plankton that are strong DMS producers, such as coccolithophorids (*5*). However, attempts to relate the DMS concentration fields to parameters indicative of marine biological activity, such as chlorophyll concentration, plant nutrients, sea surface temperature, or clear sky irradiance, all fail to produce correlation coefficients high enough to be useful. This is a great pity because a significant relation between DMS concentration and, for example, chlorophyll (which is routinely measured by satellite) would provide a convenient route for establishing DMS concentrations at much finer time and space scales than are currently possible and would reduce the need for expensive seagoing measurements.

In the meantime, we have to focus on the processes that control formation of DMS and its release to seawater, for example, zooplankton grazing (*6*) and viral attack (*7*), coupled with modeling approaches (*8*) and additional field experiments in undersampled areas. Even if the concentration field was known with adequate spatial and seasonal coverage, however, it remains difficult to convert it into a flux distribution, because the rate of transfer of DMS from sea to air is uncertain to about a factor of two (*9*). Quantification of this sea-to-air flux is a vital prerequisite for assessing the environmental impact of DMS. Progress is most likely to come once a micrometeorological technique, such as eddy correlation or eddy accumulation, is developed that can directly measure DMS fluxes across the sea surface.

References

1. J. E. Lovelock, R. J. Maggs, R. A. Rasmussen, *Nature* **237**, 452 (1972).
2. R. J. Charlson, J. E. Lovelock, M. O. Andreae, S. G. Warren, *ibid.* **326**, 655 (1987).
3. G. V. Wolfe, M. Steinke, G. O. Kirst, *ibid.* **387**, 894 (1997).
4. A. J. Kettle *et al.*, *Global Biogeochem. Cycles* **13**, 399 (1999).
5. P. S. Liss, A. D. Hatton, G. Malin, P. D. Nightingale, S. M. Turner, *Philos. Trans. R. Soc. London B* **352**, 159 (1997).
6. K. L. Daly and G. R. DiTullio, in *Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds*, R. P. Kiene *et al.*, Eds. (Plenum, New York, 1996), pp. 223–238.
7. G. Malin, W. Wilson, G. Bratbak, P. S. Liss, N. H. Mann, *Limnol. Oceanogr.* **43**, 1389 (1998).
8. A. Gabric, N. Murray, L. Stone, M. Kohl, *J. Geophys. Res.* **98**, 22805 (1993).
9. K. Suhre, *ibid.* **103**, 16433 (1998).

PERSPECTIVES: CHEMICAL PHYSICS

Interfering with Water

David C. Clary

Molecular bonds can be broken by exciting them with laser light; detection of the energy of the product atoms and molecules reveals unprecedented detail about photodissociation mechanisms (*1*, *2*). On page 1249 of this issue, Dixon *et al.* (*3*) use such techniques to show that two water photodissociation channels can mimic the two slits in Young's famous double-slit electronic interference measurement, which first demonstrated the wave nature of electrons. These remarkable molecular double slits show that even simple, ubiquitous molecules such as water still hold surprises.

Dissociation of water by sunlight occurs continually in Earth's atmosphere (*4*). Dixon *et al.*'s experiment takes a closer look at this process by exciting individual molecules of H_2O with light having a wavelength of 121.6 nm. The excitation leads to dissociation of the water molecules via

$$H_2O \rightarrow OH(N) + H \tag{1}$$

producing OH radicals in their electronic ground state but with their rotational quantum states taking particular integer quantum numbers N. A sophisticated time-of-flight laser technique is used to detect the energy of the H atoms from which N can be inferred.

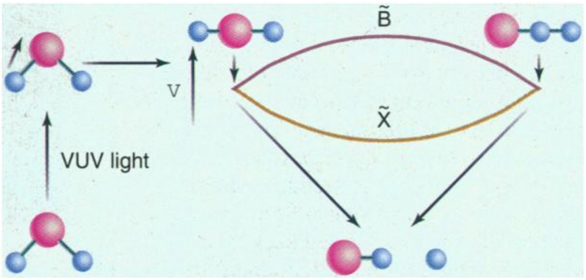
Excitation with light at 121.6 nm causes electrons in H_2O in the ground "$\tilde{X}$" electronic state to jump to antibonding orbitals, producing an electronically excited state labeled "$\tilde{B}$." In its ground electronic state, H_2O has a bent structure. If it stays bent in the $\tilde{B}$ state, dissociation to produce OH + H cannot occur because no appropriate dissociation channel can be reached from this conformation (*1*). However, if one of the H atoms moves around OH to produce linear H-O-H or O-H-H geometries, the potential energy curve for the $\tilde{B}$ state crosses that for the $\tilde{X}$ ground state (see the figure) (*5*). Such a "conical intersection" opens up a dissociation channel for H_2O to dissociate into OH and H in their electronic ground states. The change in geometry of H_2O from bent to linear leads to a considerable torque being placed on the OH molecules, which are therefore produced in highly excited rotational states, with $N = 45$ being favored (*3*).

A particularly interesting aspect of this dissociation mechanism is that two different linear geometries on the $\tilde{B}$ electronic state, H-O-H and O-H-H, can both lead to curve crossing and thus molecular dissociation, producing exactly the same OH(N) + H products (see the figure). The quantum wave functions arising from these two dissociation routes can interfere with each other to favor or disfavor the production of certain N states of OH. The experiment shows that there is a marked propensity for producing OH in odd N states for larger values of N (*3*).

To explain these results, Dixon *et al.* use a simple quantum mechanical model (*3*). The component of the molecular wave function that allows dissociation to a particular OH rotational state N is approximated as

$$\Psi_N = \psi_1 + m_N \psi_2 \tag{2}$$

where ψ_1 and ψ_2 are wave functions associated with the linear H-O-H and O-H-H geometries, respectively, on the excited state B. The curve crossing onto the X state allows both ψ_1 and ψ_2 to describe dissociation to produce OH(N) + H. m_N represents the symmetry of the rotational wave function of OH with respect to the H-O-H or O-H-H geometries. It takes values of ±1 depending on whether the rotational state N is even or odd. From Eq. 2, two terms in the probability of producing OH in rotational state N are positive, but the third "interference" term is linear in m_N and can thus be positive or negative. m_N is determined by the parity of N, and



A molecular example of Young's double-slit interference experiment. The molecule is first excited from the ground ($\tilde{X}$) state to the excited ($\tilde{B}$) electronic state. One H atom then moves around OH, the bond length of which remains constant. The potential energy curves (V) for this H-atom motion are shown schematically for the $\tilde{B}$ and $\tilde{X}$ states. The two potential curves cross for linear H-O-H and O-H-H geometries, giving two gateways for dissociation into OH(N) + H. Red, oxygen; blue, hydrogen; VUV, vacuum ultraviolet.

The author is in the Department of Chemistry, University College London, London WC1H OAJ, UK. E-mail: d.c.clary@ucl.ac.uk

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.

References

1. R. Schinke, *Photodissociation Dynamics* (Cambridge Univ. Press, Cambridge, 1993).
2. P. L. Houston, *J. Phys. Chem.* **31**, 12757 (1996).
3. R. N. Dixon *et al.*, *Science* **285**, 1249 (1999).
4. R. P. Wayne, *Chemistry of Atmospheres* (Oxford Univ. Press, Oxford, 1992).
5. D. R. Yarkony, *Mol. Phys.* **93**, 971 (1998).
6. J. N. Murrell and S. D. Bosanac, *Introduction to the Theory of Atomic and Molecular Collisions* (Wiley, Chichester, 1989).
7. W. H. Miller, *J. Chem. Phys.* **54**, 5386 (1971).

PERSPECTIVES: MATERIALS SCIENCE

Tack—a Sticky Subject

T. P. Russell and H. C. Kim

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,

---

The authors are in the Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA 01003, USA. E-mail: russell@iskara.pse.umass.edu.