Laser reveals electronically excited hydroxyl super-rotors in water photochemistry

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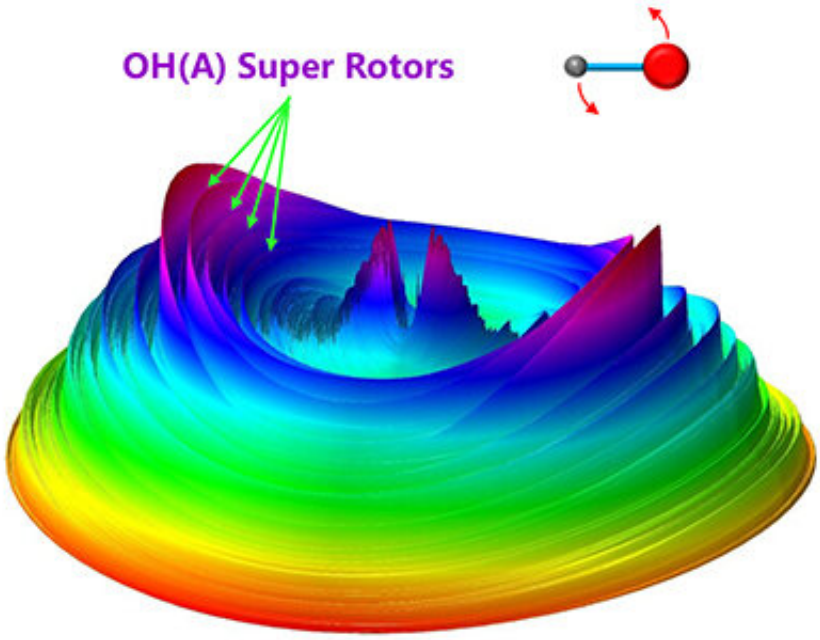

The 3-D product contour diagram from the photodissociation of H2O at 96.4 nm. Credit: CHANG Yao

The presence of high-energy radiation fields in the universe yields various superexcited molecules, which play an important role as a reaction intermediate.

Understanding the fragmentation processes of superexcited molecules is important in the upper atmospheres of planets and in the

photodissociation region (PDR) of the planetary nebula. However, the investigation of such processes in the lab is challenging due to the lack of energetic photons to excite molecules to highly excited states.

With the advent of the intense, pulsed free-electron laser (FEL) in the Dalian Coherent Light Source (DCLS) at Dalian, China, the photofragment study of molecules and radicals has become feasible for vacuum-ultraviolet (VUV) wavelengths below 100 nm using high-resolution translational energy spectroscopy.

Recently, Prof. Yuan Kaijun and Prof. Yang Xueming's group from the Dalian Institute of Chemical Physics (DICP) of the Chinese Academy of Sciences, in collaboration with Prof. Hu Xixi and Prof. Xie Daiqian from Nanjing University, electronically excited OH super-rotors in water photochemistry for the first time.

This study was published in *Journal of Physical Chemistry Letters* on August 24.

"We used VUV-FEL laser pulses with the wavelength of 96.4 nm to excite the water molecule to a high Rydberg state with the energy above its ionization potential, and then the H atom produced in the fragmentation of this superexcited water molecule was detected using HRTOF technique," said Prof. Yuan.

The experimental results indicated that the binary fragmentation channels H + OH and the triple channels O + 2H both present at 96.4 nm photolysis. Electronically excited OH super-rotors, with the internal energy just above the OH (A) dissociation energy, were observed for the first time, which were only supported by the large centrifugal barriers. The lifetime of these electronically excited OH super-rotors depended on the tunneling effect and predissociation effect.

"We recalculated the potential energy curves of OH, and found that even though the N = 36, the pure rotational level of OH was already above its dissociation limit, and the tunneling lifetime of this state through the centrifugal barrier was quite long (>2 year). However, the crossings of the ro-vibrational levels with the repulsive states caused severe predissociation," said Prof. Hu.

The predissociation rate was several orders of magnitude faster than the tunneling rate. As a result, the lifetimes of the OH super-rotors were around 370-57 ps. This suggests that these electronically excited super-rotors identified in the present work might have a role in the subsequent chemical reactions in the dense atmosphere.

More information: Yao Chang et al. Electronically Excited OH Super-rotors from Water Photodissociation by Using Vacuum Ultraviolet Free-Electron Laser Pulses, *The Journal of Physical Chemistry Letters* (2020). DOI: 10.1021/acs.jpclett.0c02320

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