1 Preamble

Our interest is to calculate the nonlinear reflection coefficient, $\mathcal{R}$. We start with equation (2) of [1]

$$\mathcal{R}_{iF} = \frac{32\pi^3\omega^2}{(n_o e)^2 c^3 \cos^2\theta} \left| T_F^{v\ell} T_F^{\ell b} (t_i^{v\ell} t_i^{\ell b})^2 r_{iF} \right|^2, \tag{1}$$

where $i = s$ or p is the incoming polarization at ω, $F = S$ or P the outgoing polarization at 2ω. θ is the angle of incidence, n_o is the electron density, e is the electron charge, and c is the speed of light. T and t are the Fresnel factors that give the transmitted fields at the vacuum–surface (vs) or the surface–bulk (sb) interfaces.

Thus, we have four different cases for $\mathcal{R}_{iF}$: $\mathcal{R}_{pP}$, $\mathcal{R}_{sP}$, $\mathcal{R}_{pS}$, and $\mathcal{R}_{sS}$. Let us derive the most explicit equations for these cases.

2 Unit Analysis

The units for $\mathcal{R}_{iF}$ should be reported in cm^2/W[1]. All terms inside the absolute value bars are adimensional, implying that $n_o e = \frac{\mathrm{pm}^2}{\mathrm{V}}$ Outside, we have

$$\frac{32\pi^3\omega^2}{(n_o e)^2 c^3 \cos^2\theta} = \frac{[\frac{1}{\mathrm{s}}]^2}{[\frac{\mathrm{C}}{\mathrm{m}^3}]^2[\frac{\mathrm{m}}{\mathrm{s}}]^3} = \frac{\frac{1}{\mathrm{s}^2}}{\frac{\mathrm{C}^2}{\mathrm{m}^6}\frac{\mathrm{m}^3}{\mathrm{s}^3}} = \frac{\frac{1}{\mathrm{s}^2}}{\frac{\mathrm{C}^2}{\mathrm{m}^3\mathrm{s}^3}} = \frac{\mathrm{m}^3\mathrm{s}^3}{\mathrm{C}^2\mathrm{s}^2} = \frac{\mathrm{m}^3\mathrm{s}}{\mathrm{C}^2}$$

3 Fresnel Factors

The Fresnel factors are given by

$$t_s^{v\ell}(\omega) = \frac{2\cos\theta}{\cos\theta + k_{z\ell}(\omega)}, \tag{2}$$

$$t_p^{v\ell}(\omega) = \frac{2\cos\theta}{\epsilon_\ell(\omega)\cos\theta + k_{z\ell}(\omega)}, \tag{3}$$

$$t_s^{\ell b}(\omega) = \frac{2k_{z\ell}(\omega)}{k_{z\ell}(\omega) + k_{zb}(\omega)}, \tag{4}$$

$$t_p^{\ell b}(\omega) = \frac{2k_{z\ell}(\omega)}{\epsilon_b(\omega)k_{z\ell}(\omega) + \epsilon_\ell(\omega)k_{zb}(\omega)}. \tag{5}$$

where $k_{zj}(\omega) = \sqrt{\epsilon_j(\omega) - \sin^2\theta}$ for $j = \ell$ (surface) or b (bulk). $\epsilon_b\,(\epsilon_\ell)$ is the bulk (surface) dielectric function. The Fresnel factors for the outgoing fields are $T = t(2\omega)$. We can derive these starting with $k_{zj}(\omega)$ and substitute into the Fresnel factors. From (2),

$$t_s^{vs}(\omega) = \frac{2\cos\theta}{\cos\theta + k_{zs}(\omega)} = \frac{2\cos\theta}{\cos\theta + (w/c)(\epsilon_s(\omega) - \sin^2\theta)^{1/2}}$$
$$= \frac{2\cos\theta}{\cos\theta + (w/\sqrt{2}c)(2\epsilon_s(\omega) + \cos 2\theta + 1)^{1/2}}.$$

From (3),

$$t_p^{vs}(\omega) = \frac{2\cos\theta}{\epsilon_s\cos\theta + k_{zs}(\omega)}$$
$$= \frac{2\cos\theta}{\epsilon_s\cos\theta + (w/\sqrt{2}c)(2\epsilon_s(\omega) + \cos 2\theta + 1)^{1/2}}.$$

From (4),

$$t_s^{sb}(\omega) = \frac{2k_{zs}(\omega)}{k_{zs}(\omega) + k_{zb}(\omega)}$$
$$= \frac{2(\epsilon_s(\omega) - \sin^2\theta)^{1/2}}{(\epsilon_s(\omega) - \sin^2\theta)^{1/2} + (\epsilon_b(\omega) - \sin^2\theta)^{1/2}}$$
$$= \frac{2(2\epsilon_s(\omega) + \cos 2\theta + 1)^{1/2}}{(2\epsilon_s(\omega) + \cos 2\theta + 1)^{1/2} + (2\epsilon_b(\omega) + \cos 2\theta + 1)^{1/2}}.$$

Lastly, from (5),

$$t_s^{sb}(\omega) = \frac{2k_{zs}(\omega)}{\epsilon_b(\omega)k_{zs}(\omega) + \epsilon_s(\omega)k_{zb}(\omega)}$$
$$= \frac{2(2\epsilon_s(\omega) + \cos 2\theta + 1)^{1/2}}{\epsilon_b(\omega)(2\epsilon_s(\omega) + \cos 2\theta + 1)^{1/2} + \epsilon_s(\omega)(2\epsilon_b(\omega) + \cos 2\theta + 1)^{1/2}}.$$

4 r_{iF} Terms

Finally, the r_{iF} terms are

$$\begin{aligned} r_{pP} = \sin\theta\epsilon_b(2\omega)[\sin^2\theta\epsilon_b^2(\omega)\chi_{\perp\perp\perp} + k_{zb}^2(\omega)\epsilon_s^2(\omega)\chi_{\perp\parallel\parallel}] \\ +\epsilon_s(\omega)\epsilon_s(2\omega)k_{zb}(\omega)k_{zb}(2\omega)[-2\sin\theta\epsilon_b(\omega)\chi_{\parallel\parallel\perp} \\ + k_{zb}(\omega)\epsilon_s(\omega)\chi_{\parallel\parallel\parallel}\cos(3\phi)], \end{aligned}$$

$$r_{sP} = \sin\theta\epsilon_b(2\omega)\chi_{\perp\parallel\parallel} - k_{zb}(2\omega)\epsilon_s(2\omega)\chi_{\parallel\parallel\parallel}\cos(3\phi),$$

$$r_{pS} = -k_{zb}^2(\omega)\epsilon_s^2(\omega)\chi_{\parallel\parallel\parallel}\sin(3\phi),$$

$$r_{sS} = \chi_{\parallel\parallel\parallel} \sin(3\phi),$$

where ϕ is the azimuthal angle. χ is the second-order susceptibility tensor with the following relations[1],

$$\begin{aligned}
\chi_{\perp\perp\perp} &\equiv \chi_{zzz}, \\
\chi_{\perp\parallel\parallel} &\equiv \chi_{zxx} = \chi_{zyy}, \\
\chi_{\parallel\parallel\perp} &\equiv \chi_{xxz} = \chi_{yyz}, \\
\chi_{\parallel\parallel\parallel} &\equiv \chi_{xxx} = -\chi_{xyy} = -\chi_{yyx}.
\end{aligned} \tag{6}$$

Expanding these expressions, we obtain

$$\begin{aligned}
r_{pP} = \sin\theta\epsilon_b(2\omega)[&\sin^2\theta\epsilon_b^2(\omega)\chi_{\perp\perp\perp} + k_{zb}^2(\omega)\epsilon_s^2(\omega)\chi_{\perp\parallel\parallel}] \\
&+\epsilon_s(\omega)\epsilon_s(2\omega)k_{zb}(\omega)k_{zb}(2\omega)[-2\sin\theta\epsilon_b(\omega)\chi_{\parallel\parallel\perp} \\
&\qquad + k_{zb}(\omega)\epsilon_s(\omega)\chi_{\parallel\parallel\parallel}\cos(3\phi)],
\end{aligned}$$

$$r_{sP} = \sin\theta\epsilon_b(2\omega)\chi_{\perp\parallel\parallel} - k_{zb}(2\omega)\epsilon_s(2\omega)\chi_{\parallel\parallel\parallel}\cos(3\phi),$$

$$r_{pS} = -k_{zb}^2(\omega)\epsilon_s^2(\omega)\chi_{\parallel\parallel\parallel}\sin(3\phi),$$

$$r_{sS} = \chi_{\parallel\parallel\parallel}\sin(3\phi),$$

References

[1] J. E. Mejia, B. S. Mendoza, M. Palummo, G. Onida, R. Del Sole, S. Bergfeld, and W. Daum. Surface second-harmonic generation from Si (111)(1x1) H: Theory versus experiment. *Physical Review B*, 66(19):195329, 2002.

[1] for this symmetry group.