Vibrational energy transfer among adsorbate modes: Picosecond dynamics on stepped H/Si(111)

K. Kuhnke,^{a)} M. Morin,^{b)} P. Jakob,^{c)} N. J. Levinos, Y. J. Chabal, and A. L. Harris AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 28 April 1993; accepted 9 July 1993)

Direct measurements of interadsorbate vibrational energy flow among Si-H stretching modes on hydrogen-terminated, stepped vicinal H/Si(111) surfaces are made. A two-color picosecond infrared method is used in which one vibrational mode is pumped by a resonant infrared pulse and other vibrational modes are probed by vibrationally resonant sum frequency generation to observe energy transfer. The surfaces are prepared by chemical etching in HF solutions and have monohydride-terminated (111)- (1×1) terraces, and average terrace widths of approximately five atoms. Two types of surfaces, differing in having either monohydride- or dihydride-terminated steps, are examined. The results on both surfaces confirm that interadsorbate energy transfer competes efficiently with energy relaxation to the substrate. On the dihydride-stepped surface, the energy flow is analyzed to give a relatively complete kinetic model of the energy equilibration pathways. The model confirms that the fast relaxing dihydride-terminated steps (60–120 ps lifetime) drain a large fraction ($\sim 2/3$) of the terrace Si-H mode energy (the terrace mode intrinsic lifetime is fit to be ~ 1.4 ns). The model is consistent with terrace-step energy transfer by dipole-dipole coupling between Si-H oscillators. On the monohydride-stepped surface, the experimental results suggest even stronger terracestep coupling, but the monohydride step lifetime is long (>500 ps) and does not drain the terrace mode energy. The coupling of the monohydride steps to the terraces by dipole interactions is in fact calculated to be strong enough so that the step and terrace modes mix, and detailed kinetic analysis of the monohydride-stepped surface is therefore ambiguous because of strong spectral interactions of the modes.

I. INTRODUCTION

Measurements of surface vibrational energy flow quantify fundamental molecule-surface interactions that control vibrational energy equilibration in surface chemical processes. When the molecule-surface interactions are strong, and when intramolecular relaxation itself is fast, as have been found for adsorbates at metal surfaces,¹⁻³ then interadsorbate interactions can be neglected. However, for weaker molecule-surface interactions, as for simple adsorbates on insulator⁴ or semiconductor⁵ surfaces, interadsorbate energy flow can become important in vibrational equilibration. We present here direct measurements of interadsorbate vibrational energy flow on a semiconductor surface. Equilibration pathways for Si-H stretching modes on hydrogen-terminated, stepped vicinal Si(111) surfaces are mapped using a two-color infrared method in which one vibrational mode is pumped and other vibrational modes are probed to directly observe energy transfer. The results show that because of the intrinsically long (~ 1 ns) lifetime of the Si-H stretching mode on flat (111) terraces,⁵ interadsorbate terrace-to-step vibrational energy

transfer can dominate the relaxation of terrace oscillators. In addition, complex intrastep vibrational energy transfer processes are resolved.

Well-ordered, stepped hydrogen-terminated surfaces are obtained by chemical preparation of samples cut vicinal to the (111) plane.^{6,7} These samples show one Si-H stretching mode at the same frequency as on the flat (111) surface, assigned to the vibration of Si-H oscillators on (111) terraces.⁶ Other well-separated modes are assigned to Si-H vibrations at the steps.⁶ Either monohydride- or dihydride-terminated steps are prepared by cutting vicinal to the (111) plane along different surface azimuths. The geometries of the steps in the two cases, formulated on the basis of both detailed IR absorption measurements and *ab initio* quantum chemical calculations,⁶⁻⁸ are shown in Fig. 1.

The present results extend previous one-color experiments⁹ which suggested, but could not clearly show, that terrace-step energy transfer takes place on these surfaces. The results demonstrate unambiguously that the terrace and step Si–H vibrational modes on these surfaces are strongly coupled, and that the strength of the coupling is consistent with estimates of dipole–dipole interactions among the Si–H oscillators. The extent to which the coupling can be resolved into a kinetic map for energy flow differs between the surfaces with dihydride-terminated steps and the surfaces with monohydride-terminated steps. On surfaces with dihydride-terminated steps, the short lifetime step-localized modes are confirmed to act as energy drains for the longer lifetime terrace-localized Si–H modes.

^{a)}Present address: Institut de Physique Experimentale, EPFL, Lausanne, Switzerland.

^{b)}Present address: Department of Chemistry, University of Ottawa, Ottawa, Canada.

^{c)}Present address: Fakultat für Physik, E20, Technical University of Munich, 8046 Garching, Germany.



FIG. 1. Surface and adsorbate geometries of the chemically prepared hydrogen-terminated vicinal Si(111) surfaces (a) miscut in the $\langle \overline{112} \rangle$ direction creates dihydride steps [H(1), H(2), and H(3) label the Si-H bonds involved in the three step modes]; (b) miscut in the $\langle 11\overline{2} \rangle$ direction creates monohydride steps with two different monohydride Si-H bonds in each step repeat unit. For both surfaces, the 9° miscut used in this study gives terraces with an average of four to five rows of Si-monohydride oscillators.

On this surface, energy transfer between step and terrace modes, as well as among the step modes themselves, can be resolved into a kinetic map for energy flow. The kinetic map suggests that particular step normal modes account for most of the coupling to the substrate. On surfaces with monohydride-terminated steps, the "step" and "terrace" vibrational modes are more strongly coupled and are therefore delocalized to some extent. The strong coupling results in large spectral saturation of all modes when one mode is pumped. The strong coupling and delocalization make it more difficult to disentangle strong spectral interactions from kinetic effects, but a rough kinetic model for this surface is also presented, assuming that the step and terrace modes equilibrate very rapidly and decay together.

Section II presents the experimental method. Section III presents the measured sum frequency generation (SFG) and excitation spectra and the pump and probe transient results for both the dihydride- and monhydridestepped surfaces. In the discussion in Sec. IV, the transients of both surfaces are analyzed and described by a linear kinetic model. The extent to which the adsorbate modes are spatially separated and the effects of modemode screening are also discussed. Section V summarizes the conclusions. The formula used to determine the kinetic model is derived in the Appendix (Sec. VI).

II. EXPERIMENT

A vibrational mode is excited by a resonant infrared (IR) pump pulse. The maximum excitation achieved by the pump pulse is 10%-20%, which is low enough so that the total excitation is approximately linear with the incident IR intensity. Vibrationally resonant sum frequency generation (SFG) monitors the pathways of the energy relaxation.^{1,3} The SFG signal probes the time evolution of the excitation in the pumped mode or in a different adsorbate mode. Nonresonant SFG signal is negligible for the H/Si(111) system.^{5,9,10} The resonant SFG signal, generated by overlapping a visible probe pulse with an IR probe pulse that is resonant on a transition of interest, is proportional to $(n_0 - n_1)^2$, where n_1 and n_0 are the fractional populations of the excited and ground states of the probed transition. The fractional population of the excited state at delay τ_d from the pump in a transient experiment is therefore¹

$$n_1(\tau_d) = \frac{[1 - r^{1/2}(\tau_d)]}{2},\tag{1}$$

where $r=S(\tau_d)/S_{eq}$, $S(\tau_d)$ is the SFG probe signal at a particular probe delay, and S_{eq} is the SFG signal in the equilibrium (no excitation) system. The equation assumes that no significant excitation of higher states is created by the pump. This is valid for the Si-H stretching mode, whose excited state transition is shifted 80 cm⁻¹ from the fundamental,¹⁰ well outside the pump bandwidth of <5 cm⁻¹ full width at half-maximum (FWHM). To simplify notation when discussing the excited state population of several modes, we also define the excitation of mode *i* as $\eta_i \equiv n_1 \pmod{i}$.

Figure 2 shows the experimental arrangement. The mode-locked Nd:YAG laser produces 70 ps pulses at 532 nm wavelength with a repetition rate of 76 MHz. These synchronously pump two dye lasers operating with sulforhodamine *B* dye, providing two independently tunable frequencies ~600 nm. Dye laser I is operated with a birefringent filter and an etalon to narrow its spectral width to about 2 cm⁻¹. This laser cannot be scanned and is used as a fixed frequency source in all experiments. Dye laser II is usually operated with only a three-plate birefringent tuning element, giving a spectral bandwidth of 4.5 cm⁻¹ FWHM, and can be wavelength scanned under computer control. In some experiments, dye laser II is also used at fixed frequency with an etalon, so that both pump and probe have 2 cm⁻¹ resolution.

Approximately 5% of the energy of the 1.06 μ m IR pulses from the Nd:YAG laser is used to seed a 40 Hz regenerative amplifier. The regenerative amplifier provides a frequency-doubled output of 50 mJ per pulse at 532 nm which amplifies the two red beams in two three-stage rhodamine 640 dye amplifiers. About 5% of one of the amplified red beams is split off for use as the visible probe pulse. The visible beam is spatially filtered, then focused to a spot with ~1.5 mm diameter on the surface.

J. Chem. Phys., Vol. 99, No. 8, 15 October 1993

Downloaded 02 May 2005 to 134.105.248.20. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp



FIG. 2. A scheme of the optical system for the two color pump and probe experiment. KTP=KTP frequency doubling crystal.

The two amplified red beams are shifted into the IR region near 5 μ m wavelength by stimulated electronic Raman scattering in an atomic cesium vapor within the heat pipe.¹¹ After filtering out remaining visible light and spurious IR frequencies, the two IR beams are focused to the surface on a spot with less than 400 μ m diameter. The energy densities are 7 mJ cm⁻² for the IR pump pulse, 3 mJ cm⁻² for the IR probe pulse, and 3 mJ cm⁻² for the visible probe pulse. The pump and probe IR beams are overlapped within the larger visible spot before each experiment by maximizing the pump-induced excitation in an easily observable mode. The SFG signal is normalized for each pulse to the energy of the incident IR probe to account for IR energy fluctuations. Fluctuations in the visible probe beam are a negligible source of noise in the experiments and are neglected.

Dye laser II is scanned to obtain SFG spectra and is used as the tunable excitation source in excitation spectra. It determines the spectral resolution in all scanned experiments. Although the scanning resolution is broader than the 1 cm⁻¹ adsorbate vibrational linewidth, it is narrower than the mode separation on the dihydride-stepped surface. However, for scanned excitation spectra of the monohydride-stepped surface, the pump bandwidth is nearly as broad as the mode separation. Fixed frequency transient measurements on this surface are carried out using etalons in both lasers, so that both pump and probe resolve single modes.

The etalon in dye laser I gives a pulse length of 30 ps, an improvement in time resolution compared to the earlier investigation.⁹ While dye laser II could potentially operate with a 10 ps pulse, it is instead operated with a 30 ps pulse by misadjusting its cavity length, since the longer pulse substantially improves infrared generation efficiency in the cesium atomic vapor.

Hydrogen-terminated vicinal Si(111) samples with either dihydride-terminated steps (cut 9° off the $\langle 111 \rangle$ plane along the $\langle \overline{112} \rangle$ azimuth) or monohydride-terminated steps (cut 9° off the $\langle 111 \rangle$ plane along the $\langle 11\overline{2} \rangle$ azimuth) are prepared by chemical etching as described elsewhere.⁶ The two types of samples both have average terrace lengths of 19.8 Å. The mean numbers of terrace rows are 4.6 and 5.3 for the monohydride- and dihydride-stepped surfaces, respectively.¹² After preparation, a sample is quickly mounted in an ultrahigh vacuum (UHV) chamber purged with N₂. The chamber is pumped down to $\sim 10^{-9}$ mbar, as previously described.¹³ Experiments are carried out with the sample at room temperature ($\simeq 300$ K). The scattering plane in all experiments is perpendicular to the direction of the step edges.

The samples are considered "clean" as long as peak widths remain below the laser resolution, and the nonresonant background remains below a few percent of the resonant peak height. A newly prepared sample typically remains clean for several weeks in the vacuum chamber. Some of the transient results on weak modes of the dihydride-stepped surface are averages of up to ten data sets from several days. The excitation in an easily observed mode (A or C_2) is measured immediately before or after each transient, and is used to scale the transients when averaging the data from different runs. The transients on Aand C_2 with pump and probe on the same mode are also used for adjusting the zero of the probe delay. The instantaneous SFG response of an evaporated gold film^{1,3} is used to show that probe delay zero coincides with the steepest part of the rising edge in those transients. The SFG response of the gold film also provides an IR-visible pulse cross-correlation measurement of 50 ps FWHM.

III. RESULTS

A. A 9° miscut H/Si(111) surface with dihydride steps

The SFG spectrum of the dihydride-stepped surface [Fig. 3(a)] reproduces the earlier measurement⁹ with a slightly lower spectral resolution. The spectrum shows three peaks, which have been previously labeled in IR absorption experiments⁶ as A, C_2 , and C_3 . Peak A is the Si–H stretching mode of the terrace. Peaks labeled C_i (i=1-3) correspond to modes localized at the steps. C_2 and C_3 are assigned to out-of-phase and in-phase stretching vibrations, respectively, of the two Si–H oscillators which are labeled H(2) and H(3) in Fig. 1(a). Quantum chemical calculations have shown that these two oscillators are strongly coupled by steric interaction, although they are bonded to different silicon atoms.^{6,8} The mode C_1 , which is not seen



FIG. 3. (a) The SFG spectrum at equilibrium for the 9° miscut dihydride-stepped surface; (b) the excitation spectrum of mode C_2 with probe delay set to 40 ps. Excitation calculated according to Eq. (1) in the text.

in the SFG spectrum, is assigned to a mode which mostly involves the Si-H stretching motion of the H(1) oscillator: the quantum chemical calculation shows that H(1) is vibrationally decoupled from the motion of H(2) and H(3). These assignments are somewhat counterintuitive, since one would normally expect the step dihydride oscillators H(1) and H(2) to be coupled to give a symmetric and asymmetric stretching mode.¹⁴ The electronic structure calculations indicate, however, that the steric interaction with H(3) on the lower terrace couples H(2) and H(3), while decoupling the two dihydride oscillators H(1) and H(2), and both IR and Raman measurements are qualitatively consistent with this assignment. This coupling makes H(3) part of the step mode and therefore reduces the average number of oscillators in the terrace mode of the dihydride-stepped surface from 5.3 to 4.3.

Figure 3(b) shows an excitation spectrum in which the fractional population of the excited state $(1-r^{1/2})/2$ for the C_2 mode is monitored while scanning the pump IR beam wavelength with a fixed probe delay of 40 ps. This two-color experiment measures which pump frequencies lead to a change in the excited state population of mode C_2 40 ps later. The delay of 40 ps is chosen because it is near the maximum in the transient excitation for all of the probed modes, given the pump pulse width. The baseline level between 2110 and 2130 cm⁻¹ represents true zero excitation in mode C_2 , confirmed by comparison of the C_2 probe signal with and without the pump. Therefore, the excitation spectrum does not show a nonresonant back-



6117

FIG. 4. C_2 excitation spectra of the dihydride-stepped surface at different probe delays. The left-hand scale indicates excitation in C_2 as a function of the pump IR frequency on the bottom scale. Arrows to the right of each spectrum indicate the zero of excitation for the left hand scale, and the probe delay at which the measurement was made on the right hand scale.

ground. The frequencies of the peaks labeled A, C_2 , and C_3 agree with those of the corresponding peaks in the SFG spectrum. The mode C_1 appears in the excitation spectrum along with the other three modes because all four modes are IR active⁶ and absorb pump energy. A straightforward interpretation of the excitation spectrum is that within 40 ps, a significant part of this energy is transferred to mode C_2 . The appearance of mode C_1 is consistent with the argument that its absence in the SFG spectrum is due to a lack of Raman scattering, rather than a small IR cross section.^{9,15}

A series of C_2 excitation spectra is obtained by setting the pump delay to different values (Fig. 4). The pumped frequency region in Fig. 4 is limited to the region of the modes A, C_1 , and C_2 , and, for two of the intermediate spectra, includes only modes C_1 and C_2 . The arrow to the right of each spectrum in the figure defines the zero level for the excitation on the left-hand scale and indicates the delay at which the spectrum was taken on the right-hand scale. This figure can be read as the time development of excitation in C_2 as a function of the pump frequency and of the delay between pump and probe.

The temporal development at a single pump frequency is obtained by setting the pump to one mode position and the probe to another, and scanning the probe delay. We refer to pump mode X-probe mode Y transients as " $X \rightarrow Y$." Figures 5-7 show the $X \rightarrow Y$ transients measured on the dihydride surface. Several $X \rightarrow Y$ transients were not measured; $X \rightarrow C_1$ transients cannot be measured since C_1 is



FIG. 5. Excitation transients of the dihydride-stepped surface with the SFG probe set to the C_2 mode. The IR pump is set as labeled on each graph. (Solid points) experimental data; (solid lines) the result of the kinetic model described in the text (Sec. IV B). Note the different scales on the y axes.

absent in the SFG spectrum, and the SFG signal of C_3 is weak enough so that only the direct pumping experiment $[C_3 \rightarrow C_3 \text{ (Fig. 7)}]$ gives satisfactory $X \rightarrow C_3$ transients. The $C_3 \rightarrow A$ transient is also not shown because the excitation appearing in mode A after pumping mode C_3 is less than the noise level of $\eta_A \sim \pm 0.002$.

Figures 5(c), 6(a), and 7 show transients in which pumped and probed modes are identical, giving effective lifetimes for those modes. The terrace mode A decay is slower than that of the step modes C_2 and C_3 . Table I gives the lifetime obtained from a fit of a single exponential decay to the data—480 ps for the A mode, 73 ps for C_2 , and 56 ps for C_3 . The terrace mode lifetime is very close to the previous measurement of 450 ps.⁹ The step mode lifetimes are shorter than the previous measurements, indicating that the previous measurements were limited by the time resolution of the experiment. There is no direct measurement of the lifetime of C_1 since it cannot be probed directly. The one-color transients can be adequately fit by single exponentials, despite the clear evidence from the two-color measurements, analyzed in Sec. IV, that the decays involve multiple energy transfer pathways and thus are generally superpositions of several exponential decays. This emphasizes the importance of using two-color tran-



FIG. 6. Transients of the dihydride-stepped surface with the SFG probe set to the A mode. (Solid points) experimental data; (solid lines) results of the kinetic model; (dashed lines) a transient negative component proportional to the instantaneous excitation in mode C_2 and attributed to transient changes in the intermode screening interaction between C_2 and A (see the text; Sec. IV C).

sients to probe directly the energy flow from one mode to another.

B. 9° miscut H/Si(111) surface with monohydride steps

The SFG spectrum obtained for the monohydridestepped surface [Fig. 8(a)] is similar to the one published earlier,⁹ again broader due to a lower spectral resolution. The terrace mode A appears at 2084 cm⁻¹. No strong steric interaction couples the step Si-H bonds to the terrace Si-H bonds on this surface, so only two step modes are observed in IR.^{6,8} These modes B_1 and B_2 are assigned to the asymmetric and symmetric stretching modes of coupled Si-H oscillators on adjacent step-edge silicon atoms



FIG. 7. A transient of the dihydride-stepped surface with the SFG probe set to the C_3 mode. (Solid points) experimental data; (solid line) the result of the kinetic model.

J. Chem. Phys., Vol. 99, No. 8, 15 October 1993

TABLE I. Parameters for the surface with dihydride-terminated steps.

Pump	Probe	n ₁ , maximum excitation ^a	Fit decay time (ps)	Statistical error of measurement ^b (ps)	<i>p</i> , integra pump energy ^c
A	A	0.12	480	+90/65	0.65
A	С,	0.04	490	+80/-65	0.75
C_1	Â	0.01	520	+580/-220	0.30
C	С,	0.05	120	+30/-20	0.39
Ċ,	Ā	0.01	760	+1260/-330	0.20
c,	С,	0.11	73	+17/-13	0.30
C_{1}	Ċ,	0.04	53	+15/-11	0.20
Ċ,	Ċ,	0.10	56	+35/-20	0.25

 n_1 is the maximum observed excitation in a transient [see Eq. (1)]. bStatistical error was obtained by varying the decay time until the sum of

square errors reached twice the value of the best fit. ^cp adjusts the overall height of the solid line in Figs. 5-7 (from the kinetic model) (see Sec. IV B and the Appendix).

(see Fig. 1). The step mode B_2 at 2089 cm⁻¹ appears in the SFG spectrum, while the B_1 step mode at 2071 cm⁻¹ is too weak to be seen clearly in the SFG spectrum.

The excitation spectrum, probing the B_2 mode at 30 ps probe delay, is shown in Fig. 8(b). All modes observed by IR spectroscopy appear distinctly in this spectrum. The straightforward interpretation, as with the excitation spectrum of the dihydride surface, is that all modes absorb IR energy and transfer a significant fraction of it within 30 ps to the B_2 mode. The strong appearance of the B_1 mode in the excitation spectrum supports the argument that its ab-

H/Si(111) 9° MONOHYDRIDE STEPS



FIG. 8. (a) The SFG spectrum at equilibrium for the 9° miscut monohydride-stepped surface; (b) the excitation spectrum of mode B_2 , with the probe delay set to 30 ps. Excitation is calculated according to Eq. (1) in the text.



FIG. 9. Transients of the monohydride-stepped surface with the SFG probe set to the A mode. The IR pump is set as labeled on each graph. (Solid points) experimental data; (solid lines) results of the kinetic

sence in the SFG spectrum is due to a weak Raman contribution to the SFG susceptibility in the geometry of the present experiment.¹⁵

model. Note the different scales on the y axis.

The measured transients on the monohydride-stepped surface are presented in Figs. 9 and 10. The linewidth of the pump beam is reduced to 2 cm⁻¹ in the transients $A \rightarrow B_2$ and $B_2 \rightarrow A$ to limit the direct pumping of the neighboring mode to less than 2%. The transients with identical pump and probe frequencies on the modes A and B_2 in Figs. 9(a) and 10(c) show decay times of 600 and 690 ps, respectively (Table II). These values are smaller than those obtained in the previous investigation,⁹ where 820 and 1100 ps, respectively, were measured. The difference may be due to differences in sample quality (see the discussion in Sec. IV D).

IV. DISCUSSION

The most important conclusion from the two-color measurements is that transient changes are measured in most of the measured surface modes whenever a single mode is pumped. The results argue that all of the modes are therefore coupled to some degree. This coupling can, in principle, be due to either energy transfer from one mode to another, or to instantaneous changes in the spectra of the probed modes due to anharmonic or dipole interactions with the pumped mode even in the absence of energy transfer. It is sometimes difficult to distinguish these effects in transient spectroscopy. We begin the discussion with the most certain qualitative conclusions regarding energy transfer on the dihydride-stepped surface (Sec. IV A), and



FIG. 10. Transients of the monohydride-stepped surface with the SFG probe set to the B_2 mode. (Solid points) experimental data; (solid lines) results of the kinetic model.

proceed to a kinetic model for that surface based on the less certain assumption that all spectral transients are due to energy transfer alone (Sec. IV B). We discuss the effects of dipole screening and anharmonic coupling on the kinetic model in Sec. IV C. The energy flow on the monohydridestepped surface is discussed in Sec. IV D. The dipole screening effects between terrace and step modes on the monohydride-stepped surface makes the energy transfer process less clear than for the dihydride-stepped surface.

TABLE II. Parameters for the surface with monohydride-terminated steps.

Pump	Probe	n_1 maximum	Fit decay time (ps)	Statistical error of measurement ^b (ps)	<i>p</i> , integral pump energy ^c
- ump	11000	excitation	time (ps)	measurement (ps)	
A	A	0.18	600	+70/-70	1.26
A	B_2	0.11	1100	+270/-160	0.81
B_1	Ă	0.05	700	+140/-130	0.36
B_1	B_2	0.04	550	+100/-80	0.32
B_2	Ā	0.04	600	+130/-100	0.32
$\overline{B_2}$	B_2	0.17	690	+90/-80	1.00
$\bar{B_2}$	$\vec{B_2}$	d	280	+55/-45	

 ${}^{a}n_{1}$ is the maximum observed excitation in a transient [see Eq. (1)]. ^bStatistical error was obtained by varying the decay time until the sum of square errors reached twice the value of the best fit.

^cp adjusts the overall height of the solid line in Figs. 9 and 10 from the kinetic model (see Sec. IV D and the Appendix).

^dFast component of the $B_2 \rightarrow B_2$ transient.

A. Primary energy transfer processes on the dihydride-stepped surface

The excitation spectra in Figs. 3(b) and 4 illustrate that the C_2 mode is excited when any of the four modes A through C_3 is pumped. The decay time of the C_2 excitation depends greatly on which mode is pumped, indicating that energy flow into (or through) the C_2 mode is determined by the lifetimes of the other modes. The single exponential fits of the various $X \rightarrow Y$ transient curves, listed in Table I, fall into three groups. First, when A is pumped $(A \rightarrow C_2)$ or probed $(C_1 \rightarrow A, C_2 \rightarrow A)$, the decay time is ~500 ps within the error limits of the measurements. This value is consistent with the 480 ps lifetime of A in the direct measurement $(A \rightarrow A)$ and is a strong indication that A acts as an energy reservoir. Energy flows into other modes from A for ~ 500 ps, and when energy is transferred into A from a short lifetime mode, it decays with a 500 ps lifetime. Second, the C_2 , C_3 mode transients ($C_2 \rightarrow C_2$, $C_2 \rightarrow C_3$, and $C_3 \rightarrow C_2$) are fast with similar decay times of ~ 60 ps, consistent with strong coupling between these modes. Third, the $C_1 \rightarrow C_2$ decay time is intermediate (120 ps), providing an indirect probe of the C_1 lifetime, which is longer than the other two C modes.

The $C_1 \rightarrow A$ and $C_2 \rightarrow A$ data, showing that the A mode excitation survives long beyond the short lifetime of the pumped C modes, confirm that energy is exchanged between the terrace mode (A) and the step modes (C_1-C_3) . Shifts or intensity changes in the A mode due only to screening or anharmonic coupling with the pumped Cmodes can be ruled out since the C modes have relaxed within 100 ps, while the excitation in A persists for ~ 500 ps. This qualitatively confirms the argument made previously⁹ that step-terrace energy transfer occurs on these hydrogen-terminated surfaces. On the other hand, a negative signal spike is seen at short probe delays in both the $C_1 \rightarrow A$ and $C_2 \rightarrow A$ transients. This spike cannot correspond to energy transfer and is assigned to transient changes in the mode-mode dipole screening which lasts only as long as the pumped C modes remain excited. The dipole screening is discussed further in Sec. IV C.

The previous one-color measurements, made with longer pulses, could not determine unambiguously whether the step modes all have similar energy decay times, which would imply strong intermode coupling on the steps.⁹ The present measurements indicate that the C_1 mode is distinct from the (C_2, C_3) modes, both of which have similar dynamics. The quantum chemical calculation of the normal modes for the dihydride step assign the C_2 and C_3 modes to the out-of-phase and in-phase stretching modes of the strongly coupled H(2) and H(3) hydrogens^{6,8} [Fig. 1(a)]. The strong coupling between these two modes is consistent with the generally observed strong coupling between different hydrogen stretching modes involving the same set of bonds. The same quantum chemical calculation assigns the C_1 mode to an isolated stretching mode of the H(1) hydrogen at the top of the step, involving almost no motion of the H(2) and H(3) hydrogens. It is reasonable, therefore, that the C_1 mode lifetime is different than the other two C modes.

А

The distinction between the lifetimes of the C_1 and the C_2 , C_3 modes is valid even if the observed transients are not all due to energy transfer from the pumped modes to the probed modes. Instantaneous changes in the probed mode signal due to anharmonic coupling or dipole screening from the pumped mode must still decay in approximately the excitation lifetime of the pumped mode. Somewhat different conclusions about the energy flow are reached depending on whether or not the transients involve, e.g., anharmonic shifts, but the basic argument about relative lifetimes does not change. Independent of the nature of the coupling, the C_2 and C_3 modes have similar lifetimes ~ 60 ps, the C_1 mode has a lifetime approximately twice as long (~ 120 ps), and both are substantially shorter than the A mode lifetime of ~ 480 ps.

B. Kinetic model of the dihydride-stepped surface

The energy flow pathways of the Si-H stretching modes can be described with a linear kinetic model. The intermode couplings, as well as the individual mode relaxation rates, can be obtained by assuming that all transients are due to energy transfer [with the exception of the early time negative spikes in Figs. 6(b) and 6(c)], and that the observed excitation, calculated for the transients in Figs. 5-7 by Eq. (1), is a direct measure of the population of the excited state for the probed mode. The rate of change of energy in mode *i* can then be written

$$\frac{d}{dt}[\eta_{i}(t)] = -c_{ii}\eta_{i} + \sum_{j \neq i} c_{ij}[\eta_{j}(t) - \eta_{i}(t)], \qquad (2)$$

where $\eta_i \equiv n_1 \pmod{i}$ is the excitation of mode *i*, c_{ij} is the coupling constant between modes *i* and *j*, and c_{ii} is the coupling of mode *i* to the substrate. The solution for the excitation as a function of time in a pump *j*, probe *i* experiment is outlined in the Appendix. With C defined as the matrix of coupling coefficients, we can define the elements d_{kk} of the diagonal matrix **D** as the eigenvalues of **C**, and the rows of a matrix **U** as the eigenvectors of **C**. Then the solution is

$$\eta_i(t) = \sum_k e^{-d_{kk}t} u_{ki} u_{kj} p_j, \quad t \ge 0.$$
(3)

Here, p_j is the integral excitation in the pumped mode; it is the maximum excitation which would be observed in mode *j* in the absence of decay channels (all $c_{ij}=0$). The solution is a sum of exponential decays, each with a magnitude determined by the factor $u_{ki} \cdot u_{kj}$. The solution is convoluted with the instrumental time resolution for finite pump and probe pulse lengths.

The density of states for the terrace mode is 4.3 times larger than for each of the step modes because of the ratio of oscillators per mode on the terrace vs on the step. The approximately four or five rows of Si-H oscillators of the terrace are coupled by dipole coupling and form a set of normal modes with various phase relations both across and along the terrace. Only the in-phase mode across the terrace (and k=0 along the terrace) has an observable dynamic dipole moment. The problem is essentially identical



 C_2

450 ps

FIG. 11. The kinetic model for energy flow on the dihydride-stepped surface with a 9° miscut. The area of the plates corresponds to the multiplicity of the modes (assumed to be 5 for the terrace A mode, 1 for the others). The cross section of the connecting lines is roughly proportional to the intermode energy coupling constants, whose reciprocal value is printed at each line.

to calculation of the normal modes of finite domains on the H/Si(111) surface.¹⁶ The kinetic model therefore assumes five normal modes (each would have dispersion in k along the terrace) representing the various phase relationships across the terrace, only one of which is pumped and probed. By explicitly breaking the terrace oscillators into an observable A mode and four other modes, we retain the symmetry $c_{ij}=c_{ji}$ in Eq. (2). We choose the coupling among the terrace modes to be equal to the terrace mode dephasing time of 10 ps. We also assume that a given step mode is coupled identically to the five terrace modes. This is not a restriction because the terrace mode equilibration is fast.

The kinetic model is used to establish which pathways of energy transfer are consistent with the data. Therefore, the coupling parameters c_{ij} are varied until a qualitative fit to the measured transients is obtained. For each transient curve, the integral absorbed pump p_i is used to adjust the height of the fitting function in order to match the data. One test of the result is that the p_i values should roughly agree for different experiments in which the same mode is pumped.

The kinetic model which gave the best qualitative description of the data is shown in Fig. 11. The resulting kinetic curves are shown as solid lines in Figs. 5-7. The integral absorbed pump energies p_i used to match the magnitude of the transients are listed in Table I. The fit of the experimental data with this simple model is reasonably good, as shown by the solid lines in Figs. 5-7, and indicates that such a model is in general consistent with the data. It is not, however, unique and depends on the assumption that the observed kinetics are in fact due entirely to energy transfer. The most important qualitative feature of the model, which we believe must be true of any successful kinetic scheme, is that the terrace modes are coupled to the step modes with rate constants of $\sim (500 \text{ ps})^{-1}$, in order to account for the shortened lifetime of the terrace mode, as well as the observed flow of energy from excited step oscillators into the terrace. Other features which will generally be true in any successful kinetic scheme include the strong intermode coupling of the C_2 and C_3 step modes to account for the large excitation transfer in the $C_3 \rightarrow C_2$ transient and the strong coupling of these modes to the substrate because they show a fast relaxation time. In addition, the C_1 mode must be more weakly coupled to the C_2 and C_3 modes, and shows a weaker coupling to the substrate since it has a longer decay time in the $C_1 \rightarrow C_2$ transient. While these qualitative features must be retained, the actual coupling values in Fig. 11 are of course dependent on details of the model and we discuss some of the uncertainties below.

Two notable features of the kinetic model are determined by the particularly fast rise time and signal strength of the transient $A \rightarrow C_2$. These include the fact that only C_2 is coupled directly to A and that the drain of A to the substrate is slower than 1000 ps. In order to couple A and C_2 as strongly as possible but maintain the long decay of A, the coupling of A to C_1 and C_3 had to be small. These coupling constants are simply dropped in the resulting model. The intrinsic drain time of mode A also had to be lengthened to 1400 ps. This lifetime was originally believed to be close to 950 ps because it should be equal to the well-established lifetime of mode A on the flat Si(111) surface.^{5,9} However, an alternative explanation of the data may be that the $A \rightarrow C_2$ transient is affected by an instantaneous dipole coupling artifact, to be discussed in Sec. IV C and that the actual $A-C_2$ coupling is weaker. Then the overall coupling of the terrace modes to the steps could be somewhat smaller, perhaps as low as $(550 \text{ ps})^{-1}$, and could be distributed among both of the spectrally close C_1 and C_2 modes. (The proposed Forster dipole coupling, discussed below, would be very inefficient between spectrally separate A and C_3 modes, and this coupling has been assumed to be very small in any case.) The intrinsic decay time of the terrace would then be closer the flat surface value of 950 ps.

Other effects of modifying the strong $A-C_2$ coupling would also occur. Because of the strong $A-C_2$ coupling, combined with the relatively long A mode lifetime, the present model attempts to remove the necessary strong C_2 , C_3 -substrate coupling by one step from the A mode, so that C_2 is coupled weakly and C_3 is coupled much more strongly to the substrate. If the $A-C_2$ coupling were in fact weaker, this asymmetry could be reduced, so that both C_2 and C_3 could be coupled relatively strongly to the substrate. The coupling of C_1 to the C_2 , C_3 modes is not subject to severe restrictions as long as the overall decay of the C_1 mode is retained by adjusting the C_1 -substrate coupling.

The integral excitation p values used for the fits in Figs. 5-7 are shown in Table I. The two values obtained for each pumped mode agree within 50%. This variation is at least due partly to experimental variations (laser pump energy, spatial beam overlap, etc.). The p values for the modes $A/C_1/C_2/C_3$ can be approximated as 1/0.5/0.3/0.3. Assuming that the beams are incident in the step-up ($\langle 11\overline{2} \rangle$) direction and making use of the screened dipole moments of the modes obtained from polarized IR spectroscopy,¹⁷ we calculate for the relative IR cross section in our exter-

nal scattering geometry 1/0.5/0.3/0.1. Except for the C_3 mode, the excitation ratios therefore agree with the expected excitation. Step-down scattering gives 1/0.04/0.8/1, which does not agree well with the values obtained from the model. We take the experimental results as evidence that the scattering was in fact carried out in the step-up direction.¹⁸

The terrace-to-step transfer rate of $(450 \text{ ps})^{-1}$ for each terrace mode, which is derived from our kinetic model that takes into account energy transfer in both directions, is somewhat larger than the value of $(750 \text{ ps})^{-1}$ obtained⁹ by neglecting back transfer from the step to the terrace. As noted above, the present rate may actually be as low as $(550 \text{ ps})^{-1}$. In any case, the terrace-to-step energy transfer accounts for approximately 1/2 to 2/3 of the energy flow from the terrace normal modes.

A terrace-to-step transfer rate in the range of (450-550 ps) $^{-1}$ is consistent with the previous⁹ estimate of (500–600 ps)⁻¹ based on Forster energy transfer from the Si-H oscillators of the terrace to those of the step, calculated using the known geometries, line positions, and transition dipole moments of the Si-H modes. That calculation assumed that pairwise, uncorrelated interactions among individual Si-H oscillators transferred energy from an excited mode to other modes on the surface. The assumption of uncorrelated single oscillators is rationalized on the basis that the transfer time (~ 500 ps) is much longer than the dephasing time of the modes (10 ps at 300 K). The present result therefore confirms that dipole coupling is the most probable mechanism for terrace-step energy transfer, and illustrates the substantial effect of the Si-H dynamic dipole moment on the dynamics of the overlayer. The strong dipole coupling, however, raises issues of mode delocalization and screening effects on the surface, which we discuss in the next section.

C. Dynamic screening in the transients of the dihydride-stepped surface

The kinetic model assumed that the normal modes of the surface are localized to either step or terrace. However, the energy transfer between terrace and step is attributed to dipole-dipole coupling, and this coupling should be included in the calculation of the surface normal modes. The coupling tends to extend the vibrational motion associated with each normal mode to adjacent oscillators. We have carried out normal mode calculations for the monohydride- and dihydride-stepped surfaces. Details of the calculation will be presented elsewhere.¹⁹ On the dihydride-stepped surface, using the step normal modes from the quantum chemical calculations^{7,8,20} and including dipole coupling between terrace and step, we find that the overlap is mostly between the terrace and C_1 ; ~5% of the energy of the terrace mode is on H(1) and $\sim 7\%$ of the energy of C_1 is on the terrace. The C_2 and C_3 modes remain essentially localized.

Although the normal mode calculation is approximate, neglecting higher order multipole effects and changes in the substrate electronic screening near steps, it shows qualitatively that the modes remain localized to steps or terraces on the dihydride-stepped surface. This supports a picture of energy transfer from one localized species to another and therefore indirectly supports the argument that dipole coupling determines the step-terrace energy flow. This is because the alternative mechanism of anharmonic coupling between step and terrace is probably unimportant in the dynamics for localized modes since the cross anharmonicity must be small for Si-H oscillators separated by at least two silicon atoms.

The extent of delocalization on the dihydride-stepped surface is not, however, completely negligible. Intensity borrowing will occur between step and terrace oscillators due to dynamic dipole screening, a spectroscopic manifestation of the $\sim 5\%$ mode delocalization. Transient changes in the screening are expected to occur upon excitation of any mode involved in the interaction. This is because the interaction is proportional to the dynamic dipole moments of the two interacting modes and the effective dynamic dipole moment changes upon excitation.^{19,21} The negative spikes at early time in the $C_1 \rightarrow A$ and $C_2 \rightarrow A$ transients in Figs. 6(b) and 6(c) are assigned to this effect, consistent with the fact that they last only as long as the C mode excitation. The effect should be reversed in the $A \rightarrow C_2$ transient (*positive* excitation in C_2), since oscillator strength is preserved in the interaction.²¹ We estimate that ~30% of the observed excitation in the $A \rightarrow C_2$ transient may be due to a transient change in the screening.¹⁹ Since that component is instantaneous, it may explain the initial fast rise of the data above the line from the kinetic model. It also suggests that in attempting to fit the $A \rightarrow C_2$ data without correcting for the intensity borrowing, we overemphasize the $A-C_2$ interaction.

Finally, we note that the clear separation of the step and terrace modes does not hold for the intermode coupling among the step modes. Strong intermode anharmonic interactions cannot be ruled out for these modes. We are encouraged by the ability to fit the entire set of kinetic data by a single kinetic model, and we emphasize that essential conclusions regarding differences in step mode lifetime are valid even if anharmonic coupling is present.

D. Interpretation of the monohydride-stepped surface kinetics

The dynamics of the Si-H stretching modes on the monohydride-stepped surface are different from the dynamics on the dihydride surface. All transients show decay times of 600 ps or more (Table II). The step modes do not show a fast relaxation, and the terrace mode lifetime is not shortened to the same extent as on the dihydride-stepped surface. This agrees with previous measurements,⁹ although the present transient measurements tend to be somewhat ($\sim 30\%$) faster than those measured previously. One exception is the $A \rightarrow B_2$ transient lifetime of ~ 1100 ps, which is similar to the decay times observed before.

The fast rise times and large excitation levels that are observed on the monohydride-stepped surface, even when the probed mode is different than the pumped mode, indicate that intermode energy transfer is rapid. This suggests a simple picture of fast equilibration (<100 ps) among all three adsorbate modes followed by a collective slow decay. However, under this assumption, we would expect to observe the same decay times for all transients. The fact that different decay times are observed (Table II) is either due to experimental uncertainties in the lifetimes, with $A \rightarrow B_2$ particularly spurious, or is an indication that such a simple model cannot hold up. From a set of measurements of the transient $A \rightarrow A$ on the *dihydride*-stepped surface taken on different days, we found that the uncertainty of the decay time in the measurements is probably larger than the statistical error from a single decay. These large fluctuations are only observed in transients with a slow decay and may arise from defect or step distributions that are inhomogeneous on a macroscopic scale. On the monohydridestepped surface, it is not always possible to eliminate dihydride-terminated kinks⁷ that might act as energy drains just as they do on the fully dihydride-stepped surface. Variations in their local density might contribute to variations in the otherwise slow decay of the monohydridestepped surface.

An additional complication in the dynamics of the monohydride-stepped surface arises from the normal mode calculation, which predicts substantial delocalization due to dipole coupling. The terrace A mode and the step B_2 mode are only separated by 5 cm^{-1} , so the dipole interaction between them is strong. The normal mode calculation indicates that 37% of the energy in the A "terrace" mode is located on the two step oscillators and 44% of the energy of the B_2 mode is on the terrace oscillators.¹⁹ The B_1 mode is more weakly interacting, with 2% of its energy on the terrace oscillators. This overlap of terrace and step modes is consistent with fast energy transfer, but it can also create large transient spectral changes due to excitation-induced changes in the dipole screening. In addition, there may be strong anharmonic interactions since the modes involve a common set of Si-H oscillators. These effects may also change the nature of the intermode energy transfer, since the modes need not couple by spatial dipole energy transfer.

An application of the linear kinetic model to the monohydride-stepped surface indicates additional problems in assuming that the kinetics result simply from energy transfer dynamics. For instance, in order to fit the transients (Figs. 9 and 10), we attempted to use the obvious scheme in which all three modes equilibrate rapidly and then relax together to the substrate. The effective decay time of the whole system determines the total coupling to the substrate, which can be partitioned arbitrarily among the three modes. The initial rapid decay of the $B_2 \rightarrow B_2$ transient can be assigned to the initial fast energy flow from the pumped B_2 mode into the other modes. This initial decay component then sets an upper limit on the rate of the intermode equilibration since a very large rate would lead to instantaneous equilibration even during the pumping process. For instance, the absence of such an initial fast decay in the $A \rightarrow A$ transient on both the monohydride- and dihydride-stepped surfaces is due to the very fast energy equilibration among the five terrace modes assumed to oc-

J. Chem. Phys., Vol. 99, No. 8, 15 October 1993

Downloaded 02 May 2005 to 134.105.248.20. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp

TABLE III., Kinetic model parameters for the monohydride-stepped surface.

Coupling between modes	Inverse rate constant (ps)		
A and substrate	1000		
B_1 and substrate	400		
B_2 and substrate	400		
A and B_1	30		
A and B_2	30		
B_1 and B_2	30		
Among terrace modes	12		

cur in the terrace dephasing time of ~ 10 ps. The initial fast decay of the $B_2 \rightarrow B_2$ transient is fitted under the arbitrary assumption that the modes A, B_1 , and B_2 are coupled by equal rate constants.

The inverse rate constants used for the fits are shown in Table III, while the integrated pump energy values p are shown in Table II, and the solid lines in Figs. 9 and 10 illustrate the resulting dynamics. The wide scatter in the pvalues indicates one problem with the model. There is a ratio of 1:3 in the best fit integral pump energies between $B_2 \rightarrow A$ and $B_2 \rightarrow B_2$. Although this difference might be accounted for by introducing a large dipole screening interaction among the normal modes, this effect itself invalidates the assumption that the transients are primarily a quantitative measure of energy flow. We conclude that a simple model which assumes that the transients are only due to energy transfer, and that fast energy equilibration occurs, does not describe the data adequately.

To summarize, pumping any Si-H stretching mode on the monohydride-stepped surface causes signal changes in other observable modes which are as large as those in the pumped mode itself. This behavior contrasts with the range of coupling strengths observed on the dihydridestepped surface and is interpreted as evidence of strong dipole-dipole coupling among the Si-H stretching modes of the surface. The strong coupling probably creates modes that are not localized to step and terrace, but involve different motions of the entire set of Si-H bonds. The modes may have strong screening interactions and strong anharmonic interactions. Together with experimental uncertainties due to sample variation, the strong coupling between Si-H oscillators makes kinetic interpretation difficult on the monohydride-stepped surface.

V. CONCLUSION

Energy transfer between vibrational adsorbate modes is investigated by a two-color IR-pump and SFG-probe experiment on two vicinal H/Si(111) surfaces with the same step density. The lifetime measurements on the dihydride-stepped surface reveal a significant transfer of energy between step and terrace. The two-color pump and probe scheme also allows the investigation of two modes that are not observed in SFG since they absorb IR energy and transfer a significant part of it to a mode that is observed in SFG. A linear kinetic model is applied to obtain both step-terrace energy transfer times and intermode en-

ergy transfer times for modes on the steps. The terracestep energy transfer is a very important relaxation channel, accounting for $\sim 2/3$ of the energy decay of the terrace. The step modes, while all decaying faster than the terrace, fall into two groups, with the C_2 and C_3 modes decaying in 60 ps and the more weakly coupled C_1 mode decaying in 120 ps. The separation of the step dynamics is consistent with quantum chemical calculations that indicate a separation of the C_1 mode from the other two. The step-terrace transfer time is consistent with the previous suggestion that terrace-step energy transfer is mediated by dipole-dipole coupling. A normal mode calculation confirms that the step and terrace modes remain localized despite the dipole coupling and supports the argument that step-terrace energy flow is due to spatial energy flow on the dihydridestepped surface. The small amount of delocalization does lead to screening effects that cause some uncertainty in levels of excitation transferred, and uncertainty in the early time dynamics.

The normal mode calculation for the monohydridestepped surface indicates that step and terrace modes interact strongly enough by dipole coupling so that they are no longer localized to step and terrace. The observed transients confirm the strong coupling, but detailed kinetic interpretation is complicated by the lack of separation of modes. The strong dipole coupling is predicted to lead to transient changes in dipole screening interactions, as well as anharmonic effects, may contribute to the observed experimental transients. Although the detailed mechanism of energy transfer is not determined precisely on the monohydride-stepped surface, all of these interactions are predicted to lead to fast equilibration among all adsorbate modes. Despite this fast equilibration, the modes all show a relatively slow collective decay, consistent with the argument that the monohydride-step modes do not act as energy drains because of a long intrinsic lifetime.

ACKNOWLEDGMENTS

The authors thank J. Tully and K. Raghavachari for helpful discussions. K. K. gratefully acknowledges fellowship support by a Feodor-Lynen Fellowship from the A.v.-Humboldt Foundation.

APPENDIX: A LINEAR MODEL FOR THE ENERGY FLOW KINETICS

We wish to solve the equation

$$\frac{d}{dt} [\eta_i(t)] = -c_{ii}\eta_i + \sum_{j \neq i} c_{ij} [\eta_j(t) - \eta_i(t)], \quad (A1)$$

where the c_{ij} 's are symmetric with regard to interchange of indices because of energy conservation. We give a short derivation of the solution using matrix diagonalization. Other methods can be used.²²

If we define a vector η which contains the excitation of mode *i* as its *i*th component, we can write Eq. (A1) as

$$\frac{d}{dt}\boldsymbol{\eta} = -\mathbf{C}\boldsymbol{\eta},\tag{A2}$$

where the elements of the matrix C are c_{ij} . The solution is

$$\boldsymbol{\eta}(t) = e^{-Ct} \boldsymbol{\eta}(0), \tag{A3}$$

where the exponential function of the matrix is defined by the power expansion of the exponential function using matrix multiplications and additions. The matrix C can be written in terms of a diagonal matrix D consisting of C's eigenvalues and a matrix U consisting of C's eigenvectors in its rows

$$\mathbf{C} = \mathbf{U}^{-1} \mathbf{D} \mathbf{U}. \tag{A4}$$

Since C is symmetric, D is real. Substituting for C in Eq. (A3) and recognizing that in any power of C,

$$\mathbf{C}^{n} = \mathbf{U}^{-1} \mathbf{D}^{n} \mathbf{U}, \tag{A5}$$

and that an exponential of the diagonal matrix **D** is itself a diagonal matrix with the diagonal elements $\exp(-d_{kk})$, we obtain the solution

$$\eta_i(t) = \sum_k \left\{ e^{-d_{kk}t} u_{ki} \sum_j \left[u_{kj} \eta_j(0) \right] \right\},\tag{A6}$$

where d_{kk} and u_{ki} are elements of the matrices **D** and **U**, respectively, and use has been made of the relation \mathbf{U}^{-1} $=\mathbf{U}^{T}$, since **C** is real and symmetric. In the two-color experiment that we want to model, one mode is pumped at t=0 and thus the sum over *j* reduces to one element $\eta_{j}(0)$ $=p_{j}$, where p_{j} is the integrated number of excitations produced by the pump pulse, proportional to the total pump energy absorbed by mode *j*. Since the intermode transfer rates are in some cases close to the pumping rate, the actual maximum excitation observed in the experiment is sometimes much less than p_{j} . The excitation in *i* due to pumping *j* becomes Eq. (3) of Sec. IV B.

The solution has the properties (1) for N coupled modes, the solution is a sum of N exponentials; (2) the excitation in mode *i* is proportional to the energy pumped into mode j (linear response); (3) the excitation of mode iafter pumping mode j [namely $\eta_{i \to i}(t)$] is proportional to the result obtained for the reversed experiment $[\eta_{i \rightarrow j}(t)]$. The two experiments give identical results when the same pump intensity is achieved in both modes. The integral pump excitation p_i depends on both the intensity of the pump beam and the absorption cross section of the mode. The observed excitation for a finite pulse length is a convolution of Eq. (3) of Sec. IV B with the pulse shape. Due to the coupling between modes, the maximum excitation observed in mode j is smaller than p_i . An extreme example is the A mode whose equilibration with the other four terrace modes is fast compared to the pump pulse length.¹⁶ In this case, an amount of $p_A = 0.65$ pumped into A, which would saturate that mode if the pump pulse were very short, leads to a maximum excitation in A of only $(\eta_A)_{max}$ =0.12, not approaching complete saturation $(\eta=0.5)$ at any time during the pump pulse.

- ¹A. L. Harris, L. Rothberg, L. H. Dubois, N. J. Levinos, and L. Dhar, Phys. Rev. Lett. **64**, 2086 (1990); A. L. Harris, L. Rothberg, L. Dhar, N. J. Levinos, and L. H. Dubois, J. Chem. Phys. **94**, 2438 (1991).
- ²J. D. Beckerle, M. P. Casassa, R. R. Cavanagh, E. J. Heilweil, and J. C. Stephenson, Phys. Rev. Lett. 64, 2090 (1990); J. D. Beckerle, R. R. Cavanagh, M. P. Casassa, E. J. Heilweil, and J. C. Stephenson, J. Chem. Phys. 95, 5403 (1991).
- ³M. Morin, N. J. Levinos, and A. L. Harris, J. Chem. Phys. 96, 3950 (1992).
- ⁴An extreme example is the millisecond lifetime of CO physisorbed on NaCl, which results in the population of high vibrational levels of CO by Trainor pumping; H.-C. Chang and G. E. Ewing, Phys. Rev. Lett. 65, 2125 (1990); J. Electron Spectrosc. Relat. Phenom. 54/55, 27 (1990).
- ⁵P. Guyot-Sionnest, P. Dumas, Y. J. Chabal, and G. S. Higashi, Phys. Rev. Lett. **64**, 2156 (1990); P. Guyot-Sionnest, P. Dumas, and Y. J.
- Chabal, J. Electron Spectrosc. Relat. Phenom. 54/55, 39 (1990). ⁶P. Jakob and Y. J. Chabal, J. Chem. Phys. 95, 2897 (1991).
- ⁷P. Jakob, Y. J. Chabal, K. Raghavachari, R. S. Becker, and A. J. Becker, Surf. Sci. 275, 407 (1992).
- ⁸K. Raghavachari, P. Jakob, and Y. J. Chabal, Chem. Phys. Lett. 206, 156 (1993).
- ⁹M. Morin, P. Jakob, N. J. Levinos, Y. J. Chabal, and A. L. Harris, J. Chem. Phys. **96**, 6203 (1992).
- ¹⁰P. Guyot-Sionnest, Phys. Rev. Lett. 67, 2323 (1991).
- ¹¹A. L. Harris and N. J. Levinos, Appl. Opt. 26, 3996 (1987).
- ¹² Reference 9 incorrectly listed 5.5 hydrogens per terrace on the dihydride-stepped surface.
- ¹³P. Dumas and Y. J. Chabal, Chem. Phys. Lett. 181, 537 (1991).
- ¹⁴ Y. J. Chabal and K. Raghavachari, Phys. Rev. Lett. 54, 1055 (1983).
 ¹⁵ M. Hines, Y. J. Chabal, T. D. Harris, and A. L. Harris (to be pub-
- lished).
- ¹⁶ P. Jakob, Y. J. Chabal, and K. Raghavachari, Chem. Phys. Lett. 187, 325 (1991); P. Jakob, Y. J. Chabal, K. Raghavachari, and S. B. Christman, Phys. Rev. B 47, 6839 (1993).
- ¹⁷This calculation is based on the angles of the dynamic dipole moments measured in internal reflection experiments (Ref. 6) and assumes that the effective dielectric constant of the Si-H layer is 2.0, consistent with Ref. 6.
- ¹⁸ Both the internal reflection IR absorption and external SFG experiments are relatively insensitive to the direction of scatter with respect to the up and down step directions. Spontaneous Raman measurements are not symmetric and can distinguish the step direction spectroscopically (see Ref. 15). Tracking sample direction by x ray would answer the question, but was not done.
- ¹⁹K. Kuhnke, A. L. Harris, P. Jakob, M. Morin, and Y. J. Chabal (to be published).
- ²⁰K. Raghavachari (private communication).
- ²¹See Ref. 16 and references therein for discussions of normal modes which include dipole coupling.
- ²²See, e.g., Erik V. Bohn, The Transform Analysis of Linear Systems, Addison-Wesley Series in Electrical Engineering (Addison-Wesley, New York, 1963).