Two-Phonon Bound State for the Hydrogen Vibration on the H/Si(111) Surface

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The $v_{1\to2}$ hot band of the Si-H stretching vibration of the H/Si(111) 1×1 surface is investigated using picosecond sum-frequency generation. The hot band is probed after directly exciting the fundamental $v_{0\to1}$ and is found to be 90 cm^{-1} lower than the fundamental. The shift is consistent with the Si-H anharmonicity in the gas phase and a small dispersion (11 cm^{-1}) for the surface layer, implying a strong two-phonon bound state.

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The vibrational spectroscopy of the normal modes of adsorbates is already a major source of information on their binding sites and configurations on the surface [1,2]. Extension to the spectroscopy of higher vibrational levels would be necessary to investigate other important parameters such as anharmonicity and dissociation energy [1]. Yet, overtone spectroscopy of surface monolayers is difficult and has been performed in only a very few systems. For infrared absorption spectroscopy, the cross sections of overtones and combination bands of monolayers are very weak and mostly undetectable except when enhanced by Fermi resonances [2]. For electron-energy-loss spectroscopy (EELS), overtone spectra have been observed in more systems, but the low resolution often prevents a clear distinction between overtones and double-loss processes [1,3]. In this report, a sequential *two-color* sum-frequency generation scheme (SFG) has been devised to observe clearly the $v_{1\to2}$ hot band of the surface Si-H stretching mode after excitation of the $v=1$ state.

The value of the frequency shift observed for the $v=2$ state (90 cm^{-1}) is important because it depends on the relative strength of the bond anharmonicity *and* of the lateral interaction. In polyatomic molecules, for example, bond anharmonicity and bond-bond interaction compete to give a localized or delocalized character to the higher vibrational levels [4]. Similarly, in bulk media, in contrast with two-phonon states where the two vibrational quanta are delocalized, there can be a *two-phonon bound state* with the two quanta localized over only a few neighboring bonds [5-7]. The existence of this two-phonon bound state is favored by a large anharmonicity but depends also on the strength of the lateral interaction and on the density of states, itself affected by the dimensionality [5-7]. While surface two-phonon bound states have been already discussed in relation with EELS [8,9], the small signals and low resolution given by EELS have not allowed a quantitative discussion of the anharmonicity. In this Letter, the determination of the frequency shift of the $v=2$ state with a good resolution makes it possible to confidently assign the observed absorption to a surface two-phonon bound state.

The unreconstructed monohydride-terminated H/Si(111) surface has been prepared by chemical etching in an ammonium fluoride solution [10]. It remains stable in a gas environment. Its Si-H vibrational modes are known from Fourier-transform infrared-absorption spectroscopy (FTIR) [10] and EELS [11] investigations. The Si-H stretching vibration is at 2083.7 cm [10]. Time-resolved measurements have shown that its lifetime is 0.9 ns at room temperature [12], and its dephasing time is 13 ps [13].

For the two-color surface spectroscopy, the experimental setup is similar to previous experiments [13] with the difference that pump and probe ir beams are now independently tunable. The two infrared beams are generated by the difference frequency of the tunable emission from infrared dye lasers around 1400 nm and the 1064-nm radiation from a Nd-doped yttrium aluminum garnet laser in $AgGaS_2$ crystals. They are tunable from 4 to 8 μm. The pulses are 7 ps long with a 3-cm^{-1} bandwidth. The pump infrared beam, 80 μJ over a 400-μm-diam spot, is resonant with the $v_{0\to1}$ transition and goes through a variable optical delay. The probe infrared beam is tunable, with 30 μJ overlapped within the pump spot. It is synchronized to the visible beam, 150 μJ at 532 nm, and the infrared-visible sum-frequency photons are detected. For the experiment, the sample was kept at room temperature, in a cell filled with argon to minimize contamination from the air. The beams are incident on the sample at around 60° incidence angle through a CaF_2 window.

Figure 1 shows that, after pumping the v_1 state, the probe SFG spectrum exhibits the expected saturation of the fundamental transition. In addition, the very clear resonance of the $v_{1\to2}$ hot band is observed at 1994 cm^{-1}. The shape and strength of the fundamental and of the hot-band transitions are studied as a function of delay of the pump. Figure 2 shows the effect of saturation on the $v_{0\to1}$ transition. It recovers with the previously measured 0.9 ± 0.05-ns lifetime, but in addition, this two-color experiment shows evidence for a small negative shift, a slight broadening, and asymmetry. The strongest effect is seen during the coherence time (for a delay less than 15 ps) after which the residual shift is less than 1 cm^{-1}. Figure 3 shows the SFG spectra of the $v_{1\to2}$ hot band. It has a dispersive shape that is accounted for by

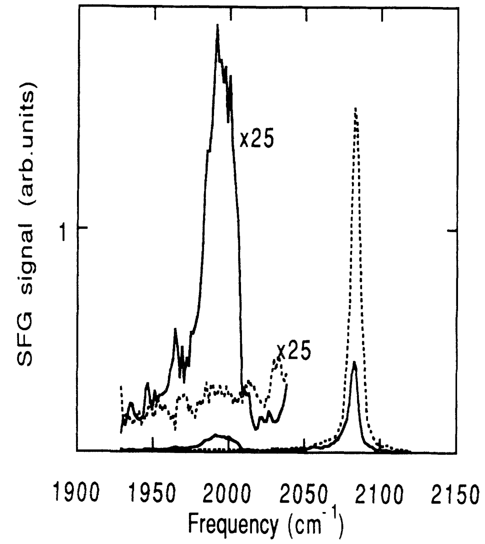

FIG. 1. SFG spectra of the fundamental and hot-band transitions. The solid line is obtained 30 ps after the pump beam at 2084 cm^{-1}. The dashed line is obtained with no pump.

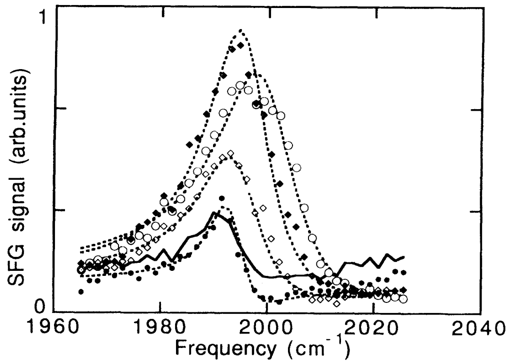

FIG. 3. SFG spectra of the hot band at different delays from the pump. The spectra are taken with 30 μJ in the probe beam; 30 ps (○); 300 ps (◆); 500 ps (◇); and 1.35 ns (●). The solid line is also taken at 30-ps delay but with the pump power reduced by a third. The dotted lines are fits as described in the text.

interference with a nonresonant background. The nonresonant background was sometimes larger on other samples and it increased with contamination. Extended scans from 1840 to 2125 cm^{-1} showed no other structures of more than 10% of the hot-band intensity. The spectral changes as a function of delay are stronger than for the $v_{0\to1}$ transition.

To analyze the data, the SFG spectra are fitted as an interference between a fixed nonresonant background and the resonant susceptibility, $\chi_R = Ae^{i\phi}/(\nu-\nu_r-i\gamma)$, convoluted with a Gaussian laser linewidth of 3 cm^{-1}. The strength A, center frequency ν_r, half-width γ, and phase ϕ are used as parameters. In the fits, the frequencies are precisely determined. There is a larger uncertainty for the strengths and linewidths since these are correlated, and the phase ϕ was found to be 155° ± 10°. The fitting values are shown in Fig. 4. It is found that the center frequency of the hot band varies as a function of time delay and power from 2000 cm^{-1} at high excitation and short delay to 1994 cm^{-1} at low excitation or long delay. The same center frequency is obtained for spectra taken at long delay and high saturation compared with short delay and low saturation. This shows that the 6-cm^{-1} shift is not due to the dynamical evolution of the system, but to the overall density of excited oscillators and it implies some nonlinear response of the system. The width is also affected, as 2γ varies from about 16 cm^{-1} at high excitation to less than 5 cm^{-1} at low excitation.

A first important result of these measurements is that the $v_{0\to1}$ transition is well separated from the hot-band

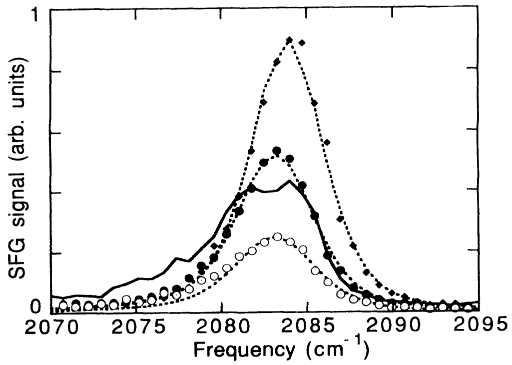

FIG. 2. SFG spectra of the fundamental transition at different delays from the pump. The spectra are taken with 3 μJ in the probe beam to avoid saturation broadening; pump off (◆); 30 ps (○); and 500 ps (●). The dotted lines are fits as described in the text. The solid line is taken at 0-ps delay.

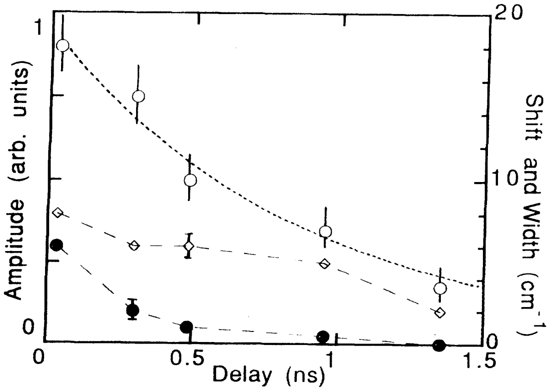

FIG. 4. Values used for the fits of the hot-band spectra in Fig. 3. (○) Amplitude; the dotted line is a exponential fit with T_1 = 0.9 ns. On the right-hand scale are shown the half-width (◇) and the frequency shift from 1994 cm^{-1} (●). The dashed lines are guides for the eye.

transition. This had been a central assumption in the earlier time-resolved studies of this system [12,13]. Second, from Fig. 3, the strength of this transition is found to decay approximately with the same time dependence as the recovery of the $v_{0\to1}$ transition. This confirms that in previous measurements [12], the lifetime of the v_1 state itself had been indeed measured, and not that of intermediate states. From the fits, the strength of the hot-band transition A_{12} can also be compared with the strength of the unsaturated fundamental, A_{01}. The experimental ratio is $A_{12}/A_{01}=0.45\pm0.05$ and it agrees well with the following simple estimate: For SFG, the strengths are a function of the state populations, the infrared transition dipole moments, and the Raman polarizabilities, such that

$$A_{i,i+1}\approx\Delta n_{i,i+1}\frac{\partial\mu}{\partial x}\bigg|_{i,i+1}\frac{\partial\alpha^{(1)}}{\partial x}\bigg|_{i,i+1}.$$

In the harmonic approximation, $\partial\mu/\partial x|_{i,i+1}$ varies with the quantum number as $\sqrt{i+1}$ and, when the optical frequencies are well below the electronic transitions, $\partial\alpha^{(1)}/\partial x|_{i,i+1}$ also varies as $\sqrt{i+1}$ [14]. Since, when the overtone is observed, the reduced intensity of the fundamental indicates an excited population $n_1=0.25$, one then expects $A_{12}/A_{01}=(\sqrt{2})^2 n_1=0.5$ which is close to the measured value.

The observed shift, 90 cm^{-1}, is significantly larger than the typical shift induced by anharmonicity for the isolated Si-H bond in silanes ($2\Gamma=68$ cm^{-1}) [4]. As mentioned earlier, to analyze the $v_{1\to2}$ frequency, one should investigate the effect of the lateral interaction of the Si-H v_1 stretching band. In bond-charge model calculations [15], the lateral interaction of the Si-H stretching mode makes the one-phonon band shift downward away from the Brillouin-zone center. Though the calculated dispersion is about $W=45$ cm^{-1} [15], values for the dynamic dipole and the isolated mode frequency obtained from infrared absorption spectroscopy indicate that the dispersion should be only about 10 cm^{-1} downward [16], and suggest that most of the lateral interaction is due to dipole-dipole coupling. Recent EELS data indicate also a dispersion of less than 18 cm^{-1} [17]. In this system, the anharmonicity is therefore significantly larger than the dispersion and a two-phonon bound state must exist. While the states made of two phonons (ν_i,q_i) form a continuum between $2\nu_{01}$ and $2\nu_{01}-2W$, the bond anharmonicity 2Γ is an attractive interaction that reduces their energy by localizing the two quanta on the same bond. The frequency of the two-phonon bound state thus formed, ν_2, depends on the two-phonon density of states $g(\nu)$ and is such that [5–7]

$$-\frac{1}{2\Gamma}=\int\frac{g(\nu)}{\nu_2-\nu}d\nu. \tag{1}$$

For the Si-H stretch, the flat dispersion at the Brillouin-zone edges is expected to lead to a one-phonon density of states strongly peaked at the bottom of the band ν_1-W. The two-phonon density of states at $q=0$ will then be similarly peaked at $2(\nu_1-W)$. In this case, from Eq. (1), the frequency of the two-phonon bound state at $q=0$ should be about $\nu_2=2(\nu_1-W)-2\Gamma$. Since $\nu_2-\nu_1$ is the experimentally determined frequency, its 90-cm^{-1} shift from ν_1 should then be $2W-2\Gamma$.

Given the strongly covalent nature of this system, one can assume that the anharmonicity of the Si-H bond is not much modified as a surface species compared to the gas-phase value of $2\Gamma=68$ cm^{-1}. This anharmonicity would imply a dispersion W of about 11 cm^{-1} for the Si-H stretch in accordance with infrared and EELS results. Note that a larger anharmonicity would require a smaller dispersion. In any case, the large anharmonicity and small interaction give a very local character to this surface two-phonon bound state [6]. Assuming a Morse potential for the Si-H bond, the calculated dissociation energy ranges from 4.1 to 3.1 eV for $2\Gamma=68$ cm^{-1} and $2\Gamma=90$ cm^{-1}, respectively. For this surface the Si-H dissociation energy is not known but it should range from 3.5 to 3.2 eV [18]. This is therefore also consistent with a large anharmonicity and consequently a small disperson, of the order of 10 cm^{-1} or less. When the dispersion is measured independently (e.g., by EELS), then the exact anharmonicity can be extracted from the present measurement. This system is in fact an excellent test for the understanding of two-phonon spectra at surfaces from which one hopes to refine our knowledge of the adsorbate-surface potential.

Also observed in this experiment are the shifts and broadenings of the fundamental and hot-band transitions. Renormalizations of frequencies are well known in the interaction of radiation with atomic systems and electronic transitions of semiconductors [19]. Very generally, they are due to anharmonic interactions. The same concepts also apply here although their physical implementations are different. For this experiment on H/Si(111), as shown in Fig. 2, different effects are seen for delays before and after dephasing occurs (i.e., for times shorter or longer than T_2). The experimental time resolution does not, however, allow us to investigate in detail the spectra within the coherence time and these will not be discussed here. On the other hand, for the spectral changes seen at high saturation in the incoherent regime, a few mechanisms can be suggested. First, in this system, the dipole-dipole interaction seems the dominant source of interaction. Therefore, as the saturation reduces the polarizability, the reduced interaction could induce a shift that is a fraction of the coupling strength W. Alternatively, as $v=1$ relaxes, probably to bending modes and surface phonons [12], anharmonic coupling between these nonthermalized modes and the stretching mode can induce shifts and broadening [10]. Anharmonic interactions between the stretching phonons results also directly from the on-site anharmonicity responsible for the bound state so that frequency renormalization is expected [6]. Finally, dispersion might also affect the spectra. Indeed, after the dephasing time, $T_2 = 13$ ps, there will be some diffusion of the highly excited $q=0$ phonon into the band so that the second step actually probes the transition between the $v=1$ and $v=2$ bands. That loss of spatial coherence (as opposed to temporal coherence) will be investigated at lower temperatures in the future.

Interestingly, similar spectral changes at high saturation have been recently observed for the $v_{0\to 1}$ transition of the CO stretching mode for CO/Pt(111) [20]. There, T_1 and T_2 are essentially similar so that both coherence and population play a role and should be considered. Which general physical mechanism can quantitatively reproduce these observations still remains to be explored.

In conclusion, the picosecond sum-frequency spectroscopy of the $v_{1\to 2}$ hot band of the surface Si-H stretch has allowed the first precise observation of a surface two-phonon bound state. The large measured shift of 90 cm^{-1} is mostly due to the anharmonicity and the lateral interaction is expected to be less than 11 cm^{-1}. This state must therefore be well localized. With an independent knowledge of the disperson of the fundamental mode, it will be possible to extract rigorously the anharmonicity of the bond. Compared with direct spectroscopy of the $v=0$ to $v=2$ overtone, the two-step approach implemented here has the advantage of higher sensitivity. On the other hand, this method requires relatively high saturation levels that can induce shifts and broadening of the spectra. This is evidence for a nonlinear phonon interaction that will be important to understand for future studies such as surface vibrational energy transfer or infrared photodesorption.

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[1] H. Ibach and D. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, San Francisco, 1982).

[2] Y. J. Chabal, Surf. Sci. Rep. **8**, 211 (1988).

[3] S. Lehwald, H. Ibach, and H. Steininger, Surf. Sci. **117**, 342 (1982).

[4] L. Halonen and M. S. Child, Mol. Phys. **46**, 239 (1982).

[5] F. Bogani, J. Phys. C **11**, 1283 (1978); **11**, 1297 (1978); F. Bogani, R. Giua, and V. Schettino, Chem. Phys. **88**, 375 (1984).

[6] J. C. Kimball, C. Y. Fong, and Y. R. Shen, Phys. Rev. B **23**, 4946 (1981).

[7] T. Holstein, R. Orbach, and S. Alexander, Phys. Rev. B **26**, 4721 (1982).

[8] J. C. Ariyasu and D. L. Mills, Phys. Rev. B **28**, 2389 (1983).

[9] L. J. Richter, T. A. Germer, J. P. Sethna, and W. Ho, Phys. Rev. B **38**, 10403 (1988).

[10] P. Dumas, Y. J. Chabal, and G. S. Higashi, Phys. Rev. Lett. **65**, 1124 (1990).

[11] P. Dumas and Y. J. Chabal, Chem. Phys. Lett. (to be published).

[12] P. 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. Related Phenom. **54/57**, 27 (1990).

[13] P. Guyot-Sionnest, Phys. Rev. Lett. **66**, 1489 (1991).

[14] Andreas C. Albrecht, J. Chem. Phys. **33**, 1475 (1961).

[15] L. Miglio, P. Ruggerone, G. Benedek, and L. Colombo, Phys. Scr. **37**, 768 (1988); U. Harten *et al.*, Phys. Rev. B **38**, 3305 (1988).

[16] P. Jacob, Y. J. Chabal, K. Raghavachari, and P. Dumas, Phys. Lett. (to be published).

[17] C. Stuhlmann and H. Ibach (private communication).

[18] B. M. Rice, L. M. Raff, and D. L. Thompson, Surf. Sci. **198**, 360 (1988).

[19] S. Schmitt-Rink, D. S. Chemla, and H. Haug, Phys. Rev. B **37**, 941 (1988), and references herein.

[20] J. D. Beckerle, R. R. Cavanagh, M. P. Casassa, E. J. Heilweil, and J. C. Stephenson, J. Chem. Phys. (to be published).