

Lifetime of an Adsorbate-Substrate Vibration: H on Si(111)

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Picosecond sum-frequency-generation measurements of the unreconstructed, ideally H-terminated Si(111) surface reveal that the lifetime of the Si-H stretching vibration is 0.8 ± 0.1 ns.

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The energy flow between adsorbed species and surfaces controls many dynamical processes. For instance, diffusion involves the spatial hopping of adsorbates while thermal and photoinduced desorption and reaction involve the breaking of the adsorbate-substrate bond via vibrational excitation. Thus the energy relaxation of the adsorbate-substrate vibrations bears directly on the overall dynamics of the adsorbate-substrate interaction.

The measurements of surface vibrational relaxation have, however, proven very difficult. In the past, the infrared *linewidth* of an adsorbate vibration was often thought to be dominated by its lifetime¹ T_1 (e.g., 1-ps lifetime results in 5-cm^{-1} linewidth). Later, however, temperature-dependence measurements of vibrational linewidths clearly showed that pure dephasing (T_2) is often the dominant contribution.^{2,3} (For an ordered adlayer, vibrational dephasing may be intraband scattering arising from anharmonic coupling to lower-frequency modes such as adsorbate bending modes or substrate phonons.) Even if the linewidth is temperature independent, one is unsure whether it is due to lifetime or inhomogeneous broadening.⁴ Direct time-resolved measurements are therefore required to determine the lifetime of the vibration.

We present here such a measurement for the Si-H stretch for an ideally H-terminated Si(111) surface, characterized by a *single* Si-H stretch vibration at 2083.7 cm^{-1} polarized purely perpendicularly to the surface.⁵ This surface, stable in air, is extremely homogeneous with a concentration of defects and impurities less than 10^{-4} .^{5,6} Furthermore, in contrast to the many relaxation channels available to molecules on metals (electronic, intramolecular) with strong dynamic dipoles (intermolecular), the Si-H stretching mode can only relax via anharmonic coupling to one H mode (Si-H bend) or to the substrate motion (Si phonons). The absence of resonant electronic excitation and the large energy difference between the Si-H stretch mode and the other vibrational modes [$\nu_{\text{Si-H bend}} = 637\text{ cm}^{-1}$ (Ref. 7) and

$\nu_{\text{phonon}} \leq 500\text{ cm}^{-1}$] implies that a long lifetime is expected. The temperature dependence of the Si-H stretch linewidth^{6,8} implies, in fact, that this mode is anharmonically coupled to both the Si-H bend and a Si surface phonon at a lower frequency, leading to a well-defined (dephasing or T_2) broadening.⁶ Such a well-defined system is all the more interesting in that it is the only one for which molecular-dynamics calculations with no adjustable parameters (i.e., based on *ab initio* calculations) have been performed.³

To measure the lifetime (T_1) of this vibration, the method of transient bleaching is used in conjunction with the surface nonlinear optical technique of sum-frequency generation (SFG) that has been recently demonstrated as a versatile surface infrared spectroscopic tool.⁹ In the past, transient bleaching has been widely applied to the determination of T_1 in liquids^{10,11} and for adsorbates on high-surface-area material.¹² Recently, SFG measurements of the energy relaxation of a C-H stretch mode from a Cd stearate monolayer on optically flat metal surfaces have also been performed,¹³ opening the way for studies of *simpler adsorbates* on well-characterized single-crystalline surfaces.

In SFG, the surface is illuminated synchronously by a visible and a tunable infrared pulse. Through the nonlinear response of the surface a coherent radiation is generated at the sum frequency of the inputs (in the visible), thus detectable with a high-sensitivity photomultiplier. Because it is a second-order nonlinear process, it is intrinsically surface sensitive for a centrosymmetric substrate such as silicon.⁹

Separating the resonant ($\chi_R^{(2)}$) and nonresonant ($\chi_{NR}^{(2)}$) contributions, the SFG signal is given by¹⁴

$$S = 128\pi^3 \frac{\omega_{\text{SF}}}{\hbar c^3} |L_{\text{SF}}^l L_{\text{vis}}^m L_{\text{ir}}^n|^2 |\chi_{NR,lmn}^{(2)} + \chi_{R,lmn}^{(2)}|^2 \frac{U_{\text{vis}} U_{\text{ir}}}{AT}, \quad (1)$$

where L accounts for the Fresnel factors that relate the surface fields (l, m, n stand for x, y, z) to the incident and

emitted radiation. ω_{SF} is the sum frequency, U_{vis} and U_{ir} are the energies of the visible and infrared incident pulses, and A and T are their overlapping area and duration, respectively. In the case of hydrogen on Si(111), the vibration is only along the surface normal z , and the dominant microscopic susceptibility should be $\alpha_{zzz}^{(2)}$. Therefore, the resonant contribution to the signal is given by the only nonzero component of the macroscopic tensor

$$\chi_{\text{R}zzz}^{(2)} = N\alpha_{zzz}^{(2)}, \quad (2)$$

where N is the surface coverage and $\alpha_{zzz}^{(2)}$ is given by

$$\alpha_{zzz}^{(2)} = \Delta\rho_{vg} \frac{\langle g | er_z | v \rangle M_{zz}}{\hbar(\omega_{\text{ir}} - \omega_{vg} + i\Gamma_{vg})} \quad (3)$$

and

$$M_{zz} = \sum_s \left[\frac{\langle v | er_z | s \rangle \langle s | er_z | g \rangle}{\hbar(\omega_{\text{SF}} - \omega_{sg})} - \frac{\langle v | er_z | s \rangle \langle s | er_z | g \rangle}{\hbar(\omega_{\text{SF}} + \omega_{sv})} \right], \quad (4)$$

where g and v stand for ground ($v=0$) and first excited state ($v=1$), respectively, and er_z is the dynamic dipole moment.

In our scheme an intense infrared pulse resonant at ω_{vg} pumps the ground state into the $v=1$ state. After a varying delay, the difference between the population of the ground state and the excited vibrational state $\Delta\rho_{vg}$ is then probed by SFG from a pair of a weaker infrared beam and a visible beam. If the nonresonant contribution $\chi_{\text{NR}}^{(2)}$ is small and if the resonance $v=1$ to $v=2$ is sufficiently far removed (as is the case for this Si-H stretch due to anharmonicity¹⁵) then, from Eqs. (1) and (3), the signal is just proportional to the square of $\Delta\rho_{vg}$. Therefore, as for transient bleaching, one measures a ground-state recovery time. If the excited state lives longer than the intermediate states it decays to, the ground-state recovery time is the mode lifetime T_1 and a single exponential decay is obtained. Otherwise, a multiple exponential decay can be obtained.

In our experimental setup, we start from an actively mode-locked and Q -switched Nd-doped yttrium-aluminum-garnet (Nd:YAlG) laser generating 1.064- μm radiation in a 200-ps pulse of 100 mJ at 10 Hz. The tunable infrared is generated by difference-frequency mixing the Nd:YAlG radiation and the output of a traveling-wave dye laser in a AgGaS₂ crystal.¹⁶ We obtain a tunable output around 2000 cm^{-1} in a 200-ps pulse with 70 μJ after a germanium Brewster plate. The infrared is then separated into a pump and a probe beam. The pump goes through a variable delay line and is incident on the surface at 60° with 50 μJ in a 800×250- μm^2 spot. The probe is at 50° with 4 μJ in a 400×125- μm^2 spot to facilitate the overlap. The visible pulse (532 nm), synchronized with the probe, is incident at 70° in a large spot of 2×0.5 mm^2 . All beams are p

polarized. From the measured infrared absorption and natural linewidth (0.9 cm^{-1}) of the Si-H mode⁶ we can estimate, with our 3- cm^{-1} resolution, that 50 μJ in our pump beam at 60° should lead to a 25% saturation (i.e., $\rho_v=0.25$) if the pulse duration is smaller than T_1 . The SFG signal from the probe should then decrease by 75%. The probe beam itself leads to a much smaller saturation that will not affect the measurements.

The preparation of the sample is described in detail elsewhere.^{5,6} Briefly, polished Si(111) wafers are first thermally oxidized (=900 Å oxide) to move the interface away from the polishing damage. After HF removal of the thick oxide, they are reoxidized chemically to generate a thin protective oxide layer. The final removal of this oxide is done prior to the experiment with a buffered HF:NH₄F solution.⁶ This preparation reproducibly yields a hydrophobic unreconstructed and ideally H-terminated Si(111) surface that is stable in laboratory air for hours. The observed infrared absorption line at room temperature is shown in Fig. 1(a). Its width (0.9 cm^{-1}) is completely dominated by dephasing.⁶

Although the infrared cross section is small, the SFG signal is fairly strong because of a significant Raman cross section and the *perfect polar ordering of the surface*. As can be seen in Fig. 1(b), the nonresonant contribution for the unsaturated spectrum is very small even with our laser of limited resolution. As expected from the previous estimate, the saturation is easily observable. Such a saturation immediately implies that the mode lifetime is longer than the pulse width. In Fig. 1(c) we show the spectrum obtained with the pump coming 200 ps before the probe beam. The saturation of the absorption leads to a 60% decrease of SFG signal in good agreement with the estimate. The asymmetry of the last

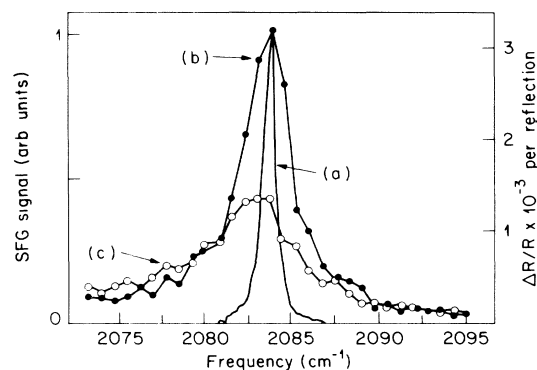


FIG. 1. Spectra of the Si-H stretch: (a) Linear absorption taken with multiple-internal-reflection Fourier-transform infrared spectrometer with 0.3 cm^{-1} resolution (solid line) using a Nicolet 740 interferometer. The vertical scale on the right represents the absorption per reflection. (b) SFG spectrum taken with the pump blocked (solid circles). (c) SFG spectrum taken with the pump incident 200 ps before the probe beam (open circles). The lines are just connecting the experimental points.

spectrum is due to the relative increase of the non-resonant contribution.

The ground-state recovery time is then directly obtained by varying the delay between the pump and probe and measuring the remaining saturation. At each delay t , the SFG signals with the pump on and off are measured for 200 pulses and the ratio $r(t) \equiv \text{SFG}(\text{pump on})/\text{SFG}(\text{pump off})$ is taken a total of 10 times. For the long delays, signal averaging is increased threefold. We obtain a statistical uncertainty of about $\pm 2\%$ in the ratio $r(t)$. Systematic errors could arise if changes in overlap and energy density occur as the path length of the pump is varied over 60 cm (2 ns). These were minimized by a slight defocusing of the pump and a careful alignment.

To present the data, we define $\rho \equiv 1 - r^{1/2}$. Then from Eq. (3), $\rho = 1 - |\Delta\rho_{\text{vg}}| \approx 2\rho_v$. The data are presented in Fig. 2 where $\ln(\rho)$ is plotted versus the time delay. It should be emphasized here that the Si-H bending mode at 637 cm^{-1} should have a much faster decay than the stretching mode because of its smaller energy difference with the substrate phonons ($\leq 500 \text{ cm}^{-1}$).³ As a consequence, the relaxation time should be dominated by the lifetime of the Si-H stretch vibration itself. Within our accuracy, we observe a straight line over two lifetimes, clearly not limited by the laser temporal resolution. Thus, from this measurement, a single lifetime $T_1 = 0.8 \pm 0.1 \text{ ns}$ can be assigned to the Si-H stretch vibration.

This lifetime is very long compared to what one would in general assume for chemisorbed molecules on surfaces. It illustrates the fact that the Si-H stretching mode is well decoupled from the bending mode and the substrate phonons. In addition, unlike molecules on metals, transfer to electronic excitations cannot occur since

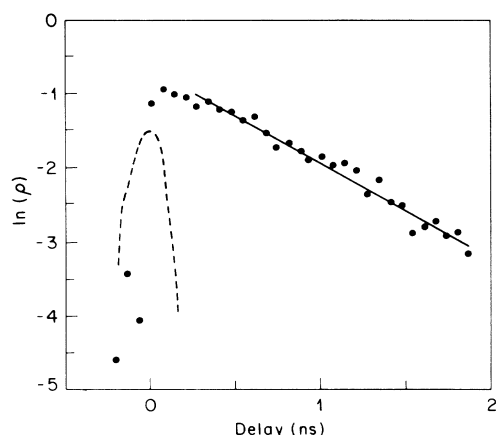


FIG. 2. Logarithm of $\rho = 1 - r^{1/2}$, where r is the ratio of the probe SFG signals with the pump on and off. The straight line is a least-squares fit giving $T_1 = 795 \text{ ps}$. The dotted line is the cross correlation of the pump with the visible pulse (temporal resolution).

the band-gap energy is much larger than the vibrational quantum. *Ab initio* molecular-dynamics simulations have, however, predicted a lifetime in excess of 20 ns for the monohydride modes on the Si(100) surface.³ As the relaxation time is determined by the adsorbate-surface potential, the discrepancy implies that the H-Si interaction must be refined.

Alternatively, transient-bleaching experiments may produce an artificially short lifetime for a variety of reasons. First, phonon-phonon scattering could thermalize the Si-H excitation among its phonon band in a similar manner as nearly degenerate modes would thermalize in a molecule. Additionally, transfer to upper phonon bands could happen similarly to Treanor's pumping for gas-phase studies.¹⁷ In both cases, the population of the $(v=1, q=0)$ state would be reduced. Because we see only one exponential decay down to nearly *complete recovery*, we can deduce that this thermalization of the stretching vibrations among themselves is either faster than the probe pulse or would take longer than the lifetime of the vibration.¹⁸ It does therefore not affect our measurement. Diffusion of surface excitations has also recently been considered.² Grating experiments might be able to observe this effect but, in our experiment, the pump spot is too large to allow any appreciable leakage of the excitation density.

Next, the high saturation levels needed for detection purposes might induce a variety of phenomena such as multiphonon absorption, monolayer heating, and desorption. However, multiphoton absorption is negligible in this case because the anharmonicity (60 cm^{-1}) is much larger than the pump-induced broadening. This is confirmed by the reasonable agreement obtained between our measured and estimated saturation. Laser-induced desorption was estimated from time-dependent studies of the SFG signal, giving an upper limit of 10^{-6} monolayer per pulse. Monolayer heating can be accurately estimated from the change in vibrational frequency between the pump and probe spectra [Figs. 1(b) and 1(c)] because the Si-H frequency depends sensitively upon temperature.⁶ We place an upper limit of a 100-K increase for the Si-H temperature upon irradiation. Finally, our samples were placed in a cell filled with helium with no changes in T_1 , confirming that the ambient gas has no observable effect on the Si-H vibrational lifetime. Therefore, for this system, possible experimental artifacts are negligible, indicating that a refinement of the theoretical model should be attempted.

In conclusion, this work constitutes the first measurement of the lifetime of an adsorbate-substrate vibration. The system, ideal in many respects, gives a clear, single exponential decay of a spectrally well-defined vibrational mode. This measurement, along with the thorough linewidth study,⁶ gives a complete experimental characterization of the anharmonic coupling between the Si-H stretch and the lower-frequency modes. Such results

stringently constrain future theoretical modeling of adsorbate-substrate interactions.³ Furthermore, this long Si-H stretch lifetime may allow various surface photophysics experiments to be done, such as multiphoton absorption, selective desorption, and chemical reaction.

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