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Tracking Ultrafast Chemical Reactions at the Aqueous Interface with Femtosecond Time-Resolved HD-VSFG Spectroscopy

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Abstract

There have been numbers of reports suggesting that chemical reactions at the water interfaces are different from the reactions in the bulk phase. However, it is very difficult to directly investigate chemical reactions at the water interfaces because of lack of suitable experimental methods. Heterodyne-detected vibrational sum frequency generation (HD-VSFG) spectroscopy is a powerful technique to study interfaces.¹ Combined with the pump-probe method, HD-VSFG has been extended to time-resolved measurements, which opened a new door to investigate ultrafast dynamics at interfaces.² HD-VSFG spectroscopy enables us to directly measure the spectrum of the second-order susceptibility ($\chi^{(2)}$) although conventional VSFG spectroscopy with homodyne detection can only provide the spectra of the absolute square of $\chi^{(2)}$ ($|\chi^{(2)}|^2$). This advantage of HD-VSFG becomes even more critical in the time-resolved measurements which detect the pump-induced change of the spectra. In fact, homodyne time-resolved VSFG can provide the pump-induced change of $|\chi^{(2)}|^2$ ($\Delta|\chi^{(2)}|^2$) but it is very difficult to interpret it. In contrast, time-resolved HD-VSFG directly gives $\Delta\chi^{(2)}$ spectra and, in particular, the imaginary part of $\Delta\chi^{(2)}$ ($\Delta\text{Im}\chi^{(2)}$) can be directly compared to the time-resolved infrared and Raman spectra which correspond to $\Delta\text{Im}\chi^{(1)}$ and $\Delta\text{Im}\chi^{(3)}$ spectra, respectively. Fully utilizing this advantage of HD-VSFG, we developed UV-excited time-resolved HD-VSFG spectroscopy which enables tracking photochemical reactions and short-lived intermediates at aqueous interfaces.³

Very recently, we succeeded in tracking the photochemical reaction of phenol at the water interface.⁴ We observed several transients at the interface with femtosecond time resolution, and they were attributed to the reaction intermediates that also appear in the reaction in the solution phase. Surprisingly, however, it was found that dynamics at the interface is drastically accelerated, compared to the corresponding reaction in solution. We consider that this marked difference arises from the unique solvation structure around phenol at the interface,⁵ which significantly changes the relevant excited-state potential energy surface of phenol at the water interface. Largely different solvation environments at the interface is expected for all kinds of molecules, implying generality of the observation in our study, i.e., great difference in chemical reactions between the interface and the bulk.

Keywords water interface, ultrafast dynamics, photochemistry, time-resolved spectroscopy, nonlinear spectroscopy, sum-frequency generation, heterodyne detection

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