Non-equilibrium quantum states in atmospheric chemistry

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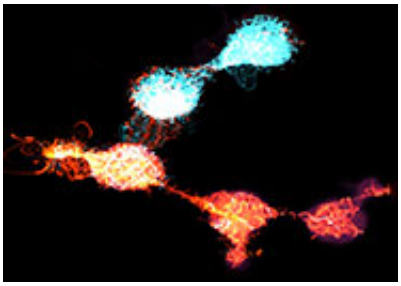

An artist's impression of O_2 'intercepting' the beta-hydroxy vinyl (BHV) radical. The hot orange colours represent non-equilibrium quantum states, while the cooler blue colours represent equilibrium quantum states.

(Phys.org)—Research that sheds new light on the microscopic chemical physics driving one of the most important reaction sequences in atmospheric chemistry is published in *Science* today by Dr David Glowacki from the University of Bristol's School of Chemistry, in collaboration with an international team including experimentalists and theoreticians based in Leeds, Cambridge, and Chicago.

The Earth's atmosphere is a huge chemical reactor where sunlight (rather than heat) starts off chemical chain reactions that ultimately control the fate of greenhouse gases and atmospheric pollutants. Within the Earth's atmosphere (and more generally), one of the most important classes of chemical reactions are so-called 'association reactions', where one molecule (call it A) reacts with another molecule (call it B).

Chemical physicists have known for a long time that molecules can exist in both high energy and low energy quantum states, often referred to as 'equilibrium' and 'non-equilibrium' states, respectively. For arbitrary A + B reactions taking place in the Earth's atmosphere, the nearly universal assumption is that, prior to reaction, both A and B are in their equilibrium states.

Earth's atmosphere is composed of 20 per cent O_2, meaning that O_2 is a participant in most atmospheric reaction sequences. Contrary to the assumption that atmospheric association reactions always involve reactants in equilibrium states, Dr Glowacki and colleagues show that, for association reactions of the type O_2 + B, there is a high probability that O_2 'intercepts' B before its non-equilibrium quantum states have relaxed to equilibrium.

The authors present compelling experimental and computational evidence showing that this occurs during the atmospheric degradation of acetylene, which is an important tracer of atmospheric pollution and also plays an important role in the formation of atmospheric particulates.

Furthermore, Dr Glowacki and colleagues show that that the products produced when O_2 intercepts another molecule's non-equilibrium quantum states are different from those produced when the states are in equilibrium.

Using detailed mathematical models to unravel the timescales of non-equilibrium quantum state relaxation, the researchers speculate that the interception of non-equilibrium quantum states by O_2 is likely to be important for a range of chemical reactions in Earth's atmosphere, with possibly unexpected chemical reaction outcomes.

Dr Glowacki said: "Ultimately, this work improves our fundamental understanding of the microscopic chemical physics driving one of the

most important reaction sequences in atmospheric chemistry, and paves the way for further studies of non-equilibrium systems within nature."

More information: 'Interception of excited vibrational quantum states by O_2 in atmospheric association reactions' by D. R. Glowacki et al in *Science*.

Provided by University of Bristol