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Surface Infrared Spectroscoopy at U4IR

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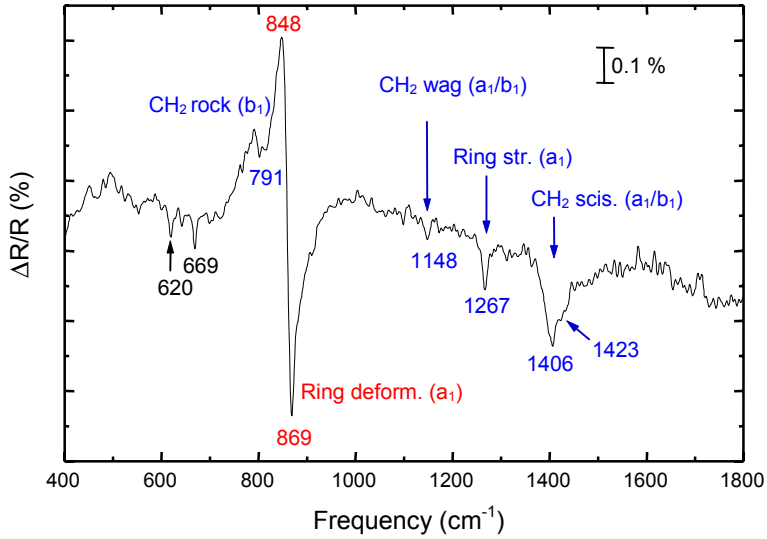
Beamline(s): U4IR

We have recently begun an effort to use infrared surface vibrational spectroscopy (IRAS) as a probe for adsorbate binding and reaction on metal single-crystal and nanoparticle surfaces. These experiments are being performed on the U4IR beam line at the NSLS, whose low frequency capabilities (100 – 1000 cm^{-1}) are ideally suited for investigating vibrational modes that are strongly coupled to bonding to the surface. Initial experiments have focused on the chemisorption of ethylene oxide (EO) on Ag(111) which is related to the selective oxidation of ethylene to ethylene oxide on supported Ag catalysts. Of particular interest is the ring opening reaction of EO to form a Ag-O-CH_2-CH_2-Ag metallocycle which is thought to be the reaction intermediate whereby oxygen atoms are added to the ethylene double bond. As the first step, we obtained the IR vibrational spectrum of EO/Ag(111) at coverages up to a monolayer. The most striking feature in the IRAS spectrum is the band centered around 860 cm^{-1}, which exhibits a persistent "derivative" line shape as shown in the accompanying figure. This band is assigned to the C-O-C ring deformation mode and involves motion of the oxygen atom through which the molecule is bound to the Ag surface. Similar line shapes have been seen in IRAS of CO/Cu(100) and H/Mo(W)(100), and are attributed to a Fano-like interference between a sharp vibrational resonance and the background electron-hole pair excitation continuum. Such non-adiabatic couplings often play a key role in the dephasing of adsorbate vibrational motions and may also lead to desorption via specific modes which are otherwise poorly matched to thermally excited phonons at the metal surface (≤ 150 cm^{-1} for Ag). Theoretical models predict variations in line shape with surface temperature and we are currently investigating this effect, as well as the influence of surface coverage and the density of surface defects.



IRAS spectrum of ethylene oxide adsorbed on Ag(111) at sub-monolayer coverages at a surface temperature of 92 K.