Breaking up water: Controlling molecular vibrations to produce hydrogen

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Natural gas (methane) can be converted into hydrogen (H2), which is used in clean energy, synthetic fertilizers, and many other chemicals. The reaction requires water and a nickel catalyst. Methane and water molecules attach on the catalyst's surface, where they dissociate into their atomic components. These then recombine to form different compounds like H2 and CO. Previous research has focused mainly on understanding how methane dissociates, but experimental constraints have limited research into water dissociation. Publishing in *Science*, EPFL scientists have used lasers to determine for the first time how specific vibrations in a water molecule affect its ability to dissociate. The experimental results were used to optimize theoretical models for water dissociation (University of New Mexico), which can impact the design of future catalysts.

Methane is widely used on an industrial scale to produce hydrogen, which is used as a clean fuel and as raw material to produce ammonia used for synthetic fertilizers. The process used is referred to as 'steam-reforming' because it involves methane gas reacting with water steam. This reaction requires a metal catalyst that allows the molecules to dissociate and recombine efficiently. But while the details of methane dissociation have been studied for over a decade, the way water molecules separate has remained elusive.

Fine-tuning vibrations with lasers

The team of Rainer Beck at EPFL, have shown that water dissociation depends strongly on the internal vibrations between its hydrogen and oxygen atoms. In a molecule, the atoms are not static but instead may vibrate in different ways. In a water molecule, the two oxygen atoms can vibrate like a scissor ("scissoring"), or can stretch back and forth either together ("symmetrical stretching") or in turns ("asymmetrical stretching"). "These 'stretches' between the oxygen and the hydrogen atoms play a big role in how well or poorly the water molecule can dissociate on a catalyst", says Beck.

Controlling different types of vibrations is the key to understanding a water molecule's ability to dissociate under mild conditions. Employing nickel as a catalyst – commonly used in steam reformation – the team used lasers to precisely control how water molecules are being excited. "If you heat up the system with e.g. a flame, you excite all the degrees of freedom at the same time", explains Beck. "You also increase its kinetic energy, so all the water molecules hit the nickel surface at higher speeds, but you have no control over the individual vibrations of the atoms. With a laser, we can selectively excite one type of vibration, which allows us to measure one energy state at a time."

The data showed that the degree of stretching vibrations between the hydrogen and oxygen atoms in a water molecule determines its ability to dissociate react on the catalyst. This happens because the laser adds energy to the water molecules, increasing vibrations to the point where they break up on the catalyst's surface. This point is called a 'transition state', where the water molecules are ready to react. "Ideally, we want to deform the molecules before the hit the surface, in a way that we have biased the structure towards the transition state", says Beck. "This is why laser-selected vibrations are more efficient that just heating up the entire system: we are putting the energy where it needs to be to break the water molecule's bonds."

From experiment to theory

The unprecedented ability to excite specific types of vibrations allowed theoreticians at the University of New Mexico to calculate all the forces between the atoms and the nickel catalyst surface, and simulate what happens when the water molecule hits the catalyst surface with each type of vibration. Without these experimental measurements, such calculations would lack accuracy.

"With our data, the theoreticians can directly compare their model to the experimental data one vibration type at a time, which is far more accurate", says Beck. "This allows for the optimization of dissociation models that can then better predict how other molecules than water or methane will react on a given surface. Our state-resolved experiments are meant to guide the development of predictive theory."

This optimization of theoretical models can also lead to the faster and more efficient development of catalysts for a range of industrial and commercial chemical reactions. As Beck explains: "You can use a computer model to e.g. vary the spacing of the atoms of the catalyst or change the structure of its surface. This is a cheaper or more efficient way to find a good catalyst, rather than having to do trial-and-error experiments. But in order to trust theoretical model, we need this data to test them against."

More information: Hundt PM, Jiang B, van Reijzen ME, Guo H, Beck RD. 2014. Vibrationally Promoted Dissociation of Water on Ni(111). *Science*, 2 May 2014

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