

A novel microscope reveals the miracle of molecular oxygen

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Artist's impression of the interaction of the triplet state (blue arrows) of an individual pentacene molecule (black and white) with an oxygen molecule (red). Credit: Jascha Repp

Researchers at the University of Regensburg track the first step in the reaction of one single dye pigment with oxygen at an unprecedented



resolution.

Why do the colors of a t-shirt fade over time in the sun? Why do you get a sunburn, and why do the leaves of a tree turn brown in autumn? These questions all have one theme in common—the interplay between dye pigments and ambient <u>oxygen</u>. Every child learns about this chemical reaction in school, which is the <u>oxidation process</u> in the air that we breathe. So what could possibly be left to research?

Oxygen is an astonishing molecule in that it is magnetic. In liquid form, at very low temperatures, it can be picked up by a magnet much like iron filings can. This property is related to the electrons in the oxygen. All molecules are made up of <u>atomic nuclei</u> and electrons, which behave like miniscule needles of a compass. Usually, these needles arrange in pairs pointing in opposite directions so that their magnetic forces cancel out. In an oxygen molecule consisting of two oxygen atoms, however, the two compass needles point in the same direction, making oxygen magnetic.

Dye molecules, such as those used to color a t-shirt, are not magnetic because the compass needles of the electrons point in opposite directions. When light shines on such a molecule, a certain color of the light will be absorbed, giving the dye its characteristic appearance. In this process of light absorption, the energy of the light is transferred to an electron in the dye molecule, breaking the original pairing of two electrons and allowing the compass needle of the excited electron to spontaneously change its alignment. When this process happens, the electron can no longer return to its original state. The dye molecule becomes magnetic, entering what is referred to as a "triplet state."

An international research team directed by Prof. Jascha Repp has now succeeded in revealing how this triplet energy is transferred from one single dye molecule to one single oxygen molecule. This process is integral to everyday life, where many oxidation reactions proceed via the



excited triplet state. As long as the molecule resides in this state, it retains the energy imparted on it by the light, thereby facilitating chemical reactions. Most <u>chemical reactions</u>, such as combustion, require some initial energy such as a spark to begin.

A complete dissipation of the energy within the dye molecule necessitates another reversal of the alignment of the electronic compass needle, which is a slow and improbable process. Alternatively, the light energy within the dye molecule, which corresponds to a magnetic energy, may simply transfer to a further magnetic molecule, such as oxygen—a process much like flipping one bar magnet by rotating another one nearby. This transfer of energy deexcites the dye molecule, but it tends to make the oxygen molecule itself highly reactive, ultimately destroying the dye molecule. This effect can be seen in bleached t-shirts or sunburns, where the <u>dye molecules</u> are the pigments in the skin.

The team has succeeded in tracking this transfer of energy between the dye and the oxygen molecule directly in space, without destroying the dye molecule. To do this, single molecules were placed on a surface and cooled to very low temperatures close to that of the universe. Using a so-called "atomic force microscope" consisting of a very fine needle with just one single atom at its tip, the researchers were able to image the individual atoms of the dye molecule by scanning the tip across it. By applying a sequence of electrical pulses to the dye molecule, they could drive it into the magnetic triplet state in a controlled fashion. The energy transfer from this excited triplet state to oxygen <u>molecules</u> nearby was then tracked in time by measuring miniscule changes in the force acting on the tip.

This novel approach, reported in *Science*, allowed the researchers to probe many different geometries of the arrangement of dye molecule and oxygen. In this way, the interplay between molecular arrangements



on the atomic level and the speed at which such energy transfer occurs could be resolved for the first time. The scientists now aim to finally be able to formulate an underlying microscopic framework of fundamental oxidation reactions. In addition to the inconvenient fading of t-shirts, such an interplay between molecular triplet excitations is of central significance to a range of technological developments, such as in organic light-emitting diodes (OLEDs) and organic solar cells, in photocatalytic energy conversion and photosynthesis, and in photodynamic cancer therapy.

More information: Atomically resolved single-molecule triplet quenching, *Science* (2021). <u>science.sciencemag.org/cgi/doi ...</u> <u>1126/science.abh1155</u>

Provided by University of Regensburg

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