Reconstruction of Raman Spectra of Two-Layer Diffusive Media: Model-Based Approach in Time-Domain

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ABSTRACT

We propose a novel analytical time-domain model for migration of Raman scattered photons in inhomogeneous two-layer diffusive media. Based on this model, the methods for reconstruction of the Raman spectra of the two layers are developed, tested in simulations and validated on phantom measurements data.

Keywords: Diffuse Optics, Raman scattering, time-domain, layered-media, model, reconstruction

1. INTRODUCTION

Highly scattering media, such as biological tissues are interesting for the application of Diffuse Optics techniques. These non-invasive techniques allow sensitivity of up to few centimetres in depth of the tissue. Combining with Raman spectroscopy, greater chemical specificity is achieved – molecules of the medium are distinguished by their vibrational states, encoded in the Raman wavelength shift.

There are several Diffuse Raman techniques that can be applied to extract chemical information from different depths in the diffusive medium: Spatially Offset Raman Spectroscopy (SORS),[1, 2] Frequency Offset Raman Spectroscopy (FORS),[3] Transmittance Raman Spectroscopy (TRS)[4] and Time-Domain Diffuse Raman Spectroscopy (TD-DRS).[5–7] SORS, FORS and TD-DRS are useful when examining layered structures, finding its application in fields such as medical diagnostics,[8] food and pharmaceuticals analysis, security and cultural heritage. However, the methods proposed so far for decoupling the spectra of layered structures are not model-based. Spectra of the layers at different depths are rather qualitatively or empirically estimated. Signals from later time gates in TD-DRS[7] or from larger source-detector distances in SORS contribute to the reconstruction of spectral components of deeper layers. Earlier time gates in TD-DRS are rejected, and in SORS – scaled subtraction is used to eliminate the spectral components from superficial layers.[1]

Here we propose a new model for Diffuse Raman in Time-Domain, exploiting the advantages of Time-Domain Diffusion Equation used for modelling the photon migration processes in diffusive media. Information about Raman spectra of the layers is encoded in the pathlengths covered by photons visiting different layers. Based on this model, the developed reconstruction methods enable simple, fast and mathematically rigorous retrieval of Raman spectra of the two-layered medium. The novel model relies on the heuristic approximation – the assumption that the optical properties of the medium are the same on excitation and Raman emission wavelengths.[9–11]

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2. MODEL

The two-layer reflectance geometry is represented in Figure 1. Source excitation wavelength is denoted by λ, while Raman emission wavelength is denoted by λ_e. Mean pathlength covered by photons in layer k is $v_k\langle t_k\rangle = -\frac{1}{R(t)}\frac{\partial R(t)}{\partial \mu_{abk}}$, with reflectance $R(t)$ at time instant t, speed of light in the medium v_k, average time spent by photons in layer k, $\langle t_k\rangle$, and background absorption coefficient μ_{abk} for layers $k = 1, 2$. The probability of Raman scattering event in layer k along small distance dl is μ_{sRk}dl. Applying the heuristic approximation, it is possible to derive the expression for Raman reflectance signal at time t

$$R_e(\lambda_e, t) \approx R(\lambda, t) \cdot \left[\mu_{sR1}(\lambda_e)v_1\langle t_1\rangle + \mu_{sR2}(\lambda_e)v_2\langle t_2\rangle\right]. \quad (1)$$

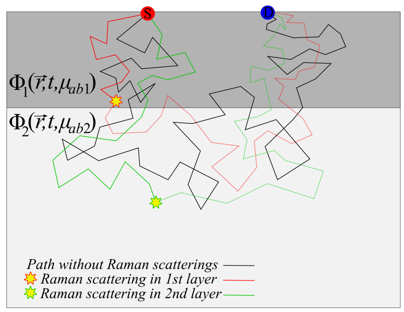

Figure 1. Two-layer reflectance geometry with exemplary photon paths and Raman scattering events

Since the relation between Raman reflectance and Raman scattering coefficients in layers 1 and 2 is linear, the system of equations for unknown Raman spectra ($\mu_{sR1,2}(\lambda)$) can be written in the matrix form

$$\mathbf{R_e}(\lambda_i) = \mathbf{W} \cdot \mathbf{S}(\lambda_i), \quad (2)$$

where $\mathbf{R_e}(\lambda_i)$ is the time-gated measurements column vector $(N_g \times 1)$, $\mathbf{W}$ is the gated sensitivity matrix $(N_g \times 2)$, and $\mathbf{S}(\lambda_i) = \begin{bmatrix}\mu_{sR1}(\lambda_i) & \mu_{sR2}(\lambda_i)\end{bmatrix}^{\mathrm{T}}$ is the spectrum (2×1) to be reconstructed. To solve the inverse problem, matrix $\mathbf{W}$ is calculated from forward model's equation (1) and diffuse two-layer model described in literature.[12,13] With sufficient number of time-gated measurements, the linear system for unknown Raman scattering coefficients is overdetermined and can be easily solved by least-square method. The solution is obtained for each wavelength separately.

3. METHODS AND RESULTS

The reconstruction methods proposed here were tested in simulations and validated on experimental data obtained from two-layer cylindrical tissue-mimicking phantom made of silicone (top layer) and marble (bottom layer).[7]

In the simulation study of the effect of various parameters on the reconstruction of the spectra of the two layers, we found that the most significant parameters are thickness of the top layer and number of photon counts detected. To have optimal conditions for separating the spectra of the two layers, top layer should not be thicker than 10 mm, while one would need at least 10^6 photon counts.

The results of the reconstruction from the phantom measurements are represented in 2. The comparison between the reconstructed and reference spectra for silicone (left) and marble (right) is given to highlight the accuracy of the method in terms of peak position reconstruction and decoupling of the spectra of the two layers. The background subtraction as well as normalization was applied on the reconstructed spectra.

4. CONCLUSION

For the first time, the model-based reconstruction of the Raman spectra of the two-layered medium was performed. The results of the reconstruction from phantom measurements are promising, the spectral components of top and bottom layers were separated well. The model can be futher generalized for many-layer geometries. Potential application is in clinical diagnostics or security.

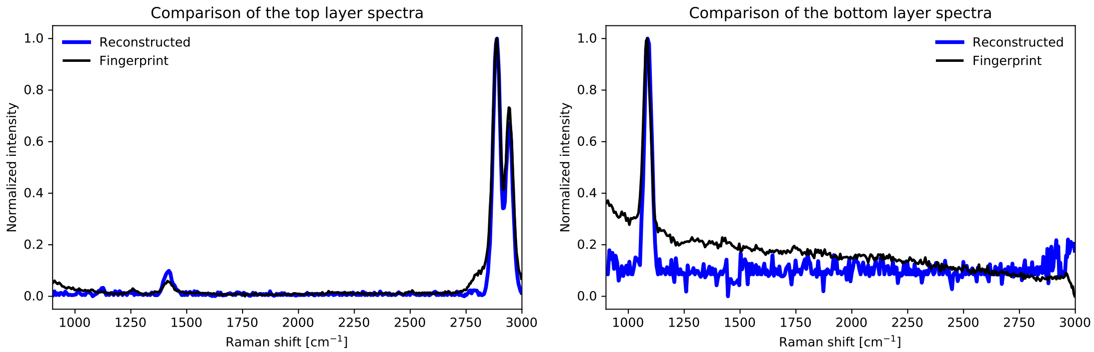

Figure 2. Comparison between the reconstructed and reference spectra of the top layer (left) and bottom layer (right)

ACKNOWLEDGMENTS

This project is funded by EU H2020 MSCA-ITN project "Photonics for Healthcare: multiscale cancer diagnosis and therapy" (PHAST-ETN), grant Agreement no. 86018.

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