POLARIZED LIGHT and the asymmetry of life

SNAPSHOT: The study of polarization properties of light forms a fascinating chapter in the history of science, generating key developments in physics, chemistry, and biology. Vitkin highlights the history and physics of polarized light, and discusses its relation to the intriguing asymmetric nature of molecules from living tissues.

he notion of light polarization originated in connection with an optical curiosity. About 1670, it was noticed that when an object was viewed through certain crystals (e.g., calcium carbonate), two images appeared. This phenomenon of seeing double was called "double refraction," and it baffled the leading scientists of the day. Even Newton was perplexed by it. Unable to find a suitable explanation, he speculated, rather vaguely, that the light particles may differ among themselves in a fashion analogous to the opposing poles of a magnet. For over a hundred years, double refraction remained a mystery. Then in 1808, Malus, still looking for an explanation, noticed that the windows of an adjacent palace did not appear double when viewed through a calcium carbonate crystal. Apparently, the window reflected only one class of light particles. Recalling Newton's speculation about opposite poles, he suggested that the reflected light was "polar-

Shortly thereafter, the wave theory of light came into prominence, and the notion of transverse oscillations was used to explain the two different polarization states that produce the double-vision effects in the trouble-some crystals. When light passes through certain materials, the ordered arrangement of atoms interacts differently with the two incident polarization states. The light thus separates into two beams of mutually perpendicular vibration planes, and because of different velocities in the material, the slower beam refracts more than its faster counterpart. The observer viewing an object through the crystal (in any direction other that down the "optic axis") sees two emerging beam and thus two images of an object.

Once the concept of transverse light waves was established, researchers realized that polarization states other than linear or unpolarized were possible. A particularly interesting case was that of circularly polarized light. In this instance, the vibration vector sweeps out a circle as the light propagates. Because the circle can be swept out in two opposite directions (say, with respect to the observer viewing the oncoming beam), there are two circular polarization states are possible. Although circularly polarized light is somewhat less common in nature

than linearly polarized light, both are "equally" fundamental descriptions of a light wave (in fact, circular polarization is more "fundamental" in the quantum-mechanical view of the photon). In other words, any beam of arbitrary polarization (including natural, or unpolarized light) can be represented as a suitable combination of mutually orthogonal linearly or circularly polarized waves.

Molecular stereochemistry

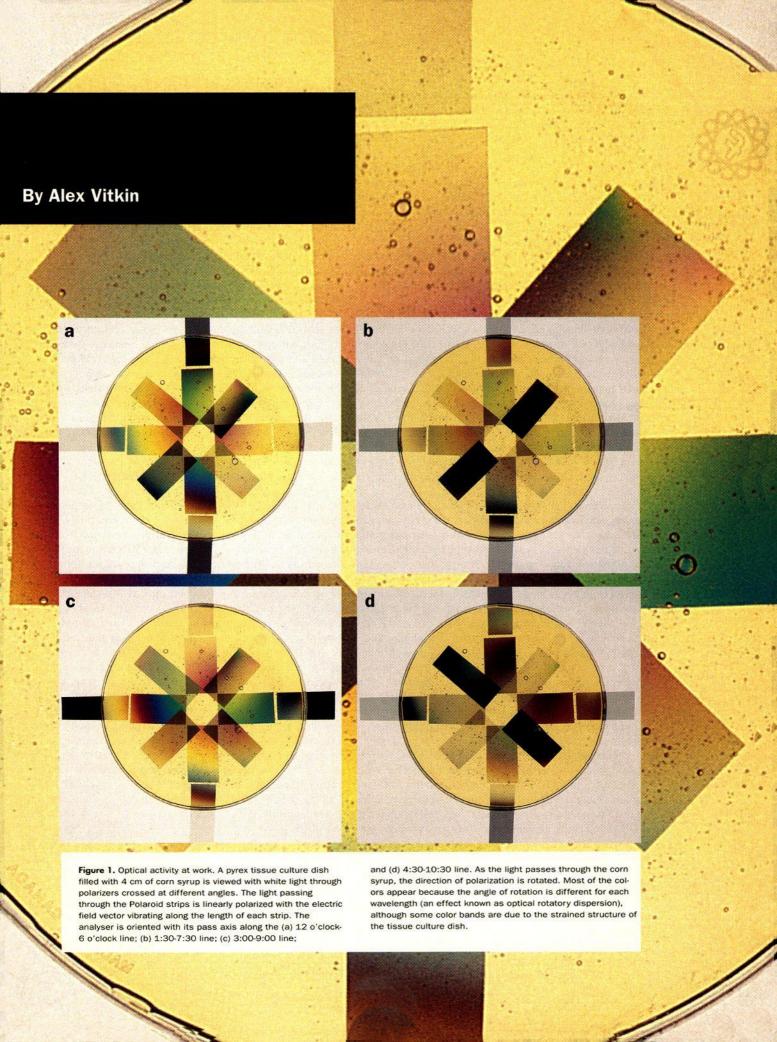
The whole idea of polarization makes sense because otherwise identical light beams interact differently with matter depending on their polarization state. To understand why these differences may be important, we must go back to the experiments of Biot, Pasteur, and others.

Biot noticed that certain liquids, such as turpentine, and certain solutions, such as sugar in water and camphor in alcohol, rotate the plane of polarization of linearly polarized light. He termed this unusual property optical activity.¹

Louis Pasteur, a young chemist, decided to investigate this effect for his doctoral research. He studied the troublesome case of racemic and tartaric acids. The two substances appeared to have identical compositions $(C_4H_6O_6)$, yet differed in their properties. For example, a solution of tartaric acid rotated the plane of linearly polarized light, whereas racemic acid did not.

This was problematic for chemists at the time—Dalton's atomic theory was still in its infancy, atoms were barely accepted as convenient if fictional descriptive tools—but the basic notion that different molecules had different atomic content was beginning to take hold. And yet here was a case of isomers (from a Greek words meaning "equal proportions") that was threatening the fundamental conclusion of the budding atomic theory.

Pasteur was able to rescue the situation. He formed salts of the two acids and closely examined the resultant crystals with a hand lens. The optically active crystals of tartaric acid seemed asymmetric, as expected. The optically inactive crystals of racemic acid were also asymmetric, but with a difference: Some were exactly as the tartaric crystals, while others seemed like their mirror



images! Pasteur therefore concluded that the reason for racemic acid's optical inactivity was that it was a mixture of tartaric acid and its mirror-image twin, with the two parts neutralizing each other's effect.

This situation is analogous to that of crystalline quartz, which was also known to exist in two different crystallographic structures. In a particular quartz crystal, identical repeating units of silicon dioxide wind in a helical fashion about the optic axis; another quartz crystal may exist with opposite circulation sense (like a right-handed and a left-handed spiral). Slowly, and with the support of Biot, this interpretation of symmetrical and asymmetrical crystals (and their combinations) prevailed, and the isomer affair did not put an end to Dalton's atomic theory.

It still seemed strange, however, that optical activity could occur in a liquid, a medium specifically characterized by its lack of order. After all, an array of molecules in a crystal could twist linearly polarized light or cause double refraction by the very nature of the ordered molecular arrangement. But a collection of sugar molecules tumbling this way and that in water? There are no crystals in solution, only molecules, and surely there is no inherent asymmetry in that to systematically change the polarization state of the passing light! In fact, molten or fused quartz, neither of which are crystalline, are not optically active. But what if the molecules themselves are asymmetric?

An extension of atomic theory that pictured molecules as a collection of atoms connected to each other in a definite arrangement on a two-dimensional plane (with lines between symbols to represent the bonds) was being developed in the 1860s by Kaluke, a German chemist. However, these Tinker-Toy models were considered highly schematic utility tools for working out some structures and reactions, no more "real" than atoms themselves. Building on the work of Pasteur and Kaluke, van't Hoff, a Dutch chemist, described optical activity of molecules in solution using a three-dimensional representation of a carbon atom attached to four different atoms or groups of atoms. Such a carbon atom came to be called "asymmetric carbon," and it turns out that nearly every optically active substance (other than some solid crystalline "helixes," such as quartz) has at least one asymmetric carbon atom.

After bitter debates, the van't Hoff system was accepted, and van't Hoff himself received the first Nobel Prize in chemistry in 1901. So, the study of polarization phenomena has provided insight into the physics of light, helped save Dalton's atomic theory, and established the 3-D use of Kaluke structures by showing that both elemental composition and spatial arrangement were important in determining the nature of the molecule!

Biotic molecular asymmetry

And then a particularly strange phenomenon was noticed in connection with optical activity. Chemists found it essentially impossible to produce an optically active substance by chemical synthesis in a test tube. And yet, asymmetric compounds, in which only one member of the twin pair is present, abound in nature.

Scientists began to realize that compounds that are not found in both asymmetric forms are associated with life—they are found only in living tissue or in matter that was once living tissue. This realization of "chiral" (from the Greek word for "handed") exclusivity of living tissue generated much excitement and speculation in the mid- to late-1800s.

Was this asymmetry a manifestation of that elusive vital life force that separated animate from inanimate matter? Theological and science-fictional interpretations aside, Pasteur himself realized its importance; in 1860, he remarked that molecular asymmetry was "... the only well marked line of demarcation that can at present be drawn between the chemistry of dead matter and the chemistry of living matter ..."

An extensive study and tabulation of optical and structural asymmetry of various biotic molecules was undertaken by a German chemist Emil Fischer in the late 1800s. For a structural standard he chose glyceraldehyde, a simple sugar-like compound with only one asymmetric carbon. He would then work out possible structural arrangements of more complicated molecules with more than one asymmetric carbon and decide if the molecules were related to either D-glyceraldehyde or L-glyceraldehyde standard (D = dextro and L = levo, Latin for right and left, respectively, referring here to the structural rather than optical asymmetry of the molecule⁴).

When possible, he would also measure optical activity and assign a "+" for dextro-rotation and "-" for levo-rotation. For example, glucose in living tissues is related structurally to D-glyceraldehyde and is dextrorotatory, thus designated D(+). On the other hand, fructose is structurally of the same family, but opposite in optical activity (at least at the examined wavelength), and is D(-). The relationship between optical and structural isomerism depends on the nature of the groups attached to the asymmetric atom, and their complex interplay that affects the polarization dipole induced in each side group by the light wave. A striking conclusion of Fischer's studies dealt with the aforementioned life asymmetry. He discovered that all sugars in living tissues (with very minor exceptions) are D-type.

Further studies revealed that the fundamental building blocks of tissues, the amino acids, are all essentially L-type. Similarly, all nucleic acids were later shown to be D-type. So it appears that in all organic life forms, only one of the two possible mirror-image twins exists. A rather important, if puzzling, conclusion reached via studies of light polarization originating with the problem of doubly-refracting crystals two hundred years prior!

Reasons for asymmetry

Several explanations have been put forward for the observed asymmetry of life molecules.⁵ The simplest one is that it is the result of sheer randomness (a scientific name for this effect is spontaneous symmetry breaking). Having gained an upper hand by chance in the primordial ocean, L-type amino acids grew more complex and formed more numerous macromolecules than their coexistent D-type twins. The "L chains" may

have reached a necessary level of complexity first, and then, in a chance combination with evolving (D-type) nucleic acids, began multiplying. This activity furthered the slight L-D imbalance in their favor to the point of exclusion of the D-type amino acid structures. And the rest is history, due to the amplifying effect of millions of years of bio-evolution!

Alternatively, non-conservation of parity in weak interactions⁶ may account for biotic symmetry breaking. According to the standard model of elementary particles, electromagnetic and weak interactions are both manifestations of the electroweak force. The latter distinguishes between left and right through "weak charged currents" and "weak neutral currents," as measured by the W and Z forces, respectively. (These subtle forces were predicted in the late 1960s by Steven Weinberg, Abdus Salam, and Sheldon Glashow. Their findings were later confirmed experimentally.⁷) These asymmetric forces are extremely small, and their effect on the chemical properties of molecules has not been observed. Nevertheless, in theory, the presence of the asymmetric Z force causes the biologically dominant L-form of some amino acids to possess a lower ground-state energy than its mirror-image twin.8

A related mechanism involving weak interaction results from beta decay. The emitted electron, upon passage through some materials, emits a bremsstrahlung photon⁹ that is circularly polarized. Most of the produced photons are left-circularly polarized because the electron itself is "asymmetric" due to parity violation in weak nuclear decay. The circularly polarized photon would interact somewhat differently with opposite configurational isomers. The overall result may be that D-type amino acids are less easily formed and more easily broken down once formed than their L-type counterparts.¹⁰

Another explanation for biotic structural asymmetry invokes the difference in the amount of left versus right circularly polarized solar irradiation at the Earth's surface over the course of the day. Coupled with higher afternoon temperatures, and faster reaction rates at elevated temperatures, the left-circularly polarized light component that is more prevalent in the afternoons may have a larger effect than the right-circularly polarized light component that is more prevalent in the mornings. Why and how this will lead to a preponderance of L-type amino acids and D-type nucleic acids is not clear, but this asymmetry of circular light polarization over the course of the day may certainly be the cause.

Emerging applications

Although these historical episodes and tentative explanations have lead us away from the discussion of light polarization, let us not ignore the numerous practical current applications of polarization effects in various branches of science and technology. Imaging through turbid media, testing of chiral purity of pharmaceutical drugs, remote sensing of planetary atmospheres, optical stress analysis of structures, and crystallography of biochemical complexes are just a smattering of its diversified uses. To date, the study of polarization properties of light has lead to important insights into fundamental

Experimenting with polarized light

The interaction of polarized light with optically active substances is quite easy to demonstrate experimentally (See Fig. 1). Alternatively, one can try the following experiment:

- Fill a long cylindrical tube (such as a graduated cylinder ≈ 1 m long) with corn syrup.
- With a linear polarizer inserted between the tube and the source, illuminate from below at a slight angle to the cylinder's axis.

The resultant waxing and waning spiral would make any neighborhood barber proud! The effect is most striking with all room lights out. A HeNe beam works nicely for a well-defined monochromatic spiral; alternatively, a collimated white light beam produces a beautiful dispersion effect (try an overhead projector with a dark slide with a hole in it as the source).

To view Mother Nature's chiral creations take a close look at dung beetles. Under natural light, they look shiny grey to matte black. Nothing much changes when they are viewed under right circularly polarized light. But what happens when you illuminate them with left-circularly polarized light, the bugs acquire a distinct green shine!¹²

problems in physics, chemistry, and biology. In all three fields, new developments are emerging.

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- 4. He had a 50-50 chance of correctly assigning one of the asymmetric forms to one of the two structural formulas of the molecule. As it turned out, he guessed right. Seventy years later, J.M. Bijvoet and his colleagues determined the absolute configurations of molecules using anomalous x-ray scattering. See J. M. Bijvoet et al., "Determination of the absolute configuration of optically active compounds by means of x-rays," Nature 168, 271-2 (1951).
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- 8. From statistical mechanics, this energy difference predicts that L-amino acids should outnumber D-amino acids by 1 part in 10¹⁷! Can such an infinitesimal difference be the cause of the asymmetry, even with millions of years of bio-evolution to amplify it?
- A bremsstrahlung photon is emitted by charged particles when they decelerate; from German meaning "breaking radiation."
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