Infrared Spectroscopy and Vibrational Relaxation of CH₃ and CD₃ Stretches on Synthetic Diamond Nanocrystal Surfaces

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Infrared spectra of CH₃ and CD₃ stretches on intensively annealed, fully hydrogenated diamond crystallites are reported. By hydrogenating synthetic diamond nanocrystals at 1000 °C, a single sharp CH₃ vibrational absorption, accompanied by several weak satellites at higher frequency, has been observed at 2835.5 cm⁻¹. The bandwidth of the sharp feature is 4.5 cm⁻¹ and is insensitive to the temperature of measurement at 100–300 K. For CD₃ stretches, however, immensely broad bands centered at 2110 cm⁻¹ with widths of 30 cm⁻¹ were recorded. The dramatic difference in bandwidth reveals a vibrational relaxation lifetime of ≈0.2 ps for the CD₃ stretch on the surface. From the results of mixed isotope experiments, it is suggested that the single band at 2835.5 cm⁻¹ should be assigned to the CH stretch on C(111)-1 × 1, and the high-frequency satellites should be attributed to the stretches of CH₃ (x = 1–3) on corners, edges, or other defect sites of the crystallites. The severe band broadening in CD₃ is interpreted as a major result of the near-resonant coupling of the transition dipole of the adsorbate with the second-order optical phonons of the substrate, from which a relaxation time of ≈3 ps is predicted for CH on C(111)-1 × 1.

Introduction

One of the recent breakthroughs in material science is the synthesis of diamond and diamond-like films at low temperatures and low pressures.¹⁻³ The films can be formed by simple chemical vapor deposition (CVD), which involves discharging gas mixtures of H₂ and CH₄ above metal or semiconductor substrates, with typical crystal growth rates of 1–10 μm/h. Advances in the technology have been rapid,⁴ yet the mechanism of diamond film formation by CVD is complex and remains unclear. Several experimental⁵⁻⁷ and theoretical⁸ efforts have been oriented toward gaining a better understanding of the key intermediates and reaction steps during the growth. From studies of Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and X-ray photoemission spectroscopy (XPS) on the surfaces of single crystals, it is now known that hydrogen atoms play a crucial role in the diamond growing process.⁹ In the presence of H, the surface carbon atoms can sustain the sp³ electronic configuration that is essential for diamond growth. It is remarkable that only 5% coverage of adsorbed hydrogen atoms will transform C(111) from (2 × 1), the graphite-like surface structure, to (1 × 1), the surface structure of diamond.¹⁰

Spectroscopic methods have also been applied to elucidate the mechanism of CVD diamond film growth. There have been three major experimental approaches to explore adsorbate vibrations on a single crystal surface: infrared spectroscopy (IRS), sum-frequency generation (SFG), and high-resolution electron energy loss spectroscopy (HREELS). Both SFG and HREELS have been employed successfully to observe CH stretches on C(111). On a natural diamond C(111)-1 × 1 surface, SFG showed a single C–H resonance at ≈2830 cm⁻¹ with an instrument-limited bandwidth of 10 cm⁻¹.¹¹ The position of the resonance could vary a few wavenumbers, depending on how well the single crystal surface was annealed.¹²

On epitaxially grown diamond surfaces, HREELS revealed single broad bands centered at ≈2840 and ≈2927 cm⁻¹ for C(111) and C(100), respectively.¹³ The bands were so broad (nearly 100 cm⁻¹) that conclusive assignment of the features to either CH or CH₃ could not be made. The direct IR absorption technique is evidently more advantageous in this regard because of its higher spectral resolution; however, the technique is limited by its lack of surface sensitivity and specificity. Despite the difficulty, D'Evelyn and co-workers¹⁴,¹⁵ have employed an attenuated total reflection (ATR) technique coupled with a Fourier transform infrared (FTIR) spectrometer and succeeded in observing the CD, bending modes on the (100) surface of single crystal diamond. The ATR spectra exhibited features at 901 and 1125 cm⁻¹ with bandwidths of ≈20 cm⁻¹. The band broadening is believed to be a combined result of surface heterogeneities and efficient coupling of the bends with high-frequency surface phonons (Debye frequency ≈1500 cm⁻¹).¹⁶

To better characterize the atomic hydrogen on diamond surfaces, the CH stretching modes should be investigated because they are off-resonant with diamond lattice vibrations and are thus less complicated. A large body of experimental data related to this subject can be found in the literature,¹¹,¹³–¹⁵,¹⁷–²⁷ however, due to the complexity caused by x varying from 1 to 3, inconclusive results and controversial spectroscopic assignments exist. For example, Ando, Kamo, Sato, and co-workers,²⁴ who pioneered the use of FTIR to investigate the CH stretching motions on polycrystalline diamond powders, assigned the doublet observed at 2840 and 2930 cm⁻¹ to the symmetric and antisymmetric stretches of surface CHₓ (x = 2 or 3) species. Additional broad features appearing within the doublet were attributed to different forms of the CHₓ stretches on different crystal faces based on the variation of the spectra as a function of hydrogenation temperature and time. They further attributed a broad feature at 2855–2870 cm⁻¹ to CH on C(111)-1 × 1 or C(100)-2 × 1. The
between the vibrationally excited adsorbate and the substrate we are allowed to further explore the rate of energy transfer on polycrystalline surfaces. On the basis of careful assignment, possible only on intensively annealed and fully hydrogenated samples, we can make cautious conclusions. With the aid of mixed isotope and experimental results which suggest that the vibrational relaxation of CH, stretches on diamond surfaces is rapid; the CH, stretching motions could be relaxed in several picoseconds.

Experimental Section

The setup and methodologies used in this experiment are similar to Ando et al.24 and Chen et al.28 and thus only a brief discussion will be presented here. The sample, composed of synthetic diamond nanocrystals (100 nm in diameter, Kay Industrial Diamond), was prepared by careful removal of graphitic carbon atoms and other possible metallic contaminants on the surfaces before hydrogenation. Adopting the recipe of Mitsuda et al.,10 we cleaned the diamond surfaces with concentrated H2SO4—HNO3 (3:1) acid mixture heated up to 100 °C for 20 min, followed by thorough rinsing with deionized H2O. Drops of the diamond—water suspensions were deposited on single crystal silicon wafers, which were then dried in a hydrocarbon-free glass desiccator to form a thin film. The polycrystalline film prepared in this way has a typical thickness of 4 μm.

The diamond film was hydrogenated by microwave discharge of pure molecular hydrogen in a chemical vapor deposition reactor (ASTeX) evacuated by a turbomolecular pump. The flow rate of the hydrogen through the reactor was maintained at 200 sccm/min during the hydrogenation. With the use of 2 kW microwave power and a hydrogen pressure of 30–60 Torr regulated by a gate valve, the temperature of the hydrogen plasma near the Si substrate surface was varied from 750 to 1100 °C, measured by a single wavelength radiation pyrometer (Optex). Uncertainty of the temperature measurement was ±50 °C. The hydrogenation conditions were maintained for 30 min to ensure complete saturation of the surfaces with atomic hydrogen. Two gaseous samples, H2 (Matheson, 99.99%) and D2 (Isotec, 99.8%), were used without further purification. After hydrogenation, the sample mounted on the Si substrate was transferred through ambient air and positioned in a dry nitrogen-purged FTIR spectrometer within 5 min to minimize contamination. The FTIR spectrometer (Bohem MB100) collected absorption spectra at room temperature from 1800 to 3200 cm⁻¹ using liquid nitrogen-cooled InSb (Cincinnati Electronics) as a detector and an air-dried sample without hydrogenation as a reference. In the region of interest, we did not observe any spurious absorptions related to the Si substrate, and loss of the intensity due to light scattering from the nanocrystals was insignificant. The absolute frequency of the FTIR was calibrated against the well-documented ro-vibrational transitions of atmospheric H2O near 3 μm and was determined to be accurate within 0.5 cm⁻¹. Spectral resolution of the spectrometer was set at 2 cm⁻¹ throughout the experiments.

In addition to the FTIR, a Raman image microscope (Renishaw) was used to characterize the diamond crystallites before and after the hydrogenation. The spectral resolution was 1 cm⁻¹, with the slit width of the micro Raman spectrometer set at 5 μm. The effect of the intensive hydrogenation at high temperatures was evident from the alteration of the characteristic Raman profiles25,30 of diamond and graphite at 1332 and 1580 cm⁻¹, respectively. Change of the lattice structure of the nanocrystals due to the hydrogenation was examined by a X-ray diffractometer looking at the characteristic diamond reflections at (111) and (400).30 The general morphology and particle size distribution of the crystallites were investigated using a scanning electron microscopy (SEM). From the SEM images, we determined that the diamond particles are irregular in shape, and their sizes are all smaller than 500 nm.

Results and Discussion

During the course of this experiment, we noticed that the spectral profiles of the CH, stretching motions on diamond surfaces depended strongly on how well the samples were prepared and hydrogenated. A systematic investigation focusing on the effects of hydrogenation temperature (T_h) and film thickness (T_f) was undertaken. Figure 1 shows three representative CH, stretch spectra taken at room temperature. The three samples were hydrogenated at temperatures of T_h = 750 and 1000 °C with film thicknesses of T_f = 1 and 8 μm. Two groups of broad absorptions, centered near 2840 and 2930 cm⁻¹ and similar to those of Ando et al.,24 were recorded at T_h < 1000 °C and T_f > 8 μm. However, at T_h = 1000 °C and T_f = 8 μm, we observed a dramatic sharpening of the absorption peaks. The sharpening reveals a three well-resolved features at 2835, 2921, and 2934 cm⁻¹ with undeconvoluted bandwidths of less than 6 cm⁻¹ (see Figure 1a,b). Further increase of the hydrogenation temperature to 1100 °C did not show any change. The spectrum, however, can be simplified by reducing the thickness of the sample for hydrogenation. As the film thickness was reduced from 8 to 1 μm, only the two bands at 2835 and 2921
IR Spectroscopy of CH₃ and CD₃

Figure 2. Spectrum of CH₃ stretch on a diamond nanocrystal film fully hydrogenated at 1000 °C. Thickness of the film is about 1 μm. The overlaid curve is a fit using three Gaussian functions as shown underneath. The feature centered at 2835.8 cm⁻¹ has an fwhm of 4.6 cm⁻¹. The fringes in the background, with peak separation of roughly 4 cm⁻¹, are due to etalon effects from the 0.3 mm thick Si(100) substrate.

The position of the most prominent peak agrees with the C–H stretch absorption on C(111)-1 × 1 measured by SFG to within 5 cm⁻¹.¹¹ The peak has a full width at half-maximum (fwhm, Γ) of 4.6 cm⁻¹ obtained by fitting to a Gaussian band shape. Deconvolution of the instrument resolution of 2 cm⁻¹ suggests Γᵣ ≈ 4 cm⁻¹. The bandwidth of 4 cm⁻¹ sets a lower limit for the vibrational relaxation lifetime of the CH₃ stretch on a diamond surface to be 10¹⁸ > 1 ps.

We emphasize that our present experimental approach and results differ from those of Ando et al.²⁴ in many ways. First, the hydrogenation conditions are considerably different between these two sets of experiments. Besides the hydrogenation temperature, the hydrogen pressure, flow rate, and microwave power used in this study are 2–7 times higher than theirs.²⁴ The intensive treatment of our samples should have ensured thorough hydrogenation and annealing of the synthetic diamond powders. Second, we have systematically investigated the influence of film thickness on hydrogenation. The thickness of the sample used for hydrogenation in this work is much less than theirs, thereby allowing hydrogenation and etching to be completed in 30 min. Third, in this experiment we used a direct absorption method, whereas they used diffuse reflection spectrometry (DRS). The DRS spectra are plotted in terms of the Kubelka–Munk function, which does not directly relate the intensities and bandwidths of the spectra to the spectroscopic properties of the adsorbate.²¹ We have attempted reploting their best spectrum obtained at 900 °C in a standard absorbance format and found that the resulting spectrum is similar to ours in Figure 1a. The dramatic sharpening of the features as seen in Figure 1a–1c was not found by these authors.

1. Hydrogenation. Diamond is the thermodynamically metastable form of carbon; it converts to graphite gradually at elevated temperatures.²² When taking Raman spectra before and after hydrogenation, we observed that formation of graphitic carbon occurred in all the samples hydrogenated from 750 to 1100 °C. A similar finding of the graphite scattering band at 1580 cm⁻¹ has been reported by Ando and co-workers.²⁶ It is highly unlikely that any of the sharp features in Figure 1b should be assigned to CH₃ on graphite since the sp² CH stretches have been reported¹⁹,²⁰ to resonate at frequencies higher than 3000 cm⁻¹. In addition, the powder X-ray diffraction pattern of the sample clearly showed the characteristic diamond (111) peak at 2θ = 44°.³⁰ The observations of the graphitic carbon indicate that the rate of graphite formation exceeds the rate of graphite etching at temperatures as low as 750 °C for diamond in a hydrogen plasma. The result is somewhat unexpected since the presence of atomic hydrogen has the effect of suppressing graphite formation.²⁴ Nevertheless, in this work we found that the graphite formation was not too extensive. In a simple test, the sample hydrogenated at 1000 °C was oxygenated in a furnace at 600 °C for 1 h. All the graphite scattering bands were extinguished, and only the diamond Raman peak at 1332 cm⁻¹ remained with a bandwidth of 2 cm⁻¹. We have also found that the rate of the graphite formation depends strongly on the rate of hydrogen flow. In a separate experiment, where a flow rate of 10 sccm/min was used, the sample had considerably more graphite, and the total band area of the CH₃ absorptions on the diamond surface was decreased by a factor of 4.

Figure 3 displays the infrared spectra of a typical CVD diamond film grown on a silicon substrate at 800 °C in our laboratory.²⁸ The overall breadth of the feature is more than 100 cm⁻¹, accompanied by a relatively sharp band at 2830 cm⁻¹. We note that the broad features observed at temperatures lower than 1000 °C in Figure 1 show many similarities to that found in the CVD film.²¹,²² From 750 to 1100 °C, the spectral features sharpened accordingly but decreased in their total absorption band areas. A possible explanation for this observation is that these broad features are associated with the stretches of CH₃ on defect diamond sites and/or on diamond-like residues which have been resistant to our hot acid treatment. Conceivably, the high-temperature hydrogenation process etched away these imperfect materials,³³ transformed them into graphitic carbon, and consequently reduced the integrated CH₃ infrared absorption intensities. An additional effect of the hydrogenation at high temperature is annealing. Annealing under appropriate conditions can improve the general morphology of crystallites, which has been demonstrated in other materials as well, such as halides and oxides.³⁴ For MgO in particular, sintering at 1073 K in the presence H₂O vapor yielded nanocrystals predominantly in cubic shape, which essentially minimized the number of edge, corner, and defect sites. It is now known in many semiconductors that smaller crystallites (with size less than 1 μm) have
measurements to verify the assignment and also to explore the experiment, we have performed systematic mixed isotope origin of the sharp features in Figure 1b. Figure 4 shows the features predominantly due to CH, on C(111).

Another interesting possibility of the simplification of the spectra in Figure 1 is that the hydrogenation at 1000 °C is selective. The thermal desorption of hydrogen and deuterium atoms on C(100) and (111) single crystal surfaces has been explored carefully by a number of authors.\textsuperscript{10,37,38} They found the temperature-programmed desorption (TPD) for C(100) and C(111) peaking at 980 and 1080 °C, respectively. The peak positions varied ±50°, depending on heating rates and also on the preparation of the crystal surfaces. At 1200 °C, the hydrogen atoms are completely desorbed, inducing a (2 × 1) reconstruction on both surfaces. In the extensive studies of thermal hydrogenation of diamond crystallites (with size smaller than 0.5 μm), Ando et al.\textsuperscript{24c} found two maxima with an intensity ratio of 1:3 at 950 and 1100 °C, respectively, in their TPD spectra. The positions of the two maxima match well with those on single crystal surfaces, indicating that the crystallites have many (100) and (111) faces exposed. The important implication conveyed by the TPD results is that selective hydrogenation or dehydrogenation is possible if the crystallites are hydrogenated at ≈1000°C. In the present experiment, the optimum temperature of the hydrogenation to obtain the sharpest infrared features is 1000 ± 100 °C, close to the expected value. The selection could have greatly simplified the spectrum and yielded absorption features predominantly due to CH, on C(111).

2. Band Assignment and Absorption Intensity. In a series of papers,\textsuperscript{34,25} Ando et al. assigned the broad doublet observed at 2840 and 2930 cm\textsuperscript{-1} to the symmetric and antisymmetric stretches of CH, (x = 2 or 3) on the diamond surface. In this experiment, we have performed systematic mixed isotope measurements to verify the assignment and also to explore the origin of the sharp features in Figure 1b. Figure 4 shows the mixed isotope spectra in the region of 3 μm as a function of the mole fraction (f\textsubscript{H}) of H\textsubscript{2} in H\textsubscript{2}/D\textsubscript{2} mixtures.

We argue that the features observed at 2840 and 2930 cm\textsuperscript{-1} cannot be assigned exclusively to the symmetric and antisymmetric stretches of adsorbed CH\textsubscript{2} or CH\textsubscript{3} as postulated by Ando, Kamo, Sato, and co-workers.\textsuperscript{24} If the doublet at 2840 and 2930 cm\textsuperscript{-1} is indeed a result of interbond coupling which yields symmetric and antisymmetric normal mode vibrations,\textsuperscript{25,40} a new band representing the decoupled C–H stretch should emerge in the middle of the doublet when isotopes are mixed in. However, in the studies of H–D exchange kinetics,\textsuperscript{26} they did not observe this effect. Since we also fail to make this observation, the two groups of absorptions must come from different origins and most likely they originate from CH\textsubscript{2} on different adsorption sites. This conclusion is also supported by the large variation of the absorptions, particularly at 2835 cm\textsuperscript{-1}, with hydrogenation temperature and film thickness as shown in Figure 1. We believe that the sharp single feature at 2835 cm\textsuperscript{-1} is not due to CH on C(100)-2 × 1; for example consider the selective hydrogenation at 1000 °C mainly on C(111) as discussed in the previous section. The monohydride C(100)-2 × 1:H with one hydrogen per surface carbon atom has been predicted by \textit{ab initio} calculations\textsuperscript{8} to be more thermodynamically stable than other phases, such as C(111)-1 × 1:H. The (2 × 1) phase, involving the formation of dimer bonds between pairs of surface carbon atoms, has a structure markedly different from that of C(111)-1 × 1:H. It would be an unusual coincidence for the CH stretch on C(100)-2 × 1 to resonate at the same frequency (≈2830 cm\textsuperscript{-1}) as CH on C(111)-1 × 1.\textsuperscript{11}

On the basis of the agreement in frequency and bandwidth with that of the single crystal experiment using SFG,\textsuperscript{1} we assign the singlet at 2835.5 cm\textsuperscript{-1} to CH on a well-annealed C(111)-1 × 1 surface. We tentatively attribute the weak features at higher frequencies to CH\textsubscript{2} chemisorbed on edges and corners of the C(111) nanocrystals. It is likely that the weak feature at 2921 cm\textsuperscript{-1} in Figure 1c is due to the CH stretch on C(100) since its location is consistent with that observed by HREELS on epitaxially grown C(100).\textsuperscript{13} It is also possible that the small doublet at 2922 and 2935 cm\textsuperscript{-1} in Figure 1b is due to CH\textsubscript{2} on C(100) since the splitting of 13 cm\textsuperscript{-1} is comparable in magnitude to that measured for SiH\textsubscript{2} on Si(100).\textsuperscript{41} D'Evelyn and co-workers\textsuperscript{14,15} have carefully discussed the chemistry of hydrogen on C(100) and concluded that the presence of a full coverage of CH\textsubscript{2} on C(100)-1 × 1 is highly improbable because of extreme steric repulsion between neighboring hydrogen atoms.

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*Uncertainties in the measurement of band center ν and width Γ are ±0.5 cm\textsuperscript{-1} and ±10% for CH, and ±10 cm\textsuperscript{-1} and ±20% for CD.; f\textsubscript{H} is the mole fraction of H\textsubscript{2} in the H\textsubscript{2}/D\textsubscript{2} mixtures.
In order to have CH$_2$ on C(100), the surface has to reconstruct to a structure of (3 $\times$ 1):1.33H.

In Table 1, we list the precisely measured band centers and bandwidths obtained from the isotope substitution experiments for $f_0 = 0.0-1.0$ and their tentative assignments. The regular shift of band origins and increase of bandwidths due to isotope mixing have been observed in other surface systems as well,$^2$$^4$$^3$ and they have been understood to be a result of intermolecular electrostatic interactions between neighboring adsorbates. The interactions, to the first-order approximation, are of dipolar type, and therefore the red shifts provide valuable information about the size of the dipole moment of the adsorbate. The shift also depends upon surface coverage. In the present work, saturation of the diamond surfaces should have been achieved by the intense hydrogenation treatment such that each surface carbon is covered by one hydrogen atom. The regular red shifts in band centers of Figure 4 should represent dynamic shifts that are due to transition dipole couplings between adsorbates.$^3$$^4$$^4$

A complete theoretical analysis of the isotopic substitution effect has been given by Persson and Ryberg$^5$ for vertical dipoles, like CO, adsorbed on metal surfaces. The theory can be applied here since the SFG measurement has demonstrated that the CH bond is aligned perpendicularly on the C(111)-1 $\times$ 1 surface. For H and D on diamond, the transition dipoles of CH$_3$ and CD$_3$ are much smaller than that of CO on metals. In addition, the coupling between CH and CD vibrations is negligible since the stretching frequencies of the two isotopes are separated by more than 700 cm$^{-1}$. We thus simplify the Persson-Ryberg theory and relate resonance frequency ($\nu$) to mole fraction ($f$) as$^5$$^6$

$$(\nu/\nu_0)^2 \approx 1 + f_\alpha U(1 + f_\alpha U)$$  (1)

where $\nu_0$ is the resonance of a single isolated isotope in the monolayer, and $\alpha$ and $\alpha_\alpha$ are vibrational and electronic polarizabilities of the adsorbate, respectively. The parameter $U$ is defined as $a^{-3/3}$, where $a$ is the unit cell constant of the two-dimensional lattice of interest and $S = \sum (r_{ij})^{-3}$ is a lattice sum written in terms of the dimensionless separation distance ($r_{ij}$) of molecules $i$ and $j$, given in integral value of $a$.

The diamond C(111)-1 $\times$ 1 surface is hexagonally structured with a lattice constant of $a = 2.52 \pm 0.02$ Å.$^7$ The sum for such a two-dimensional lattice has been evaluated precisely to be $S = 11.0342.47$ Fitting of the four data sets in Table 1 to eq 1 reveals that the electronic polarizability of the CH is too small to be determined meaningfully. Assuming $\alpha_\alpha \approx 0$, we obtain $\alpha \approx 0.012$ Å$^3$. As has been shown elsewhere,$^8$ the vibrational polarizability is related to the integrated absorption cross section of the adsorbate along its molecular axis by $\sigma_\nu = 4\pi\alpha \nu_\nu^3$. This yields $\sigma_\nu \approx 1.2 \times 10^{-17}$ cm/molecule for the stretching motion of CH on the diamond C(111)-1 $\times$ 1 surface. The cross section of $\sigma_\nu \approx 1.2 \times 10^{-17}$ cm/molecule is large for an atomic species chemisorbed on a dielectric surface; it is only a factor of 3 smaller than that of simple hydrocarbon molecules in the gas phase, such as HCN, C$_2$H$_2$, and CH$_4$.$^9$$^9$

The present analysis provides a crude estimate of the size of the transition dipole for CH on C(111)-1 $\times$ 1. It would be more desirable to investigate the band shifts, line broadening, and other effects in detail on the surfaces of single crystals. These effects, however, are small and may be undetectable using HREELs. Attempts to observe CH$_2$ on C(100) and C(111) by direct infrared absorption spectroscopy, to the best of our knowledge, have not yet been successful. Use of FTIR-ATR appears to be a promising method; however, it has been demonstrated by D'Evelyn and co-workers$^1$$^4$$^5$ that self-absorption of the diamond substrate essentially makes the infrared

Figure 5. Comparison of the stretch profiles of CH$_3$ and CD$_3$ on diamond crystallites (a) hydrogenated and (b) deuterated in pure H$_2$ or D$_2$ at 1000 °C. Thickness of the sample is about 4 μm. The fringes in the background of (b), with peak separation of roughly 4 cm$^{-1}$, are due to etalon effects from the 0.3 mm thick Si(100) substrate.

region from 1600 to 2800 cm$^{-1}$ opaque and does not allow spectra of either CH$_3$ or CD$_3$ stretches to be obtained easily. The question of how to unambiguously identify the CH$_3$ and CD$_3$ in various forms on different faces of a single crystal diamond remains mostly unanswered.

3. Lifetime Broadening. In Figure 4, we did not show the spectra in the region of CD$_3$ stretching because most of the bands are too broad to be observed. As shown in Figure 5a, at $f_0 = 1.0$, the features at 2150 cm$^{-1}$ are immensely broadened with an FWHM of more than 100 cm$^{-1}$ for the entire absorption manifold. The two partially resolved peaks at $\approx 2130$ and $\approx 2190$ cm$^{-1}$ correspond to the weak broad satellites at $\approx 2860$ and $\approx 2930$ cm$^{-1}$ of the CH$_3$, (see Figure 5a). They are more closely spaced, and the D/H frequency ratio 2190/2930 $\approx 2130/2860 = 0.74$ is in accord with an isotope shift.$^9$$^9$ The most dramatic feature of the spectra is the breadth of the absorptions, which are nearly 10-fold wider than that of the CH$_3$ stretch. In particular, the absorption corresponding to 2835 cm$^{-1}$ of the C–H is incorporated completely in the 100 cm$^{-1}$ wide manifold. Assuming that the ratios of the frequency shifts are identical for all the features, we estimate that the unobserved absorption should be located at $\approx 2110$ cm$^{-1}$. The value is close to 2113 cm$^{-1}$ measured by HREELS for CD$_3$ on an epitaxially grown C(111) surface.$^5$ The CD/C(111) band is unobservable here because of severe band broadening, which decreases the intensity of the sharp singlet relatively more than other bands.

The severe band broadening has also been observed by Ando et al.$^8$ in their isotope exchange experiment, but no interpretations were given. Estimation of the broadening can be made by deconvoluting the band with three Lorentzian functions; however, the deconvolution is too arbitrary since there are many possible ways of fitting the nearly structureless absorption manifold. We therefore provide an estimate by utilizing the bands that are partially resolved at 2835 and 2930 cm$^{-1}$ for CH$_3$ and the corresponding features at 2110 and 2190 cm$^{-1}$ for CD$_3$. In Figure 5a, the relative peak intensity of the two bands at 2835 and 2930 cm$^{-1}$ is 7:1, whereas it is about 1:1 in Figure
The difference reveals a bandwidth of $\Gamma_0 \approx 30$ cm$^{-1}$ for the CD stretch on C(111)-1 $\times$ 1 at 2110 cm$^{-1}$. The band broadening of 30 cm$^{-1}$ cannot be solely a result of heterogeneity in the adsorbate transition frequency (in cm$^{-1}$), $\epsilon = (n + i\kappa)^2$ is the complex dielectric constant, $n$ is the refractive index, and $\kappa$ is the extinction coefficient of the diamond crystal. For a horizontal dipole, the ratio is reduced by a factor of 2. Calculation of the nonradiative relaxation time using this formula is difficult since the static molecule-surface distance $D$ is hard to define. The theory is useful, however, because it provides a first estimation of the relative relaxation lifetimes of CH$_2$ versus CD$_2$ on the surface. To estimate $\tau_{\text{HD}}$, we note that the radiative rate for a free molecule in space is proportional to $v^2\mu^2$, where $\mu$ is the oscillating dipole between two transition states. Since $n$ is insensitive to $v$, $n \gg \kappa$, and $D$ is nearly identical for both isotopes, for dipoles aligned either vertically or horizontally on the surface, we have

$$k_{\text{rad}}(H)/k_{\text{rad}}(D) \approx k_{\text{rad}}^2/k_{\text{rad}}^2$$

For molecular vibrations, the ratio of the transition dipoles of the two isotopes is $\mu_2/\mu_1 \approx (m_2/m_1)^{1/2}$, where $m_1$ and $m_2$ are the reduced masses of molecules $a$ and $b$, respectively. In the regions of 3 and 5 $\mu$m, the optical extinction coefficients of diamond are $\kappa_D \approx 2 \times 10^{-5}$ and $\kappa_D \approx 4 \times 10^{-4}$, respectively, and thus we have $k_{\text{rad}}(H)/k_{\text{rad}}(D) \approx 0.07$. Since we have found $k_{\text{rad}}(D) = \tau_{\text{HD}}^{-1} \approx 5 \times 10^2$ s$^{-1}$, the vibrational relaxation lifetime of the CH$_2$ stretch on the diamond surface is estimated to be $\tau_{\text{HD}} \approx 3$ ps. The Fourier transform line width of the lifetime is nearly 2 cm$^{-1}$, which is a factor of 2 smaller than what we observed in Figure 2.

The relaxation time of 3 ps for the chemisorbed CH$_2$ is much shorter than that observed for SiH$_2$ on a Si(111) single crystal surface, where a lifetime of 0.9 ns was found. The exceedingly rapid relaxation is quite unusual on dielectric crystal surfaces but can be immediately understood when inspecting the optical transitions of the diamond substrate. In the wavelength range 2-10 $\mu$m, diamond has a unique infrared absorption (with bandwidth of $\approx 400$ cm$^{-1}$), which has been attributed to the second-order optical lattice vibrations. The absorption, peaking at 5 $\mu$m, is infrared-allowed, and thus the lattice vibrations can couple efficiently with the CD$_2$ stretching motions resonant in the same region. The short lifetime is a direct outcome of the resonant coupling of the adsorbate with the second-order phonons of the substrate through transition dipoles. The match of the resonances at 3 $\mu$m is estimated to be a factor of 10 poorer at 5 $\mu$m. The mismatch accounts for the large difference in the bandwidths of the two isotopic adsorbates. We note that the near-resonant coupling can cause a large frequency shift as well. As a result of Fermi resonance, the frequencies of CH$_2$ and CD$_2$ can be shifted to different extents by the diamond phonons. The deviation of the frequency ratio, 2113/2835 $= 0.745$ as discussed earlier, from the reduced mass ratio, $\sqrt{2} = 0.707$, could be one of the consequences of the Fermi resonance effect.

The present treatment can explain some features of the bands observed by Struck and D'Evelyn, who determined widths of $\approx 20$ cm$^{-1}$ for both CD (at 901 cm$^{-1}$) and CD$_2$ (at 1125 cm$^{-1}$) bands on a C(100) single crystal. At the region of bending, diamond has an absorption strength of $K_D \approx 2 \times 10^{-3}$. In the gas phase, the bending modes of carbon hydrides usually have integrated absorption cross sections, $\sigma$, as large as the stretches. Since $\sigma$ is proportional to $\mu^2$, by taking into account the frequency difference of the two vibrations, the oscillator strength of the stretch is calculated to be nearly 2 times smaller. Assuming a horizontal dipole, we estimate from eqs 2 and 3 a lifetime-broadened bandwidth of 2 cm$^{-1}$. The estimate is a factor of 10 smaller than the observed value, presumably because the effects of surface heterogeneities have not yet been taken into account.

While the classical electromagnetic theory predicts the radiationless energy transfer rate of the vibrationally excited molecules on diamond reasonably well, it could be oversimplified. There are at least two possible competing channels for the vibrational relaxation. As has been pointed out by Sun et al., the channel via the near-resonant coupling between the stretch and the two bends could also be responsible for a large portion of the energy transfer process. Although the channel involves indirect coupling, it could yield a relaxation rate comparable to that of the direct coupling. Mapping out completely the details of the vibrational energy partition in these two channels will be interesting. During the course of their calculations, Sun et al. found that the calculated relaxation rates are extremely sensitive to the frequency mismatch of the stretch and the bends. The relaxation rate could be enhanced by more than 2 orders of magnitude (lifetime dropped from 60 to 0.3 ps) if the mismatch was reduced by 110 cm$^{-1}$. The large variation reflects the nature of the near-resonant coupling in this unique surface system.

**Conclusion**

We have demonstrated in this paper that annealing of the diamond nanocrystals at high temperatures without extensive
graphite formation can be accomplished in a high-density hydrogen plasma. The annealing, along with selective hydrogenation at 1000 °C, dramatically sharpens the infrared absorption features of the CH stretches on diamond surfaces and reveals the rapid relaxation of the vibrationally excited surface hydrides. We have provided experimental evidence that indicates, although indirectly, that the vibrational relaxation of CH stretches on diamond might occur within several picoseconds. It is striking to see that the vibrational features on nanometer-sized crystals can have bandwidths of less than 5 cm⁻¹, and furthermore, they are close to Fourier-transform limit.

In the present experiment, the thickness of the thin diamond film commonly used is 1 μm. There are thus only about 10 layers of crystallites stacked randomly on the Si substrate for interrogation, since the nanocrystals have an average diameter of 0.1 μm. This is approaching single crystal conditions. The estimated vibrational polarizability αv ≈ 0.012 Å³, together with the excellent signal-to-noise ratio (limited by the magnitude of the fringes) of the results in Figure 2, suggests that observations of the CH stretching motions on single crystals of diamond are practical.

Note Added in Proof. We learned that Shen and co-workers have recently performed a complete study of the SFG spectroscopy on C(111)-1×1 and determined the band centers to be located at 2838 and 2115 cm⁻¹ with an fwhm of 7 and 40 cm⁻¹ for surface CH and CD stretches, respectively (Chin, R. P.; Huang, J. Y.; Shen, Y. R.; Chuang, T. J.; Seki, H., submitted to Phys. Rev. B). The authors have also directly measured the vibrational relaxation time of the CH stretch on C(111)-1×1 using SFG and found that the relaxation time was comparable to their picosecond laser pulse width. Deconvolution of the measured time profile gave τ1 ≈ 3 ps (Chin, R. P.; Blase, X.; Shen, Y. R.; Louie, S. G., to be published). Compared to this value, our estimate of τ1 ≈ 3 ps is off by a factor of 6.

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References and Notes

(2) Yarbrough, W. A.; Messier, P. Science 1989, 247, 688.
(4) An entire journal, Diamond and Related Materials, has been devoted to reporting the research and development of diamond thin film technology.
Another possible consequence of the Fermi resonance is the severe band broadening observed in the CD, stretch region. The resonance may give rise to many additional broad features that were not seen in the reference spectrum taken without deuterium atoms on the surface. However, in the region of 1950–2250 cm$^{-1}$, the diamond two-phonon absorption shows little structure, with $\kappa$ varying from $3 \times 10^{-4}$ to $5 \times 10^{-4}$. The completely different absorption patterns in Figure 5a,b suggest that this consequence of the Fermi resonance is low.