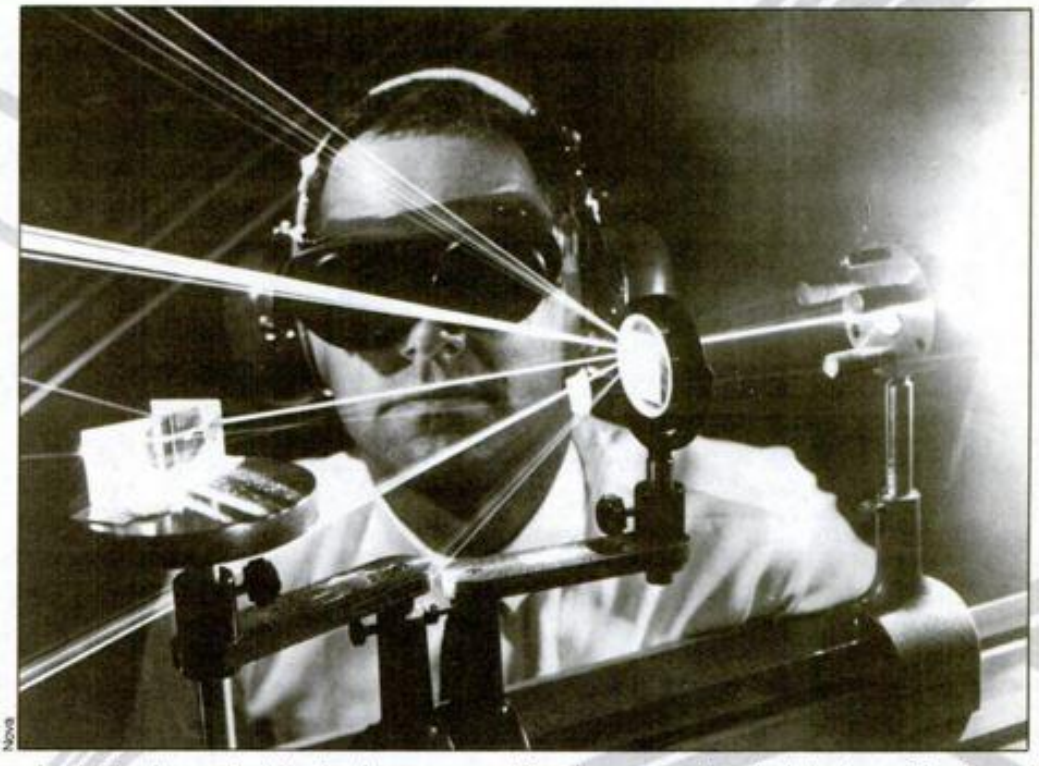
Lasers give chemists a new vision

By using lasers, chemists can look at the way molecules behave when bombarded by energies never before possible. But laser chemistry is more than just a new experimental toy, it can have applications in the semiconductor and other industries

David Andrews



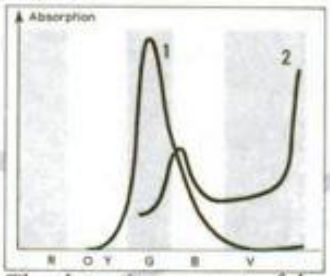
Chemists are dazzled by the new insights that lasers are providing them, even about the behaviour of familiar substances

HOW CAN we see through a brick wall? Chemists have found a way of doing the equivalent by using lasers to quietly persuade atoms and molecules to absorb two photons of light at the same time. The absorption of photons one by one accounts for almost all that we see; in contrast, two-photon absorption is a relatively new discovery, made possible by the intense power of a laser. And it looks set to provide new insights into the electronic structure of matter. Looking into the depths of optically dense materials—the chemist's equivalent of a brick wall—is just one of the applications.

When we shine white light on any object, the atoms and molecules of which it is made absorb some colours in the spectrum. It is the other, reflected colours that we see because they register an image on the retina, again by absorption of light. Yet, despite its universal importance, scientists did not understand how light is absorbed until the development of quantum mechanics and the concept of the photon early this century.

When the individual atoms or molecules of a substance absorb a single photon they use the photon's energy to change the orbitals of their electrons. According to the quantum theory, an electron orbiting an atomic nucleus can occupy only certain, specified, discrete energy levels, and hence if the photon is to be absorbed, it has to have exactly the right amount of energy to kick the electron into a higher orbital. Now, the colour of a beam of light is directly related to the energy of its photons. It follows that the structure of the atoms and molecules of a substance determines the energy, the wavelength and hence the colour of the light it can absorb.

This relationship between the colour of a substance and its molecular properties is immensely important to the chemist. At its simplest level the intensity of colour can be a guide to the concentration of a substance in solution—the basis of the science of colorimetry. Far more useful, however, is the more detailed analysis of light absorption known as spectroscopy.



The absorption spectrum of the organic dye Rhodamine 6G, for the visible region (from red, through orange, yellow, green, blue, to violet). Curve 1 shows the ordinary single-photon spectrum: most of the absorption occurs in the green-blue region. This gives the dye its deep orange colour. Curve 2 shows the strong two-photon absorption in the violet region. (Adapted from Aslandi and Tikhonov, Opt. Spectrosc. vol 37, p 446)

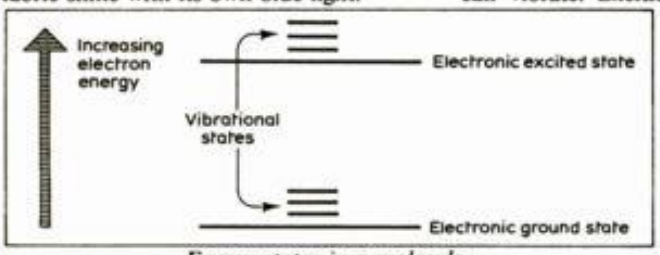
Absorption spectroscopy covers many experimental procedures, yet the underlying principle is always the same: the chemist shines light on to the sample and plots how much each wavelength is absorbed against the wavelength (or frequency) of the light.

Spectroscopy based on the absorption of visible light gives us information about the electronic structure of molecules. Other regions of the electromagnetic spectrum, such as the infrared or the microwave, provide data

Why does your shirt glow in the disco dark?

SHINY shirts are a common hazard in the ultraviolet gloom of a disco. The reason? Fluorescing optical brightners left in the fabric after washing.

Modern washing powders contain optical brightners to boost their whitening power. They absorb ultraviolet (UV) light, and re-emit it as longer wavelength blue light—they fluoresce. Normal daylight contains very little UV light. A fabric impregnated with optical brighteners is, therefore, only weakly fluorescent and so merely appears whiter than white. Under ultraviolet light, as in a disco, however, the brighteners fluoresce strongly, making the fabric shine with its own blue light.

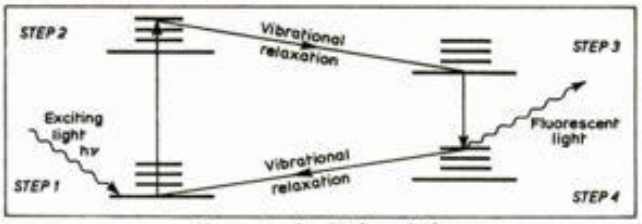


Energy states in a molecule

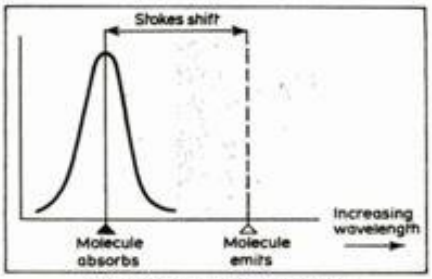
What are the steps in the molecule's fluorescent dance? When light excites a molecule, it kicks an electron into a higher energy state. From here, several things can happen. If the electron simply returns to its original (ground) state, then the molecule can re-emit the energy by fluorescing. But if that were the end of the story, the wavelength of the fluorescent light would be the same as that of the exciting light. In fact, the fluorescent light is always at a longer wavelength (lower energy). Some of the energy of the excited molecule goes in changing the way its constituent atoms vibrate.

For any molecule in its electronic ground state, there are a discrete number of ways it can vibrate. Exciting an electron in the molecule's chemical bonds loosens the binding between the atoms, in which case they ought to spring apart slightly. But because electronic transitions in a molecule take place much more rapidly than vibrational changes, the atoms are left in a "tense" condition. The molecule then relaxes to accommodate the change in binding. This slightly lowers the energy of the excited molecule.

The excited electron now falls back to the ground state, giving off fluorescent light. But the atoms in the molecule are still in the same relative position as they were in the excited state. So they have to relax again. The molecule is now energetically back where it started from.



Steps in the Stokes shift



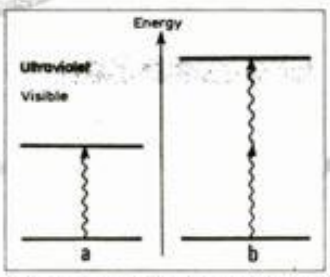
The Stokes shift observed

Because of the two vibrational relaxation steps, the original electronic excitation is slightly degraded by the time the molecule fluoresces. It is red-shifted compared with the exciting light. Scientists call this the Stokes shift. **Lionel** Milgrom

concerning molecular vibrations and rotations. There are very many molecules in even the tiniest sample, and the number of photons hitting the sample (incident photons) is vast. (Even the lowly candle emits something like fifty million billion photons every second and the sources of light used in chemical spectroscopy are very much more intense than that.) Yet there is little chance of any molecule being able to absorb more than one photon at a time, so in each case, we are dealing with the absorption of single photons by individual molecules.

With lasers the situation is entirely different. At the focus of the beam from a gas laser, the light can easily be a hundred thousand times more intense than that obtained from a powerful mercury arc lamp (a conventional spectroscopic light source). Two photons from such a laser could pass through the same molecule simultaneously. If they are both of the right frequency, the molecule may absorb both at the same time. What is interesting here is that the sample molecules will take up twice as much energy as during a normal single-photon absorption.

How can we observe two-photon absorption? One approach is to swamp our sample with light from the most powerful mode-locked laser source. Mode-locked lasers emit ultra-short (10^{-12}s) bursts of light (*New Scientist*, vol 77, p 32).

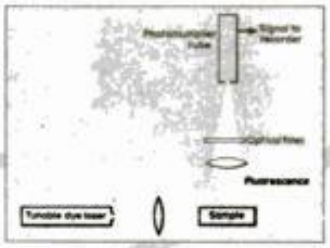


The amount of energy taken up by the molecules in a sample during two-photon absorption is twice that taken up in a single-photon absorption. Molecule (a) in this diagram is excited by the absorption of a single photon of visible light. Molecule (b), which absorbs two such visible photons from a high-intensity laser source, will reach a state of higher energy normally only achievable by absorbing a single ultraviolet photon with double the energy

This creates the largest possible flux of photons, and so increases the likelihood of two-photon absorption, which we could then monitor directly. Problems arise, however, if there are too many photons.

Laser light is so intense that it causes other multi-photon phenomena to occur. These, in turn, may ionise the sample and disrupt the molecules. Reducing the light intensity only lowers the number of molecules undergoing two-photon absorption. This would make direct monitoring difficult because the change in light intensity, before and after two-photon absorption, is too small to measure.

Another method which chemists use is to observe the fluorescent light emitted as the molecules, excited by two-photon absorption, return to a more stable state. In single-photon absorption, the fluorescent light emitted by excited molecules generally has less energy, and so a lower frequency, than the absorbed light. (This is how optical brighteners in washing powders work—they absorb energetic, but invisible, ultraviolet light, and then re-emit it as visible blue-white light.) When a molecule absorbs two photons simultaneously, however, the light it emits on its return to a more stable state has *more* energy then the individual absorbed photons—a clear indication that more than one photon is involved in the absorption process. W. Kaiser



A typical experimental arrangement to detect the fluorescence from a sample that has absorbed two photons. (The two-photon absorption spectrum of Rhodamine 6G, illustrated by curve 2 in the diagram on the previous page, was obtained in this way.) The optical filter allows through to the detector only the higher frequencies (shorter wavelengths) in the fluorescent light. These are the frequencies that result from two-photon absorption of laser-light by the sample

and C.G.B. Garrett of Bell Telephone Laboratories, New Jersey, used this method to demonstrate the two-photon process for the first time in 1961. In their experiments they irradiated fluorite crystals with intense red light from a ruby laser and observed blue fluorescence.

As the development of lasers has progressed, and the two-photon process has become easier to observe, more and more compounds have been shown to demonstrate this behaviour including inert gases, and biologically active materials such as chlorophyll and human chromosomes.

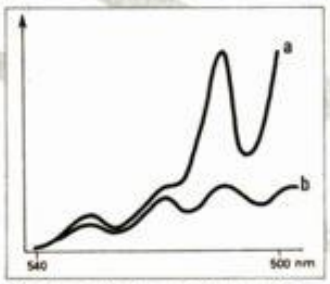
Particularly interesting are substances that are transparent to visible light but which absorb ultraviolet strongly. Now, measuring ultraviolet spectra by the usual single-photon technique is a problem at wavelengths less than 185nm because oxygen in the air and the material of the sample container (cell) also absorb photons at these wavelengths. This extra absorption interferes with the experiment. For this reason, chemists have had to develop vacuum techniques and non-absorbing cells.

Two photons of visible light may have the same energy as one ultraviolet photon. Consequently, two-photon absorption, using visible and near-visible laser light, can provide useful data on the far ultraviolet response of a substance, without the need for special techniques. In one sense, then, the process allows us to "see" into the ultraviolet.

Another useful feature of the technique is that it can excite molecules into states completely inaccessible to single-photon absorption, even with ultraviolet photons. In this way, we can obtain much more information on the electronic and vibrational structure of molecules, even well-known substances such as ammonia and benzene.

When any gas absorbs light, absorption lines that are close together in its spectrum, tend to merge. This is caused by the molecules colliding with each other and leads to a loss of valuable information. Chemists can mitigate the problem to some extent by using dyelasers to produce monochromatic (single wavelength) light. At any one time, the laser can be tuned to radiate at one frequency. Observing the sample under low pressure avoids intermolecular collisions. Molecular motions, however, also give rise to a kind of doppler effect, which also modifies the absorption, and chemists cannot entirely remove this effect.

The doppler effect is most familiar in the realm of sound—the rising note of an approaching train, for example. A similar principle applies when a photon intercepts a molecule in motion. The frequency the molecule "sees" is shifted according to its speed and direction. There is a random distribution of motions in a fluid, so identical molecules absorb at slightly different frequencies. This means that the measured spectrum is not as precise as we might wish. With two-photon absorption, we can arrange for the two photons to be absorbed from different laser beams travelling through the sample in opposite directions. In this case, the doppler shift for the two photons cancels out for every molecule and we can obtain a more precise spectrum.



The two-photon spectrum of liquid fluorobenzene taken at room temperature between the wavelengths 540nm and 500nm (roughly the green part of the visible spectrum). Trace (a) shows the result obtained using plane-polarised light and trace (b) the result for circularly polarised light. Clearly, the spectrum depends heavily on the polarisation of the photons. (Adapted from Friedrich, Van Alsten and Walters, Chem. Phys. Lett. vol. 76, p 506, 1980)

Two-photon spectroscopy differs from conventional single-photon spectroscopy in several other ways. For example, chemists can use this technique to study optically dense materials. These are substances that absorb visible light intensely. Two-photon absorption may occur outside the normal single-photon absorption range, so what little light is absorbed is uniform throughout the sample. On the other hand, the polarisation of the laser light strongly affects two-photon absorption in gases and liquids. With ordinary single-photon absorption, the polarisation of the light has little effect on liquids and gases. There is a marked difference in the two-photon absorption spectrum of, for example, liquid fluorobenzene between plane and circularly polarised light. Its analysis confirms theoretical predictions about the nature of fluorobenzene's excited state. This, in turn, gives chemists confidence in their theories.

Besides spectroscopy, there are other interesting possibilities for two-photon absorption. Chemists could use it detect impurities in a substance, even down to single-atom quantities of the impurity—levels which can be critical in the manufacture of semiconductors. In a mixture of substances, only those atoms and molecules with suitably spaced energy levels will exhibit two-photon absorption; the rest will be transparent.

Intricate three-dimensional patterns may be cut in clear plastic by focusing two laser beams inside it, and traversing the sample with the two beams. Two-photon absorption would occur only at the place where the beams cross, initiating a photochemical reaction. This would either harden or soften the plastic.

Laser-induced two-photon absorption has a great deal to offer the chemist both in fundamental research and in practical application. Moreover, researchers are developing higher order multi-photon absorption processes for laser separation of isotopes and photochemical applications. □

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