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# Surface-enhanced infrared absorption?

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## Abstract

In ultra-high vacuum (UHV) we have measured infrared transmission spectra of CO on ultra-thin films of iron grown at about 315 K on UHV-cleaved MgO(001). Even at normal incidence of light we observe several asymmetric CO stretching lines with positions, intensities and shapes dependent on film morphology. The CO stretching lines observed are enhanced by at least two orders of magnitude with respect to adiabatic values. Enhancement and asymmetry are correlated to the curvature of transmission spectra of the bare iron films which is a measure of the dynamic conductivity, i.e., of the degree of continuity of the films formed by the growth of three-dimensional epitaxial islands. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Carbon monoxide; Infrared absorption spectroscopy; Iron; Metallic films; Vibrations of adsorbed molecules

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## 1. Introduction

Infrared (IR) absorption of adsorbates on metal surfaces is commonly investigated by IR reflection–absorption spectroscopy (IRAS) at grazing incidence of light [1,2]. Because of the vanishing tangential component of the electric field at the surface of an ideal metal, IRAS probes the vibrational dipoles normal to the surface. However, there are a few results that disagree with this assumption. Careful consideration of baseline shifts as a consequence of adsorption revealed absorption lines from tangential vibrational dipoles – e.g., for frustrated CO translation on Cu(100) [3] and for a second harmonic tangential hydrogen mode on W(100) and on Mo(100) [4]– that enhance reflectivity at the resonance frequency and which are asymmetric. The lines have a Fano-like shape which means that, in a small frequency region near resonance, the reflectivity is also lowered. Langreth developed a theory for the Fano effect of adsorbate vibrational excitations interacting with the continuum of electronic transitions of free carriers [5,6]. Since this Fano effect includes interaction of adsorbate vibrations with the electric field, there remains an open question concerning excitations from the tangential field component in IRAS. Later Persson developed the new theory for anti-absorption due to dynamic interaction of electronic motion near a surface with tangential adsorbate motions that do not necessarily feel an incoming field [7,8]. When applied to adsorbates on good metals (with low scattering rates for free charge carriers) like copper for example, Persson's theory of friction between electrons and adsorbates explains experimental baseline shifts and asymmetric anti-absorption lines well [8].

No such suitable theory exists for the effect of surface-enhanced infrared absorption (SEIRA) for molecules on metal island films [9]. Like done in

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the case of surface-enhanced Raman scattering, SEIRA is dicussed in terms of field enhancement [10] and a residual chemical effect. SEIRA is investigated experimentally for large organic molecules (e.g., [11,12]) with many vibrational modes which, certainly, is a reason for the neclect of a thorough line-shape analysis [10–12]. To date, molecular orientation has not usually been taken into account in the determination of enhancement factors for absorption with metal island films regarding the case without metal [12].

In order to learn more about SEIRA we have started to investigate normal IR transmission of the small molecule CO adsorbed on epitaxial iron island films on MgO(001). It will be shown here that SEIRA really is observed for this system and that it is correlated to asymmetric line shapes which can be explained by Langreth's theory.

## 2. Experimental

Our experiments were done with an apparatus consisting of a Fourier transform infrared (FTIR) spectrometer (Bruker IFS66v/S with a liquid-nitrogen-cooled MCT detector) which is connected with an ultra-high vacuum (UHV) chamber 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 one 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 low-energy electron diffraction (LEED) system. The base pressure ($p_{\text{base}} < 2 \times 10^{-10}$ mbar) in the UHV chamber is established and maintained by an ion getter pump and an integrated titanium sublimation pump.

The MgO crystals (7 mm × 7 mm × 12 mm; purity >99.9 %) were mounted in an OHFC copper frame to allow transmission measurements. 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 mm × 7 mm) at a substrate temperature of about 315 K. For all experiments comparable deposition rates of around 0.5 nm $\text{min}^{-1}$ 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 the deposition time and quartz crystal frequency shift due to deposited iron, assuming the density of the bulk material to be 7.88 g $\text{cm}^{-3}$. The iron film thicknesses reported are accurate within ±5%. After cooling the samples to 115 K, they were exposed to CO (purity of 99.997 vol%) at partial pressures of about $10^{-8}$ mbar.

Spectra were recorded in the frequency range from 1000 $\text{cm}^{-1}$ to 7000 $\text{cm}^{-1}$ with a resolution of 32 $\text{cm}^{-1}$for the observation of iron-film growth and 4 $\text{cm}^{-1}$ for CO adsorbates. The transmission spectra were measured in normal incidence. Each spectrum is the average of 100 co-added scans sampled during an accumulation time of 7 s while the film was growing slowly, and during 22 s while the film was exposed to CO. Reference spectra were taken from bare MgO at the growth temperature for the iron-film spectra and were recorded at 115 K immediately before CO exposure to the iron films.

## 3. Results and discussion

The epitaxial growth of iron on MgO(001) has been widely investigated and is being understood with increasing success [13–16]. Starting from a UHV-produced cleavage plane at room temperature, three-dimensional (3D) islands form and grow with further deposition (at slow rates of a few monolayers per minute).

As is known from helium-atom scattering, the MgO substrate is fully covered at about 0.8 nm [15,16]. Although the so-called Schwoebel barrier for diffusion of iron on iron is easily overcome only when the temperature is above 450 K [14], there are already small crystalline facets at room temperature [13] as proved by the various distinct CO lines in our experiment.

The IR transmission spectra of Fig. 1 reflect the development of dynamic conductivity, $\sigma(\omega) \propto i\omega\epsilon(\omega)$ [$\epsilon(\omega)$ is the frequency-dependent

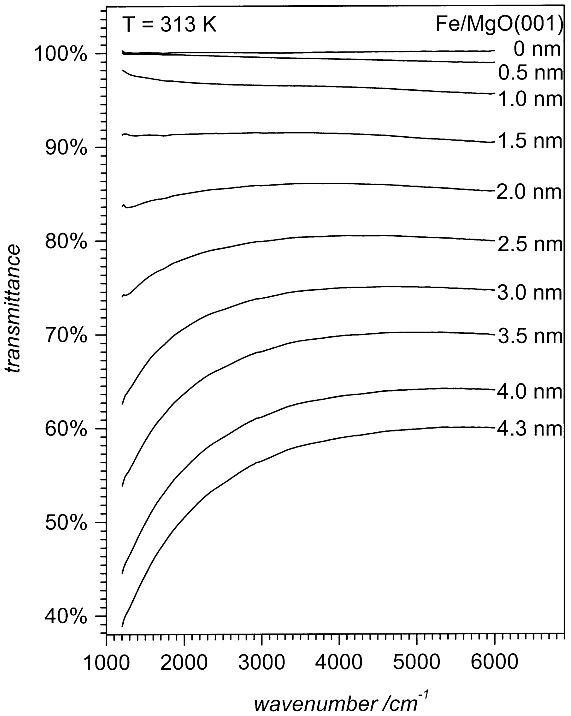

Fig. 1. Relative transmittance of iron films on MgO(001), temperature and film thickness as indicated.

dielectric function], with iron coverage (given in terms of a thickness). Clearly, the spectra contain information about the degree of continuity of the film, i.e., of integration of iron islands. Films much thinner than 0.8 nm are insulating in the static limit. Films thicker than 0.9 nm clearly show the metallic behaviour. Deeper insight into the interpretation of these spectra is given in another paper [16].

Fig. 2 shows the spectral consequences of CO adsorption for three different iron thicknesses for saturation exposures which are about 6 L (regarding IR spectra) for the three films of this adsorption experiment (but which is larger and strongly thickness-dependent for rough iron films, e.g., if evaporated onto KBr [17]). It is seen that there are strong spectral changes of baseline and strong absorption bands in the CO stretching region. At least three well-separated CO peaks appear. They can be attributed to different but well-defined adsorption sites as will be discussed in another paper [18]. Clearly, the strongest line (at about 1960 cm$^{-1}$ for 1 nm of iron) is asymmetric and the shape is different for the three samples. The baseline shift and the asymmetry of IR absorption lines indicate non-adiabatic interaction of CO vibration with electronic transitions.

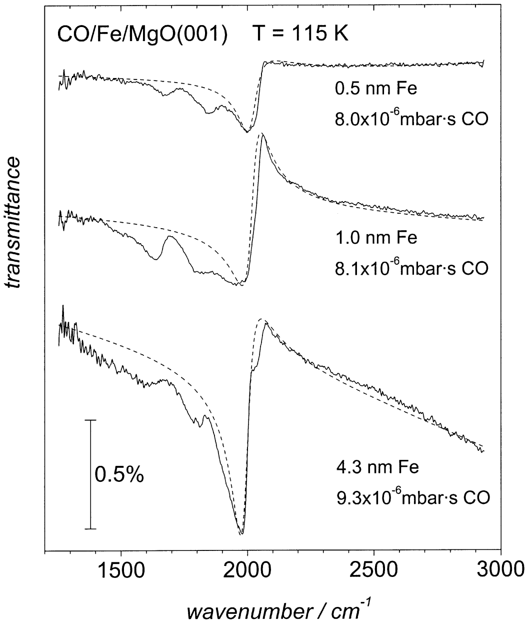

Fig. 2. Relative transmittance of Fe/MgO(001) after CO adsorption (continuous lines represent the experimental spectra, broken lines the Fano-like fit, see text); temperature, CO exposure and iron thickness as indicated. Fit parameters: $\omega_0$ is 2014 cm$^{-1}$ for 0.5 nm, 2023 cm$^{-1}$ for 1 nm and 1987 cm$^{-1}$ for 4.3 nm; $\gamma$ is 103 cm$^{-1}$ for 0.5 nm, 87 cm$^{-1}$ for 1 nm and 77 cm$^{-1}$for 4.3 nm; the asymmetry $\omega_0\tau$ is 0.4 for 0.5 nm, 1.14 for 1 nm and 0.61 for 4.3 nm. $\Theta\mu^2$ corresponds to the oscillator strength. It is (in $10^{-9}$ A V$^{-1}$) 220 for 0.5 nm and for 1 nm, but it is 500 for 4.3 nm.

After a suitable background conformation [18] (which has to be different to the background function used by Langreth) we applied the Fano-like susceptibility model function of Langreth [5,6] [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 $\omega_0$ [18]. The fit curves are shown as broken lines in Fig. 2 (for parameters see figure caption). A comparison of the fit parameters for the three samples yields two interesting pieces of information. The asymmetry (in terms of $\omega_0\tau$) is strongest for 1 nm of iron, which means a just closed film, the 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 of iron, which is the film with the highest conductivity.

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 $\Theta \approx 1.21 \times 10^{19}\ \mathrm{m}^{-2}$ is estimated by assuming full coverage (one on-top CO molecule per surface iron atom) of closely packed iron pyramids with bcc {011} facets tilted by 45° with respect to the substrate. The dipole moment $\mu$ is calculated from the IR peak area of CO on NaCl [19] (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 the substrate are considered, the adiabatic result for $\Theta\mu^2$ is $2.3 \times 10^{-9}\ \mathrm{A\ V}^{-1}$, which is about 200 times smaller than the experimental value for the 4.3 nm film.

Our results indicate Fano-like intensity borrowing [20] as an important contribution to SEIRA. The theoretical condition of a sufficiently strong electric field in the metal [6] is fulfilled for ultra-thin films in the normal transmission experiment. Additionally, the local field for CO adsorbates can be enhanced, especially inside small grooves [21] that still persist while a closed iron film on MgO(001) is continuing to grow [13,15,16].

By IRAS of CO on an annealed, 12.5 nm thick iron film on MgO (film thicker than 10 nm, which is the mean free path of free charge carriers in iron at 2000 $\mathrm{cm}^{-1}$), we observed a symmetric line at 2061 $\mathrm{cm}^{-1}$(for a saturation exposure of about 15 L regarding the IR spectrum) without any enhancement (if assuming monolayer coverage) [18].

## 4. Summary and conclusions

We have shown our first results on SEIRA for small molecules on a relatively well-known system. We observed a Fano-like effect for CO on iron thin films.

In order to increase our understanding it is necessary to investigate further the dynamic conductivity of ultra-thin metal films which is determined by the energy dependence of the optical Drude parameters, by the classical and the quantum size effect, and by the degree of integration of two-dimensionally arranged 3D islands that can change their shape during growth.

It is also important to improve our knowledge about the sticking and molecular orientation of CO on the thin metal films.

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