therefore an alternating propensity for even and odd *N* states is predicted, in agreement with the experimental observations. More detailed calculations show that the OH product rotational distributions are very sensitive to the geometry and energy of the curve crossings (*3*). As pointed out by Dixon *et al.*, the experiment constitutes a molecular example of Young's famous double-slit interference experiment (see the figure).

Oscillations in the probabilities for photodissociating molecules into rotational product states have been observed in several molecules before, including H_2O at other wavelengths of laser light. The results have often been explained by a simple model that projects the vibrational wave function of bent H_2O onto OH product rotational states (*1*). However, for initial linear H-O-H or O-H-H geometries, such a projection does not give an oscillating function. Furthermore, this model does not predict a propensity for producing OH in odd or even rotational states.

Even/odd propensities in rotational states occur in the collisions of symmetric diatomic molecules, such as N_2, with atoms and are also found in collisions involving near-symmetric molecules such as CO (*6*). They can be accounted for by a semiclassical theory that allows for quantum interference effects (*7*). However, no such propensities are expected for collisions involving highly asymmetric OH radicals. It is the crossing of two potential surfaces at two different geometries connecting with the same molecular products that leads to the new interference effect observed by Dixon *et al.*

A complete and rigorous theoretical treatment of the photodissociation of water is a major challenge. Most molecular properties can be described in terms of the Born-Oppenheimer approximation, which states that the time scales of electronic and nuclear motion are so different that they can be treated as independent. However, an increasing body of experimental and theoretical results suggests that several important molecular problems, including the photodissociation of H_2O, require a treatment beyond the Born-Oppenheimer approximation. First, the three different potential energy surfaces—$\tilde{X}$, $\tilde{A}$ and $\tilde{B}$, and the coupling terms that enable motion between these surfaces must be calculated. Then the equations describing the coupling of electronic, translational, rotational, and vibrational motion need to be solved to calculate the probabilities for forming OH in particular rotational and vibrational states. Such computations have not yet been done for the photodissociation of water but are now just within the reach of modern theoretical chemistry.

As Dixon *et al.*'s results show, the continuing development of increasingly sophisticated experimental methods to photodissociate molecules, and detect their quantum states precisely, can lead to surprises such as the "double slit" interference effect in the photo-dissociation of H_2O, representing a challenge for theory to explain.

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PERSPECTIVES: MATERIALS SCIENCE

Tack—a Sticky Subject

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The energy required to separate two objects not permanently bound together is a measure of the tack. We can all recall situations when the stickiness of a substance—such as chewing gum or partially dried paint—results in an unpleasant experience. But there are numerous situations where tack is highly desirable. Adhesive tape, rubber cement, and Post-It notes all use tack to great advantage.

Worldwide, the production and use of adhesives and tackifiers support an industry that nets tens of billions of dollars annually. Applications range from cosmetics to athletics, microelectronics to aerospace, and textiles to stationery. The sticky substances may be natural (starches or natural rubber cements, for example), organic (such as derivatives of collagen, proteins, or cellulose), or synthetic (usually polymer-based thermosets, thermoplastics, or elastomers). All of these substances are produced with the goal of controlling the energy required to separate two objects.

Despite the vast number of different adhesives and tackifiers, it remains difficult to produce a material that is sticky only when you want it to be. The ability to trigger tack at a predetermined level in response to an environmental change—for example, in temperature, pressure, or pH—thus holds tremendous potential. To gain such control requires tailoring the parameters that influence tack, not just by modifying a surface but by controlling the mechanical properties of the adhesive and the substrate to which adhesion is desired. On page 1246 of this issue, de Crevoisier *et al.* (*1*) present a unique means of manipulating tack and, by tailoring both surface and bulk properties of the substrate, taking advantage of a phase transition in a polymer from an ordered to a disordered state.

To understand the requirements for successful adhesion, consider first a hard flat surface (panel A of figure). An obvious condition for tack is that two materials wet. This is governed by the Young equation:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \qquad (1)$$

which relates the contact angle θ to the surface energy of the solid (γ_{SV}), the surface energy of the liquid (γ_{LV}), and the interfacial energy (γ_{SL}) (*2*). Wetting of the surface will occur if γ_{LV} is sufficiently less than γ_{SV} such that the reduction in the surface energy outweighs nonfavorable interfacial interactions, or if the interfacial interactions at the solid-liquid interface are sufficiently favorable to overcome any energetic penalties at the air interface.

These simple criteria have driven a tremendous amount of research on the surface modification of materials (*3*). For example, a surface can be chemically modified so that its properties vary from being hydrophobic to hydrophilic or oleophobic to oleophilic. Alternatively, materials can be made "smart," such that they respond to contact with another material or to an environmental change. Koberstein *et al.* (*4*), for example, used a functional additive with a low surface energy, preferentially segregating the additive to the surface. In contact with a second material containing an additive with a complementary functional group, wetting and adhesion were promoted by the interactions between the functional groups across the interface.

A phase transition in the substrate can also be used (*5*, *6*) to activate a response. Following the latter approach, de Crevoisier *et al.* (*1*) take advantage of an ordering transition in a polymer containing alkyl and perfluoroalkyl side chains to turn tack on and off. At low temperatures, the perfluoroalkyl side chains (which have low surface energy) segregate to the surface,

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and the polymer is crystalline and the structure fixed. At elevated temperatures, crystal melting imparts mobility to the polymer such that it can respond to external stimuli. If a hydrocarbon is brought in contact with the surface, a surface rearrangement occurs, moving the alkyl segments to and the perfluoroalkyl segments away from the interface. Such a surface reorganization is generally evidenced by a hysteresis between the advancing and receding contact angles. But the observed hysteresis is much too large for the restructuring to be confined to the surface and requires changes in the bulk of the material. As will be discussed shortly, changes in the bulk mechanical properties also dramatically alter wetting behavior.

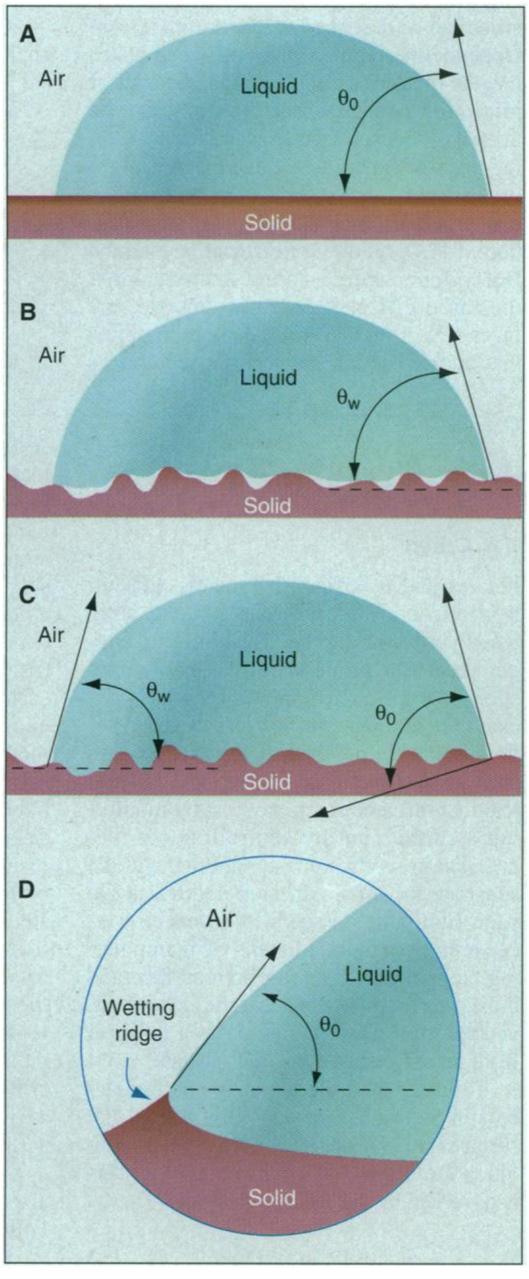
A second factor affecting tack is the surface roughness (*7–9*). If contact across the surface is incomplete (panel B of figure), the tack will be reduced in proportion to the reduction in the contact area. Conversely, if the interstices on the rough surface are filled by the second component (panel C of figure), the contact area and therefore the tack will increase. The amplitudes and lateral correlations of the surface roughness and the flow properties of the wetting component will thus dictate the wetting behavior (*10*). However, the role of surface roughness in wetting and adhesion is not yet quantitatively understood (*11*, *12*).

De Crevoisier *et al.* (*1*) control surface roughness through the melting phase transition in their material. The surface of a semicrystalline polymer is rough with crystalline lamellae protruding through the surface. Driving the polymer into the molten state causes a dramatic reduction in the surface roughness. In the molten state, the contact area between the two bodies will, in general, increase, thereby increasing the tack.

Shanahan and co-workers (*13*, *14*) noted that the viscoelastic properties of the substrate must also be considered when describing surface wetting and tack. In the case of tack, if one body is compliant, energy will be dissipated by a deformation of the soft body until failure occurs. A simple demonstration of this is to place your finger on a tacky surface. As you pull your finger away, it stretches until, hopefully, adhesive failure occurs.

The situation changes if both materials are fluid (panel D of figure). Local deformation of the substrate results in the formation of a wetting ridge. The height of this ridge and the rate at which the drop spreads are inversely proportional to the shear modulus of the substrate. The dissipation of energy into the substrate will retard or even stop the advancing front. Similar behavior is observed on dewetting (*15–17*).

This phenomenon is exploited by de Crevoisier *et al.* (*1*), who induce a phase transition in the substrate by increasing the temperature, changing it from a rigid, crystalline solid to a viscoelastic fluid. At low temperatures, the substrate is rigid with a large surface roughness and thus low tack. Above the transition, the substrate is viscoelastic with a smooth surface. This phase transition increases the tack by markedly changing the mechanical properties of the substrate. Increasing temperature further above the transition temperature decreases the viscosity of the substrate, which lowers the viscoelastic dissipative capacity of the substrate and, in turn, reduces tack again.



Changing tack. Wetting conditions affect the tack of a material. **(A)** A fluid on a solid substrate. **(B)** A fluid on a rough substrate with reduced contact area. **(C)** A fluid on a rough surface with full contact. **(D)** A fluid on a viscoelastic solid. θ_w and θ_0 are defined in (*10*).

Thus, by using a simple melting phase transition, de Crevoisier *et al.* (*1*) achieved control over the surface and bulk mechanical properties of their polymer. A delicate balance between factors that enhance and reduce tack gives rise to a maximum in the tack over a very narrow temperature range. It is, of course, no accident that the phase transition in the work of de Crevoisier *et al.* (*1*) occurs at 35°C, slightly below body temperature. Used on grips on racquets, clubs, bats, and so forth, maximum tack is achieved during use but tack is substantially reduced for dirt and foreign matter when the grip is not in use. By altering the length of the pendant side chains on the polymer, the transition temperature can be fine tuned further. De Crevoisier *et al.* (*1*) have demonstrated a highly versatile means of tailoring the tack of a material in an elegant, simple manner using its bulk properties.

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