

## Ultrafast vibrational dynamics of the free OD at the air/water interface revealed by time-resolved heterodyne-detected vibrational sum frequency generation spectroscopy

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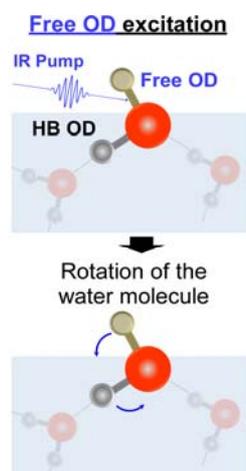
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Vibrational relaxation dynamics of the OH stretch of water at the water surface has been a subject of intensive research facilitated by recent developments in ultrafast interface-selective nonlinear spectroscopy.<sup>1</sup> We previously reported the vibrational relaxation of the free OH at the air/water interface for pure H<sub>2</sub>O and isotopically diluted water (HOD-D<sub>2</sub>O) using time-resolved heterodyne-detected VSFG (TR-HD-VSFG) spectroscopy.<sup>2</sup> In sharp contrast to a former homodyne TR-VSFG study,<sup>3</sup> we found that the vibrational relaxation T<sub>1</sub> time of the free OH at the air/H<sub>2</sub>O and air/HOD-D<sub>2</sub>O interfaces does not change with isotopic dilution. Based on the absence of the isotopic dilution effect on the T<sub>1</sub> time, it was concluded that the vibrational relaxation of the free OH proceeds predominantly with the reorientation of the topmost water molecule having the free OH, not by intramolecular energy transfer as believed so far.

In this presentation, we report the vibrational relaxation dynamics of the free OD at the air/neat D<sub>2</sub>O and isotopically diluted HOD-H<sub>2</sub>O interfaces using TR-HD-VSFG spectroscopy. The obtained results show that the T<sub>1</sub> time of the free OD does not show any detectable change with the isotopic dilution within the experimental error, as in the case of the free OH in the OH stretch region. This result further confirms that the vibrational relaxation of the free OD/OH at the water surface predominantly proceeds with the diffusive rotation mechanism and negates the predominant contribution of intermolecular energy transfer in the relaxation of the free OH that has been argued based on a recent MD simulation.<sup>4</sup> We also found that the T<sub>1</sub> time of the free OD is about twice larger than that of the free OH, being consistent with the reorientation mechanism of the vibrational relaxation.

The observed large difference in the T<sub>1</sub> time between the free OD and the free OH may suggest the involvement of the non-classical isotope effect, i.e., the nuclear quantum effect.



**Figure 1.** Schematic of the vibrational relaxation mechanism of the free OD.

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