Sun et al. Reply

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Sun *et al.* Reply: Our Letter [1] reported that the orientational distribution of free O-H groups at the air-water interface has an exponential shape. In the preceding Comment [2], Gan *et al.* raised four issues: 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 were raised in error, as explained below.

First, our *ssp* sum-frequency generation (SFG) spectra are different from the spectra reported in Refs. [3,4], which can be attributed to the narrow-band picosecond laser sources in Refs. [3–5] and the broadband femtosecond laser source in Ref. [1]. A similar difference between the picosecond and femtosecond setup can be found also in the phase-resolved data [6,7]. In any case, this difference does not affect our data analysis, as both the *ssp* and *ppp* spectra used in the analysis were obtained using the same setup.

Second, they claimed that in Ref. [1] Figs. 2(a) and 2(d) are not consistent with Figs. 3(b) and 3(c). Since Figs. 3(b) and 3(c) plot the free O-D *amplitudes*, these cannot be compared directly to the free O-D *intensity* in Figs. 2(a) and 2(d). The spectra in Figs. 2(a) and 2(d) were not normalized to the same scale; the spectra were only normalized to the 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 justified.

The third point raised is that only a narrow orientational distribution would be able to explain both the insensitivity of the *ssp* spectrum and the sensitivity of the *ppp* spectrum to beam geometries. However, a broad orientational distribution can do this as well. To illustrate this, Fig. 1 displays a comparison between a narrow Gaussian distribution [3] and our broad exponential decay distribution [1] for the beam geometries from Ref. [3]. Clearly, for both distributions, the *ssp* intensities are very similar, while the *ppp* intensity depends strongly on the geometry, which originates from the Fresnel factors, rather than from the second-order susceptibility of water. Thus, the strong dependence on the beam geometry of the *ppp* spectra is not necessarily caused by a narrow distribution function, and is fully consistent with our proposed exponential function.

Fourth, Gan *et al.* mentioned that a broad exponential decay distribution cannot explain the experimental results [4] 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 one specific case of salt

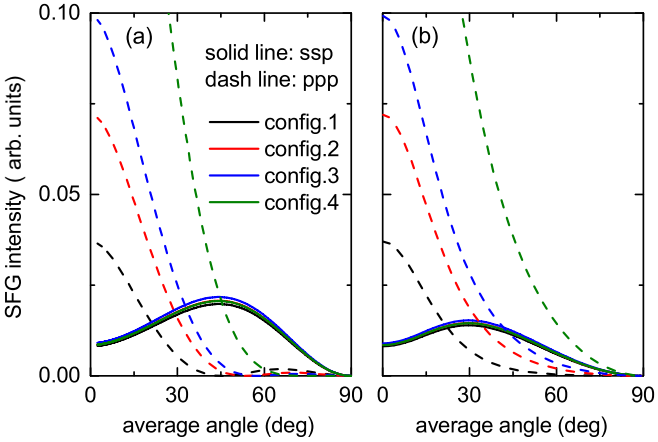

FIG. 1. Calculated SFG intensity for the free O-D peak using the same procedure as in Ref. [3] with (a) Gaussian distribution function with its width of $\sigma = 15°$ and (b) exponential decay distribution function.

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 O-H groups at the surface of water.

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[1] S. M. Sun, F. J. Tang, S. Imoto, D. R. Moberg, T. Ohto, F. Paesani, M. Bonn, E. H. G. Backus, and Y. Nagata, Phys. Rev. Lett. **121**, 246101 (2018).

[2] W. Gan, R.-R. Feng, and H.-F. Wang, preceding Comment, Phys. Rev. Lett. **123**, 099601 (2019).
[3] W. Gan, D. Wu, Z. Zhang, R. R. Feng, and H. F. Wang, J. Chem. Phys. **124**, 114705 (2006).
[4] R. R. Feng, Y. Guo, and H. F. Wang, J. Chem. Phys. **141**, 18C507 (2014).
[5] R. R. Feng, Y. Guo, R. Lu, L. Velarde, and H. F. Wang, J. Phys. Chem. A **115**, 6015 (2011).
[6] S. Yamaguchi, J. Chem. Phys. **143**, 034202 (2015).
[7] S. Nihonyanagi, R. Kusaka, K.-i. Inoue, A. Adhikari, S. Yamaguchi, and T. Tahara, J. Chem. Phys. **143**, 124707 (2015).
[8] T. Imamura, Y. Mizukoshi, T. Ishiyama, and A. Morita, J. Phys. Chem. C **116**, 11082 (2012).