

# Towards real-time molecular demolition?

**A demonstration of the successive excitations of rubidium atoms by lasers may be a model for the selective dissociation of molecules for which chemical engineers would (and will) give fortunes.**

EVEN as we marvel at how lasers are being used for the manipulation of atoms or molecules, we are assaulted by further illustrations of the tricks the laser people are waiting to play on us. Now, of course, it is a commonplace that people working with atomic or molecular beams can arrange, by irradiation with laser light of the appropriate frequency, that much of their material is in a predetermined excited state. Because the energy levels of atoms or molecules depend to some small degree on the masses of their nuclei, the same principle may yet be used commercially for the separation of isotopes. And those whose expertise is the use of insubstantial electromagnetic fields for trapping small numbers of atoms or molecules in ionic form can now use lasers detuned from some known resonant frequency to 'cool' their specimens even to the microkelvin level.

All that, and much more, is familiar, but there is plainly no end to what lies in store. Here are some recent innovations, each a surprise in itself and also suggestive of other tricks not far ahead.

Take, for example, the dissociation of molecules, which could be of great importance in the chemical industry if it could be used to push chemical reactions in some desired direction. In principle, there is no problem. Identify an excited state of the molecule in which its components are no longer bound together, work out the frequency corresponding to the excitation energy and then irradiate the material to be dissociated with laser light of that (or greater) frequency.

But there are snags. The frequencies are usually far in the ultraviolet (requiring the inconvenient use of excimer lasers, themselves dependent on chemical reactions), the process is inefficient and the products of dissociation often unspecific. So why not, instead, pump laser energy into particular vibrational states of molecules, literally to shake them apart in such a way that the products are specifically determined by the particular chemical bond attacked in this way?

On the face of things, there should be no difficulty. For one thing, molecular vibrations usually have frequencies in the infrared. Then, to a first approximation, a molecular vibration is a simple harmonic process, with the consequence (described in every textbook of quantum mechanics) that the energy levels are equally spaced. But reality differs from

the first approximation. By definition, if a molecule can shake itself apart, its potential energy cannot be a symmetrical function of the departure (for a diatomic molecule) of the internuclear distance from its equilibrium value. For molecular vibrations in general, the energy difference between successive excited states decreases as the energy increases.

So why not arrange that molecules meant to be shaken apart should be irradiated not by laser light of constant frequency but with light of a frequency that decreases as time goes by? Two years ago, S. Chelkowski, A. D. Bandrauk and P. B. Corkum suggested just that (*Phys. Rev. Lett.* **65**, 2355; 1990). Their idea was to use femtosecond laser pulses with a pre-patterned declining frequency to shake molecules apart. It is easily foretold that some future generation of chemical engineers will really be laser people in disguise, skilled at shaking molecules apart in specific ways by laser pulses of varying frequency. (The technical term is 'chirping', borrowed from acoustic analysis of bird song.)

A Dutch group has now carried through a rudimentary demonstration of the principle of chirped laser excitation, not with molecules, but with rubidium atoms. The point is simply that the valence electron of rubidium, whose ground state is the  $5s$  state, may be excited to  $5p$  and then  $5d$  by optical photons, with wavelengths of 780.2 nm and 775.9 nm respectively. The first transition is less energetic than the second by a little more than 0.5 per cent.

The difference is so small that a single laser might span the gap, with a little manipulation of its output. B. Broers, H. B. van Linden van den Heuvell and L. D. Noordam from the Institute for Atomic and Molecular Physics at Amsterdam have now shown how that can be done (*Phys. Rev. Lett.* **69**, 2063; 5 October 1992). Chirping, it appears, works as predicted. But there is a big surprise.

The source of the laser light is a pulsed dye laser, made to yield four different outputs by means of dye cells pumped by an yttrium-aluminium-garnet laser. The four sequences of pulses are mixed together in a water cell so as to produce a relatively broadband laser pulse lasting a few tens of times as long as the original (depending on the geometry), and with a predominant frequency increasing or

even (according to the geometry) decreasing over the duration of the output pulse. That is a hint of the technology the next generation of chemical engineers will have to practise.

The Amsterdam group has amply demonstrated what its readers will have expected of it: with an upward (infrequency) chirping pulse, it turns out to be possible to excite rubidium atoms with great efficiency into the second excited state ( $5d$ ). So much can be inferred from the arrangements for monitoring the population of that state, which consist of the ionization of excited rubidium atoms by more energetic laser light (at a wavelength of 532 nm) and the counting of the electrons therefrom. Upward (in frequency) chirped laser pulses behave as expected.

So where is the surprise? Chirped laser pulses whose frequency decreases over the duration of the pulse also seem to have the same effect, but even more quickly. (Remember, the first rubidium transition is less energetic, by about 0.5 per cent, than the second.) The authors describe this observation as "counter-intuitive". That is like applying the same adjective to an observation that water will spontaneously run uphill.

That the counter-intuitive mechanism is nevertheless plausible has been shown by calculation. Low-to-high frequency chirping seems fully to populate the intermediate state. Chirping in the other direction can fully populate the upper state without foot touching ground at the intermediate level. In reality, of course, none of this would be possible unless the laser pulses spanned a range of frequencies throughout their short duration.

The implications of these developments for the next generation of chemical engineers are not easily discerned. For most of us, it will be a comfort that the idea of frequency chirping as a systematic way of dissociating atomic systems has been substantiated. But the application of the technique now demonstrated to real chemical systems will evidently require a much more detailed knowledge of the details of the structure of complicated molecules than even future decades will easily acquire. Perhaps the solution is to use laser pulses shorter than a femtosecond in duration to shape the femtosecond laser pulses that shake molecules apart. Real-time molecular demolition may be the name.

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