Comment on "Angular Dependences of Third Harmonic Generation from Microdroplets"

Kasparian *et al.* [1] have studied third harmonic generation (THG) from microdroplets experimentally and theoretically. Angular THG maxima were observed around $\theta = 26°$ and 155° (several overlapping peaks after 138°), remarkably stable given the significant droplet radius fluctuations ($\pm 2\%$). Theoretically, based on the surface charge model for metal spheres, they predicted THG peaks at $\theta = 10°$ (the object of a new experiment) and 158° but none about 26°.

The surface charge model is inadequate. It assumes that the metal has high electric conductivity, so that there is no electric field inside the sphere. Thus there is no electric field on the surface of the sphere, save that in the radial direction (surface charge), to act as the source of THG. However, water is capable of THG whether or not at the droplet surface. Furthermore, this model is closely related to the specific mathematical form of the charge. One has to start from the second harmonic generation to study THG. The derivation is very involved.

We use the Green function in free space [2], applicable to spheres via the technique in [3]. If $(\mathbf{u} + i\mathbf{v}) \exp(-i\omega t)$ is the Mie field inside the droplet, then

$$\mathbf{J} = \frac{\partial}{\partial t} \chi^{(3)} [\mathrm{Re}(\mathbf{u} + i\mathbf{v}) \exp(-i\omega t)]^3 \qquad (1)$$

is the THG current, where $\chi^{(3)} = \chi^{(3)}_{xxxx}$ is one of the 21 nonzero elements of the third order tensor susceptibility of water. Equation (1) is found from a local Cartesian system, whose x axis parallels $\mathrm{Re}(\mathbf{u} + i\mathbf{v}) \exp(-i\omega t)$, so that 20 nonzero tensor components are suppressed exactly without approximation. While this exact treatment reveals little about $\mathbf{J}$ in the laboratory system, this is of little consequence when the Green function is integrated numerically (with respect to r and θ, φ-integration analytic). We use the tenth order Newton-Cotes formula and keep 300 partial waves ($l \leq 300$, $m = 1, 3$, other m lead to vanishing integrations), so that error is $<5\%$. THG is a special case of third order sum frequency (TOSF) generation, which was studied by Hill *et al.* using a method equivalent to the Green function method [4]. However, they found only the total TOSF output, either at a single frequency or averaged over a peak of Mie scattering, which was shown to depend on the overlapping between the TOSF and Mie field.

In [1], $x = ka$ varied between 79 and 83 (k being the wave number in vacuum, a the radius of the droplet), a range difficult to cover either analytically or numerically. Instead, we study four representative frequencies. Figure 1 shows the angular THG distribution when $x = 81.0000$ (nonresonant Mie field). There are two THG peaks of comparable magnitudes around $\theta = 30°$ and 140°, matching experimental results very closely. These appear to be stable, because the curve in Fig. 1 changes little at $x = 81.2750$ (nonresonant). While detailed comparisons are difficult, because the intensity scale of the experimental plot in [1] varies in different ranges of θ, Fig. 1 resembles that plot much more closely than the theoretical plot in [1]. We found more backward THG scattering at $x = 79.1475$ and 80.9943 (low and high Q resonances), which may explain the extra experimental THG peaks for $\theta > 140°$ in [1]. Their erroneous observation of four resonant peaks when $x = 81 \pm 2$ [1] (more than 40 in Mie theory) makes further comparison difficult.

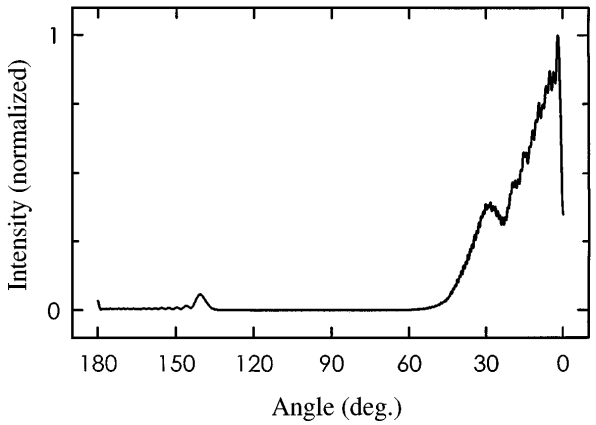

FIG. 1. Angular (in degrees) intensity distribution (in the $\varphi = 90°$ plane, normalized linear scale) of the THG far field at $x = 81.0000$, as would be seen through a polarizer in the $\varphi = 90°$ direction. The incident light is linearly polarized at the $\varphi = 0°$ plane.

In conclusion, the theoretical model in [1] should be replaced by a more adequate version. Experimental conditions should also be controlled carefully. Current fluctuations in a for droplet trains can be reduced to two parts in 10^5, so that a resonant partial wave can be selectively excited and locked onto for more than a half hour [5]. This would allow us to test, e.g., Eq. (1) to improve our knowledge of THG at the fundamental level.

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