Zero-Point Vibration of Hydrogen Adsorbed on Si and Pt Surfaces

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Hydrogen atoms adsorbed on Si(111) and Pt(111) were investigated by nuclear reaction analysis (NRA) using ^{1}H(^{15}N, $\alpha\gamma$)^{12}C. From measurements of the NRA spectrum at normal and tilted ion incidences the zero-point vibrational energies of H on Si(111) in the perpendicular and parallel directions were found to be 123.4 ± 4.6 and 44.6 ± 6.2 meV, respectively, which are consistent with harmonic potentials. The zero-point energies obtained for Pt(111)-H were 80.8 ± 3.9 and 62.1 ± 6.0 meV for perpendicular and parallel directions, respectively. These results indicate that the stretching mode is harmonic, while the bending mode is strongly anharmonic.

The interaction of hydrogen with solid surfaces has been a subject of extensive study in the past decades because it encompasses fundamental concepts of adsorption, vibration, and diffusion on surfaces. Because of its light mass, quantum effects dominate the behavior of the H atom in many cases, the most familiar phenomenon being the zero-point vibrational motion giving rise to isotope effects in dynamical processes.

In the present paper, we report first direct measurements of the zero-point vibration of H adsorbed on solid surfaces. In conventional spectroscopic techniques probing surface vibrational modes such as high-resolution electron energy loss spectroscopy (HREELS) and reflection-absorption infrared spectroscopy (RAIRS), vibrational excitation from the ground to the first-excited state is measured. In nuclear reaction analysis (NRA) using ^{1}H(^{15}N, $\alpha\gamma$)^{12}C, on the other hand, it is found that the spectral width is considerably broadened due to the momentum uncertainty originating from the zero-point vibrational motion of adsorbed H [1–4]. If H atoms are present only on the surface occupying specific adsorption sites, analysis of the NRA spectrum allows for direct measurements of the zero-point vibrational energy of H. Here we present detailed analysis of NRA spectra taken at different ion incidence angles for H on Si(111) and Pt(111) surfaces.

The Si(111)-(1 × 1)–H surface has been extensively studied both experimentally [5–8] and theoretically [9–11], and its vibrational nature has been well characterized: there are two normal modes corresponding to the stretching and bending motion of H on the surface with excitation energies of 258 and 78 meV, respectively [5–7]. Adsorption of H on Pt(111) was also studied by a variety of techniques, and H is believed to occupy the fcc threefold hollow site of Pt(111) with vibrational excitation energies of 153 and 68 meV [12–14].

In order to describe the adsorption state of H on metallic surfaces, in contrast to covalent materials like Si, a delocalized picture has been proposed [15–17]. Previous HREELS studies showed a broadening of the H-related vibrational band suggesting delocalization of the vibration-

ally excited ($\nu = 1$) state [18–21]. Furthermore, a recent theoretical study has shown that H in the vibrational ground state could be delocalized on Pt(111) to some extent [22]. Nevertheless, characteristics of the vibrational ground state are not yet clarified experimentally, because the features of both $\nu = 0$ and $\nu = 1$ states are involved in the HREELS spectrum. On the basis of the uncertainty principle, delocalization of H in real space is expected to reduce the momentum uncertainty leading to a decrease of the zero-point vibrational energy. In this Letter, we report that the zero-point vibration of H on a covalent substrate of Si(111) is quite harmonic in both perpendicular and parallel directions. On a metallic surface of Pt(111), on the other hand, the perpendicular motion is almost harmonic, while the parallel motion seems to be strongly anharmonic.

The adsorbed hydrogen was examined by the ^{1}H(^{15}N, $\alpha\gamma$)^{12}C nuclear reaction in an ultrahigh vacuum (UHV) chamber. The ^{15}N^{2+} ion beam at an energy of 6.385 MeV was monochromatized with an energy analyzer of the double-focused magnetic-sector type with an energy dispersion of 2540 mm. Both entrance and exit slit widths of the energy analyzer were carefully measured and set to 1.2 mm. The magnetic field of the analyzer was stabilized within 10^{-5} with aid of a feedback system using the proton NMR signal. The achieved energy width of the incident ion beam at 6.385 MeV is described by a triangular-shaped function with a full width at half maximum (FWHM) of 3.0 keV as shown by a dashed curve in Fig. 1.

Assuming that all hydrogen atoms are in the vibrationally ground state, the momentum uncertainty originating from the zero-point vibration broadens the NRA spectrum to a Gaussian form, $A_0 \exp[-(E - E_R)^2/\sigma_\nu^2]$. Its width σ_ν is described as follows:

$$\sigma_\nu = 2\sqrt{\frac{M_B E_{\mathrm{res}}}{M_H}\left(\frac{\sin^2\theta}{E_x} + \frac{\cos^2\theta}{E_z}\right)^{-1}}, \qquad (1)$$

where M_B and M_H are the masses of the ^{15}N ion and H, E_{res} is the resonance energy of 6.385 MeV, θ is the
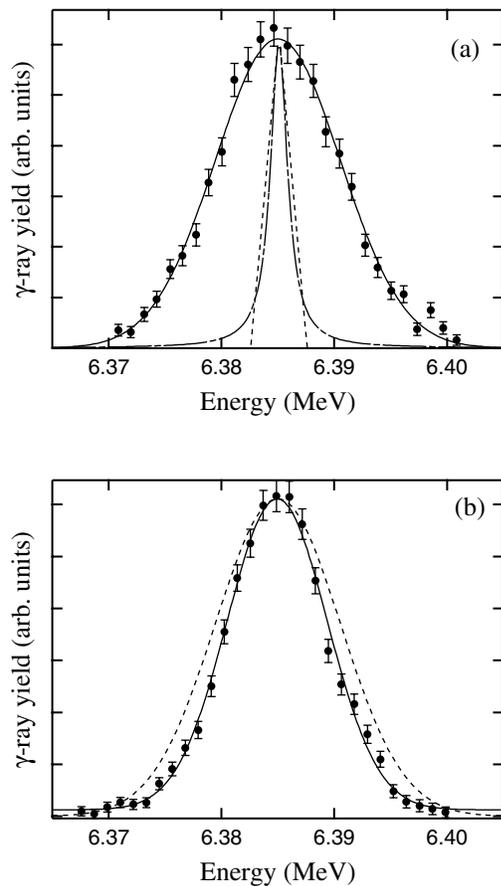
FIG. 1. Intensity profiles of the γ ray from the ^{1}H(^{15}N, $\alpha\gamma$)^{12}C nuclear reaction as a function of the incident ^{15}N beam energy taken for Si(111)-(1 $\times$ 1)–H at incidence angles of (a) 0° and (b) 40°. The solid curves are fits to a Gaussian form. The dashed and dash-dotted curves in (a) represent the energy width of the incident ^{15}N ion beam and the natural reaction width, respectively. The dashed curve in (b) is the fit curve at 0° shown in (a).

incidence angle of the ion beam with respect to the surface normal, and E_x and E_z are the zero-point vibrational energies in the directions parallel and normal to the surface, respectively [1]. A detailed analysis of the NRA spectral width therefore enables us to directly measure the real-space projection of the zero-point vibration of adsorbed H on the incident ion direction.

The Si(111)-(1 $\times$ 1)–H surface was prepared by an atomic H dose of 8000 L [23] at a sample temperature of 650 K [24] where the H coverage is saturated as measured by NRA. The sample was subsequently annealed at 670 K to remove trihydride species, which was confirmed by reduction of streaks in LEED [24]. The measurements were performed at a sample temperature of about 150 K where the population in the vibrationally excited states is 0.2% or smaller and the effect of such excited states on the NRA spectra can be neglected. For Pt(111), molecular H$_2$ of 10 L was initially dosed on the clean surface, and the NRA measurements were conducted at a sample temperature of 150–200 K. Since the H coverage was observed to

decrease under ion irradiation, the ambient pressure of H$_2$ was kept at $\sim$10^{-4} Pa to compensate for the H desorption from the surface, which maintained the H coverage constant at 1 ML. The NRA spectra were measured on two different samples under different beam tuning conditions, which were found to be essentially identical for both surfaces.

Figure 1 shows the γ-ray intensity profiles as a function of the incident ^{15}N beam energy (NRA spectrum) taken for Si(111)-(1 $\times$ 1)–H at ion incidence angles of 0° and 40° with respect to the surface normal. Also shown in Fig. 1(a) is a Lorentz function representing the natural reaction width of 1.8 keV [25,26]. The experimental data are considerably broader than both beam energy and natural reaction widths. The solid curves in Fig. 1 are fits of the data to a Gaussian function of the form of $A \exp[-(E - E_0)^2/\sigma^2]$, where E is the ion energy, and A, E_0, and σ are fit parameters. In all spectra shown in the present paper, the E_0 value representing the spectral position was the resonance energy of 6.385 MeV within the experimental accuracy. The spectral width (σ) obtained from the fit is 7.86 ± 0.12 keV for normal ion incidence and the χ^2 per degree of freedom was 0.95. After numerically deconvoluting the beam energy and reaction widths from the experimental curve in the normal incidence, the remaining width becomes 6.87 ± 0.13 keV. Following formula (1), the zero-point vibrational energy in the perpendicular direction is calculated to be 123.4 ± 4.6 meV. According to RAIRS and HREELS studies, the excitation energy of the stretching-vibrational mode ($E^s_{0\rightarrow1}$) of Si(111)-(1 $\times$ 1)–H is reported to be 258 meV, and this vibrational mode is well localized with a dispersion of $\sim$2.5 meV [5]. The zero-point energy of 123.4 meV is almost a half of the excitation energy, which indicates that the potential is quite harmonic. A previous study has shown that the anharmonic frequency shift of the $\nu = 2$ level ($E^s_{0\rightarrow1}E^s_{1\rightarrow2}$) is 11 meV [8]. The effect of the anharmonicity on the $\nu = 1$ level is expected to be smaller than that on the $\nu = 2$ level, which is consistent with the present study.

As seen in Fig. 1(b), the experimental data at an ion incidence angle of 40° are obviously narrower in width than that at 0°, the spectral width obtained from a fit to a Gaussian form being 6.29 ± 0.19 keV. After deconvolution of the beam energy and reaction widths from the fit curve in Fig. 1(b), the vibrational width is calculated to be 5.23 ± 0.20 keV corresponding to a zero-point energy of the bending mode $E_x = 44.6 \pm 6.2$ meV. According to a previous HREELS study, the vibrational excitation energy of the bending mode ($E^b_{0\rightarrow1}$) is reported to be 78 meV [6,7]. The present value of 44.6 meV is almost a half of the vibrational excitation energy implying that the potential is also harmonic in the parallel direction. The dispersion of the bending mode is also measured by HREELS and has been shown to be $\sim$2.5 meV [6,7]. The anharmonicity of the bending mode has not been measured experimentally to date, but it is theoretically shown to be smaller than that for the stretching mode [11], which is also consistent with

the present result. The parallel momentum of H originating from the zero-point energy might depend on the azimuthal direction. The experimental data, however, are symmetric with respect to the resonance energy suggesting that the zero-point motion is isotropic, which is in agreement with the theoretical calculation showing an isotropic potential in the surface parallel direction [11].

Figures 2(a) and 2(b) show the NRA spectra taken for Pt(111)-H at incidence angles of 0° and 45° from the surface normal direction ([001]) towards [1$\bar{1}$0], respectively. Both spectra reveal a maximum at the resonance energy with a slight tailing feature in the high-energy region. Although Pt does not absorb H in its bulk, this tailing observed in NRA spectra indicates that a small amount of H is present at deeper locations extending to ~5 nm from the surface. Note that this tailing feature was observed for both samples used in the present work. At this stage, we assume a certain concentration of H in the Pt bulk near the surface which yields a background in the spectra in the shape of a sigmoidal function, as clearly demonstrated for H/Pd(100) [27]. Comparing with a calibration standard, the H concentration is estimated to be 0.29% near the Pt(111) surface. The filled circles in Fig. 2 denote the data after subtraction of such sigmoidal curve as a background, and are well fitted to a Gaussian form as displayed by solid curves with χ^2 per degree of freedom of 0.58 and 0.73 for Figs. 2(a) and 2(b), respectively. The spectral widths for Figs. 2(a) and 2(b) obtained from the fits are 6.61 ± 0.10 and 6.25 ± 0.10 keV, respectively. The zero-point vibrational energies for the stretching mode (E_z) and the bending mode (E_x) are calculated to be 80.8 ± 3.9 and 62.1 ± 6.0 meV, respectively.

In previous HREELS studies, two prominent loss peaks are observed at 68 and 153 meV [12,13], and a RAIRS study has shown that the vibrational loss peak at 153 meV

FIG. 2. Intensity profiles of the γ ray from the ^{1}H(^{15}N, $\alpha\gamma$)^{12}C nuclear reaction as a function of the incident ^{15}N beam energy taken for Pt(111)-H at incidence angles of (a) 0° and (b) 45°. Open and filled circles denote the data before and after subtraction of the background with a form of a sigmoidal function. The solid curves are fits to a Gaussian form.

is dipole active assigning it to the Pt-H stretching vibrational mode [14]. This assignment is also confirmed by a theoretical calculation [28]. The zero-point vibrational energy in the surface normal direction deduced from the NRA spectrum is a half of the excitation energy of the stretching vibrational mode within our experimental accuracy, which strongly supports the idea of a harmonic oscillation for the stretching mode. On the other hand, the loss peak at 68 meV observed by HREELS is assigned to the bending vibrational mode of H on Pt(111). It is worth noting that the zero-point energy for the bending mode deduced from the NRA spectrum is comparable to this excitation energy. This result implies that the H potential in the direction parallel to the surface is anharmonic, deviating strongly from the harmonic potential even around the vibrationally ground state. The substrate phonon mode might influence the H velocity measured by NRA. The Pt bulk phonon dispersion curve shows the highest energy of ca. 25 meV at the X point [29]. Because of the mass difference, however, the velocity of the Pt atom is considerably smaller than that of H. Therefore, the effect of the Pt phonon on the H motion observed by NRA can be neglected. It should be noted that an additional loss peak is observed at 112 meV in HREELS spectra [12,13]. If this peak corresponded to the bending vibrational mode, the zero-point energy of 62.1 meV in the present study would be in good agreement with a harmonic potential. Considering that the lateral diffusion barrier reported in a helium atom scattering study is 68 ± 5 meV [30], however, the assignment of the loss peak at 112 meV to the bending mode does not seem to be probable. In the following, we discuss the lateral potential for H on Pt(111) assuming that the vibrational excitation energy of the bending mode is 68 meV.

In order to realize the anharmonic potential in the parallel direction, we tentatively analyze the data on the basis of a Morse potential in a first approximation. The energy levels, $E(v)$, are expressed as $\hbar\omega_0(v + 1/2)\{1 - \hbar\omega_0(v + 1/2)/4D\}$ where v, ω_0, and D are the vibrational quantum number, harmonic frequency, and dissociation energy, respectively. Substituting the energy levels of 61 and 129 meV for the $v = 0$ and 1 states, respectively, the dissociation energy D is calculated to be 136.3 meV. In the parallel motion, dissociation corresponds to diffusion to the neighboring site, and the diffusion barrier [$D - E(0)$] leads to 74.2 meV. If we choose a different potential with the form of $V(x) = -D/\cosh^2(x/a)$ instead of a Morse potential where x, D, and a are the lateral displacement, diffusion barrier, and nearest neighbor distance, a similar value of 68.6 meV for the diffusion barrier is obtained. The activation energy for surface diffusion of H on Pt(111) measured by the helium atom scattering method is 68 ± 5 meV [30], which is in good agreement with the present analysis. The adsorption site of H on Pt(111) is the fcc hollow site [31,32]. According to recent density functional calculations [33,34], the adsorption energy of
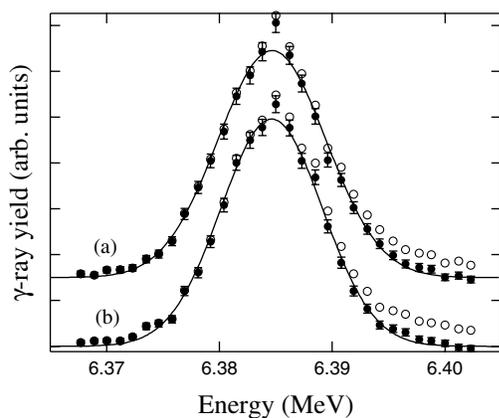
H on Pt(111) is reported to be similar for atop, bridge, hcp hollow, and fcc hollow sites suggesting that the potential is very flat. In fact, the diffusion barrier is 125 meV for the path from the fcc hollow to atop site, and 20–30 meV from fcc hollow to hcp hollow via the bridge site [34]. In the present study, the NRA spectrum was measured in the direction towards [$1\bar{1}0$], which corresponds to the direction between the atop and bridge from the fcc hollow site.

The wave function of H adsorbed on metallic surfaces is sometimes claimed to be delocalized over the surface in its vibrationally excited state. Considering the fact that the vibrational excitation energy of 68 meV is comparable with the barrier for surface diffusion, the $\nu = 1$ state is considered to be located near the potential maximum, where the tunneling between the neighboring sites is expected to be remarkably enhanced inducing delocalization of the $\nu = 1$ state. A recent theoretical investigation of H on Pt(111) has shown that the H atom could be delocalized in the vibrationally ground state in the low-coverage regime [22]. Nevertheless, the extent of the H wave function is calculated to be 0.026 nm from the zero-point energy of 61 meV on the basis of the harmonic analysis indicating strong localization at the adsorption site. The present measurements were performed at saturation coverage, while the theory treats the surface with a H coverage of 1/4. The H-H interaction at high coverages might strongly suppress the delocalization.

In conclusion, we have shown that the NRA technique enables us to directly probe the zero-point motion of H on surfaces. On Si(111), it was found that the zero-point energies of H are in good agreement with the idea of a harmonic oscillation in both parallel and perpendicular directions. On Pt(111), on the other hand, the perpendicular motion is almost harmonic while the parallel motion seems to be strongly anharmonic.

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