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Low-temperature observation of the softened C-H stretching vibrations of cyclohexane on Rh(111)

Takanori Koitaya, Atsushi Beniya, Kozo Mukai, Shinya Yoshimoto, and Jun Yoshinobu[*]
The Institute for Solid State Physics, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan

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The C-H stretching vibrations of cyclohexane on Rh(111) were investigated using infrared reflection absorption spectroscopy between 20 and 89 K. At 20 K, the softened C-H stretching band consists of several sharp peaks, ranging from 2500 to 2700 cm^{-1}. The wide-range distribution of the softened C-H stretching peaks results from inhomogeneity of adsorption environments. With increasing the substrate temperature, each softened C-H stretching peak becomes significantly broadened, but the normal C-H stretching peaks are little changed. These results indicate that the local interaction between the softened C-H species and the Rh(111) surface is sensitive to a thermally excited low-energy mode. The temperature-dependent broadening of a soft mode at low temperature is analyzed using a vibrational dephasing model, where the softened C-H stretching mode is anharmonically coupled with a thermally excited frustrated translation mode.

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Vibrational spectra of alkanes adsorbed on metal surfaces often show the presence of significantly redshifted and broadened C-H stretching bands.[1–14] These features were first observed by Demuth *et al.* using high-resolution electron energy loss spectroscopy in the cases of cyclohexane on Ni(111) and Pt(111),[1] and called as the “soft mode.” The soft mode has been attributed to the C-H bonds directly interacting with metal surfaces. Hence, elucidation of the softening mechanism is essential to understand the interaction between alkanes and metal surfaces, and the reaction processes of heterogeneous catalysis. Theoretical studies have shown that the origin of the redshift of softened C-H vibrations is the electronic interaction between the adsorbate and the substrate. The previous density-functional theory (DFT) calculations of polyethylene on metal surfaces have revealed that the redshift of C-H stretching vibrations is due to the hybridization between occupied substrate states and unoccupied molecular orbitals.[15] *Ab initio* cluster calculations have shown that electron donation from metal states to molecular Rydberg orbitals is important in the case of cyclohexane on the Cu(111) surface.[16,17] However, the mechanism of the line broadening has not been understood well, because detailed analysis of the soft mode was difficult due to their broad feature. Hostetler *et al.* suggested that the broadness of the soft mode was associated with an inhomogeneous broadening mechanism due to structural inhomogeneity of the $\mathrm{C\text{-}H\cdots M}$ interaction.[7] On the other hand, Witte *et al.* reported that the energy dissipation via the creation of electron-hole (e-h) pairs played a key role in the broadening of the soft mode in the case of octane on Ru(0001).[18]

In this Brief Report, we report on temperature-dependent infrared reflection adsorption spectroscopy (IRAS) of cyclohexane on Rh(111) at a low-temperature range from 20 to 89 K. Previous studies have reported that cyclohexane adsorbs on fcc (111) metal surfaces with the chair conformation whose carbon skeleton is nearly parallel to the surface.[3,5,6,12,19] The observed softened C-H stretching bands were assigned to three axial C-H stretching vibrations pointing to metal atoms. So far, the soft mode of cyclohexane was regarded as a very broad band.[2,4,5,8,12] For example, the C-H soft mode of cyclohexane on Cu(111) had a full width at half maximum (FWHM) of about 70 cm^{-1} at 95 K,[5] and a FWHM larger than 200 cm^{-1} was reported on Pt(111) at 95 K.[4] On the other hand, here we have found that the C-H soft band of cyclohexane on Rh(111) consists of sharp peaks at low temperature. Furthermore, the widths of these peaks strongly depend on the substrate temperature. These experimental results indicate that the broadening of an individual peak of the soft modes is caused by the vibrational dephasing through anharmonic coupling with a low-energy frustrated translation mode (an external mode of adsorbed molecules).

There are three main line-broadening mechanisms in vibration at surfaces:[20] (i) inhomogeneity of adsorption sites (inhomogeneous broadening), (ii) the vibrational energy dissipation through the excitation of e-h pairs and/or lattice phonons, and (iii) the vibrational phase relaxation (dephasing). The vibrational dephasing of adsorbed molecules has been studied in detail about CO on single crystal metal surfaces by IRAS and theoretical calculations.[21–25] These studies have revealed that the peak broadening of the CO stretching mode can be explained by the dephasing, which is triggered by anharmonic coupling with thermally excited low-energy external modes. However, little is known about vibrational dynamics of larger organic molecules including cyclohexane.

Details of the experimental apparatus and the sample preparation were described in our previous report.[26] Briefly, all experiments were carried out using an ultrahigh vacuum chamber. The base pressure was 6.0×10^{-11} Torr. Before each experiment, the Rh surface was cleaned by several cycles of Ne^{+} sputtering, annealing at 1050 K, followed by O_2 treatment, and flashing at 1300 K. Cyclohexane (Wako chemicals, $>99.5\%$ purity), which was degassed by several freeze-pump-thaw cycles, was introduced into the chamber through a pulse gas dosing system. While dosing of cyclohexane molecules, the Rh sample was heated at 160 K, where the multilayer is not formed, and the submonolayer molecules are sufficiently mobile on the surface. After a few minutes, the Rh sample was cooled to the measured temperature, and IR spectra were recorded with a 2 cm^{-1} resolution.

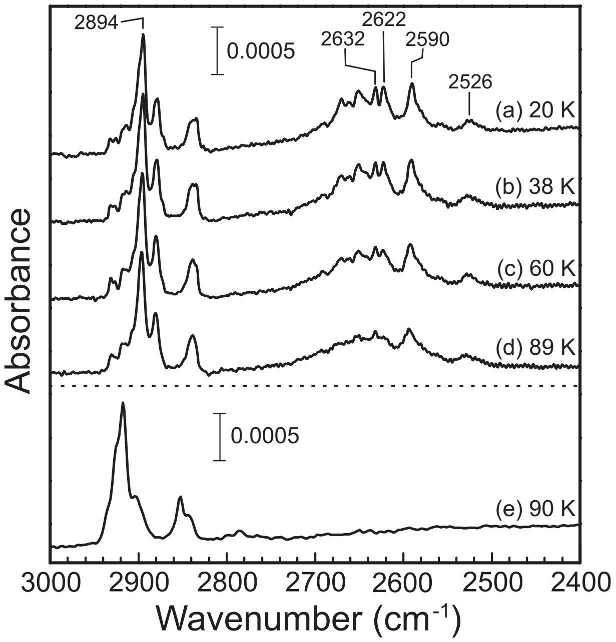

FIG. 1. (a)–(d) IRAS spectra of cyclohexane on Rh(111) at a near saturation coverage as a function of substrate temperature. (e) The IRAS spectrum of cyclohexane on H-saturated Rh(111) at 90 K.

An IRAS measurement of cyclohexane on the hydrogen saturated Rh(111) surface was also carried out at 90 K, and its spectrum was recorded at a resolution of 4 cm^{-1}.

Figure 1 shows a series of IRAS spectra of cyclohexane on Rh(111) at a near saturation coverage as a function of the substrate temperature. The C-H stretching bands were observed from 2400 to 3000 cm^{-1}. The softened C-H stretching band between 2800 and 2400 cm^{-1} consisted of several sharp peaks at 20 K. If cyclohexane has a single adsorption state on Rh(111), only three softened C-H peaks would be observed at most. The observed multiple peaks indicate that cyclohexane molecules take several different adsorption states on Rh(111). In fact, we observed sharp low-energy electron diffraction (LEED) spots, which showed that cyclohexane molecules formed an ordered but incommensurate phase on Rh(111) from 20 to 90 K. These experimental results show that there are several adsorption states, i.e., several axial C-H$\cdots$M environments. It has been elucidated that the soft C-H vibrations are quite sensitive to the distance from a metal surface.[15] Therefore, the inhomogeneity of the C-H$\cdots$M environments causes the wide-range distribution (about 250 cm^{-1}) of the soft modes of cyclohexane on the Rh(111) surface.

On the other hand, no soft mode was observed between 2700 and 2500 cm^{-1} in the IRAS spectrum of cyclohexane on the H-saturated Rh(111) surface [Fig. 1(e)]. Witte *et al.* performed near-edge x-ray absorption spectroscopy of octane on clean and H-saturated Ru(0001) surfaces, and they revealed that the presence of adsorbed H atoms prohibits the formation of octane-metal hybrid orbitals.[18] Hence, the difference in IRAS spectra is consistent with the previous theoretical study; the redshift of the softened C-H stretching peaks is caused by the electronic interaction between the adsorbate and the substrate.[15]

It should be noted that all peaks of the soft modes became considerably broadened with increasing temperature. At 89 K, the soft modes were so broad that individual peaks cannot be resolved. The present results clearly show that the energy dissipation through the e-h pair creation is not the main cause of the present peak broadening because it should be nearly independent of temperature.[20,27] In addition, the decay of a high-frequency mode such as C-H stretching vibrations requires multiphonon creation, which has a very small probability.[20,28] Thus, these energy dissipation processes are not the origin of the temperature-dependent broadening of the softened C-H modes. Furthermore, the possibility of the temperature-dependent inhomogeneous broadening, e.g., order-disorder phase transition, can be ruled out for the following reasons. LEED spots of a cyclohexane submonolayer at 90 K were as sharp as those measured at 20 K, suggesting that cyclohexane molecules retained the same adsorption phase over the measured temperature region. In addition, our scanning tunneling microscopy study at 100 K showed that the domain size of the ordered cyclohexane layer was sufficiently large, often more than 200 Å. This means that the most of cyclohexane molecules are located inside the domain. Thus, the present temperature-dependent broadening of the soft mode cannot be explained by lifetime or inhomogeneous broadening mechanisms. According to the previous He-atom scattering (HAS) experiments, the observed energies for frustrated translation modes of alkanes on metal surfaces are small enough to be thermally excited at temperature below 90 K.[29] Hence, the change in the soft modes at such a low-temperature region indicates that the temperature-dependent broadening of the individual softened C-H mode is triggered by thermal excitation of a low-energy frustrated mode of adsorbed cyclohexane.

In order to obtain further insight into the broadening mechanism of the soft modes at low temperature, we focus on the soft mode at 2590 cm^{-1} since this mode is well isolated from other soft modes. However, it should be noted that the peak at 2590 cm^{-1} is not a single peak, but overlaps with small peaks which are observed as an asymmetric tail of the 2590 cm^{-1} peak. Here, we approximately treat the 2590 cm^{-1} peak as a single peak since it is difficult to decompose the soft modes unambiguously. In the analysis, backgrounds of the normal-mode region (3000–2800 cm^{-1}) and the soft-mode region (2800–2450 cm^{-1}) were represented by straight lines. The validity of this approximation was checked by control experiments, which were carried out by the same procedure without dosing of cyclohexane molecules, and showed that backgrounds of two regions can be fitted well by straight lines. Figure 2(a) shows the FWHM of the soft mode at 2590 cm^{-1}, and a width of a normal mode at 2894 cm^{-1} is also presented for comparison. A FWHM (Γ) is given by $\Gamma=\sqrt{\Gamma_{\mathrm{exp}}^2-(\Delta E)^2}$, where ΔE is the spectrometer resolution and Γ_{exp} is a measured width, which is defined simply as the difference between the two values of the wavenumber at which the absorbance is equal to half of its maximum value. The linewidth of the soft mode starts to increase by about 40 K. On the other hand, the width of the normal mode was nearly constant over the observed temperature range. Thus, the soft C-H mode is more sensitive to

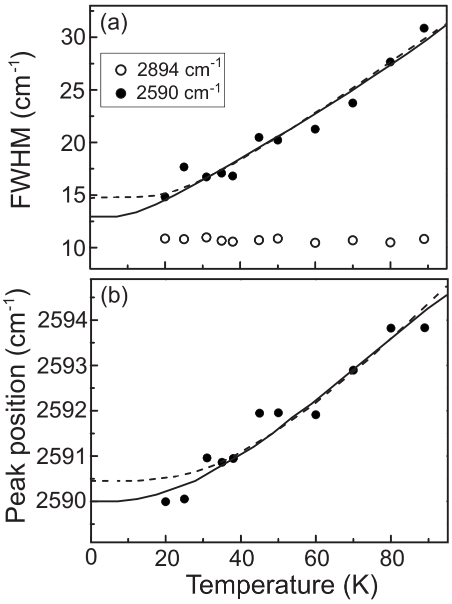

FIG. 2. (a) FWHMs and (b) peak positions of a softened C-H stretching peak at 2590 cm^{-1} (closed circles) as a function of temperature. FWHMs of a normal C-H peak at 2894 cm^{-1} are also shown (open circles). FWHMs and peak positions of the soft mode are fitted by the dephasing model (Ref. 23). The solid line is the result using values of $\omega_0=24$ cm^{-1}, $\delta\omega=23$ cm^{-1}, and $\eta=4.1$ cm^{-1}, and the dashed line represents the result of $\omega_0=56$ cm^{-1}, $\delta\omega=46$ cm^{-1}, and $\eta=13$ cm^{-1}.

the frustrated motion than the normal C-H mode.

Figure 2(b) shows the peak position of the soft mode at 2590 cm^{-1} as a function of temperature. The peak at 2590 cm^{-1} as well as a small peak at 2526 cm^{-1} shifts higher in wavenumber with increasing temperature. In contrast, the peak positions of the soft modes above 2600 cm^{-1} show little change at higher temperature than 20 K. The previous DFT study of cyclohexane adsorbed on the Pt(111) surface has revealed that adsorbed cyclohexane is most stable at a hollow site with the three softened C-H bonds positioned over three on-top sites.[30] In addition, the extent of the C-H mode softening correlates with the strength of the cyclohexane-metal interaction.[3] Therefore, the peaks at lower frequencies could be attributed to the softened C-H bonds of cyclohexane on a favorable hollow site. Thermal excitation of a low-energy frustrated mode causes a displacement of these C-H bonds from on-top sites, and thus induces weakening of C-H$\cdots$M interaction. This is consistent with the blueshift of the peak at 2590 cm^{-1}. On the other hand, peaks above 2600 cm^{-1} may be derived from the softened C-H bonds of cyclohexane, which does not locate at a favorable hollow site, as suggested by the incommensurate LEED spots. In this case, the frustrated translational motion may not necessarily induce a peak shift, which will be discussed later in detail.

As described above, a thermally excited frustration mode can induce the vibrational phase relaxation (dephasing). Assuming that the 2590 cm^{-1} peak is attributed to the softened C-H species positioned over an on-top site, the peak broadening and the peak shift of the softened C-H peak at 2590 cm^{-1} can be analyzed more quantitatively using the dephasing model proposed by Persson and Ryberg.[22,23] They have modeled that a high-energy mode (frequency Ω) is anharmonically coupled with a single low-energy mode (frequency ω_0) which can thermally exchange their energy with substrate phonons. Characteristic parameters used in this model are $\delta\omega$ and η: $\delta\omega$ is a parameter of anharmonic coupling between high- and low-energy modes and η is a friction parameter that describes energy dissipation of a low-energy mode into a substrate. Here, we calculated the line shape $I(\omega)$ using equations derived by Persson and Ryberg within the Markoff approximation,[23] and we obtained FWHMs and peak positions numerically. The contributions of other temperature-independent factors, i.e., energy relaxation and inhomogeneous broadening, to FWHMs are treated as a constant and added to the calculated values. To determine the energy of the low-frequency mode ω_0, we refer to previous HAS experiments.[31] Several n-alkanes and cyclohexane on Cu(100) have almost the same energy (~ 56 cm^{-1}) for the frustrated translation normal to the surface (FT$_z$).[32] In addition, the FT$_z$ frequency of adsorbed octane does not critically depend on a kind of the substrate.[29] Therefore, here we assume a similar value of 56 cm^{-1} for the FT$_z$ mode of cyclohexane on Rh(111). Other frustrated modes have been rarely observed by HAS experiments. Only the frustrated translation of octane parallel to the Cu(111) surface (FT$_\parallel$) has been detected at the frequency $\omega_0 \sim 24$ cm^{-1}.[29] Here, we assume the ω_0 value of 24 cm^{-1} as a FT$_\parallel$ mode.

In Fig. 2, the calculated FWHMs and peak shifts are presented by solid lines ($\omega_0=24$ cm^{-1}) and dashed lines ($\omega_0=56$ cm^{-1}). As a result of fitting to experimental data of FWHMs and peak positions, $\delta\omega$ value of 23 cm^{-1} (46 cm^{-1}) and η value of 4.1 cm^{-1} (13 cm^{-1}) are obtained for the FT$_\parallel$ (FT$_z$) mode. In the Persson-Ryberg model, when $\delta\omega$ is positive there should be an asymmetric tail on the higher-frequency side of the spectra. The observed peak shape seems to be inconsistent with the model. We think that the shoulder on the lower-frequency side is due to small peaks which overlap to the peak at 2590 cm^{-1}. Hence, the obtained values of parameters in this study could contain some error due to the single peak approximation. In particular, the FWHMs at higher temperatures may be overestimated because of the overlapping with surrounding peaks. Nevertheless, it is reasonable to attribute the broadening of the soft mode to the vibrational dephasing since the peak broadening at such low temperatures cannot be explained by other broadening mechanisms as discussed already.

The calculated peak shift of $\omega_0=24$ cm^{-1} is in better agreement with experimental data than that of $\omega_0=56$ cm^{-1} at lower temperature. The peak positions are expected to be less affected by surrounding small peaks than the peak widths. This was confirmed by peak fittings assuming several peaks around the 2590 cm^{-1} peak; positions of a fitted 2590 cm^{-1} peak were almost the same as those of an unfitted peak, i.e., the experimental results shown in Fig. 2(b). Therefore, the FT$_\parallel$ mode is more likely to cause the vibrational dephasing, rather than the FT$_z$ mode.

We think that other soft modes above 2600 cm^{-1} are also broadened by the dephasing although these show little peak shift. According to the Persson-Ryberg model, the vibrational dephasing causes a peak shift. In this model, however, it is assumed that adspecies adsorb on high-symmetry sites, and a frustrated motion causes a monotonous increase or decrease in a bond force constant, e.g., CO adsorbed on Ni(111) (Ref. 23) and Ru(001).[25] In the case of cyclohexane on Rh(111), we attribute the soft mode at 2590 cm^{-1} to the axial C-H at on-top sites, and other soft modes above 2600 cm^{-1} to those at low-symmetry sites. Therefore, the Persson-Ryberg model may be applicable only to the analysis of the 2590 cm^{-1} peak. Soft modes above 2600 cm^{-1} could also be affected by thermal excitation of a frustrated mode. However, an obvious peak shift does not necessarily occur due to their low-symmetry adsorption states, where the peak can shift to higher or lower frequencies, depending on a direction of the $\mathrm{FT}_{\parallel}$ mode.

In the previous studies, the origin of the broad C-H soft modes were attributed to inhomogeneous broadening[7] or damping of the vibrational motion via the e-h pair excitation.[18] However, these studies were carried out above 80 K. The observed soft mode may already be broadened by thermal excitation of a frustrated mode. The present study clearly shows that a low-temperature measurement is essential to discuss the broadening mechanisms in the case of weakly adsorbed molecules.

In summary, the C-H stretching vibrations of cyclohexane on Rh(111) were investigated by IRAS in a low-temperature region. The IRAS measurement at 20 K clearly shows that the softened C-H stretching band of cyclohexane consists of several sharp peaks which are distributed over a wide range, from 2500 to 2700 cm^{-1}. This is a consequence of inhomogeneity of adsorption states. Moreover, the peak width of each soft mode strongly depends on temperature. The observation of the soft modes as a function of temperature indicates that a thermally excited frustrated mode plays an important role in the temperature-dependent broadening of each soft mode; the broadening process can be explained by the vibrational dephasing scheme. Analysis of an observed peak using the dephasing model by Persson and Ryberg indicates that a low-frequency mode coupled with the softened C-H stretching mode could be a frustrated translation parallel to the surface.

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*Corresponding author; yoshinobu@issp.u-tokyo.ac.jp

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