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Femtosecond time-resolved vibrational SFG spectroscopy of CO/Ru(0 0 1)

Ch. Hess [a,b], M. Wolf [a,b,*], S. Roke [c], M. Bonn [c]

[a] *Fritz-Haber-Institut der MPG, Faradayweg 4–6, 14195 Berlin, Germany*
[b] *Fachbereich Physik, Institut fur Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany*
[c] *Leiden Institute of Chemistry, P.O. Box 9502, 2300 RA Leiden, The Netherlands*

Abstract

Vibrational sum-frequency generation (SFG) employing femtosecond infrared (IR) laser pulses is used to study the dynamics of the C–O stretch vibration on Ru(0 0 1). Time-resolved measurements of the free induction decay (FID) of the IR-polarization for 0.33 ML CO/Ru(0 0 1) exhibit single exponential decays over three decades corresponding to dephasing times of $T_2 = 1.94$ ps at 95 K and $T_2 = 1.16$ ps at 340 K. This is consistent with pure homogeneous broadening due to anharmonic coupling with the thermally activated low-frequency dephasing mode together with a contribution from saturation of the IR transition. In pump–probe SFG experiments using a strong visible (VIS) pump pulse the perturbation of the FID leads to transient line shifts even at negative delay times, i.e. when the IR–VIS SFG probe pair precedes the pump pulse. Based on an analysis of the time-dependent polarization we discuss the influence of the perturbed FID on time-resolved SFG spectra. We investigate how coherent effects affect the SFG spectra and we examine the time resolution in these experiments, in particular in dependence of the dephasing time.

Keywords: Vibrations of adsorbed molecules; Sum frequency generation; Non-linear optical methods; Carbon monoxide; Ruthenium

1. Introduction

The dynamics of vibrational excitations, energy exchange and relaxation in adsorbate systems is of fundamental importance for a microscopic understanding of molecular processes at interfaces, in particular in surface reactions [1]. Among various vibrational spectroscopies infrared–visible (IR–VIS) sum-frequency generation (SFG) is a surface sensitive non-linear optical technique, which allows to study vibrational spectra of adsorbates and molecular orientations with high sensitivity and molecular specificity even at ambient conditions [2]. Using ultrashort laser pulses the dynamics of energy and phase relaxation of vibrational excited states can be investigated directly in the time domain [3]. For example the energy relaxation time T_1 of the vibrational population induced by an IR pump pulse can be measured by SFG spectroscopy without assumptions about the contribution to the linewidth of pure dephasing and inhomogenous broadening [4].

* Corresponding author. Address: Fachbereich Physik, Institut fur Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany. Tel.: +49-30-838-56060; fax: +49-30-838-56059.

E-mail address: wolf@physik.fu-berlin.de (M. Wolf).

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Furthermore, time-resolved SFG spectroscopy has great potential to investigate reaction intermediates and the coupling between different vibrational modes during the course of a surface reaction, since molecular vibrations of absorbates can provide direct insights into the formation and breaking of chemical bonds at surfaces. In such experiments the reaction is initiated by an ultrafast pump pulse and its temporal evolution is monitored by recording transient SFG spectra of the adsorbate layer on an ultrafast timescale. So far two experiments have been reported using time-resolved SFG spectroscopy as a molecule specific probe. Bandara et al. studied the conversion between two formate species adsorbed on NiO(1 1 1) with 30 ps time resolution [5]. Using femtosecond time-resolved SFG spectroscopy the dynamics of the C–O stretch vibration on Ru(0 0 1) and its coupling to low-frequency vibrational modes have been studied after femtosecond laser excitation leading to desorption of CO [6]. In the latter experiments IR-broadband SFG spectroscopy was employed to record vibrational snapshots without tuning the IR frequency.

The technique of SFG relies on the fact that the second-order non-linear susceptibility is non-vanishing at the interface of centro-symmetric materials [2]. This enables the generation of an electric field oscillating at the sum frequency of the two incidents fields, where energy and parallel momentum must be conserved. If the incident IR field is resonant with a vibrational transition, the signal is resonantly enhanced. For the broadband-IR pulse in our experiment, this enhancement will occur only at frequencies within the IR bandwidth that are resonant with the vibrational transition [6–8].

The principle setup for the three different types of broadband-IR SFG spectroscopy described in this paper is shown in Fig. 1. In all three experiments, a broadband (temporally short) IR pulse induces an IR-polarization (i.e. a coherent oscillation of CO dipoles). This macroscopic vibrational polarization decays due to dephasing (typically within a few picosecond) as the different CO molecules lose their mutual phase relation and no longer interfere constructively (although the individual molecular dipoles may still oscillate). In

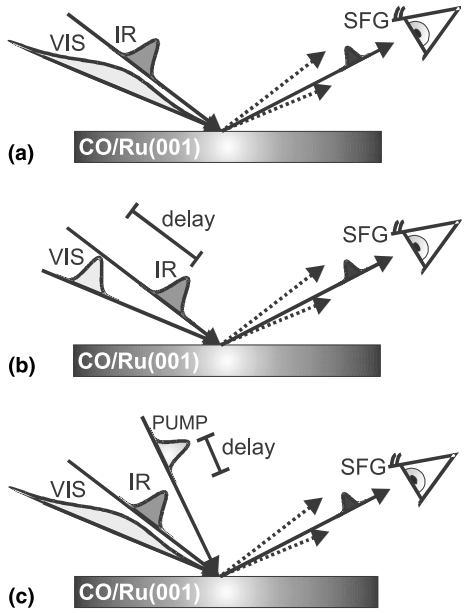

Fig. 1. Principle of (time-resolved) broadband-IR SFG spectroscopy: (a) scheme for broadband-IR–VIS SFG spectroscopy; (b) scheme for time-resolved SFG spectroscopy for T_2 determination. The transient vibrational polarization induced by a fs-IR pulse is upconverted with a fs-VIS pulse; (c) scheme for pump/SFG-probe spectroscopy. Broadband-IR SFG spectroscopy is used as a probe method to monitor the changes of the adsorbate/substrate system induced by a pump pulse (see text).

the first type of experiment (frequency-resolved broadband-IR SFG spectroscopy, Fig. 1a), the whole time-trace of the polarization induced by the IR pulse is upconverted to a virtual electronic level with a temporally long (i.e. spectrally narrow) VIS pulse. The width of the resulting spectrum of the emitted SFG light is solely determined by the vibrational resonance (and the experimental frequency resolution) because the linewidth of the VIS pulse is very narrow, and the spectral components of the IR-polarization are determined only by the vibrational resonance, and not by the width of the IR pulse. Hence, in this type of experiment one has excellent frequency resolution that can be used to determine the vibrational linewidth Γ. This approach of frequency-resolved broadband-IR SFG spectroscopy allows to record vibrational SFG spectra with extremely high sensitivity using multi-channel detection ($<10^{-3}$ ML for CO on Ru(0 0 1) [9]).

In a second experiment, shown schematically in Fig. 1b, the time-evolution of the IR-polarization is measured, which is the so-called time-resolved free induction decay (FID) measurement. Again, an ultrashort IR pulse coherently excites the CO oscillators which decay due to dephasing. The buildup and decay of the vibrational polarization can be probed with an ultrashort VIS upconversion pulse which is delayed with respect to the IR pulse. The emitted SFG signal is spectrally integrated and recorded as a function of delay between the IR and VIS pulses. From the exponential decay of the SFG intensity at positive delays between the IR and VIS pulse the dephasing time T_2 is obtained. Since the upconversion pulse is temporally short, this type of experiment does not allow for spectral resolution. It should be noted that the time-resolved FID experiment is the time-domain equivalent of the frequency-domain SFG experiment, since the linewidth can be related to the dephasing time according to $\Gamma = 2/T_2$ for a homogeneous linewidth [3].

For real-time probing of photoinduced surface reactions using SFG as a molecule specific probe a three pulse pump-probe scheme is used. The principle of this pump/SFG-probe spectroscopy is depicted schematically in Fig. 1c. An intensive fs-pump pulse induces a surface reaction (e.g. desorption or dissociation) and the resulting transient changes of an adsorbate vibrational mode are probed by broadband-IR SFG spectroscopy by varying the delay between the pump pulse and the pair of SFG probe pulses. Note, that in this configuration the time delay between the broadband IR and the narrowband VIS upconversion pulse is kept fixed. An important advantage of this approach is that it provides both temporal and spectral resolution: the time resolution in this experiment is determined by the duration of the pump and the IR pulses (as in Fig. 1b), whereas the frequency resolution is determined by the spectral width of the VIS-upconversion pulse (as in Fig. 1a). However, the SFG spectrum is determined by the Fourier transform of the time-dependent polarization induced by the IR pulse. Therefore, the perturbation of the FID by the pump pulse will affect the time-resolved SFG spectrum, resulting in pump-induced changes in the SFG signals even at delay times below zero. Also, time-dependent changes of the vibrational frequency (e.g. due to transient heating and cooling of the surface) have to be taken into account. It is the intention of this paper to discuss these effects, especially the influence of the FID on the transient SFG spectra and the time resolution of this pump/SFG-probe scheme.

2. Experimental

The experiments were carried out in an ultrahigh vacuum chamber (base pressure 10^{-10} mbar) equipped with standard surface science tools. A commercial Ti:sapphire laser system delivers 800 nm, 110 fs pulses with a pulse energy of 4.5 mJ at 400 Hz. For the time-resolved experiments reported here the repetition rate is reduced to 20 Hz to minimize the effect of surface heating. For the pump/SFG-probe measurements one third of the pulse energy is used to excite the surface with a 800 nm "pump" pulse (typical absorbed fluence 55 J/m^2). [1] The remaining energy is used to pump an OPG/OPA providing tunable ($\lambda = 2$–10 μm), broadband-IR pulses (bandwidth ~150 cm^{-1} (FWHM)) with an energy of typically 20–30 μJ and approximately 150 fs pulse duration. The portion of the 800 nm pulse which is not converted in the OPG/OPA-process is spectrally narrowed down to 7 cm^{-1}, and is used for upconversion to obtain spectrally resolved SFG spectra (see Fig. 1a and c). In case of time-resolved measurements of the FID (FID-SFG) the ultrashort "pump" pulse (800 nm, 110 fs, ~30 J/m^2) is used for upconversion of the IR-polarization (Fig. 1b). The SFG signal which is radiated from the surface is focused into a spectrograph with a 1200 g/mm grating and dispersed across an intensified CCD detector. For all experiments reported here a $(\sqrt{3} \times \sqrt{3})$-CO structure on Ru(0 0 1), corresponding to a CO coverage of 0.33 ML, was prepared starting form

[1] The reported fluences were corrected to reproduce the frequency shift of the C–O stretch for $T < 400$ K and are consistent with the fluences determined from the beam profile [10].

saturation coverage followed by annealing according to Ref. [10]. An extensive description of the complete experimental set-up as well as the procedure for surface cleaning and characterization can be found elsewhere [10,11].

3. Results and discussion

3.1. Free induction decay

In the following we discuss the time-resolved measurements of the FID (FID-SFG) of CO/Ru(0 0 1), as schematically depicted in Fig. 1b. The top panel of Fig. 2 depicts a monologarithmic plot of the spectrally integrated SFG intensity versus the IR–VIS delay of the C–O stretch at 95 K and a coverage of 0.33 ML. In order to perform the FID experiments with high temporal resolution ultrashort VIS-upconversion pulses are used. As has been shown theoretically [12], for negligible overlap between the IR and VIS pulse, T_2 does not dependent on the shape of the pulses. From the exponential decay of the SFG intensity at positive delays ($I_{SFG} \sim e^{-t/\tau}$) the dephasing time $T_2 = 2\tau$ is determined to be 1.94 ± 0.02 ps at 95 K. [2] In an earlier FID study of the C–O stretch of CO/Cu(1 1 1) at 93 K a similar value of $T_2 = 2 \pm 0.3$ ps was obtained [13]. The solid line through the data represents the result of a calculation for a two-level system using the optical Bloch equations including spatial effects due to the finite spot sizes and the angles of the laser beams overlapping at the surface [6]. An important result of this measurement is that the FID can be described by a single exponential decay over several orders of magnitude. This corresponds to a Lorentzian lineshape in the frequency domain and therefore a homogeneously broadened vibrational resonance.

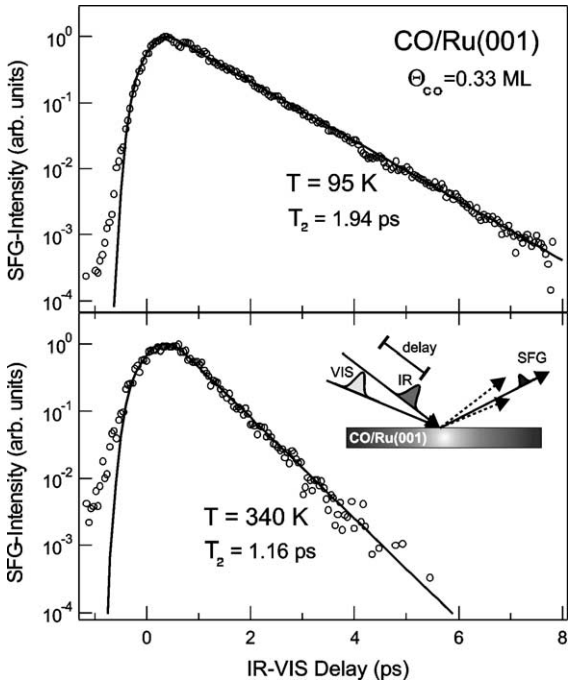

Fig. 2. FID of the C–O stretch vibration of CO on Ru(0 0 1) at temperatures of 95 and 340 K and a coverage of 0.33 ML, together with the result of a calculation according to a two-level system as solid line. The scheme for time-resolved SFG is shown schematically as inset. At 95 K a dephasing time T_2 of 2 ps (top) is observed, at 340 K $T_2 = 1.2$ ps (see text).

To study the influence of temperature on the dephasing time the FID of the C–O stretch was recorded also at 340 K. The experimental data is shown at the bottom of Fig. 2 together with the result of the two-level calculation (solid line). At this temperature T_2 is determined to be 1.16 ± 0.04 ps. Comparison with the value of T_2 obtained at 95 K shows that the C–O stretch vibration dephases faster at higher temperature. Both population relaxation and pure dephasing contribute to the width of a homogeneously broadened line according to $\Gamma = 2/T_2 = 1/T_1 + 2/T_2^*$ [14], with T_2 the overall dephasing time, T_1 the population lifetime, and T_2^* the pure dephasing time. The T_1-population decay of the high-frequency C–O stretch on Ru(0 0 1) is attributed to electron–hole pair excitation in the substrate [15] and can be regarded to be temperature independent [16]. Therefore the temperature dependence of T_2 must originate from pure dephasing. From previous FTIR studies on CO/Ru(0 0 1) it is well known that the dephasing of the high-frequency C–O stretch is due to anharmonic coupling to the low-frequency frustrated translational mode (47 cm^{-1})

[2] Note, that T_2 describes the exponential decay of the IR-polarization (i.e. $I_{SFG} \sim |P(t)|^2$).

[17]. The increasing rate of population in this low-frequency mode with increasing temperature leads to faster dephasing of the C–O stretch vibration which is associated with a faster decay of the IR-polarization.

According to this FTIR study, increasing the temperature from 100 to 350 K leads to an increase in linewidth from 3.5 cm^{-1} to about 4.6 cm^{-1}, respectively [17]. From our time-resolved measurements we obtain a linewidth $\Gamma = 2/T_2$ of 5.5 cm^{-1} at 95 K and 9.2 cm^{-1} at 340 K. The larger linewidth compared to the FTIR result is attributed to a contribution from saturation of the fundamental transition of the C–O stretch with the IR pulse. Due to dipole–dipole coupling between the CO molecules, which leads to energy delocalization within the adlayer, saturation of the IR transition does not lead to a spectrally separated excited-state absorption but an increase in linewidth due to excitation and vibrational energy delocalization, as has been demonstrated previously [18]. The different contributions to the linewidth from saturation broadening at 95 and 340 K are attributed to the slightly different diameters of the IR focus used in the FID experiments.

To summarize this part, the FID contains information on the vibrational lineshape. The observed monoexponential decay over three decades strongly suggests that homogeneous broadening dominates the linewidth. With this approach the linewidth can be studied directly in the time domain, but due to the small intensity of the SFG signal saturation effects could not be avoided in the present study. As shown above, these effects can significantly affect the measured linewidth. Nevertheless, it should be noted that the temporal evolution of the vibrational polarization can strongly influence transient SFG spectra obtained in pump/SFG-probe experiments, as will be shown in the following.

3.2. Time-resolved sum-frequency generation

In a pump/SFG-probe experiment according to Fig. 1c the time-domain vibrational polarization $P(t)$ is upconverted with a temporally long (spectrally narrow) upconversion pulse. One of the goals of such an experiment is to obtain the time-dependent frequency $\omega(t)$ and linewidth $\Gamma(t)$ of a vibrational resonance of reaction intermediates, since these quantities contain information about the potential energy surface and the relaxation dynamics along the reaction pathway. The pump-induced changes in $\omega(t)$ and $\Gamma(t)$ will occur during the buildup and decay of the polarization $P(t)$ induced by the IR probe pulse. Ideally, one would like access directly the instantaneous frequency and the linewidth $\omega(t)$ and $\Gamma(t)$, but this is impossible due to limitations imposed by the finite time-bandwidth product. In the pump–probe experiments of Fig. 1c we essentially obtain the Fourier transform of $P(t)$, which in principle contains all the information about $\omega(t)$ and $\Gamma(t)$. To extract this information a careful analysis based on model calculations is required [19].

Fig. 3 shows transient SFG spectra of the C–O stretch after excitation with 800 nm/110 fs pump pulses, starting at a temperature of 340 K and a

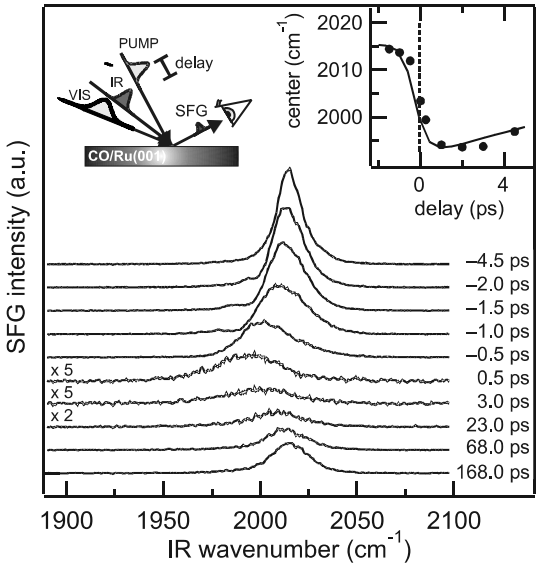

Fig. 3. Transient SFG spectra of the C–O stretch vibration after excitation with 800 nm/110 fs pump pulses with a fluence of 55 J/m^2, starting at a temperature of 340 K and coverage of 0.33 ML. Under these conditions CO desorption takes place. The scheme for the pump/SFG-probe experiment is shown schematically as inset. As indicated by the dashed line at zero delay the C–O stretch frequency shifts already at negative delay times due to the perturbed FID of the vibrational polarization (see text).

coverage of 0.33 ML [6]. The excitation by the pump pulse results in a transient heating of the surface to approximately 1000 K, leading to desorption of about 50% of the CO molecules. Under these extreme conditions the C–O stretch frequency exhibits a strong transient redshift, which is the result of anharmonic coupling of the C–O stretch to low-frequency frustrated modes [6,8,15]. As indicated in the inset, this frequency shift sets in already at negative delays between the pump and the SFG probe and is a consequence of the finite decay time of the vibrational polarization induced by the IR pulse. As shown above, the IR-polarization of the C–O stretch decays with a time constant $T_2 = 1.2$ ps at 340 K. Therefore, on the timescale of this decay, the pump pulse disturbs the FID (perturbed FID) leading to spectral changes even at negative delays, as can be seen, for example, at a delay of -0.5 ps (Fig. 3). A similar behavior has been observed previously for CO/Pt(1 1 1) [20].

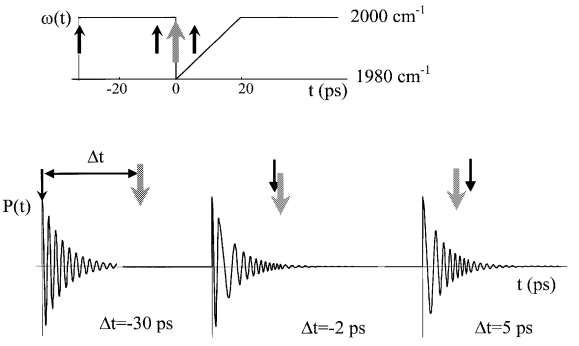

Fig. 4. Description of the model used to study the effect of the FID induced by an ultrashort IR pulse on the transient SFG spectra. Top: The pump-induced frequency response of the vibrational resonance used to model TR-SFG spectra. The resonance frequency $\omega(t)$ of the C–O stretch is assumed to respond instantaneously to the excitation by the pump pulse and to relax to its original value linearly within 20 ps. For pump–probe delay times of -30, -2 and 5 ps and $T_2 = 1$ ps the time dependence of the induced polarization $P(t)$ is depicted.

3.3. Modeling of time-resolved SFG spectra

To obtain insights how the transient SFG spectra are influenced by a perturbed FID we have performed model calculations of time-resolved SFG spectra for a simple scenario of the time-dependent frequency $\omega(t)$ and linewidth $\Gamma(t)$ of a vibrational resonance. In this model, which is illustrated in the upper panel of Fig. 4a, the frequency of the resonance (the C–O stretch) is assumed to shift instantaneously upon excitation with the pump pulse. Such a scenario would correspond to an ultrafast (electron-mediated) excitation of the adsorbate. Although CO desorption from a Ru(0 0 1) surface is known to be a phonon-driven process with a finite coupling time between the phonons and the adsorbate [10], the assumption of the model used here allows us to separate the effect of the perturbed FID from the finite energy transfer rate between the substrate and the adsorbate. In the model a shift of the resonance frequency back to its original value is chosen to occur linearly with time on a timescale of 20 ps as shown in Fig. 4. This approximation allows us to obtain analytical solutions for the SFG spectra. We calculate the SFG spectrum at various time delays Δt between the pump and the IR pulse of the SFG probe according to the following equation (as in [19]):

$$I_{\mathrm{SFG}}(\omega, \Delta t) \sim \left| \int \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\omega t} P_{\mathrm{IR}}(t; \Delta t) E_{\mathrm{VIS}}(t) \right|^2$$

Here $P_{\mathrm{IR}}(t; \Delta t)$ is the time-dependent polarization at a given delay time Δt – this quantity depends parametrically on the delay time – as determined by:

$$P_{\mathrm{IR}}(t; \Delta t) = \chi(t; \Delta t) E_{\mathrm{IR}}(t)$$

with $\chi(t, \Delta t)$ being the time domain susceptibility representing the vibrational resonance. For simplicity the IR field E_{IR} is assumed to be a delta-function and the VIS field a continuous-wave field. These approximations hardly affect the outcome of the calculations, as evidenced by comparison to full numerical calculations using the two-level Bloch equations [6,19]. For the sake of clarity and simplicity, the linewidth or, equivalently, the dephasing time is kept fixed. The calculated spectra are depicted centered around the IR-resonance ω_0.

The lower panel of Fig. 4 depicts the time-dependent polarization $P(t)$ for $T_2 = 1$ ps, at delays of -30, -2 and 5 ps between the pump and the

IR pulse. At large negative delay ($\Delta t = -30$ ps), the pump pulse arrives long after the probe pulse, which is too late to perturb the decay of the coherent polarization. As the polarization, $P(t)$, oscillates with the frequency of the vibrational resonance, it also changes when the resonance frequency changes after the excitation by the pump pulse. If this frequency change occurs at small negative delays (e.g. -2 ps) the polarization changes on a timescale of the dephasing time T_2. At small positive delays $P(t)$ also changes with time. As the SFG spectrum is determined by the Fourier transform of $P(t)$, a change in the polarization necessarily results in a change of the SFG spectrum. A larger T_2 corresponds to a longer decay time of the polarization and hence a large time window to modify $P(t)$ and hence the SFG spectrum. This is demonstrated in Fig. 5 which compares calculated SFG spectra for the pump-induced frequency changes of Fig. 4 at several delay times. The upper panel shows three SFG spectra for $T_2 = 1$ ps which approximates the situation of the pump/SFG-probe experiment at 340K with respect to the dephasing time (see Figs. 2 and 3). At -30 ps a single Lorenzian peak appears because the pump pulse arrives long after the IR puls, where $P(t)$ has already decayed and is not perturbed by the pump pulse. For delay times of -2 and 5 ps $P(t)$ changes during its decay, resulting in SFG spectra with a distorted lineshape which is not present at $\Delta t = -30$ ps.

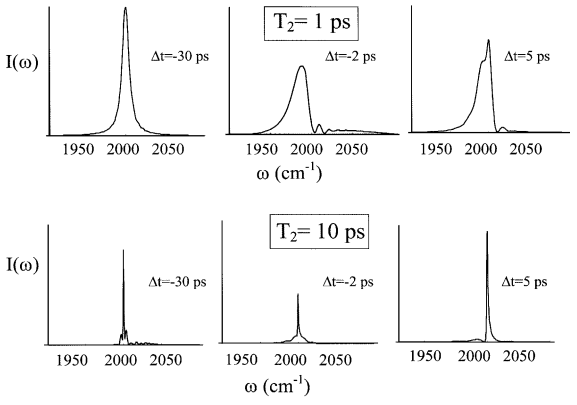

Fig. 5. TR-SFG spectra for the pump-induced change in Fig. 4 at delay times -30, -2, 5 ps and $T_2 = 1$ ps (upper panel) and $T_2 = 10$ ps (lower panel). The thick arrows indicate the pump pulse while the thin arrows represent the probe pulse. For delays $\Delta t \gg T_2$ the pump pulse has no influence on the decay of the vibrational polarization leaving the SFG spectrum undistorted (see text).

These effects become even more pronounced when T_2 is increased to 10 ps (lower panel of Fig. 5). A longer T_2 leads to a smaller linewidth and a slower decay of the polarization. If $P(t)$ is set up 30 ps prior to arrival of the pump pulse, there will still be some vibrational polarization at the surface, which will be modified by the pump. The SFG spectrum for -30 ps is therefore no longer a single peak. Fig. 5 demonstrates that quite different SFG spectra can be obtained within the time span of T_2. The results of our model calculations show qualitatively that in a pump/SFG-probe experiment in which the dynamics of a vibrational resonance is investigated, unperturbed SFG spectra are expected to be observed only for negative delays much longer than the dephasing time, i.e. for $\Delta t \ll -T_2$, so that the polarization has fully decayed when the pump pulse arrives. In case of the C–O stretch vibration of CO/Ru(0 0 1) the frequency shift at negative delays (see Fig. 3) clearly demonstrates the perturbation of the FID by the pump pulse due to the finite decay time of the vibrational coherence.

An important question which arises from the observed pump-induced spectral changes is how the time-resolution of our pump/SFG-probe scheme is influenced by the dephasing time T_2. Fig. 6 shows three calculated SFG spectra at pump–probe delays of 200 fs, 1.2 ps and 3.0 ps, for $T_2 = 1$ ps. The pump-induced frequency response used in this calculations is same as in Fig. 4. Even for relatively closely spaced delay times the SFG spectra are clearly different. To quantify the change in the SFG spectrum, we use the absolute difference ΔI between two integrated SFG spectra at a given delay time and zero ($\Delta t = 0$). Comparing this difference ΔI (i.e. the change in the SFG spectra) for the same T_2 yields a measure of the achievable time resolution. Fig. 6 shows ΔI as a function of the delay time for three different dephasing times. The dashed line indicates a 1% change in the integrated spectrum of $T_2 = 1$ ps at zero pump–probe delay—as an estimate of the experimental sensitivity. It can be seen that a larger T_2 would lead to a better

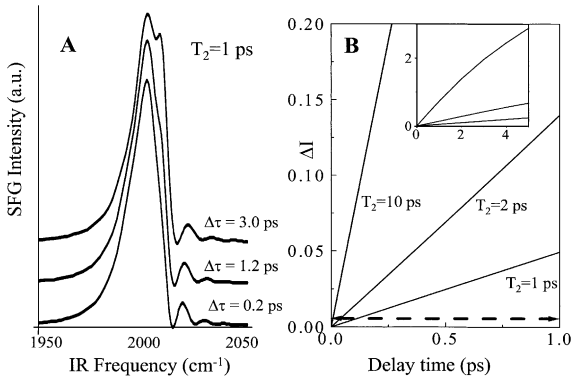

Fig. 6. Calculations illustrating the time resolution in the time-resolved SFG experiment: (A) SFG spectra for $T_2 = 1$ ps at delay times of 200 fs, 1.2 and 3.0 ps. The transient change in the frequency is same as in Fig. 4. (B) A plot of the fractional change in the integrated SFG intensity ΔI vs delay time Δt for $T_2 = 1$, 2 and 10 ps. The straight dashed line indicates a 1% change in a SFG spectrum at zero delay for $T_2 = 1$ ps as an estimate of the typical experimental sensitivity. The inset shows the changes for larger delay times.

time resolution (more rapidly developing changes in the spectrum as a function of delay time). Although this result may seem counter-intuitive as the polarization decays slower, it is a consequence of the fact that the SFG intensity is determined by the Fourier transform of the time-dependent polarization. For longer T_2's the spectral features are sharper, and therefore more sensitive to (small) changes of the polarization. However, it should be noted that within the time window of T_2 a detailed understanding of the experimental results is accessible only via a detailed model, which describes the relaxation dynamics as well as the frequency shifts as a function of time.

4. Summary

In summary, time-resolved SFG spectroscopy is demonstrated to be a powerful tool to study vibrational dynamics at surfaces directly in the time domain. Measurements of the FID (FID-SFG) allow to determine the dephasing time T_2 as shown for CO/Ru(0 0 1) ($T_2 = 1.94$ ps at 95 K and $T_2 = 1.16$ ps at 340 K). In pump/SFG-probe experiments one needs to carefully consider coherent effects to extract the relevant information from the data. In particular, these effects give rise to spectral changes even at negative delay times, and their impact on the time resolved SFG spectrum increases in magnitude with increasing dephasing times T_2. For CO on metal surfaces, due to the small T_2 value of a few ps, this does not appear to be a major constraint. On the other hand, to obtain insight into the response of the system at very short delay times ($\Delta t \leqslant T_2$), additional information and analysis based on model calculations is necessary.

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