

Far Infrared Reflection Absorption of CO on Ultrathin Metal Films: Start of Experiments

A. Priebe, G. Fahsold, and A. Pucci (Kirchhoff-Institut f. Physik Heidelberg)

Abstract No. Prie8541

Beamline(s): U4IR

Introduction: Non-adiabatic effects at surfaces should be relevant for surface-enhanced infrared absorption, surface enhanced Raman scattering, catalysis, sensor development, etc. Infrared reflection absorption spectroscopy (IRAS) can give information about such dynamic interactions of adsorbates with the underlying metal. From previous experiments¹⁻⁶ it is known that IR absorption of adsorbate vibrations on metal surfaces could be strongly modified by the dynamic interactions with electronic excitations^{7, 8}. The results are baseline shifts¹ and unusual spectral features like Fano-type adsorbate vibrational lines in transmittance spectra⁴⁻⁶ and anti-absorption peaks in IRAS^{2,3}. These effects should be particularly strong for ultrathin metals⁹.

Methods and Materials: During our first beamtime at U4IR in June 2000 we studied in-situ prepared ultrathin iron films on MgO(001) with respect to far IR spectral changes due to CO for the first time. For the in-situ metal film deposition we used an electron impact evaporator (Omicron) connected to the ultrahigh vacuum (UHV) chamber at the U4IR beamline. The deposition rate was calibrated with the help of Auger spectra from reference films. The MgO surface was prepared by cleavage in air and by heating to 720 K in UHV. The high density of surface defects due to cleavage in air improves the smoothness of iron films compared to Fe on MgO cleaved in UHV¹⁰. The infrared spectra were taken at grazing incidence from 200 cm⁻¹ to 600 cm⁻¹ with the Nicolet Vacuum Magma Interferometer at U4IR and a Si bolometer detector. The intensity reflected from bare MgO and few-nm-iron covered MgO was sufficiently high (not only in the reststrahlen region) to allow sufficiently quick accumulation of spectra.

Results: We were able to characterize the MgO substrate at 100K (the temperature of the CO adsorption experiments) by an analysis of the spectral changes with respect to MgO at room temperature, the optical data of which are well known. Fe deposition strongly changed the reflectivity at the TO phonon frequency of MgO at about 390 cm⁻¹ (see **Figure 1**). Exposure of CO lead to further spectral changes around the TO frequency of MgO. From this step-like structure we can calculate the adsorbate-induced changes of the relaxation rate of the free charge carriers in the metal films. Such additional relaxation leads to baseline shifts in IRAS at surfaces of thick metals with low bulk relaxation rates like Cu⁷ but not to baseline shifts for IRAS of adsorbates on Ni¹¹ and on Fe¹².

Conclusions: With spectroscopy in the UHV chamber at U4IR it is possible to determine the dynamic conductivity of ultrathin metal films and their changes due to adsorbates in the far infrared.

Acknowledgments: We would like to thank the U4IR science staff M. Pilling and C. Hirschmugl for their help in preparing and conducting the experiments. Financial support by the Deutsche Forschungsgemeinschaft is greatly appreciated.

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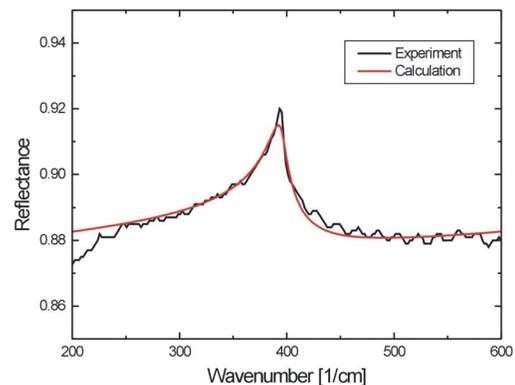


Figure 1. Reflectance of 9 Å Fe (deposited at 300K substrate temperature) on MgO(001) with respect to reflectance of the MgO substrate at 300K. The polarization of the light and the accurate angle of the grazing incident light are as fixed by the optimum beamline optical path. No polarizer was used. Calculation for 70% polarization in the plane of incidence and for 85° as the angle of incidence. For the dynamic conductivity of the iron film a Drude-type model was applied as explained in Ref.10.