Translational Energy Transfer from Molecules and Atoms to Adsorbed Organic Monolayers of Long-Chain Amphiphiles

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Time-of-flight studies of monatomic and diatomic gases scattered from long-chain, amphiphilic monolayers are reported. The extent of energy transfer can be correlated with the rigidity of the chains and the gas/surface mass ratio. Surface vibrational modes responsible for the energy transfer are suggested.

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Molecular-beam scattering is a powerful tool for the study of the dynamics of gas-surface energy transfer. It has been used to study characteristics of various surfaces, and how they interact with impinging (probe) molecules or atoms.[1] The surfaces studied have typically been either single-crystal or polycrystalline inorganic materials. The use of inorganic surfaces in these studies has both historic and scientific basis, since the preparation of clean, well-defined inorganic surfaces has become a rather standard (although often difficult) process, as a result of years of research in the field. In addition, surface-analysis techniques are now able to give precise information on the structure and chemical purity of the surface. In contrast, organic surfaces are not as easily prepared or characterized, which has led to a paucity of information on them. This is despite their importance in nature and industry, and the fact that they are well known to alter radically the characteristics of an inorganic surface on which they lie.[2] Significant progress has been made in recent years toward the development of stable, structured monolayer assemblies consisting of long-chain amphiphiles.[3] These assemblies can be constructed on solid supports in close-packed, ordered structures, exposing a variety of chemical functionalities at the outer monolayer interface.[4] This development has opened the possibility of our producing organic surfaces exhibiting a variety of planned chemical and physical properties. Such structures have obvious importance in design of heterogeneous catalysts, and control of gas-surface energy transfer.

This Letter summarizes the first reported study of molecules and atoms scattered from organized monolayer surfaces. By use of the time-of-flight (TOF) technique, the extent of translational energy exchange in encounters of individual gas atoms and molecules (probes) with such organic surfaces was determined. In addition, we hoped to observe the influence of processes unique to ordered monolayers on the scattering phenomena. Besides penetration of the probe into the monolayer, three low-frequency surface modes could conceivably absorb the incident kinetic energy: (a) concerted waving motion of the chains parallel to the surface plane; (b) hindered rotation of the end group; (c) vibration along the chain axis. By variation of the chain constituents, it is possible to control the manner in which these modes can interact with an impinging species. This is unachievable in inorganic crystal surfaces.

Three different monolayers were studied.[3-5] They are schematically shown in Fig. 1. Two are very similar, having polar heads attached to the surface, and long methylene chains exposing a methyl group at the end. Monolayers of *n*-octadecyltrichlorosilane (OTS)—an eighteen-carbon chain with covalent silane attachment at the surface—were prepared on glass and polished quartz slides, polished silicon single-crystal wafers, and cleaved mica substrates by means of the self-assembly technique. Monolayers of Cd(II) arachidate were transferred by the Langmuir-Blodgett method to freshly cleaved LiF(100) faces. The alkyl chains of these two monolayers are similar, the main difference being in the nature of attachment to the surface. Infrared spectroscopy has shown the orientation of the alkyl chains to be close to

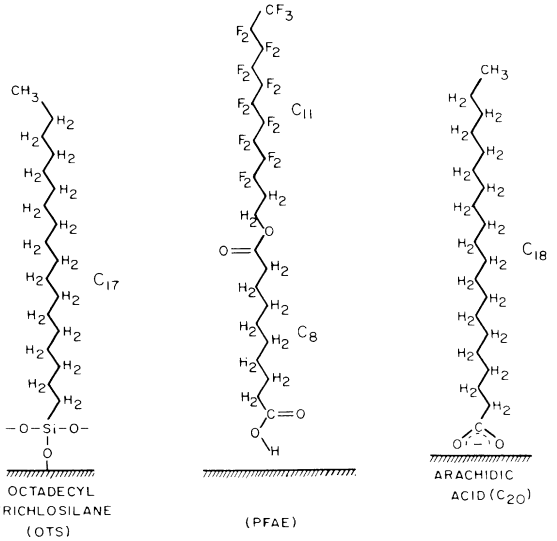

FIG. 1. Representations of the three monolayers studied: *n*-octadecyltrichlorosilane (OTS), perfluorinated acid ester (PFAE), and Cd(II) arachidate (C_{20}).

perpendicular to the substrate (within ca. 10°) for both of these monolayers.[3,6] The third monolayer, perfluorinated acid ester (PFAE), was used to test the effect of lower surface energy and heavier chain constituents. This monolayer, also prepared by self-assembly on glass,[6] is entirely fluorinated over the outer eight carbons of the chain, exposing the $-CF_3$ group. Freshly cleaved LiF(100) faces were used to estimate the time resolution of the experiment in the case of elastic scattering.

The TOF studies were made in a three-tiered vacuum chamber. From the nozzle expansion region, the pulsed molecular beam (R. M. Jordan Co., nominal 50-μs width) expands through a skimmer into the sample chamber where it is collimated and then strikes the surface of the sample, which is mounted on a rotatable mount. The quadrupole mass spectrometer (UTI model 100 C) is located 40 cm from the sample and differentially pumped. If it is positioned closer, sample degradation occurs. Overall angular resolution is 5°. The nozzle-sample-detector angle is fixed at 60°. The TOF trace, triggered from the firing of the pulse nozzle, is averaged by use of a PC-controlled digital scope (Gould) over 500–2000 shots. The scattered signal was easily discerned when superimposed on the rising peak of unpumped gas from each nozzle pulse. Appropriate background subtraction was made, and the TOF traces were analyzed only up to the point where the difference between directly scattered and background ion signals was significant.

A preliminary study was made of the angular scattering distribution. Whereas scattering of He from LiF yielded strong scattered signals with specular and diffraction peaks observable, the monolayers all gave a weak, diffuse pattern centered about the surface normal. Such patterns may be indicative of a dirty or rough surface, and so it is worthwhile to emphasize here some of the qualities of these monolayers. Because these surfaces are of low energy (< 20 dyn/cm compared with > 1000 dyn/cm for typical metal surfaces),[7,8] we do not expect them to become contaminated even under the mild vacuum conditions (10^{-7}–10^{-6} Torr) of this experiment. No change in contrast angles measured before and after the experiment could be observed. This indicated that neither contamination nor deterioration of the monolayer structure occurred.[3,4,9] In addition, two recent publications have shown that similar surfaces remain clean, as measured by Auger spectroscopy[9] and LEED.[10] These surfaces, prepared in the former case by self-assembly and in the latter case by the Langmuir-Blodgett method, are by necessity prepared under atmospheric conditions and then transferred to vacuum for study without further cleaning. With respect to surface roughness, we have prepared the monolayers on the mica, silicon crystal, and LiF crystals in order to see if the surface smoothness would affect the scattering patterns. X-ray studies have shown that the roughness of OTS prepared on polished Si wafers is of the order of tenths of angstroms.[11] Cleaved mica and LiF surfaces are atomically smooth. It is reasonable to assume that their smoothness is preserved upon coating with ordered monolayers. The fact that every substrate yielded the same diffuse scattering pattern indicates that scattering properties of these monolayers are substrate independent.

TOF data gave supporting evidence for the above results. The TOF patterns obtained at different angles were identical within the accuracy of the experiment. Therefore we may presume that there is no component which contributes to particular angles only. Measurements of the TOF patterns reported here were generally made at normal deflection angle, and incident angle of 60°.

Before data analysis, TOF traces were shortened to preclude the nozzle-surface distance (12 cm) and take into account the gas pulse width. The ion flight time and spreading effect of the ionization volume were small corrections which were made on the derived parameters. Because the equations chosen for the fitting[12,13] were velocity flux equations, they were transposed to density and the time frame in order to match the experimental curve. Two phenomena are included in the expression. The first component describes a Maxwellian stream at the surface temperature for probes which have completely accommodated to the surface. The second component is a distribution with both width and mean speed free to vary. We designate this nonequilibrated portion the stream component [second term in Eq. (1)]. The advantage of this equation is that it allows characterization of the part of the scattered curve which is not described by a Maxwellian stress at the surface temperature:

$$I=(B/t^2)\exp[(-m/2k_BT)(L^2/t^2)] + (A/t^2)\exp[-W(L/tv_s-1)^2]. \quad (1)$$

Here I is the signal intensity, m the mass of the gas, k_B Boltzmann's constant, and T the surface temperature which was fixed at 300 K. For the stream component, the width factor is $W=\gamma M_a^2/2$, M_a being the aerodynamic Mach number and γ the heat-capacity ratio C_p/C_v, but we attach importance to W only as a measure of the width of the distribution (narrow for large W). The other quantities are stream velocity v_s, surface-detector distance L, and time t. A and B are the normalization constants for the stream and Boltzmann components, respectively.

In Fig. 2, TOF traces for He scattered from PFAE, LiF, and Cd(II) arachidate are displayed. The latter is similar to scattering from OTS on any of the substrates. Simulations obtained by fitting with Eq. (1) are overlaid on the experimental curves. From the curve fittings, best-fit values were obtained for W, v_s, A, and B. The fits were excellent, and unique with respect to parameter adjustment. In fact, the major source of uncertainty in the parameters is reproducibility between runs which

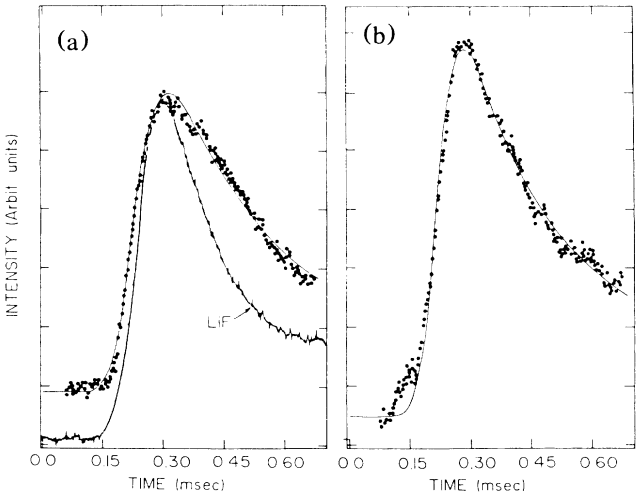

FIG. 2. Fitted TOF simulations (solid lines) overlaid on the experimental trace (dots) for He scattered from (a) OTS (with LiF curve underlaid for width comparison), and (b) PFAE.

averaged $\pm 8\%$ for v_s and $\pm 10\%$ for large W, approaching 100% for $W \approx 1$. Integration yielded the relative weights of the two components. In Table I the data are presented in two forms: On the left side the experimentally measured average energy loss and width of the distribution are displayed. On the right side the parameters obtained from the fitting are shown.

The data analysis was designed to give a both physically intuitive and simple representation of the results. It is important to note that for our unseeded beams, the incident kinetic energy is only very slightly larger than the most probable velocity of a Maxwellian stream leaving a room-temperature surface.[13] This difference is larger for the diatomic gases. Exiting kinetic energy of the probe therefore gives only partial information on the extent of energy transfer at the surface. For this reason, the width of the scattered distribution is an important measure of the extent of energy transfer because an increase of the width represents a loss of coherence between incoming and outgoing distributions. The kinetic-energy loss is probably dominated by partial migration into and tortuous exit from among the chains. This process may also contribute to coherence loss to a degree determined by the nature of probe and surface. This phenomenon will be expressed by a larger stream fraction with a low velocity v_s, in addition to possible diminution of W.

For He scattered from PFAE, it is clear that the stream portion is described by an exceptionally high width factor. In fact, W is almost identical to that obtained for He scattered from LiF (for LiF, the width factor was 11.6 with 70% stream). The kinetic-energy loss for this component is also quite low. This is indicative of a hard-impact, nearly elastic collision. It is interesting to contrast these data with those for He scattered from OTS, and Ar scattered from PFAE. The former gives a distribution which is essentially thermalized. The latter gives a width much smaller than the He case, but large enough to be considered nonthermalized. These differences may be understood by consideration of the mass ratio $\mu = (\text{gas mass})/(\text{surface mass})$ for the different cases. μ is small for He scattered from PFAE whether the surface unit is taken to be CF_3 or merely F. Energy transfer is poor because of the mismatch in masses. When the probe is the more massive Ar, the nearly even mass ratio allows significant energy transfer to occur. The OTS, besides being lighter, is also less rigid than the perfluorinated surface. Its behavior is more like a soft mattress than a hard wall.

The hard-cubes model[14] was used to simulate the He-PFAE results. A good fitting was obtained if the total

TABLE I. Measured and fitted parameters for TOF Distribution.

		Measured values				Fitted parameters		
Gas	Surface	E_i[a] (10^{-13} erg) ($\pm 5\%$)	E_F[b] (10^{-13} erg) ($\pm 10\%$)	Percentage kinetic energy loss[c] ($\pm 10\%$)	Normalized[d] FWHM (± 0.1)	W[e]	Percent stream[f]	v_s[e] (cm/sec)
He	PFAE	1.0	0.72	28	0.38	10	23	1.6×10^5
	OTS	1.0	0.57	43	0.62	1.0	100	1.4×10^5
Ar	PFAE	1.0	0.96	4	0.48	5.0	25	5.5×10^4
	OTS	1.0	0.71	29	0.47	3.6	42	3.6×10^4
O_2	PFAE	1.4	0.90	36	0.49	3	19	5.9×10^4
	OTS	1.4	0.80	43	0.49	2	53	5.2×10^4
NO	PFAE	1.5	0.68	54	0.43	2	63	5.2×10^4
	OTS	1.5	0.76	49	0.56	0.5	39	5.4×10^4

[a]Translational energy of incoming beam determined by fast ion gauge.

[b]Average translational energy of scattered distribution.

[c]$(1 - E_F/E_i) \times 100$.

[d]Full width at half maximum (FWHM) of scattered distribution divided by its average velocity.

[e]From Eq. (1).

[f]Integrated intensity for relative contribution of second component in Eq. (1), after conversion to flux distribution.

incident velocity was substituted for the incident normal velocity, and $\mu = 0.08$. This corresponds to a "surface mass" of about 50 u. Although the systems studied gave significant tangential momentum transfer which is not allowed in the hard-cubes model, our aim was to see if a meaningful value could be obtained for the surface mass. The correspondence attained lends support to the notion of an impulsive, angle-independent collision between the He and the CF_3 end group.

The results for the diatomic molecules lack information on internal energy disposal, and hence are not as easily understood. Oxygen, however, seems to follow trends similar to the monatomic gases. Separate experiments are under way to probe internal energy changes in NO scattered from these surfaces.

In summary, ordered monolayers of long-chain amphiphiles have been shown to demonstrate unique properties in the scattering of gaseous atoms and molecules. Whereas a high extent of thermalization always occurs, an indirectly scattered component is observed which appears to be dependent on μ and the monolayer rigidity. The diffuse scattering which is observed could be due to either structural or thermal effects. Whereas the methyl groups introduce a certain degree of roughness, monolayers prepared on atomically smooth surfaces do not show any specular component, even for diatomic molecules which should be less sensitive to this structure because of their size. For this reason we must consider the role of thermal scattering. Because significant tangential momentum transfer has occurred, the surface modes involved in the scattering must have a component perpendicular to the carbon skeleton. In terms of the three surface modes described earlier, the end-group rotation and concerted waving motion could lead to kinetic-energy transfer in this direction. A low-frequency beating mode of the coupled C-C oscillators could conceivably provide good energy matching with the incoming probe. However, this motion is directed perpendicular to the surface and thus cannot explain the scattering observed. For PFAE, the CF_3 group seems to control the scattering.

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