Observation of the Low-Energy External Vibrations of Benzene on Rh(111)

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The low frequency vibrations of benzene molecules adsorbed on Rh(111) have been investigated with inelastic He atom scattering. Well resolved energy losses of 13.1, 12.9, and 12.7 meV were observed for the pure benzene $(2\sqrt{3}\times 3)$ structure, the $CO+C_6H_6$ $c(2\sqrt{3}\times 4)$rect and (3×3) structures, respectively. As these are the first experimental data for vibrations of a large adsorbed molecule in this energy regime extended Hueckel calculations were used to identify the observed mode as the frustrated translation of the benzene molecule parallel to the surface.

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Knowledge about vibrations at thermal energies (<20 meV) is of crucial importance for understanding the basic thermodynamical properties of thin organic films on solid substrates. Also structural properties (e.g., occupation of different adsorption sites) at finite temperatures will depend—via entropy contributions [1]—on the excitation spectrum in the thermal energy regime. Whereas relevant data for two-dimensional systems is rather scarce so far, vibrations in the bulk of molecular crystals have in the past been studied extensively by optical spectroscopies and, with reduced resolution but without the rather stringent selection rules, by inelastic scattering of neutrons [2].

For molecules adsorbed on solid surfaces the above techniques are not applicable because of intensity problems. Most of the available information has been provided by electron energy loss spectroscopy (EELS) [3] which is inherently surface sensitive. Using mainly EELS and to a lesser extent infrared spectroscopy (IRS) [4] the internal intramolecular vibrations for a large number of adsorbed molecules have been determined. The only external modes observed until recently are the frustrated translations perpendicular to the surface and in a few cases the frustrated rotation with frequencies above 30 meV. Because of its even greater surface sensitivity and high resolution He atom scattering (HAS) [5] was the first technique so far in detecting the thermodynamically relevant low-frequency vibrations [6]. Only recently librations of adsorbed CO molecules have also been seen with EELS [7,8], IRS [9], and Raman spectroscopy [10]. The relevance of these low-energy modes for determinations of adsorbate geometries has been demonstrated for a number of systems [11,12]. For example, structurally sensitive methods may provide erroneous results for the tilt angle of adsorbed diatomics if the thermal occupation of the low-energy modes is not considered [11].

So far these low-energy vibrations for chemisorbed systems have only been observed for CO chemisorbed on a variety of transition metal surfaces; the only polyatomic molecule studied so far has been NH_3 adsorbed on Fe(110) [13]. The energy of frustrated translations parallel to the surface for even larger chemisorbed molecules is difficult to estimate as we expect two opposite trends: an increase in the interaction strength with the substrate as a result of the larger number of atoms which will tend to raise the frequency and on the other hand the higher mass, which of course will lower the frequency. In addition for large molecules the lateral forces are expected to depend sensitively on the amount of registry between the structure of the molecules and that of the substrate. In the only previous attempt to detect low-energy vibrations of a larger molecule adsorbed on a transition metal surface measurements were carried out with inelastic neutron scattering for benzene adsorbed on Raney nickel, a polycrystalline material with a high surface area [14], but in a search for modes at lower energies only Ni phonons were found.

In this study we present the first experimental data on the low-energy dynamics of a large chemisorbed hydrocarbon molecule, benzene. The adsorption of benzene on Rh(111) is one of the most extensively studied cases of an aromatic molecule chemisorbed on a metal substrate. In previous work it has been established that for surface temperatures of 300 K and below both benzene and CO adsorb associatively on Rh(111) [15]. Whereas pure benzene has only a weak tendency to order on this surface, coadsorption of CO leads to an additional stabilization and at least two well ordered overlayers, $c(2\sqrt{3}\times 4)$rect and (3×3), are formed. LEED-$I(V)$ calculations carried out for the two benzene+CO overlayers [$c(2\sqrt{3}\times 4)$rect [16], (3×3) [17]] indicate that the benzene molecule occupies a threefold hollow site with the molecule rotated such that three of the C-C bonds are atop substrate atoms. These results were confirmed by STM investigations [18]. For the pure benzene phase $(2\sqrt{3}\times 3)$ the occupation of bridge sites has been proposed [15]. The vibrational spectrum of benzene molecules adsorbed on Rh(111) has been investigated with

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EELS [19,20]. In addition to the internal benzene vibrations, which were found to be slightly shifted with respect to the gas-phase values, two modes at lower frequencies (42.8 and 68.2 meV) were observed, which have been assigned by isotope substitution to external modes involving a stretch of the Rh-C bond.

The HAS time-of-flight apparatus has been described previously [21]. The Rh(111) crystal used in these experiments was cleaned using standard procedures involving sputtering with Ar ions at 800 eV and annealing to 1200 K. Prior to the adsorption of benzene and/or CO the cleanliness of the surface was monitored with an x-ray photoelectron spectroscopy (XPS) system and no contaminations exceeding 0.5% of a monolayer were observed. Both benzene and CO of better than 99.9% purity were admitted through leak valves and the pressure during exposure was less than 5×10^{-8} mbars, at a base pressure of 5×10^{-11} mbars. The three different overlayers as well as the clean surface were investigated with both HAS and LEED. In the case of the overlayers containing CO the previously published LEED diffraction patterns [15] could be reproduced. In the case of the pure benzene layer LEED investigations are hampered by the extreme sensitivity of the structure to trace amounts of CO (which are always produced by the degassing of the LEED electron gun filament). Therefore this structure was characterized with HAS angular distributions.

Figure 1 shows a series of representative He-atom time-of-flight spectra and angular distributions recorded for identical beam energies for the clean (above) and a pure benzene-covered $(2\sqrt{3}\times3)$ Rh(111) surface at 160 K (second from top) and for the two CO stabilized structures. For the clean surface only one energy-loss peak corresponding to excitation of a surface Rayleigh phonon is seen in this energy range. From these data the dispersion curve of the Rayleigh wave on clean Rh(111) has been determined [22]. The energy-loss spectrum in Fig. 1(b) shows a new feature at an energy loss of about 13.1 meV which emerges upon adsorption of benzene molecules in addition to the Rayleigh mode which is still seen through the benzene layer but with about half the intensity. The appearance of the new peak is accompanied by a strong increase of the diffuse elastic signal which is attributed to disorder within the adsorbed layer [23].

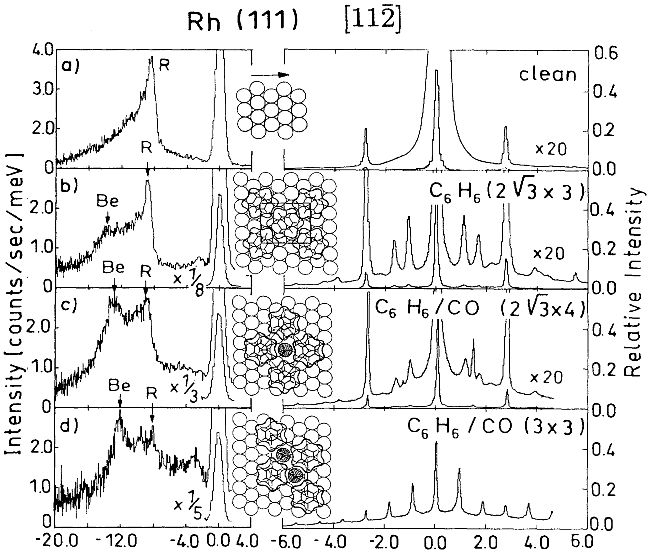

FIG. 1. On the left side He atom energy-loss spectra for (from top to bottom) the clean Rh(111) surface (a), the pure benzene $(2\sqrt{3}\times3)$ overlayer (b), and the two CO-containing overlayers, $c(2\sqrt{3}\times4)$rect (c), and (3×3) (d) are shown, while the corresponding He atom diffraction angular distributions with the proposed arrangements of benzene are displayed on the right side. All spectra were recorded at 160 K along the [11$\bar{2}$] direction with the exception of the energy-loss spectrum for the $c(2\sqrt{3}\times4)$rect overlayer, which was recorded along the [1$\bar{1}$0] azimuth. All spectra were taken at the same kinematical conditions ($k_i=7.8$ Å^{-1}, $\theta_i=38°$) in order to facilitate a direct comparison. In some time-of-flight spectra small energy-loss peaks are visible in the energy region below 5 meV. Careful studies have revealed that these features are artifacts caused by reflection of He atoms in the detector.

In Figs. 1(c) and 1(d) typical He atom time-of-flight spectra for the CO containing more densely packed $c(2\sqrt{3}\times4)$rect phase and the (3×3) phase are shown. Here the benzene-induced vibrations appear at 12.9 and 12.7 meV, respectively, slightly shifted to smaller energies. This lowering of the frequencies was the only difference observed with respect to the pure $(2\sqrt{3}\times3)$ surface and there was no evidence for a splitting resulting from different adsorbate sites. It is interesting to note that EELS experiments also indicate a lowering of the 43 meV mode to 39 meV with increasing CO coverage [19]. This is consistent with the shift from a bridge to a hollow-site structure which according to the calculation of Garfunkel *et al.* [24] leads to a slight 10% bond weakening. As in the latter case the dispersion curves were found to be flat and the energies for the surface Rayleigh mode were similar. However, as apparent from a comparison of the intensities in Fig. 1 the excitation probabilities for the different modes increase with increasing CO concentration in the layers without affecting the Rayleigh mode intensities. The former observation could be due to slight structural changes accompanying the CO adsorption [25].

Figure 2 presents a compilation of all the energy-loss features from more than 50 time-of-flight measurements at different incident and final scattering angles for the pure benzene $(2\sqrt{3}\times3)$ surface. There it is seen that the 13 meV mode is almost entirely independent of the wave vector over the entire range indicating only a negligible lateral coupling of the molecules with each other. This is consistent with the relatively large distance between the benzene molecules of 5.6, 6.6, and 7.5 Å in the structures

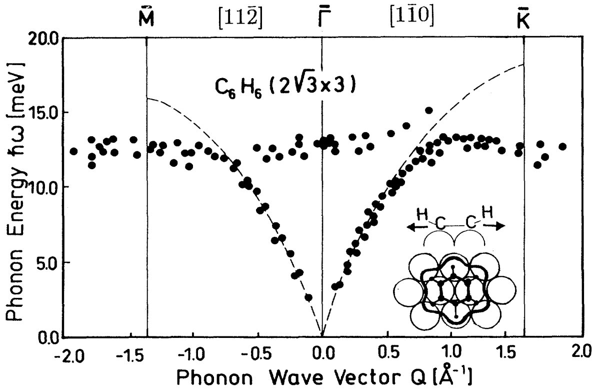

FIG. 2. Dispersion of the energy-loss features observed in the He atom time-of-flight spectra for the $(2\sqrt{3}\times3)$ overlayer on Rh(111) along the [11$\bar{2}$] direction. The dotted line shows the expected position of the Rayleigh mode of the clean surface. The structure of benzene assumed in the calculations is indicated in the inset.

of Fig. 1, respectively, which is greater than the root mean square dimer distances in a cluster of 5.2 Å [26]. On closer examination there is evidence for an avoided crossing where the mode crosses the Rayleigh mode. Since the Rayleigh mode is largely transversal polarized and thus mostly orthogonal to the longitudinal motion of the frustrated translation this hybridization should be weak. For instance, it is not seen in the reverse case of the coupling of the longitudinal surface resonance to a transversal adsorbate mode as in Ar on Pt(111) [27]. Here the situation is, however, closer to that recently studied for CO on Cu(100) where a similar hybridization was seen to enhance the inelastic intensities in the crossing region [25] and attributed to the longitudinal component of the Rayleigh mode.

At phonon energies above the adsorbate mode the Rayleigh mode of the clean surface is no longer seen. Mass-loading effects of the benzene molecule are not enough to describe the observed softening. Since the benzene molecule (78 amu) rests on 3 Rh atoms (103 amu) the effect on the zone boundary frequency can be estimated to be $[(3\times103)/(3\times103+78)]^{1/2}=89\%$. A more likely explanation is provided by noting that since the benzene molecule sits on several Rh atoms it will tend to dampen the short wavelength phonons. From the diameter of the H atoms in a benzene ring of approximate $D=5.6$ Å we calculate a cutoff wave vector of $Q_c=2\pi/D=1.1$ Å^{-1}. This lies close to the Q vector (0.75 Å) at which the Rayleigh mode disappears.

No clear evidence for vibrations of the CO molecule embedded between the benzene molecules was found, although for CO adsorbed on the clean Rh(111) surface the frustrated translation of this molecule at 5.7 meV could be clearly observed [22].

In order to facilitate the assignment of the energy-loss features in our time-of-flight spectra extended Hueckel calculations as described in Ref. [24] have been carried out. These calculations involve severe simplifications and their results should be interpreted with care, but in previous work it has been demonstrated that the adsorption geometry for benzene on Rh(111) is described correctly [24]. In the present study we have used the same parameters and adsorbate structure (which involves an upward bending on the H atoms) as described by Garfunkel *et al.* [24] in order to calculate the potential energy curve for small lateral displacements away from the center threefold-hollow binding site of a planar, triangular shaped Rh cluster containing 15 atoms. Only translations parallel to the surface were considered; the height was kept fixed at the calculated equilibrium distance of 2.0 Å [24]. In principle this procedure yields a two-dimensional potential energy surface (PES), but because of the threefold symmetry of the adsorption site the frustrated translation parallel to the surface will consist of two degenerate modes [28], so that the energy of the corresponding vibration parallel to the surface can be calculated from a one-dimensional cut through the PES.

The calculated data for a one-dimensional potential cut along the [1$\bar{1}$0] direction, which was found to be strongly anharmonic, were then interpolated by a polynomial, and the eigenvalues were determined numerically. An energy of 11.9 meV was found for the first vibrational transition (frustrated translation parallel to the surface). Results for smaller cluster sizes indicate that this good agreement is to some extent fortuitous. We believe, however, that the results of the calculations provide additional support of our mode assignment.

Note, however, that this assignment is not in agreement with results of model calculations using empirical external force fields [29], where much lower frequencies are obtained for the $c(2\sqrt{3}\times4)$rect and (3×3) phases, namely, 3.5 and 5.2 meV for the frustrated translation parallel and perpendicular to the surface, respectively. These calculations cannot be correct since they predict the incorrect geometry.

Considerable effort was devoted to the detection of the frustrated translation of the benzene molecules perpendicular to the surface at 68.2 or 42.8 meV, as seen in EELS [19,20]. No observation of an adsorbate mode at such higher energies with HAS has been reported previously, which has been attributed to a reduction in sensitivity of helium atom scattering at such high energy transfers due to a sharp drop off in coupling matrix elements and an obscuring large multiphonon background [6]. In this case, however, we were able to observe a weak feature in several time-of-flight spectra one of which is shown in Fig. 3 which could unambiguously be assigned to the frustrated translation perpendicular to the surface at 42.8 meV in agreement with the EELS data.

In conclusion the present Letter reports the first observation of the frustrated translation mode for a large hy-

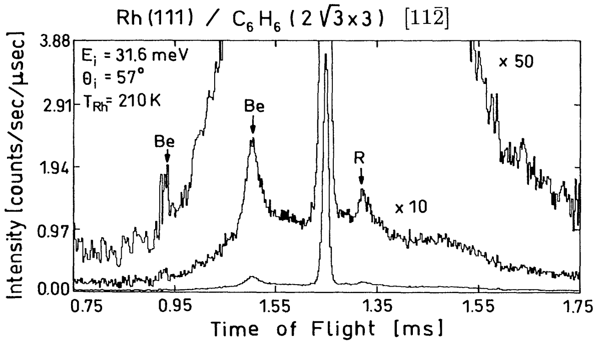

FIG. 3. He atom time-of-flight spectrum for the $(2\sqrt{3}\times 3)$ overlayer on Rh(111) at a surface temperature of 210 K for an incident energy of 31.6 meV. Note the weak feature at a flight time of 0.93 ms, which corresponds to an annihilation of a benzene vibration at 43 meV.

drocarbon molecule adsorbed on a solid surface. The observed frequency agrees well with the results of extended Hueckel calculations, indicating that these low energy vibrations probe properties of the interactions between chemisorbed molecule and metal surface, the description of which requires a proper treatment of the chemical interaction between substrate and the π system of the molecule. It will be interesting to compare this vibrational energy with that of benzene molecules adsorbed on other surfaces in order to find out whether small differences in adsorbate-substrate interaction have a considerable influence on the energy of this mode, as is the case for CO adsorbed on various metal surfaces [28]. As the vibrational amplitude (parallel to the surface) for this mode is more than 0.1 Å it has to be considered also for the structure analyses reported for these systems (see the recent Letter by Over, Moritz, and Ertl for the case of CO on Ru(0001) [12]) and can possibly explain the present disagreement between LEED-$I(V)$ calculations [16,17], which find a rather strong Kekule distortion of the adsorbed benzene molecule, and UPS data [30], where an effective C_{6v} symmetry of the adsorbed molecule is observed.

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