Angular Dependence of Sticking Coefficients on Tungsten*

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The sticking coefficients s of H_2, D_2, N_2, CO, and CO_2 have been measured as a function of angle of incidence on the (100) and (110) planes of W. s generally increases towards grazing incidence as predicted by a classical model involving energy dissipation by phonon production. However for H_2 and D_2 on W(110), s decreases markedly towards grazing incidence. This suggests the existence of a threshold for energy transfer.

While sticking coefficients are experimentally found to vary by orders of magnitude between different gases, substrates, and crystal planes,[1] the mechanisms of energy transfer in gas-surface collisions are still matters of speculation. A key obstacle in interpreting such data is the fact that most data are obtained by exposing the surface to an isotropic flux of gas, i.e., by averaging over incident angles. Only a few molecular-beam studies of adsorbing gases have been published, and they have either focused on the reflected portion of the beam[2] or used a polycrystalline substrate.[3]

We report here measurements of the angular dependence of the sticking coefficients of several gases on two low-index planes of W. We find generally significant angular dependences. In most cases, our results can be interpreted classically, but for H_2 and D_2, the data do not appear to be compatible with classical theories. We believe that these results yield significant information on the potential energy surface and the mechanisms of energy transfer in gas-surface collisions and on the interpretation of molecular-beam experiments.

Our molecular-beam apparatus was a 2-liter Pyrex chamber containing a mass spectrometer. A directed gas flux from a Pyrex capillary 1 mm in diameter and 25 mm long impinged on a rotatable single-crystal disk positioned ~7 cm from the capillary so that the entire front face of the disk received a uniform flux with an angular divergence of ~2°. The crystal was cut and polished such that both faces were within 2° of the stated orientation. The cyrstal was heated by electron bombardment to 2500°K. Incident angles φ could be determined to within ±2°. The system was pumped primarily by a tantalum-film getter pump with a measured pumping speed of ~80 l/sec.

Crystals were cleaned by heating in O_2 and by

flashing repeatedly to 2500°K. The flash-desorption spectra of H_2 and CO at saturation confirmed that the surfaces were free of carbon and oxygen.[4] All data reported here were obtained at room temperature. A steady-state flux through the capillary was established such that a coverage of ~0.1 monolayer was attained in 300 sec. Amounts adsorbed in a 200-sec interval were measured as a function of φ by measuring areas under flash-desorption spectra. Adsorption from the background was compensated for by determining the coverage with the crystal perpendicular to the beam. Adsorption on edge areas, a few percent of that on the faces, was corrected for. Contaminant coverages were always less than 10% of those of the gas being studied.

The difference between the amounts adsorbed at an angle φ and at 90°, $A(\varphi) - A(90°)$, is proportional to $s(\varphi)\cos\varphi$. The accuracy of the data for $A(\varphi) - A(90°)$ was such that they could be fitted by an expression of the form $a\cos\varphi + b\cos3\varphi$. Thus one obtains

$$s(\varphi) = s(0)[1 - 4b\sin^2\varphi/(a+b)]. \tag{1}$$

In Fig. 1 are displayed typical data for CO on W(100) and H_2 on W(110). For $\varphi > 60°$, amounts adsorbed from the beam could not be determined accurately because of the relatively larger background contribution. The solid lines in Fig. 2 are curves fitted to experimental data as described above. We see that $s(\varphi)$ increases slightly with increasing φ except for H_2 and D_2 on W(110), where $s(\varphi)$ decreases sharply with increasing φ.

Condensation requires that the normal component of the kinetic energy of the incident gas molecule, $2kT_g\cos\varphi$, be transferred to the surface during the collision. This could occur either by generation of phonons in the substrate, by excitation of conduction electrons, or by electronic interactions involving chemical-bond formation. We have recently examined the angular depen-
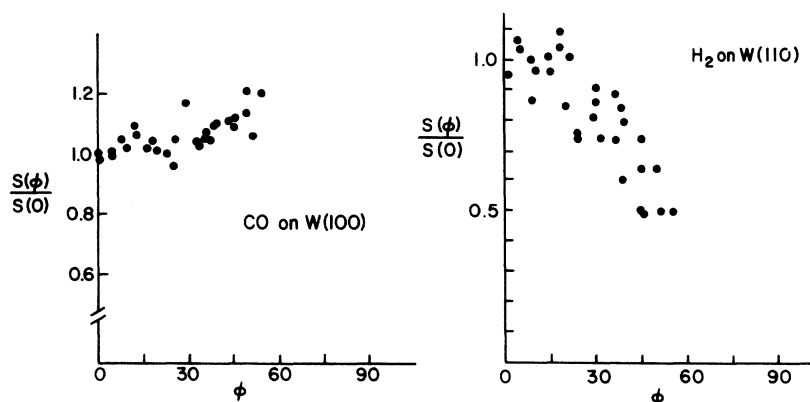
FIG. 1. Typical data of $s(\varphi)/s(0)$ for CO on W(100) and H_2 on W(110).

dence of $s(\varphi)$ predicted by a simple classical model in which the gas-surface interaction potential is assumed to be a one-dimensional square well.[5] This model should be qualitatively correct for light gases on low-index planes because the collision time is short compared with the response time of the heavy substrate atoms and the potential experienced by an incident molecule should be reasonably uniform parallel to the surface. Our model (and, we believe, classical lattice theories in general) predicts that s generally *increases* towards grazing incidence since less energy must be transferred for condensation to occur. The results for all gases except H_2 and D_2 are described qualitatively by this model. The dashed lines in Fig. 2 are curves calculated for CO on these planes.

For H_2 and D_2, classical theories appear to fail. On W(100), s is predicted[5] to increase by a factor

of ~4 between 0 and 60°, whereas s actually increases by only ~5%. On W(110), classical theories predict the *wrong sign* for the angular dependence of s. Since s decreases while the amount of energy to be transferred decreases, we infer that the incident gas molecule may require a minimum perpendicular component of kinetic energy for energy transfer to occur. Also the absence of a marked isotope effect between H_2 and D_2 suggests that the threshold involves the kinetic energy rather than the momentum of the gas molecule.

This threshold could arise if a potential barrier existed at the surface. A potential barrier has been proposed to explain the deviations of desorption fluxes from $\cos\varphi$ which are observed in some gas-solid systems[6] (but not the ones considered here). Calculations including a potential barrier in the square-well model[7,5] yield qualitatively the right shape of $s(\varphi)$ but do not reproduce other re-
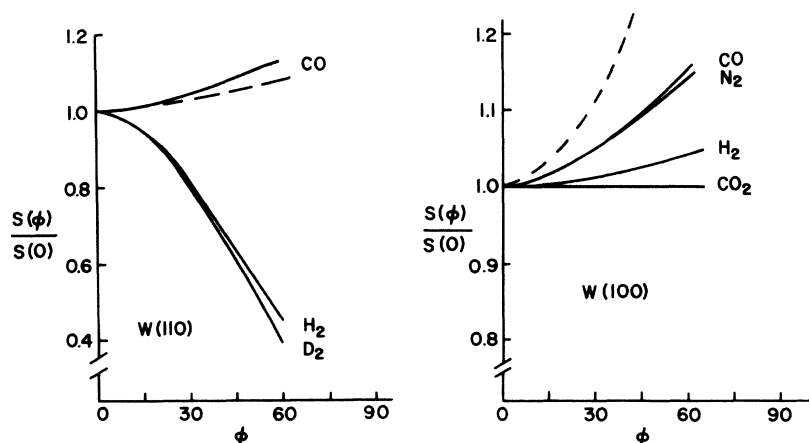

FIG. 2. Curves of $s(\varphi)/s(0)$ fitted to experimental data according to Eq. (1). Dashed curves are calculated for CO according to the square-well model (Ref. 5).

cent experiments in this laboratory[7] on the gas-temperature dependence of the angle-averaged sticking coefficient s for H_2 on $W(110)$ and on the isotope effect for s between H_2 and D_2. A calculation using the square-well potential and quantized motion of the surface atoms gives the correct form for $s(\varphi)$ but predicts that the angle-averaged sticking coefficient s increases with increasing gas temperature, which is at variance with our recent experiments.

These results demonstrate a significant dependence of the sticking coefficient on the angle of incidence. This can have an important bearing on the interpretation of molecular-beam—surface experiments and on catalysis in situations where fluxes may not be isotropic. The results also indicate that our present knowledge of the interaction potential and the energy transfer process in gas-surface collisions is inadequate and that momentum transfer from the gas to the surface probably cannot account for all the features of condensation rates.

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Superionic Conductors: Theory of the Phase Transition to the Cation Disordered State

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We suggest that it is the interaction of interstitial cation defects with the strain field they induce which is primarily responsible for the phase transition to the cation disordered state of the superionic conductor. This idea is developed in terms of a simple model that yields an analytic solution for the phase transition and relates the necessary strength of the interaction to anomalously large free volumes of cation interstitial formation.

The so-called "superionic conductors," typified by the cation disordered phases of the silver halide-chalcogenides and their various derivatives (e.g., AgI, Ag_2S, Ag_3SI, $RbAg_4I_5$), exhibit remarkable physical properties.[1] Structurally, they may be characterized as consisting of a relatively rigid crystalline framework composed of the nonconducting ionic species, with the conducting cations, usually Ag^+ or Cu^+, distributed in a statistically disordered fashion among the available sites offered by the crystalline nonconducting framework. There are usually several, and sometimes many, possible sites per conducting cation. As was first recognized by Strock[2] in 1934, the exceptionally high ionic conductivity[1] and liquidlike levels of cation diffusivity[1] of these solids result from an almost moltenlike state of the disordered cation species. Interestingly, the physical picture of these disordered cations as having "arrived" from some sort of melting transition is emphasized by the fact that the disordered cation state typically arises as a result of a first-order structural phase transition from a lower-temperature crystalline phase in which the cations are crystallographically ordered. At the transition to the ordered phase the ionic conductivity drops discontinuously by several orders of magnitude to the relatively low levels of ionic conductivity characteristic of typical ionic solids.[1] The accompanying heat of transition is comparable to that of a normal melting transition.[3]

An as yet unresolved problem in the study of this interesting class of solids is an elucidation of the physics behind the unique phase transition to the superionic conductor phase. It is the purpose of this Letter to present a theoretical model of such a phase transition.

In the low-temperature phase $(T < T_c)$ one can imagine that a small fraction of the ordered conducting cation species becomes thermally pro-