Treanor Pumping Vibrational Transport on Si(111)-H

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Contents

I. ABSTRACT

The study of vibrational dynamics at semiconductor surfaces has a long and important history, with Si(111) playing a central role. Mechanistic elucidation at these surfaces has obvious, important implications in many key areas throughout surface science and offers fundamental understanding of many surface chemical processes. Previously, sum frequency spectroscopy generation (SFG) has played a major role in the determination of vibrational properties at hydrogen passivated silicon surfaces. Impressive work completed by Chabal, Dumas and Guyot-Sionnest elucidated a detailed picture of first excited state vibrational energy transfer along terrace Si(111) surfaces and those with various step defects by measuring T_1 lifetimes of adsorbate species with two-color transient-bleaching SFG. This resonant V-V, or Forster hopping, is important in almost all vibrational transport regimes at crystal semiconductor surfaces. A well studied phenomena in the gas phase, non-resonant V-V (vibrational-vibrational), or Treanor pumping vibrational transport, is relatively unknown on surfaces, and has been observed in only a few isolated systems. This is most notable for CO on various surfaces. More recently, the long-standing goal of mode-selective IR photodissociation at surfaces has been achieved on hydrogen passivated Si(111) using a high-power, tunable infrared free electron laser (FEL) in resonance with the $\nu_{0\to1}$ stretching mode of the terrace Si-H bond. The combination of this study and that of a coadsorbed hydrogen/deuterium system exhibiting an extreme isotope effect suggests an entirely new vibrational transport mechanism leading to these effects. It is the hypothesis of this work that a Treanor pumping, non-resonant V-V vibrational transfer mechanism may be, for the first time, observed on a hydrogen passivated Si(111) surface by use of an appropriately tuned FEL and subsequent SFG probe. This will be observed as the occupation of hot-band vibrational states (at least the ν_2 state) that are anharmonically decoupled from the laser (i.e., the linewidth of the FEL pulse is not in resonance with any but the first excited state stretching mode). Further, successful exploitation of this effect will correctly explain the mechanism of the unprecedented mode-selective chemistry observed by Liu et. al., and lead to further important developments in a new regime of energetic transfer processes at surfaces.

II. INTRODUCTION

A comprehensive understanding of vibrational dynamics and energy flow at surfaces is required to understand the huge variety of processes that take place in adsorbed monolayers on highly ordered crystals. Silicon surfaces, not surprisingly, have generated a huge amount of both experimental and theoretical interest in part because of their importance for industrial processes such as semiconductor growth. At the same time, work specific to surfaces offers unique opportunities to study condensed phase processes that are often obscured in disordered, bulk media. The development of literally hundreds of techniques specific to ordered crystal surfaces is a testament to this fact. Second harmonic generation (SHG) and sum frequency generation (SFG) non-linear spectroscopies offer previously unprecedented surface selectivity when studying the vibrational properties of adsorbed surface species. This is due to selection rules disallowing the non-linear processes in environments with inversion symmetry, such as in bulk solid-phase crystals and gases. Pulse-probe SFG is an idea platform for the study of vibrational dynamics at silicon surfaces.

The application of pulse-probe SFG to reconstructed silicon crystals is not without precedent.[1, 2] Since the advent of the technique, SFG has been used to study vibrational energy transfer and adsorbate vibrational lifetimes in a variety of silicon-adsorbate surfaces, on terraces and on interesting imperfections and steps.[3–6] The first measurement of vibrational lifetimes on such surfaces using transient bleaching SFG was published in 1990.[3] It was expected and shown in this work that the T_1 lifetime for the Si(111)-H stretching mode was quite long, on the order of 800 ps. This was correctly explained as being due to poor vibrational coupling to other available modes (phonon coupling or coupling to low-frequency bending modes) and a lack of other dominant intermolecular redistribution channels as would be expected for more complex adsorbate species, such as dipole-dipole coupling or electron-hole pair generation on metal substrates.[2] Multiphoton absorption leading to vibrational ladder climbing in this case was assumed to be negligible due to strong Si(111)-H bond anharmonicity, which was significantly larger than the IR pump linewidth. Resonant excitation of the $\nu_{1\to2}$ and higher vibrational states does not occur because the laser is not in resonance with those transitions. Although the authors did observe some desorption, this was attributed to substrate heating through phonon mode coupling as measured by a shift in the vibrational frequency in the SFG spectrum after some significant delay from the pulse.

Further work in this area aimed at elucidating the transfer of vibrational energy between varying Si-H adsorbate species by monitoring transient bleaching at Si(111) step sites after IR irradiation coupled with stretches on terrace sites.[6] Vibrational lifetimes for the monohydride step species were estimated in subsequent years to be even longer than those at terraces (≈ 1000 ps). A robust picture of this vibrational energy flow seemed almost complete by 1993. It was suggested during the course of this work that the long vibrational lifetimes of hydrogen-passivated Si(111) could be exploited and give rise to mode-selective bond scission at the surface, a long-sought goal. However, this seemingly simple phenomena was not observed until 2006. All previous work in this area, regardless of substrate and adsorbate, indicated that coupled IR irradiation into an adsorbate-surface or intra-adsorbate bond yielded thermal, statistical desorption.[7–12] This confirmed that the mechanism was in fact due to phonon mode coupling or laser-induced heating of the substrate, yielding statistical, thermal desorption of all species present on the surface by scission of the adsorbate-surface bond.

In 2006, a return to the simple Si(111)-H surface and incorporation of a high-fluence free electron laser (FEL) yielded surprising and unprecedented results.[13] For the first time, clear evidence for non-thermal desorption was seen. Desorption of H_2 was observed when the FEL was coupled to the Si-H stretching mode on a surface coadsorbed with excess deuterium over a long period of time (seconds). A surprising isotope effect was seen as almost no HD or D_2 desorption was observed. The thermal experiment on a 50:50 hydrogen/deuterium passivated Si(111) surface yields statistical desorption of H_2:HD:D_2 in the ratio 1 : 4.3 : 16.9, whereas the observed desorption yield in this study was 1 : 0.04 : 0.005. This is in stark contrast to any mechanism previously identified. All previously observed thermal and electronic desorption mechanisms can be clearly ruled out. The direct ladder climbing mechanism, in which a number of vibrational states are populated by sequential excitation with the FEL, could be ruled out by the use of sufficiently narrowband FEL pulses. This work suggests that the creation of very hot-band vibrational states on silicon surfaces may be possible by implementing an appropriately tuned FEL laser and driving a non-resonant V-V vibrational energy transfer mechanism. This is the Treanor pumping process, proposed first in 1968 for the description of vibrational energy pooling in the gas phase.[14] This behavior has not previously been observed on any but a few systems with adsorbed CO[15–17], and may be reasonably predicted under strong FEL illumination by understanding properties of

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the Si(111) surface. Impressive simulation work by Tully et. al. had previously dismissed the possibility of driving non-resonant V-V transfer at the silicon surface.[16] It is the contention of this work that this is in fact incorrect. The factors leading to such a dismissal may be reasonably overcome by the incorporation of the FEL with its unique properties, which will continuously drive the system into non-equilibrium states where Treanor pumping may occur. This prediction is described in detail below. Successful exploitation of this mechanism leads to the observed result: mode-selective bond scission at the silicon surface.

Step sites on the silicon surface offer another interesting possible experiment making use of the Treanor pumping process. Depending on the results of the first part of this study, it may be possible to selectively excite and desorb species that reside only at step sites. This was the contention of Cohen et. al. some years ago.[18] However, this possibility should be met with some skepticism. It may be significantly more difficult than on the bulk substrate: the process will be geometrically constrained and fewer adsorbate collisions will result in less hot-band excitation due to non-resonant transfer. Further skepticism of this mechanism should be considered as the V-V resonant delocalization rate to terrace sites may be faster than the non-resonant Treanor process may be pumped. Even still, the non-resonant process may also transfer energy to terrace instead of step sites. In short, every possible energy transfer process that is possible on terraces may be possible between step and terrace sites, rapidly delocalizing the energy away from steps. This problem is insignificant on the bulk terrace experiment: resonant vibrational delocalization is acceptable as the experiment is being performed on a large site. Results from experiments on the Si(111) terraces will give reasonable information as to the rate of the non-resonant pumping process and therefore guide possibilities for geometrically-selective chemistry. However, if a rapid non-resonant process is possible, this effect may be significant at step sites.

III. STATED GOALS AND HYPOTHESES

The current work aims to show the existence of an important new vibrational transport mechanism observed under high-fluence mode-selective excitation with a free electron laser. The unique properties of the free electron laser drive the hydrogen passivated silicon system into a highly non-equilibrium state resulting in non-resonant V-V vibrational energy transfer (Treanor pumping). This work will constitute the first observation of such phenomena on

silicon and correctly explain the mechanism of previously observed mode-selective hydrogen desorption. The hypotheses of this work may be summarized as:

- Treanor pumping may be observed and lead to the formation of very high-lying vibrational excited states (ν_2 or greater) for this first time on a silicon substrate by implementation of a narrowband chirped FEL pulse train (micropulse structure) followed by broadband SFG.

- Treanor pumping is theorized to occur on the ideally terminated Si(111)-H (1x1) surface. It is this surface that will be interrogated.

- The competition of the non-resonant pumping process with standard relaxation mechanisms for excited adsorbate species will be investigated.

- The rate of the non-resonant pumping processes is unknown and may proceed before of after the saturation and subsequent delocalization of energy in low lying vibrational states leading to a phonon-band structure at the $\nu_{0\rightarrow1}$ and $\nu_{1\rightarrow2}$. Information identifying the existence of higher-lying vibrational modes from the current experiment are available in both of these cases, though it is expected that the phonon-band structure in the hydrogen adlayer will not be observed, as explained later.

- Upon identification of significant Treanor pumping (i.e., when the $\nu_{2\rightarrow3}$ vibrational transition is observed), the T_1 lifetime of the $\nu_{0\rightarrow1}$ transition will be determined using transient bleaching SFG. The lifetime of this bond will be markedly shorter than has been seen on a non-Treanor pumping surface. This will be due to the new rate associated with the non-resonant mechanism driving adsorbate species away from the $n = 1$ vibrational state.

- This mechanism is the principal driving force in the observation of the mode-selective bond scission at the silicon surface.

- Can this effect also be exploited on surface steps, as well as terraces? Observation of the Treanor pumping process on terraces will shed light on this possibility.

IV. FUNDAMENTALS

The following section summarizes known physical and mechanistic aspects of the systems to be investigated and the properties of techniques used to probe their structure in the present work.

A. The Si(111) Surface

The Si(111) surface is an ideal platform for the study of surface vibrational energy transfer processes occurring on semiconductors. The industrial importance, ease of preparation and study, as well as the scientifically interesting aspects of this surface have led to a wealth of experimental and theoretical work in this area.[1, 2] The hydrogen-passivated (1x1) Si(111) structure exhibits a simple diamond-lattice structure shown below in Figure 1.[19]
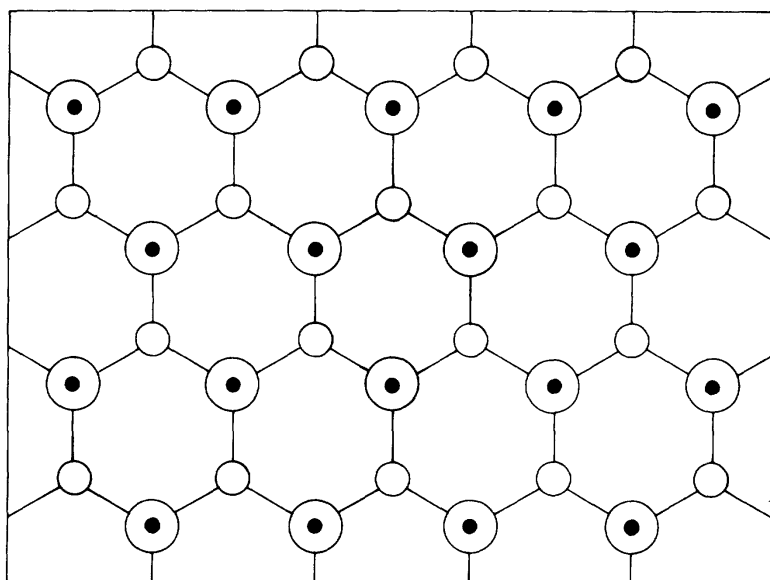

FIG. 1: Terrace structure of hydrogen-passivated (1x1) Si(111) surface as viewed from above. Large open circles are the top silicon layer, while small open circles are the silicon atoms in the second layer. Small black dots indicate hydrogen adatom sites.[19]

Preparation of clean, flat Si(111) surfaces has been shown to be experimentally simple at atmospheric pressure and temperature.[20, 21] Subsequent etching with hydrofluoric acid protects the surface from further degradation due to oxidation or contamination before experimental study in an ultra high vacuum chamber. Miscuts and surface imperfections

lead to surfaces with stepped features. Both monohydride and dihydride stepped surfaces are easily prepared but cutting off-axis with the (111) plane. These techniques are described elsewhere, and the resultant surfaces are shown in Figure 2.[6]
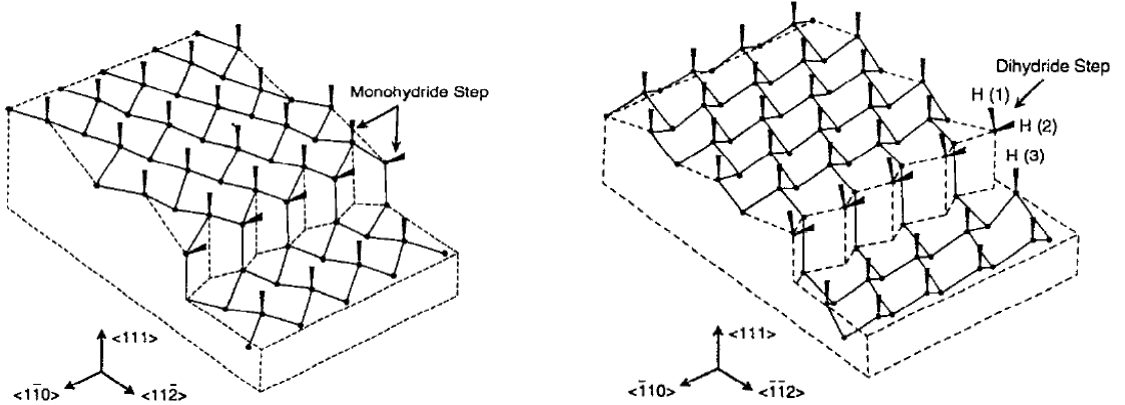

FIG. 2: (LEFT) Monohydride stepped surface prepared by 5-degree off-(111) axis cut in the $\langle 11\bar{2}\rangle$ direction. (RIGHT) Dihydride stepped surface prepared by 9-degree off-(111) axis cut in the $\langle \bar{1}12\rangle$ direction.[6]

First-vibrational state stretching and bending mode frequencies for hydrogen-terminated Si(111) have been well characterized by many methods, from electron energy loss spectroscopy (EELS) to sum frequency generation (SFG) techniques.[22, 23] These indicate a Si(111)-H $\nu_{0\rightarrow1}$ frequency at 2084 cm^{-1} and a Si(111)-H bending mode at 636 cm^{-1}. Monohydride step modes differ in frequency from that of the terrace mode by 51.8 cm^{-1}, although there is some inconsistency in this value across work completed recently.[6, 13] The Si(111)-H bond exhibits significant anharmonicity in its vibrational mode distribution. The $\nu_{1\rightarrow2}$ has been found to be 90 cm^{-1} lower than that of the fundamental band after its excitation. This is due to both the 68 cm^{-1} fundamental anharmonicity of the Si-H bond as well as effects originating from the surface interaction.[4] However, higher-lying vibrational states are of great interest here and have not been appropriately characterized or understood due to the difficulty of populating these states with mode-selective methods. Certainly, these states are easily populated upon substrate heating, as there are no "secret" energetic pathways available on this surface.[12] The energetics of hydrogen desorption from silicon surfaces is well understood. The energy needed to break two Si-H bonds is approximately 7.0 eV, and the energy released from the formation of H-H is approximately 4.5 eV.[1] In contrast,

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resonant excitation of the Si-H stretch requires photons in quanta of 0.26 eV. The diffusion barrier of hydrogen on Si(111) is 1.5 eV.[24] Therefore the Si-H bond must absorb multiple quanta before associative desorption may occur.

Significant previous work has been done to elucidate the vibrational energy transfer mechanisms and dynamics at these surfaces. Impressive work completed by Chabal et. al. indicates surprisingly long T_1 vibrational lifetimes for both the terrace and step Si-H modes, measured at 820 and 1100 ps, respectively.[3, 5, 6] These values depend on the detailed structure of the surface adlayer, though they are consistently on the order of 1 ns. In contrast, small dihydride steps exhibit much shorter vibrational lifetimes, and act as vibrational energy drains for energy initially localized on terrace sites. These terraces and steps were found to have T_1 vibrational lifetimes of 420 and 100 ps, respectively. This work was consistent with Si-H oscillator dipole-dipole coupling on the surface leading to vibrational energy transfer between terrace sites and step sites, and subsequent relaxation to other Si-H vibrational modes and to surface phonons. This resonant V-V transfer is the Forster mechanism described with some detail in the following section. Longer dihydride steps, prepared by a smaller angle cut through the bulk crystal, do not exhibit this step energy drain behavior. Phonon modes on the Si(111)-H surface are sufficiently low-lying that the redistribution of vibrational energy to the surface is generally unfavorable, accounting for the relatively long lifetime of the Si-H stretching vibration observed on silicon surfaces. In fact, relaxation of the initially excited Si-H terrace stretching mode requires redistribution of that energy into both low-lying bending and surface phonon modes. This may be equally well explained by the relatively low Debye frequency observed for Si(111), at 448 cm^{-1}.[16]

Under high-temperature annealing, the Si(111) surface undergoes a reconstruction to a (7x7) configuration, shown in Figure 3.[1, 13] Further, under these high temperature conditions ($\approx$ 1000 K), hydrogen is desorbed from the surface yielding a clean, unpassivated surface. The clean (7x7) surface may be verified by a strong low-energy electron diffraction (LEED) pattern.

Upon hydrogen dosing and cracking using a tungsten filament, the clean Si(111) surface may be covered with H atoms. This coverage may be verified by the Si(111)-(1x1) LEED pattern. The details of the surface preparation process in ultra-high vacuum (UHV) conditions are discussed later.
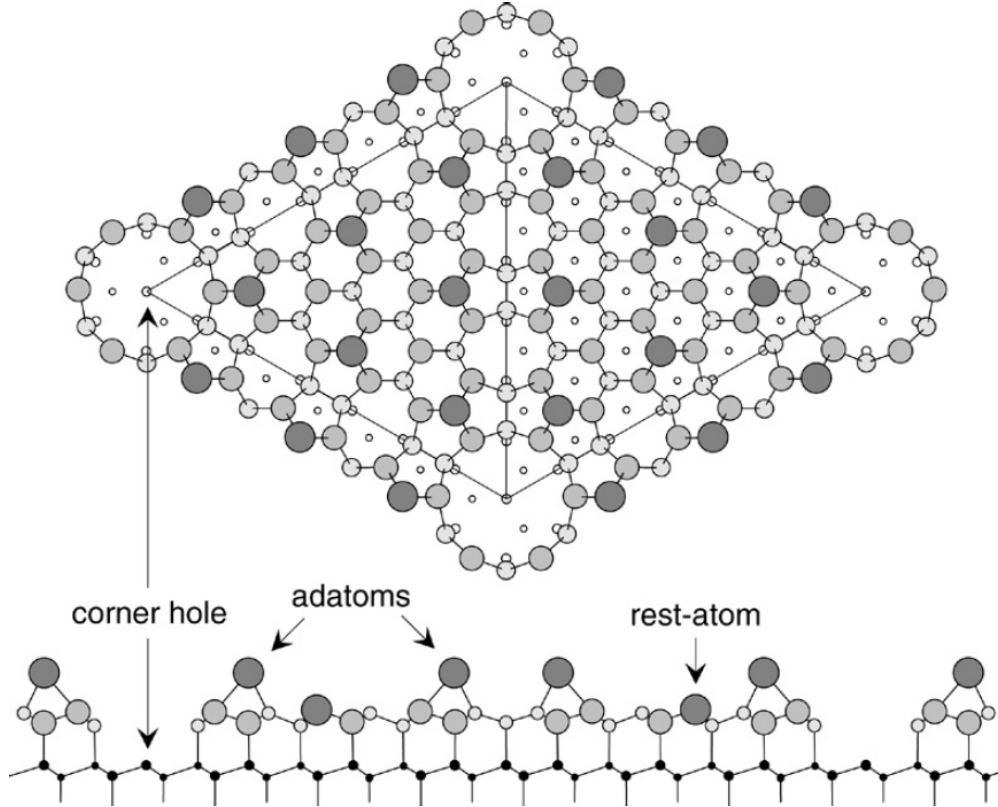
FIG. 3: Schematic representation (both top and size views) of the Si(111) surface reconstructed into a (7x7) unit cell.[1]

B. Free Electron Laser Pulse Characteristics

The free electron laser provides an ideal platform for the study of non-equilibrium resonant excitation at surfaces, in part due to the increased power, repetition rate and time width of micropulses, and wide frequency and spectral linewidth tuning properties. The present work will make use of each of these important laser properties. The description of free electron laser theory and operation may be found in many articles and reviews. Described here are the salient pulse characteristics that make this IR laser particularly interesting in driving the phenomena of Treanor pumping on the Si(111) surface.

Free electron lasers are relatively unique in that they are widely tunable (2-10 μm) throughout the IR frequency range. This is particularly advantageous when attempting mode-selective chemistry, as it is possible to tune the laser exactly to the mode of interest across a wide range of possible absorbing species. The FEL pulse is made up of a packet of "micropulses", which together form a macropulse. The micropulses in the experiment are

approximately 1 ps wide and may have per-pulse power of up to 40 μJ. The macropulse power may vary and reach beyond 100 mJ/pulse, however the laser is generally operated at 40 mJ/pulse. The structure of the macropulse is summarized in Figure 4.[25]
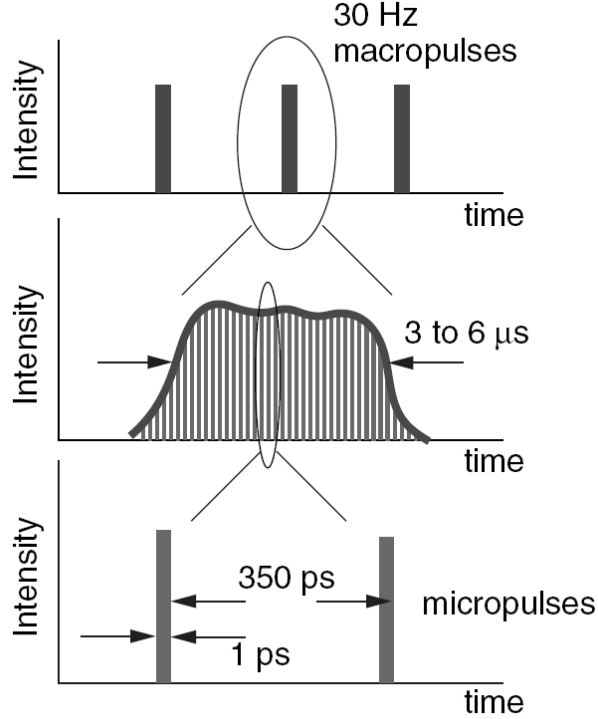

FIG. 4: General outline of the FEL macropulse and micropulse structure in time.[25]

This structure is particularly advantageous in this study. The time delay between micropulses is less than half the T_1 relaxation time of the Si(111)-H bond, which when tuned in resonance with the $\nu_{0\rightarrow1}$ stretching mode of the surface, will yield a saturated first excited state. Further, the pulses are repetitive over 3-6 μm, meaning that the surface will have a substantial amount of time within a fully saturated window in which to distribute vibrational energy. The Forster and Treanor V-V transfer processes are known to take place within this time frame. The FELIX (Free Electron Laser for Infrared eXperiments) FEL at Vanderbilt University is ideally suited for this study, and its salient pulse characteristics are summarized in Table I.[26]

These characteristics, when considered together, may be used to selectively excited the first excited state stretching mode of the Si(111)-H with sufficiently small enough wavelength as to not direct couple energy into the second excited state stretching transition. It also

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Wavelength	5-100	μm
Wavenumber	2000-100	cm^{-1}
Spectral Width	0.4-7	%
Polarization	Linear	–
Micropulse Duration (FWHM)	6-100	Optical Cycles
	(may be $\approx$ 1 ps)	
Micropulse Energy	1-40	μJ
Micropulse Power	0.5-100	MW
Micropulse Rep. Rate	25-1000	MHz
Macropulse Duration	< 10	μs
Macropulse Rep. Rate	< 10 - > 30	Hz

TABLE I: FELIX FEL pulse characteristics.[26]

allows the use of a "pulse train" of micropulses to saturate the first excited state species and maintain a saturated excited state for a substantial period of time. It is known from previous experimental study that desorption on the hydrogen passivated Si(111) surface is observed well within the time scale of the macropulse.[13] Therefore it is expected that the desired Treanor-type mechanism will be observed within the duration of the first macropulse.

It should be noted that FEL+SFG studies have been discussed and completed previously.[27–29] However, the current methodology requires a two-color FEL+SFG IR pump-probe. It is advantageous therefore to separate the pulse and probe in this experiment, and use a second IR laser for generation of the narrow-band visible light and broad-band IR light necessary for the SFG probe. This system is described later.

C. Forster V-V Transfer

The Forster resonant V-V transfer process is well known on many surfaces, and arises primarily because of dipole-dipole coupling of surface adsorbate species. This resonant mechanism has been seen previously on hydrogen passivated silicon surfaces, as discussed

earlier. Typically it is assumed that nearest neighbor species on the surface may undergo this resonant exchange process. The two species are isoenergetic before and after the transfer.

Consider two nearest neighbor species, one in its $n = 0$ and the other in its $n = 1$ vibrational state. The resonant exchange proceeds by a transfer of one vibrational quanta from the excited state species to the ground state species. On most surfaces, the rate of this process is several orders of magnitude larger than that of other vibrational processes, such as non-resonant transfer. This is masked by the rapid dephasing process. The T_2 lifetime on Si(111)-H, for instance, is approximately 11 ps, though there is some uncertainty in this value.[2] Regardless, rapid dephasing will initially localize the excited state vibrational energy to just those modes that were initially excited. This will be followed by eventual delocalization to all resonant modes on the surface. The basic mechanism of this process is shown in Figure 5.

$$|\nu+1\rangle + |\nu\rangle \rightarrow |\nu\rangle + |\nu+1\rangle$$
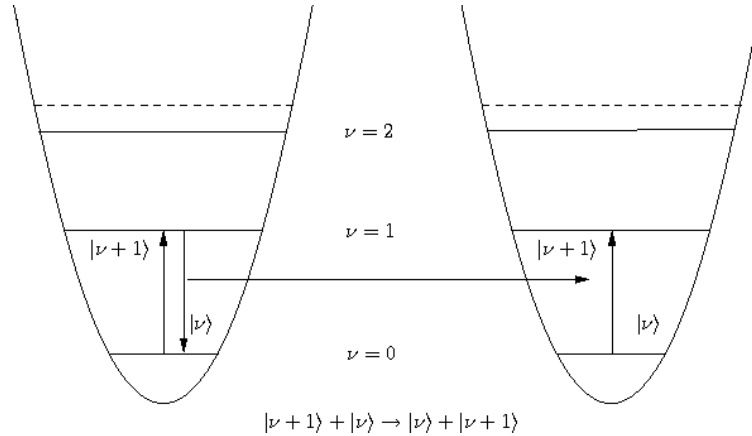
FIG. 5: Basic resonant Forster hopping mechanism for V-V energy transfer.

The rate dependence of this process has been well studied on some more complex surfaces, such as CO/Ru(001).[30–32] On these systems, not surprisingly, it was found that surfaces with higher adsorbate monolayer coverage share the excitation energy across all adsorbed CO species, leading to a delocalized phonon-like band in the adlayer of the substrate. This was explained by an increase in the exchange residence time, or the inverse of the vibrational "hopping time", between adsorbate species on the surface.

However, this process has not been observed on the hydrogen passivated Si(111) surface. SFG studies of ideally terminated (1 ML) Si(111)-H surfaces show clear resolution of both the $\nu_{0\rightarrow1}$ and $\nu_{1\rightarrow2}$ transitions.[4] In this study, an 80 μJ pulse, 7 ps long in resonance with

the $\nu_{0\to1}$ transition was used as the pulse. The population ratio between the first excited and ground states was given as $A_{12}/A_{01} \approx 0.45$.

This Forster mechanism is responsible for the V-V transfer behavior observed by Chabal, Dumas and Guyot-Sionnest, discussed previously. The lack of any phonon-band structure in the adlayer is beneficial for the study of other possible V-V transfer mechanisms, such as Treanor pumping. It is expected that population of each vibrational transition will be well resolved by the SFG study without interference from any phonon-type excitation. However, this study will saturate the first excited state population of the adlayer for an extremely long time. Therefore there is some possibility of forming a delocalized structure in the adlayer. The degree to which this will be observed is to the best of current knowledge, unknown. However, the Forster hopping rate on the surface is still relatively slow, therefore the population of higher-lying states should still be well resolved.

D.   Treanor V-V Transfer

A model for the vibrational relaxation of anharmonic oscillators with exchange-dominated collisions was first proposed for gas-phase species by Treanor et. al. in 1968.[14] It is for Treanor that the process is named.

Consider two anharmonic oscillators both in the $n = 1$ vibrational state. The non-resonant exchange process proceeds by the transfer of a vibrational quanta from one oscillator to the other, leaving the first oscillator in its ground state and the other in its second excited state. This is roughly summarized as the process A(1) + A(1) → A(0) + A(2), or similarly A(1) + A(2) → A(0) + A(3). However, as the majority of diatomic species are anharmonic (Si(111)-H being no exception), the products are lower in energy than the reactants by the anharmonicity. The leftover energy must lead to an increase in the translational energy of the products, as required by conservation. Assuming a steady supply of initially excited species and a Treanor rate that exceeds that of any vibrational relaxation processes, then a series of Treanor processes may populate very high-lying vibrational states. The Treanor pumping process is illustrated in Figure 6.

This has been observed in a variety of gas phase systems. A particularly interesting gas-phase case is that of CO, since studies of CO on surfaces have also elucidated non-resonant V-V transfer processes. By pumping the $\nu_{0\to1}$ vibrational transition, gas phase CO has

$$|\mu\rangle + |\nu\rangle \rightarrow |\mu - 1\rangle + |\nu + 1\rangle + |q\rangle$$
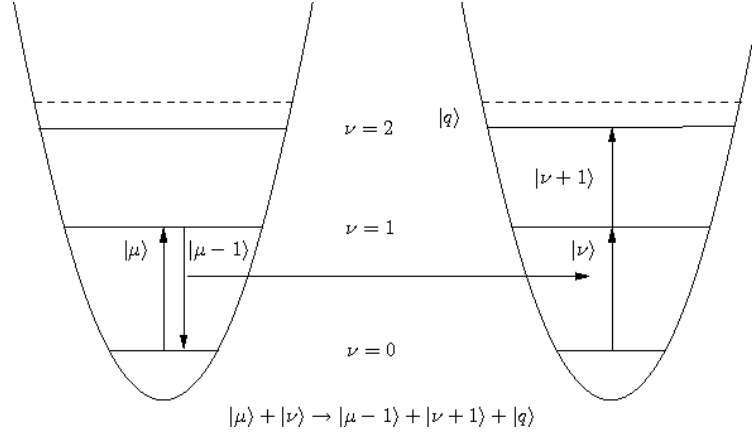
FIG. 6: Basic non-resonant Treanor pumping mechanism for V-V energy transfer.

been promoted to the $n = 42$ vibrational level. On surfaces, adsorbate molecules have been observed in their $n = 15$ vibrational state. However, this process has never been observed for the Si(111)-H system.[16]

Impressive work completed by Tully et. al. indicates that strong system-bath coupling impedes the Si(111)-H system from undergoing any vibrational energy pooling due to non-resonant transfer[15, 16]. There is a large frequency mismatch between the Si-H stretch frequency and the Debye frequency of Si(111) (448 cm^{-1}, the theoretical maximum vibrational frequency for the crystal system). However, vibrational relaxation times on the order of a nanosecond are much to fast to allow time for any Treanor-type mechanism. They suggest that the study of the hydrogen passivated Ge(111) system may reduce the vibrational relaxation rate the Ge(111)-H stretching mode and therefore allow for a non-resonant pooling process to occur. This hypothesis is due in part to the reduced Debye frequency of Ge (260 cm^{-1}). No experiments on Ge(111) to this end have been performed. It is the contention of the work presented here that a non-resonant transfer mechanism is possible on Si(111) by use of an appropriate FEL system, making use of chirped micropulses to avoid rapid relaxation processes on the surface by constantly saturating the first vibrational state.

E. Sum-Frequency Generation

Sum frequency generation (SFG) spectroscopy is the ideal platform to probe the vibrational state populations of the FEL-illuminated hydrogen passivated Si(111) system in a time-dependent fashion, due to the ultrafast nature and surface selectivity of the SFG

probe. Surfaces constitute regions where centrosymmetry is broken, which is required for the observation of the non-linear process. Many articles are reviews concerning the application and theory of SFG are available in the literature.[27, 33–40] The typical geometrical scheme for an SFG experiment is shown in Figure 7.[40]
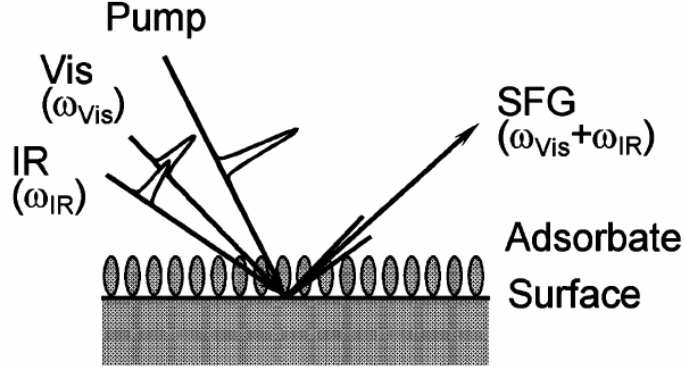

FIG. 7: Scheme for pump-probe IR-Visible SFG.[40]

The basic mechanism of this process is conceptually simple. The broadband IR-Visible SFG probe is comprised of a narrowband visible pulse combined with a broadband IR pulse, which are coincident on the surface in time. Emission of the SFG signal is observed only by non-centrosymmetric media, and is therefore selective only at the surface of the semiconductor crystal. This surface selectivity relies on the fact that the second-order nonlinear susceptibility is nonvanishing at interfaces. Therefore the SFG signal is obtained by generation of an electric field E_{SFG} from the two incident fields E_{VIS} and E_{IR}. As for all systems, conservation of energy and conservation of momentum must be observed. Therefore the energy of the SFG signal is the sum of the visible and IR quanta incident on the surface. The surface selectivity of SFG is its most significant advantage over IR and Raman techniques.

Consider a surface with adsorbate species in both the ground and first vibrationally excited state, such as indicated in Figure 8. A picosecond pulse of narrowband visible light, typically at 800 nm, is coincident on the surface with a broadband IR pulse a spectral width of approximately 150 cm^{-1}. The SFG signal is enhanced in spectral regions where the IR quanta are in resonance with vibrational transitions at the surface, such that the observed SFG signal has maxima at the sum frequency $\omega_{SFG} = \omega_{VIS} + \omega_{IR}$. Here, ω_{IR} is in resonance with the vibrational mode of interest at the surface. This general mechanism is detailed in Figure 8.
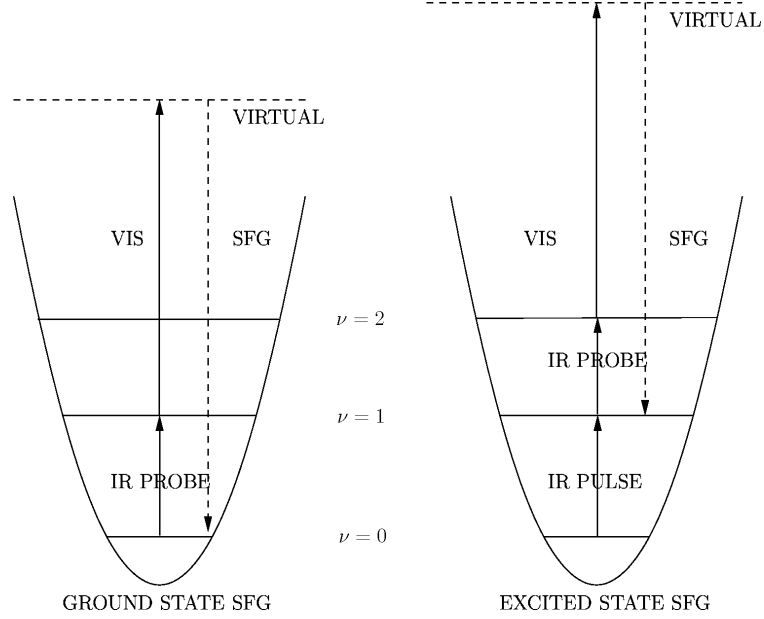
FIG. 8: Ground state and excited state SFG mechanisms.

In the SFG experiment, the narrowband visible light should not be in resonance with any significant electronic transition of continuum of states at the surface. In the case of the ground state, the IR pulse resonantly excites the $\nu_{0\to1}$ transition. This IR pulse is upconverted by the spectrally narrow visible pulse and the SFG emission is detected. The narrowband visible signal is responsible for the resolution obtained in the SFG spectra. In more complex situations, such as the three-level system shown in Figure 8, a pump pulse is used to excite a population of oscillators from the ground state to the first vibrationally excited state. In anharmonic systems, such as the Si(111)-H bond, the $\nu_{1\to2}$ vibrational transition occurs at a lower frequency than that of the $\nu_{0\to1}$ transition, and therefore they may be mutually resolved by an appropriately narrow visible pulse SFG experiment. This three-level experiment is relatively commonplace and has been observed on a variety of systems. Saturation of the first vibrational transition leads to bleaching and reduction of the SFG signal observed for the $\nu_{0\to1}$ mode, and production of the excited state signal. The ratio of the signals may be used to experimentally determine the non-equilibrium vibrational state distribution at any time. More complex situations, where some saturation of both the first and second excited state transitions take place may yield a resonance for the $\nu_{2\to3}$ vibrational transition, which due to anharmonicity of the bond is also spectrally separated from the first and second transition resonances.

A scheme for a typical broadband SFG instrument is shown in Figure 9.[40] This instrument is nearly identical to the SFG module to be used in the current study, and therefore subsequent reference to this instrument will be denoted simply by the "SFG module". In this instrument, a Mode-locked Ti:Sapphire laser is used to generate 800 nm light, which is then converted into an approximately 2 ps 800 nm pulse with a FWHM of approximately 5 cm^{-1}. It should be noted that this spectral width is much smaller than that of the anharmonicity of the Si(111)-H bond, and will therefore easily resolve the occupation of varying vibrational levels. The Ti:Sapphire pulse is also used to create a broad-band IR pulse of varying frequency with a spectral width of 150 cm^{-1} FWHM. Detection of the SFG signal from the surface is accomplished with a polychromator with a charge-coupled device (CCD), indicated in the figure. The specifics and theory of pulse stretching and optical parametric oscillation (OPO)/differential frequency generation (DFG) devices is described in reviews previously cited.
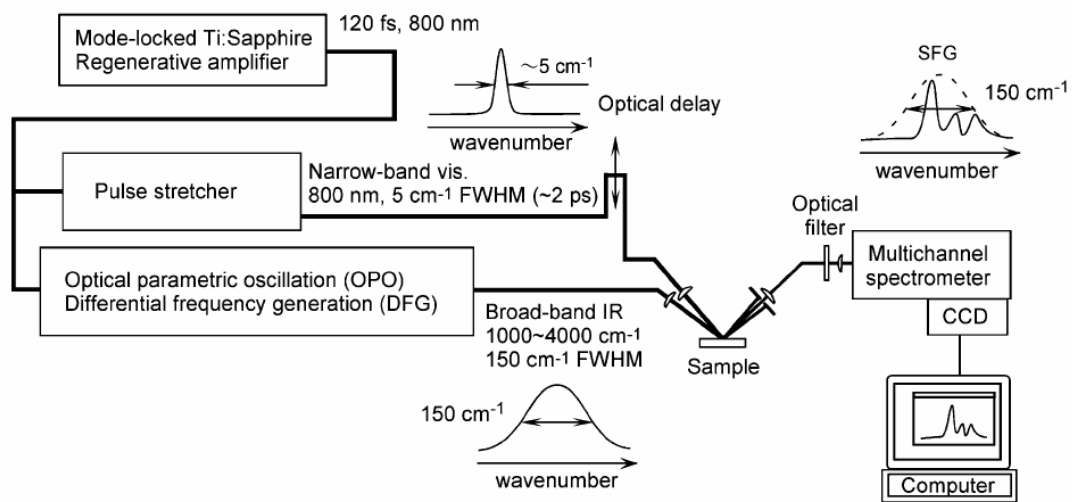

FIG. 9: Typical broad-band SFG system.[40]

The basic system described above will be coupled to an existing FEL source (such as the FELIX laser) for the detection of hot-band vibrational state occupation on the hydrogen passivated silicon surface.

Previous study of the first excited state vibrational transport on hydrogen passivated silicon surfaces made use of two-color transient bleaching SFG. The current experiment may be regarded as a two-color SFG experiment. The first "color", or narrowband IR pulse is generated from the FEL, and the second "color" broadband SFG probe is generated via the

module described above. Previous experiments have had success in implementing the SFG technique without the use of a separate SFG Ti:Sapphire laser for the production of the IR pulse, instead relying on the micropulse IR generated by the FEL in combination with a simple narrowband visible pulse.[29] Here, the multi-laser apparatus is particularly useful for two major reasons. First, the use of the FEL micropulse for the IR probe does not allow for broadband excitation. Broadband SFG is vital to the study since it is desired to observe multiple resonances in the vibrational ladder on the surface. Secondly, the probe should be positioned outside of the micropulse window such that the vibrational structure may be determined while maintaining saturation of the first excited transition.

V. PROPOSAL

The following details the basic experimental strategy for the production and observation of Treanor pumping on hydrogen passivated Si(111).

A. General Strategy

The general, point-by-point strategy for the current work is summarized as follows:

- Modification of a current FEL apparatus (FELIX) with a broadband SFG system similar to the system detailed previously.

- Preparation of hydrogen passivated Si(111) surfaces.

- Treanor pumping will be observed by the production of hot-band vibrational populations by implementation of a narrowband chirped FEL pulse train (micropulse structure) followed by broadband SFG. Some variable delay between the FEL and SFG onset will used to probe the ultrafast vibrational dynamics.

- On ideally terminated Si(111)-H surfaces, investigate at what point during the FEL macropulse is population of the second and nth vibrationally excited states observed.

- How does this production rate compare with the previously known vibrational relaxation process on the Si(111)-H surface?

- Upon identification of significant Treanor pumping (i.e., when the $\nu_{2\to3}$ vibrational transition is observed), the T_1 lifetime of the $\nu_{0\to1}$ transition will be determined using transient bleaching SFG. The lifetime of this bond will be markedly shorter than has been seen on a non-Treanor pumping surface. This will be due to the new rate associated with the non-resonant mechanism driving adsorbate species away from the $n = 1$ vibrational state.

- Use this data to interpret known resonant bond scission data previously discussed.

- Then, is it logical to expect that geometrically-resolved excitation and desorption would be possible by exploitation of this mechanism?

B. Instrument Configuration

A schematic diagram of the proposed instrument for use in this study is shown in Figure 10. This instrument is relatively simple in that the majority of the setup has been previously documented and is available with any current FEL configuration. In this case, a similar FEL configuration to that used by Liu et. al. will be used.[13] The laser will be tuned to provide approximately 100 mJ per macropulse on an area of approximately 0.5 mm^2. This instrument configuration was shown to provide mode-selective desorption in the previous work. This typical setup provides a spectral linewidth of approximately 50 cm^{-1}, which is well within the bond anharmonicity of Si(111)-H and therefore sufficient to probe only the first vibrational excited state transition at 4.8 μm, or ≈ 0.26 eV, 2084 cm^{-1}. The instrument includes an ultra-high vacuum (UHV) chamber in which a clean Si(111) crystal is placed. The LEED and quadrupole mass spectrometer (QMS) modules, while available on current FEL instrumentation, are not necessary for the observation of the desired phenomena in this study, though their utility may arise in troubleshooting qualitatively the desorption process and confirming the Si(111) crystal structure before the onset of an experiment, respectively.

The broadband SFG module will be built onto to the FEL UHV chamber, and has been previously described in detail.[40] The Ti:Sapphire laser will produce 4 mJ of 800 nm light with a time width of 120 fs and 400 Hz repetition rate. An optical parametric oscillator is pumped producing tunable IR pulses in the rage 1-2.5 μm. Broadband IR pulses are subsequently produced by difference frequency mixing (DFG) with a bandwidth of approximately
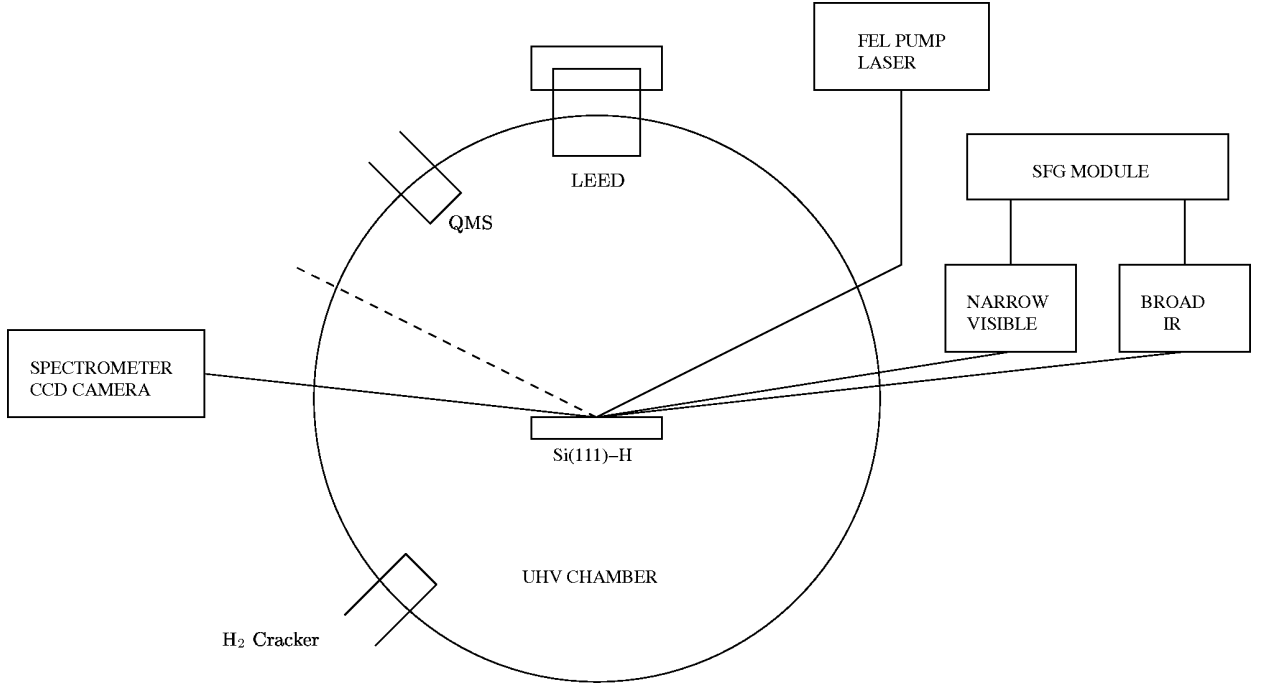
FIG. 10: Schematic diagram of the experimental instrument setup.

150 cm^{-1} and pulse energies of approximately 20 μJ. A pulse shaper is used to convert residual 800 nm light into spectrally narrow visible pulses with bandwidth 5-8 cm^{-1}. The temporal spread of the visible pulse is approximately 2 ps. The visible pulse is passed through a variable delay and the VIS and IR signals are temporally overlapped outside the UHV chamber. The incident angle is approximately 70 degrees with respect to the surface normal. This configuration typically yields visible pulse energies of approximately 4 μJ and IR pulse energies of 10 μJ. The resultant SFG signal is detected using a standard chromatographic separation and CCD camera. The theory of the operation of these components is not presented here, as it is an established method. The reader is encouraged to read the variety of reviews concerning the SFG method cited in this proposal.

C. Surface Preparation

Simple, standard methods for the preparation of initially hydrogen passivated Si(111) surfaces exist and produce some of the best known crystal surfaces ever observed, and are previously described in the preceding sections. These surfaces are prepared in air by wet chemical etching with HF and introduced as clean, ideally terminated unreconstructed

Si(111)-H surfaces into the UHV chamber. Subsequent annealing desorbs the initial adsorbed hydrogen to form a clean Si(111) (7x7) reconstructed surface. An ideally terminated Si(111)-H (1x1) surface is easily prepared at low temperature by H_2 cracking with a tungsten filament heated to 2000 K at a hydrogen dose pressure of 3×10^{-6} Torr for 120 seconds. Temperature programmed desorption spectra of this surface shows a single peak at 820 K, indicating that only the monohydride phase is present on the surface. [13] Further, a strong Si(111) (1x1) LEED pattern has also been observed using this method.

D. Standard Procedure

The standard procedure is detailed as follows:

- Introduce prepared HF etched hydrogen passivated Si(111) surface into the UHV chamber.

- Heat to desorb hydrogen and observe (7x7) reconstruction.

- Prepare hydrogen passivated surfaces by methods described in the previous section. An ideally terminated Si(111)-H (1x1) surface is generated.

- Fire FEL.

- Within the first macropulse, survey the vibrational state distribution by SFG in a time-resolved fashion. At what point during the macropulse is the second vibrationally excited state significantly populated? Or, is the population of this state able to be determined within the first macropulse? The observation of this state is expected for this system.

- Whether or not the $n = 2$ vibrational state is observed, measure the transient bleaching SFG signal of the $\nu_{0 \to 1}$ transition and compare the relaxation rate to previously known exponential free induction decays. Extract the new lifetime of this mode. This will require first doing the non-FEL, equilibrium SFG experiment to establish the base response of the unexcited system.

The theoretical model of the observed SFG response is shown in Figure 11. After some number of micropulses, the SFG probe is fired and the resulting signal yields information as

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to the vibrational state distribution of the Si(111)-H stretching modes. Observation of the $\nu_{2\to3}$ SFG transition is the only absolutely necessary observation for the corroboration of the hypothesis for this work, though the observation of even higher-lying vibrational states cannot be ruled out and may further complement our understanding of this mechanism.
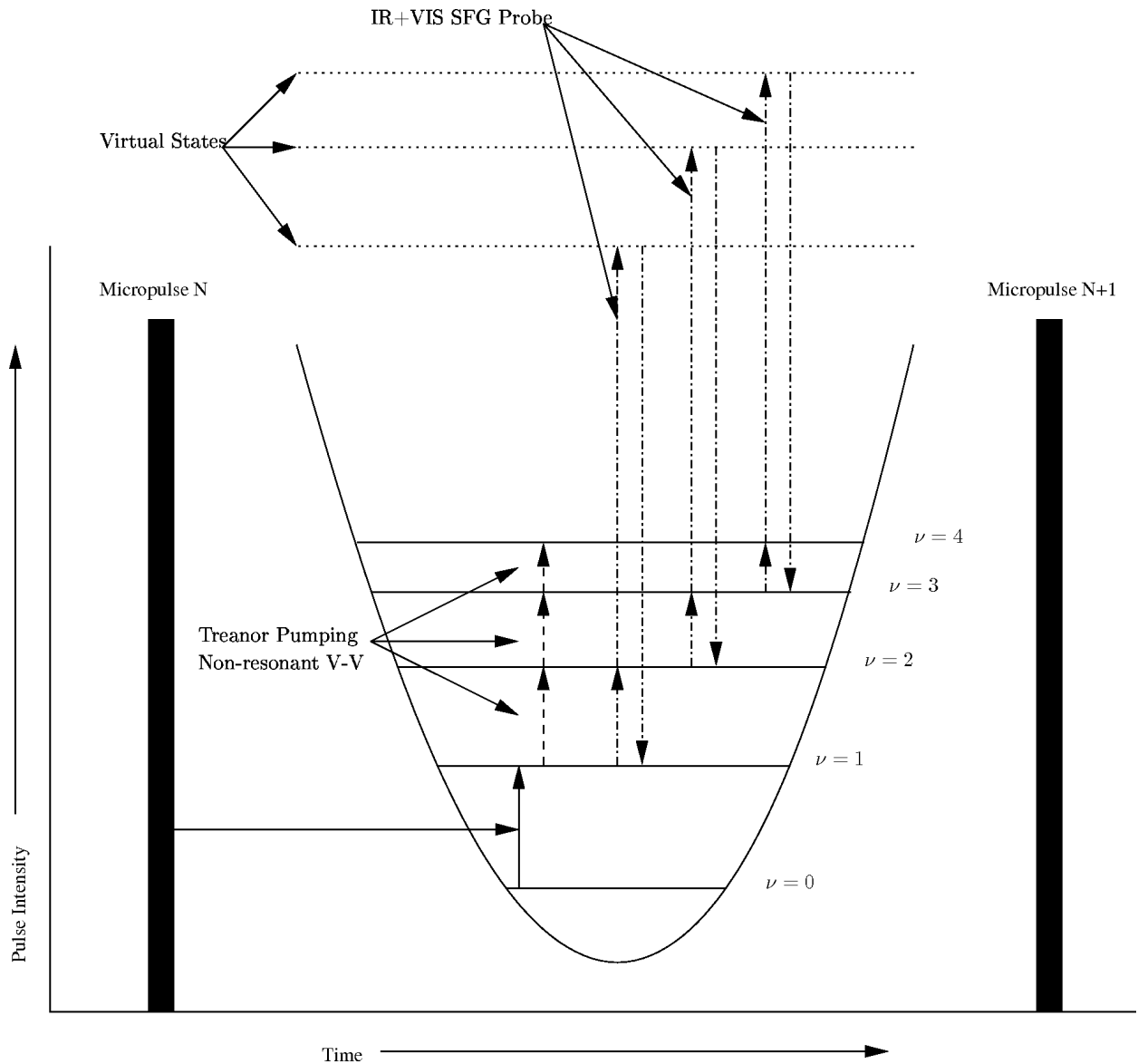

FIG. 11: General outline for the pulse-probe experiment including non-resonant Treanor pumping transfer to high-lying vibrational states and subsequent SFG detection.

Note that in the figure, the timescale and pulse intensity refer only to the micropulse structure. The inset is included to detail the various processes that may be occurring between micropulses of the FEL. It is between these micropulses that SFG will be done to determine

what modes are significantly populated and what the characteristic T_1 vibrational relaxation time is for the $n = 1$ excited state for the system undergoing Treanor pumping. In the figure, only the upward ladder climbing mechanism is indicated as occurring in the Treanor non-resonant V-V transfer, though such a ladder climbing will be concurrently associated with a relaxation by one vibrationally excited state in some other adsorbate species.

VI.   RESULT ANALYSIS AND DISCUSSION

The first results obtained by this study will be phenomenological in nature and qualitative, though they have broad implications for the understanding of this surface. The most important result initially will be whether or not occupation of the ν_2 vibrational state is observed at some time during the first FEL macropulse. It is expected that for the Si(111)-H (1x1) system being interrogated that Treanor pumping does occur within the first FEL macropulse. Therefore occupation of the ν_2 and higher vibrational states must occur.

The rates of these processes, however, are relatively unknown, and lead to some uncertainty as to whether or not these transitions will be observed in the SFG spectra. To a reasonable first approximation, the constant pumping of the $\nu_{0 \rightarrow 1}$ transition with chirped FEL micropulses lead to the formation of what can be thought of as an "artificial ground state". Certainly, relaxation of the $n = 1$ vibrationally excited state does occur on the timescale of the gap between micropulses. However, this gap is less than half the T_1 lifetime and so the approximation of a steady state of oscillators in their first vibrationally excited states is conceptually valid.

Now consider the process leading to the formation for the $n = 2$ vibrational state on the surface by the Treanor pumping mechanism. Observation of the $\nu_{2 \rightarrow 3}$ SFG signal relies on the occupation of the $n = 2$ state by a significant population of adsorbate species. This can only occur if the rate of the Treanor pumping process is competitive with or is greater than the rate of vibrational relaxation away from the $n = 2$ excited state. The T_1 relaxation time for the $n = 2$ vibrational state has been previously observed and is on the order of 1 ns in non-Treanor pumping systems.[4] Further complicating the interpretation of this observation is the fact that subsequent Treanor pumping steps, their rates unknown, may also occur by a variety of processes, including the A(2) + A(2) $\rightarrow$ A(1) + A(3), and the A(1) + A(2) $\rightarrow$ A(0) + A(3) non-resonant processes. Any adsorbate species returned to

the ground state $n = 0$ will be quickly converted back to the artificial ground state $n = 1$, ensuring that there will be a steady population of first excited state species as well as a steady population, however short-lived, of the $n = 2$ species produced by Treanor pumping. All of the factors leading to this ladder climbing severely complicate the interpretation of the observed SFG signal. The observation of the $\nu_{2\rightarrow3}$ SFG transition would establish that some Treanor pumping must occur on the surface, and that the mechanism competes with the relaxation of the $n = 2$ excited state by whatever channels are available to it. The absence of this observation does not at all exclude the non-resonant process, though its existence must be measured using another method, described next.

The other major piece of data obtained in this study is the transient bleaching SFG signal of the $\nu_{0\rightarrow1}$ between FEL micropulses after some reasonable delay through the FEL macropulse such that Treanor pumping is expected to be occurring. This transient bleaching SFG experiment is a standard method used to measure the lifetimes of vibrationally excited states with SFG, and has been applied to the hydrogen passivated silicon surface previously.

The T_1 vibrational lifetime is measured by fitting the decay of the transient SFG signal with a single exponential. The decaying signal is given by

$$1 - [S(t_d)/S_0]^{1/2}, \tag{1}$$

and is plotted again the pulse-probe delay. Here, $S(t_d)$ is the SFG probe signal at some pulse-probe delay and S_0 in an ground state (equilibrium) system. A single exponential fit yields the T_1 vibrational lifetime, which on Si(111)-H terrace sites has been previously measured to be 950 ± 80 ps. The fractional population of the excited state at delay t_d from the pump pulse is given by

$$n_1(t_d) = \left[1 - r^{1/2}(t_d)\right]/2, \tag{2}$$

where r is the ratio $S(t_d)/S_0$. An experimental study of the Si(111)-H surface with a single exponential fit of the decaying transient is shown in Figure 12.[5]

The exponential decay is obtained by fitting the exponential function

$$N_t = N_0 \exp[-\lambda t], \tag{3}$$

and extracting the T_1 lifetime by the inverse of the decay constant λ. If all standard
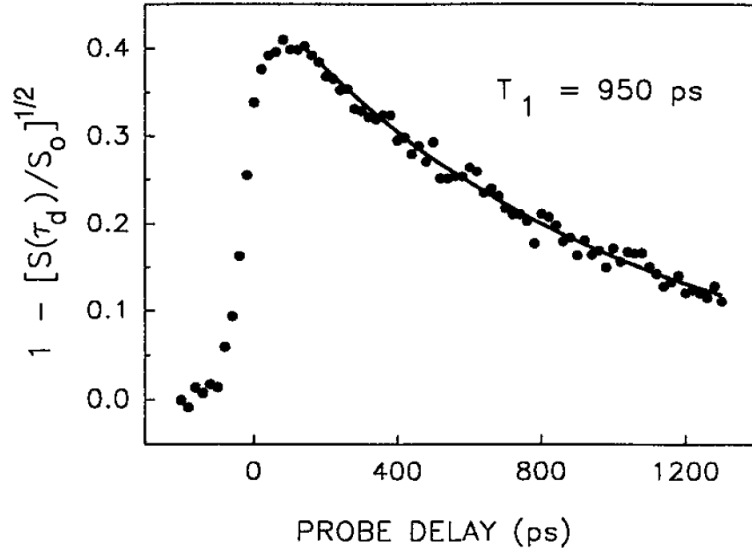
FIG. 12: Experimental and exponential fit of the decaying transient of the terrace Si(111)-H first vibrationally excited mode. Black dots indicate the experimental SFG response and the solid line indicates the exponential fit yielding a T_1 lifetime of 950 ps.[5]

vibrational relaxation processes without non-resonant transfer are grouped, we can describe this decay rate as $T_{1,standard}$ from the inverse of $\lambda_{standard}$. If then a second, isolated group of relaxation processes are introduced, such as the rates associated with the various non-resonant Treanor processes, then the total decay exponential is given by the sum of two exponentials as

$$N_t = N_0 \exp[-(\lambda_{standard} + \lambda_{treanor})t], \tag{4}$$

where $\lambda_{treanor}$ is the decay constant associated with the non-resonant Treanor pumping processes. The inverse of the Treanor decay constant gives $T_{1,treanor}$, the lifetime of the first excited state due to non-resonant relaxation and pumping processes.

It is tempting to consider that the Treanor lifetime derived from the transient bleaching mechanism is a function of only a single mechanism, just as it may be tempting to consider that only one mechanism is responsible for the vibrational relaxation process observed on the standard system. However, this is not the case for either lifetime, and therefore theoretical modeling would be a very appropriate next step in the understanding of this process. In the case of the Treanor pumping rate constant, movement away from the $n = 1$ state may occur by a theoretically infinite number of non-resonant processes, though the onset of significant

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diffusion (and desorption) across the Si(111)-H surface will likely limit the number of discrete non-resonant processes that occur before a continuum of vibrational states is observed on the surface. It is estimated that the barrier for enhanced diffusion requires vibrational ladder climbing to the sixth vibrationally excited state, and therefore non-resonant transfer to higher states is neglected. Therefore the theoretically possible non-resonant processes yielding departure from the first vibrationally excited state may be summarized as

$$A(1) + A(n) \rightarrow A(0) + A(n+1) \qquad \text{where} \qquad n = 1 - 5. \qquad (5)$$

Certainly here the A(1) + A(1) → A(0) + A(2) process is the most important term, as it is the first pumping step required to observe the non-resonant V-V process. However, the A(1) + A(2) → A(0) + A(3) process is also extremely important. If in the qualitative work described above the SFG $\nu_{2 \rightarrow 3}$ transition is not observed, then the second vibrationally excited state must be left with a rate greater than that of the A(1) + A(1) → A(0) + A(2) pumping process. Because the mode-selective desorption experiment has been observed (as previously discussed), it is assumed that the Treanor mechanisms specific to the second vibrationally excited state must be fast in relation to the relaxation process through standard surface mechanisms. Therefore it is expected that the rate limiting non-resonant transfer mechanism is the initial promotion into the second vibrationally excited state, followed by rapid further non-resonant transfer to higher-lying states.

There is some previous work and general thought on the validity of this proposed mechanism. Tully et. al. observed rapid promotion to very high vibrational states theoretically, up to states near the desorption threshold of CO on NaCl(100), without significant population of the intermediate vibrational modes.[15, 16] Further, the non-resonant process yields species that are lower in vibrational energy compared to the reactant species. Conservation of energy requires that the excess energy be observed in an increase in the translational energy of the adsorbate, which may possibly lead to an increased collision rate between species in their $n = 2$ vibrational states and other excited state adsorbates on the surface.

A.   A Note on Step Sites

Cohen et. al. originally proposed the FEL Si(111)-H experiment with step sites in mind, as discussed previously.[18] It was their goal to localize vibrational energy in the step

sites only, thereby promoting reactivity at those sites. Successful exploitation of this effect would have obvious and important implications for semiconductor growth (step-flow growth and imperfection reduction) and catalytic reactivity on step sites. However, the formalism developed in the current proposal suggests that this process is unlikely to be reasonable on all but surfaces with extremely slow T_1 relaxation and poor intra-adsorbate coupling between step and terrace sites. This is not the case on the Si(111)-H system. The vibrational energy flow between step sites and terrace sites observed by Chabal et. al. indicate strong terrace-step Forster coupling, leading to a rapid delocalization of the vibrational energy across all sites, not just those in resonance with the pump laser at the step. In general, all of the vibrational redistribution and relaxation channels observed on terraces have been shown to exist at similar rates between the terrace and step species. This includes Forster and Treanor processes. Therefore is it expected that this method will not be capable of localizing energy at step sites, and that semiconductor growth under FEL conditions, while faster due to the increased vibrational temperature of the substrate, will not show any significant selectivity toward step sites.

VII.   ORIGINALITY

This study constitutes the first observation Treanor pumping, non-resonant V-V energy transfer on a silicon surface. It utilizes a simple but novel method for the production and observation of hot-band vibrationally excited states without the use of resonant excitation of higher-lying modes. The combination of the micropulse time distribution and power coupled to a full broadband SFG system facilitates this study. Further, the mechanism of mode-selective desorption at the Si(111) surface is investigated and shown to be due to the non-resonant Treanor pumping mechanism. It is expected that this work will drive further development in this area, as there are very few limits to this techniques applicability to other surfaces. The possibility of doing mode-selective bond cleavage of the substrate-adsorbate bond on a variety of surfaces and adlayer species is an exciting prospect. Further fundamental study of this and other systems may drive new theory on the rate processes of V-V transfer mechanisms at surfaces. The importance of such vibrational properties ensures that such development will yield new applications in the area of semiconductor surface science.

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