Coherent Processes at Surfaces: Free-Induction Decay and Photon Echo of the Si-H Stretching Vibration for H/Si(111)

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Using short infrared pulses and sum-frequency up-conversion, the dephasing of the transient polarization of the Si-H adsorbate-substrate vibration is followed in real time. At 120 K, dephasing due to homogeneous linewidth or inhomogeneous broadening are separated.

The vibrational spectra of adsorbates on surfaces have been a major source of information on their bonding and their various sites of adsorption.[1,2] In addition, when the linewidth is homogeneous, its temperature dependence can be used to obtain important information about the dynamics of the molecule-surface interaction.[2-4] Indeed, the dephasing time T_2 is given by the linewidth since $\Delta\omega = 2/T_2 = 1/T_1 + 2/T_2^*$. Combined with measurements of the vibration lifetime T_1, the pure dephasing time T_2^* can be extracted. Unfortunately, even single-crystal surfaces have some defects, so that inhomogeneous broadening can become the major source of the linewidth, preventing the extraction of dynamical information. It is therefore of fundamental interest to be able to separate the homogeneous linewidth out of an inhomogeneous line. In bulk and gaseous media, this has been achieved with techniques such as the photon echo[5] or hole burning. Extending these to surfaces would be a very valuable improvement. For adsorbates on surfaces, persistent hole burning has been demonstrated in the visible range[6] but the weak photophysical effects of vibrational excitations may prevent its application to the infrared range. For photon echos, difficulties are the small amount of scatterers available on a surface (10^{14} cm^{-2}) and the need to discriminate the bulk signal. Lately, the nonlinear optical technique of sum-frequency generation (SFG) was shown to be a versatile surface vibrational spectroscopy.[7] With ultrafast time resolution, a surface photon echo should be observable.[8]

This Letter presents the first observation of coherent processes, free-induction decay (FID) and photon echo, for the stretching vibration of the monohydride Si-H of the ideally H-terminated silicon (111) surface. This highly ordered surface, chemically prepared,[9,10] has been well characterized experimentally and theoretically.[10-12] Surface infrared spectroscopy has shown that the stretching vibration (at 2083.7 cm^{-1} at room temperature) has a temperature-dependent linewidth due to dephasing from a weak anharmonic coupling with 210 ± 25-cm^{-1} silicon phonons.[10] This is in accord with the recent observation of several surface phonon bands (with distinct polarization) in this range.[11,12] To determine if one specific phonon band is responsible for the Si-H

linewidth, high-resolution linewidth measurements at lower temperature are needed. However, such measurements with 0.06-cm^{-1} resolution show a linewidth limited to 0.3–0.2 cm^{-1} below 150 K, depending on the sample preparation and UHV introduction.[13] In contrast, the lifetime T_1 of the vibration is about 1.4 ns at 120 K implying a lifetime-limited linewidth of only 0.004 cm^{-1}.[14] It is therefore important to determine whether the remaining linewidth is due to inhomogeneities of the system and to extract the homogeneous linewidth. In this work, FID and photon echo at 120 K show clearly that the linewidth is inhomogeneous. The measured natural linewidth ($0.12 + 0.01$ cm^{-1}) favors the phonon at 190 cm^{-1}, perpendicularly polarized, as the source of dephasing.

In the experiment, a coherent vibrational polarization of the adsorbate is induced by short resonant infrared pulses and its evolution is then monitored by up-conversion with surface infrared-visible SFG.[7] In this scheme the electronic polarizability seen by an incident visible pulse $E_{vis}(x,t)e^{i\omega_{vis}t}$ is modulated by the Raman tensor $\partial\alpha/\partial q$ and the coherent vibrational polarization between the $v=0$ and $v=1$ states, $\mu_{01}(x,t)e^{i\omega_{01}t}$. This gives rise to a coherent polarization at the sum of the frequency, $P_{sf}(x,t)$,

$$P_{sf}(x,t) = N\frac{\partial\alpha}{\partial q}\left[\frac{\partial\mu}{\partial q}\right]^{-1}\mu_{01}(x,t)E_{vis}(x,t), \quad (1)$$

where N is the surface density of adsorbates and q is the normal mode. This sum-frequency polarization generates a coherent radiation with an intensity proportional to $|P|^2$ so that the SFG follows the square of the magnitude of the vibrational polarization. The surface wave vectors $k_{01,x}$ of $\mu_{01}(x,t)$ and $k_{vis,x}$ of $E_{vis}(x,t)$ determine the direction of the SFG such that $k_{sf,x} = k_{01,x} + k_{vis,x}$. If the vibration is excited by a single pulse, its polarization decays with time due to the loss of coherence of the oscillators. This is the free-induction decay. For a sequence of pulses, there are echos in the vibrational polarization that are reflected in the SFG.

A flash-lamp–pumped Nd-doped yttrium-aluminum-garnet laser, with an intracavity GaAs plate, generates short pulses at 1.064 μm (10 Hz, 11 ps, 40 mJ).[15] The

tunable infrared (4–7 μm, 7 ps, 60 μJ, 4-cm^{-1} bandwidth) radiation is obtained by the difference-frequency technique from the 1.064-μm laser and a near-infrared dye laser in a AgGaS$_2$ crystal.[16] Visible light at 0.532 μm is obtained by doubling the 1.064-μm radiation in a 1-cm potassium dihydrogen phosphate crystal. The cross correlation of the visible and ir pulse obtained by SFG from a silver surface is 11 ps (FWHM) with a 4-ps decay time over the first 2 orders of magnitude. This gives the time resolution of the experiment. For the measurements, three beams are needed. The visible beam is incident on the sample with 100 μJ over 1 mm^2 at 57° incidence. The ir is split into two beams, ir1 and ir2. ir1 is incident on the sample with 4 μJ at 50° and ir2 with 35 μJ at 73°. Both are focused to about 400 μm. They can be attenuated with thin Mylar sheets. All beams are p polarized.

The samples are polished silicon (111) wafers oriented at less than 0.5°. After chemical preparation, the sample is introduced into a UHV chamber under argon flow. The chamber is first slowly pumped with a sorption pump, and then a turbomolecular pump brings the pressure down to 1×10^{-9} mbar in 16 h.[14] The sample is clamped to a stainless-steel reservoir which can be filled with liquid nitrogen. The lowest temperature achieved on the sample surface is 120 ± 5 K. It is facing a sapphire window which is used as the entrance and exit window for the laser beams.

For the FID, one monitors the decaying vibrational polarization after only one excitation pulse. One of the two infrared beams is therefore blocked and the surface polarization is monitored by SFG with the visible beam coming at a variable delay. The results are shown in Fig. 1(a) for two different temperatures, 300 and 120 K. The signals were about 500 times larger than the noise (0.01 count/shot). 13- and 35-ps polarization decay times are observed at 300 and 120 K, corresponding to 0.8- and 0.3-cm^{-1} linewidth. This is in fair agreement with infrared measurements.[9,10]

For quantitive purposes, one assumes a Gaussian distribution of frequencies of variance σ for the inhomogeneous broadening and one also assumes a two-level system. This is justified here because the anharmonicity of the Si-H stretching vibration should be about 60 cm^{-1},[17] very large compared to the linewidth. For pulses much shorter than the coherence times, the polarization induced by a resonant field is calculated simply.[5,18] In the case of a single excitation pulse at time 0, the surface polarization remaining at time $t > 0$ is

$$\mu_{01}(x,t) = i\mu_{01}\sin\theta_j \exp(-t/T_2)$$
$$\times \exp(-2\pi^2\sigma^2 t^2)\exp(-ik_{j,x}x), \quad (2)$$
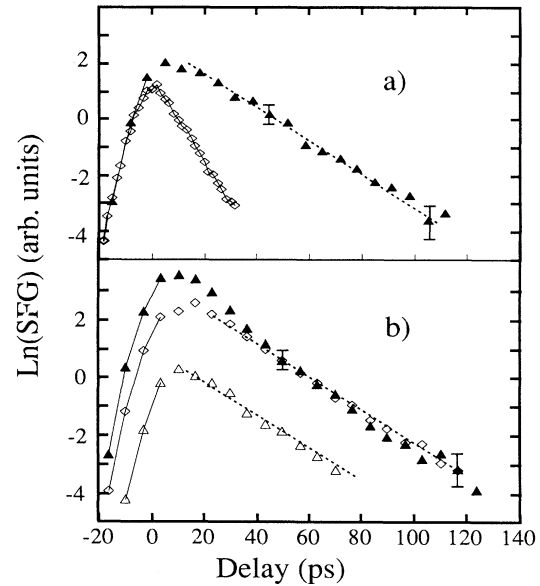

FIG. 1. Logarithmic plot of the SFG free-induction-decay signal as a function of green delay. (a) With the ir1 beam at 300 K ($\Diamond$) and at 120 K ($\blacktriangle$). (b) At 120 K with the ir2 beam at three attenuation levels (1, $\blacktriangle$; $\frac{1}{3}$, $\Diamond$; $\frac{1}{27}$, $\triangle$). The dashed line is a guide for the eye.

where the indice j stands for the infrared beam (ir1 or ir2). θ_j has the standard definition, $\theta_j = (1/\hbar)\int\mu_{01} \times E_j(t)dt$. The term $\exp(-t/T_2)$ comes from the irreversible dephasing of the single oscillator while the term $\exp(-2\pi^2\sigma^2 t^2)$ is due to the dephasing between oscillators at different frequencies. From Eq. (2), it appears that FID measurements cannot, in general, determine whether the linewidth is homogeneous[19] since a model (here a Lorentzian natural line shape and a Gaussian broadening) is needed, just as in line-shape measurements.

It should be stressed that the measurements must be taken at low enough powers to avoid additional effects. Indeed, at high power, a significantly faster decay is observed as shown in Fig. 1(b) for the FID with ir2. This occurs even for delays long compared to the pulse width. It seems therefore that the dephasing is accelerated for large coherent amplitude. Several interpretations are possible, but a definite one will require further analysis. It was, however, important to avoid this effect and the power used in the following was lowered such that the free-induction decay was unmodified.

For the photon echo, the two infrared beams are incident on the surface and overlap. The first pulse (ir1) comes at $t = 0$ and ir2 comes at a later time t_1, such that $t_1 > 0$. The surface vibrational polarization at $t > t_1$ is then given by[5,18]

$$\mu_{01}(x,t) = i\mu_{01}\sin\theta_1\sin^2\frac{\theta_2}{2}\exp\left(-\frac{t}{T_2}\right)\exp[-2\pi^2\sigma^2(t - 2t_1)^2]\exp[-i(2k_{2,x} - k_{1,x})x], \quad (3)$$

where only the term that leads to the echo has been conserved. Equation (3) shows that in the limit of large inhomogeneous broadening, the polarization is peaked at $t = 2t_1$, and hence the name photon echo. This is due to the rephasing of the oscillating dipoles by the second pulse. On the other hand, for no broadening, it is peaked at $t = t_1$ and then has an exponential decay. From the dynamic dipole moment of the transition $\mu_{01} = 10^{-19}$ esu,[10] the rotation θ_2 induced by ir2 should be close to π for the central part of the spot. From this estimate and Eqs. (2) and (3), it appears that the echo signal, with the sequence ir1 and then ir2, should be of the same magnitude as the free-induction decay with beam ir1. It should therefore be readily detectable. The direction of the sum-frequency signal is such that $k_{sf,x} = 2k_{2,x} - k_{1,x} + k_{vis,x}$.

The photon-echo signal is indeed easily observed, and at the maximum energy for ir2 the largest photon-echo signal was only about a factor of 2 smaller than obtained in the FID with ir1. The signal is purely resonant, is found at the expected angle of observation, and disappears when one of the two ir beams is blocked. To avoid the power effects mentioned earlier, the energy of the ir2 beam is reduced below 10 μJ where there is no further change in the free-induction-decay time. At these energies, the signal shows an approximately quadratic dependence with the ir2 power and a linear dependence with ir1, as expected from Eq. (3). At room temperature, an echo signal has been obtained but the time resolution of the experiment was too slow to resolve it. On the other hand, at low temperature, the coherence time is much longer than the experimental resolution. Figures 2 and 3 show the photon-echo signal for various delays of ir2 at 120 K. The solid lines are fits using Eq. (3). No attempt has been made to incorporate the finite time resolution of the measurement. T_2 and σ being the only adjustable parameters, a fairly good fit is obtained for $T_2 = 85 \pm 7$ ps and $1/\sqrt{2}\pi\sigma = 75 \pm 8$ ps. Both times are still an order of magnitude shorter than the lifetime T_1. T_2 is precisely obtained because, on the logarithmic plot, the tangent common to all curves has slope $2/T_2$. The corresponding homogeneous linewidth (FWHM) is 0.12 ± 0.01 cm^{-1} while the inhomogeneous broadening is 0.23 ± 0.03 cm^{-1}. The linewidth of the convoluted Voigt profile would therefore be 0.3 cm^{-1} in perfect agreement with the linewidth obtained by FID. In Fig. 3, the same data have been plotted showing the SFG signal as a function of green delay versus the ir2 beam $(t - t_1)$ for various delays (t_1) of ir2 vs ir1. Since homogeneous and inhomogeneous broadenings are of the same order, the maximum of the SFG signal arrives increasingly later than the ir2 pulse. At long delay, the echo of surface polarization is broad, about 70 ps as expected from $1/\sqrt{2}\pi\sigma$.

For several measurements on various samples, it has been found that the inhomogeneous broadening could vary by a factor of 2, down to 0.13 cm^{-1}, while the homogeneous linewidth is virtually unchanged. This inhomogeneity is affected by slight variations in the sample preparation, the sample cut orientation, and the vacuum conditions leading to physisorbed or contaminating layers. A systematic study of these effects is in progress.

The direct implication of this measurement is that at 120 ± 5 K the linewidth is definitely inhomogeneously broadened and the homogeneous linewidth of the Si-H stretching vibration of 0.12 ± 0.01 cm^{-1}. In the mechanism proposed by Dumas, Chabal, and Higashi, based on linewidth measurements at higher temperatures, a phonon between 190 and 235 cm^{-1} is responsible for the dephasing through a quartic anharmonic coupling term.[10] In this range, the silicon surface presents one mode at 190 cm^{-1} polarized perpendicular to the surface and one at 220 cm^{-1} polarized parallel,[11,12] both at the K point in the Brillouin zone. With a phonon of frequency ω, the temperature dependence of the linewidth is $\Delta v \sim e^{\hbar\omega/kT}$
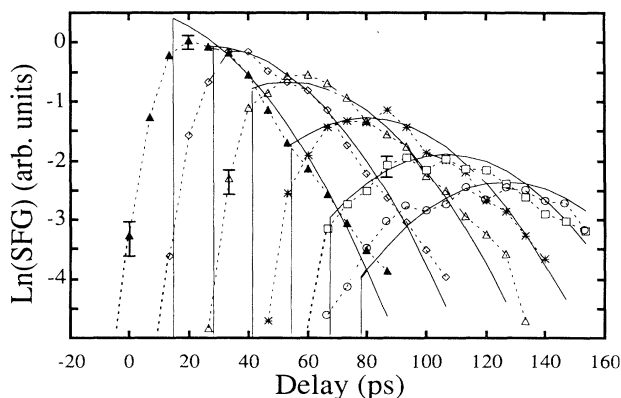

FIG. 2. Logarithmic plot of the SFG echo signal as a function of green delay. The data points connected by dashed lines are shown for several ir2 delays: 15 ps, ▲; 28 ps, ◇; 42 ps, △; 55 ps, *; 68 ps, □; 78 ps, O. The solid lines are fits obtained as described in the text.
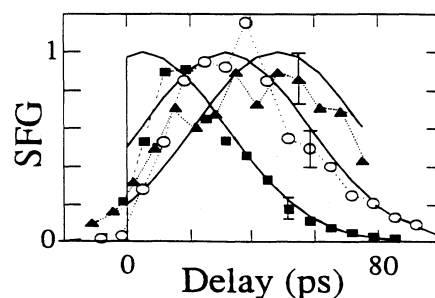

FIG. 3. SFG echo signal as a function of delay between the green and the second ir pulse (ir2) for several delays of ir2 with ir1: ■, 28-ps delay; O, 55-ps delay; ▲, 75-ps delay. The fits are the solid lines. They are normalized to 1 and the data are normalized with the same constant.

$\times(e^{\hbar\omega/kT}-1)^{-2}$.[2-4,10] Given a room-temperature linewidth of 0.85 cm^{-1},[10] the linewidth at 120 K (including 0.004 cm^{-1} from the lifetime) should then be 0.105 cm^{-1} for a 190-cm^{-1} phonon and 0.095 cm^{-1} for a 220-cm^{-1} phonon. Both numbers are close to the present experimental value but the error bars favor the lower energetic phonon. Although it has been shown that perpendicular substrate vibration (such as the 190-cm^{-1} phonon) cannot effectively couple to the adatom perpendicular vibration through the adatom-surface anharmonicity[20] (in this case H-Si), the anharmonicity of the Si-Si bonds can still be the source of an efficient coupling. Clearly, the present result should motivate further theoretical investigations. With photon-echo measurements at lower temperature, a precise picture is likely to emerge for the dephasing of this system.

In conclusion, this work presents the first time-resolved measurements of the dephasing of a surface vibration on single-crystal surfaces. By up-conversion with SFG, free-induction decay and the photon echo have both been observed for the transient surface polarization. Therefore, it became possible to separate the homogeneous linewidth from an inhomogeneously broadened surface vibration. This was shown for the particular system H/Si(111). With improved signals, these surface photon-echo measurements will find applications in many systems and they will improve our knowledge of the molecule-surface interaction by refining spectroscopic data.

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