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Sum-Frequency Generation at interfaces: a Fresnel story

II. Analytical expressions for multilayer systems

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The well-known formalism for Sum-Frequency Generation reflected or transmitted by a three-layer system involves three equations defining the emitted SFG intensity, the effective nonlinear susceptibility, and a set of Fresnel factors specific to the three-layer system. We generalize the equations to a N-layer system, where all media have non-vanishing thicknesses, by leaving the first two equations unchanged and modifying only the Fresnel factors. These universal Fresnel factors bear all the complexity of light propagation and interference in the system, in amplitude and phase. They are analytically known anywhere in the N-layer system, either at any interface or in any of the bulks, and share common expressions for the three beams, incoming or emitted, of the SFG process in reflection. Enclosing of an ultrathin layer (e.g. a molecular monolayer) in the system does not modify the Fresnel factors except for boundary conditions at this layer, as in three-layer case. Specific rules are elaborated to simplify systems comprising macroscopic layers. Equations for the four and five layer systems are explicitly provided. Simulations in the four-layer system allow to recover the results of the transfer matrix formalism, to a lower complexity cost for SFG users. Finally, when several interfaces in the system produce SFG signals, we show that it is possible to probe only the most buried one by canceling all the SFG responses except at this last interface, generalizing the results of the three-layer system.

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I. INTRODUCTION

Second-order nonlinear optical techniques, like Second Harmonic generation (SHG) or Sum-Frequency Generation (SFG), have a straightforward interest in analyzing the properties of surfaces and interfaces because of their peculiar properties. In short, they are essentially blind towards a centrosymmetric bulk whereas interfaces, where this symmetry is broken, become the main source of the output signal. In addition, as they change the color (frequency) of their output as compared to their inputs, every measured photon carries information specific from the interfaces. Finally, they extract spectroscopic information in the infrared (of vibrational nature) or the visible (electronic) ranges provided that the laser sources used to generate them are made tunable or broadband.

SFG spectroscopy becomes in fact a routine technique for molecular studies at interfaces, with standard procedures for data analysis. The original system under study is however often too complex for a straightforward application of this nonlinear spectroscopy tool. The system is often transformed into a simplified interface for a model study aiming at elucidating the key properties at stake in the full system. In particular, deeply buried interfaces in multilayer systems may be modelled by open interfaces for an easy access by the SFG beams. In this case, the system consists of two or three layers, namely the outside medium (air, vacuum or a transparent window), the molecular film, and the substrate, in order to elucidate the chemical and physical mechanisms at stake in catalysis or electrochemical reactions, or the peculiar configurations adopted by the molecules at the surfaces of various liquids. A lot of applications have been published concerning the study of molecules adsorbed on, or in close contact with, a solid substrate, potentially buried¹⁻³ and electrically charged,^{4,5} or interacting at a liquid interface.⁶⁻⁹ Molecules at nanostructured interfaces are now commonly addressed either.¹⁰⁻¹³

However, the complexity of heat, charge and matter exchange, together with conformation changes and long-time stability in operando systems makes it rather needful, after the model interfaces, to tackle more realistic systems *in situ*. Such complex studies may include the influence of molecular orientation¹⁴ or of vibrational and vibronic coupling¹⁵⁻¹⁷ on the electron transfer at a molecule-substrate junction in a dye-sensitized solar cell; the anodic and cathodic sides of an operating fuel cell;¹⁸ buried interfaces in organic micro-electronic devices involving molecular components like conducting polymers, graphene or

organic semiconductors.¹⁹⁻²¹

Burying the interfaces by piling up stacks of matter makes sample design but also SFG data analysis difficult due to the existence of these additional layers, and of the additional interfaces that come with them. In a few works, analysis of deeply buried interfaces in systems comprising more than three layers has been attempted.²²⁻²⁷ Whatever the number of layers, the nonlinear process is always represented by the creation of a local surface nonlinear polarization $\mathbf{P}(\omega_3)$, proportional in the dipolar approximation to the product of the electric fields $\mathbf{E}(\omega_1)$ and $\mathbf{E}(\omega_2)$ of the incoming light beams (with $\omega_3 = \omega_1 + \omega_2$ for SFG), emitting in turn light at the new frequency, eventually detected in the far field in reflection or transmission. In other words, we have

$$P_{\alpha}^{[k]}(\omega_3) = \sum_{\beta\gamma} \chi_{\alpha\beta\gamma}^{(2)} E_{\beta}^{[k]}(\omega_1) E_{\gamma}^{[k]}(\omega_2) \quad (1)$$

where the proportionality factor is the surface second-order susceptibility $\chi^{(2)}$, a third-rank tensor, and (α, β, γ) represent Cartesian coordinates. When the number of media grows, so does the number of interfaces and accordingly the number of nonlinear polarization sources. However, the emitted electric fields at the SFG frequency at the various interfaces just sum up in the far field, so that, from a nonlinear optical point of view, there is no difference between interfaces composed of 2 or N media.

The difficult point encountered in the quantitative and spectroscopic description of the phenomenon does not lie in the nonlinear process itself. It arises from the fact that the electric fields and polarizations are local quantities, to be evaluated in the medium [k] where the nonlinear process actually takes place. These local fields are related to the far fields, the ones that are controlled and measured by the experimenter, through the Fresnel factors. These factors encompass all the linear optics at stake in the propagation, reflection, refraction and interferences undergone by the light waves from the far field to the local position of the nonlinear interaction. While equation 1 remains universal whatever the number of layers and experimental tunable factors, the Fresnel factors on the other hand depend on the nature of the interface and of its constituents, on the angles of incidence and on the wavelengths involved. This can be summarized by the equation linking the intensity of the output to those of the input:

$$I_R(\omega_3) = \frac{8\pi^3(\omega_3)^2}{c^3 n_3^{[1]} n_1^{[1]} n_2^{[1]} (\cos \theta_3^{[1]})^2} |\chi_{eff}^{(2)}|^2 I(\omega_1) I(\omega_2) \quad (2)$$

where I_R is measured in reflection, intensities are defined by $I(\omega_i) = \frac{cn_i^{[1]}}{2\pi} |\mathbf{E}^0(\omega_i)|^2$ with \mathbf{E}^0 the far field, $n_i^{[1]}$ and $\theta_i^{[1]}$ the refractive index and angle of incidence of beam i (frequency ω_i) in incident medium [1], respectively. In this equation, the Fresnel factors have shifted from the fields to the nonlinear susceptibility itself, modifying it into an effective surface susceptibility which bears all the burden of the linear optics. As a matter of fact, we have :

$$\chi_{eff}^{(2)} = \sum_{\alpha\beta\gamma} F_\alpha(\omega_3) e_\alpha^{[1]}(\omega_3) F_\beta(\omega_1) e_\beta^{[1]}(\omega_1) F_\gamma(\omega_2) e_\gamma^{[1]}(\omega_2) \chi_{\alpha\beta\gamma}^{(2)} \quad (3)$$

where $\mathbf{e}^{[1]}(\omega_i)$ are the polarization vectors of the electric fields in the plane perpendicular to their direction of propagation. For practical applications, factors $e^{[1]}$ represent the decomposition of electric field \mathbf{E}_i^0 on their (\mathbf{s}, \mathbf{p}) basis, projected onto the $(\mathbf{x}, \mathbf{y}, \mathbf{z})$ laboratory frame. Such a projection is necessary in order to account for the symmetry properties of tensor $\chi^{(2)}$, linked to the interface. We also note that the Fresnel factors have identical expressions for the three beams, which is a universal property whatever the structure of the interface in a reflection SFG experiment.²⁸⁻³⁰ For completeness, the corresponding equations in transmission are:

$$I_T(\omega_3) = \frac{8\pi^3(\omega_3)^2}{c^3 n_3^{[N]} n_1^{[1]} n_2^{[1]} (\cos \theta_3^{[N]})^2} |\chi_{eff,T}^{(2)}|^2 I(\omega_1) I(\omega_2). \quad (4)$$

and

$$\chi_{eff,T}^{(2)} = \sum_{\alpha\beta\gamma} F_\alpha^T(\omega_3) e_\alpha^{[N]}(\omega_3) F_\beta(\omega_1) e_\beta^{[1]}(\omega_1) F_\gamma(\omega_2) e_\gamma^{[1]}(\omega_2) \chi_{\alpha\beta\gamma}^{(2)} \quad (5)$$

where the last medium of the system is labelled [N].

Eq. 2 and 4 are universal whatever the complexity of the interface, whereas Eq. 3 and 5 contain all the details of the system: number and thicknesses of the layers, indices of refraction, angles of incidence. Evaluation of the Fresnel factors is thus an ineludible step during data analysis as it allows retrieving the sought-after quantity $\chi^{(2)}$, characteristic of the species acting as the source of the nonlinear process, from experimental data. It is therefore necessary to calculate their amplitude and phase from dedicated formulas, using all tunable experimental parameters as inputs. The formulas for two layer (2L) and three layer (3L) systems have been known for long.³¹ In the latter case, when the middle layer [2] becomes thicker than the wavelengths of light, Fresnel factors also account for the phase differences induced by beam propagation coupled to the interference between all reflected beams bouncing up and down in this layer. Such an interference may lead to interesting

situations, completely independent on the nonlinear process itself, for the example the vanishing of the SFG response of one of the two interfaces in a three layer system.^{30,32,33} Even if a universal formulation of the Fresnel factors in this case is not always achieved,³⁴⁻³⁸ their description has become robust and rather straightforward.

The problems arise when the number of layers reaches four or more. Partial determination of an analytic expression of Fresnel factors has been made in the four layer case, under the hypothesis that one of the layers has a vanishing thickness.²²⁻²⁴ To our knowledge, there is no analytical expression of Fresnel factors for a generic four-layer system, and all the more for a N-layer system, to be plugged into Eq. (2) to (5). Such complex systems may still be addressed using several theoretical methods. The transfer matrix approach allows to express the electric fields at various interfaces or media through matrix products applied to the external fields,^{25,27,39-41} even beyond dipolar approximation.⁴² Each interface crossing results in the append of two matrices in the transfer matrix product, one accounting for the reflectivity properties and the second one for the phase factors. The (4×4)-matrix formalism developed by Berreman,⁴³ and applied later on to nonlinear optics,⁴⁴ allows to introduce flexibility in the symmetries of the layers beyond in-plane anisotropy,⁴⁵ or beyond dipolar approximation.⁴⁶ Finally, the mixed (4×4)-transfer matrix approach⁴⁷ generalizes the transfer matrix equations to anisotropic materials. All these techniques give access to the numerical computation of the desired quantities, but they do not provide the analytical expressions of the various internal fields in terms of reflection (or transmission) coefficients and phase factors. They are well adapted to automated simulations, in particular when the number of layers is high. On the other hand, analytical formulas offer some advantages: they may be analyzed *per se* in order to provide predictions about their output before performing any simulation. A good example is provided by the analysis of the conditions required to achieve canceling of the SFG process at the first interface in a three-layer system, as recalled above.^{30,32,33} In addition, analytical formulas allow easy plug and play into the well-established formalism for three layer systems. It is easily conceivable that current SFG users would like to keep the same tools and concepts they are accustomed to for their data analysis, even for multilayer interfaces. Finally, Fresnel factors for arbitrary depth inside the system (i.e. in between interfaces) are easier to access by analytical means as they represent a continuous function of depth. Such depth-dependent factors are interesting for *in situ* analysis of film growth⁴⁸ or bulk SFG production⁴⁹ in multilayer systems.

In this article, we provide analytical formulas for Fresnel factors in a generic N-layer system by elaborating on the formalism proposed by Abelès.⁵⁰ The factors depend on the location of the nonlinear polarization source, so we provide formulas for a polarization located at one of the (N-1) interfaces, but also at any arbitrary depth inside the bulk of one of the layers. These Fresnel factors have a simple form (i.e. as x, y and z-factors), which can be directly plugged into the usual SFG equations (2) to (5). They may be obtained by the direct application of algebraic formulas or using a recurrence relation. Their analysis shows that a layer with negligible thickness has no influence on the factors of the whole system, except for boundary conditions, similarly to the well-known three-layer case.^{30,31} We also propose a way to account for the specificity of macroscopic layers inside the system: the user may decide whether to take the Fabry-Pérot effect into account, or not. In the latter case, the system splits in two subsystems on each side of the macroscopic layer. We explicitly take the four and five layer systems as examples and provide the "plug and play" formulas for SFG users. Results for the 4-layer system both match the simplified versions found in the literature and reproduce at low cost the simulations performed using the transfer matrix formalism. Having access to analytic formulas also allows to analyze and predict without simulation the conditions required to switch off the SFG produced at any interface inside the N-layer film. In particular, we show that it is possible, by adapting the rules established for the three layer system,³⁰ to predict without simulation the design of samples in which the SFG process vanishes at all interfaces except the last one, allowing to probe the most buried interface in a multilayered system.

II. FRESNEL FACTORS IN A MULTILAYER FILM

We consider the Sum-Frequency Generation (SFG) process as sketched on Fig. 1. All beams travel in a common (\mathbf{x}, \mathbf{z}) plane of incidence, with \mathbf{z} axis perpendicular to the interface and pointing "up" (i.e. towards the incoming light beams). The generic sample is sketched on Figure 1(B): N media, separated by N-1 plane interfaces located at $z = z^{[k]} \leq 0$ with $k = \{1, \dots, N-1\}$, each layer described by its own refractive index $n^{[k]}$ and thickness $d^{[k]} = z^{[k-1]} - z^{[k]}$. The SFG process may happen at any depth inside the film. As for notations, we index quantities (refractive indices n, angles of incidence θ , electric field amplitudes E...) in the following way. Subscripts incorporate s/p polarizations, beam number ($i = 1, 2, 3$) and

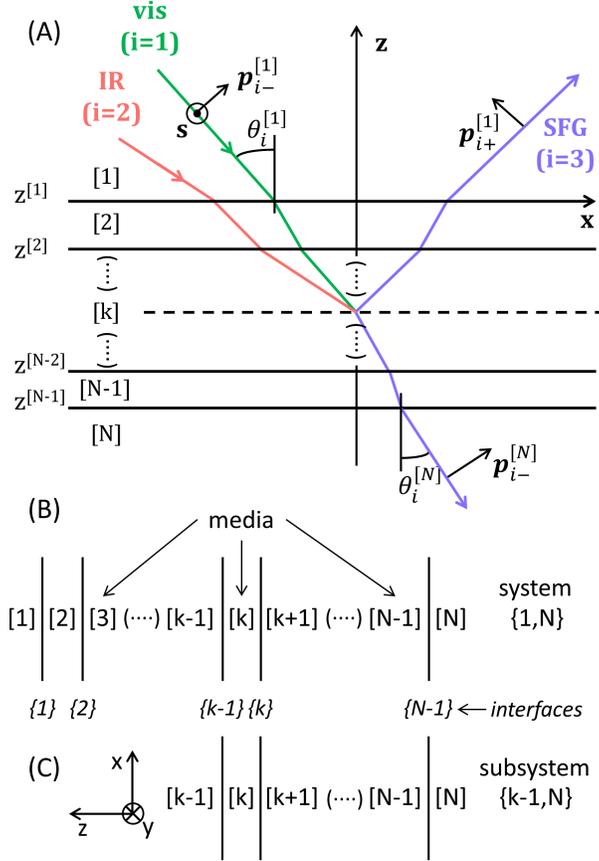


FIG. 1. (A) Sketch of the SFG process in the N-layer model. Multiple beam reflections and refractions at every interface are not shown for clarity. Definitions of the multilayer systems: (B) full system $\{1, N\}$; (C) subsystem $\{k-1, N\}$.

component ($\alpha = x, y, z$). Superscripts focus on the position where a quantity is evaluated: $[k]$ when defined inside a layer and $\{k\}$ at an interface. For reflection r^{ij} and transmission t^{ij} coefficients, superscript (ij) means that beam travels from $[i]$ towards $[j]$. The beam number subscript will be skipped every time it is possible without ambiguity.

As explained in the Introduction, we focus on Eq. 3 (or Eq. 5 when appropriate), to be plugged into Eq. 2 and 4. Our goal is to provide analytical expressions for the electric fields at any depth $z \leq 0$ inside the sample, thus defining the Fresnel factors applicable to these equations. As we address the linear optical properties of the stack, only one light beam (frequency ω , far field amplitude E^0) is necessary, entering the system from medium [1] with angle of incidence $\theta^{[1]}$, refracted into $\theta^{[k]}$ in each layer $[k]$, transmitted to medium $[N]$ with far field amplitude $E^{[N]}$, with $n^{[1]} \sin \theta^{[1]} = n^{[k]} \sin \theta^{[k]} = n^{[N]} \sin \theta^{[N]}$. We define the following

parameters: $\beta^{[k]} = \frac{\omega}{c} n^{[k]} d^{[k]} \cos \theta^{[k]}$ is the phase delay induced by propagation through layer $[k]$ and $\xi^{[k]} = e^{2i\beta^{[k]}}$.

In order to achieve our goal, we rely on the compact formalism proposed by Abelès,⁵⁰ summarized in subsequent publications^{51,52} and recently applied to the SFG case.^{32,53} The principles of this optical description of interfaces are recalled in Appendix A. The Fresnel factors relating the far field amplitudes and the local fields at arbitrary depth inside the film are generally defined in the following way:

$$F_x = \frac{E_x}{E_p^0 \cos \theta^{[1]}}, \quad F_y = \frac{E_y}{E_y^0} \quad \text{and} \quad F_z = \frac{E_z}{E_p^0 \sin \theta^{[1]}} \quad (6)$$

The detailed derivation of the following formulas can be found in Appendices B and C for s (y factors) and p polarized (x and z factors) light, respectively. They incorporate quantities $\xi^{[k]}$ defined above, and reflection coefficients $r_{s/p}^{j,j+1}$ at each interface $\{j\}$ as

$$r_s^{j,j+1}(\omega) = \frac{n^{[j]} \cos \theta^{[j]} - n^{[j+1]} \cos \theta^{[j+1]}}{n^{[j]} \cos \theta^{[j]} + n^{[j+1]} \cos \theta^{[j+1]}} \quad (7)$$

$$r_p^{j,j+1}(\omega) = \frac{n^{[j+1]} \cos \theta^{[j]} - n^{[j]} \cos \theta^{[j+1]}}{n^{[j+1]} \cos \theta^{[j]} + n^{[j]} \cos \theta^{[j+1]}}. \quad (8)$$

All expressions below make use of the ruled product, marked with a dagger (\dagger) superscript, which we define as follows: when a product is evaluated under this rule, all factors of the form $(r_{s/p}^{j,j+1})^2$ are set to 1.

A. At the interfaces between two media

At the various interfaces, we calculate the local electric field amplitudes to deduce the Fresnel factors to apply to incoming beams. For the outgoing SFG beam, the same formulas apply as detailed in Part II C.

1. First interface $\{1\}$

$$F_x^{\{1\}} = \frac{(1 - r_p^{12})^\dagger \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \quad (9)$$

$$F_y^{\{1\}} = \frac{(1 + r_s^{12})^\dagger \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger} \quad (10)$$

$$F_z^{\{1\}} = \frac{(1 + r_p^{12})^\dagger \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \quad (11)$$

The numerators in these equations do not simplify with the denominators because of the ruled products with $r_{s/p}^{12}$ at the numerator.

As an illustration of the handling of the ruled product, we detail the numerators above:

$$\begin{aligned} (1 - r_p^{12})^\dagger \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger &= (1 - r_p^{12})^\dagger [1 + \xi^{[2]} r_p^{1,2} r_p^{2,3}]^\dagger \prod_{j=3}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger \\ &= [1 - r_p^{12} + \xi^{[2]} r_p^{1,2} r_p^{2,3} - \xi^{[2]} r_p^{2,3}]^\dagger \prod_{j=3}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger \\ &= (1 - r_p^{12})(1 - \xi^{[2]} r_p^{2,3})^\dagger \prod_{j=3}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger \end{aligned} \quad (12)$$

$$\begin{aligned} (1 + r_s^{12})^\dagger \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger &= [1 + r_s^{12} + \xi^{[2]} r_s^{1,2} r_s^{2,3} + \xi^{[2]} r_s^{2,3}]^\dagger \prod_{j=3}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger \\ &= (1 + r_s^{12})(1 + \xi^{[2]} r_s^{2,3})^\dagger \prod_{j=3}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger \end{aligned} \quad (13)$$

$$\begin{aligned} (1 + r_p^{12})^\dagger \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger &= [1 + r_p^{12} + \xi^{[2]} r_p^{1,2} r_p^{2,3} + \xi^{[2]} r_p^{2,3}]^\dagger \prod_{j=3}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger \\ &= (1 + r_p^{12})(1 + \xi^{[2]} r_p^{2,3})^\dagger \prod_{j=3}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger \end{aligned} \quad (14)$$

The alternate formulas below explicitly show the proportionality of the $F^{\{1\}}$ factors to the Fresnel factors of the {1,2} two-layer system: $(1 - r_p^{12})$ for x, $(1 + r_s^{12})$ for y and $(1 + r_p^{12})$ for z:

$$\begin{aligned}
F_x^{\{1\}} &= (1 - r_p^{12}) \frac{1 - \xi^{[2]} r_p^{23}}{1 + \xi^{[2]} r_p^{12} r_p^{23}} \quad \text{for } N = 3 \\
&= (1 - r_p^{12}) \frac{(1 - \xi^{[2]} r_p^{23})^\dagger \prod_{j=3}^{N-1} [1 + \xi^{[j]} r_p^{j-1, j} r_s^{j, j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1, j} r_p^{j, j+1}]^\dagger} \quad \text{for } N \geq 4
\end{aligned} \tag{15}$$

$$\begin{aligned}
F_y^{\{1\}} &= (1 + r_s^{12}) \frac{1 + \xi^{[2]} r_s^{23}}{1 + \xi^{[2]} r_s^{12} r_s^{23}} \quad \text{for } N = 3 \\
&= (1 + r_s^{12}) \frac{(1 + \xi^{[2]} r_s^{23})^\dagger \prod_{j=3}^{N-1} [1 + \xi^{[j]} r_s^{j-1, j} r_s^{j, j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1, j} r_s^{j, j+1}]^\dagger} \quad \text{for } N \geq 4
\end{aligned} \tag{16}$$

$$\begin{aligned}
F_z^{\{1\}} &= (1 + r_p^{12}) \frac{1 + \xi^{[2]} r_p^{23}}{1 + \xi^{[2]} r_p^{12} r_p^{23}} \quad \text{for } N = 3 \\
&= (1 + r_p^{12}) \frac{(1 + \xi^{[2]} r_p^{23})^\dagger \prod_{j=3}^{N-1} [1 + \xi^{[j]} r_p^{j-1, j} r_s^{j, j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1, j} r_p^{j, j+1}]^\dagger} \quad \text{for } N \geq 4
\end{aligned} \tag{17}$$

2. *Arbitrary interface {k-1}, with $3 \leq k \leq N - 1$*

$$\begin{aligned}
F_x^{\{k-1\}} &= \frac{(1 - r_p^{k-1,k})^\dagger \prod_{j=k}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \prod_{j=2}^{k-1} [1 - r_p^{j-1,j}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \\
(k \leq N - 2) \rightarrow &= \frac{(1 - \xi^{[k]} r_p^{k,k+1})^\dagger \prod_{j=k+1}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \prod_{j=2}^k [1 - r_p^{j-1,j}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \\
(k = N - 1) \rightarrow &= \frac{(1 - \xi^{[N-1]} r_p^{N-1,N})}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \prod_{j=2}^{N-1} [1 - r_p^{j-1,j}] \prod_{j=2}^{N-2} e^{i\beta^{[j]}} \quad (18)
\end{aligned}$$

$$\begin{aligned}
F_y^{\{k-1\}} &= \frac{(1 + r_s^{k-1,k})^\dagger \prod_{j=k}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger} \prod_{j=2}^{k-1} [1 + r_s^{j-1,j}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \\
(k \leq N - 2) \rightarrow &= \frac{(1 + \xi^{[k]} r_s^{k,k+1})^\dagger \prod_{j=k+1}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger} \prod_{j=2}^k [1 + r_s^{j-1,j}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \\
(k = N - 1) \rightarrow &= \frac{(1 + \xi^{[N-1]} r_s^{N-1,N})}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger} \prod_{j=2}^{N-1} [1 + r_s^{j-1,j}] \prod_{j=2}^{N-2} e^{i\beta^{[j]}} \quad (19)
\end{aligned}$$

$$\begin{aligned}
F_z^{\{k-1\}} &= \left(\frac{n^{[1]}}{n^{[k-1]}} \right)^2 \frac{(1 + r_p^{k-1,k})^\dagger \prod_{j=k}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \prod_{j=2}^{k-1} [1 + r_p^{j-1,j}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \\
(k \leq N-2) \rightarrow &= \left(\frac{n^{[1]}}{n^{[k-1]}} \right)^2 \frac{(1 + \xi^{[k]} r_p^{k,k+1})^\dagger \prod_{j=k+1}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \prod_{j=2}^k [1 + r_p^{j-1,j}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \\
(k = N-1) \rightarrow &= \left(\frac{n^{[1]}}{n^{[N-2]}} \right)^2 \frac{(1 + \xi^{[N-1]} r_p^{N-1,N})}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \prod_{j=2}^{N-1} [1 + r_p^{j-1,j}] \prod_{j=2}^{N-2} e^{i\beta^{[j]}} \quad (20)
\end{aligned}$$

3. Last interface $\{N-1\}$

$$F_x^{\{N-1\}} = \frac{\prod_{j=2}^{N-1} e^{i\beta^{[j]}} \prod_{j=1}^{N-1} [1 - r_p^{j,j+1}]}{N-1 \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \quad (21)$$

$$F_y^{\{N-1\}} = \frac{\prod_{j=2}^{N-1} e^{i\beta^{[j]}} \prod_{j=1}^{N-1} [1 + r_s^{j,j+1}]}{N-1 \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger} \quad (22)$$

$$F_z^{\{N-1\}} = \left(\frac{n^{[1]}}{n^{[N-1]}} \right)^2 \frac{\prod_{j=2}^{N-1} e^{i\beta^{[j]}} \prod_{j=1}^{N-1} [1 + r_p^{j,j+1}]}{N-1 \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \quad (23)$$

The formulas for y-polarization are deduced from x-polarization by replacing r_p with r_s and changing all minus signs to plus signs. The formulas for z-polarization are very close to their counterparts for y-polarization after the substitution of r_s by r_p , only differing by the continuity conditions represented by the ratio of the squared refractive indices. As the z-component is not continuous and differs on either side of interface $\{k-1\}$, they are valid

in medium [k-1]. On the other side of the interface, i.e. in medium [k], the factor must be multiplied by $(n^{[k-1]}/n^{[k]})^2$.

Having established analytical formulas makes it possible to analyze their content. As for the numerators, the last two products involved in Eq. 18-20 could have been anticipated: (i) the first one involves the product of the local field coefficients ($1 - r_p^{j,j+1}$ for x, $1 + r_s^{j,j+1}$ for y or $1 + r_p^{j,j+1} = -1$ for z), related to the transmission coefficients, at all interfaces {j} up to {k-1}: if any of them vanishes, no beam is transmitted to layer [k]. This is why the alternate formulas provided in Eq. 15-20 explicitly show such products up to and including interface {k-1}. These terms represent in fact the various boundary conditions at all interfaces involved along beam propagation. We note that the exact cancellation of any of these transmission coefficients at some interface j is rather hypothetical as it would require $r_p^{j,j+1} = 1$ for x, $r_s^{j,j+1} = -1$ for y or $r_p^{j,j+1} = -1$ for z, hence one of the conditions $n^{[j]}, n^{[j+1]} = 0$ ⁵⁴ or $\theta^{[j]}, \theta^{[j+1]} = 90^\circ$ (achievable only for attenuated total reflection at the critical angle). However, we can get near cancellation when angles of incidence become either very big, close to critical ATR angle or when $|n^{[j+1]}| \gg$ (or \ll) $|n^{[j]}|$, for example at a dielectric-metal interface; (ii) the second product simply accounts for the total phase acquired upon beam propagation after traveling through the [k-1] first layers of the system. We study the denominator in more details below.

4. Recurrence relations

The algebraic formulas above (Eq. 9-23) provide the Fresnel factors at any interface in any system. Their application to deduce explicit analytical formulas is complicated by the presence of ruled product. Here we provide an alternate way to obtain these formulas, by deducing the factors for the (N+1)-layer system from those of the N-layer system or, alternatively, from the factors at the first layer of each system comprising between 2 and N layers.

All the Fresnel factors above encompass denominator

$$D_{s/p}^{N-layer} = \prod_{j=2}^{N-1} \left[1 + \xi^{[j]} r_{s/p}^{j-1,j} r_{s/p}^{j,j+1} \right]^\dagger, \quad (24)$$

common to all of them. The first step is thus to write down this denominator. The dagger product involved here may seem abstruse at first sight, but the analysis of the structure of

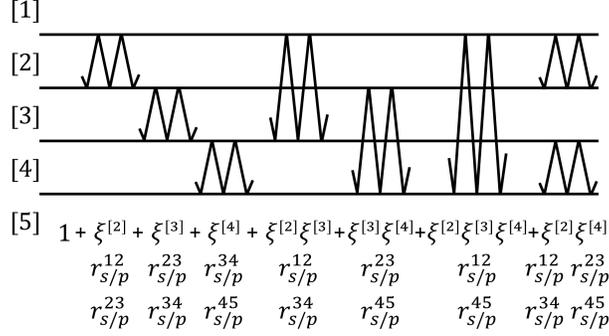


FIG. 2. Principle of calculation of the interference terms in multilayer systems, illustrated in the $N = 5$ case.

each term in the final sum makes it possible to easily implement the result using a graphic help (Fig. 2). For a system with N media, there are $N-2$ sandwiched layers introducing $N-2$ dephasing terms $\xi^{[j]}$, each corresponding to the bouncing of a beam inside layer $[j]$. The denominator is constructed by enumerating and summing the 2^{N-2} possible products $\prod \xi^{[j]}$. The amplitude associated to each of these terms is graphically determined as the reflectivity factors $r_{s/p}$ necessary to constraint the beam to bounce inside the corresponding layers, written in the order of increasing layer numbers. When adjacent layers are involved, the beam goes through their common border without reflection, the corresponding reflectivity term disappears, and this is just what the dagger ruled product accounts for. As an application, we can directly read on Fig. 2 the eight terms of the denominator for the 5-layer system:

$$\begin{aligned}
D_{s/p}^{5-layer} = & 1 + r_{s/p}^{12} r_{s/p}^{23} \xi^{[2]} + r_{s/p}^{23} r_{s/p}^{34} \xi^{[3]} + r_{s/p}^{34} r_{s/p}^{45} \xi^{[4]} + r_{s/p}^{12} r_{s/p}^{34} \xi^{[2]} \xi^{[3]} \\
& + r_{s/p}^{23} r_{s/p}^{45} \xi^{[3]} \xi^{[4]} + r_{s/p}^{12} r_{s/p}^{45} \xi^{[2]} \xi^{[3]} \xi^{[4]} + r_{s/p}^{12} r_{s/p}^{23} r_{s/p}^{34} r_{s/p}^{45} \xi^{[2]} \xi^{[3]} \xi^{[4]} \quad (25)
\end{aligned}$$

Starting with the x-component, the factors for the $(N+1)$ -layer system may be deduced from those of the N -layer system using the following rules (established by the analysis of the algebraic formulas):

- (i) write down denominator $D_{s/p}^{(N+1)-layer}$ using the method exposed above;
- (ii) replace all denominators $D_p^{N-layer}$ in x-factors by $D_p^{(N+1)-layer}$;
- (iii) deduce x-factor at interface $\{k+1\}$ in the $(N+1)$ -layer system from factor at interface $\{k\}$ in the N -layer system (for all $1 \leq k \leq N-1$) by rewriting the numerator

while increasing all indices in the superscripts by 1 (e.g. $r_p^{12}r_p^{23}\zeta^{[2]} \rightarrow r_p^{23}r_p^{34}\zeta^{[3]}$), then multiply by $e^{i\beta^{[2]}}(1 - r_p^{12})$;

- (iv) deduce x-factor at first interface in the (N+1)-layer system by writing down denominator $D_p^{(N+1)-layer}$ at the numerator while replacing r_p^{12} by -1 , then multiply by $(1 - r_p^{12})$;
- (v) deduce y-factor from x-factor by replacing r_p by r_s and changing all minus signs to plus signs;
- (vi) deduce z-factor from x-factor by changing all minus signs to plus signs;
- (vii) modify the boundary condition $(n^{[1]}/n^{[k]})^2$ in the z-factor to $(n^{[1]}/n^{[k+1]})^2$ or $(n^{[1]}/n^{[k+2]})^2$ to evaluate the local field in medium [k+1] or [k+2].

Recurrence starts with the 2-layer case, for which we have $F_x = 1 - r_p^{12}$, $F_y = 1 + r_s^{12}$ and $F_z = 1 + r_p^{12}$ in medium 1 (the 2-layer case may even be seen as the result of the recurrence applied to the 1-layer case, i.e. $F_x = F_y = F_z = 1$). Application to the 3-layer system leads to the formulas analyzed in details in Ref. 30. The 4-layer system is explicitly detailed in Part III C, and the 5-layer case in the Supplementary Material.

In the end, evaluating all the x-factors at the N interfaces in a (N+1)-layer system is equivalent to evaluating the x-factors at the first interface of all systems from 2 to (N+1) layers using rule (iv), then applying rule (iii) as many times as needed. These recurrence methods give access to the analytical formulas for any N-layer system, but also provide a way leading to an algorithm for the automated evaluation of their numerical values.

B. In the bulk of a medium between two interfaces

As explained in the introduction, for the analysis of SFG produced during film growth⁴⁸ or in the bulk of a layer inside a multilayer system,⁴⁹ it is also possible to define Fresnel factors $F(z)$ at any depth z located into medium [k]. We define the dephasing induced by the propagation into this medium $\beta^{[k]}(z) = \frac{\omega}{c}n^{[k]}(z^{[k-1]} - z) \cos \theta^{[k]} \geq 0$.

1. *In medium [2]*

$$F_x^{[2]}(z) = \frac{\left[e^{i\beta^{[2]}(z)} - r_p^{2,3} \xi^{[2]} e^{-i\beta^{[2]}(z)} \right]^\dagger \prod_{j=3}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} [1 - r_p^{12}] \quad (26)$$

$$F_y^{[2]}(z) = \frac{\left[e^{i\beta^{[2]}(z)} + r_s^{23} \xi^{[2]} e^{-i\beta^{[2]}(z)} \right]^\dagger \prod_{j=3}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger} [1 + r_s^{12}] \quad (27)$$

$$F_z^{[2]}(z) = \left(\frac{n^{[1]}}{n^{[2]}} \right)^2 \frac{\left[e^{i\beta^{[2]}(z)} + r_p^{23} \xi^{[2]} e^{-i\beta^{[2]}(z)} \right]^\dagger \prod_{j=3}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} [1 + r_p^{12}] \quad (28)$$

2. *In medium [k], with $3 \leq k \leq N - 2$*

$$F_x^{[k]}(z) = \frac{\left[e^{i\beta^{[k]}(z)} - r_p^{k,k+1} \xi^{[k]} e^{-i\beta^{[k]}(z)} \right]^\dagger \prod_{j=k+1}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \prod_{j=2}^k [1 - r_p^{j-1,j}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \quad (29)$$

$$F_y^{[k]}(z) = \frac{\left[e^{i\beta^{[k]}(z)} + r_s^{k,k+1} \xi^{[k]} e^{-i\beta^{[k]}(z)} \right]^\dagger \prod_{j=k+1}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger} \prod_{j=2}^k [1 + r_s^{j-1,j}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \quad (30)$$

$$F_z^{[k]}(z) = \left(\frac{n^{[1]}}{n^{[k]}} \right)^2 \frac{\left[e^{i\beta^{[k]}(z)} + r_p^{k,k+1} \xi^{[k]} e^{-i\beta^{[k]}(z)} \right]^\dagger \prod_{j=k+1}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \prod_{j=2}^k [1 + r_p^{j-1,j}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \quad (31)$$

3. In medium [N-1]

$$F_x^{[N-1]}(z) = \frac{e^{i\beta^{[N-1]}(z)} - r_p^{N-1,N} \xi^{[N-1]} e^{-i\beta^{[N-1]}(z)}}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \prod_{j=2}^{N-1} [1 - r_p^{j-1,j}] \prod_{j=2}^{N-2} e^{i\beta^{[j]}} \quad (32)$$

$$F_y^{[N-1]}(z) = \frac{e^{i\beta^{[N-1]}(z)} + r_s^{N-1,N} \xi^{[N-1]} e^{-i\beta^{[N-1]}(z)}}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger} \prod_{j=2}^{N-1} [1 + r_s^{j-1,j}] \prod_{j=2}^{N-2} e^{i\beta^{[j]}} \quad (33)$$

$$F_z^{[N-1]}(z) = \left(\frac{n^{[1]}}{n^{[N-1]}} \right)^2 \frac{e^{i\beta^{[N-1]}(z)} + r_p^{N-1,N} \xi^{[N-1]} e^{-i\beta^{[N-1]}(z)}}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \prod_{j=2}^{N-1} [1 + r_p^{j-1,j}] \prod_{j=2}^{N-2} e^{i\beta^{[j]}} \quad (34)$$

It may be checked that $F^{[k]}(z = z^{[k]})$ is equal to $F^{\{k\}}$ as calculated from Eq. 18-20, and that all the results in this section coincide with those in Ref. 30 for a three-layer system.

C. Application to SFG process

The equations above provide the general transformation of the far field in medium [1] into the local field at any depth z in the multilayer system. If a nonlinear sheet is placed at this depth, these equation may be plugged into Eq. 3 to reconstruct the effective nonlinear susceptibility. This supposes that the Fresnel coefficient for the emitted SFG beam is identical to those for the incoming beams. This has been shown in the previous article³⁰ using the external point of view, but it is also possible to check it directly from the equations 29 to 31. They are composed, in this order, of a Fabry-Pérot term, multiplied by the two products described above: one proportional to the local field coefficients (or boundary conditions) and a propagation dephasing term. As for the latter, incoming and outgoing beams share the same dephasing as they travel the same distance whatever their direction of propagation. As for the Fabry-Pérot term, ray-tracing inside the successive layers from [2] to [k-1] shows that incoming and outgoing beams experiment the same reflections at interfaces and dephasing upon exchanging the roles of rays going "out" (with increasing z) and "in" (with decreasing z), respectively. This is also valid in layer [k], represented by the first term at numerator in Eq. 29-31, summing up two terms travelling "in" and "out", respectively.³⁰ In fact, the

only difference between incoming and outgoing beams lies in the boundary conditions, because they obviously don't cross the interfaces in the same directions. In the same line, the emission coefficient transforming the nonlinear polarization into an electric field^{28,30} in medium [k], where it actually happens, is proportional to $1/n_3^{[k]} \cos \theta_3^{[k]}$, to be compared to $1/n_3^{[1]} \cos \theta_3^{[1]}$ showing up in Eq. 2. This issue is solved by a recursive use of

$$\frac{1}{n_3^{[j-1]} \cos \theta_3^{[j-1]}} t_{s/p}^{j-1,j}(\omega_3) = \frac{1}{n_3^{[j]} \cos \theta_3^{[j]}} t_{s/p}^{j,j-1}(\omega_3) \quad (35)$$

where $t_{s/p}^{j-1,j}$ is the transmission coefficient from medium [j-1] to medium [j]. For s polarization, we use $1 + r_s^{j-1,j} = t_s^{j-1,j}$, leading to

$$\frac{1}{n_3^{[1]} \cos \theta_3^{[1]}} \prod_{j=2}^k [1 + r_s^{j-1,j}] = \frac{1}{n_3^{[k]} \cos \theta_3^{[k]}} \prod_{j=k}^2 t_s^{j,j-1} \quad (36)$$

This equation shows that the boundary condition term for SFG emitted in medium [k] and transmitted to medium [1] is equal to that corresponding to the SFG emission in medium [1], coupled to transmission from medium [1] to medium [k], as for an incoming beam.

For the x-factor, we use $1 - r_p^{j-1,j} = 1 + r_p^{j,j-1} = \frac{n^{[j-1]}}{n^{[j]}} t_p^{j,j-1}$ to get

$$\frac{1}{n_3^{[1]} \cos \theta_3^{[1]}} \prod_{j=2}^k [1 - r_p^{j-1,j}] \cos \theta_3^{[1]} = \frac{1}{n_3^{[k]} \cos \theta_3^{[k]}} \prod_{j=k}^2 [t_p^{j,j-1}] \cos \theta_3^{[k]}. \quad (37)$$

In other words, p-polarized SFG emission in medium [k] projected onto x axis and transmitted to medium [1] is equal to emission in medium [1] projected onto x axis and transmitted to medium [k]. For the z-factor, we use $1 + r_p^{j-1,j} = \frac{\cos \theta^{[j-1]}}{\cos \theta^{[j]}} t_p^{j,j-1}$ and Snell's law to get

$$\frac{1}{n_3^{[1]} \cos \theta_3^{[1]}} \frac{(n_3^{[1]})^2}{(n_3^{[k]})^2} \prod_{j=2}^k [1 + r_p^{j-1,j}] \sin \theta_3^{[1]} = \frac{1}{n_3^{[k]} \cos \theta_3^{[k]}} \prod_{j=k}^2 [t_p^{j,j-1}] \sin \theta_3^{[k]} \quad (38)$$

showing that the Fresnel factor defined for an incoming beam identically applies to p-polarized SFG emission in medium [k] projected onto z axis and transmitted to medium [1]. The boundary conditions belonging to the straight Fresnel factors of the SFG beam quantify p-polarized SFG emission by the nonlinear polarization located in medium [k], then transmitted throughout (k-1) interfaces to the far field in medium [1]. Equations 36-38 show that such boundary conditions are identical to those applied to any incoming far field, taking into account the emission factor defined in Eq. 2. The Fabry-Pérot, boundary condition and dephasing terms, thus the whole Fresnel factors are equal for the SFG outgoing

and the incoming beams. We recover in the expressions above the universality of the Fresnel factors in the generic case of the N-layer system.

When SFG is emitted and measured in transmission, the Fresnel factors for the SFG beam differ from the ones determined above because they now account for the propagation of a beam generated in medium [k] and travelling towards the far field in medium [N]. However, from the universality property, we know that, whatever the polarization, such Fresnel factors for the transmitted SFG beam are equal to those applying to an incoming beam travelling from layer [N] to layer [k], provided that emission factor from Eq. 4 is used. They may be deduced from the formulas above by appropriately swapping the indices, i.e. transforming $\{1, 2, \dots, k-1, k, \dots, N-1, N\}$ into $\{N, N-1, \dots, k, k-1, \dots, 2, 1\}$. As propagation phases are now calculated from the last interface, $\sum_{j=2}^{N-1} \beta_3^{[j]}$ must be subtracted from the total phase to account for the common origin of the phases at $z = 0$. Explicit formulas for SFG in transmission in the three-layer system may be found in Ref. 30.

Beyond these general equations, we show below how they must be adapted to two specific cases, namely ultrathin and macroscopic layers, and how they apply to the four-layer case.

III. SPECIAL CASES

For practical applications, we stress on the essential differences between thin, microscopic and macroscopic layers. The calculations above suppose that the layers are "microscopic", i.e. thick enough not to neglect the Fabry-Pérot and interference effects due to beam propagation. In the two parts below, we consider the transformation of these equations when one layer becomes very thin, or instead very thick.

A. Thin layers

We examine what happens when one of the layers (medium [h], refractive index $n^{[h]}$) has a thickness small when compared to the wavelengths of light, or even tending to zero ($d^{[h]} \ll \lambda/2\pi$, leading to $\beta^{[h]} \rightarrow 0$ and $\xi^{[h]} \rightarrow 1$). In the three-layer system, we have in this situation (with $h = 2$), whatever the polarization, $r^{123} \rightarrow \frac{r^{12} + r^{23}}{1 + r^{12}r^{23}} = r^{13}$. Layer [2] becomes blank for linear optics⁵⁵ and, as for nonlinear optics, the main consequence is the equivalence between 2L and 3L models apart from continuity conditions for the z-

component.³⁰ Here we show that this result generalizes in the N-layer system: the Fresnel factors applicable to layer [h] are equal to the Fresnel factors of the same system where layer [h] has been removed (this new system being called $\{N \setminus h\}$), apart from continuity conditions for the z-component. In order to show this, we plug $\xi^{[h]} = 1$ into Eq. 19 in order to calculate the Fresnel factor for s-polarization at any interface $\{k-1\}$ in the system (generalization for arbitrary z is straightforward using Eq. 30). Developing the denominator using $r^{h-1,h+1} = \frac{r^{h-1,h} + r^{h,h+1}}{1 + r^{h-1,h}r^{h,h+1}}$ (valid for s and p polarizations) gives

$$\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger = \prod_{\substack{j=2 \\ \{N \setminus h\}}}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger \times (1 + r_s^{h-1,h} r_s^{h,h+1}) \quad (39)$$

where the product for the last term is not ruled. For $h \leq k$, factors $(1 + r_s^{h-1,h})(1 + r_s^{h,h+1})$ appear at the numerator, which simplify using

$$1 + r_s^{h-1,h+1} = \frac{(1 + r_s^{h-1,h})(1 + r_s^{h,h+1})}{1 + r_s^{h-1,h} r_s^{h,h+1}} \quad (40)$$

and Eq. 19 becomes:

$$F_y^{\{k-1\}} = \frac{(1 + \xi^{[k]} r_s^{k,k+1})^\dagger \prod_{j=k+1}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger}{\prod_{\substack{j=2 \\ \{N \setminus h\}}}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger} \prod_{\substack{j=1 \\ \{N \setminus h\}}}^{k-1} [1 + r_s^{j,j+1}] \prod_{\substack{j=2 \\ \{N \setminus h\}}}^{k-1} e^{i\beta^{[j]}} \quad (41)$$

For $h \geq k+1$, the same factor $(1 + r_s^{h-1,h} r_s^{h,h+1})$ appears as a normal product both at the numerator and denominator, and after simplification, Eq. 19 becomes:

$$F_y^{\{k-1\}} = \frac{(1 + \xi^{[k]} r_s^{k,k+1})^\dagger \prod_{\substack{j=k+1 \\ \{N \setminus h\}}}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger}{\prod_{\substack{j=2 \\ \{N \setminus h\}}}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger} \prod_{j=1}^{k-1} [1 + r_s^{j,j+1}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \quad (42)$$

The same procedure leads to analogous results for x- and z-components. For the latter, factor $(n^{[1]})^2 / (n^{[h]})^2$ (Eq. 20 and 31) is the only reminder of the presence of [h] layer. Otherwise, this layer has become blank for linear and nonlinear optics, as is layer [2] with a negligible thickness in a three-layer system.^{30,55} Consequently, in a N-layer system, all layers having

thicknesses smaller enough than the wavelengths of light may be discarded, reducing the complexity of the system, in order to focus only on the thick layers where interferences occur. Conversely, this means that it is possible to model a multilayer system by increasing at will the number of layers as soon as they have a negligible thickness and their indices of refraction are introduced to modulate the Fresnel z-factors. This option is interesting for example when the nonlinear polarizations happen to be generated at any interface where the refractive index differs from both bulk indices.³² Choosing the right index for such an interface layer is a classical puzzle for SFG spectroscopy, and several options have been proposed, based on variations on a Lorentz model,^{31,56,57} molecular dynamics simulations^{58,59} or ellipsometry measurements⁶⁰ It is also possible to define the interface by several sublayers, or even a continuous variation of the refractive index as a function of depth.⁶¹

B. Macroscopic layers

The equations in Part II take full account of the Fabry-Pérot (F-P) effect due to interferences between all the beams propagating and bouncing inside a generic layer [k] after multiple reflections at the {k-1} and {k} boundaries. This analysis is correct as long as the system allows long range propagation and overlap of the multiply reflected beams. When layer [k] becomes thick, or even macroscopic, these hypotheses suffer from several restrictions. In practical SFG experiments, these thick layers are in general made of wafers, plates or windows not originally designed for perfect F-P effect, or in any case too thick to perfectly achieve it. It is known that even manufactured F-P resonators may suffer from imperfections, due to non-parallel plane surfaces or non-planar boundaries, either slightly spherical or roughened.^{62,63} Quantitatively, the upper bound of the misalignment of two adjacent plane interfaces in the system (i.e. non-parallelism) leading to an incomplete F-P effect is a fraction of the wavelength.⁶⁴ It is therefore more easily reached for thick layers, whereas it may be neglected when the thickness of the interfering layer is roughly up to the order of magnitude of the wavelength. In addition, contrary to optical set-ups designed for F-P analysis, SFG experiments usually make use of small and focused beams at high angles of incidence. In these kinds of geometries, it is easy to see that the multiple beams inside a thick layer [j] experiment a drift in position which quickly leads to loss of spatial overlap, all the more as beam overlap is usually experimentally optimized at one of the interfaces, not in the middle

of the thick layer. When ultrashort pulses are involved, we may also expect that the pulses, originally overlapped in time, acquire a progressive time delay as a consequence of their different propagation speeds (i.e. group velocities), leading to a decreasing efficiency of the nonlinear process when multiple reflections are involved. Finally, for Gaussian beams, the nonlinear phenomenon essentially takes place close to the overlapping beam centers where the intensities of the input beams are maximal, and the multiply reflected beams quickly shift away from this small optimal zone.

As a consequence, it seems reasonable to give the possibility to the user to simplify the model by treating thick layers in a different way as for their Fresnel factors. When the thickness becomes macroscopic (typically for $d^{[k]} \gg \lambda_{IR}$), it is possible to adapt the implementation and the magnitude of the F-P effect to the experimental geometry and sample properties. In particular, when multiple reflections are completely neglected in layer [k], all terms specific to this phenomenon must be discarded. This means that a beam entering macroscopic layer [k] is allowed to reflect on the next interface {k} (to ensure consistent boundary conditions there) but not backwards on interface {k-1} and further. As a consequence on the formulas, terms containing $\xi^{[k]} r_{s/p}^{k-1,k}$ can be dropped from the F-P denominator in Eq. 18-20 and 29-31, as illustrated in the examples in Part III C.²²

Considering the general Fresnel factor in medium [k] from Eq. 29-31, we see that the denominator for a macroscopic layer [k] separates as

$$\prod_{j=2}^{N-1} \left[1 + \xi^{[j]} r_{s/p}^{j-1,j} r_{s/p}^{j,j+1} \right]^\dagger = \prod_{j=2}^{k-1} \left[1 + \xi^{[j]} r_{s/p}^{j-1,j} r_{s/p}^{j,j+1} \right]^\dagger \prod_{j=k+1}^{N-1} \left[1 + \xi^{[j]} r_{s/p}^{j-1,j} r_{s/p}^{j,j+1} \right]^\dagger \quad (43)$$

when $\xi^{[k]} r_{s/p}^{k-1,k} = 0$. For the y-component (identical relationships apply to x and z components), Eq. 30 separates into

$$F_y^{[k]}(z) = \frac{\prod_{j=2}^{k-1} e^{i\beta^{[j]} z} \prod_{j=1}^{k-1} [1 + r_s^{j,j+1}] \left[e^{i\beta^{[k]}(z)} + r_s^{k,k+1} \xi^{[k]} e^{-i\beta^{[k]}(z)} \right]^\dagger \prod_{j=k+1}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger}{\prod_{j=2}^{k-1} \left[1 + \xi^{[j]} r_{s/p}^{j-1,j} r_{s/p}^{j,j+1} \right]^\dagger \prod_{j=k+1}^{N-1} \left[1 + \xi^{[j]} r_{s/p}^{j-1,j} r_{s/p}^{j,j+1} \right]^\dagger} \quad (44)$$

This formula expresses the full factor inside layer [k] as the (regular) product between the factor at the last interface {k-1} inside layer [k] of the {1;k} subsystem (Eq. 22) and the factor inside the first medium (i.e. layer [k]) of the {k;N} subsystem. This second factor has not been calculated above, but may be reconstructed from Eq. 10 by changing (1,2) into

(k,k+1) and replacing first term $[1 + r_s^{k,k+1}]^\dagger$ by the full function of $\beta^{[k]}(z)$, or from Eq. 27 by changing (2,3) into (k,k+1) and discarding the terms involving $r_s^{k-1,k}$. In other words, as seen from macroscopic layer [k], the system can formally be split into two independent subsystems {1;k} and {k;N}. If the reflection process at the k interface is moreover neglected (i.e. $r_{s/p}^{k,k+1} = 0$) then $F_y^{[k]}(z)$ reduces, as could be anticipated, to

$$F_y^{[k]}(z) = \frac{\prod_{j=2}^{k-1} e^{i\beta^{[j]}} \prod_{j=1}^{k-1} [1 + r_s^{j,j+1}]}{\prod_{j=2}^{k-1} \left[1 + \xi^{[j]} r_{s/p}^{j-1,j} r_{s/p}^{j,j+1}\right]^\dagger} e^{i\beta^{[k]}(z)}, \quad (45)$$

and accordingly for x and z factors. In this case, the whole system is reduced to the upper subsystem {1;k}, and the Fresnel factors combine transmission from layer [1] to layer [k] and a mere forward propagation phase inside layer [k]. The lower subsystem {k;N} has no influence on the value of the electric field inside layer [k].

C. Four-layer system

As a straightforward application of the general results, we list here the Fresnel factors applicable to the SFG process at the three interfaces of a four-layer system (the five-layer system is addressed in the Supplementary Material). Such a four-layer description is interesting for example when studying molecular layers deposited on top of a substrate which spontaneously oxidizes in air, thus inserting an additional oxide layer into the three-layer system;^{26,65} when a gap layer is experimentally present between medium 1 and the interface, for example in ATR configuration;²³ when the presence of a liquid environment makes it necessary to probe the interface through a transparent substrate;²² when the media have to be decomposed into a surface layer and a bulk layer.²⁴

From the results for the N-layer system, we can write the Fresnel factors linking the far field amplitude in medium [1] to the local fields at

interface {1}:

$$F_x^{\text{interface 1}}(\omega_i) = \frac{(1 - r_p^{12})(1 - \xi^{[2]}r_p^{23} + \xi^{[3]}r_p^{23}r_p^{34} - \xi^{[2]}\xi^{[3]}r_p^{34})}{1 + \xi^{[2]}r_p^{12}r_p^{23} + \xi^{[3]}r_p^{23}r_p^{34} + \xi^{[2]}\xi^{[3]}r_p^{12}r_p^{34}} \quad (46)$$

$$F_y^{\text{interface 1}}(\omega_i) = \frac{(1 + r_s^{12})(1 + \xi^{[2]}r_s^{23} + \xi^{[3]}r_s^{23}r_s^{34} + \xi^{[2]}\xi^{[3]}r_s^{34})}{1 + \xi^{[2]}r_s^{12}r_s^{23} + \xi^{[3]}r_s^{23}r_s^{34} + \xi^{[2]}\xi^{[3]}r_s^{12}r_s^{34}} \quad (47)$$

$$F_z^{\text{interface 1}}(\omega_i) = \frac{(1 + r_p^{12})(1 + \xi^{[2]}r_p^{23} + \xi^{[3]}r_p^{23}r_p^{34} + \xi^{[2]}\xi^{[3]}r_p^{34})}{1 + \xi^{[2]}r_p^{12}r_p^{23} + \xi^{[3]}r_p^{23}r_p^{34} + \xi^{[2]}\xi^{[3]}r_p^{12}r_p^{34}} \quad (48)$$

interface {2}:

$$F_x^{\text{interface 2}}(\omega_i) = \frac{e^{i\beta^{[2]}}(1 - r_p^{12})(1 - r_p^{23})(1 - \xi^{[3]}r_p^{34})}{1 + \xi^{[2]}r_p^{12}r_p^{23} + \xi^{[3]}r_p^{23}r_p^{34} + \xi^{[2]}\xi^{[3]}r_p^{12}r_p^{34}} \quad (49)$$

$$F_y^{\text{interface 2}}(\omega_i) = \frac{e^{i\beta^{[2]}}(1 + r_s^{12})(1 + r_s^{23})(1 + \xi^{[3]}r_s^{34})}{1 + \xi^{[2]}r_s^{12}r_s^{23} + \xi^{[3]}r_s^{23}r_s^{34} + \xi^{[2]}\xi^{[3]}r_s^{12}r_s^{34}} \quad (50)$$

$$F_z^{\text{interface 2}}(\omega_i) = \frac{e^{i\beta^{[2]}}(1 + r_p^{12})(1 + r_p^{23})(1 + \xi^{[3]}r_p^{34})}{1 + \xi^{[2]}r_p^{12}r_p^{23} + \xi^{[3]}r_p^{23}r_p^{34} + \xi^{[2]}\xi^{[3]}r_p^{12}r_p^{34}} \left(\frac{n^{[1]}}{n^{[2]}} \right)^2 \quad (51)$$

and interface {3}:

$$F_x^{\text{interface 3}}(\omega_i) = \frac{e^{i\beta^{[2]}}e^{i\beta^{[3]}}(1 - r_p^{12})(1 - r_p^{23})(1 - r_p^{34})}{1 + \xi^{[2]}r_p^{12}r_p^{23} + \xi^{[3]}r_p^{23}r_p^{34} + \xi^{[2]}\xi^{[3]}r_p^{12}r_p^{34}} \quad (52)$$

$$F_y^{\text{interface 3}}(\omega_i) = \frac{e^{i\beta^{[2]}}e^{i\beta^{[3]}}(1 + r_s^{12})(1 + r_s^{23})(1 + r_s^{34})}{1 + \xi^{[2]}r_s^{12}r_s^{23} + \xi^{[3]}r_s^{23}r_s^{34} + \xi^{[2]}\xi^{[3]}r_s^{12}r_s^{34}} \quad (53)$$

$$F_z^{\text{interface 3}}(\omega_i) = \frac{e^{i\beta^{[2]}}e^{i\beta^{[3]}}(1 + r_p^{12})(1 + r_p^{23})(1 + r_p^{34})}{1 + \xi^{[2]}r_p^{12}r_p^{23} + \xi^{[3]}r_p^{23}r_p^{34} + \xi^{[2]}\xi^{[3]}r_p^{12}r_p^{34}} \left(\frac{n^{[1]}}{n^{[3]}} \right)^2 \quad (54)$$

with $\xi^{[j]} = e^{2i\beta^{[j]}}$ and $\beta^{[j]} = \frac{\omega}{c}n^{[j]}d^{[j]} \cos \theta^{[j]}$. For z-component, these Fresnel factors at interface {k} apply in medium [k]. For the same interface in medium [k+1], the continuity condition must be taken into account by using $\left(\frac{n^{[1]}}{n^{[k+1]}} \right)^2$ instead of $\left(\frac{n^{[1]}}{n^{[k]}} \right)^2$.

It is interesting to compare these results to the few examples of four-layer systems in the literature.^{22–24} In Ref. 22, after reordering the interface numbers, the probed interface (yyz component) is buried between media [3] and [4] (interface {3}). Letting aside the coefficient relating to the entrance inside the first prism, the y-component coefficient reads (Eq. A5)

$$\frac{(1 + r_s^{12})(1 + r_s^{23})(1 + r_s^{34})}{1 + \xi^{[3]}r_s^{23}r_s^{34}}. \quad (55)$$

Comparing with Eq. 53 shows several discrepancies. We understand that layer [2] (the substrate) is considered macroscopic and that no Fabry-Pérot nor phase delays are taken into

account in this medium. Applying the rule defined in Part III B, we drop terms containing $\xi^{[2]}r_s^{12}$ and recover their formulas, except factor $e^{i\beta^{[3]}}$ which shows that the origin of the phases is probably set at interface {3}. The z-component reads

$$\frac{\frac{n^{[1]}}{n^{[2]}}(1+r_p^{12})\frac{n^{[2]}}{n^{[3]}}(1+r_p^{23})\frac{n^{[3]}}{n^{[4]}}(1+r_p^{34})}{1+\xi^{[3]}r_p^{23}r_p^{34}}\left(\frac{n^{[4]}}{n^{[m]}}\right)^2 \quad (56)$$

where $n^{[m]}$ is the index of refraction of the thin nonlinear sheet inside medium 4. Leaving aside as above the $\xi^{[2]}r_s^{12}$ factors and the propagation phases in media [2] and [3], we should find

$$\frac{(1+r_p^{12})(1+r_p^{23})(1+r_p^{34})}{1+\xi^{[3]}r_p^{23}r_p^{34}}\left(\frac{n^{[1]}}{n^{[m]}}\right)^2. \quad (57)$$

The missing $n^{[1]}/n^{[4]}$ factor is more easily understood when considering also their x-component, which surprisingly has the same amplitude as their z-component (apart from the boundary conditions), which should not be the case. We understand that the formulas provide in fact, probably mistakenly, the amplitudes of the p-polarized local field in medium [4], rather than its x- and z-components. Reintroducing factors $\cos\theta^{[4]}/\cos\theta^{[1]}$ and $\sin\theta^{[4]}/\sin\theta^{[1]} = n^{[1]}/n^{[4]}$ in the formulas for x and z, respectively, allows to recover the expected Fresnel factors. This example illustrates how the calculation of Fresnel factors is very dependent of the approximations made during the definition of the system, and, as already pointed out, the specificity of macroscopic layers.

Another interfacial system is described as composed of four layers with one vanishing thickness²³ or five layers with two vanishing thicknesses.²⁴ In the former, the nonlinear sheet is located in medium [3] at the interface with medium [4]. The coefficient for the y-component is expected to follow from Eq. 53. The thickness of layer [3] is then considered negligible, leading to $\beta^{[3]} = 0$ and $\xi^{[3]} = 1$. Eq. 53 becomes

$$F_y^{\text{interface } 3}(\omega_1) = \frac{e^{i\beta^{[2]}}(1+r_s^{12})(1+r_s^{23})(1+r_s^{34})}{1+r_s^{23}r_s^{34}+\xi^{[2]}r_s^{12}(r_s^{23}+r_s^{34})} \quad (58)$$

We illustrate the mechanism used in Part III A and divide numerator and denominator by $1+r_s^{23}r_s^{34}$. Using $\frac{r_s^{23}+r_s^{34}}{1+r_s^{23}r_s^{34}} = r_s^{24}$, leading to $1+r_s^{24} = \frac{(1+r_s^{23})(1+r_s^{34})}{1+r_s^{23}r_s^{34}}$, we get as expected the y Fresnel factor of the three layer system where layer 3 has been removed:

$$F_y^{\text{interface } 3}(\omega_1) = \frac{e^{i\beta^{[2]}}(1+r_s^{12})(1+r_s^{24})}{1+\xi^{[2]}r_s^{12}r_s^{24}} \quad (59)$$

Simple manipulations of the original equation for $L_1^{(4)}$ in Ref. 23, essentially introducing the explicit values of $r_{s/p}$, allows retrieving an identical expression. The same manipulations

lead as expected for the z-component $L_2^{(4)}$ to

$$F_z^{\text{interface } 3}(\omega_2) = \frac{e^{i\beta^{[2]}}(1+r_p^{12})(1+r_p^{24})}{1+\xi^{[2]}r_p^{12}r_p^{24}} \left(\frac{n^{[1]}}{n^{[3]}}\right)^2 \quad (60)$$

For the SFG y-component, we note that the emission factor turns down to $G^{(4)} = \frac{2i\pi\omega_3}{cn^{[1]}\cos\theta^{[1]}}L_1^{(4)}$, in accordance with the usual factors in Eq. 2. In Ref. 24, the full system is composed of five layers, in which two are nonlinear media with vanishing thicknesses. The same procedure for manipulating the equations leads to recover the same Fresnel factors as with our formulas, provided that the vanishing thicknesses are taken into account.

As illustrated here, our general formulas allow to recover those of the literature. However, for most published SFG analysis of four-layer systems, one of the layers has a vanishing thickness, leading to final equations converging towards a three layer system. It is possible to find some examples where explicitly non-vanishing thicknesses have been studied.^{40,66} In these cases, the use of the transfer matrix formalism does not allow the determination of analytical Fresnel factors and therefore may not be directly compared to our expressions. However, it is possible to compare the numerical results of both methods. In Fig. 3, we tackle some of the calculations of Ref. 66 using the same definition of the four-layer system (air/PTCDI-C₈/SiO₂/Si) and the same sources for the refractive indices. We note that the plotted $|F_{ijk}^{\{1,2\}}| = |F_i^{\{1,2\}}(\omega_3)F_j^{\{1,2\}}(\omega_1)F_k^{\{1,2\}}(\omega_2)|$ reproduce all the features seen on the original $|T_{\{1,2\}}^{ijk}|$ transfer coefficients. The main small differences lie in the relative amplitudes of the coefficients, which are mainly linked to the definition of the transfer coefficients versus Fresnel factors. For example, a better agreement is obtained when our zyy component at interface {1} is corrected by factor $(n_3^{[1]}/n_3^{[2]})^2$, suggesting that the nonlinear polarization at this interface is set in medium [1] in the original publication, instead of medium [2] as we do.

IV. MULTIPLE NONLINEAR SOURCES

In a multilayer film, several interfaces may give birth to a nonlinear polarization. The SFG signals they emit sum up and interfere in the global response of the interface. From Eq. 3, we see that such interferences have their origin in the relative values, in amplitude and in phase, of their nonlinear susceptibility tensors and of their Fresnel factors. In order to exploit the specificity of SFG spectroscopy towards interfaces, it becomes interesting to

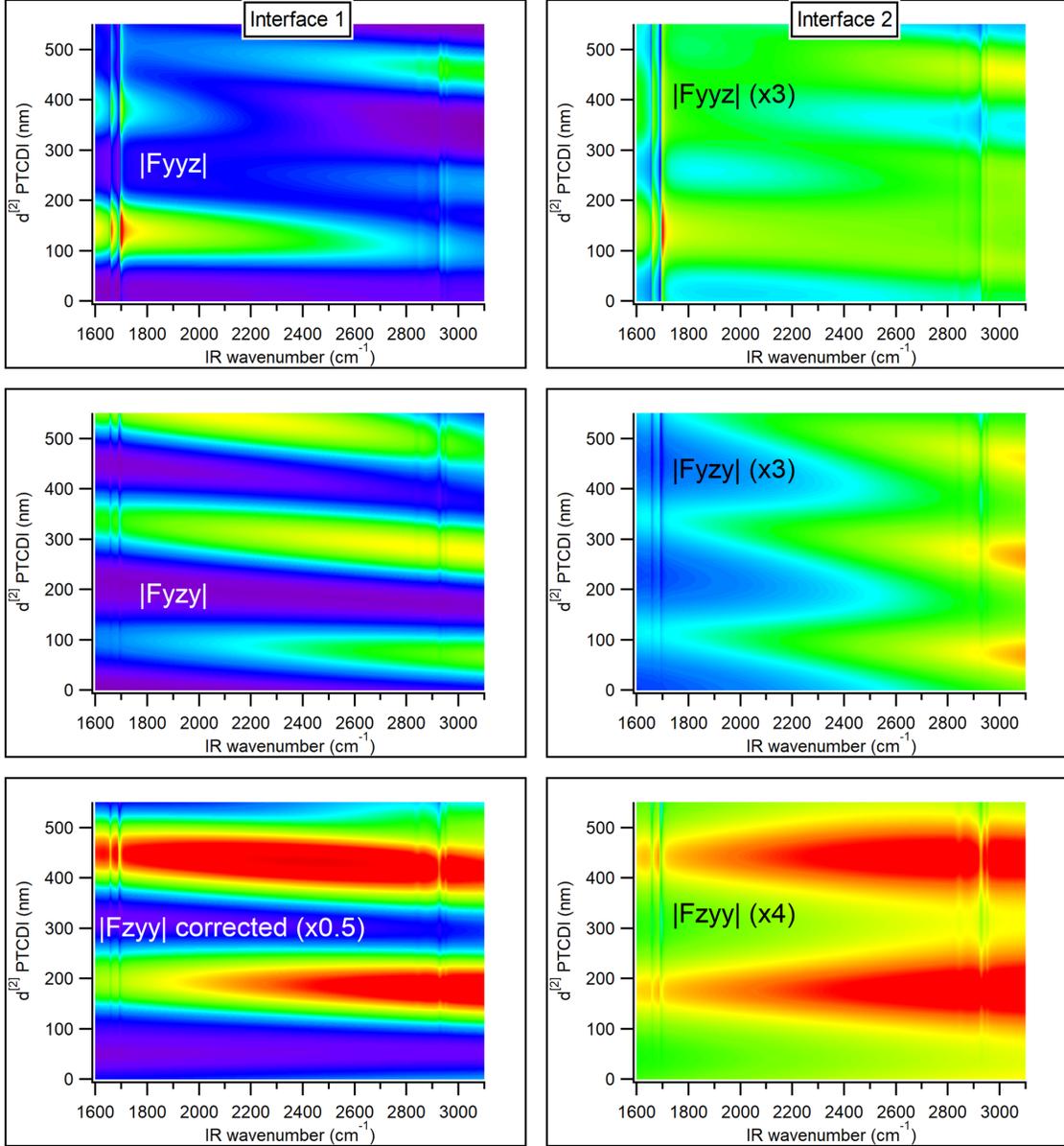


FIG. 3. Amplitude of the complex Fresnel factors (all scales identical) for the SFG process at the four-layer {air/PTCDI-C₈/SiO₂/Si} interface described in Ref. 66. Tunable parameters are the IR wavenumber and the thickness of the PTCDI-C₈ layer. For zyy term at interface {1}, best intensity match with the original publication is obtained after correction by $(n_3^{[1]}/n_3^{[2]})^2$.

look for the specific experimental conditions which lead to the decrease, ideally down to cancellation, of the response of one (or several) interfaces while keeping the interface of interest at a high signal level. The three-layer case has been addressed in the previous article³⁰ and elsewhere.³² Here we focus on the four-layer and N-layer systems.

A. Four-layer system

The conditions leading to the cancellation of one of the electric fields at one of the three interfaces in the four-layer system directly follows from Eq. 46-54, more precisely from their numerators. We immediately see that the fields at the last interface {3} cannot exactly vanish (for the reasons recalled in Part II A). The fields at next-to-last interface {2} may vanish under the same conditions as in the three-layer system³³ (see the complete discussion in Ref. 30) applied to the last two media, i.e. adapted from layers [2] and [3] to layers [3] and [4]. The analysis of this previous article is thus still valid when applied to the last two layers of the system. Finally, cancelling one of the fields at interface {1} implies to cancel the numerator of one of Eq. 46-48. Considering first the y-component, we have to solve $1 + \xi^{[2]}r_s^{23} + \xi^{[3]}r_s^{23}r_s^{34} + \xi^{[2]}\xi^{[3]}r_s^{34} = 0$. Such an equation depends on many parameters: four indices of refraction $n^{[1]}$, $n^{[2]}$, $n^{[3]}$, $n^{[4]}$, two layer thicknesses $d^{[2]}$, $d^{[3]}$ and $\theta^{[1]}$, making it difficult to establish general rules. There are therefore potentially various sets of parameters leading to the cancellation of a field at interface {1}. However, such a cancellation does not happen in the general case, as is exemplified in Fig. 3 where points with the lowest values represent between 6% and 11% of the maxima at interface {1}, and between 22% and 31% at interface {2}. Of course, interesting contrast is still achievable when comparing the full Fresnel factors at interfaces {1}, {2} and {3}.⁶⁶

We may however consider a particular case interesting for its practical application: we suppose that the parameters of layers [3] and [4] have been optimized so that the y-component of the electric field cancels at interface {2}, i.e. $\xi^{[3]}r_s^{34} = -1$.^{30,33} Plugging this condition in the cancelling condition at interface {1} gives:

$$1 + \xi^{[2]}r_s^{23} + \xi^{[3]}r_s^{23}r_s^{34} + \xi^{[2]}\xi^{[3]}r_s^{34} = 1 + \xi^{[2]}r_s^{23} - r_s^{23} - \xi^{[2]} = (1 - r_s^{23})(1 - \xi^{[2]}) = 0 \quad (61)$$

leading to $\xi^{[2]} = 1$, which is easily achieved for a series of thicknesses $d_i^{[2]}$ for layer [2], fulfilling the condition

$$d_i^{[2]} = \frac{m\lambda_i}{2n_i^{[2]}\cos\theta_i^{[2]}} \quad (62)$$

for $m \geq 0$, the case $m = 0$ being obvious. We note that the cancelling condition at interface 1 does not depend on the value of r_s^{23} . This means that, when the electric field along y cancels at the next-to-last interface {2}, it also easily cancels out at interface {1} just by adjusting the thickness of medium [2]. In a similar way, for the x-component, under the

cancelling condition at interface {2}: $1 - \xi^{[3]}r_p^{34} = 0$, we may cancel the electric field at interface {1} under the condition

$$1 - \xi^{[2]}r_p^{23} + \xi^{[3]}r_p^{23}r_p^{34} - \xi^{[2]}\xi^{[3]}r_p^{34} = 1 - \xi^{[2]}r_p^{23} + r_p^{23} - \xi^{[2]} = (1 + r_p^{23})(1 - \xi^{[2]}) = 0 \quad (63)$$

and the same calculation for the z-component leads to $(1 - r_p^{23})(1 - \xi^{[2]}) = 0$. The cancelling conditions for the three components are therefore all identical (Eq. 62).

Beyond cancelling conditions, we also understand from this analysis that the periodicities in $\xi^{[2]}$ and $\xi^{[3]}$ play a role in the contrast factors from layer to layer. Of course, only the values of the full numerators of the Fresnel factors provide the exact contrast. Nevertheless, if media [2] and [3] have refractive indices not too far apart, we may expect that the conditions on $(d^{[2]}, d^{[3]})$ leading to a maximum {2}/{1} contrast will also induce further maxima for a series of thicknesses $(d^{[2]} + m\lambda_i/2n_i^{[2]}\cos\theta_i^{[2]}, d^{[3]} + p\lambda_i/2n_i^{[3]}\cos\theta_i^{[3]})$. Interestingly, the simulations in Ref. 66 (Figure 5) show indeed clear periodic fluctuations in the maxima of the contrast factors, whatever the polarizations, with orders of magnitude for their periods $\lambda_{vis,SFG}/2n_{vis,SFG}^{[2]}\cos\theta_{vis,SFG}^{[2]} \sim 230 - 260nm$ along $d^{[2]}$ and $\lambda_{vis,SFG}/2n_{vis,SFG}^{[3]}\cos\theta_{vis,SFG}^{[3]} \sim 290 - 330nm$ along $d^{[3]}$, respectively.

As a conclusion, if the design of layers [3] and [4] of the system (i.e. $n_i^{[3]}, d_i^{[3]}, n_i^{[4]}$), probed by light with wavelength λ_i under the angle of incidence $\theta_i^{[1]}$ (leading to $\theta_i^{[3]}$ and $\theta_i^{[4]}$ by Snell's law), leads to fulfill the condition for the cancellation of one component of the electric field at interface {2}, then a mere adjustment of the thickness of layer [2] to a value fulfilling Eq. 62 also leads to the simultaneous cancellation of the same component of the electric field at interface {1}. By a careful design of the system, it is therefore possible to probe by SFG only the last interface of a four-layer system while keeping the two other interfaces SFG-silent. In particular, if a three-layer system is originally designed in order to probe only the last interface (i.e. the other one is made silent), then it is possible to deposit or add other layers on top of the sample and keep them silent as long as they fulfill Eq. 62.

B. N-layer system

As shown along the detailed proof below, we may generalize the previous result to a N-layer system. If the system is designed in order that the SFG produced by the next-to-last interface (interface {N-2}) cancels out (because one component of one electric field cancels

out following the various conditions listed in Ref. 30), it is possible to achieve the cancellation of the same component of that electric field at all other interfaces $\{k-1\}$, from $k=2$ to $N-2$, providing that the thicknesses $d^{[k]}$ are adjusted according to the condition of Eq. 69, valid for the three components of the field. In other words, in such a N -layer system, all interfaces except the last one become SFG-silent. Conversely, it is possible to adjust the value of $d^{[1]}$ in such a system (e.g. using a half integer value for m in Eq. 69) to build a N -layer system where only the first and last interfaces coherently produce SFG radiation (interfering with each other) while all others remain silent, in a way comparable to a conventional three-layer system, where the SFG signals from both interfaces usually interfere.^{32,36}

The demonstration relies on Eq. 18 to 20. Focusing on the y -component, we may cancel the electric field at the $\{N-2\}$ interface by fulfilling the equality $1 + \xi^{[N-1]}r_s^{N-1,N} = 0$. We recover for the last two layers of the N -layer system the same conditions as in Ref. 30 for the three-layer system. We have for the $\{N-3\}$ interface the cancellation condition:

$$(1 + \xi^{[N-2]}r_s^{N-2,N-1})^\dagger [1 + \xi^{[N-1]}r_s^{N-2,N-1}r_s^{N-1,N}]^\dagger = 0 \quad (64)$$

and, by plugging in $1 + \xi^{[N-1]}r_s^{N-1,N} = 0$, we get

$$(1 - \xi^{[N-2]})(1 - r_s^{N-2,N-1}) = 0 \quad (65)$$

so that condition $\xi^{[N-2]} = 1$ is sufficient to extend the cancellation to interface $\{N-3\}$. Recursively, we consider now interface $\{k-1\}$ and suppose that the y -component of the electric field vanishes for interfaces $\{k\}$ to $\{N-2\}$, represented by the conditions $1 + \xi^{[N-1]}r_s^{N-1,N} = 0$ and $\xi^{[j]} = 1$ for $k+1 \leq j \leq N-2$. We rewrite the cancellation condition at interface $\{k-1\}$ as

$$(1 + \xi^{[k]}r_s^{k,k+1})^\dagger \prod_{j=k+1}^{N-2} [1 + r_s^{j-1,j}r_s^{j,j+1}]^\dagger [1 - r_s^{N-2,N-1}]^\dagger = 0 \quad (66)$$

Applying the rules of the ruled product in inverse order from factors $r_s^{N-2,N-1}$ to $r_s^{k,k+1}$, and more precisely using recursively equalities like

$$[1 + r_s^{N-3,N-2}r_s^{N-2,N-1}]^\dagger [1 - r_s^{N-2,N-1}]^\dagger = [1 - r_s^{N-3,N-2}]^\dagger [1 - r_s^{N-2,N-1}] \quad (67)$$

leads to the transformation of Eq. 66 into

$$(1 + \xi^{[k]}r_s^{k,k+1})^\dagger [1 - r_s^{k,k+1}]^\dagger \prod_{j=k+1}^{N-2} [1 - r_s^{j,j+1}] = (1 - \xi^{[k]}) \prod_{j=k}^{N-2} [1 - r_s^{j,j+1}] = 0 \quad (68)$$

This shows by induction that the y-component of the electric field may also be cancelled at interface $\{k-1\}$ by constructing $\xi^{[k]} = 1$, that is choosing thickness $d^{[k]}$ as

$$d_i^{[k]} = \frac{m\lambda_i}{2n_i^{[k]} \cos \theta_i^{[k]}} \quad (69)$$

for $m \geq 0$. Demonstrations for x- and z-components follow the same track and lead to the same result.

V. CONCLUSION

We believe that surface SFG spectroscopy will apply in the future to more and more complex systems to study buried interfaces. Instead of modifying the Fresnel paradigm for surface SFG to adapt to these new conditions, the present article proposes to extend this simple description, made up of two simple equations involving well-defined quantities, and adapt it to the particularities of multilayer systems. The evolution thus only applies to the Fresnel factors, leaving the rest unchanged. We hope that this article thus establishes a link between present and future uses of second-order nonlinear spectroscopies.

Interestingly, the Fresnel factor concept may be extended to the magnetic terms involved in the nonlinear process, as fully described in Ref. 67. A generalization to the N-layer system, following the same steps as here,⁵⁰ seems rather straightforwardly accessible, as has already been attempted using the (4×4)-matrix formalism.⁴⁶ It would give birth to new and simple rules for interferences between SFG processes of electric dipole and magnetic origins, for example involving chiral molecules or magnetic nanoparticles, even when both processes occur at two distinct interfaces separated by several media. Of course, in this case, care should be taken to discriminate between surface and bulk origin of the signals. In the same line, extension to bulk quadrupolar higher order terms has been proposed for multilayers in the transfer matrix frame,⁴² and detailed modellings exist for the three-layer system under the Fresnel formalism.⁶⁸ As our formulas include the generic z-dependent Fresnel factor at any point inside the N-layer system, and considering the equivalence of magnetic and quadrupolar contributions to an effective electric dipolar description,^{69,70} a generic description in the N-layer system of surface and bulk nonlinear responses induced by electric dipole, magnetic and quadrupolar contributions appears reachable.

Appendix A: General formalism

In the Abelès formalism, each interface $\{k\}$ between layers $[k]$ and $[k+1]$ is represented by a vector $\mathbf{Q}^{\{k\}}$ gathering the two tangential components of the electromagnetic field at this interface (i.e. continuous across the interface). Specifically, we have, for the s-polarization,

$$\mathbf{Q}_s^{\{k\}} = \begin{bmatrix} U_s^{\{k\}} \\ V_s^{\{k\}} \end{bmatrix} = \begin{bmatrix} E_y^{\{k\}} \\ H_x^{\{k\}} \end{bmatrix} \quad (\text{A1})$$

and for the p-polarization,

$$\mathbf{Q}_p^{\{k\}} = \begin{bmatrix} U_p^{\{k\}} \\ V_p^{\{k\}} \end{bmatrix} = \begin{bmatrix} H_y^{\{k\}} \\ E_x^{\{k\}} \end{bmatrix} \quad (\text{A2})$$

where \mathbf{E} and \mathbf{H} stand for the electric and magnetic fields, respectively. Contrary to the T-matrix formalism, one matrix $\mathbf{M}^{[k]}$, characteristic of each layer $[k]$, gathers amplitude and phase information for the transfer from one layer to the other. This leads to the following relations for s polarization, with $p^{[k]} = n^{[k]} \cos \theta^{[k]}$:

$$\mathbf{M}_s^{[k]} = \begin{bmatrix} \cos \beta^{[k]} & -\frac{i}{p^{[k]}} \sin \beta^{[k]} \\ -ip^{[k]} \sin \beta^{[k]} & \cos \beta^{[k]} \end{bmatrix} = \frac{e^{-i\beta^{[k]}}}{2} \begin{bmatrix} 1 + \xi^{[k]} & \frac{1}{p^{[k]}}(1 - \xi^{[k]}) \\ p^{[k]}(1 - \xi^{[k]}) & 1 + \xi^{[k]} \end{bmatrix} \quad (\text{A3})$$

and, symmetrically for p polarization, using $q^{[k]} = \cos \theta^{[k]}/n^{[k]}$:

$$\mathbf{M}_p^{[k]} = \begin{bmatrix} \cos \beta^{[k]} & -\frac{i}{q^{[k]}} \sin \beta^{[k]} \\ -iq^{[k]} \sin \beta^{[k]} & \cos \beta^{[k]} \end{bmatrix} = \frac{e^{-i\beta^{[k]}}}{2} \begin{bmatrix} 1 + \xi^{[k]} & \frac{1}{q^{[k]}}(1 - \xi^{[k]}) \\ q^{[k]}(1 - \xi^{[k]}) & 1 + \xi^{[k]} \end{bmatrix} \quad (\text{A4})$$

The relations:

$$r_s^{12} = \frac{p^{[1]} - p^{[2]}}{p^{[1]} + p^{[2]}}; \quad 1 + r_s^{12} = \frac{2p^{[1]}}{p^{[1]} + p^{[2]}}; \quad 1 - r_s^{12} = \frac{2p^{[2]}}{p^{[1]} + p^{[2]}} \quad (\text{A5})$$

and

$$r_p^{12} = \frac{q^{[1]} - q^{[2]}}{q^{[1]} + q^{[2]}}; \quad 1 + r_p^{12} = \frac{2q^{[1]}}{q^{[1]} + q^{[2]}}; \quad 1 - r_p^{12} = \frac{2q^{[2]}}{q^{[1]} + q^{[2]}} \quad (\text{A6})$$

follow from the definitions of $p^{[k]}$ and $q^{[k]}$.

The optical properties of the system are obtained in successive steps:

1) evaluate the total matrix \mathbf{M} of the system

$$\begin{bmatrix} U^{\{1\}} \\ V^{\{1\}} \end{bmatrix} = \mathbf{M}^{[2]} \dots \mathbf{M}^{[N-1]} \begin{bmatrix} U^{\{N-1\}} \\ V^{\{N-1\}} \end{bmatrix} = \mathbf{M} \begin{bmatrix} U^{\{N-1\}} \\ V^{\{N-1\}} \end{bmatrix} \quad (\text{A7})$$

2) calculate the global reflection $r_{s/p}^{\{1,N\}} \equiv r_{s/p}^N$ and transmission $t_{s/p}^{\{1,N\}} \equiv t_{s/p}^N$ coefficients of the system for s and p incident polarisations:

$$r_s^N = \frac{(m_{11} + m_{12}p^{[N]})p^{[1]} - (m_{12} + m_{22}p^{[N]})}{(m_{11} + m_{12}p^{[N]})p^{[1]} + (m_{12} + m_{22}p^{[N]})} \quad (\text{A8})$$

$$t_s^N = \frac{2p^{[1]}}{(m_{11} + m_{12}p^{[N]})p^{[1]} + (m_{12} + m_{22}p^{[N]})} \quad (\text{A9})$$

$$r_p^N = \frac{(m_{11} + m_{12}q^{[N]})q^{[1]} - (m_{12} + m_{22}q^{[N]})}{(m_{11} + m_{12}q^{[N]})q^{[1]} + (m_{12} + m_{22}q^{[N]})} \quad (\text{A10})$$

$$t_p^N = \frac{n^{[1]}}{n^{[N]}} \frac{2q^{[1]}}{(m_{11} + m_{12}q^{[N]})q^{[1]} + (m_{12} + m_{22}q^{[N]})} \quad (\text{A11})$$

3) evaluate $\mathbf{Q}^{\{1\}}$ and $\mathbf{Q}^{\{N-1\}}$ using, for s polarized far field \mathbf{E}^0 :

$$\mathbf{Q}^{\{1\}} = \begin{bmatrix} U^{\{1\}} \\ V^{\{1\}} \end{bmatrix} = \begin{bmatrix} 1 + r_s^N \\ p^{[1]}(1 - r_s^N) \end{bmatrix} E_y^0 \quad (\text{A12})$$

$$\mathbf{Q}^{\{N-1\}} = \begin{bmatrix} U^{\{N-1\}} \\ V^{\{N-1\}} \end{bmatrix} = \begin{bmatrix} 1 \\ p^{[N]} \end{bmatrix} t_s^N E_y^0 \quad (\text{A13})$$

and, for p polarized far field \mathbf{E}^0 :

$$\mathbf{Q}^{\{1\}} = \begin{bmatrix} U^{\{1\}} \\ V^{\{1\}} \end{bmatrix} = \begin{bmatrix} 1 + r_p^N \\ q^{[1]}(1 - r_p^N) \end{bmatrix} n^{[1]} E_p^0 \quad (\text{A14})$$

$$\mathbf{Q}^{\{N-1\}} = \begin{bmatrix} U^{\{N-1\}} \\ V^{\{N-1\}} \end{bmatrix} = \begin{bmatrix} 1 \\ q^{[N]} \end{bmatrix} n^{[1]} t_p^N E_p^0 \quad (\text{A15})$$

4) calculate $\mathbf{Q}^{\{k-1\}}$ for $3 \leq k \leq N-1$ in the system, taking into account the fact that $\mathbf{M}^{[k]}$ matrices allow backward progression (from [N] to [1]) into the successive layers:

$$\mathbf{Q}^{\{k-1\}} = \begin{bmatrix} U^{\{k-1\}} \\ V^{\{k-1\}} \end{bmatrix} = \prod_k^{N-1} \mathbf{M}^{[j]} \begin{bmatrix} U^{\{N-1\}} \\ V^{\{N-1\}} \end{bmatrix} \quad (\text{A16})$$

With equations A12-A16, all \mathbf{Q} vectors of the system, hence the field components at all interfaces, are known.

5) evaluate the fields into medium [k] at an arbitrary depth $z^{k-1} \geq z \geq z^k$ using:

$$\mathbf{Q}^{[k]}(z) = \mathbf{N}^{[k]}(z) \begin{bmatrix} U^{\{k-1\}} \\ V^{\{k-1\}} \end{bmatrix} \quad (\text{A17})$$

with $\mathbf{N}^{[k]}(z)$ accounting this time for forward progression in layer [k]. Defining $\beta^{[k]}(z) = \frac{\omega}{c}n^{[k]}(z^{[k-1]} - z)\cos\theta^{[k]} \geq 0$ and $\xi^{[k]}(z) = e^{2i\beta^{[k]}(z)}$, we have, for s polarization:

$$\mathbf{N}_s^{[k]}(z) = \begin{bmatrix} \cos\beta^{[k]}(z) & \frac{i}{p^{[k]}}\sin\beta^{[k]}(z) \\ ip^{[k]}\sin\beta^{[k]}(z) & \cos\beta^{[k]}(z) \end{bmatrix} = \frac{e^{-i\beta^{[k]}(z)}}{2} \begin{bmatrix} 1 + \xi^{[k]}(z) & \frac{1}{p^{[k]}}(\xi^{[k]}(z) - 1) \\ p^{[k]}(\xi^{[k]}(z) - 1) & 1 + \xi^{[k]}(z) \end{bmatrix} \quad (\text{A18})$$

and for p polarization:

$$\mathbf{N}_p^{[k]}(z) = \begin{bmatrix} \cos\beta^{[k]}(z) & \frac{i}{q^{[k]}}\sin\beta^{[k]}(z) \\ iq^{[k]}\sin\beta^{[k]}(z) & \cos\beta^{[k]}(z) \end{bmatrix} = \frac{e^{-i\beta^{[k]}(z)}}{2} \begin{bmatrix} 1 + \xi^{[k]}(z) & \frac{1}{q^{[k]}}(\xi^{[k]}(z) - 1) \\ q^{[k]}(\xi^{[k]}(z) - 1) & 1 + \xi^{[k]}(z) \end{bmatrix} \quad (\text{A19})$$

6) Finally, the three components of the electric field at any position inside medium [k] follow from the definitions of U and V as

$$E_x^{[k]}(z) = V_p^{[k]}(z), \quad E_y^{[k]}(z) = U_s^{[k]}(z) \quad \text{and} \quad E_z^{[k]}(z) = U_p^{[k]}(z) \frac{n^{[1]}}{(n^{[k]})^2} \sin\theta^{[1]}. \quad (\text{A20})$$

The proportionality factor between the components of the electric field inside the film and the far electric field defines the Fresnel factors:

$$F_x^{[k]}(z) = \frac{E_x^{[k]}(z)}{E_p^0 \cos\theta^{[1]}}, \quad F_y^{[k]}(z) = \frac{E_y^{[k]}(z)}{E_y^0} \quad \text{and} \quad F_z^{[k]}(z) = \frac{E_z^{[k]}(z)}{E_p^0 \sin\theta^{[1]}} \quad (\text{A21})$$

The point is now to provide analytic expressions for these formulas.

Appendix B: Beam with s polarization

We first focus on the incident s-polarized case and define the numerators \mathcal{N} and denominators \mathfrak{D} of the reflection and transmission coefficients:

$$r_s^N = \frac{\mathcal{N}_s^{[N]}}{\mathfrak{D}_s^{[N]}} \quad t_s^N = \frac{2p^{[1]}}{\mathfrak{D}_s^{[N]}} \quad (\text{B1})$$

We recall the definition of the "ruled product", marked with a dagger (\dagger) superscript in the following: when a product is evaluated under this rule, all factors of the form $(r_s^{k-1,k})^2$ are set to 1. From Eq. A8, we have

$$\mathfrak{D}_s^{[N]} = (m_{11} + m_{12}p^{[N]})p^{[1]} + (m_{12} + m_{22}p^{[N]}) \quad (\text{B2})$$

with $\mathbf{M} = \mathbf{M}^{[2]} \dots \mathbf{M}^{[N-1]}$ and

$$\mathfrak{D}_s^{[N+1]} = (m_{11}^{[+1]} + m_{12}^{[+1]}p^{[N+1]})p^{[1]} + (m_{12}^{[+1]} + m_{22}^{[+1]}p^{[N+1]}) \quad (\text{B3})$$

with $\mathbf{M}^{[+1]} = (\mathbf{M}^{[2]} \dots \mathbf{M}^{[N-1]})\mathbf{M}^{[N]}$. Using the expression of $\mathbf{M}^{[N]}$ from Eq. A3, we have:

$$\begin{aligned}\mathfrak{D}_s^{[N+1]} &= \frac{e^{-i\beta^{[N]}}}{2} \left[\frac{p^{[N]} + p^{[N+1]}}{p^{[N]}} \mathfrak{D}_s^{[N]} + \xi^{[N]} \frac{p^{[N]} - p^{[N+1]}}{p^{[N]}} \mathfrak{D}_s^{[N]}(-p^{[N]}) \right] \\ &= \frac{e^{-i\beta^{[N]}}}{1 + r_s^{N,N+1}} \left[\mathfrak{D}_s^{[N]} + \xi^{[N]} r_s^{N,N+1} \mathfrak{D}_s^{[N]}(-p^{[N]}) \right]\end{aligned}\quad (\text{B4})$$

where the second $\mathfrak{D}_s^{[N]}$ is evaluated using $-p^{[N]}$, instead of $p^{[N]}$ in Eq. B2. From Eq. B4, we see that factor $p^{[N]}$ in $\mathfrak{D}_s^{[N]}$ may only appear as $p^{[N-1]} - p^{[N]}$ or as $p^{[N-1]} + p^{[N]}$, leading (after division by $p^{[N-1]} + p^{[N]} = 1 + r_s^{N-1,N}$) to $r_s^{N-1,N}$ and 1, respectively. Evaluating $\mathfrak{D}_s^{[N]}(-p^{[N]})$ is thus equivalent to exchanging the factors of $r_s^{N-1,N}$ and 1 in $\mathfrak{D}_s^{[N]}$. In other words, we have

$$\mathfrak{D}_s^{[N]}(-p^{[N]}) = (r_s^{N-1,N})^\dagger (\mathfrak{D}_s^{[N]})^\dagger \quad (\text{B5})$$

and

$$\mathfrak{D}_s^{[N+1]} = \frac{e^{-i\beta^{[N]}}}{1 + r_s^{N,N+1}} (\mathfrak{D}_s^{[N]})^\dagger [1 + \xi^{[N]} r_s^{N-1,N} r_s^{N,N+1}]^\dagger \quad (\text{B6})$$

Having established the induction step, the value of $\mathfrak{D}_s^{[N]}$ follows:

$$\mathfrak{D}_s^{[N]} = \frac{\prod_{j=2}^{N-1} e^{-i\beta^{[j]}}}{\prod_{j=2}^{N-1} [1 + r_s^{j,j+1}]} (\mathfrak{D}_s^{[2]})^\dagger \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger \quad (\text{B7})$$

Finally, Eq. B1 gives, for the two-layer system:

$$\mathfrak{D}_s^{[2]} = \frac{2p^{[1]}}{1 + r_s^{12}} \quad (\text{B8})$$

and

$$\mathfrak{D}_s^{[N]} = \frac{2p^{[1]} \prod_{j=2}^{N-1} e^{-i\beta^{[j]}}}{\prod_{j=1}^{N-1} [1 + r_s^{j,j+1}]} \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger \quad (\text{B9})$$

where the last term is called $D_s^{N-layer}$ in the main text. Numerator $\mathcal{N}_s^{[N]}$ follows exactly the same induction step (Eq. B6) leading to a relation analogous to Eq. B7. In this case however, we have by definition:

$$\mathcal{N}_s^{[2]} = r_s^{12} \mathfrak{D}_s^{[2]} = r_s^{12} \frac{2p^{[1]}}{1 + r_s^{12}} \quad (\text{B10})$$

leading to

$$\mathcal{N}_s^{[N]} = \frac{2p^{[1]} \prod_{j=2}^{N-1} e^{-i\beta[j]}}{N-1} (r_s^{12})^\dagger \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1, j} r_s^{j, j+1}]^\dagger \prod_{j=1} [1 + r_s^{j, j+1}] \quad (\text{B11})$$

or, equivalently, for $N \geq 4$,

$$\mathcal{N}_s^{[N]} = \frac{2p^{[1]} \prod_{j=2}^{N-1} e^{-i\beta[j]}}{N-1} (r_s^{12} + \xi^{[2]} r_s^{23})^\dagger \prod_{j=3}^{N-1} [1 + \xi^{[j]} r_s^{j-1, j} r_s^{j, j+1}]^\dagger \prod_{j=1} [1 + r_s^{j, j+1}] \quad (\text{B12})$$

From Eq. B9 and B12, we get the quantities of interest:

$$t_s^N = \frac{E_y^{\{N-1\}}}{E_y^0} = F_y^{\{N-1\}} = \frac{\prod_{j=2}^{N-1} e^{i\beta[j]} \prod_{j=1}^{N-1} [1 + r_s^{j, j+1}]}{N-1 \prod_{j=2} [1 + \xi^{[j]} r_s^{j-1, j} r_s^{j, j+1}]^\dagger} \quad (\text{B13})$$

$$r_s^N = \frac{(r_s^{12})^\dagger \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1, j} r_s^{j, j+1}]^\dagger}{N-1 \prod_{j=2} [1 + \xi^{[j]} r_s^{j-1, j} r_s^{j, j+1}]^\dagger} \quad (\text{B14})$$

We note that the two products at the numerator and denominator in Eq. B14 do not simplify because of the ruled product with r_s^{12} at the numerator. To complete Eq. A12, we also need:

$$1 + r_s^N = \frac{E_y^{\{1\}}}{E_y^0} = F_y^{\{1\}} = \frac{(1 + r_s^{12})^\dagger \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1, j} r_s^{j, j+1}]^\dagger}{N-1 \prod_{j=2} [1 + \xi^{[j]} r_s^{j-1, j} r_s^{j, j+1}]^\dagger} \quad (\text{B15})$$

and

$$1 - r_s^N = \frac{(1 - r_s^{12})^\dagger \prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1, j} r_s^{j, j+1}]^\dagger}{N-1 \prod_{j=2} [1 + \xi^{[j]} r_s^{j-1, j} r_s^{j, j+1}]^\dagger}. \quad (\text{B16})$$

Denominators $\mathfrak{D}_s^{[N]}$ are common to all quantities, and only the last product in Eq. B9 remains after simplification with $\mathcal{N}_s^{[N]}$. A graphical help is provided in the main text to evaluate this

ruled product. To construct $\mathcal{N}_s^{[N]}$ from the 2^{N-2} terms in $\mathfrak{D}_s^{[N]}$, one only needs to remove r_s^{12} factors in the 2^{N-3} terms where they appear, and multiply the 2^{N-3} other terms by r_s^{12} . This symmetry accounts for the $(1 + r_s^{12})$ and $(1 - r_s^{12})$ factorizations in $1 + r_s^N$ and $1 - r_s^N$, respectively.

Some aspects of the formulas above could have been anticipated: (i) one could have expected the transmission coefficient to be proportional to the numerator of Eq. B13. The first term accounts for the total phase acquired upon beam propagation after crossing the whole system. The second term is simply the product of the transmission coefficients across all the interfaces: if any of them vanishes, no beam is transmitted to layer [N]; (ii) identically, if $(1 + r_s^{12})$ is to vanish (this hypothesis is rather theoretical as it would require $n^{[1]} = 0$ ⁵⁴ or $\theta^{[1]} = 90^\circ$, but it is possible to get close to it when $|n^{[2]}| \gg |n^{[1]}|$, for example at a dielectric-metal interface), so will the total electric field at the first interface, and accordingly the total reflected field by the N-layer system $(1 + r_s^N)$, hence the proportionality to $(1 + r_s^{12})$ in Eq. B15.

The next step is to calculate $\mathbf{Q}^{\{k-1\}}$, hence the electric field at each interface $\{k-1\}$, for $3 \leq k \leq N - 1$, using Eq. A16. In this equation, we recognize the matrix linking input and output $\tilde{\mathbf{Q}}$ vectors of system $\{k-1, N\}$ composed of the last $N-k+2$ layers [Figure 1(C)]. From the above, we know how to calculate its properties, and we call \tilde{r}_s^N and \tilde{t}_s^N its reflection and transmission coefficients, respectively. For this system

$$\tilde{\mathbf{Q}}^{\{k-1\}} = \begin{bmatrix} \tilde{U}^{\{k-1\}} \\ \tilde{V}^{\{k-1\}} \end{bmatrix} = \begin{bmatrix} 1 + \tilde{r}_s^N \\ p^{[k-1]}(1 - \tilde{r}_s^N) \end{bmatrix} E_s^{\{k-1\}} = \prod_k^{N-1} \mathbf{M}^{[j]} \begin{bmatrix} \tilde{U}^{\{N-1\}} \\ \tilde{V}^{\{N-1\}} \end{bmatrix} \quad (\text{B17})$$

and

$$\tilde{\mathbf{Q}}^{\{N-1\}} = \begin{bmatrix} \tilde{U}^{\{N-1\}} \\ \tilde{V}^{\{N-1\}} \end{bmatrix} = \begin{bmatrix} 1 \\ p^{[N]} \end{bmatrix} \tilde{t}_s^N E_s^{\{k-1\}} \quad (\text{B18})$$

leading to

$$\begin{bmatrix} 1 + \tilde{r}_s^N \\ p^{[k-1]}(1 - \tilde{r}_s^N) \end{bmatrix} = \prod_k^{N-1} \mathbf{M}^{[j]} \begin{bmatrix} 1 \\ p^{[N]} \end{bmatrix} \tilde{t}_s^N \quad (\text{B19})$$

Turning back to the full $\{1, N\}$ system, we have

$$\mathbf{Q}^{\{k-1\}} = \begin{bmatrix} U^{\{k-1\}} \\ V^{\{k-1\}} \end{bmatrix} = \prod_k^{N-1} \mathbf{M}^{[j]} \begin{bmatrix} 1 \\ p^{[N]} \end{bmatrix} t_s^N E_y^0 \quad (\text{B20})$$

and the electric field amplitude $E_y^{\{k-1\}} = U^{\{k-1\}}$ at the interface between layers [k-1] and [k] follows:

$$E_y^{\{k-1\}} = \frac{t_s^N}{\tilde{t}_s^N} (1 + \tilde{r}_s^N) E_y^0. \quad (\text{B21})$$

From the definition (Eq. 6), we may calculate the Fresnel factor at interface {k-1}: $F_y^{\{k-1\}} = E_y^{\{k-1\}}/E_y^0$. This leads, for $3 \leq k \leq N-1$ (cases $k=2$ and $k=N$ have been addressed in Eq. B15 and B13, respectively), to

$$F_y^{\{k-1\}} = \frac{(1 + r_s^{k-1,k})^\dagger \prod_{j=k}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger} \prod_{j=2}^{k-1} [1 + r_s^{j-1,j}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \quad (\text{B22})$$

The last two terms on each line were predictable for the same reasons as listed above for the analysis of Eq. B13: the deeper the fields enter the system, the bigger the propagation phase, whereas any cancellation at an interface {j} between {1} and {k-1} (i.e. $1 + r_s^{j,j+1} = 0$) cancels the electric field $E_y^{\{k-1\}}$.

In a final step, the electric field inside any layer is calculated using Eq. A17 and A18, leading to

$$E_y^{[k]}(z) = U^{[k]}(z) = \frac{e^{-i\beta^{[k]}(z)}}{2} \left[(\xi^{[k]}(z) + 1) U^{\{k-1\}} + \frac{1}{p^{[k]}} (\xi^{[k]}(z) - 1) V^{\{k-1\}} \right] \quad (\text{B23})$$

where

$$\frac{V^{\{k-1\}}}{E_y^0} = p^{[k-1]} \frac{(1 - r_s^{k-1,k})^\dagger \prod_{j=k}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger} \prod_{j=2}^{k-1} [1 + r_s^{j-1,j}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \quad (\text{B24})$$

This simplifies using $\frac{p^{[k-1]}}{p^{[k]}} (1 - r_s^{k-1,k}) = 1 + r_s^{k-1,k}$, leading to the expression of the Fresnel factor valid for any depth z inside any layer k in the film $F_y^{[k]}(z) = E_y^{[k]}(z)/E_y^0$. For $3 \leq k \leq N-2$, we have

$$F_y^{[k]}(z) = \frac{\left[e^{i\beta^{[k]}(z)} + r_s^{k,k+1} \xi^{[k]} e^{-i\beta^{[k]}(z)} \right]^\dagger \prod_{j=k+1}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger} \prod_{j=2}^k [1 + r_s^{j-1,j}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \quad (\text{B25})$$

For $k = 2$, Eq. B25 holds with the last term dropped, and, for $k = N - 1$, Eq. B25 becomes

$$F_y^{[N-1]}(z) = \frac{e^{i\beta^{[N-1]}(z)} + r_s^{N-1,N} \xi^{[N-1]} e^{-i\beta^{[N-1]}(z)}}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_s^{j-1,j} r_s^{j,j+1}]^\dagger} \prod_{j=2}^{N-1} [1 + r_s^{j-1,j}] \prod_{j=2}^{N-2} e^{i\beta^{[j]}} \quad (\text{B26})$$

It may be checked that $E_y^{[k]}(z = z^{[k]})$ is equal to $E_y^{\{k\}}$ as calculated from Eq. B22, and that all the results in this section coincide with those in Ref. 30 for a three-layer system.

Appendix C: Beam with p polarization

The formalism being fully symmetric between $p^{[k]}$ and $q^{[k]}$ when switching from s to p polarization, t_p^N and r_p^N are obtained from Eq. B13 and B14 by simply changing r_s factors into r_p . From Eq. A14 and A20, we have $E_x^{\{1\}} = q^{[1]} n^{[1]} (1 - r_p^N) E_p^0 = (1 - r_p^N) E_p^0 \cos \theta^{[1]}$ and $E_z^{\{1\}} = (1 + r_p^N) E_p^0 \sin \theta^{[1]}$ as expected. For the transmitted fields, we get

$$E_z^{\{N\}} = \frac{(n^{[N-1]})^2}{(n^{[N]})^2} E_z^{\{N-1\}} = \frac{(n^{[1]})^2}{(n^{[N]})^2} \sin \theta^{[1]} t_p^N E_p^0 \quad (\text{C1})$$

and the z-component Fresnel factor at interface $\{N-1\}$, evaluated in medium $[N-1]$, is

$$F_z^{\{N-1\}} = \frac{(n^{[1]})^2}{(n^{[N-1]})^2} \frac{\prod_{j=2}^{N-1} e^{i\beta^{[j]}} \prod_{j=1}^{N-1} [1 + r_p^{j,j+1}]}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \quad (\text{C2})$$

proportional to the product of all $(1 + r_p^{j,j+1})$ for the same reasons as for y component. For the x-component, we have $E_x^{\{N\}} = q^{[N]} n^{[1]} t_p^N E_p^0 = \frac{n^{[1]}}{n^{[N]}} \cos \theta^{[N]} t_p^N E_p^0$. In order to recover the expected dependence in $(1 - r_p^{j,j+1})$, we note that

$$1 + r_p^{j,j+1} = \frac{n^{[j+1]} \cos \theta^{[j]}}{n^{[j]} \cos \theta^{[j+1]}} (1 - r_p^{j,j+1}) \quad (\text{C3})$$

leading at interface $\{N-1\}$ to

$$F_x^{\{N-1\}} = \frac{E_x^{\{N\}}}{E_p^0 \cos \theta^{[1]}} = \frac{E_x^{\{N-1\}}}{E_p^0 \cos \theta^{[1]}} = \frac{\prod_{j=2}^{N-1} e^{i\beta^{[j]}} \prod_{j=1}^{N-1} [1 - r_p^{j,j+1}]}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \quad (\text{C4})$$

At interface $\{k-1\}$, $E_x^{\{k-1\}} = V^{\{k-1\}}$ is continuous and may be evaluated as for the y component, using

$$Q^{\{k-1\}} = \frac{t_p^N}{\tilde{t}_p^N} \begin{bmatrix} 1 + \tilde{r}_p^N \\ q^{\{k-1\}}(1 - \tilde{r}_p^N) \end{bmatrix} n^{[1]} E_p^0 \quad (\text{C5})$$

leading to

$$E_x^{\{k-1\}} = E_p^0 \frac{n^{[1]}}{n^{[k-1]}} \cos \theta^{\{k-1\}} \frac{(1 - \xi^{[k]} r_p^{k,k+1})^\dagger \prod_{j=k+1}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} [1 - r_p^{k-1,k}] \prod_{j=1}^{k-2} [1 + r_p^{j,j+1}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \quad (\text{C6})$$

The Fresnel factor for x-components at interface $\{k-1\}$ is defined as $F_x^{\{k-1\}} = E_x^{\{k-1\}} / E_p^0 \cos \theta^{\{1\}}$.

Introducing Eq. C3, we transform it for $3 \leq k \leq N - 2$ into

$$F_x^{\{k-1\}} = \frac{(1 - \xi^{[k]} r_p^{k,k+1})^\dagger \prod_{j=k+1}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \prod_{j=1}^{k-1} [1 - r_p^{j,j+1}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \quad (\text{C7})$$

For $k = N - 1$, as in Eq. B22, the same equation applies with the numerator replaced by $(1 - \xi^{[N-1]} r_p^{N-1,N})$. Finally, we recall here for $k = 2$ that $F_x^{\{1\}} = 1 - r_p^N$ (formula follows from Eq. B16) and refer to Eq. C4 for $k = N$.

The z-component is not continuous and differs on either side of interface $\{k-1\}$. In medium $[k-1]$, we get for the z-component $F_z^{\{k-1\}} = E_z^{\{k-1\}} / E_p^0 \sin \theta^{\{1\}}$

$$F_z^{\{k-1\}} = \frac{(n^{[1]})^2}{(n^{[k-1]})^2} \frac{(1 + \xi^{[k]} r_p^{k,k+1})^\dagger \prod_{j=k+1}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \prod_{j=1}^{k-1} [1 + r_p^{j,j+1}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \quad (\text{C8})$$

for $3 \leq k \leq N - 2$. For $k = N - 1$, the same equation applies with the numerator replaced by $(1 + \xi^{[N-1]} r_p^{N-1,N})$; for $k = 2$ we have seen that $F_z^{\{1\}} = 1 + r_p^N$ (to be evaluated using Eq. B14); for $k = N$, Eq. C2 can be used.

Finally, the fields at an arbitrary depth z inside layer $[k]$ follow from Eq. A17. From

$$E_x^{[k]}(z) = V^{[k]}(z) = \frac{e^{-i\beta^{[k]}(z)}}{2} [(\xi^{[k]}(z) - 1) q^{[k]} U^{\{k-1\}} + (\xi^{[k]}(z) + 1) V^{\{k-1\}}] \quad (\text{C9})$$

using the same procedure as for y component, and $\frac{q^{[k-1]}}{q^{[k]}}(1 - r_p^{k-1,k}) = 1 + r_p^{k-1,k}$, we get for $3 \leq k \leq N - 2$

$$F_x^{[k]}(z) = \frac{\left[e^{i\beta^{[k]}(z)} - r_p^{k,k+1} \xi^{[k]} e^{-i\beta^{[k]}(z)} \right]^\dagger \prod_{j=k+1}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \prod_{j=1}^{k-1} [1 - r_p^{j,j+1}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \quad (\text{C10})$$

and

$$F_z^{[k]}(z) = \frac{(n^{[1]})^2}{(n^{[k]})^2} \frac{\left[e^{i\beta^{[k]}(z)} + r_p^{k,k+1} \xi^{[k]} e^{-i\beta^{[k]}(z)} \right]^\dagger \prod_{j=k+1}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger}{\prod_{j=2}^{N-1} [1 + \xi^{[j]} r_p^{j-1,j} r_p^{j,j+1}]^\dagger} \prod_{j=1}^{k-1} [1 + r_p^{j,j+1}] \prod_{j=2}^{k-1} e^{i\beta^{[j]}} \quad (\text{C11})$$

Again, for $k=2$, the last terms in Eq. C10 and C11 are dropped. For $k=N-1$, the numerators become $e^{i\beta^{[N-1]}(z)} - r_p^{N-1,N} \xi^{[N-1]} e^{-i\beta^{[N-1]}(z)}$ and $e^{i\beta^{[N-1]}(z)} + r_p^{N-1,N} \xi^{[N-1]} e^{-i\beta^{[N-1]}(z)}$ in Eq. C10 and Eq. C11, respectively.

SUPPLEMENTARY MATERIAL

See Supplementary Material for the details of the Fresnel factors for the five-layer system.

CONFLICT OF INTEREST

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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