Vibrational spectra of hydrogen on diamond C(111)-(1 × 1)

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Infrared-visible sum-frequency generation was used to obtain vibrational spectra of hydrogen on C(111). From a fully relaxed (1×1) surface, a single sharp peak at ~ 2830 cm^{-1} was observed, which can be identified as the CH stretch mode from H on top sites. With the surface freshly transformed from (2×1) to (1×1), however, another peak at a higher frequency was detected. This is attributed to H adsorbed on a metastable (1×1) structure.

Hydrogen on diamond C(111) is a subject of great current interest since it plays an important role in the growth of diamond films by vapor deposition.[1] However, despite the rather extensive effort in the past, understanding of the system is still not complete. The low-energy electron-diffraction (LEED) work[2] showed that upon hydrogen adsorption, the reconstructed C(111)-(2×1) surface is transformed into a (1×1) bulk-terminated structure, but few details are known. The electron-energy-loss spectroscopy (EELS) results[3] suggested that the adsorption forms CH_3 groups truncating the dangling bonds of the (1×1) surface, while the He scattering and diffraction data[4] and the angular distribution of protons desorbed by electron stimulation[2,5] from H/C(111)-(1×1) favored a simple hydrogen truncation of the bulk (H on top sites). Recently, infrared-visible sum-frequency generation (SFG) has been proven to be an effective tool for surface vibrational spectroscopic studies.[6] It can be applied to any interface accessible by light and is ideally suited for investigation of hydrogen adsorption on diamond. Here, we report the first results on H/C(111) using this technique. We have found, for H on a fully relaxed (1×1) surface, a single CH stretch peak at ~ 2830 cm^{-1} in the vibrational spectrum with an intrinsic full width less than 10 cm^{-1}. This, together with the polarization dependence of the spectrum, assures the monohydride adsorption geometry of H sitting on top C(111) sites. We have also found, together with LEED and optical second-harmonic generation work, that adsorption of only a few percent of a full monolayer of H was sufficient to induce the (2×1)→(1×1) phase transformation.[7] The CH stretch mode observed on a freshly formed (1×1) surface at a low H coverage without annealing, however, showed up as a peak at a higher frequency (2860 cm^{-1}), suggesting the freshly formed surface might not be fully relaxed. The full surface relaxation could be effected by either high-temperature annealing (without hydorgen desorption) or higher surface coverage of H.

The experimental setup for the SFG measurements has been described elsewhere.[6] Briefly, the sum-frequency output from a sample surface was generated by overlapping a 25-ps visible light pulse at 0.532 μm and a 25-ps

tunable infrared pulse on the surface. It is known that the output is proportional to the absolute square of the surface nonlinear susceptibility $\chi_s^{(2)}$, which can be written as[6]

$$\chi_s^{(2)} = \chi_{NR}^{(2)} + \chi_R^{(2)},$$

$$\chi_R^{(2)} = \sum_Q \frac{A_Q}{\omega_{IR} - \omega_Q + i\gamma_Q},$$

(1)

where $\chi_{NR}^{(2)}$ is the nonresonant contribution, ω_{IR} is the infrared laser frequency, and A_Q, ω_Q, and γ_Q denote, respectively, the strength, the resonant frequency, and the damping coefficient of the Qth vibrational mode. A theoretical fit of $|\chi_s^{(2)}|^2$ vs ω_{IR} with the observed SFG spectrum using Eq. (1) allows us to deduce $\chi_{NR}^{(2)}$, A_Q, ω_Q, and γ_Q. The different tensor components of $\chi_s^{(2)}$ can often be determined from measurements with different polarization combinations of input and output beams. In simple cases, the results can yield information about the orientation of a group of atoms associated with a specific vibrational mode.[8] For example, consider a carbon monohydride stretch mode on a diamond C(111)-(1×1) surface. It can be shown, from $\chi_R^{(2)} = N_s \langle \alpha^{(2)} \rangle$, that the two relevant elements of $\chi_R^{(2)}$ are

$$\chi_{yyz}^{(2)} = \chi_{xxz}^{(2)} = N_s \alpha_{\xi\xi\xi}^{(2)}[\frac{1}{2}(1-r)\langle \sin^2\theta\cos\theta \rangle + r\langle \cos\theta \rangle],$$

(2)

$$\chi_{yzy}^{(2)} = \chi_{xzx}^{(2)} = \chi_{zyy}^{(2)} = \chi_{zxx}^{(2)} = \frac{1}{2}N_s\alpha_{\xi\xi\xi}^{(2)}(1-r)\langle \sin^2\theta\cos\theta \rangle.$$

Here, N_s refers to the surface density of the C-H bonds, $\alpha^{(2)}$ is the nonlinear polarizability of the C-H bond with its two independent nonvanishing elements being $\alpha_{\xi\xi\xi}^{(2)}$ and $\alpha_{\zeta\zeta\xi}^{(2)}$, where ξ and ζ denote directions parallel and perpendicular to the bond, respectively, $r \equiv \alpha_{\zeta\zeta\xi}^{(2)}/\alpha_{\xi\xi\xi}^{(2)}$ and is estimated to be 0.14 for C-H from Raman polarizability measurements,[9] z is along the surface normal and x-y in the surface plane, θ is the angle between z and the C-H bond, and the angular brackets denote an orientational average. Knowing $\chi_{yyz}^{(2)}$ and $\chi_{yzy}^{(2)} = \chi_{zyy}^{(2)}$, Eq. (2) can then be used to deduce the information about the C-H orientation. Experimentally, $\chi_{yyz}^{(2)}$ can be obtained with an s(sum-frequency, output)-s(visible, input)-p(infrared, input) polarization combination, and $\chi_{yzy}^{(2)}$ and $\chi_{zyy}^{(2)}$ with s-

p-s and *p-s-s* combinations, respectively.

The sample was situated in an ultrahigh-vacuum (UHV) chamber with a base pressure of $< 5 \times 10^{-10}$ torr. It was a type-IIa natural diamond cleaved and polished along (111) with a dimension of $3 \times 3 \times 0.25$ mm^3. The surface obtained by polishing with olive oil and subsequent chemical cleaning and baking at 450°C in UHV was found to be fully covered by H.[10] By heating the surface to 1150°C, all H could be desorbed and the surface was reconstructed from (1×1) to (2×1). Hydrogen could be readsorbed on the surface by dosing H via hot-filament-induced dissociation of H$_2$.

For the clean C(111) surface, our LEED pattern revealed a (2×1) surface structure.[2,7] When the surface was dosed to a H coverage of ∼5% of a monolayer, both the LEED pattern and the optical second-harmonic signal from the surface indicated that the surface had begun to convert from (2×1) to (1×1). The SFG measurement also started to register a peak at 2860 cm^{-1} [peak positions, widths, and strengths reported here and in the following are values obtained from the fit to the observed spectra using Eq. (1), spectral resolution was limited to 10 cm^{-1} by our infrared source]. With continuous H dosage, this peak first increased in strength, reached a maximum at ∼42% monolayer H coverage, and decreased afterward to nearly zero at full monolayer H coverage. In the meantime, another peak at ∼2830 cm^{-1} showed up and grew monotonically with the increase of H coverage. The spectral variation described above is illustrated in Fig. 1. We note that the vibrational spectra reported here are very different from those obtained by EELS.[3] The strength of the 2860-cm^{-1} peak could be transferred to the 2830-cm^{-1} peak by annealing the sample at ≥ 700°C. Annealing not only eliminated the former completely, but also made the latter narrower, presumably due to a relief of surface strain set in by the surface structural transformation. After the (1×1) surface was annealed, the 2860 cm^{-1} would not appear again with further desorption or readsorption of H or with any H coverage on the surface. The strength of the ∼2830-

FIG. 2. SFG spectra of H/C(111) from a fully relaxed (1×1) surface with different surface H coverages resulting from thermal desorption: 100% ML (solid squares); 49% ML (open squares); 29% ML (open circles); 14% ML (open triangles).

cm^{-1} peak could then be used to estimate the H surface coverage. Figure 2, for example, shows how the H surface coverage decreases by thermal desorption as reflected in the reduction of the 2830-cm^{-1} peak in the SFG spectrum. A close examination of the spectra as a function of H surface coverage reveals an approximately linear shift of the peak given by $\omega_{CH} = 2834 - 6.62x$, with $0 < x \leq 1$ denoting the H coverage in terms of a percentage of a full monolayer. The polarization dependence of the 2830-cm^{-1} peak is depicted in Fig. 3. It is seen that while the *s-s-p* SFG spectrum exhibits the peak clearly, the *s-p-s* and *p-s-s* spectra are barely detectable. This immediately suggests that the C-H bonds must be mainly along the surface normal since then only the *p*-polarized infrared input can excite the C-H stretch vibration. An analysis of the spectra of Fig. 3 using Eq. (2) yields a mean angular spread of the bond orientation of ∼60° if the average bond direction is taken to be along the surface normal. This agrees with the conclusion derived from electron-stimulated ion desorption by Hamza, Kubiak, and Stullen.[2] The polarization dependence of the 2860-cm^{-1} peak is very similar to that of the 2830-cm^{-1} peak, indicating that the CH bonds responsible for this peak must
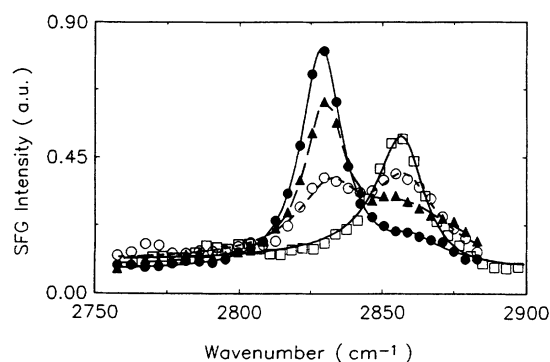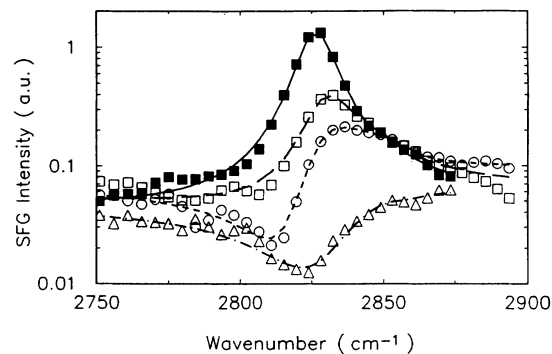

FIG. 1. SFG spectra of H/C(111) from a freshly formed (1×1) surface with different surface H coverages: 42% ML (open squares); 51% ML (open circles); 68% ML (solid triangles); 77% ML (solid circles). The (2×1) to (1×1) phase transition was induced by H adsorption. The H coverage were estimated from the overall strength of the resonant modes using the full H coverage as a reference.
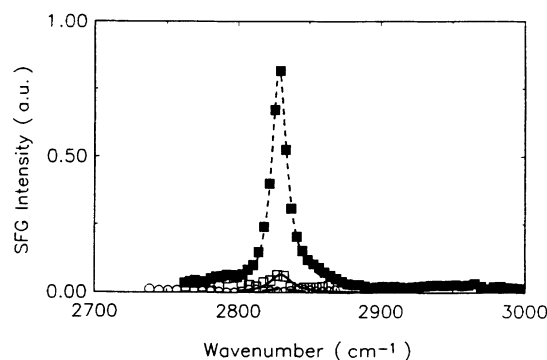

FIG. 3. SFG spectra of a well-annealed H-terminated C(111)-(1×1) surface, obtained with different polarization combinations: solid squares for the *s*(sum-frequency, output)-*s*(visible, input)-*p*(infrared, input) polarization combination, open squares for the *p-s-s* combination, and open circles for the *s-p-s* combination.

also be along the surface normal.

The above results strongly support the picture of atomic H adsorbed on top sites of $C(111)$-(1×1).[2,4] We can estimate the frequency of such a surface C-H stretch mode from the known C-H stretch frequency (2992 cm^{-1}) of CHD$_3$ in the gas phase.[11] Assuming that the spring constants for the CH vibration of the two cases are the same and the diamond surface can be approximated by a rigid wall with an infinite mass, we find $\omega_{CH} = 2875$ cm^{-1} for the surface CH stretch along the surface normal. This is close to what we have observed. The corresponding CH bond length is estimated to be 1.11 Å following Ref. 11. A much more sophisticated total-energy calculation predicting the C-H vibrational frequency and the anharmonicity for H/$C(111)$-(1×1) has been carried out by Zhu and Louie.[12]

The observation of the 2860-cm^{-1} mode, which can be annealed away, suggests that there may exist a metastable (1×1) phase on $C(111)$ resulting from a H-adsorption-induced phase transition from (2×1) to (1×1). A π-bonded chain model has been proposed to be the most energetically favorable structure for the (2×1) surface.[13] A conversion from the π-bonded chain structure to the bulk-truncated (1×1) surface would involve a rather complicated rearrangement of bonds. It is conceivable that a metastable (1×1) phase might exist with slightly different bond angles and bond lengths from the truncated (1×1),[14] although we do not know the exact configuration of that structure. Apparently, both annealing and sufficiently high H coverage can cause this surface to relax to the more stable bulk-truncated (1×1) surface, whereas transition in the reverse direction seems impossible. To obtain the metastable (1×1) structure, the surface must be first reversed back to (2×1) by desorbing all H and then dosed with a small amount of H to induce the surface restructuring.

We have also used SFG to study surface modification of $C(111)$ resulting from dosing of CH^4 through a hot filament. Dissociation of CH$_4$ at the filament would yield H and CH$_x$ ($x = 1,2,3$), which could be adsorbed on $C(111)$. A sufficiently high surface coverage by the adsorbates led again to the surface structural transformation from (2×1) to (1×1).[7] In the case of a saturated surface coverage, our SFG spectrum shows clearly the presence of CH$_3$, H, and a trace of CH$_2$ adsorbed on the surface. Upon further dosing of H, the surface density of CH$_3$ decreased very significantly and that of H increased. Detailed results of this investigation will appear in a later publication.[15]

In summary, we have obtained, using the SFG technique, the vibrational spectra of H/$C(111)$. The spectra for H on a fully relaxed $C(111)$-(1×1) surface are dominated by a single sharp peak that can be identified as the C-H stretch from atomic hydrogen adsorbed on top sites. The spectra for H on a freshly converted, but unrelaxed, $C(111)$-(1×1) surface are, however, dominated by a sharp peak at a higher frequency. This suggests that in the adsorbate-induced phase transition of $C(111)$ from (2×1) to (1×1), there may exist an intermediate metastable (1×1) surface structure.

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