$  [2]. The fit curves are shown as broken lines in Fig. 2 (for the parameters see the figure caption). A comparison of the fit parameters for the three samples yields two interesting informations: The asymmetry (in terms of  $\omega_0\tau$ ) is strongest for 1 nm Fe which means a just-closed film and which is of a thickness range where the conductivity change with thickness is the largest. The oscillator strength (in terms of  $\Theta\mu^2$ ) is greatest for 4.3 nm which is the film with the highest conductivity but which still has a rough surface [6,7].

In order to evaluate an enhancement factor we estimated the adiabatic value for  $\Theta\mu^2$ . (At 115 K we could not detect CO adsorption on MgO.) The value

$\Theta \approx 1.21 \times 10^{19} \text{ m}^{-2}$  is estimated assuming full coverage (one on-top CO per surface Fe) of closely packed Fe-pyramides with bcc {0 1 1} facets tilted by  $45^\circ$  with respect to the substrate. The dipole moment  $\mu$  is calculated from the IR peak area of CO on NaCl [12] (which yields an effective dynamic charge of about 0.4 elementary charges per ion) and the  $\omega_0$  value. If only dipole components tangential to substrate are considered the adiabatic result for  $\Theta\mu^2$  is  $2.3 \times 10^{-9} \text{ A/V}$  which is about 200 times smaller than the experimental value for the 4.3 nm film. The theoretical value corresponds to the Lorentzian band (with  $\gamma = 70 \text{ cm}^{-1}$ ) also shown in Fig. 1.

Our results indicate Fano-like intensity borrowing [13] as an important contribution to SEIRA. The theoretical condition of a sufficiently strong electric field in the metal [11] is fulfilled for the ultrathin films in the normal transmission experiment. Additionally, the local field for CO-adsorbates can be enhanced, especially inside small grooves [14] which still persist while a closed Fe-film on MgO(0 0 1) further grows [5,6].

By reflection absorption measurements of CO on annealed 12.5 nm Fe on MgO (film thicker than 10 nm which is the mean free path of free charge carriers in iron at  $2000 \text{ cm}^{-1}$ ) we observed a sharp symmetric line at  $2061 \text{ cm}^{-1}$  (for saturation exposure of about  $19 \times 10^{-6} \text{ mbar s}$ , regarding the IR spectrum) without any enhancement, see Fig. 2. Assuming monolayer coverage of upright CO molecules on Fe(0 0 1) and using the aforementioned effective charge the (unpolarized) peak areas is estimated to be  $0.095 \text{ cm}^{-1}$  within classical theory [15]. The measured peak area is about  $0.1 \text{ cm}^{-1}$ .

#### 4. Summary and conclusions

We showed our first results on SEIRA for small molecules on a relatively well known system. We observed a Fano-like non-adiabatic effect for adsor-

bates. This is certainly the main part of the chemical effect in SEIRA.

In order to understand more it is necessary to investigate further the dynamic conductivity of ultrathin metal films as a consequence of the specific growth process.

Also the knowledge of sticking and molecular orientation of CO (i.e. on adsorption) on thin metal films has to be improved.

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