Light - in the service of chemistry

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The UN General Assembly has proclaimed 2015 as the International Year of Light and Light-based Technologies (IYL 2015). It is the perfect excuse for a series of articles about light in chemistry. Enjoy!

Thinking of light we usually think of visible light, in the wavelength range 400-700 nm, but we may consider light more generally as a kind of electromagnetic radiation – from the high energy side of the spectrum (γ and x-ray) to the low energy end (infrared, micro- and radio waves).

We may also include fast electrons as they share both particle (photon) and wave behaviour with light. Light has strong connections with chemistry – historically, as fire was long the dominating source of light – today light in the shape of various spectroscopic methods provides the major information source for almost any kind of molecular systems, from the simplest – small single molecules - to the most complex – the living cell.

Infrared light is typically generated by hot matter, a hotplate on your stove and although we cannot see it, we can feel IR radiation as heat on our faces.

White light – from a light bulb or the sun – is a mix of lights of many colours of the spectrum as shown when refracted through a prism or as the rainbow in the sky (Isaac Newton 1672).

X-rays are generated by an electric discharge as Wilhelm Konrad Röntgen discovered in 1895. With typically 50 kV accelerating electrons across a spark gap, their kinetic energy (50 keV) is enough to excite atomic electrons which, when falling back, give rise to X-ray fluorescence of similar energy.

Historically scientists have contributed quite differently to the understanding of light.

Chemist Lavoisier classified light as an element (1789), while much earlier (1672), Robert Hook had already presented a theory based on observations of refraction, suggesting that light was waves with vibrations oscillating perpendicular to the propagation direction.

Hook is famous for his book Micrographia (1665) showing how to use a microscope to observe nature – he was first to coin the biological term 'cell'.

In 1678 Christiaan Huygens presented a theory assuming that elementary waves are emitted in all directions in a medium (aether) and then slowed down when entering a denser medium – this explained accurately how a light beam refracts at a surface (Snell's law: $n_1 \sin u_1 = n_2 \sin u_2$ with n_1 and n_2 the refractive indices of the two media and u_1 and u_2 the angles that the beam forms with the normal to the surface).

Thomas Young showed in a seminal experiment (1802) that light shining on two parallel slits recombines (diffracts) after passage in a way consistent with interference between two waves: bright and
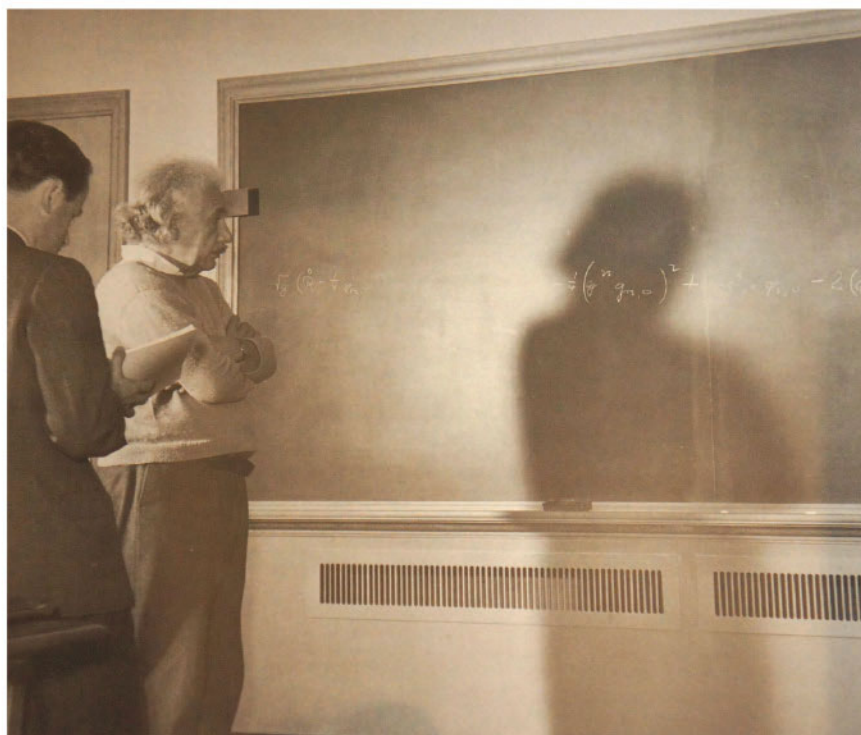
For the rest of my life I want to reflect on what light is. 1916

Albert Einstein in front of the black board. (picture owned by Ahmed Zewail, Nobel prize in chemistry 1999).

dark fringes indicating constructive and destructive interference.

Young's double-slit experiment with light, which has an exact correspondence for electrons showing diffraction too, can be seen as a corner stone of quantum mechanics. 100 years later it was postulated (Planck 1900, Einstein 1905) that light is absorbed and emitted as packets known as photons, each with an energy

$$E = h\nu \qquad (1)$$

with h being the Planck's constant (6.6261×10^{-34} J s) and ν the light frequency. ν is related to the wavelength (λ) according to: $\lambda\nu = c$ with c the velocity of light. The fact that light thus exhibits properties of both waves and particles is referred to as the wave-particle duality.

By assuming that light consists of discrete energy packets, Einstein wrote an equation that explained why the energy of photoelectrons (electrons emitted from some metals when irradiated with light) was dependent only on the frequency of the incident light and not on its intensity. It earned him the Nobel Prize in physics for the discovery of the "photoelectric effect".

But back to chemistry - one of the first important chemical applications of light was in optical activity: the phenomenon that the plane of polarized light is rotated when passing through a solution or a crystal. Jean-Baptiste Biot found that some quartz crystals rotated the plane of polarized light while others rotated it to the same extent but in the opposite direction.

In 1815 he showed that turpentine rotates plane polarized light, and observed the same effect with some solids (sugar, tartaric acid) when dissolved in water. He realized that this ability of some substances in solution must mean that the effect is a molecular property.

In 1848 Louis Pasteur noticed that sodium ammonium tartrate forms two different kinds of crystals that are mirror images of each other, much as the right hand is a mirror image of the left hand. By separating one type of crystal from the other, manually under a magnifying glass, he was able to prepare two samples of this compound which had opposite optical rotations.

Ergo, macroscopic asymmetry was related to microscopic, molecular asymmetry!

In 1874 Jacobus Henricus van't Hoff, proposed that the phenomenon of optical activity was related to how atoms in molecules are located in space. van't Hoff, the first Nobel Laureate in Chemistry (but awarded for other things) made chemist Kolbe furious – how could anybody dare to claim that atoms are "arranged in the Universe" – a good example of the common resistance to new ideas that precede paradigm change.

Thus, the optical activity of certain carbon compounds (such as tartaric acid) could be explained as a result of an 'asymmetric carbon atom' having four bonds pointing towards four different neighbours at the apices of a tetrahedron: there will be two different ways of ordering the four atoms that correspond to opposite mirror images.

Stereochemistry was born!

Michael Faraday, about whom James Clerk Maxwell said that he was the greatest theoretical physicist, had little mathematical ability but was a divinely gifted experimentalist with brilliant intuition. In fact he was also a great chemist (he was the first to isolate benzene!).

In 1845 he discovered that virtually any transparent material, when exposed to a ➜
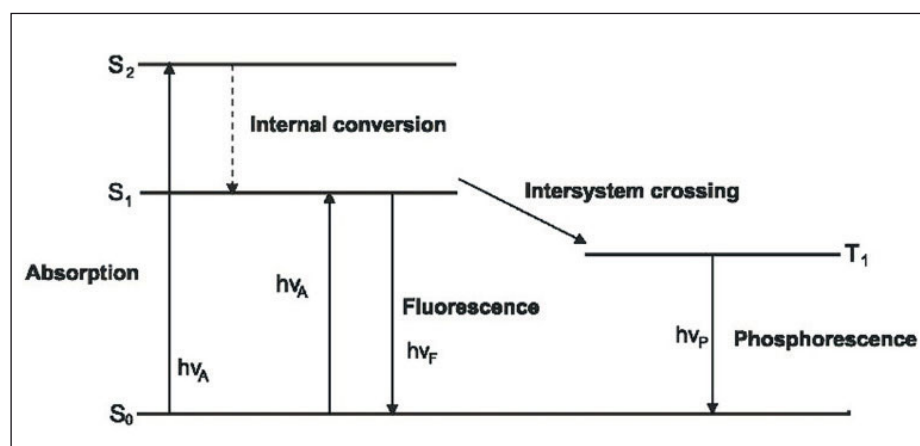

Fig 1. 'Jabłonski' (pronounced jabwonski) energy diagram showing principles for light interactions with molecules: absorption of one photon ($h\nu_A$) excites the molecule from ground state (S0) to, e.g., first singlet state (S1). Then different things may happen: a photon ($h\nu_F$) emitted as fluorescence or, after radiationless transfer ('intersystem crossing') to triplet state (T1), emitted later as phosphorescence ($h\nu_P$).
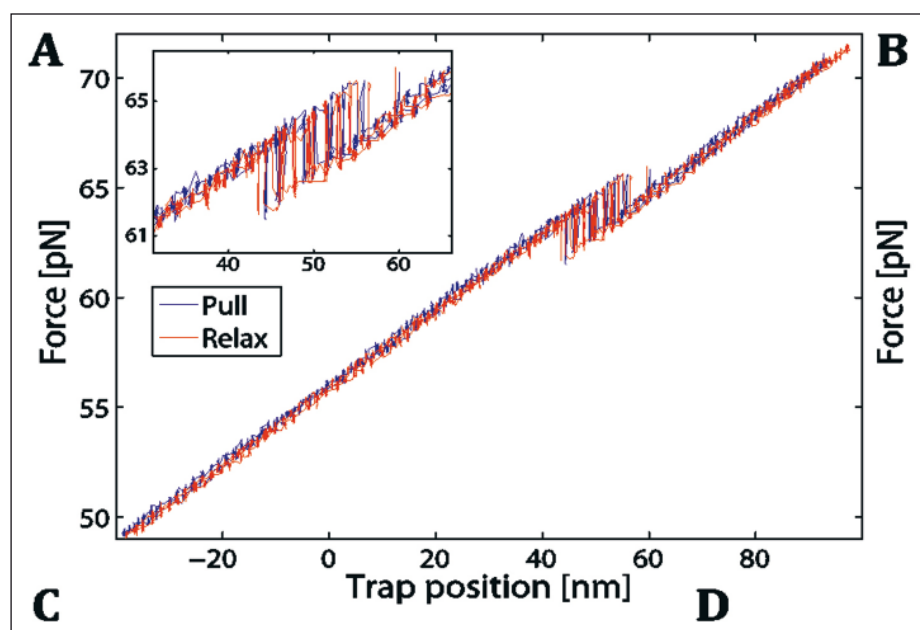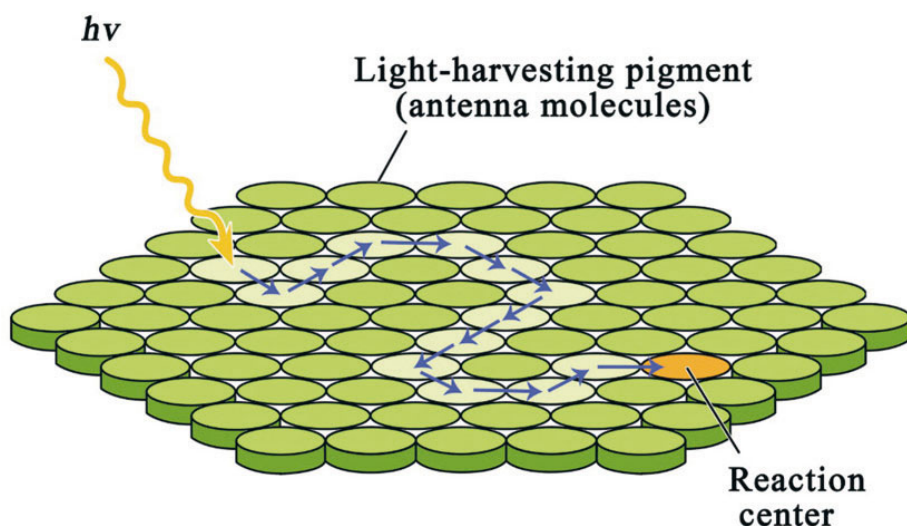

Fig 2. Single-molecule Optical Tweezers experiment. Force versus stretch distance for double-stranded guanine-cytosine rich DNA double helix. At 63 pico-Newton a reversible transition between B-form DNA and a 51% longer DNA conformation is seen.

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Light-harvesting pigment (antenna molecules)

Reaction center

magnetic field in the direction of light propagation exhibits optical rotation of plane-polarized light just like chiral molecules did.

In one strike his discovery showed that light and electromagnetism are related! Today magnetic circular dichroism (MCD) is a spectroscopic tool for analysing the symmetry properties of molecular excited states. MCD is in fact the imaginary part of the complex refractive index differential between left and right circularly polarized light - the real part being exactly the optical rotation that Faraday discovered.

Faraday also pioneered field theory with his 'lines of force' to which Maxwell's and Einstein's later formalistic descriptions relate. In contrast to Maxwell, though, who thought that light must propagate through an aether, Faraday claimed his lines of force may penetrate also into vacuum. In this aspect he was closer to Einstein whose relativity theory does not assume any aether. This assumption is also a prerequisite for how stellar optical observations are interpreted in terms of current cosmological models for the birth and expansion of the Universe.

The theory of modern spectroscopy relies on quantum mechanics. In 1888 Janne Rydberg in Lund had found a formula that very accurately predicted the wavelengths of lines in the hydrogen spectrum and which the Danish physicist Niels Bohr (1913) could explain as transitions of electrons between circular orbits of different radii around the proton.

As late as in 2012 the Rydberg constant ($R = 1.09737315685395 \times 10^7$ m^{-1}) and the electron spin g-factor were the two most accurately known fundamental constants.

The most important, general equation for all forms of spectroscopy is the Fermi-Dirac Golden rule for the probability P(ν) that a transition between two states i (initial)

and f (final) will occur due to interaction with radiation – for example explaining absorption of light by a molecule:
$$P(\nu)= (1/h) \left| \int \Psi_f{}^* V \Psi_i d\tau \right|^2 \rho_f \qquad (2)$$
Here Ψ_i and Ψ_f in the integral (over all space) are wavefunctions for initial and final states of the molecule(s) ($\Psi_f{}^*$ = complex conjugate of Ψ_f). ρ_f is the density of (final) states and V is a time-dependent operator for the interaction energy of the electric and magnetic field vectors of light, oscillating at light frequency ν, with the correspondingly fluctuating electric and magnetic dipole moments in the molecule. Maximum P is observed at resonance, i.e. when ν fulfills the condition of Eq (1), so that the energy difference between the energy levels is $E_f - E_i = h\nu$

Equation (2) explains absorption but also which radiation will be emitted when a molecule descends from a higher-energy excited state to the ground state (fluorescence). It also explains the mechanism for FRET (Förster Resonance Energy Transfer) by which the electric dipolar fields of two molecules interact through space with each other so that excitation energy from one molecule may be transferred to the other.

FRET is a useful method for measuring distances in bio-macromolecular contexts. Eq (2) is also basis for how chlorophyll molecules in plants collect and transfer solar energy to the photosynthetic reaction centre. Incidentally, an application in Nuclear Magnetic Resonance (NMR) spectroscopy, where the "light" is in the radiofrequency range, is the nuclear spin dipolar correspondence of FRET: the so-called Nuclear Overhauser Effect (NOE).

NOE is widely used for assessing the through-space distances (around 0.3 nm) between nuclei in molecules, and besides x-ray diffraction; NMR is the most important method for structure determination as it applies also to solutions.

All this represents only a fraction of the developments central for the understanding of light and for spectroscopy. Resonant interactions like absorption and fluorescence represent interactions that involve the permanent exchange of energy with molecules - corresponding to the mentioned imaginary part of a generalized refractive index.

Photochemistry (which we have omitted here) is when light absorption and excitation of molecules lead to chemical reactions. In addition, many applications also involve non-resonant or elastic interactions, i.e. various ways of scattering light. Instead, they involve the real part of the refractive index. Since no energy is then dissipated, these methods are sometimes more sensitive as they can exploit long light paths, and were therefore developed early.

Raman spectroscopy, x-ray diffraction, optical Kerr effect and optical tweezers all belong to the scattering category. The latter two phenomena are worth mentioning as they reflect some interesting properties of photons.

The Optical Kerr effect (predicted by Buckingham in 1956 and experimentally pioneered by Kielich in 1959) is when strong laser radiation by the electric fields of photons gives rise to anisotropy in polarizable media, including aligning molecules.

Optical tweezers exploit the momentum of photons impacting on dielectric (non-absorbing) particles. If an intense laser beam is focused on a dielectric particle surrounded by a medium of a different refractive index, the light scattering at the surface will, depending on the divergence of the light and due to conservation of momentum, confer forces that can be focused to keep the particle in a "trap". (Ashkin 1969). This technique was used by Steven Chu (1997 Nobel Prize in physics) for cooling and trapping atoms.

More recently it was also used for applying stretch forces to single molecules of double-stranded DNA: Bosaeus (2012) found that at a defined force (64 pN) a 60 base-pair long DNA reversibly shows a conformational change to become about 50% longer but remains a base-paired double helix.

Remarkably, this change corresponds to precisely the stretched structure that DNA adopts in complexes with genetic recombination enzymes. 🅺

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