Damping of Molecular Motion on a Solid Substrate: Evidence for Electron-Hole Pair Creation

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The damping of molecular motion relative to a solid substrate was investigated by high-resolution vibrational spectroscopy in the far-infrared regime. For octane adsorbed on a hydrogen-passivated Ru(0001) surface the experimental linewidths observed by He-atom scattering for the frustrated translation normal to the surface are in accord with a damping by phonon emission, but a strong broadening is found for the clean Ru substrate. This enhanced friction is related to an increase in the rate of electron-hole (*e-h*) pair creation due to the presence of hybrid metal-molecule electronic states which are absent for the hydrogen passivated surface. Data from near-edge x-ray absorption spectroscopy provide direct evidence for these differences in electronic structure. Results from IR spectroscopy strongly suggest that the soft C-H bands observed for these systems are also related to the formation of these hybrid electronic states. [S0031-9007(97)04947-8]

An important topic in gas-surface interaction is the nature of the energy exchange between an impinging gas particle and the substrate. Whereas on insulators the energy transfer will comprise only excitation and deexcitation of substrate phonons and/or molecular vibrations, on conductors an additional energy dissipation via the excitation of electron-hole (*e-h*) pairs is possible. So far, attempts to directly identify the excitation of *e-h* pairs in high-resolution experiments for light molecules scattered off solid surfaces have failed, in accord with theoretical calculations. In case of He atoms with an energy of 22.6 meV impinging on a Cu surface at 16 K, theoretical calculations yield an integrated probability for electron-hole pair creation of 10^{-5} [1], which is about 4 orders of magnitude smaller than the experimentally determined total inelastic cross section. The recent experimental [2] and theoretical [3,4] success in advancing the understanding of the microscopic origins of friction has created substantial interest in a related topic, namely, that on the mechanism underlying the damping of molecular motion relative to a solid substrate. For some lubricant molecules it has been proposed that the electronic contributions to friction become so large that the *e-h* pair creation dominates damping by phonon emission (e.g., octane/Cu(001) [5]).

In the present study the damping of molecular motion was measured by high-resolution spectroscopy of the frustrated translation normal to the surface. This FT_z mode is a particular external vibration and corresponds to a translation of the whole molecule. The dissipation of translational energy into the substrate manifests itself in a decrease of vibrational lifetime. In order to precisely monitor the line shape and the frequency of these low-energy vibrations with frequencies in the far-infrared regime (typically below 100 cm^{-1}, or 12.4 meV), we have employed high-resolution He-atom scattering (HAS) to study the low-energy vibrations of octane (C$_8$H$_{18}$),

a prototype lubricant molecule, adsorbed on clean and hydrogen-passivated Ru(0001) substrates. In a second set of experiments using IR spectroscopy we demonstrate that the anomalous strong damping reported here for the external vibration of octane on a clean Ru(0001) surface correlates with the occurrence of so-called "soft bands" in the C-H stretch regime. This phenomenon was first observed about 20 years ago [6], but as of yet has not been completely understood despite significant effort [7]. Finally, a third set of experiments carried out using near-edge x-ray absorption spectroscopy (NEXAFS) demonstrates that the anomalies discussed above correlate with the formation of metal-molecule hybrid orbitals which couple the molecular motion to the metal substrate electronic degrees of freedom and thus lead to a strong increase in electron-hole pair creation.

The inelastic HAS experiments were carried out in a UHV time-of-flight apparatus (base pressure 8×10^{-11} mbar) which is described elsewhere [8]. The NEXAFS experiments were recorded at the electron synchrotron BESSY (beam line HE-TGM2). The IR data were obtained in a third UHV system equipped with a Bruker 66v Fourier-transform infrared spectrometer with an energy resolution of 4 cm^{-1}. In all three different systems a Ru(0001) crystal was cleaned by Ar-ion sputtering (600 eV, 1 μA/cm^2) followed by several cycles of oxygen adsorption at 300 K (10 L) and heating up to 1100 K. Finally the crystal was heated up to 1570 K to desorb the oxygen. Prior to the experiments described here the cleanliness and the structural quality of the surface had been checked by x-ray photoelecron spectroscopy (XPS) and low-energy electron diffraction. Exposing the clean Ru(0001) surface to hydrogen at room temperature or below results in the formation of a saturation (1×1) H overlayer which has been characterized thoroughly in a number of previous works [9]. Octane monolayers were

prepared by condensing a multilayer at around 120 K and subsequently annealing at 200 K which is below the monolayer desorption temperature (230 K) [10]. For the octane monolayers on both clean and hydrogen-covered Ru(0001) well defined He-atom diffraction peaks revealed the presence of ordered octane overlayers [11] with the C-C-C plane of the molecule parallel to the surface [12], similar to the case of octane on Cu(111) [13].

The left panel of Fig. 1 shows a set of He-atom energy loss spectra for a monolayer of octane adsorbed on the clean and hydrogen-covered Ru(0001) surface. The dominating feature is an octane induced energy loss peak at 7.6 meV, which is typical for hydrocarbons physisorbed on metal surfaces [10,14]. From an analysis of the variation of the excitation probability with the transfered wave vector, Δk, this feature has been identified as the external vibration polarized normal to the surface (FT_z mode) [10]. For the present HAS measurements kinematic conditions were carefully chosen to minimize excitations of substrate phonons, which have been determined previously for both the clean and the hydrogen-passivated surface [15]. The second loss peak at 9.9 meV has been identified as an internal octane vibration in a previous study [16].

After correcting for the finite resolution of the apparatus [14] a FT_z-mode linewidth of 0.56 meV is found for the hydrogen-saturated surface. As for the similar system of octane adsorbed on Cu(111) [14] this value is somewhat

smaller than that computed for pure phononic damping (0.7 meV) for a substrate with the elastic constants of Ru [17].

For the octane monolayer on the clean Ru(0001) surface the peak assigned to the FT_z mode is found at about the same energy (7.3 meV), thus implying the absence of any strong bonding interactions between octane and the clean surface, e.g., resulting from hydrogen-bond formation. Such a chemical interaction would significantly increase the binding energy and, correspondingly, the FT_z-mode frequency. The octane thermal desorption spectra recorded for the clean and hydrogen-saturated Ru(0001) surface yielded desorption maxima at 255 and 233 K, respectively, which confirms an almost constant binding energy for both surfaces.

Inspection of Fig. 1 reveals significant differences, however, as regards the FT_z energetic half-width. For octane adsorbed on the clean surface the analysis described above yields a half-width of 2.5 meV (FWHM), substantially larger than for the H-saturated surface. Since the He-atom angular distributions recorded for the octane adlayer on both the clean and hydrogen-covered surfaces exhibit the same degree of order [11], we feel that any inhomogenuous broadening can be ruled out. Consequently, we attribute this strong increase in linewidth to a reduced lifetime, or increased damping, of the FT_z mode.
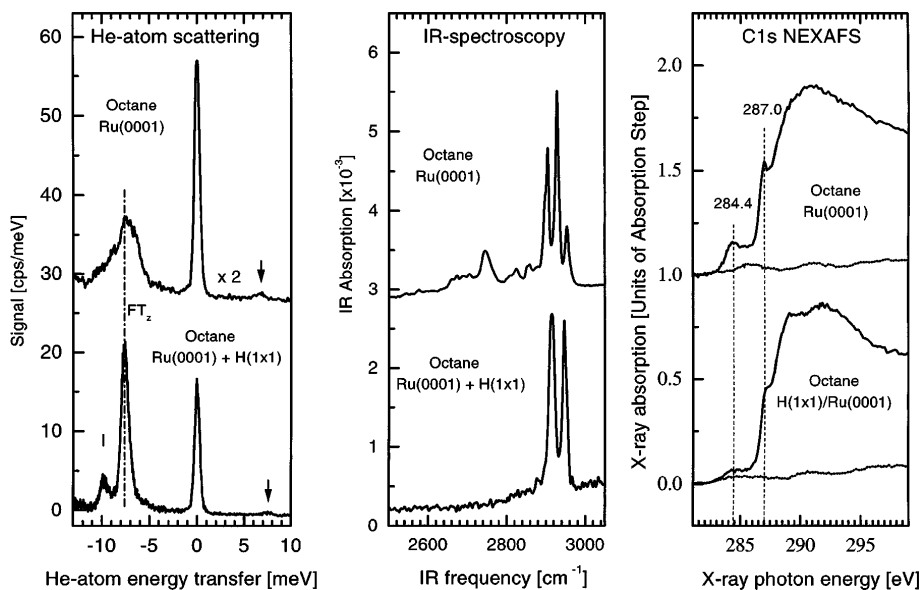

FIG. 1. Compilation of typical spectra obtained from applying different types of spectroscopy to monolayers of octane molecules adsorbed on clean (top) and hydrogen saturated Ru(0001) surfaces (bottom). All spectra were recorded for sample temperatures between 100 and 115 K. The left panel shows HAS energy loss spectra obtained for scattering along the [$1\bar{1}00$] azimuth at an angle of incidence of 40° and for an incident He atom beam energy of 22.7 meV. The loss peak at 7.6 meV is assigned to the frustrated translation of the molecule normal to the surface (FT_z mode). In the center panel infrared absorption spectra recorded at grazing incidence of the C-H stretch vibration bands are displayed. Note the so-called soft bands in case of adsorption on the clean Ru surface between 2650 and 2750 cm^{-1}. In the right panel soft x-ray absorption spectra for the carbon $1s$ edge are shown. For comparison near-edge x-ray absorption fine structure (NEXAFS) spectra recorded prior to adsorption are also included (dashed lines).

The observed peak broadening for the external vibration is accompanied by another vibrational anomaly, namely, the occurrence of a soft C-H stretch vibration band as evident from the IR data displayed in the center panel of Fig. 1. The IR spectrum recorded for the hydrogen-saturated surface (actually D has been used to monitor possible exchange processes) reveals C-H stretch vibrations localized in -CH_2- and -CH_3 subunits at 2915 and 2946.5 cm^{-1}, respectively, as well as a C-H bending mode at 1454 cm^{-1} and a weak feature related to a -CH_2- rocking vibration at 722 cm^{-1}. These vibrational bands and also those observed for the clean surface (see below) are in close agreement with the previous work by Hostetler *et al.* [18] for octane adsorbed on clean and hydrogen-covered Pt(111) surfaces. In the spectrum obtained for the clean surface these bands are slightly shifted in frequency to 2904, 2928, 1449, and 725 cm^{-1}, respectively. The feature of main interest here is the broad C-H bands at around 2650–2750 cm^{-1}. These bands are highly anomalous since they are strongly redshifted (in this case about 150 cm^{-1}) and exhibit a untypically large linewidth. These so-called soft bands were first seen for cyclohexane on Pt(111) and Ni(111) by Demuth, Ibach, and Lehwald [6] and have since then been observed for many other saturated hydrocarbon/metal adsorbate systems [7]. Despite significant interest (in particular in connection with the H-bond activation playing a key role in many catalytic processes) a complete understanding of the microscopic origins for the softening and the large linewidth of this mode is still lacking.

Frequently, the formation of hydrogen bonds to the metal surface has been proposed [6,7,19] in part due to the fact that a similar softening of stretching vibrations is observed for hydrogen-bonded molecules [20]. Although a hydrogen bond is considerably weaker than the covalent C-H bond it should give rise to an increased binding energy to the substrate. Saturating the clean surface with hydrogen should essentially remove such interactions. We therefore consider the fact that the FT_z frequency normal to the surface does not show any pronounced differences between the two chemically different substrates (see above) as strong evidence for the absence of significant C-H bonding between the molecule and the clean Ru(0001) surface.

In order to explain the large linewidth of the "soft" C-H stretch modes the presence of combination bands has been proposed, resulting from a mixing of the high-energy internal vibrations with low-energy external vibrations [7]. In the present HAS spectra one type of these low-energy vibrations with an energy of 7.6 meV is identified. One other low-energy vibration is expected for the present adsorption geometry, a frustrated translation parallel to the surface. Presumably, due to the very low excitation probability this mode could not be seen for the present surface, but experimental data for a similar system [octane on Cu(111) [21]] and theoretical work for butane adsorbed on Pt(111) [22] suggest that this energy is

around 4 meV. Our HAS data show that the frequencies of these vibrations are virtually the same for the two different substrates. Since the IR data shown in Fig. 1 demonstrate the absence of the anomalous broadening for the H-saturated substrate, the large width of the shifted C-H bands cannot be due to combination bands arising from coupling to low-energy modes.

Inspection of Fig. 1 reveals that the occurrence of the broadened C-H stretch modes correlates with a strong linewidth increase of the low-energy FT_z mode by about the same amount ($\approx$30 cm^{-1}, or 3.6 meV). In the latter case contributions from combination bands can be excluded [the only other low-energy excitation is the vibration parallel to the surface with energies around 4 meV (see above) and a very small excitation probability [23]]. Since the elastic constants of the substrate governing the damping by emission of phonons into the substrate are unchanged upon adsorption of hydrogen [24], the additional damping of the FT_z mode must be related to the only other channel available for energy dissipation on a metal substrate, the excitation of *e-h* pairs.

Whereas for higher frequency vibrations (with energies above the bulk phonon bands) of chemisorbed atoms or molecules *e-h* excitation is the dominating channel for energy dissipation [25], for the present case of a physisorbed molecule the electronic coupling to the substrate should be very weak, and as a result low-frequency vibrations should be almost exclusively damped by emission of acoustic phonons [17]. The occurrence of electronic friction proposed above for low-energy vibrations of octane on Ru(0001) is thus surprising and of course implies at least a weak electronic coupling, in contrast to the hydrogen substrate, where the large broadening of the FT_z mode is absent.

As regards to these electronic structure differences it is rather unfortunate that an application of ultraviolet photoelectron spectroscopy, the standard tool to study the electronic structure of substrates and their adsorption induced modification, is hampered since the small density of states induced by the adsorption of the octane molecule is superimposed on a large background due to the metal density of states. This makes a quantitative evaluation difficult, in particular in the region close to the Fermi edge where the contribution of metal *d* states is strongest [19]. We have therefore used C 1s NEXAFS spectroscopy. This technique is only sensitive to electronic states for which the projection on the atomic C 2p orbitals is finite [26]. Pure metal states are therefore not visible, as demonstrated by the NEXAFS spectra recorded prior to octane adsorption (shown as dashed line in the right panel of Fig. 1). For a full monolayer of octane adsorbed on the clean Ru(0001) surface the NEXAFS spectrum reveals a peak at 287.0 eV. This feature is caused by excitations into molecular Rydberg orbitals and is commonly observed for saturated hydrocarbons [27]. In addition a pronounced, broad peak at around 284 eV appears, just above the C

$1s$ XPS energy, the threshold for excitations from C $1s$ core levels into empty states of metal character [26]. The presence of this peak, which has been seen for other saturated hydrocarbon/metal substrate combinations in previous work [26,27], directly implies the existence of hybrid orbitals with contributions from both metal substrate and octane molecule. A comparison with the corresponding data for the H-saturated surface reveals a strong reduction of the peak at 284 eV, in accord with the expected weaker electronic interaction between the octane molecules and the hydrogen-saturated substrate.

With these results on the electronic structure of the adsorbed octane molecules a consistent picture emerges which is able to qualitatively explain all the rather different experimental results reported here. The hydrogen-saturated Ru(0001) surface shows only little electronic interaction with the adsorbed octane molecules since the presence of the H atoms prohibits a chemical interaction with the octane molecular orbitals as revealed by the NEXAFS data, the small linewidth of the external FT_z mode, and the absence of the anomalous soft modes in the IR data. On the clean ruthenium surface the metal d states can interact with the octane molecular orbitals and, as a result, a small density of hybrid states is created, which, however, do not give rise to a substantial binding energy [28]. These hybrid states couple the molecule to the substrate and a relative motion of the whole molecule with respect to the surface (as in case of the FT_z mode) or parts of it (as in case of the C-H stretch vibration) affects these hybrid states and leads to energy dissipation via creation of e-h pairs. The resulting linewidth (around 30 cm^{-1}) appears to be equal for the low-energy FT_z mode and the high-energy internal C-H stretch vibrations, in agreement with theoretical work where the e-h pair induced damping has been found to be independent of vibrational frequency [25].

Of course it would be highly desirable to corroborate the present experimental findings by a detailed first-principles theoretical analysis. However, such an analysis appears to be a formidable task since previous theoretical work on NEXAFS results for the free octane molecule indicated the importance of using very large basis sets for adequately representing the octane Rydberg states [27]. Since the present experimental data demonstrate that these Rydberg states play a key role in the metal/molecule electronic hybridization, equally large basis sets will also have to be used when investigating the adsorbate-substrate complex. We expect, however, that the strong interest in understanding the related C-H bond activation at metal surfaces will eventually provide the motivation for the required effort.

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