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Infrared linewidths and vibrational lifetimes at surfaces: H on Si(100)

J. C. Tully, Y. J. Chabal, Krishnan Raghavachari, J. M. Bowman,* and R. R. Lucchese†
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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The temperature dependence of the natural linewidth of an adsorbate-substrate mode, Si-H, has been measured for the first time. Molecular-dynamics simulations of the infrared line shapes, with the use of an accurate *ab initio* force field and a novel stochastic method to include quantum effects, are in good agreement with experiment. Linewidths are shown to be dominated by pure dephasing above 250 K and by inhomogeneities at low temperature. The vibrational lifetime, computed to be $\simeq 10^{-8}$ s, contributes negligibly to the linewidth.

Knowledge of the rates and pathways of vibrational energy flow is critical for understanding thermal and laser-induced dynamical processes at surfaces. Recent advances in high-resolution infrared spectroscopy of adsorbate vibrations[1–4] promise to provide valuable information. Extraction of dynamical parameters may not be straightforward, however. Although it is common to associate a linewidth with a vibrational lifetime, experience from condensed-phase spectroscopy suggests caution. Even when inhomogeneous effects can be eliminated, linewidths may have little to do with lifetimes. Pure dephasing processes, i.e., fluctuations of the vibrational frequency due to anharmonic coupling to surrounding modes, generally dominate condensed phase homogeneous linewidths, particularly at high temperatures.[5,6]

In the present work we attempt to identify the contributions of energy relaxation and pure dephasing to the vibrational linewidth of a well-ordered adsorbate on a single-crystal surface. We report the first measurements of the temperature dependence of the linewidth of an adsorbate-substrate mode, Si-H, over the range 40–500 K. The Si(100)-(2×1)H surface provides an ideal model system. The stretching mode (~ 2100 cm^{-1}) is well removed from the substrate phonon (≤ 500 cm^{-1}) and electronic absorptions. Further, for the "monohydride" phase, in which there is only one H bonded to each Si atom, the structure and vibrational parameters have been accurately determined.[7] To interpret the measurements, we have computed the vibrational lifetimes and linewidths directly via molecular-dynamics simulation. The calculation of infrared absorption spectra by molecular dynamics was inspired by recent successful implementation of this approach by other workers.[8,9] However, in order to accurately describe pure dephasing broadening we have developed a new stochastic procedure, described below, to introduce certain quantum effects into the equations of motion. We have employed accurate *ab initio* force fields and dipole moment functions in the simulations, with no adjustable parameters. This represents the first *a priori* calculation in full dimensionality of the homogeneous infrared line shape of a localized mode in a condensed phase system. The combination of experimental and theoretical results provides strong evidence that pure dephasing processes dominate the Si-H stretch linewidths at temperatures above 250 K.

Experiments were performed on a Si(100)-(2×1) surface with hydrogen overlayer prepared as described previously.[7,10] The resulting monohydride phase is characterized by repeated units consisting of a symmetric Si-Si dimer with one H atom bound to each Si. Infrared spectra of the Si-H stretch were obtained with an apodized resolution of 0.3 cm^{-1} for $T \leq 280$ K and 0.6 cm^{-1} for $T > 280$ K by a multiple internal reflection technique described elsewhere.[10] A typical spectrum (Fig. 1, solid curve) exhibits two peaks, an antisymmetric stretch at about 2090 cm^{-1} and a symmetric stretch at about 2100 cm^{-1}. The actual center frequency depends on the temperature and features a 4.1 cm^{-1} red shift from 40 to 500 K. The sample temperature could be maintained within 1 K during the time of the measurement (~ 15 min) by means of a specially designed manipulator[11] and the linewidths were quite reproducible for a variety of

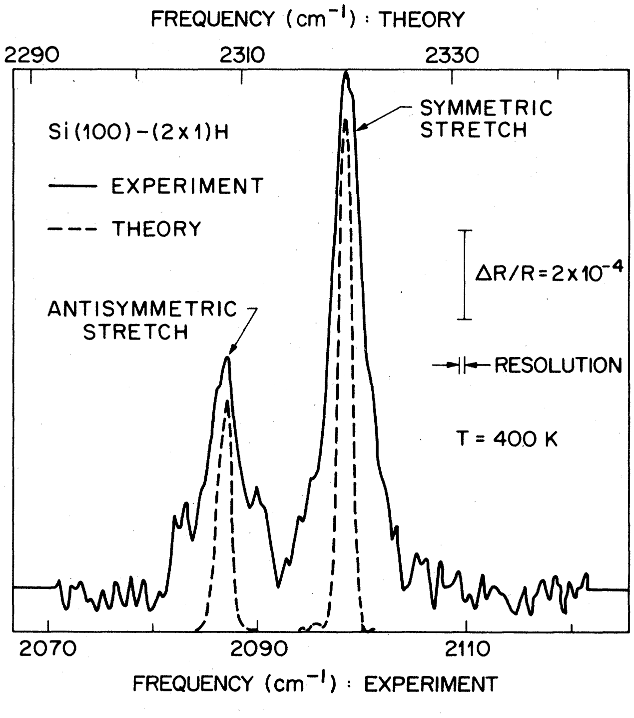

FIG. 1. *Solid curve:* Raw infrared spectrum at $T = 400$ K obtained from subtracting the clean surface spectrum from that of the monohydride surface prepared by H saturation exposure at 250 °C. The apodized resolution is 0.6 cm^{-1}. *Dashed curve:* Theoretical spectrum obtained from Eq. (2) for $T = 400$ K. Note the shift in scale.

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samples and after repeated cleaning and dosing with H. However, the error bar (± 0.25 cm^{-1}) is systematic in nature and depends mostly on the sample quality. A similar set of data was also taken for deuterium for which the two normal modes occur in the 1525-cm^{-1} region.[7]

Molecular-dynamics calculations were carried out for a slab containing 16 H atoms, 16 first-layer Si atoms, and 12 second-layer Si atoms, i.e., 8 monohydride (H-Si-Si-H) units. The Si-Si interactions were taken to be those employed in a previous calculation,[12] derived from a bulk force field due to Tubino, Piseri, and Zerbi.[13] Si-H interactions were evaluated by means of *ab initio* Hartree-Fock calculations with the polarized 3-21G* basis set[14] using a Si_2H_6 cluster[7] to represent the local environment. Diagonal and off-diagonal stretch and bend force constants, including non-negligible cubic, and quartic terms, were calculated. This level of theory has been shown to accurately reproduce the vibrational splitting due to chemical interaction of the two Si-H groups in the dimer and the associated deuterium isotope effects.[7] Although the calculated force constants are about 10% too large, typical of quantum chemical calculations of this type, the force field is otherwise expected to be accurate, including off-diagonal force constants and anharmonic terms.[15] The changes in the dipole moments associated with the normal modes of vibration of the monohydride structure were evaluated using the larger 6-31G** basis set,[16] with inclusion of electron correlation effects by means of Moller-Plesset perturbation theory through fourth order.[17] The accuracy of the computed dynamic dipole moments has been documented by comparison to experimental infrared intensity and polarization data.[7] The resulting dynamic dipole-moment function was employed in the dynamics simulations to calculate infrared absorption intensities and lateral dipole-dipole interactions.

Two types of molecular-dynamics calculations were carried out, one to obtain vibrational lifetimes and another to simulate infrared absorption spectra. The lifetime calculations were performed in the following way: Classical mechanical equations of motion were numerically integrated for the 44-atom slab of H and Si atoms. In addition to the force field described above, friction and Gaussian white-noise random forces were applied to the edge atoms of the slab, as described previously,[12] to account for energy flow between the slab and the missing remainder of the solid. The friction and random forces were constrained to satisfy the fluctuation-dissipation theorem so that the slab maintained the desired temperature.[12] However, the temperature T_{QC} was chosen by the quasiclassical procedure

$$T_{QC}=\frac{\hbar\omega_D}{k}\left[\frac{1}{2}+\frac{\exp(-\hbar\omega_D/kT)}{1-\exp(-\hbar\omega_D/kT)}\right] , \tag{1}$$

where $\hbar$ and k are Planck and Boltzmann constants, T is the actual temperature, and ω_D is the Debye frequency taken to be 500 cm^{-1}. It has been demonstrated for a simple collinear model that multiphonon vibrational relaxation rates calculated by this stochastic trajectory method with the quasiclassical temperature of Eq. (1) are in quantitative agreement with quantum-mechanical rates calculated for the same model for all temperatures, even approaching 0 K.[18] In the present calculation one quantum (2300 cm^{-1}) of energy was initially deposited in the symmetric stretch of each H-Si-Si-H unit, i.e., the $k=0$ level was excited, and the remainder of the positions and momenta were chosen from a Boltzmann distribution at temperature T_{QC}. The trajectory was then integrated and the decay of energy in the Si-H stretch modes monitored as a function of time. Energy relaxation was found to be so slow that even for the longest trajectories integrated, 2.6×10^{-10} s, less than 1% of the energy in the Si-H stretch modes was dissipated. Similar results were obtained for the antisymmetric stretch. Thus, we can make only a rough estimate of the vibrational lifetime of the Si-H stretch, $\tau_H \gtrsim 2\times10^{-8}$ s. When all H atoms were replaced by D atoms, using the same force fields, vibrational lifetimes were shortened sufficiently to calculate more reliable estimates ranging from $\tau_D=1.0\pm0.5\times10^{-9}$ s at 500 K to $\tau_D=3.0\pm1.5\times10^{-9}$ s at 0 K. Thus, it appears that the vibrational lifetime contributes negligibly to the observed infrared linewidths for the Si-H and Si-D stretch modes ($\sim10^{-3}$ cm^{-1} for H and $\sim10^{-2}$ cm^{-1} for D).

The next molecular-dynamics calculation was direct simulation of the infrared absorption spectrum. The absorption intensity, $I_i(\omega)$ at frequency ω (polarization $i=x,y,$ or z) was computed from the expression

$$I_i(\omega)\propto\int\langle\mu_i(t)\mu_i(0)\rangle e^{-i\omega t}dt , \tag{2}$$

where brackets indicate ensemble average over many trajectories. The dipole-moment function, $\mu_i(t)$, was computed along each trajectory and the power spectrum equivalent of Eq. (2) evaluated.[8] Typically, the results of 8 trajectories of 2.6×10^{-10} s duration were averaged. As suggested from the study of small model systems,[9] the initial energy of the Si-H stretch mode was chosen half way between the $v=0$ and $v=1$ levels. Furthermore, the white-noise random force was replaced by a filtered random force, $R(t)$, obeying the following relationship

$$\langle R(t)R(0)\rangle=\tfrac{1}{3}\pi\hbar^{-1}k^2T^2\gamma\exp(-\pi kTt/3\hbar) , \tag{3}$$

where γ is the friction constant; i.e., an approximate "quantum" fluctuation-dissipation theorem was employed.[19] With this ansatz, the resulting equilibrium populations of vibrational modes approximate the correct quantum-mechanical distributions, a requirement for obtaining the correct Arrhenius-type temperature dependence of pure dephasing linewidths.

A typical computed spectrum is shown in Fig. 1 (dashed curve). Note that the frequency scale of the theoretical curve has been shifted 222 cm^{-1} relative to experiment to account for the $\approx$10% overestimate of the calculated force constants as described above. Experimental and calculated splittings and intensities are in good agreement. Calculated linewidths are somewhat smaller than experimental.

Experimental (closed circles) and calculated (open squares) linewidths are compared in Fig. 2. At low temperatures, the experimental linewidths level off at about 0.9 cm^{-1}. This residual linewidth which varies from sample to sample and with sample preparation is almost certainly due to inhomogeneous broadening. Therefore, we have extracted an approximate homogeneous part of the linewidth (Fig. 2, triangles) by subtracting the 0.9 cm^{-1} inhomogeneous contribution from the experimental points. The calculated widths are in reasonable accord with the adjusted experimental widths, particularly with regard to temperature dependence. In fact, the agreement achieved is remarkable for a theory with no adjustable parameters. The discrepan-

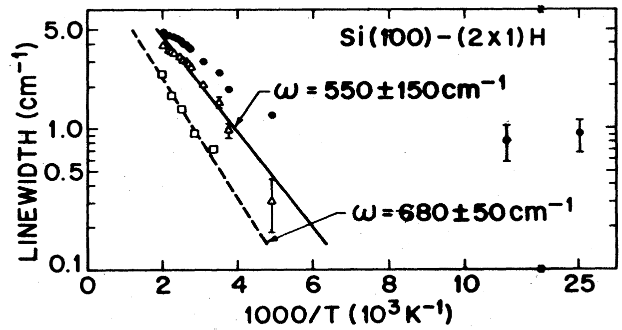

FIG. 2. Experimental linewidth (closed circles) obtained from Lorentzian fit to the data and proper deconvolution of the apodized resolution function. The error bar represents mostly the reproducibility from sample to sample (±0.25 cm^{-1}). The triangles are obtained by subtracting from the experimental linewidth the inhomogeneous contribution of 0.9 cm^{-1} (see text). The squares are the calculated linewidths. Statistical uncertainty of calculated points is ±0.4 cm^{-1}.

cies of about a factor of 2 could easily result from approximations inherent in the semiclassical simulation technique[19] and/or inaccuracies in the *ab initio* force field. Furthermore, experimental and theoretical linewidths for the Si-D stretch in Si(100)-(2×1)D are in equally good agreement.

Calculated linewidths are essentially entirely due to pure dephasing. Dipole-dipole interactions make a negligible contribution to both linewidth and lifetime. The major mechanism for dephasing is the anharmonic coupling between the Si-H bending mode and the Si-H stretch. The dominance of this mechanism is manifested in the slope of a straight-line fit through the calculated points of Fig. 2.[20] When converted to wave numbers, the slope is ~680 ± 50 cm^{-1}, in close agreement with the 700 cm^{-1} (theoretical) activation energy for exciting the bending mode. Note that the slope of a straight-line fit through the adjusted experimental points of Fig. 2 (triangles) yields an activation energy of 550 ± 150 cm^{-1}, in at least rough accord with the experimental bending frequency[21] of 635 cm^{-1}. Additional evidence for the dominance of pure dephasing is provided by the Ge(100)-(2×1)H system for which above 250 K the logarithm of the experimental linewidth versus inverse temperature can be well fit[22] by a straight line with slope ~500 cm^{-1}, again close to the bending vibration of ~550 cm^{-1}.

In summary, from high-resolution measurements of temperature-dependent linewidths coupled with calculations carried out in full dimensionality with accurate force fields, we conclude that for the system studied at temperatures above 250 K the infrared linewidth is essentially entirely due to pure dephasing processes, with a major contribution from anharmonic coupling between the Si-H stretching and bending motions.

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[*] Permanent address: Department of Chemistry, Illinois Institute of Technology, Chicago, IL 60616.

[†] Permanent address: Department of Chemistry, Texas A&M University, College Station, TX 77843.

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