

Interadsorbate vibrational energy flow on stepped vicinal H/Si(111) surfaces

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We report direct measurements of the vibrational energy flow among Si-H stretching modes on hydrogen-terminated stepped vicinal Si(111) surfaces using a two-color, infrared pump/sum frequency generation probe scheme in which one vibrational mode is pumped and another one is probed. The results, which follow the vibrational energy equilibration, reveal that interadsorbate energy transfer from the terrace to the step can be the dominant relaxation channel of the terrace oscillators. Two types of surfaces have been examined. Both have monohydride terminated terraces, but one has monohydride and the other dihydride terminated steps. On the dihydride stepped surface, the terrace Si-H vibrational energy is drained by the short lifetime step modes. The energy flow on the dihydride terminated surface occurs between terrace-localized and step-localized modes and can be resolved into a kinetic model of the vibrational energy equilibration process. Stronger interadsorbate dipole couplings, on the monohydride stepped surface, delocalize the terrace and step modes and make it difficult to separate the energy flow from direct Si-H oscillators excitation. We suggest that on this surface there is a rapid equilibration of all the Si-H stretching modes followed by their collective decay. Estimates of dipole-dipole energy transfer rates are consistent with the kinetic model results and confirm the role of dipolar interactions in vibrational energy flow on the hydrogen-terminated silicon surfaces.

1. INTRODUCTION

The relative importance of vibrational energy in interfacial reactions depends on the rate at which it equilibrates with the surface compared to the reaction rate. A rapid transfer of the adsorbate vibrational energy to the substrate simply leads to a temperature increase of the bulk, but if the vibrational excitations do not dissipate rapidly they can become important in surface reactions. Recent direct measurements[1-10] of vibrational energy transfer rates have begun to quantify the fundamental adsorbate/substrate interactions controlling the vibrational energy equilibration pathways. For carbon monoxide on metallic surfaces, fast vibrational relaxation rates are observed[6,9] and have been explained in terms of strong, non-adiabatic, vibration/electron couplings[6,9,11]. In the case of larger adsorbates on metallic substrates, intramolecular vibrational channels have been found to be important[1,2] in the vibrational relaxation process. For these large and small adsorbates on metallic surfaces, vibrational energy thermalisation is occurring locally from a single

molecule to the substrate. Small adsorbates on semiconductor[7,8] or insulator[10] surfaces display a different dynamic behaviour because the adsorbate/substrate interactions are weaker and intramolecular channels are absent, and therefore interadsorbate energy transfer is found to play an important role in the vibrational energy equilibration.

We report here on direct measurements of interadsorbate energy transfer on hydrogen-terminated stepped vicinal Si(111) surfaces[7,8]. We examine the influence of steps on the adsorbate vibrational energy relaxation processes by quantifying the effects of the nature of the step termination (monohydride and dihydride) on the vibrational relaxation rates using a two-color infrared/sum frequency generation method in which one vibrational mode is pumped and another vibrational mode is probed. The data show that steps influence the relaxation rate of the terrace Si-H oscillators through interadsorbate energy transfer and that their role depends on the step termination.

The extremely well-ordered hydrogen-terminated stepped vicinal Si(111) surfaces used in this study are obtained by a novel chemical preparation[12]. The

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chemical preparation gives narrow, well resolved vibrational absorption bands[13] associated with the step and terrace Si-H stretching modes and also steps which are straight over hundred of angstroms and evenly distributed as seen in STM[14]. The dihydride and monohydride stepped surfaces are obtained by cutting the Si(111) surfaces along different azimuths. The idealized surface geometries of both types of stepped surfaces shown in Fig. 1 are based on IR polarisation studies and ab-initio calculations[13], and are discussed further below.

The two-color measurements show unequivocally that interadsorbate energy transfer between all the Si-H oscillators is occurring on both the dihydride and monohydride stepped surfaces. The effect of steps on the terrace mode via interadsorbate energy transfer is found to be important because it occurs at rates which are competitive with the slow intrinsic monohydride Si-H relaxation of 950 ps.

In section 2, the sample preparation and optical approach are described. Section 3 presents the sum frequency generation spectra, excitation spectra and transient spectra for the dihydride and monohydride stepped surfaces. These results are discussed and analysed with a linear kinetic model in section 4. Dipole-dipole coupling as an interadsorbate energy transfer mechanism is also discussed in section 4. A summary of the conclusions is presented in section 5.

2. EXPERIMENTAL

The exceptionally well-ordered hydrogen-terminated vicinal Si(111) surfaces used in this study were prepared by a buffered HF etch described elsewhere[12,13]. In brief, the chemical method consist in putting the high-resistance, thermally oxidized silicon samples through two chemical oxydation (Shiraki solution) and etching (buffered HF, pH=6.6) cycles followed by rinsing with deionized water. The samples are then rapidly introduced in a vacuum chamber purged with nitrogen. The vacuum system is pumped down to the low 10^{-9} Torr range following a procedure which minimizes contamination[7,8,13,15]. No filament is used during the experiments to prevent sample degradation. Following these precautions, samples can be kept clean for up to 3 weeks, based on the SFG linewidths and intensities.

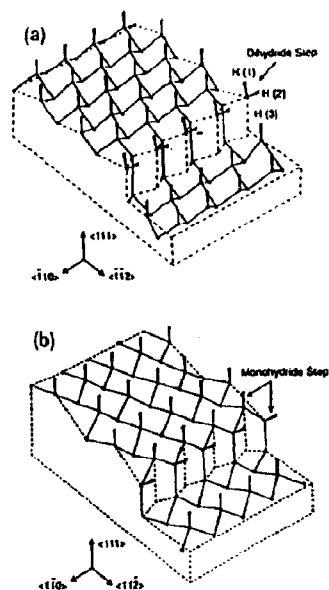


Fig. 1: Structure of the hydrogen-terminated stepped vicinal Si(111) surfaces: (a) Dihydride stepped surface cut along the $\langle 11\bar{2} \rangle$ azimuth. H(1), H(2) and H(3) are the hydrogens involved in the step normal modes, discussed in the text. (b) Monohydride stepped surface cut along the $\langle 11\bar{2} \rangle$ azimuth.

The flat and stepped Si(111) surfaces prepared by HF etching have been shown by IR[12,20] and STM[12,14] to be well-ordered. The stepped surface geometries suggested by these studies are shown in Fig. 1. In this study, the pH of the buffered HF was adjusted to obtain very narrow Si-H stretching modes in the IR absorption spectra, and straight, evenly distributed, single steps as shown by STM. For both surfaces, the terraces are unreconstructed and terminated by a (1x1) hydrogen overlayer in which the monohydrides are separated by 3.84 Å. The dihydride terminated stepped surface is obtained by miscutting the Si(111) sample by 9° in the $\langle 11\bar{2} \rangle$ direction and is shown in Fig. 1(a). For an unrelaxed surface, the average terrace length is 19.8 Å and has 5.3 monohydrides across, and the step height is 3.14 Å. The steps are terminated by dihydrides lying in a plane perpendicular to both the step edge and the (111) plane. The monohydride stepped surface is obtained by a miscut of 9° of the Si(111) surface in the $\langle 11\bar{2} \rangle$ direction and is illustrated in Fig. 1 (b). The average terrace length and step height are the

same as the dihydride stepped surface, but the average number of monohydrides per terrace is reduced to 4.6. Two different types of monohydrides, one perpendicular to the (111) plane and the other almost parallel to the (111) plane, form the step unit cell.

The excited state relaxation rates of the Si-H stretching modes on the vicinal Si(111) surfaces are measured directly using an IR pump/sum frequency generation (SFG) probe scheme[1-8]. In this pump/probe approach a resonant, intense, short, infrared pulse excites a vibrational mode from the ground state to its first excited state. The excited state vibrational population of this mode or another coupled mode is monitored with IR/visible SFG. Sum frequency generation which as now become a proven ultrafast vibrational spectroscopy has been described in detail elsewhere[1-8,17]. Briefly, sum frequency generation is a non-linear spectroscopy which originates from the second order molecular polarisability. A coherent molecular polarisation at the vibrational frequency is created by an infrared field. A coherent visible field overlapped spatially and temporally with the IR field interacts with the IR molecular polarization and generates a new molecular polarisation at the sum of the frequencies of the IR and visible fields. This latter molecular polarisation radiates the sum frequency signal. The strength of the resonant SFG signal depends on both the infrared transition dipole and the Raman susceptibility. The radiated SFG signal is weak, typically 1 to 100 photons but is collimated, directional and monochromatic and can be detected very efficiently. Being a second order process sum frequency mixing is only allowed in a non-centrosymmetric medium, such as an interface hence SFG is a surface specific spectroscopy. Non-resonant contributions to the SFG signal can arise from non-centrosymmetric substrates and the adsorbate layer, and interfere with the resonant signal giving rise to complex lineshapes[3]. In this study, bulk silicon is centrosymmetric and essentially background free SFG spectra are obtained for the hydrogen-terminated stepped vicinal Si(111) surfaces. For IR and visible pulses shorter than the population relaxation lifetime, the vibrationally resonant sum frequency signal can be shown[1-8] to be proportional to $(n_0 - n_1)^2$, where n_0 and n_1 are, respectively, the fractional population of the ground and excited vibrational state of the probed mode. The change in the population differences is equal to the

normalized pump-induced change in the square root of the SFG signal as defined in the following equation:

$$1 - \left[\frac{S(\tau_d)}{S_0} \right]^{1/2} = \Delta n_1(\tau_d) - \Delta n_0(\tau_d) \quad (1)$$

where S_0 is the SFG signal without the IR pump and $S(\tau_d)$ is the SFG signal at a delay τ_d from the pump. Δn_0 and Δn_1 are the pump-induced changes in the fractional population of the ground and excited state, respectively.

The experimental two-color set-up has been described in detail elsewhere[8]. This set-up gives two short (≈ 30 ps), intense (≈ 10 μJ), infrared pulses independently tunable between 1900 and 2300 cm^{-1} , and a visible probe beam of similar pulse length. A small fraction of the IR probe is split off and used to normalize the SFG signal. The IR pump and probe, and visible probe beams are focused on the silicon surface. The pulses energy densities at the surface are approximately; 7 mJ cm^{-2} for the IR pump, 3 mJ cm^{-2} for both the IR and visible probe. Finally, the beams are overlapped spatially and temporally by optimizing the instantaneous SFG response of a gold surface. On gold, the IR-visible pulses cross-correlation is ≈ 50 ps FWHM.

3. RESULTS

3.1 Dihydride stepped surface

The SFG spectrum of the Si-H stretching region of the dihydride stepped Si(111) surface is shown in Fig. 2. There are 3 modes in the SFG spectra. The mode labelled A at 2083 cm^{-1} is assigned to the monohydrides on the terraces and occurs at the same frequency as the monohydride stretching mode on the flat Si(111) surface[4,12]. The two other SFG modes are related to the step. They are the C_2 mode at 2102 cm^{-1} and the C_3 mode at 2136 cm^{-1} . The C_1 step mode at 2094 cm^{-1} observed in IR absorption[13] is absent.

The excitation spectrum of the C_2 step mode is displayed in Fig. 3. In this spectrum the excited state population of the C_2 mode, at a fixed SFG probe delay of 40 ps, is monitored while the pump frequency is scanned across the Si-H stretching

region. Changes in the C_2 intensity are observed when any of the IR active Si-H stretching modes: A, C_1 , C_2 and C_3 are excited. Assuming that the excitation spectrum consists only of energy transfer, the C_2 mode would be strongly coupled to all other modes and receive a significant fraction of the Si-H energy. The strong depletion of the C_2 mode when the C_1 mode is pumped indicates that the C_1 mode can adsorb and transfer IR energy. Its absence from the SFG spectra is probably due to our scattering geometry which makes the Raman anti-Stokes transition small and difficult to detect as has been shown by recent Raman measurements[22].

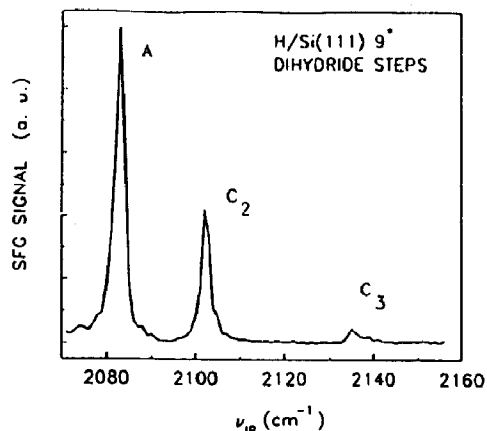


Fig. 2: SFG spectrum of the dihydride stepped Si(111) surface at room temperature. A; terrace mode, C_2 and C_3 ; step modes.

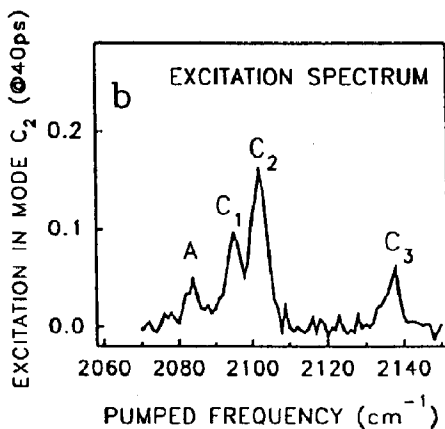


Fig. 3: SFG excitation spectrum of the C_2 mode of the dihydride stepped surface at a probe delay of 40 ps.

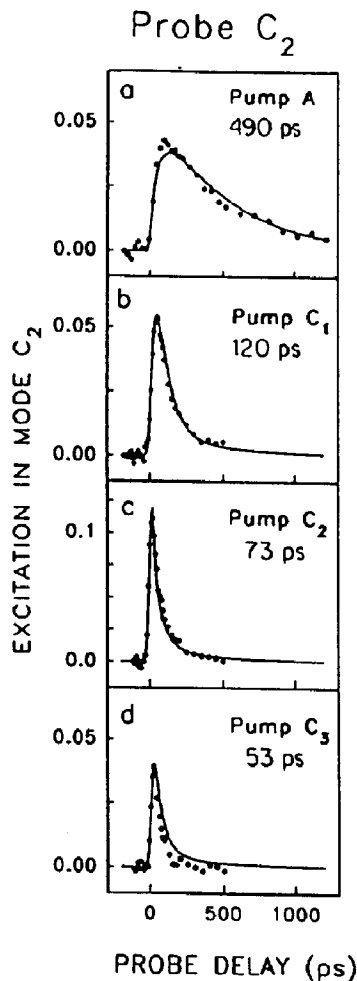


Fig. 4: Transient spectra of the C_2 mode on the dihydride stepped Si(111) surface. Solid points, experimental data; solid line, kinetic model fit.

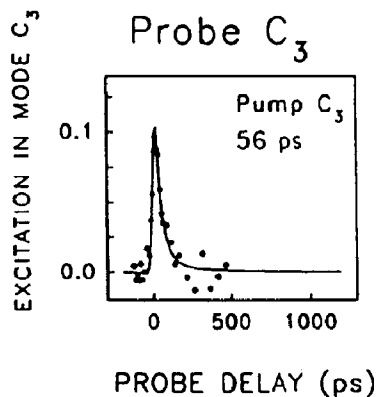


Fig. 5: Transient spectrum of the C_3 mode on the dihydride stepped Si(111) surface. Solid points, experimental data; solid line, kinetic model fit.

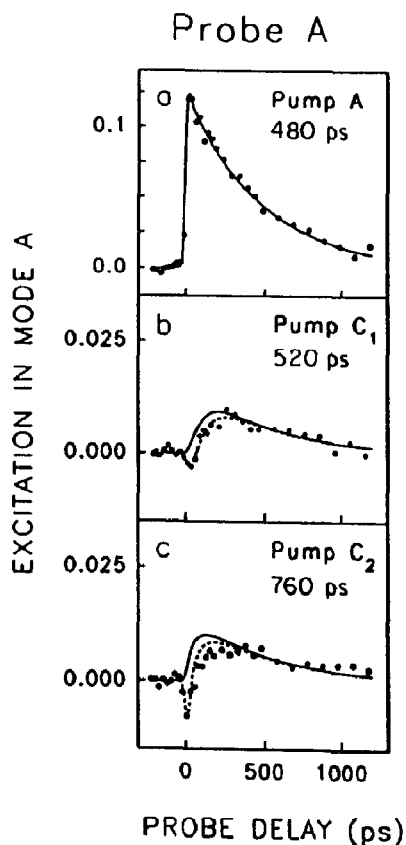


Fig. 6: Transient spectra of the A mode on the dihydride stepped Si(111) surface. Solid points, experimental data; solid line, kinetic model fit; broken line, transients negative component proportional to the C_2 excitation (see refs. 8, 19).

The excited state vibrational population dynamics of the A, C_2 and C_3 modes at different pump frequencies are shown in Fig. 4, 5, and 6. These spectra consist in pumping one mode and probing the same or another mode as a function of the time delay between the pump and probe pulses. The data are analysed using a single exponential fit and the resulting lifetimes are shown in Fig. 4, 5, and 6. The solid line fit to the data is obtained by a kinetic model[8] which consist of multiexponential decay rates and is described the next section. To simplify the following discussion, the set of pump X mode \rightarrow probe Y mode is denoted as X \rightarrow Y. The two-color lifetime measurements reveal the main characteristics of the energy flow on the dihydride stepped surface.

Pumping and probing the same mode shows that the lifetime of 480 ps of the terrace mode A is slower than the C_2 (73 ps) and C_3 (56 ps) step modes, but is two times faster than the flat Si(111) value of 950 ps. The excitation of the C_2 mode lasts ≈ 6 times longer (≈ 500 ps) when the A mode is pumped. The reverse process of probing the A mode and pumping the C_2 or C_1 modes shows that the lifetime of the A mode is similar (≈ 600 ps) to the A \rightarrow A process (480 ps). These last two results can only be explained by energy transfer since coherent or anharmonic effects do not last longer than the pumped mode excitation. The $C_1 \rightarrow C_2$ lifetime of 120 ps is an indirect measurement of the C_1 lifetime. The C_1 mode therefore relaxes at a slower rate than the other 2 step modes. The $C_1 \rightarrow A$ and $C_2 \rightarrow A$ transient spectra show a complex response at early delay that cannot be fitted adequately by a single exponential decay or with the kinetic model. An empirical inclusion of the dynamical dipole effects[8] by adding a negative going signal proportional to the excitation of the C_2 mode to the kinetic model fit improves the fit of these experimental data and is shown as a dotted line in Fig. 6.

3.2 Monohydride stepped surface

The SFG spectrum of the monohydride stepped surface in Fig. 7 shows two Si-H stretching modes.

There is the terrace monohydride mode A at 2083 cm^{-1} and a very intense step mode, B_2 , at 2089 cm^{-1} . As in the case of the dihydride stepped surface, one IR active step mode[13], B_1 (2071 cm^{-1}), is absent in the SFG spectrum.

The excitation spectrum of the B_2 mode at a probe delay of 30 ps is shown in Fig. 8. Changes in the B_2 intensity are seen at pump frequencies corresponding to all the IR active modes: A, B_1 and B_2 . Assuming once again that the observed changes in the excitation spectrum arise exclusively from energy transfer, these results indicate that the B_2 mode is coupled to all the Si-H stretching modes and that a significant fraction of the vibrational energy is transferred to it. The strong appearance of the B_1 mode in the excitation spectrum shows that this mode can store and transfer vibrational energy and that its absence in the SFG spectra is probably due to a small Raman cross-section and/or a poor scattering geometry for the detection of the Raman anti-Stokes transition.

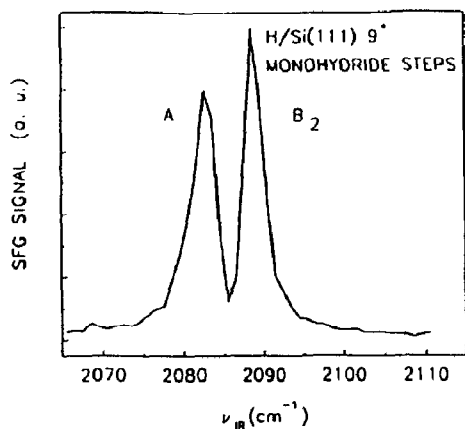


Fig. 7: SFG spectrum of the monohydride stepped Si(111) surface at room temperature. A, terrace mode; B₂, step mode.

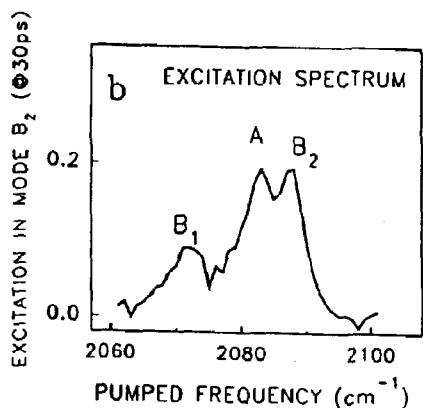


Fig. 8: SFG excitation spectrum of the B₂ mode on the monohydride stepped Si(111) surface at a probe delay of 30 ps.

The six possible two-color transient spectra of the two SFG active modes, A and B₂, are shown in Fig. 9 and 10. Care was taken to reduce the laser linewidth to ≈ 2 cm⁻¹ for the A \rightarrow B₂ and B₂ \rightarrow A transients in order to limit direct pumping to less than 2%. The data are analysed using the same kinetic energy flow schemes and the results are shown on the Figs. 9 and 10. The decays of the A and B₂ modes of 600 and 690 ps, respectively, are identical within the experimental errors[8]. All the other two-color transient have similar lifetimes of ≈ 600 ps, except the

A \rightarrow B₂ lifetime which is longer at 1 100 ps.

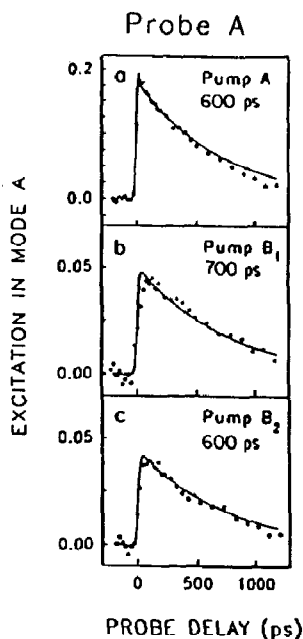


Fig. 9: Transient spectra of the A mode on the monohydride stepped Si(111) surface. Solid points, experimental data; solid line, kinetic model fit.

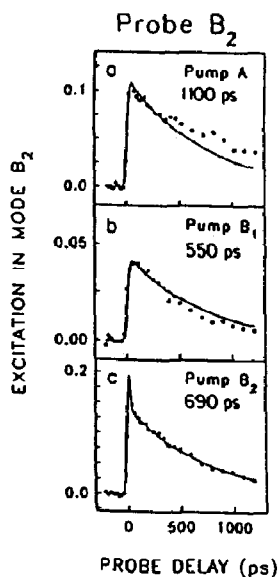


Fig. 10: Transient spectra of the B₂ mode on the monohydride stepped Si(111) surface. Solid points: experimental data; solid lines: kinetic model fit.

4. DISCUSSION

The two-color transient measurements clearly show that on both dihydride and monohydride stepped surfaces the Si-H stretching modes are strongly coupled. The observed transient changes in the SFG intensity seen in other modes when pumping one mode can originate from different interadsorbate coupling mechanisms. The most likely processes are energy transfer leading to a change in the excited state population, dipolar interactions giving rise to intensity borrowing effects[19] and coherent artefacts[21]. In the following we discuss the contributions of all of these processes to the two-color transient spectra and conclude that in all cases the transients are caused primarily by energy transfer. We analyse the results of the dihydride stepped surfaces first and show that energy transfer between localized modes is occurring. A linear kinetic model[8] of the vibrational energy flow is then developed and applied to the dihydride stepped surface results. The analysis of the monohydride stepped surface results gives less definitive conclusions about the vibrational energy flow. We show that unlike the dihydride stepped surface, strong interadsorbate couplings which cause the delocalization of the terrace and step modes[19] makes it difficult to separate energy transfer and direct excitation. Finally, we discuss dipole-dipole coupling as an interadsorbate energy transfer mechanism.

4.1 Interpretation of the dihydride stepped surface results

The close proximity of the dihydride step with the monohydride H(3) on the lower terrace modifies significantly the vibrational spectrum. The nature of the three normal modes formed by the three coupled Si-H oscillators has been studied by IR-polarisation[13], Raman spectroscopy[22], and ab-initio calculations[16]. Strong steric interactions are predicted, by ab-initio calculations, to cause a noticeable step relaxation consisting of a 22° upward rotation of the dihydride. Raman scattering experiments[22] confirm the step relaxation. The ab-initio calculations gives the following mode assignment: Using the labels of Fig. 1(a), the C_3 mode is assigned to the symmetric stretching mode involving the Si-H(2) and Si-H(3) bonds while the C_2 mode is the asymmetric mode of the Si-H(2) and Si-

H(3) bonds. The C_1 mode involves only the Si-H(1) bond. Preliminary Raman measurements suggest an almost complete uncoupling of the three Si-H bonds[22]. In this paper we used the ab-initio definition of the step normal modes.

On the dihydride stepped surface, the presence of steps affects significantly the excited state lifetime of the terrace Si-H stretching modes. From the two-color transient measurements the main characteristics of the energy transfer process are determined to be the following: All the two-color transients involving the terrace A mode either as a pumped or probed mode have similar lifetimes of ≈ 500 ps. If the transient spectra consist only of energy transfer then energy would be transferred from the A mode to the short lifetime step mode as long as the A mode is excited (≈ 500 ps). In the reverse process, energy transferred to the A mode from the short lifetime step modes is dissipated in ≈ 500 ps. The fact that the excitation in the A mode survives longer than any of the step mode excitation in the $C_1 \rightarrow A$ and $C_2 \rightarrow A$ transients can only be accounted for by energy transfer. This is at the heart of our conclusion that vibrational energy transfer between the terrace and step is occurring on the dihydride stepped surface. The results suggest that the short lifetime step modes act as drains for the vibrational energy of all the Si-H oscillators.

The transients involving the pair of C_2 and C_3 modes all have a short lifetime of approximately 60 ps. The similar lifetimes are evidence of strong coupling between these modes and they are consistent with the C_2 and C_3 modes being the asymmetric and symmetric modes involving the Si-H(2) and Si-H(3) bonds. In this mode assignment, energy is exchanged rapidly between the C_2 and C_3 modes and they then relax at the same rate. The longer lifetime of 120 ps of the strong $C_1 \rightarrow C_2$ excitation shows that all step modes are coupled but that the C_1 mode differs from the other two step modes. Assignment of the C_1 mode to the Si-H(1) stretching mode could explain its slightly different dynamics.

The short lifetimes of the dihydrides step modes are very likely due to the presence of higher frequency modes. An HREELS study[23] of the dihydride stepped surface has shown the presence of a scissor mode at 910 cm^{-1} , which can reduce the number of phonons needed to deexcite the Si-H stretching modes from 4, for a monohydride on a flat surface, to a more efficient 3 phonons process.

4.2 Interpretation of the monohydride stepped surface results

The Si-H stretching modes vibrational relaxation rates on the monohydride stepped surfaces are noticeably different than those measured on the dihydride stepped surface. Lifetimes of 550 ps or more are measured. The terrace monohydride A→A lifetime of 600 ps is intermediate between the dihydride stepped (480 ps) and the flat surface (950 ps) lifetimes. In contrast to the dihydride step modes, the asymmetric and symmetric unit cell step modes B₁ and B₂ relax at a rate similar to that of the terrace monohydride (≈600 ps). This result proves that the effect of steps on the terrace monohydrides relaxation depends on the nature of their termination. If interadsorbate energy transfer is occurring on both surfaces, their different vibrational dynamics can be explained by the fact that the short lifetime dihydride steps rapidly dissipate the terrace energy whereas the longer lifetime monohydride steps do not.

The rapid and significant depletion observed when different modes are pumped and probed indicates that sizeable interadsorbate energy transfer is occurring on the monohydride stepped surface. The simplest interpretation of these results is that there is a rapid energy equilibration between all the Si-H oscillators, in less than 100 ps, followed by a collective decay of ≈600 ps. Within the experimental uncertainties[8], all transient measurements, except the A→B₂ give support to this model. We note that although a significant depletion occurs in the A→B₂ transient, the experimental errors are rather large. This is caused by variations between different sets of measurements which are larger than the error on a single measurement, and may be caused by sample quality problems.

The strong coupling between the monohydride stretching modes complicates the interpretation of the transient results. In the SFG spectra and more spectacularly in the IR absorption spectra[13] intensity borrowing, indicative of strong dipolar interactions, makes the step modes the dominant feature of the vibrational spectrum. Intensity borrowing reflects the fact that terrace and step modes become delocalized because of strong dipolar interactions[24]. A normal mode calculation[19] which quantifies this effect suggests that 37% of the terrace mode energy is in the step oscillators and 44% of the energy of the B₂ mode is in the terrace oscillators. The B₁ mode further away

in energy from the A mode has only 2% of its energy on the terrace oscillators. In contrast, on the dihydride stepped surface only a slight delocalization (≈5%) of the C₁ and the A mode is predicted. This calculation gives further support to fast interadsorbate energy transfer on the monohydride stepped surface. However, because of the strong interadsorbate couplings, it is likely that processes other than energy transfer will be present in the transient spectra[19]. Important transient spectral shifts are likely to occur because of intensity borrowing changes during mode excitation. Also anharmonic interactions are expected because of the proximity of the Si-H bonds. The fundamental nature of the interadsorbate energy transfer process can be completely changed by these effects since they do not involve through space energy transfer.

4.3 Kinetic model of interadsorbate energy transfer

The eight and six two-color transient measurements on the dihydride stepped and monohydride stepped surfaces, respectively, give a large base of data on which to build a linear kinetic model of vibrational energy flow. Nevertheless, simplifying approximations, based whenever possible on experimental measurements, need to be done to obtain quantitative estimates of the energy flow. The most important approximation of this model is the assumption that all the transient spectra are only due to change in the vibrational excited state population of the probed mode. This approximation has been shown recently to be somewhat inadequate by calculations[19] which indicate that substantial dipolar coupling occurs on both the monohydride and dihydride stepped surfaces, and that they cause noticeable changes in the transient spectra. This model nevertheless gives a useful global view of the energy flow although it is an oversimplified one. Within these limitations, we use the kinetic model to fit all the transient spectra of a given surface with a single set of interadsorbate and adsorbate/substrate transfer rates. In our model[8], the rate of excitation in a mode *i* is given by the following equation:

$$\frac{d\eta_i(t)}{dt} = -c_{ii}\eta_i + \sum_{j \neq i} c_{ij}[\eta_j(t) - \eta_i(t)] \quad (2)$$

where η is the excited state population, c_{ij} is the

coupling constant between mode i and j , and c_{ii} is the coupling constant of mode i with the substrate. The solution of this equation is a sum of exponential decays that can be expressed by the following equation:

$$\eta_i(t) = \sum_k e^{-d_{kk}t} u_{ik} u_{kj} p_j \quad (3)$$

where d_{kk} is a coupling constant. $u_{ik}u_{kj}$ can be seen as the weight of a decay channel in the overall decay process. p_j is the maximum energy absorbed by the mode j in absence of decay channels ($c_{ij}=0$). The relative values of p for the different modes are used to adjust the amplitude of the kinetic model fit to the experimental data.

A terrace is represented by five oscillators where only one is pumped or probed. We assumed a rapid equilibration between the terrace oscillators and we choose the coupling rate between the terrace oscillators to be equal to the dephasing time (≈ 10 ps)[15]. With this assumption a step mode is coupled identically to all five terrace modes.

The best fit of the kinetic model of all the dihydride stepped surface transients are shown as solid lines in Fig. 4, 5 and 6. The fits are relatively good for almost all the transient spectra. The results confirm the central role of energy transfer to the steps in the relaxation of the terrace modes: Up to 2/3 of the terrace energy is transferred to the steps because of an efficient terrace-to-step energy transfer rate of $(450 \text{ ps})^{-1}$. In this approximate model, the C_2 mode would be the central element in the interadsorbate energy flow process since it is strongly coupled to all the other modes. Since only the C_2 mode would be coupled to the terrace modes, transfer to the C_2 mode accounts for $\approx 65\%$ of the energy relaxation of the terrace Si-H oscillators. The energy received by the C_2 mode from the terrace oscillators is transferred mainly to the C_1 and C_3 modes in less than 100 ps. The vibrational energy is then dissipated by these step modes by transfer to other types of vibrational modes in 140 ps or less. We note inconsistencies in this model. The terrace mode A has a longer lifetime (1 400 ps) than on the flat Si(111) surface (950 ps). Furthermore, although this model reproduces the results adequately it is not consistent with dipole-dipole calculations[7,8,19] which predict coupling of both the C_1 and C_2 modes with the terrace mode A.

This disagreement might be due to the neglect of the dynamic screening effect. Clearly, further work is needed to develop a kinetic model which would include both dipolar effects and adequate coupling among the adsorbates and with the substrate.

Table 1: Kinetic model interadsorbate coupling lifetimes on the monohydride stepped surface.

Coupled modes	Lifetime (ps)
A-substrate	1000
B ₁ -substrate	400
B ₂ -substrate	400
A-B ₁	30
A-B ₂	30
B ₁ -B ₂	30
A-A	12

On the monohydride stepped surface, the application of the kinetic model gives an inconsistent fit of the population changes in the transient data. This inconsistency lies in our assumption that the transient changes are only due to energy transfer. In the case of the monohydride stepped surface, this approximation is not adequate because of the important mode delocalization which makes direct excitation an important process. Nevertheless, we have used a scheme of fast equilibration between all the Si-H oscillators to mimic the direct excitation and to reproduce the fast component observed in the B₂→B₂ transient. This results in the intermode couplings rates of $\approx (30 \text{ ps})^{-1}$ or more shown in Table 1. The resulting fits are shown as a solid line in Fig. 9 and 10. They qualitatively reproduce the observed transient. Although the details of the energy transfer process can not be resolved by such a simple kinetic model, it is clear that the Si-H stretching modes are strongly coupled and that vibrational energy is exchanged. It is likely that on the monohydride stepped surface there is a rapid equilibration of all the

The very rapid energy transfer between terrace and step compared to the measured excited state lifetimes gives additional support to a rapid equilibration of terrace and steps modes followed by their slow collective relaxation.

5. SUMMARY

We have followed the vibrational energy equilibration pathways of Si-H stretching modes on hydrogen-terminated stepped vicinal Si(111) surfaces with a two-color IR pump/SFG probe spectroscopy. The measurements reveal the central role of interadsorbate energy transfer in the vibrational relaxation process. The extent of surface vibrational energy flow occurring on both type of stepped surfaces is determined by the combination of the strength of the dipolar interactions between the Si-H oscillators and the nature of the step termination.

On the dihydride stepped surface, the dominating feature of the vibrational energy relaxation process is found to be the draining of the terrace Si-H oscillators energy by short lifetime step modes. From the two-color vibrational lifetime measurements three distinct characteristics of the energy transfer process emerge: Firstly, whenever the terrace mode is pumped and/or probed a lifetime of ≈ 500 ps is measured. Secondly, shorter lifetimes of ≈ 100 ps are measured in the case of energy transfer among the step modes. Thirdly, the step modes are found to form two groups; the strongly coupled C_2 and C_3 modes with identical lifetimes (≈ 70 ps) and the C_1 mode which has a slightly longer lifetime (≈ 120 ps). By combining all the two-color lifetime measurements we have been able to construct a simple kinetic model of the energy flow pathways which suggests that the terrace oscillators relax by transferring a significant fraction of their energy ($\approx 65\%$) to the step modes. Finally, we suggest, based on energy transfer rate calculations, that interadsorbate energy transfer is occurring via dipole-dipole interactions.

On the monohydride stepped surface, the interadsorbate coupling is stronger, but the long lifetime step modes can not act as drains for the terrace modes and the terrace lifetime is longer than on the dihydride stepped surface. The two-color transient measurements reveal that, in contrast to the dihydride stepped surface, all the Si-H vibrational

lifetimes are similar (≈ 600 ps). Although this result seems to be simple, the determination of the detailed kinetic of the energy flow is complicated by the strong interadsorbate couplings. A normal mode calculation[19] shows that the most important effect of the strong dipole coupling between the adsorbates is a substantial delocalization of both step and terrace modes of $\approx 40\%$ which results in the simultaneous excitation of the modes. Therefore it is difficult to differentiate energy transfer from spectroscopic effects. We can only suggest that on the monohydride stepped surface there is a fast equilibration of all the modes followed, most probably, by a slow collective decay of ≈ 600 ps.

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