due in part to uncertainties in the assumed values of model parameters. It may also imply that charge exchange in the outer regions of the solar system removes some of the neutral hydrogen (*22*). More detailed analysis of pick-up ion data, planned for the future, should help to resolve these questions.

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23. We are grateful to the many individuals at the University of Maryland, the University of Bern, the Technical University of Braunschweig, the Max-Planck-Institut fur Aeronomie, and the Goddard Space Flight Center who have contributed to the SWICS experiment. We have benefited from discussions with C. Gloeckler, J. R. Jokipii, M. A. Lee, E. Möbius, and E. C. Stone. This work was supported by NASA/JPL contract 955460, the Swiss National Science Foundation, and the Bundesminister fur Forschung und Technologie of Germany.

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Directionally Aligned Helical Peptides on Surfaces

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Directionally oriented peptide layers 1000 angstroms thick were constructed by polymerization on gold and indium-tin-oxide glass. A key feature is the use of an appropriately functionalized surface on which the initiation sites for polymerization are spaced at distances consistent with the helical diameter of the peptide. Completely helical polyalanine and polyphenylalanine layers have been constructed. The helicity of the polyalanine layer was completely retained after heating at 180°C for 7 days.

The rational design and preparation of materials for a wide range of practical applications, such as information storage and processing, requires protocols for the assembly of molecular units into supramolecular arrays. For example, optical switches based on second-order nonlinear effects require materials with unidirectional alignment of axes of molecular polarizability over domains that exceed the wavelength of the light (*1–4*). Several techniques for the alignment of organic materials have been investigated, making use of single-crystal materials, liquid crystals, Langmuir-Blodgett films, poled polymers, and host-guest inclusion complexes. However, none of the techniques have provided a satisfactory solution addressing all of the requirements for devices, including such practical issues as long-term stability to both heat and light. Recent reports have described thin multilayers built by sequential deposition of monolayers (*5*), as well as thin films formed by the cross-linking of monolayers (*6*). We describe a complementary approach that provides a directionally organized assembly of large molecules built by polymerization on a gold surface.

Peptides have received little attention as optical switching materials, in part because methods that result in unidirectional alignment have been lacking (*7–11*). Nonetheless, a helical peptide has characteristics similar to crystalline urea, with a network of hydrogen bonds extending from one end of the chain to the other (Fig. 1) (*12*). Thus, we sought a method for the assembly of helical peptides for which the axes of all molecules point in the same direction. However, the helical arrangement is favored over the β-pleated sheet only when there are more than 10 amino acid residues in the polymer, and at that size, homogeneous peptides are quite insoluble. As a result, we focused our attention on the formation of peptides on a surface by in situ polymerization and chose the [100] face of gold as a relatively flat substrate to which suitable "seeds" could be attached and from which the polymers could be grown (*13–15*).

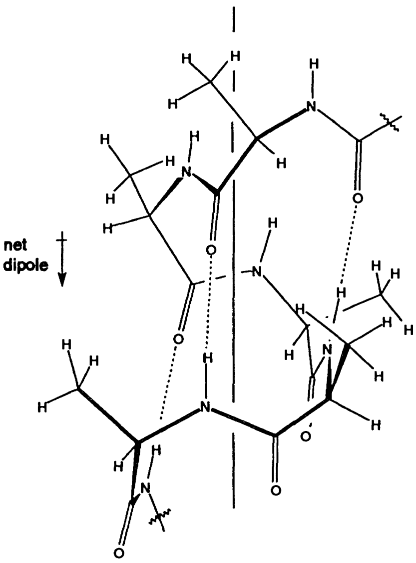
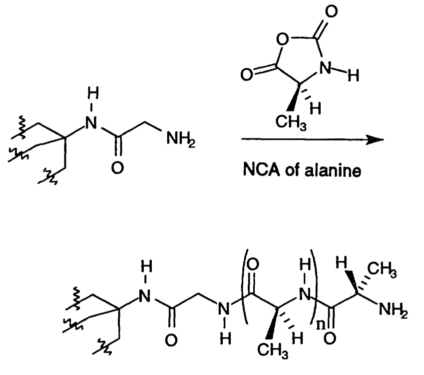


Fig. 1. Helical polyalanine showing the net macroscopic dipole resulting from the summation of the electrostatics of the individual, constituent amide groups.

The interatomic spacing on the Au [100] surface is substantially smaller (4.1 Å) than the diameter of a helical peptide ($\sim$9 Å for polyalanine) (Fig. 2A). Thus, it is essential that the seeds deposited on the surface each occupy at least 9 Å; to this end, we prepared the aminotrithiol (*16*) "tripod" **1** (Fig. 2B). This compound adheres tightly to evaporated gold surfaces (on a thin layer of chromium on silicon), and treatment of such a surface-bound layer of **1** with the *N*-carboxyanhydride (NCA) of alanine in acetonitrile led to the growth of a substantial layer of polyalanine.



The thickness and helicity of this material can be determined by comparison of the grazing-angle Fourier transform infrared (FTIR) spectrum (*17*) of this layer (Fig. 3A) with, respectively, a commercial sample of polyalanine (Fig. 3B) and a layer of

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24 alanine units prepared by the successive addition of trialanine with the Merrifeld protocol (Fig. 3C) (*18*). The infrared (IR) spectrum of the helical peptide formed by polymerization on gold (Fig. 3A) exhibits extremely narrow absorptions for the amide I and II bands and for the N–H stretch (*19*). Furthermore, the absorption of the helical polymer layer is approximately 30 times that of the 24-mer layer, consistent with about 600 alanine units. The spectra recorded before and after this surface layer of polyalanine was annealed for 7 days at 180°C and 1 torr are identical (*20*).

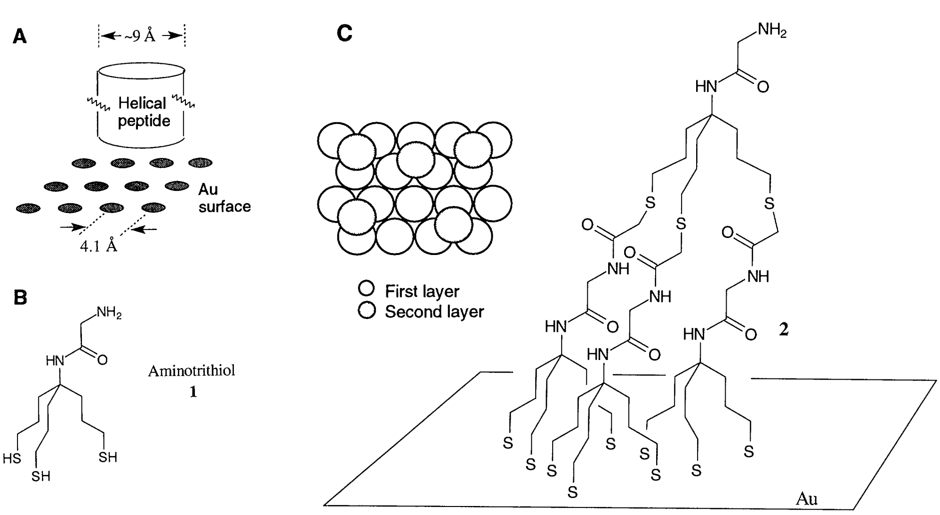


Fig. 2. (**A**) Schematic representation of the Au [100] surface and a cylinder representing the diameter of helical polyalanine. (**B**) Structure of the aminotrithiol **1**. (**C**) Double layer (**2**) of aminotrithiol **1** on gold.

The directional axis of the helix can, in principle, be determined by examination of the intensity variation of the amide I IR spectral band with both perpendicularly and horizontally oriented light. This band should be much stronger when the electric vector of the light is oriented parallel with the axis. Unfortunately such experiments cannot be conducted on metal surfaces because the horizontal components of all IR modes are inactivated by the conducting nature of the surface. Thus, to examine this question, we built helical polyalanine layers on indium-tin-oxide (ITO)–coated float glass using (MeO)$_3$Si(CH$_2$)$_3$NH$_2$ for attachment (*21*). The amide I absorptions in horizontally and vertically polarized light cannot be directly compared because the semiconducting nature of the ITO coating damps horizontal components. Nonetheless, the γ_{sym} and γ_{asym} C–H stretching modes of the methyl groups can be used for cross reference between spectra because the three-dimensional shape of the methyl group makes the magnitudes of these modes essentially independent of orientation. Comparison of IR spectra of helical polyalanine on ITO glass taken with vertically (Fig. 3D) and horizontally (Fig. 3E) polarized light reveals that the intensity of the amide I and II bands is greatly attenuated (relative to the

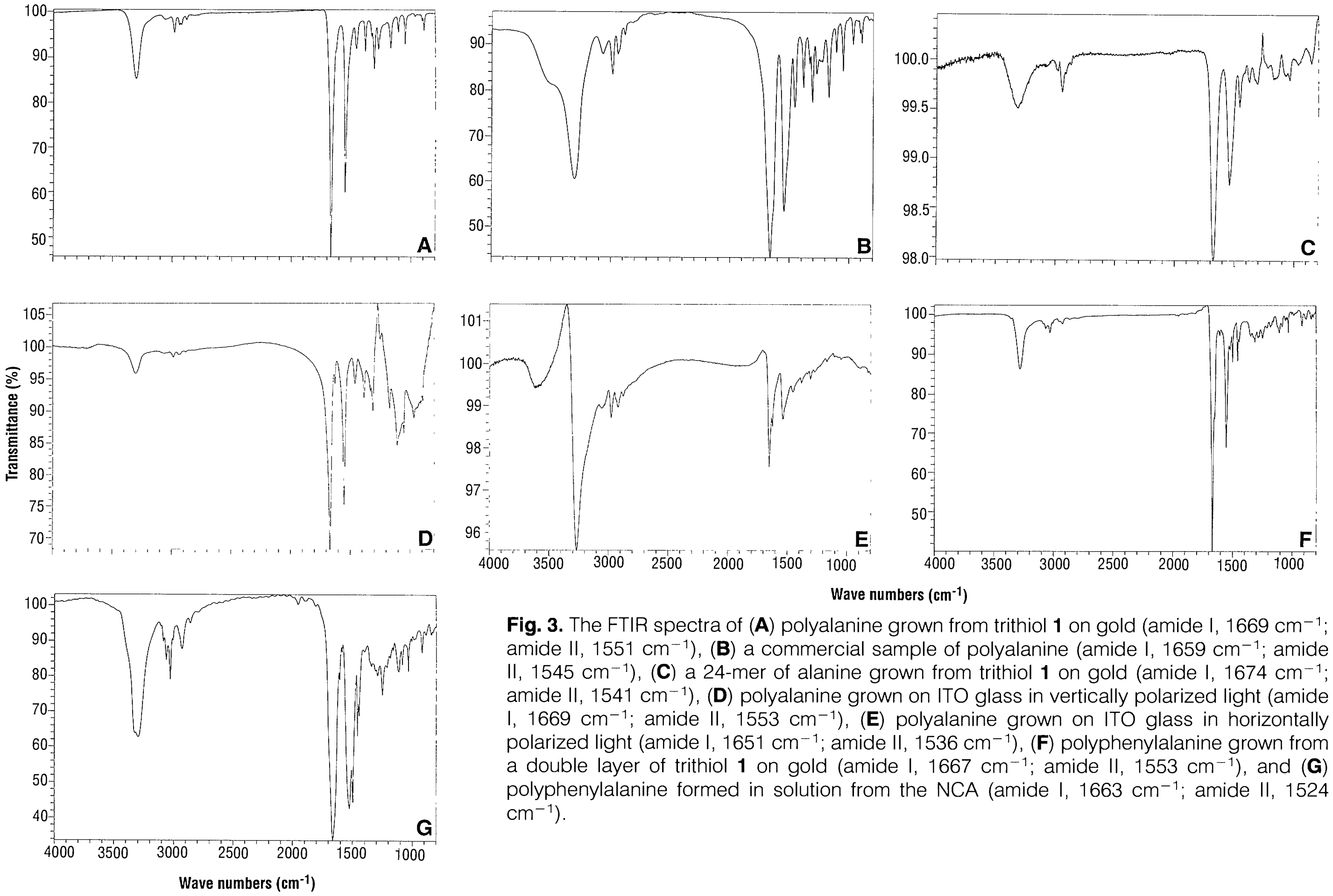
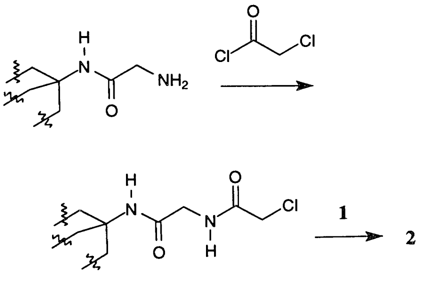


Fig. 3. The FTIR spectra of (**A**) polyalanine grown from trithiol **1** on gold (amide I, 1669 cm^{-1}; amide II, 1551 cm^{-1}), (**B**) a commercial sample of polyalanine (amide I, 1659 cm^{-1}; amide II, 1545 cm^{-1}), (**C**) a 24-mer of alanine grown from trithiol **1** on gold (amide I, 1674 cm^{-1}; amide II, 1541 cm^{-1}), (**D**) polyalanine grown on ITO glass in vertically polarized light (amide I, 1669 cm^{-1}; amide II, 1553 cm^{-1}), (**E**) polyalanine grown on ITO glass in horizontally polarized light (amide I, 1651 cm^{-1}; amide II, 1536 cm^{-1}), (**F**) polyphenylalanine grown from a double layer of trithiol **1** on gold (amide I, 1667 cm^{-1}; amide II, 1553 cm^{-1}), and (**G**) polyphenylalanine formed in solution from the NCA (amide I, 1663 cm^{-1}; amide II, 1524 cm^{-1}).

methyl C–H stretching modes) in the latter. Thus, we conclude that the axes of the helices are aligned mainly normal to the surface. The relative intensities of the amide bands compared with the methyl group C–H modes when vertically polarized light is used are similar for the helical peptide on both the ITO glass (Fig. 3D) and the gold surface (Fig. 3A). We conclude that the orientations of the helices on the two surfaces are similar.

Because the aminotrithiol **1** occupies a space on the surface only slightly larger than that required by helical polyalanine, it seemed unlikely that peptides with larger side chains would grow from this seed. Indeed, attempts to grow a polymer from the NCA of phenylalanine were unsuccessful. To prepare a surface with seed units spaced further apart, we reacted the aminotrithiol **1** on the surface of gold with chloroacetyl chloride, forming a tris-α-chloroamide. Treatment of this layer with additional **1** produced a double layer, **2** (Fig. 2C), in which each of the free amino groups of the second layer required the surface area occupied by three aminotrithiol units of the first (~15 Å between free NH$_2$ groups) (*22*). Polymerization of the NCA of phenylalanine on this base was successful (Fig. 4) and resulted in a peptide layer with a high degree of helicity (Fig. 3F). The degree of helicity of the surface-bound peptide contrasts with the homogeneously dispersed, randomly oriented polyphenylalanine formed simultaneously in solution (Fig. 3G).



We now have the flexibility to prepare polypeptides with a wide range of side chains so as to optimize the molecular properties for particular applications. Furthermore, we anticipate that the directional alignment of the dipoles of the individual amide units can orient polar side chain substituents. The use of the aminotrithiol **1** and related species provides an opportunity for the adjustment of surface spacing so as to accommodate a variety of peptide and nonpeptide polymers and, as well, affords binding to the surface that is substantially more robust than that obtained with monothiol linkages.

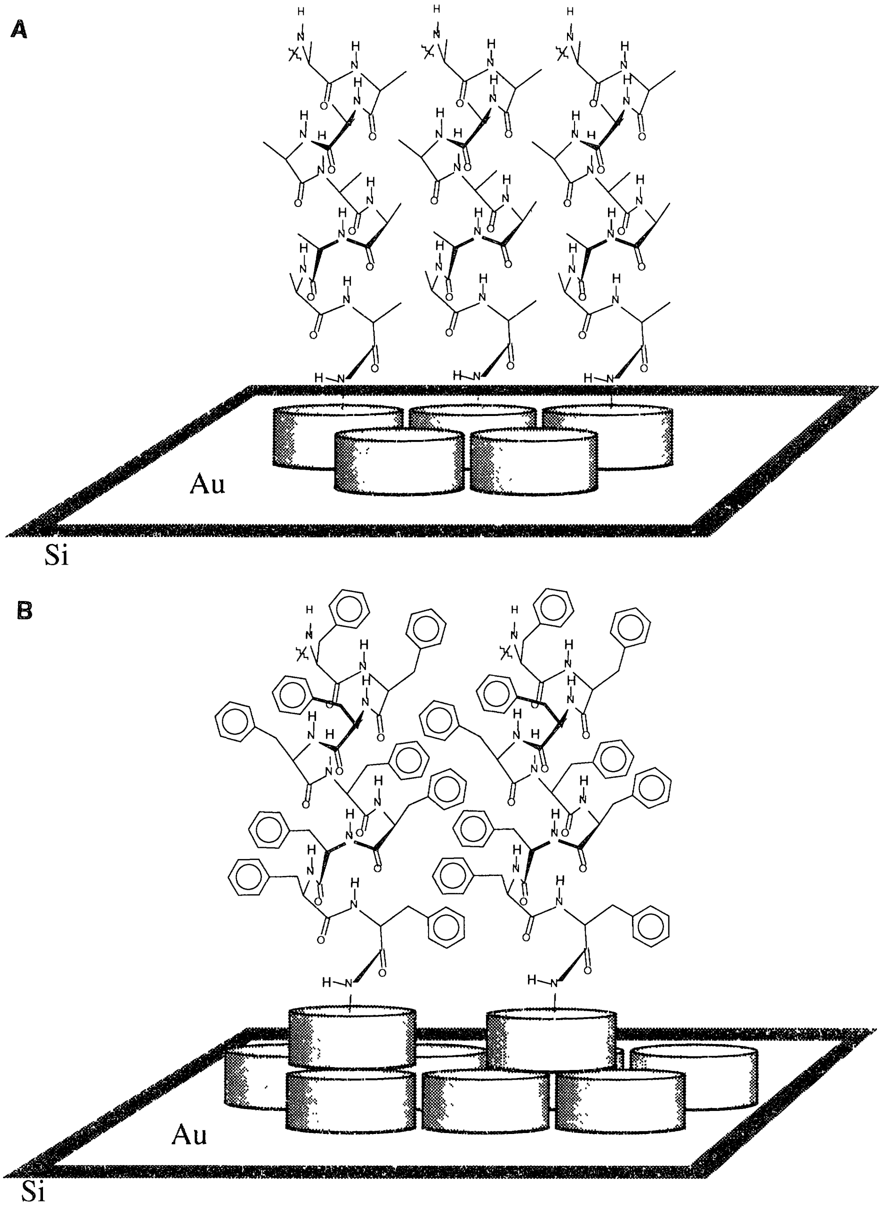


Fig. 4. Schematic representations of (**A**) polyalanine on a monolayer of the aminotrithiol **1**, and (**B**) polyphenylalanine on a double layer of **1**, where **1** is represented as a cylinder (for clarity, only one row of polymer is shown).

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16. The synthesis of this aminotrithiol was accomplished in four steps from commercial bis(homotris)[4-amino-4-(3-hydroxypropyl)-1,7-heptanediol] as follows: bis(homotris) (Aldrich) was con-

verted to the trihexyl ester with 3 equivalents of *n*-hexanoyl chloride in pyridine (90%). The triester was reacted with *N-t*-BOC-glycine (BOC, butoxycarbonyl), dicyclohexylcarbodiimide (DCC), and 4-dimethylaminopyridine (DMAP) in pyridine, forming the *N-t*-BOC-glycylaminomethane derivative of the triester (68%). Hydrolysis of the ester groups (K_2CO_3 in 95% ethanol) (94%), followed by treatment with CH_3SO_2Cl in CH_2Cl_2, yielded tris(3-methanesulfonyloxypropyl)-*N-t*-BOC-glycylaminomethane (97%). Reaction of this trimesylate with sodium thiolacetate in MeOH at reflux for 5 hours afforded the trithiolacetate ester (46%) that was converted to **1** after 5 hours at reflux in methanol and HCl (100%). Full details of this preparation will be reported separately.

17. A Nicolet (Madison, WI) 510P FTIR spectrometer equipped with a mercury cadmium telluride (MCT) detector, a Spectra Tech (Stamford, CT) model FT-80 grazing-angle (80°) reflectance accessory, and a Spectra Tech aluminum-wire grid on zinc selenide substrate polarizer.
18. Ellipsometry measurements on the polyalanine layer were highly variable, indicating uneven chain growth. Nonetheless, there was no indication of incorporation of the solvent (acetonitrile) in the layers (the layers were rinsed with ethanol and air dried before analysis). The absorptions of the 24-mer and the polymer layer in Fig. 3A are 0.009 and 0.34, respectively, from which we conclude that the polymer layer consists of approximately 900 alanine units. Each amino acid residue contributes 1.5 Å to the length of the helix, and thus, the polymer layer is 1300 to 1400 Å thick.
19. The IR spectral details of α-helical and β-pleated sheet forms of peptides have been studied in detail: see T. Miyazawa and E. R. Blout, *J. Am. Chem. Soc.* **83**, 712 (1961); D. Muller and H. R. Kricheldorf, *Polym. Bull.* **6**, 101 (1981).
20. The monolayer of **1** on gold is also quite stable and is unchanged after heating at 150°C for 2 days.
21. The procedure for modification of ITO glass was that described in K. Chen, W. B. Caldwell, C. A. Mirkin, *J. Am. Chem. Soc.* **115**, 1193 (1993); R. C. Cieslinski and N. R. Armstrong, *J. Electrochem. Soc.* **127**, 2605 (1980). The surface metal–OH groups are spaced further apart on this and other glass surfaces than are the gold atoms on a gold surface, providing room for the growth of helical polyalanine without the use of trithiol **1**. However, the greater degree of randomness and inhomogeneity of a glass surface compared with that of gold is reflected in a lower degree of order in the polymer grown on the former.
22. This layer need not be as ordered as the first, and we expect that unreacted α-chloroamide residues remain.
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Quantification of the Influence of Surface Structure on C–H Bond Activation by Iridium and Platinum

Dale F. Johnson and W. Henry Weinberg*

The trapping-mediated dissociative chemisorption of ethane on the closest packed Ir(111) surface has been investigated, and the activation energy and preexponential factor of the surface reaction rate coefficient have been measured. These results are compared to those of ethane activation on Pt(111) and on the missing row reconstructed Ir(110)-(1×2) and Pt(110)-(1×2) surfaces, allowing a quantitative determination of the effect surface structure has on the catalytic activation of C–H bonds. In the order Pt(111), Pt(110)-(1×2), Ir(111), and Ir(110)-(1×2), the activation energies for the dissociative chemisorption of ethane are 16.6, 10.5, 10.3, and 5.5 kilocalories per mole, demonstrating that the electronic and geometric effects are of approximately equal importance for ethane activation on these catalysts.

The catalytic reforming of petroleum naphtha fractions by supported bimetallic platinum and iridium catalysts is a process of great commercial importance in the fuels industry. The objective of reforming is the selective conversion of saturated hydrocarbons into high-octane aromatic components for gasoline. The overall yield of the process, however, is hampered by the competing hydrogenolysis of the feed stream hydrocarbon reactants (*1*). Also of importance in this industry is the catalytic conversion of C_1 to C_4 alkanes in natural gas into value-added fuel and feedstock chemicals (*2*). The common technological challenge relevant to these processes is the activation of the strong alkane C–H bonds: 105 kcal/mol for methane, 98 kcal/mol for primary bonds, 95 kcal/mol for secondary bonds, and 93 kcal/mol for tertiary bonds (*3*).

On supported catalysts, the metallic component is dispersed as small (10 to 100 Å) particles on high surface area substrates of alumina or silica, for example, in which a large fraction of the metal atoms may be considered as surface atoms (*1, 4*). The distinct microstructures of these crystallites induce steric and electronic differences among the catalytic sites, with those on the faceted surfaces having relatively lower reactivities than those at the edges and defects. In an effort to go beyond this qualitative description, we have undertaken a quantitative determination of the effect surface structure has on C–H bond activation.

Both platinum and iridium form face-centered-cubic lattice structures, and the four surfaces of interest in this report are Pt(111), Ir(111), Pt(110)-(1×2), and Ir(110)-(1×2). The (111) surfaces are the most stable, closest packed arrangements of surface metal atoms, whereas the (110) surfaces reconstruct into a (1×2) surface unit cell, often referred to as the "missing row" structure (*5*). A measure of the structural sensitivity of these four surfaces toward alkane activation is found in the results of ultrahigh vacuum (UHV) thermal desorption and low-energy electron diffraction studies (*6–8*). The threshold temperatures for the thermal activation of alkane C–H bonds were found to be 130 K for Ir(110)-(1×2) and 200 K for Pt(110)-(1×2). Under these UHV conditions, Ir(110)-(1×2) activates all alkanes except methane, Pt(110)-(1×2) activates only C_4 and higher alkanes, and Ir(111) and Pt(111) fail to activate saturated hydrocarbons up to C_7 and C_8, respectively.

Our understanding of the influence of surface geometric and electronic structure on catalysis has been extended considerably by recent studies of the apparent kinetic parameters of C–H bond activation on these four surfaces (*9–11*). We report here the results of experiments concerning the activation of ^{13}C-labeled ethane (C_2H_6) on Ir(111), which, when combined with recent studies of this reaction on Pt(111), Pt(110)-(1×2), and Ir(110)-(1×2), quantify the significant influence exerted by surface structure on C–H bond activation. As would be expected, the initial step in the activation of C_2H_6 is C–H (and not C–C) bond cleavage (a deuterium kinetic isotope effect was observed on all four surfaces).

The measurements on the Ir(111) surface were carried out in an ion-pumped UHV microreactor (200 liter/s) that has a base pressure of 2×10^{-10} torr and a volume of 10 cm^3 (*10, 12*). For the dissociative chemisorption of C_2H_6 over the surface temperature range that was used ($450\ \mathrm{K} < T_s < 1200\ \mathrm{K}$), the system was operated in a continuous flow mode. With the crystal held at a constant temperature, a C_2H_6 pressure of 1.0×10^{-7} torr was maintained for a reaction time, τ. The gas temperature, T_g, was always equal to the wall temperature (~300 K) because the mean-free path of C_2H_6 at this pressure was much greater than the dimensions of the microreactor. We determined the amount of dissociated C_2H_6 by titrating the carbonaceous residue on the surface after reaction with excess oxygen, producing exclusively ^{13}C-labeled CO_2 (*13*). By counting mass spectrometrically the amount of $^{13}CO_2$ that was produced, we obtained the total number of ^{13}C adatoms on the surface, N_c. The reaction conditions and times were such that the fractional coverage of ^{13}C adatoms was between 5 and 10% of a monolayer of carbidic carbon. The lower limit ensures

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