

Vibration of H Atomic Chains on Ni(110) Measured by Scanning Tunneling Microscope Light Emission Spectroscopy

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We have measured the visible light spectrum emitted by hydrogen atoms adsorbed on an Ni(110) surface, excited by the tunneling current from the scanning tunneling microscope. The spectrum contains periodic fine structures, whose period corresponds to the vertical vibrational energy of the adsorbed H atom. This energy showed the expected isotope shift when H was replaced by deuterium, and further it depended on the H-atom chain length.

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Single molecule vibrational spectroscopy using the scanning tunneling microscope (STM) is extremely powerful, because of the atomic scale spatial resolution afforded by STM [1]. Ho and his collaborators have published a series of work in which they have detected molecular vibrations of individual molecules with atomic scale spatial resolution [2]. They detected structures in the tunneling current vs voltage curve and generated the image of vibrating molecules. More recently his group demonstrated that they can obtain single molecule vibrational spectra [3] through STM light emission spectroscopy. In this method one first obtains a STM image of the sample surface, finds a target of interest (i.e., single molecule), and fixes the STM tip over it. Then one measures the spectrum of visible light emitted from the sample excited by the tunneling current [4]. Qui *et al.* observed the vibrational energies of a single molecule of ZnEtiol on AlNi(110) as fine structures in the STM light emission spectra [3]. According to their explanation, the emission occurs through the transitions of injected electrons between the vibronic states of the adsorbed molecule. This mechanism requires the accessibility of vibronic states to the tunneling electrons; i.e., the molecule has to appear in the STM image.

In this Letter we report the STM light emission spectra of the hydrogen (H) atom on Ni(110). Our new finding is that in spite of the fact that the H atom has no electronic states in the energy range accessible to the tunneling electrons (i.e., the H atom is invisible in the STM image [5]), the vibrational energy of H appears in the STM light emission spectra as fine structures. This result is very interesting, because it shows that single molecule vibrational spectroscopy by STM light emission is possible even in the absence of electronic states that produce structures in the STM image. In the present work we were able to distinguish the vibrational energy difference for different chain lengths of H atoms. This is an interesting effect that deserves further study.

The sample was single crystal Ni with the (110) surface. Its surface was cleaned by repeated cycles of Ar ion

sputtering and annealing until no contamination was detected by Auger electron spectroscopy and x-ray photoemission spectroscopy. The (1×1) surface structure of the clean Ni(110) surface was confirmed by low-energy electron diffraction (LEED). After this cleaning process, the surface was exposed to 0.6 Langmuir (L) of molecular hydrogen at room temperature. The adsorption structure of H on Ni(110) varies depending on the coverage of H and the temperature of the substrate [6]. The Ni(110)-H surface prepared at room temperature is referred to as streaky (1×2) and denoted by ST (1×2) , because its LEED pattern changes to streaky (1×2) after the exposure to molecular hydrogen [7].

The sample was transferred to a STM, which was cooled down to 80 K for light emission measurements. The tip was made of tungsten. The STM light emission spectra were measured for a sample bias voltage of $V_0 = +2.3$ V and a tunneling current of $I_0 = 2$ nA in a constant current mode. The optical detection system has already been reported [8].

Figure 1 shows a STM image of the sample. This image is consistent with the previously reported images of the ST (1×2) surface [5]. One can see rows of dark and light spots along the $[1\bar{1}0]$ direction on the terrace. The dark

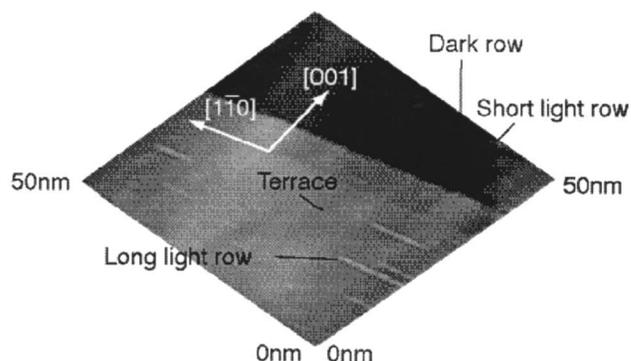


FIG. 1. STM image of the Ni(110) surface exposed to 0.6 L of molecular hydrogen.

rows are grooves with a monoatomic depth and width, created by an etching process induced by exposure to molecular hydrogen. The light rows are Ni adatoms on which H atoms are adsorbed. However, the H atoms themselves are not imaged according to the literature [5]. One can find the light rows with various lengths in the $[1\bar{1}0]$ direction in the STM image. We measured the STM light emission spectra from the light rows with a few atomic lengths (short light row) as well as those with a few tens of atomic lengths (long light row).

Figures 2(a) and 2(b) show the STM light emission spectra of the terrace and the long light row. Both spectra have the quantum cutoff [9,10] at $eV_0 = 2.3$ eV and extend towards the low-energy side. Here e is the electronic charge. To analyze the difference between these two spectra in detail, the ratio between the spectra of Figs. 2(b) and 2(a) was calculated as shown in Fig. 2(c). We see that the ratio spectrum consists of two components. One is the slowly varying component depicted by the dashed line and the other is the fine structure superimposed on the slow component [see Fig. 2(c)]. The slope of the dashed line is very small; i.e., the slowly varying component is approximately unity in the observed spectral range (1.5–2.3 eV). Hence we know that the spectra of the terrace and the light row have a common envelope. No structure

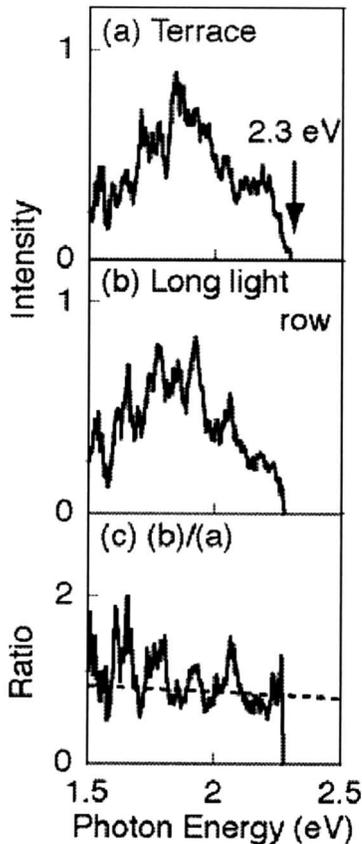


FIG. 2. STM light emission spectra of (a) the terrace and (b) the long light row. (c) is the ratio of (b) to (a).

corresponding to the fine structure is seen in the spectrum of the terrace [Fig. 2(a)]. Thus the fine structure in Fig. 2(c) is due to the spectrum of the light row.

The fine structure in Fig. 2(c) appears periodic. To determine the period, we performed Fourier transformation of the observed STM light emission spectra $S(E)$ according to

$$A(n) = \sum_{m=1}^{N+1} S\left(E_{\min} + \frac{E_{\max} - E_{\min}}{N}(m-1)\right) \times \exp\left(-2\pi i \frac{(n-1)(m-1)}{N}\right), \quad (1)$$

where E is the photon energy, $A(n)$ is the Fourier component of $S(E)$; $E_{\max} = 2.3$ eV is the quantum cutoff for the bias voltage ($V_0 = 2.3$ V) and $E_{\min} = 1.5$ eV corresponds to the low-energy detection limit of our optical system; $N + 1$ is the total channel number (1024) of the optical detector. m and n represent channel numbers of $S(E)$ and $A(n)$, respectively. Hereafter we call the spectrum $|A(n)|$ of the absolute value of the Fourier component “Fourier spectrum.”

Figure 3(a) shows the Fourier spectrum of a sinusoidal function with a period of 150 meV given by

$$S(E) = \sin\left(\frac{2\pi}{150 \text{ meV}}E\right). \quad (2)$$

Since the Fourier transformation of the sinusoidal function of Eq. (2) was performed in a finite range ($1.5 \leq E \leq 2.3$), it diverges towards $n = 1$. The periodicity in Eq. (2) produces the peak at channel number $n = 17$ in the Fourier spectrum. Hence if a spectrum $S(E)$ contains a component with a period of 150 meV, we will find a peak at $n = 17$ in the Fourier spectrum of $S(E)$. Conversely, if one finds a peak at channel n in the Fourier spectrum, the corresponding spectrum $S(E)$ contains a component with a period given by

$$150 \text{ meV} \times \frac{17-1}{n-1} = 150 \text{ meV} \times \frac{16}{n-1}. \quad (3)$$

Here we note that the origin of the Fourier spectrum is $n = 1$. The uncertainty ΔE of the period caused by the discreteness of n is estimated from

$$\Delta E = \pm \left(150 \text{ meV} \times \frac{16}{(n-1)^2}\right)^{1/2}. \quad (4)$$

Figures 3(b) and 3(c) are the Fourier spectra of the STM light emission spectra of the terrace [Fig. 2(a)] and the long light row [Fig. 2(b)], respectively. We do not see any noticeable peak in the Fourier spectrum of the terrace [i.e., in Fig. 3(b)] and the dark row (spectrum not shown), but a peak appears at $n = 18$ in Fig. 3(c). From Eq. (3) we see that this peak corresponds to a period of 141 meV with the uncertainty of $\Delta E = \pm 4.2$ meV. Hence we see that the periodic fine structure in the STM light emission

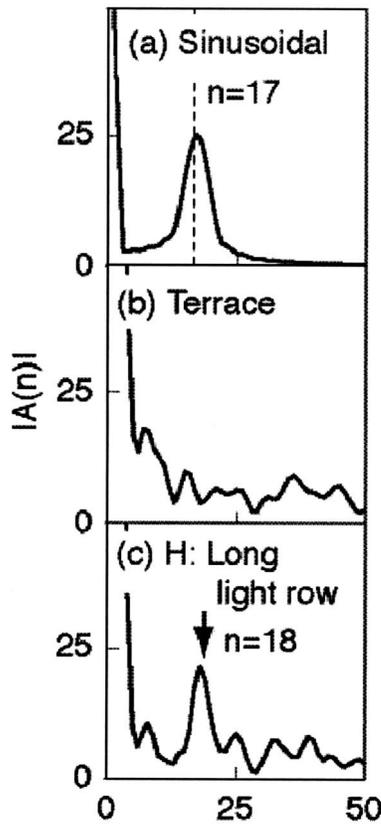


FIG. 3. (a) The Fourier spectrum of the sinusoidal function with a period of 150 meV. The peak at $n = 17$ is produced by the periodicity of the sinusoidal function. (b),(c) The Fourier spectra of STM light emissions from the terrace and the long light row, respectively. We can see the clear peak at $n = 18$ in (c).

spectrum of the long light row [Fig. 2(b)] has the period of $141 (\pm 4.2)$ meV. We note that the common envelope does not contribute to the Fourier peak at $n = 18$ because the Fourier spectrum of the terrace [Fig. 4(b)] has no peak at $n = 18$.

To identify the origin of this period, we measured the STM light emission spectra of the Ni(110) surface exposed to molecular deuterium (D) instead of H and obtained the corresponding Fourier spectra. The results are shown in Fig. 4 along with those for H. Figures 4(a) and 4(b) are the Fourier spectra of the long light row for H and D, respectively. Figure 4(a) is a copy of Fig. 3(c). In Fig. 4(b), one sees a peak at $n = 24$, which corresponds to the period of $104 (\pm 2.3)$ meV. Figures 4(c) and 4(d) are the Fourier spectra of the short light row (see Fig. 1) for H and D, respectively. The periods deduced from these Fourier spectra are $133 (\pm 3.7)$ meV and $96 (\pm 1.9)$ meV for H and D, respectively. The ratios (H/D ratios) of the period for H to that for D are $141/104 = 1.36$ and $133/96 = 1.39$ for the long and the short light rows, respectively. These ratios are close to the value $\sqrt{2} = 1.41$ expected for the H/D ratio of vibrational energies

of H and D. Thus we conclude that the periods from the Fourier spectra of the long and short light rows give the vibrational energies of the Ni-H atomic chain adsorbed on the Ni(110) surface.

We note that the vibrational energy depends on the chain length. The vibrational energies of the long light row (141 meV for H and 104 meV for D) are consistently higher than those of the short light row (133 meV for H and 96 meV for D) for both isotopes. Furthermore, the difference in the vibrational energy for D (8 meV) is significantly greater than the sum of the uncertainties ($1.9 + 2.3$ meV). Thus the vibrational energy dependence on the length of the light row must have a significant physical meaning. Such a microscopic (atomic scale) chain-length dependence of the vibrational energy could be measured only by this new technique and is not detectable by conventional macroscopic spectroscopy. This is a new development that we wish to emphasize in this Letter.

Let us compare the present results for H and D vibrational energies with the electron-energy-loss spectroscopy (EELS) results for the $ST(1 \times 2)$ surface. DiNardo *et al.* [11] and Jo *et al.* [12] reported the H vibrational energies at 76–80 meV, 117 meV, and 140 meV. The first two and the last energies were assigned to H vibrational motions parallel and perpendicular to the surface, respectively. We see that the mode observed in the present STM light emission spectra is the vibration of the H(D) atom polarized perpendicular to the surface and that the modes polarized parallel to the surface did not appear in our spectra. This is reasonable in view of the fact that the STM light emitted from a metal surface is predominantly

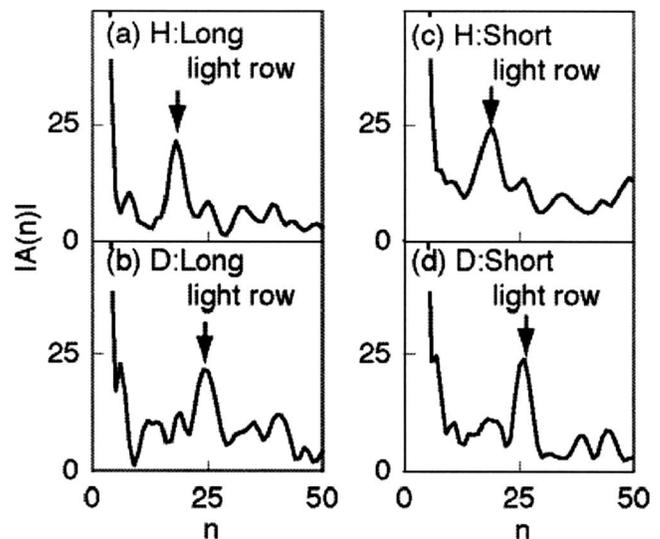


FIG. 4. (a),(c) The Fourier spectra of the STM light emissions from long and short light rows, respectively, for H. Corresponding to (a) and (c), (b) and (d) are obtained for D, respectively.

radiated by an oscillating dipole polarized perpendicular to the surface [13]. This is because an oscillating dipole polarized parallel to the surface is screened by the metal surface so that the light radiated from the parallel dipole becomes very weak relative to that from the perpendicular dipole. The oscillating dipole perpendicular to the surface couples strongly with the vibrational motion of the H atom in the same direction. Thus the STM light emission spectra are modulated by the H-atom vibration perpendicular to the surface.

As we have remarked earlier, it is interesting to find out that the vibrational energy depends on the length of the row (chain) of Ni-H(D) atoms. In the EELS measurements by DiNardo *et al.* [11] and Jo *et al.* [12], their ST(1 × 2) surface was prepared by raising the temperature of the sample with the (2 × 1) surface structure ($\theta = 1$ ML). Since their surface started from full coverage, it is reasonable to presume that this surface is predominantly covered by long chains of Ni-H, which appear as the long light rows in the STM image. Thus their vibrational energy (140 meV) agrees with our energy measured for the long light row (141 meV).

The present result that the vibrational energy of the Ni-H chain depends on its length suggests an interesting interpretation for the result reported by Nishijima *et al.* [14]. They measured the vibrational energy of the perpendicular mode at room temperature as they changed the hydrogen ambient pressure in the chamber. They found that the vibrational energy increased from 135 to 139 meV as the H pressure was increased. The increase in the ambient H pressure raises the surface coverage, which in turn means the increase of the number of long light rows (long Ni-H chains). Thus they must have observed the same vibrational energy dependence on the Ni-H-chain length that we found from our microscopic measurements. We believe that their energy range of 135–139 meV is caused by the distribution in the Ni-H chain lengths in their sample. This energy range corresponds to the difference in the vibrational energies of the long and short chains (133–141 meV) measured in the present work.

Next let us consider the isotope shift of the vibrational energy due to the replacement of H by D. The isotope shift has been reported only for the (2 × 1) and the (1 × 2) surfaces [15]. [The latter surface is seen at substrate temperatures below 150 K for $\theta = 1.5$ ML and is different from the ST(1 × 2) surface.] The H/D ratios of vibrational energies range from 1.25 to 1.43 depending on the modes. While no corresponding value for the ST(1 × 2) surface has been reported, the H/D ratios of the periods (1.36 and 1.39 for the long and the short light rows, respectively) are consistent with the H/D ratios of the vibrational energies. Thus we confirm that we have indeed measured the energy of the vibrational motion of the

H atom perpendicular to the surface from the STM light emission spectra.

In conclusion, we have measured the STM light emission spectra of the Ni(110)-ST(1 × 2)-H(D) surface. When the STM tip was located over the Ni adatom on which the H(D) atom is adsorbed, periodic fine structures were observed in the STM light emission spectra. The period of the fine structures agreed well with the vibrational energy of the H(D) atom on the Ni(110) surface. Furthermore, the period showed the expected isotope shift when H was replaced by D. Thus we conclude that the vibrational energy of the H atom on the Ni(110) surface can be determined from the STM light emission spectra. The most interesting finding is that the vibrational mode energy depends on the length of the Ni-H(D) chain. To understand the physics of this result we need a detailed theoretical analysis that takes into account the long-range interactions among the H(D) atoms in the chain.

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