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Vibrational spectroscopy using sum-frequency generation has been used to investigate the coupling between a ferromagnetic thin film and adsorbed molecules, here CO on Ni/Cu(100). The CO stretching vibration exhibits a strong magnetic contrast with a pronounced temperature dependence, underlining the high sensitivity of this adsorbate-specific spectroscopy method. Our results indicate that the strong temperature dependence is caused by dynamical changes in the surface chemical bond when the CO stretch vibration is coupled to thermally excited external vibrational modes. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4822120]

Magnetism in thin films, two-dimensional magnetism, and even single magnetic atoms have received significant attention recently[1–6] because of their potential application in molecular spintronic devices.[7,8] The ultimate information density would be reached by addressing bits in single atoms or molecules which could be arranged regularly on surfaces.[9] Experimental methods addressing the magnetic properties of adsorbed atoms or molecules are therefore highly desired. An interesting question in this context is how a magnetic surface influences the magnetic properties of an adsorbate. In particular, the coupling of the ferromagnetic film to the adsorbed molecules can induce a spin-polarization in a diamagnetic molecule.[10–12] However, such studies are challenging since they require spin-resolved techniques that are also adsorbate specific. Consequently, there are still only few studies on how the magnetic state of the substrate affects adsorbate molecules,[3,5,8,10–14] mainly employing x-ray magnetic circular dichroism (XMCD), which can be performed at synchrotron radiation sources. Here we propose a complementary table-top technique that makes use of second-order non-linear sum-frequency generation (SFG) that is an established vibrational spectroscopy.[15] Sum-frequency generation is the non-degenerate, adsorbate sensitive case of second harmonic generation (SHG). Magnetization dependent SHG (MSHG) is sensitive to the total magnetic moment of the electronic ground state and has proven useful for the study of magnetic thin films.[16]

In the present paper we explore the possibilities of extending non-linear magneto-optical techniques such as MSHG to include adsorbate sensitivity by employing magnetization dependent vibrational SFG (MSFG). In particular we report the magnetization dependent SFG signal of adsorbed CO on Ni(100) and propose MSFG as an approach to investigate the coupling between spin and vibrational degrees of freedom at the interface of a magnetic layer and a non-magnetic molecule. We find a magnetic response of the adsorbate and show that this spectroscopy method provides a local adsorbate probe of the magnetic properties of the adsorption complex.

The experiments were carried out in an ultra-high vacuum chamber with a base pressure below 1×10^{-10} mbar. The Cu(100) crystal was cleaned by cycles of argon ion sputtering followed by annealing to 850 K until a sharp 1×1 low energy electron diffraction (LEED) pattern was obtained. A 13 ML pseudomorphic Ni film[17] was deposited using an electron beam evaporator with an evaporation rate of 0.5 ML per minute. After that 0.5 ML of CO was prepared in a c(2×2) structure at 330 K. The structure was confirmed using LEED and temperature programmed desorption (TPD), which showed one distinct desorption state at 390 K. The sample was magnetized using an electromagnet with a magnetic field of ~100 G along the surface normal, which at 13 ML is the easy axis of the magnetization.[18] The SFG data were taken in remanence to avoid excessive heating of the electromagnet. The experimental geometry is schematically depicted in the top panel of Fig. 1.

The SFG experiments were run in broadband mode[19] and performed using a Ti:sapphire based amplified laser system, which provides laser pulses of 100 fs in duration and 4 mJ of pulse energy centered at 800 nm with a repetition rate of 400 Hz. Mid-infrared (IR) pulses with a full width at half maximum of 120 cm^{-1} and a centre frequency around 2000 cm^{-1} were generated by an optical parametric generator/amplifier with subsequent collinear difference frequency mixing between signal and idler output. The residual 800 nm light from the optical parametric generator/amplifier (OPG/OPA) was spectrally narrowed down to 5–8 cm^{-1} in order to provide a spectrally well-defined pulse, which up-converts the IR frequencies to the visible spectrum.

The induced non-linear SFG polarization $\mathbf{P}_{NL}$ is proportional to the electric fields of both incident beams

$$\mathbf{P}_{NL} = \chi^{(2)} \mathbf{E}_{IR} \cdot \mathbf{E}_{VIS}. \quad (1)$$

The susceptibility tensor $\chi^{(2)}$ comprises both non-resonant and resonant contributions $\chi^{(2)}_{NR}$ and $\chi^{(2)}_{R}$, respectively. The resonant term can be expressed as the coherent sum of
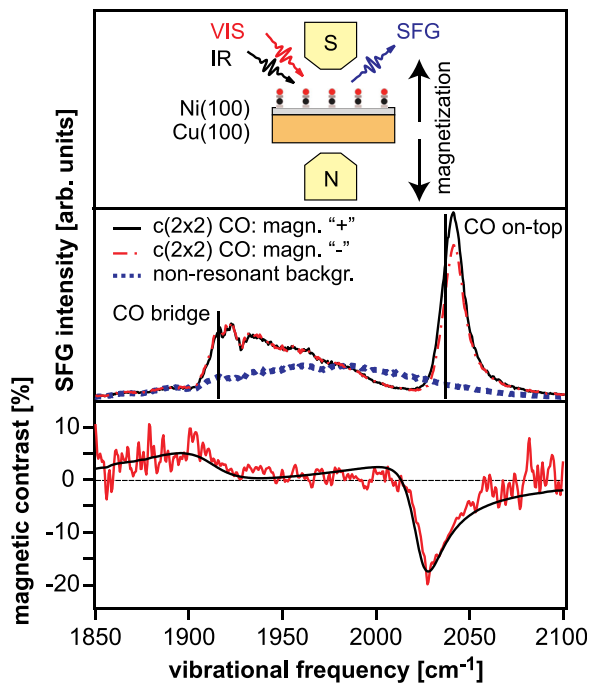
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FIG. 1. Sum-frequency generation of CO on 13 ML Ni/Cu(100) at 110 K. (top) Schematic of the experiment. (middle) Resonant SFG spectra of the CO stretch vibration of molecules adsorbed on-top and at bridge sites, respectively, in the $c(2 \times 2)$ phase for two anti-parallel magnetization directions of the Ni film (denoted by "+" and "−"). The dashed blue line indicates the non-resonant background of the clean Ni film, and the vertical bars mark the fitted resonance positions. (bottom) Spectrally resolved magnetic contrast with distinct features of opposite sign at both CO resonances.

Lorentzians of all probed molecular vibrations covered by the bandwidth of the IR pulse yielding the intensity[15]

$$I_{SFG} \propto |\mathbf{P}_{NL}|^2 \propto |\chi^{(2)}_{NR} + \chi^{(2)}_{R}|^2 I_{IR} I_{VIS} \qquad (2)$$

with

$$\chi^{(2)}_{R} = \sum_n \frac{A_n \exp(i\phi_n)}{\omega_{IR} - \omega_n + i\Gamma_n}, \qquad (3)$$

where A_n, ϕ_n, ω_n, and Γ_n denote the strength, relative phase, resonance frequency, and damping constant of the nth mode.

The middle panel of Fig. 1 displays the SFG spectra of CO adsorbed on 13 ML Ni/Cu(100) containing both resonant and non-resonant contributions.[15] The non-resonant background is determined separately from a bare Ni film and is shown as a dashed line that follows the spectral profile of the infrared pulses. The resonant contributions exhibit two features, at different frequencies, originating from CO stretching vibrations in on-top and bridge adsorption sites. The vibrational frequencies extracted from curve fitting amount to $2037\,\mathrm{cm}^{-1}$ and $1916\,\mathrm{cm}^{-1}$ and agree well with previous infrared absorption[20,21] and SFG[22] studies on CO/Ni(100).

Spectra recorded for different magnetization directions of the substrate are shown as solid and dotted-dashed lines. There is a clear asymmetry in terms of an intensity difference, in particular, around the on-top resonance, between the spectra recorded for the two opposite magnetization directions. The bottom panel of Fig. 1 shows the magnetic contrast, i.e., the

difference between the SFG spectra normalized by the sum of the SFG intensities. The magnetic contrast in our spectra exhibits remarkably large peak values of up to −20% in the frequency region of the on-top CO species. A much smaller contrast of opposite sign is observed for molecules adsorbed at bridge sites, which indicates that the MSFG technique is indeed sensitive to the local environment of the CO-Ni adsorption complex.

For a spin-polarized molecule the observation of the magnetic contrast in MSFG can be understood by analogy with MSHG, where the magnetic contrast is proportional to the magnetization of the substrate.[23] A non-zero magnetic contrast reflects the fact that some tensor components of the nonlinear susceptibility are probed with a different sign upon magnetization reversal. The magnetic contrast can be expected to be polarization dependent. In analogy with MSHG,[24] the MSFG process can be regarded as a $\chi^{(3)}$ process, which connects the nonlinear polarization $\mathbf{P}_{NL}$ with the fields $\mathbf{E} \cdot \mathbf{E} \cdot \mathbf{M}$. Symmetry arguments prevent the magnetically odd component to be observed from incoming waves with the same polarization if the magnetization axis is along the surface normal as in the present case.[23] We recorded the dependence on the polarization of the 800 nm light. As observed in the top panel of Fig. 2, the magnetic contrast vanishes when both incident beams have the same polarization and shows a maximum when the polarizations are perpendicular to each other. Overall, this demonstrates that MSFG indeed probes the asymmetry caused by the magnetic moment via a magneto-optical process similar to MSHG, yet, if tuned close to an adsorbate resonance molecular specificity is achieved with MSFG, as shown in Fig. 1. Given the similar mechanisms governing MSHG and MSFG, one can expect also MSFG to provide a magnetic contrast that is linear with the spin-polarization that is probed.

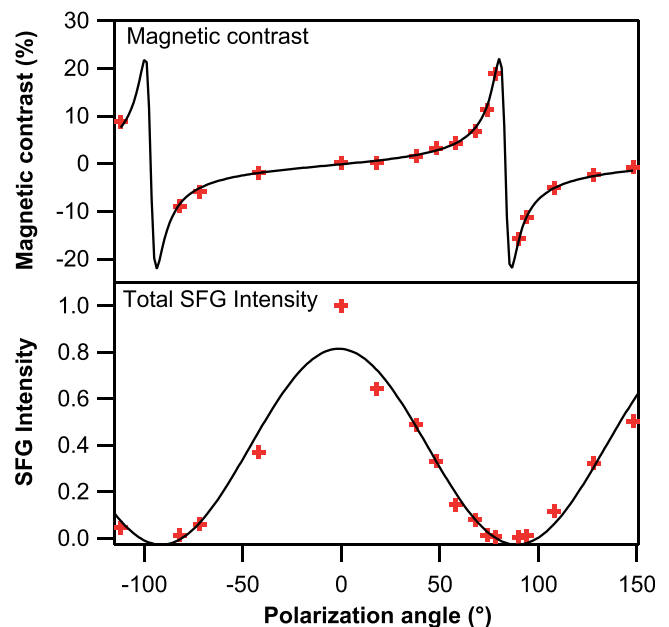

FIG. 2. Polarization dependence of the magnetic contrast (top panel) and SFG intensity (bottom panel). Experimental data points are marked by "+". Fits with the expected 180° periodicity are shown as guides to the eye. The polarization angle is the angle of polarization of the visible light, given in degrees with respect to p-polarization. The infrared light is p-polarized in all experiments.

As shown in Fig. 2 the total SFG intensity vanishes when the contrast has its maximum. A good compromise between signal and magnetic contrast was found when the **E** vector of the 800 nm light was rotated 20° with respect to the surface plane. This geometry was used for the experiments discussed in the present paper.

The peak of the magnetic contrast is clearly spectrally shifted from the peak of the vibrational resonance, which is a consequence of phase shifts between the magnetic and non-magnetic contributions to the signal,[25] resulting in different phases for the SFG resonances recorded for the two magnetization directions. This phase difference will cause the wings around the resonances to decay differently, and the reason is that we observe the maximum magnetic contrast on the low frequency side of the SFG resonance where the intensity is small and the difference between the two magnetic directions is still significant. In order to substantiate this picture we made a curve fit to our SFG data with a function consisting of a non-resonant background and two resonances, each of which has phase shifted magnetically even and odd components. We fitted the SFG spectra to both magnetization directions simultaneously to obtain a common set of parameters where only the sign of the odd component differed. The resulting magnetic contrast is plotted in the bottom panel of Fig. 1. The curve fitting suggests that the different signs of the magnetic contrast for the on-top and bridge resonances correspond to phase shifts in different directions of the magnetically odd component compared to the even component.

The observation of a magnetic contrast on the CO resonance suggests that the CO adsorption complex is spin-polarized. Previous studies have shown that CO indeed possesses some element of spin-polarization when adsorbed onto ferromagnetic surfaces. From oxygen K-edge XMCD experiments an orbital moment in the CO π^* resonance was reported,[10,11] which shows that at least the π^* level is spin-polarized. More recently spin-polarization of also the occupied orbitals of CO/Fe(110) was observed.[12] These findings are in line with calculated spin-polarizations from CO/Fe(100),[26] where orbital symmetry dependent spin-polarizations were observed and together provide a strong indication of a spin-polarized CO adsorbate.

After having established the sensitivity of MSFG to adsorbate spin-polarization and the presence of such spin-polarization in adsorbed CO we now proceed to explore also the coupling between spin-polarization and external low-frequency vibrations that are excited with increasing sample temperature.[27] Vibrational spectroscopies are, in general, sensitive to coupling between internal and external vibrational modes. One can expect that the changes in CO hybridization with the surface due to mixing with low-frequency vibrational modes that distort the adsorption geometry dynamically can affect the adsorbate spin-polarization that we observe with MSFG.

In order to examine this we recorded the magnetic contrast derived from MSFG as a function of sample temperature. Figure 3 displays such a temperature dependence for the CO on-top resonance together with the non-resonant background, which was recorded, here, also with CO adsorbed at the surface but with the IR frequency tuned off resonance in order to keep the same electronic structure as
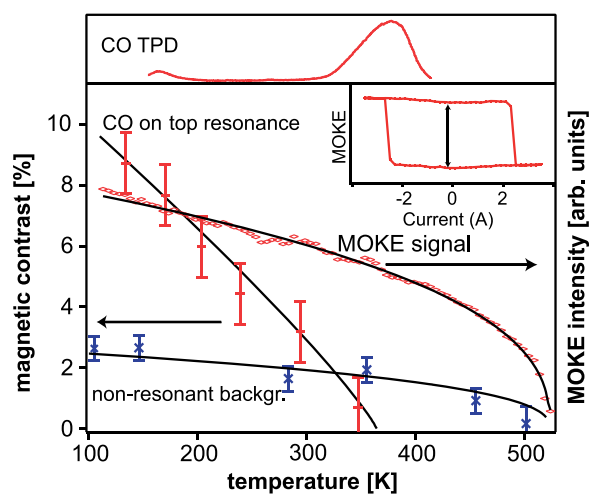

FIG. 3. Temperature dependence of the magnetic contrast derived from the spectrally integrated SFG signal of the CO on-top resonance, the non-resonant SFG background, and the MOKE signal. The top panel shows the corresponding TPD spectrum of CO, with an onset of the thermal desorption rate around 320 K. Note that the resonant SFG magnetic contrast at 350 K was recorded with a CO background pressure of 5×10^{-8} mbar to keep the coverage constant during the measurement. The coverage was confirmed *in situ* by monitoring the spectral position of the CO on-top resonance. The inset shows a MOKE curve recorded at low temperature defining the MOKE intensity plotted in this figure.

for the resonant spectra. Furthermore, the magneto-optic Kerr effect (MOKE) signal is plotted, which is commonly used to determine the magnetization of thin films.[28] Our MOKE data show the expected temperature dependence[29] with a Curie temperature of ~520 K. Note that MOKE is bulk sensitive, and one should not expect any effect from adsorbed CO. No significant changes related to the desorption of CO were observed, and the MOKE signal of the CO covered surface follows the same temperature dependence as that recorded without CO on the surface confirming these expectations. As seen from Fig. 3, the *non-resonant* SFG-derived contrast follows the same temperature dependence as the MOKE signal does. The magnetic moment at the surface thus behaves in the same way as in the bulk of the film with respect to temperature changes.

The magnetic contrast around the CO *resonance* exhibits a significantly steeper decrease with increasing temperature and is close to zero at the highest recorded temperature (~350 K) when the desorption has started and the molecules are highly mobile at the surface. This temperature is slightly below the peak maximum of the TPD (top trace in Fig. 3). At this temperature a background pressure of CO was applied to ensure that the CO coverage was constant during the experiment. The steep temperature dependence of the resonant MSFG contrast is entirely different from that of both the MOKE and the non-resonant background. It suggests that the magnetic properties are different in the close vicinity of the CO from that in the bulk of the Ni film.

The steeper decrease of the temperature dependence of the adsorbate magnetic contrast is similar to that observed for adsorbed paramagnetic molecules.[5,14] In those cases the steep decrease was explained by thermal fluctuations leading to disordering of the paramagnetic moment of the adsorbed molecules due to weak coupling to the surface.

In the present case a similar weak coupling can be expected, but the situation has to be somewhat different since the CO molecules only possess a magnetic moment due to the coupling to the surface. As the coupling is lost, one would expect not only a disordering but also a complete loss of the induced magnetic moment on the CO molecules. The steep decrease of the magnetic moment can thus be taken as an indication of a loss of magnetic coupling to the surface during vibrations.

Other explanations may, however, also explain the present data. Since the SFG technique is only sensitive to changes in dipole moment out of the surface plane a rotation of the magnetic polarization into the surface plane would also result in a loss of magnetic contrast. The on-top and bridge adsorbed CO molecules show magnetic contrasts of different sign, due to different phase shifts. One might thus interpolate between these extremes and propose that as the molecules are heated and gain the energy to start probing lower symmetry positions they will show much smaller magnetic contrast.

At the present stage we cannot unambiguously determine which mechanism is most important in providing this pronounced temperature dependence but leave this question open and welcome further investigations to shed light on this matter. Regardless of the exact mechanism for the steep decrease of the magnetic contrast with temperature, it is clear that the MSFG technique is sensitive to the coupling between spin-polarization of adsorbed molecules and the excitation of external vibrational motion.

In conclusion, we have presented a sum-frequency generation experiment probing the spin-polarization in the CO-Ni adsorption complex. We find a strong magnetic contrast of the CO on-top resonance with a temperature dependence completely different from that of ferromagnetic Ni. Furthermore we find that the properties of the MSFG technique are similar to those of MSHG, with added adsorbate sensitivity. We propose that the pronounced temperature dependence is related to excitation of external adsorbate vibrations with temperature and propose different mechanisms that would be consistent with this observation.

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