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Sun *et al.* Reply:

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Response to "Comment on Orientational Distribution of Free O-H Groups of Interfacial Water is Exponential"

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Our manuscript [1] reported that the orientational distribution of free OH groups at the air/water interface has an exponential shape. Gan *et al*.'s comment contains four points: the seeming inconsistency of our experimental results and previous reports by other groups, the seeming inconsistency of Figs. 2 and 3 in Ref. [1], the inability of the broad distribution function to account for the experimental results, and the specific case of NaF solutions. All four points are raised in error, as explained in detail below.

First, our *ssp* spectra are different from the spectra reported in Refs. [2,3,5], which is attributed to the narrowband picosecond laser sources in Ref. [2-5] and the broadband femtosecond laser source in Ref. [1]. Similar difference between picosecond and femtosecond setup can also be found in Ref. [6] and [7] reporting phase resolved data. In any case, this difference does not affect our data analysis, as both *ssp* and *ppp* spectra in the analysis were obtained at the same setup.

Second, they claimed that in Ref. [1] Figs. 2(a) and (d) are not consistent with Fig. 3(b) and (c). Since Fig. 3(b) and (c) in Ref. [1] plot the free O-D amplitudes, it cannot be compared directly to the free O-D "intensity" in Figs. 2(a) and (d). Further, the spectra in Fig. 2(a) and (d) were not normalized to the same scale; the spectra were only normalized to their infrared laser profiles. Moreover, the amplitude of the free O-D stretch mode cannot be deduced solely from the peak height of the intensity spectrum, as the other vibrational modes affect the peak height; the amplitude can be obtained only from the proper fit of the spectra. Taking these factors into account, it is clear that the direct comparison made by Gan *et al.* is not possible.

The third point raised is that only a narrow orientational distribution can explain both the insensitivity of the *ssp* spectrum and sensitivity of the *ppp* spectrum to beam geometries. However, a broad orientational distribution can do this as well. To illustrate this, we present in Fig. 1 for the beam geometries from Ref. [2] a comparison between a narrow Gaussian distribution [2] and our broad exponential decay distribution [1]. Clearly, for both distributions, the *ssp* intensity is very similar, while the *ppp* intensity depends strongly on the geometry, which has its origin rather in the Fresnel factors than in the second-order susceptibility of water. Thus, the strong dependence on the beam geometry of *ppp* spectra is not necessarily caused by a narrow distribution function, and is consistent with our proposed exponential function.

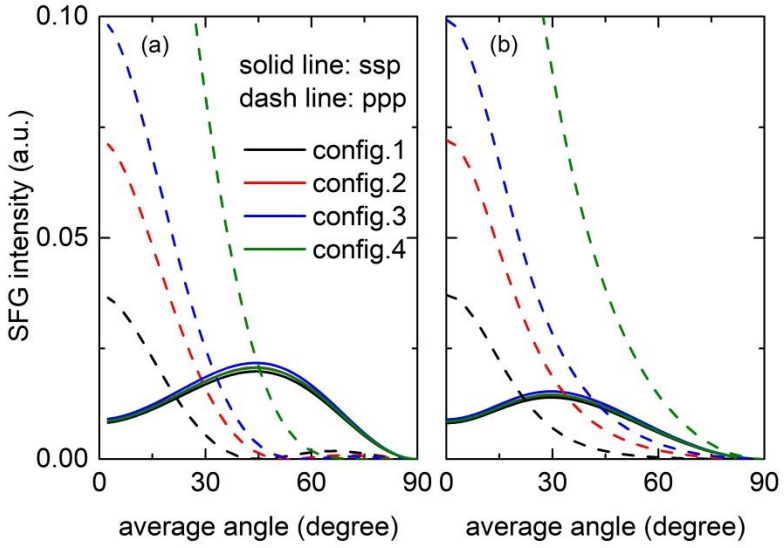

Figure 1: The calculated SFG intensity for the free OD followed the same procedure in Ref. [2] by using different distribution functions: (a) Gaussian function with $\sigma = 15^o$, (b) Exponential decay function.

Fourth, Gan *et al*. mentioned that a broad exponential decay distribution cannot explain the experimental results [5] that with increasing NaF bulk concentration, the *ppp* intensity of the free O-H decreased drastically, while the *ssp* intensity remained the same. Since the effect of salt on the interfacial water structure is complicated, it is not straightforward to comment on the specific case of salt effects. However, we would like to mention that simulations conducted by Morita and co-workers found no difference in the orientation of interfacial water for neat water and a 0.915 M NaF solution [8]. Thus, at present, we have no idea why the *ppp* signal varies with the addition of NaF. This is, however, outside the scope of Ref. [1].

In conclusion, our experimental data are fully consistent with the simulation data that reveal a broad, exponentially decaying distribution of free OH groups at the surface of water.

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