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The microscopic origins of sliding friction: a spectroscopic approach

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Abstract. The nature of the mechanism governing the damping of molecular motion relative to a solid substrate has been investigated by a systematic study of molecular frustrated translations. Using scattering of thermal energy He atoms, these vibrations located in the far-infrared regime (<15 meV) have been determined for prototype lubricant molecules, octane and other saturated hydrocarbons, adsorbed on a variety of different substrates, namely hydrogen-terminated diamond C(111), Pb(111), clean and hydrogen passivated Ru(0001) as well as on Cu(111). In most cases the lifetime of the frustrated translational modes is in good agreement with that computed from theoretical models considering only phononic damping. Exceptions to this rule (Pb(111) and Ru(0001)) are discussed. The results suggest that generally electronic contributions to sliding friction are weak; only in cases with significant electronic coupling between molecule and substrate does electronic friction dominate phononic friction.

In the case of dry friction the rupture of chemical bonds formed spontaneously when two surfaces come into close contact uses up the most part of the dissipated energy. The presence of a lubricant at the interface of the two materials not only reduces the wear resulting from this process but also significantly lowers the frictional forces and thus the amount of dissipated energy. In case of fluid film lubrication the remaining losses are governed by viscosity and can be calculated by simple hydrodynamics. About 75 years ago, however, Hardy [1, 2] realized that a single-molecular layer of lubricant is sufficient to establish the so-called boundary lubrication. In this case the energy dissipation process must comprise a direct coupling of the lubricant molecular motion and the substrate heat bath. With special devices like the surface force apparatus [3] or the atomic force microscope [4] frictional forces can be measured today on a microscopic level, and even the lateral variation of the friction when sliding objects over a periodic surface can be

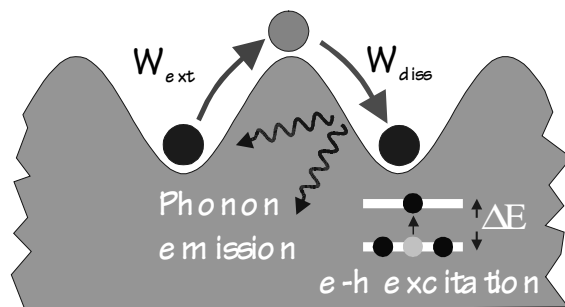


Figure 1. Schematic representation of the two basic mechanisms in sliding friction. First, external work, W_{ext} , is converted into potential energy which is then dissipated into the substrate by either phonon emission or electron–hole (e–h) pair excitation.

monitored [5]. Relatively little information, however, is available on the fundamental dissipation process by which the lateral motion is transformed into heat warming the substrate and is thus responsible for the frictional force.

When sliding a molecule along an insulator surface, translational energy can be dissipated only via emission of substrate vibrations or phonons, but in the case of a metal in addition electronic excitations are possible, see figure 1. Although in principle it should be possible to answer the basic question on the relative importance of these two mechanisms, phononic and electronic friction, by a theoretical analysis of quantitative data obtained for model systems, e.g. of quartz microcrystal balance data for noble gas atoms adsorbed on silver substrates [6], such theoretical efforts [7] are severely hampered by the fact that precise information on the lateral corrugation of the noble gas/substrate potential energy surface is not readily available [8]. Consequently, the question of the importance of electronic friction is still being debated. In particular, quantitative information for realistic molecule/substrate combinations, in addition to results for the different, rather special model systems, e.g. argon on Ag(111) and different molecules on mica, is urgently required.

On the molecular level the motion of a particle along a surface is quantized and can be described by a superposition of a special type of vibrational modes. These so-called frustrated translations, which are schematically depicted in figure 2, are of external character and generally have frequencies located in the far-infrared regime. Recently it has been demonstrated that, with a particular spectroscopic technique, scattering of thermal energy He-atoms, these vibrations can be detected in a straightforward fashion. These investigations provide two important pieces of information. From the frequency of the mode the strength of the adsorbate/substrate coupling can be determined, and the damping of the translational motion relative to the substrate can be obtained from a line-shape analysis, or a determination of the vibrational lifetimes. These results can then be used to test theoretical predictions on the absolute strength of the phononic damping [9, 10, 11], and can also provide detailed information on the importance of electronic contributions to sliding friction.

Here, we will provide a brief summary of an extensive set of experiments for a prototype lubricant molecule, octane, adsorbed on a variety of different materials with strongly differing elastic and electronic properties, ranging from the hard insulator diamond to the soft metal

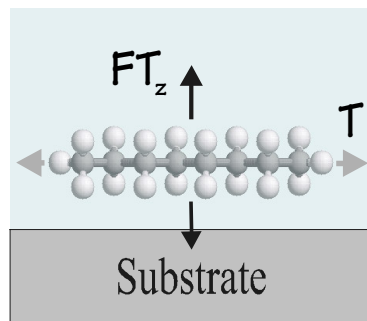


Figure 2. Schematic displacement patterns for two differently polarized frustrated translational modes of an octane molecule adsorbed on a solid surface. The vibration normal to the surface is denoted FT_z . The T-mode exhibits a polarization parallel to the substrate surface. The frequencies of both modes are located in the far-infrared regime.

lead. This systematic study demonstrates that generally the damping for molecular translations normal to solid substrates can be well described by phononic damping as given by a simple formula (see equation (1)). Two exceptions to this general rule, however, were found and will be described. We were also able to determine for the first time the frequency of the octane frustrated translation parallel to the surface, which allows us to estimate the phononic damping for the motion along the substrate. Altogether our results reveal that, in the absence of significant chemical interaction between molecule and substrate, electronic friction is negligible for damping molecular translations on metal surfaces †.

The experiments were carried out using the prototype lubricant molecule n-octane together with other members of the homologous series of n-alkanes. The molecules were adsorbed on the different substrates typically at temperatures of 180 K by backfilling an ultrahigh vacuum chamber with the corresponding gas. Adsorption was monitored by recording the intensity of thermal energy He-atoms scattered from the substrate in the specular direction (see [12] for details on the experiments) using a molecular beam apparatus which has been described in detail previously [13]. Upon exposing the substrate to the alkane vapour the He-atom reflectivity first decreases, passes through a minimum and then reaches a maximum upon completion of the monolayer. He-atom angular distributions recorded for octane monolayers on all different substrates showed well defined diffraction patterns, thus revealing the presence of high-quality, well ordered structures. Note that He atoms are particularly well suited for the investigation of molecular systems since beam damage can be strictly excluded due to the low energy of the incident particles (<40 meV in the present study). Additional experiments using other methods of surface analysis (e.g. x-ray photoelectron spectroscopy, or XPS, and low-energy electron diffraction, or LEED) confirmed the presence of precisely one monolayer. On all substrates investigated here octane adsorbs with its C-C-C-plane parallel to the substrate [14].

The frustrated translations or external vibrations of the molecule are located in the far infrared, a regime which is difficult to access with infrared or Raman spectroscopy. Also, neutron scattering is largely inapplicable; molecular vibrations on surfaces have so far only been

† This statement is correct only for commensurate overlayers. In case of incommensurability the lateral translational invariance may lead to a complete disappearance of phononic friction.

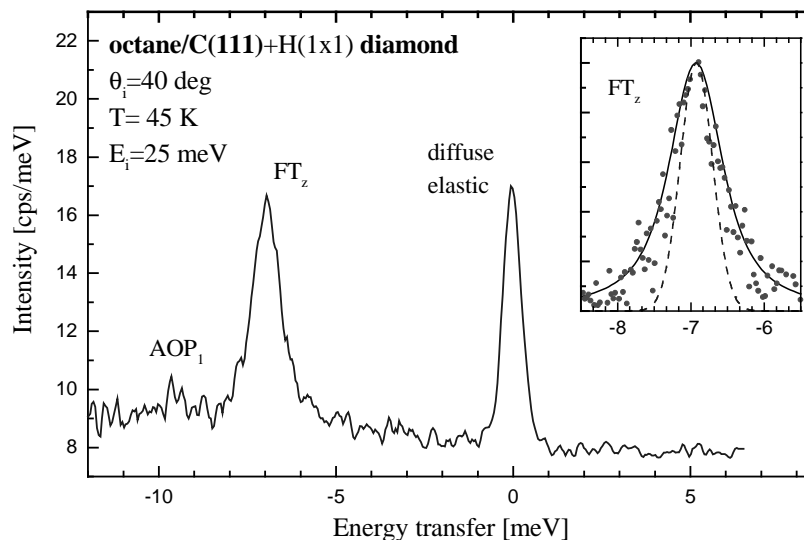


Figure 3. He-atom energy transfer spectra of a monolayer n-octane adsorbed on diamond, C(111). It shows a peak at zero energy transfer, which corresponds to diffuse elastic scattering. The intense peak around 7.0 meV can be ascribed to a frustrated translation normal to the surface (FT_z). The peak at 9.5 meV corresponds to an internal out-of-plane bending mode (AOP_1). The inset shows the experimental data (full circles) for the FT_z mode, which are compared with the apparatus response function (broken line), and a convolution of the experimental response function with a Lorentzian of linewidth 0.8 meV (full line).

studied in the case of graphite substrates [15]. We have therefore used inelastic scattering of thermal energy He atoms. This method uses a time-of-flight technique to determine the energy transfer between the He atom and the target and was originally developed for measuring surface phonons [16].

A typical result for an octane monolayer adsorbed on a hydrogen-passivated C(111) + H(1 × 1) diamond surface [17] is shown in figure 3. The He-atom energy transfer spectrum first reveals a sharp peak at zero energy transfer, corresponding to elastic, diffuse scattering indicating the presence of a small amount of defects. A comparison with the available data on the energies of the substrate phonons [18] reveals that the other discrete peaks at finite energy transfers are related to internal and external vibrations of the octane molecule. It has been demonstrated previously [19] that the peak at 9.5 meV is due to an internal out-of-plane molecular bending mode (which for the free molecule corresponds to the lowest energy internal vibration) whereas the largest peak located at 7.0 meV can be assigned to the frustrated translation of the octane molecule normal to the surface (FT_z mode). This low frequency is typical for physisorbed particles; similar FT_z frequencies are observed for noble gas atoms adsorbed on solid substrates [8].

In addition to determining the frequency of these different molecular vibrations, the knowledge of the apparatus response function makes it possible to apply a deconvolution procedure, thus yielding the intrinsic linewidth of the mode, as schematically indicated in the inset of figure 3. In the case of energy dissipation by emission of phonons into the substrate it has been proposed that, for the case of ordered adsorbate overlayers, the intrinsic halfwidth of a

frustrated (or hindered) translation either parallel or normal to the surface is given by [20]

$$\Gamma = \frac{m\omega_0^2}{A\rho \cdot c_T} \quad (1)$$

where m is the adsorbate mass, ω_0 is the frequency of the external vibration and A is the surface area occupied by the molecule. ρ and c_T correspond to the substrate mass density and the transverse speed of sound, respectively [20]. The full line in the inset of figure 3 shows a convolution of a Lorentzian with a halfwidth of 0.38 meV and the apparatus response function. This value is somewhat smaller than the theoretical value for pure phononic damping as obtained by equation (1), 0.58 meV, but the comparison indicates that the theoretical description for the damping of molecular vibrations on solid substrate by emissions of phonons into the substrate is adequate even for the hardest material available (note that electronic damping can be excluded for the insulator diamond).

Figure 4 shows similar data obtained for the case of well-ordered overlayers of octane molecules on a Cu(111) substrate. Here the FT_z frequency is shifted to slightly larger values, 7.2 meV, and the lineshape analysis yields a linewidth of 0.45 meV. As expected from equation (1), which yields a value of 1.1 meV, the damping on the soft copper substrates is larger than on the hard diamond. Together with the fact that theoretical predictions on the strength of electronic damping yield values roughly three orders of magnitude smaller [21], these results demonstrate that major contributions from damping through electronic excitations, i.e. generation of electron–hole pairs, are absent in the case of n-alkanes adsorbed on copper surfaces.

Previously it has been suggested that the damping of the so-called frustrated translation of octane polarized *parallel* to Cu and Ag substrates is dominated by electronic friction [21]. Although at first sight this statement appears to be at odds with the results presented above, it has to be considered that the efficiency of the damping strongly depends on the frequency of the corresponding frustrated translation. In fact, if this frequency ω_0 of the horizontally polarized T-mode (see figure 2) were very small, the damping would be reduced significantly since the energetic halfwidth is proportional to the square of ω_0 . In previous work this T-mode could not be seen and it was concluded that the corresponding frequency must be very small (<0.1 meV) [22]. As a result, the phononic damping as estimated by equation (1) becomes very small and drops below the theoretical estimate for electronic friction [21].

Since a knowledge of the frequency of this T-mode would also allow an important conclusion on the corrugation of the potential energy surface [8], in the present work we have made additional attempts to observe this mode. Despite significant effort, however, only on Cu(111) substrates was the quality of the He-atom energy loss spectra sufficient to unambiguously detect this mode. Here, the spectra reveal a small peak at an energy transfer of 3.0 meV, denoted ‘T’ in the data shown in figure 4. By a detailed analysis of the variation of the intensity of this peak with transferred parallel momentum, and using the results of a previous normal mode analysis for octane adsorbed on a structureless (flat) surface [19], this mode can be ascribed to the frustrated translation of the molecule parallel to the surface. This appears to be the first observation of this T-mode for a larger molecule adsorbed on a metal surface. The fact that the excitation probability for this mode is about an order of magnitude smaller than for the vibration normal to the surface explains the fact that it remained unseen in previous experiments and for other substrate materials. Briefly, the small excitation probability is due to the fact that the matrix element governing the excitation probability is roughly proportional to $|\langle \Delta k \cdot E \rangle|^2$, where Δk denotes the exchanged momentum and E the displacement vector of the molecule. Since in a

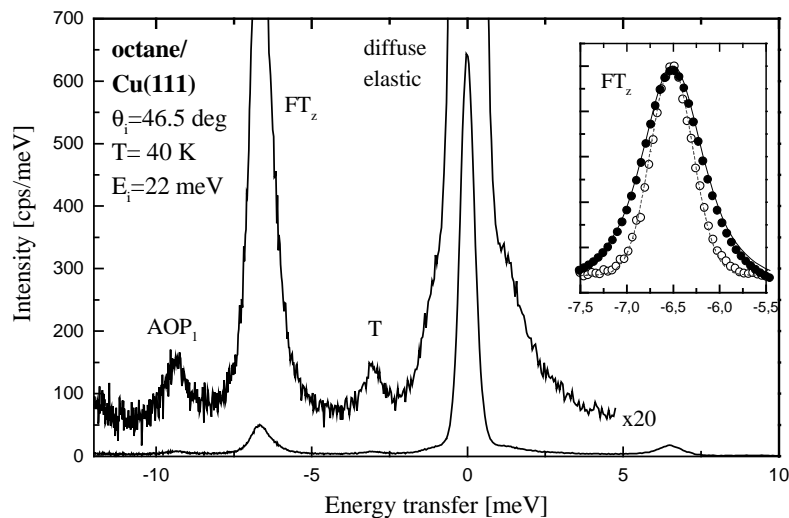


Figure 4. Energy transfer spectra of a monolayer n-octane adsorbed on Cu(111). It shows a peak at zero energy transfer, which corresponds to diffuse elastic scattering. The intense peak around 6.7 meV can be ascribed to a frustrated translation normal to the surface (FT_z) and the peak at 3.0 meV to one parallel to the surface (T). The peak at 9.3 meV corresponds to an internal out-of-plane bending mode (AOP_1). The inset shows the experimental data (full circles) for the FT_z mode, which are compared with the apparatus response function (open circles), which is well approximated by a Gaussian (broken line) and a convolution of the experimental response function with a Lorentzian of linewidth 0.45 meV (full line).

typical scattering geometry the component of k directed normal to the surface by far exceeds the parallel component, the vibrations polarized in the surface plane are strongly suppressed and modes with this polarization have not been seen in previous experiments. The fact that in the present case the mode becomes visible is due to the high structural quality of the octane overlayer.

The analysis of the peak shape as described above yields an intrinsic halfwidth of 0.29 meV for octane and 0.19 meV for the perdeuterated octane (see table 1). As expected from the smaller frequency, these values are significantly smaller than those corresponding to the FT_z modes, but even in the case of the perdeuterated octane the experimental value is about a factor of two larger than the theoretical prediction (model II) and, since contributions from inhomogeneous broadening cannot completely be excluded, sets an upper limit of about 0.17 meV to the contribution from electronic friction. This value is three orders of magnitude larger than the value of $0.2 \mu\text{eV}$ obtained theoretically by Persson and Volokitin for the similar system of ethane, C_2H_6 , adsorbed on Ag(111) [21]. Since this value for the electronic friction agrees very well with surface resistivity data [21] we feel that we can exclude a dominant contribution of electronic friction to the damping of the lateral translational motion of octane on Cu(111).

Similar data to those shown in figures 3 and 4 were recorded for octane molecules adsorbed on Pb(111), Ru(0001) and Ru(0001) + H(1×1). Additional measurements were recorded for hexane and perfluorated hexane deposited on Cu(111) and Pb(111), as well as for nonane and

Table 1. Experimental determined energies of the frustrated translation normal to the surface (FT_z) for alkanes adsorbed on different surfaces. In the third column the experimental lifetime broadening Γ_{exp} extracted from a lineshape analysis is listed. These values are compared with predictions for the phononic contribution to the lifetime broadening from two different models. Model I describes the phononic damping of the molecular motion in the limit of a single molecule adsorbed on a surface [9], whereas in model II a densely packed monolayer is considered [19]. All experimental data correspond to values at the $\bar{\Gamma}$ -point of the surface Brillouin zone, with the exception of the parallel frustrated translation of octane ($\Delta K = 0.52 \text{ \AA}^{-1}$) and of perdeuterated octane on Cu(111) ($\Delta K = 0.65 \text{ \AA}^{-1}$).

System	Mode	Experiment		Theory	
		E (meV)	Γ_{exp} (meV)	model I (meV)	model II (meV)
Octane/Cu(111)	FT_z	7.2	0.45	2.4	1.1
	FT_{\parallel}	3.0	0.29	0.07	0.08
d-octane/Cu(111)	FT_z	6.6	0.52	2.0	1.1
	FT_{\parallel}	2.8	0.19	0.06	0.08
Hexane/Cu(111)	FT_z	7.0	0.48	1.7	1.3
Nonane/Cu(111)	FT_z	6.6	0.52	2.0	1.1
Decane/Cu(111)	FT_z	6.6	0.52	2.0	1.1
Hexane/Pb(111)	FT_z	6.7	0.34	(20.4)	(2.4)
Octane/Pb(111)	FT_z	6.6	0.26	(25.4)	(2.0)
d-octane/Pb(111)	FT_z	6.2	0.32	(22.9)	(2.0)
Octane/C(111)	FT_z	7.0	0.38	0.03	0.59
Decane/C(111)	FT_z	7.0	0.32	0.04	0.61
Octane/Ru(0001)	FT_z	7.3	1.12	0.32	0.48
Octane/H/Ru(0001)	FT_z	7.6	0.42	0.38	0.52
PFH/Cu(111)	FT_z	2.8	0.63	0.17	0.4
PFH/Pb(111)	FT_z	2.4	0.76	1.3	0.7

decane on Cu(111). All results are compiled in table 1, where they are compared with theoretical predictions obtained from two different theoretical models. The comparison with the prediction of the two models, in particular in the case of the diamond substrate, reveals that model I, which has been developed for the damping of single molecules, is not applicable for the present case of well ordered, densely packed overlayers. In this case the emission of phonons into the substrate is strongly influenced by interference phenomena, which are taken into account in model II from which equation (1) [20] was obtained. (Recently, model II has been further improved, yielding a significantly better agreement with experiment [23].)

Despite good overall agreement for the FT_z -mode damping also for the heavier perfluorinated hydrocarbons adsorbed on Cu(111), strong discrepancies are present for the case of lead and ruthenium. In the first case the bulk phonon frequency is so low that continuum

theory providing the basis for the two theoretical models is no longer applicable [24]. For lead substrates, one-phonon excitation processes, owing to the low phonon frequencies, become inefficient in damping the molecular vibration. As a result, the damping of the molecular motion is strongly reduced, since the contribution from two-phonon processes is significantly smaller than that from single-phonon interactions.

In the second case, octane adsorbed on clean Ru substrates, the data in table 1 reveal a damping more than twice as strong as that expected theoretically. Comparison with the results obtained for the same molecule adsorbed on the hydrogen-passivated Ru surface demonstrates that this unexpected large damping is not due to the elastic properties of the substrate (which are virtually unchanged upon hydrogen adsorption [25]). Instead, detailed electronic structure determinations revealed that this strong coupling correlates with a weak chemical interaction between the saturated hydrocarbon and the transition metal surface and strongly suggest that in this case the energy dissipation is largely given by electronic friction [25]. A similar large linewidth has also been reported for unsaturated hydrocarbons adsorbed on Cu(100) [22].

Altogether, these results reveal that the damping of the translational motion of the prototype lubricant molecule octane normal to a solid substrate (FT_z -mode) is well described by a damping through phonon emission if two requirements are fulfilled. First, the frequency of the corresponding molecular vibration has to be significantly lower than the bulk phonon frequency. Second, the adsorption has to be dominated by physical forces; even weak chemical interactions can lead to strong contributions from electronic excitations.

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