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13. The crystallographic data for **1** are as follows. Cell constants and an orientation matrix for data collection correspond to the triclinic space group $P\bar{1}$, with a = 12.903(3) Å, b = 18.047(4) Å, c = 9.341(4) Å, α = 94.75(3)°, β = 107.94(2)°, γ = 105.79(2)°, and V (cell volume) = 1958(1) Å^3. There is one molecule, $C_{54}H_{118}Si_{12}Bi_2$, per unit cell (Z = 1), giving a formula weight of 1522.51 and a calculate density (D_c) of 1.291 g cm^{-3}. The intensity data were collected through a glass capillary on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å), and the structure was solved by direct methods with SHELXS-86 [SHELXS-86, Program for Crystal Structure Determination, G. M. Sheldrick, University of Göttingen, Göttingen, Germany (1986)]. The linear absorption coefficient, μ, for Mo-Kα radiation is 46.91 cm^{-1}. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were included at calculated positions but not refined. The final cycle of full-matrix least square refinement was based on 5630 observed reflections [$I > 3.00\sigma(I)$, where I is the observed reflection intensity] and 307 variable parameters and converged with the unweighted and weighted agreement factors equal to R = 0.044 and R_w = 0.050. Atomic coordinates, bond lengths and angles, and the other important parameters will be deposited at the Cambridge Crystallographic Data Centre.
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The Stereodynamics of a Gas-Surface Reaction

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Measurements of the influence of reactant alignment on the rates of chemical reactions provide direct information concerning the atomic motions necessary for chemical transformation. Data presented here show that at low collision energy, the dissociative adsorption of deuterium (D_2) on the (111) surface of copper has a much higher probability for broadside than for end-on collisions. Furthermore, this steric preference is sensitive to the kinetic energy of the incident molecule, almost disappearing as the energy increases to 0.8 electron volt. This study shows that the dynamic conditions of a surface chemical reaction can profoundly influence the associated steric requirements.

Reactant orientation and alignment can affect or even dictate the outcome of a chemical encounter. Such steric effects are of ubiquitous importance in chemistry. For example, the reaction $K + CH_3I \rightarrow KI + CH_3$ proceeds only when the potassium approaches the iodine end of the CH_3I molecule (*1*). More generally, the rates of bimolecular nucleophilic substitution (S_N2) reactions are thought to be almost entirely determined by steric factors (*2*). Similarly, the activity and specificity of enzymes depend strongly on their steric interactions with the substrate (*3*), which may facilitate or preclude enzyme-substrate binding. In these reactions, a specific alignment geometry is expected to be required in order to follow the path of lowest energy between reactants and products; the preferred approach geometry will therefore reflect the structure of the reaction's transition state. Detailed knowledge of steric preferences can thus provide precise information on how the atoms are moving as the chemical reaction occurs; to gain a complete understanding, we must probe the steric requirements as a function of the collision conditions, that is, the vibration, rotation, and translation of the reactant. Unfortunately, despite the large body of empirical data substantiating the importance of steric effects, little is known about how the steric requirements depend on these aspects of the reactive encounter.

Chemical reactions occurring on surfaces offer an excellent opportunity to study chemical reactions at this level of detail. The surface naturally provides an oriented reactant that can be easily manipulated in the laboratory frame (*4*). Several theoretical calculations (*5*) have predicted strong steric effects in one of the simplest and best studied gas-surface reactions, dissociative adsorption of hydrogen at a Cu surface (*6*). The results indicate that the reaction occurs preferentially when the molecule approaches with its bond parallel to the surface. These predictions have recently been qualitatively confirmed experimentally (*7–9*), but no measurements on the kinetic-energy dependence of the steric effects were reported.

Here we report measurements of the alignment of D_2 formed in the reaction of D atoms on a Cu(111) surface as a function of the kinetic energy of the desorbing D_2. At low energy, the desorbing D_2 is strongly aligned with its bond axis parallel to the surface, but the probability of this alignment decreases rapidly with increasing energy. These results imply that the dissociative adsorption of D_2 at a Cu surface shows a strong steric preference for broadside collisions when the molecules strike the surface at low translational energy. This steric preference all but disappears as the collision energy is raised above the average activation barrier for the reaction. These measurements provide insight into the geometry of the transition state and the dynamics of the reaction in the critical energy regime near the barrier.

Our experimental approach is based on the polarization dependence of an appropriately chosen resonance-enhanced multiphoton ionization (REMPI) scheme for D_2. Linearly polarized light was used to selectively ionize D_2 in specific vibration-rotation (**v**, **J**) states (*10*) whose molecular bond axis is parallel to the electric field vector (*11*). The ionization was performed in a field-free region, such that the flight time of the ions to the detector gave a measure of the velocity of the desorbing D_2. By rotating the polarization of the

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probe light so that it was either parallel or perpendicular to the surface normal vector **z** and by recording the intensities of the detected signal for these two polarizations as a function of arrival time at the detector, $I_{\parallel}(t)$ and $I_{\perp}(t)$, we determined the degree of alignment of the desorbing sample as a function of velocity. The reaction took place on a clean, well-characterized Cu(111) surface under ultrahigh vacuum. A small fraction of a monolayer of D atoms was supplied to the surface by permeation through a single crystal maintained at 925 K. Further details of the apparatus and experimental methods have been given elsewhere (*8*, *12*).

The values of $I_{\parallel}(t)$ and $I_{\perp}(t)$ obtained with the probe laser tuned to detect D_2(**v** = 0, **J** = 11) (*13*) and D_2(**v** = 1, **J** = 6) (*14*) under otherwise identical conditions (Fig. 1) show that for both states, $I_{\perp}(t)$ is greater than or equal to $I_{\parallel}(t)$ at all arrival times. This relation means that there is a higher probability for the formation of molecules with bonds perpendicular to the surface normal than for the formation of molecules with bonds parallel to the surface normal (*15*). The relative difference between $I_{\parallel}(t)$ and $I_{\perp}(t)$ depends markedly on the arrival time: It is large for large arrival times (corresponding to low translational energies) and approaches zero for short arrival times (corresponding to high translational energies).

A quantitative description of the degree of alignment can be given in terms of the quadrupole alignment parameter $A_0^{(2)}$, which is defined as twice the expectation value of the second Legendre polynomial of the cosine of the angle Θ, the angle between the D_2 angular momentum vector **J** and the surface normal **z**.

$$A_0^{(2)} \equiv \langle 3\cos^2\Theta - 1\rangle \qquad (1)$$

Two limiting cases are commonly referred to in the literature. In the case where **J** is perfectly perpendicular to the surface, $\Theta = 0$ or π, and $A_0^{(2)} = 2$. Such a situation, only strictly possible for classical motion, is referred to colloquially as "helicoptering or propeller motion," because the molecules mimic the motion of a propeller "flying" away from the Cu surface. Perfect alignment of **J** parallel to the surface, where $\Theta = \pi/2$ and $A_0^{(2)} = -1$ (colloquially referred to as "cart-wheeling motion"), is the second classical limit.

The value of $A_0^{(2)}$ can be derived directly from the ratio of $I_{\parallel}(t)$ and $I_{\perp}(t)$ (*16*) using

$$A_0^{(2)} = \frac{(4 - 8J)P}{(J + 1)(3 - P)} \ \text{(P branch)} \qquad (2)$$

$$A_0^{(2)} = \frac{(8J + 12)P}{J(P - 3)} \qquad \text{(R branch)}$$

where $P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$. Using these equations, the translational-energy dependence of $A_0^{(2)}$ can be obtained from the data of Fig. 1. We first fit the data to a model of the time-of-flight spectra (*12*) that includes the effects of convolution over our experimental conditions (Fig. 1). At ~6 μs and longer, there is some discrepancy between the fit and the data for both D_2 states (Fig. 1) resulting from background contributions and from a nonactivated desorption process in which a small number of D_2 molecules leave the surface at kinetic energies close to a Maxwell-Boltzmann distribution at the surface temperature. Here we confine ourselves to the energies greater than about 0.3 eV, that is, times shorter than 6 μs, for which the activated desorption dominates the results.

From the fitted time-of-flight curves, $A_0^{(2)}$(**v**, **J**) was obtained as a function of the arrival time (equivalent to translational energy) (Fig. 2). The degree of alignment depends strongly on the translational energy: at 0.8 eV, $A_0^{(2)} \simeq 0.1$ for both states; in contrast, at the lowest energies probed here, $A_0^{(2)}$(**v**, **J**) is about half of its maximum possible value (*17*) and apparently still increasing with decreasing energy.

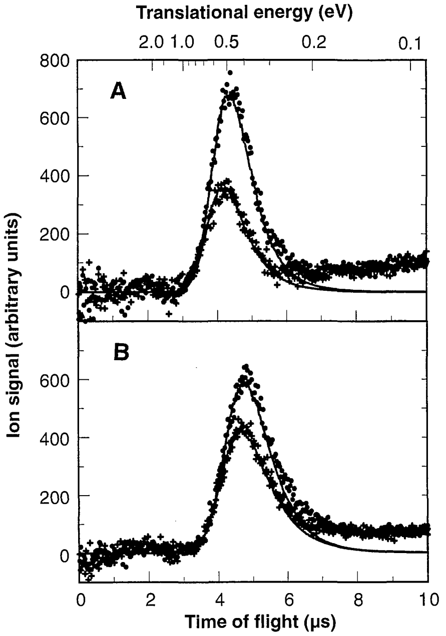

Fig. 1. Alignment-sensitive time-of-flight spectra of specific quantum states of D_2(**v**, **J**) formed by recombinative desorption from Cu(111): Results are for (**A**) D_2(**v** = 0, **J** = 11) (*13*) and (**B**) D_2(**v** = 1, **J** = 6) (*14*), each measured with the polarization of the probe laser perpendicular (●) and parallel (+) to the surface normal, but otherwise under identical conditions. The solid curves show the best fit to the experimental data obtained by a nonlinear least-squares procedure used to treat convolution over the instrumental parameters (*12*). Nonresonant and thermal backgrounds have been subtracted from the data.

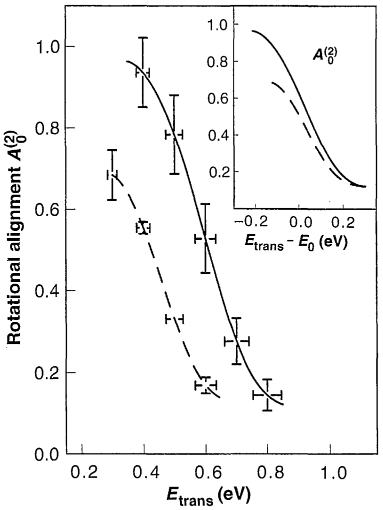

Fig. 2. The rotational quadrupole alignment moment $A_0^{(2)}$ as a function of the translational energy of the desorbing D_2 molecules in specific rovibrational quantum states, with the small effects of experimental convolution removed. The solid line shows the results for D_2(**v** = 0, **J** = 11), whereas the dashed line is for D_2(**v** = 1, **J** = 6), both obtained from the best fits to the time-of-flight spectra shown in Fig. 1. The vertical error bars reflect the uncertainties in the fits, noise in the data, and in the case of (0, 11), the difference between two independent measurements. The horizontal error bars reflect the energy resolution in the experiment. (**Inset**) $A_0^{(2)}$ plotted as a function of the difference between the translational energy E_{trans} and $E^{(\mathrm{iso})}$(**v**, **J**) (*12*), where $E^{(\mathrm{iso})}$(**v**, **J**) is the translational energy threshold for an unpolarized ensemble of molecules. The similarity between the two is even more striking when one notes that the quantum limiting value for $A_0^{(2)}$(0, 11) is 1.75, whereas that for $A_0^{(2)}$(0, 6) is 1.57.

To obtain a clearer understanding of the dramatic change in the degree of alignment observed as a function of the translational energy, we define $\mathcal{P}(\Theta)$, the classical distribution of D_2 rotational angular momentum vectors consistent with a specific value of the quantum mechanical $A_0^{(2)}$ parameter. Polar plots of $\mathcal{P}(\Theta)$ were constructed for two choices of $A_0^{(2)}$ (Fig. 3), reflecting the minimum and maximum degree of alignment obtained at different translational energies. At high translational energy, the distribution is nearly isotropic and the polar plot for $A_0^{(2)} = 0.1$ (shown as a dashed line) is nearly circular, indicating nearly equal probability for all values of Θ. At low translational energies, $A_0^{(2)} = 0.9$, resulting in a strongly peaked distribution.

It is perhaps more intuitive to discuss

these results in terms of the steric preference of the reverse reaction, obtained by applying the principle of detailed balance (7). According to this principle, the observation of preferred motion of the D_2 product of the desorption reaction, 2D(ad) $\xrightarrow{Cu}$ D_2(g) (ad, adsorbed), indicates a dynamical enhancement of the reverse reaction, D_2(g) $\xrightarrow{Cu}$ 2D(ad). The observed "helicoptering" alignment of the recombinative desorption products observed here indicates that incident D_2 dissociatively adsorbs with the highest probability when it collides with its bond parallel to the surface. The dependence of the alignment on energy indicates that this steric preference is strong at low translational energies (~0.3 eV) and decreases rapidly with increasing translational energy to nearly zero at 0.8 eV.

It is well known that for dissociative adsorption of D_2 on Cu to occur, an activation barrier in the potential-energy surface (6) of the molecule-surface system has to be overcome. Therefore, a steric preference for dissociation of molecules undergoing broadside collisions can be easily understood as arising from a smaller activation barrier for broadside collision of the molecule with the surface than for a collision involving a tilted configuration. Two competing factors could influence the translational-energy dependence of the steric preference: (i) realignment effects and (ii) changes in the ratio of the anisotropy energy to the available kinetic energy.

In principle, reactant molecules approaching a surface in an unfavorable alignment can be realigned by the anisotropic interaction potential between the reactant and the surface, in a manner that brings them closer to the lowest energy pathway for the reaction. When such a "steering" (18, 19) effect is strong, the initial alignment of the reactant becomes irrelevant, and a strong steric preference in the reaction probability is not expected. Such a steering effect is expected to become increasingly important as the translational energy of the reactant is lowered because the time spent under the influence of the anisotropic part of the potential is expected to increase as the translational energy is lowered. Consequently, we would predict a decrease in the steric preference (or a lowering of the alignment of the desorption products) at low translational energy if the steering dynamic is dominant in the D_2-Cu(111) system. We observe the opposite trend; thus, steering effects do not play a large role at the collision energies probed here.

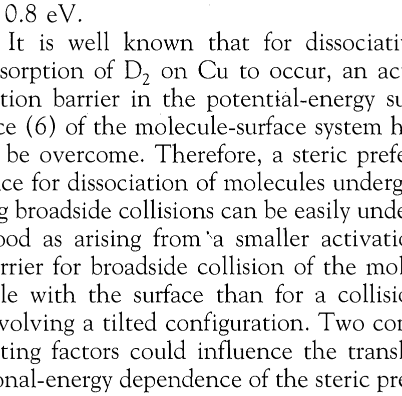

Fig. 3. Polar plot of $\mathcal{P}(\Theta)$, the classical probability distribution of the angle between the D_2 angular momentum unit vector **J** and the surface normal unit vector **z**, defined as $\mathcal{P}(\Theta) \equiv \frac{1}{2} + \frac{5}{4} \cdot A_0^{(2)} \cdot P_2(\cos \Theta)$, where $P_2(x)$ is the second Legendre polynomial. The minimum observed alignment corresponds to $A_0^{(2)} = 0.1$ (dotted curve), and the maximum observed alignment corresponds to $A_0^{(2)} = 0.9$ (solid curve).

Next, we consider the changing ratio of the anisotropy energy relative to the kinetic energy in excess of the activation barrier. At the lowest kinetic energy, only those molecules oriented close to the minimum-energy configuration in the transition state are able to dissociate. As the kinetic energy of the incident D_2 is increased, molecules with a wider range of alignments are able to dissociate, and the steric preference decreases, in agreement with our measurements. We can gain further support for this interpretation of the energy dependence of the steric effect by considering more carefully how much energy is available to overcome the anisotropy of the dissociation barrier. The energy available for this purpose is not simply the total kinetic energy of the incident molecules. Rather, it is the kinetic energy in excess of that required for dissociative adsorption. It is known from experiments that are not sensitive to reactant alignment that the kinetic energy required to overcome the dissociation barrier depends markedly on the (**v**, **J**) state (12). The dissociative adsorption thresholds $E^{(\mathrm{iso})}(0, 11)$ and $E^{(\mathrm{iso})}(1, 6)$ have been previously determined (20) [$E^{(\mathrm{iso})}(\mathbf{v}, \mathbf{J})$ indicates the threshold for a specific (**v**, **J**) state averaged over alignment]. The variation of $A_0^{(2)}$ with the energy available to overcome the anisotropy energy, $E_{\mathrm{trans}} - E^{(\mathrm{iso})}(\mathbf{v}, \mathbf{J})$, for (0, 11) and (1, 6) are comparable (Fig. 2, inset). The similarity of these two curves is evidence for the fact that it is the translational energy E_{trans} above and beyond the dissociative threshold energy that is capable of overcoming the anisotropy energy.

The reactions of deuterium and its isotopomers on Cu are useful for studying surface stereodynamics. Unfortunately, the polarization-sensitive and state-specific detection of these molecules is difficult. Improvement of the detection sensitivity (for example, by using four-wave–mixing techniques) promises to allow measurements of the stereodynamics of this model reaction over the full range of reactant motion of chemical interest.

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10. Here, **v** and **J** refer to, respectively, the vibrational and rotational quantum numbers of the detected quantum state of D_2. We used REMPI for this work. Vacuum ultraviolet light at a frequency of ~105 nm was generated by frequency-tripling 5-ns pulses of 315-nm light in Xe. This light was used to resonantly excite D_2 in the $B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ absorption system. The residual untripled light was used to ionize the *B* state.
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13. The $\mathbf{J} = 11$ state was probed using the *P*(11) line of the $\mathbf{v}' = 7 \leftarrow \mathbf{v}'' = 0$ band of $B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$.
14. The $\mathbf{J} = 6$ state was probed using the *R*(6) line of the $\mathbf{v}' = 8 \leftarrow \mathbf{v}'' = 1$ band of $B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$
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