Chemistry

Ivars Peterson reports from Washington, D.C., at the annual meeting of the American Association for the Advancement of Science

Chemist in the driver's seat

Many chemical reactions occur extremely rapidly. Chemical bonds break and form in a matter of femtoseconds; atoms shift positions in mere picoseconds. In such cases, what happens during the first tiny fraction of a second often determines how quickly and readily a particular chemical reaction proceeds. That sensitivity also provides an opening that chemists can exploit for manipulating reactions by directly intervening in the initial stages. The recent development of sophisticated equipment for generating strings of closely spaced laser pulses – each pulse only a few femtoseconds long – now makes such manipulation on a submicroscopic scale conceivable.

"By using a proper sequence of short light pulses, the experimentalist can get in there and alter what happens – can control rather than just watch," says chemist Graham R. Fleming of the University of Chicago.

Quantum mechanics makes this kind of control possible. In studying reaction rates, chemists generally picture the atoms and electrons involved in these processes as particles. They tend to ignore the quantum-mechanically determined interference effects possible when waves associated with particles such as electrons add together as they meet peak-to-peak or cancel each other as they meet peak-to-trough. Although such complicated effects undoubtedly occur, chemists usually assume that interactions between these electron waves and waves associated with nearby molecules would smooth out any peaks and troughs into tiny, random ripples before anything of chemical interest happens.

However, some reactions occur so fast that one can't ignore quantum-mechanical effects, Fleming says. In such cases, molecular vibrations and other motions have too little time to wash out wave effects. Indeed, computer simulations show that electron waves can produce an orderly interference pattern that persists through the first moments of a chemical reaction. These models predict that such a pattern would have a substantial influence on how rapidly the reaction proceeds.

To demonstrate this wave effect in the laboratory, Fleming and his collaborators developed a special laser system for generating pairs of femtosecond pulses of visible light so that successive pulses are either in phase (two peaks) or out of phase (one peak and one trough). They studied the effect of these pairs of pulses on electrons in iodine molecules by measuring the amount of light given off by the pulse-excited molecules.

The researchers discovered they could control how much the iodine gas fluoresced by changing the phase relationship between successive pulses. They got less light when the two pulses entered the gas out of phase and more light when the pulses were in phase, confirming that quantum interference had occurred. In other words, the first pulse would excite electrons in the iodine molecules, and the second pulse, depending on its phase, would either cancel or augment the effect of the first.

"We've demonstrated the simplest kind of control of molecular dynamics," Fleming says. "It remains to be seen whether this technique can be applied to systems of more general interest."

Fleming suggests that quantum effects may play a key role in photosynthesis, explaining why the first step – the transfer of an electron – actually occurs much more rapidly and efficiently than predicted by calculations based on conventional theory. By including quantum effects in their calculations, chemists could probably come closer to predicting the correct rate, Fleming says. Someday, researchers may even understand the process well enough to use light pulses to interrupt or accelerate electron transfer, thereby influencing the rate of photosynthesis.

Space Sciences

Uncertainties surface over Hubble 'fix'

NASA wants a second opinion about treating its troubled eye in the sky.

Optical problems have impaired the Hubble Space Telescope's vision since NASA launched the instrument last April 12. A panel advising the space agency on how to compensate for the telescope's incorrectly shaped primary mirror and recurring "jitters" handed over its conclusions to NASA officials in a 120-page "strategy" report on Jan. 15. But now the space agency is assembling a second team of scientists and engineers to reevaluate the first group's unanimous recommendations.

Development of a package of corrective mirrors, which spacewalking astronauts would install in December 1993, figures prominently in the strategy panel's recommendations. This box of mirrors – called COSTAR, for Corrective Optics Space Telescope Axial Replacement – should correct the optical distortion afflicting three of the telescope's scientific instruments: its faint-object spectrograph, high-resolution spectrograph and faint-object camera. However, uncertainties about COSTAR's potential cost and development time justify seeking a second opinion, says Charles J. Pellerin, head of astrophysics at NASA's Office of Space Science and Applications in Washington, D.C.

"We're moving as aggressively as we can to see if [COSTAR] should be done," he says, adding that there are at least two schools of thought on the proposed project. While one side feels COSTAR would improve the three instruments' performance, the other side would rather reserve COSTAR's projected budget on the chance the money may be needed to guarantee the timely completion of two already planned "second-generation" instruments.

One of them, an imaging spectrometer slated for installation in 1996, would be five times as sensitive as any of the instruments that COSTAR would benefit, Pellerin says. (Sensitivity, however, is not always the only important trade-off. For instance, though Pellerin says the new spectrometer could resolve dimmer emissions than Hubble's existing faint-object camera, it will lack the camera's array of 48 interchangeable filters – important for examining those objects at different wavelengths or degrees of polarization, notes F. Duccio Macchetto, the camera's chief scientist at the Baltimore-based Space Telescope Science Institute.)

NASA's second-opinion panel should report back to the space agency in April. Pellerin notes that should this group back COSTAR, NASA should have time to complete the device in time to include it in a Hubble servicing already scheduled for 1993. During that space shuttle mission, astronauts will install another new Hubble instrument – an improved wide-field and planetary camera.

Asked whether NASA really needs a second opinion on Hubble's recommended fixes – especially COSTAR – Macchetto noted that the director of the Space Telescope Science Institute, the organization which coordinates Hubble's research, selected the first panel. "I truly support the idea of having a panel of people who . . . are not directly connected with the telescope" reevaluate the need for COSTAR, he said.

The first advisory panel also recommended fixing the telescope's jitters. This slight shaking, caused in part by temperature related expansion and contraction of Hubble's power-providing solar panels (SN: 11/10/90, p.295), also reduces the sharpness of the telescope's pictures and spectra. Engineers on the Hubble project have tried shaking the telescope (with its gyros) to better understand and possibly reduce the jitter-susceptibility of replacement solar panels. Results of this test, Macchetto says, are expected shortly, leaving time to modify the new panels so that shuttle astronauts can install them in 1993.

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