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Quantifying Raman Photon Generation Depth via Diffusion Modeling

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Abstract: In this work, we propose a model derived from diffusion theory of the generation depth of Raman photon with respect to the time of arrival. © 2025 The Author(s)

1. Introduction

Diffuse Raman is an emerging field with great promise. It can combine the unique chemical capabilities of Raman spectroscopy with the depth-sensitivity capabilities of diffuse optics. To probe and distinguish the depth of Raman signals several approaches exist such as Spatially Offset Raman Spectroscopy (SORS) [1] which exploits different distances between light injection and detection, Frequency Offset Raman Spectroscopy (FORS) [2] exploits the different optical properties at different wavelengths, Transmission Raman Spectroscopy (TRS [3]) works in transmission and is independent on depth, and Time-Domain Diffuse Raman Spectroscopy (TD-DIRS) [4, 5], which utilizes the photon arrival time.

The main parameter in the analysis of a diffuse Raman signal is the average generation depth of the detected photons, which we will define as z_{Raman} . It differs from the commonly known average penetration depth [6], as the elastic scattering does not carry information on a single point, but along its pathlength, while the Raman generation carries the chemical information of a single point where the photon experienced the inelastic scattering.

In this work we present the first rigorous modellization of the average Raman photon generation depth given the optical properties of the material.

2. Model

Following [7], we can model the Raman signal starting from a system of two coupled diffuse equations:

$$\left(\frac{1}{v} \frac{\partial}{\partial t} - D \nabla^2 + \mu_a \right) \Phi(\mathbf{r}, t) = q(\mathbf{r}, t) \quad (1a)$$

$$\left(\frac{1}{v_e} \frac{\partial}{\partial t} - D_e \nabla^2 + \mu_{ae} \right) \Phi_e(\mathbf{r}, t) = q_e(\mathbf{r}, t) \quad (1b)$$

Where we have at the probing and emission wavelengths: the speed of light v, v_e , the diffusion coefficient $D = \frac{1}{3\mu'_s}, D_e = \frac{1}{3\mu'_{s,e}}$, the reduced scattering coefficient $\mu'_s, \mu'_{s,e}$ and the absorption coefficient μ_a, μ_{ae} . The resulting field can be calculated by convolving the two Green functions, considering the linearity of the problem. Similar to ref. [6] we can calculate the probability density function $f(z|t)$ of a photon arriving at time t to be generated at a depth of z . This is done by considering the Raman emission by a small thickness Δz region at depth \bar{z} , normalized by the total reflectance $R_e(\rho, t)$.

$$f(\bar{z} | t) = \frac{1}{R_e(\rho, t)} \frac{R_e(\bar{z} + \Delta \bar{z} | \rho, t) - R_e(\bar{z} | \rho, t)}{\Delta \bar{z}} = \frac{1}{R_e(\rho, t)} \frac{\partial R_e(\bar{z} | \rho, t)}{\partial \bar{z}}. \quad (2)$$

Given the probability density function, we can calculate the average generation depth by:

$$z_{Raman}(t) = \int \bar{z} f(\bar{z} | t) d\bar{z}. \quad (3)$$

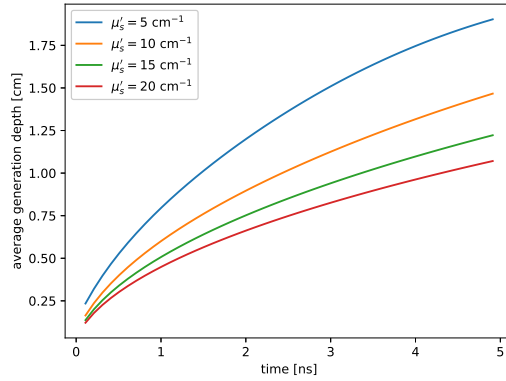


Fig. 1. Average generation depth of Raman photons, varying the scattering and assuming $\mu'_s = \mu_{se}$ and $\mu_a = \mu_{ae} = 0.1 \text{ cm}^{-1}$.

By developing all the calculations assuming a semi-infinite medium, we can find $R_e(\bar{z} | \rho, t)$, by solving the convolution:

$$R_e(\rho, t) = \frac{1}{2A} \int \Phi(\mathbf{r}, \mathbf{r}', t, t') \Phi_e(\mathbf{r}', t') d\mathbf{r}' dt' \quad (4)$$

Where A is obtained from the extrapolated boundary condition [8].

We can find $\frac{\partial R_e(\bar{z} | \rho, t)}{\partial \bar{z}}$:

$$\begin{aligned} \frac{\partial R_e(\bar{z} | \rho, t)}{\partial \bar{z}} &= \frac{\mu_{sR}}{2A\pi^2} \sqrt{\frac{v v_e}{16DD_e}} \exp\{-\mu_{ae} v_e t\} \int \frac{\exp\{-\mu_{sR} v t' - \mu_{ab} v t' + \mu_{ae} v_e t'\}}{\sqrt{t'(t-t') [4Dv t' + 4D_e v_e (t-t')]} \times \\ &\times \exp\left\{-\frac{\rho^2}{4Dv t' + 4D_e v_e (t-t')}\right\} \left[\exp\left\{-\frac{(\bar{z} - z_S)^2}{4Dv t'}\right\} - \exp\left\{-\frac{(\bar{z} + z_S + 2z_E)^2}{4Dv t'}\right\} \right] \times \\ &\times \left[\exp\left\{-\frac{(-\bar{z})^2}{4D_e v_e (t-t')}\right\} - \exp\left\{-\frac{(\bar{z} + 2z_{Ee})^2}{4D_e v_e (t-t')}\right\} \right] dt'. \end{aligned} \quad (5)$$

This result can be extended to the continuous wave case for SORS by solving this problem, considering the time-independent solution, and calculating:

$$f_{CW}(\bar{z} | \rho) = \frac{1}{R_{e,CW}(\rho)} \frac{\partial R_{e,CW}(\bar{z} | \rho)}{\partial \bar{z}}, \quad (6)$$

3. Results and Discussion

In Fig. 1 we show the average depth of generation with respect to the time of arrival of photons assuming different reduced scattering coefficients (μ'_s). We can clearly observe the dependence of the time of arrival which encodes the generation depth, and secondly, we can observe the dependence on μ'_s , whose increase limits the penetration of photons and reduces the likelihood of the generation at higher depths. In Fig. 2, we show the average depth of generation and we show that the average generation depth varies with the difference in absorption between the probing and Raman wavelength.

4. Conclusion

We have proposed a model for the calculation of the average generation depth of Raman photons through diffusion theory and evaluated its monotonic dependence with the time of arrival and the limiting depth probing capabilities of higher μ'_s .

5. Acknowledgment

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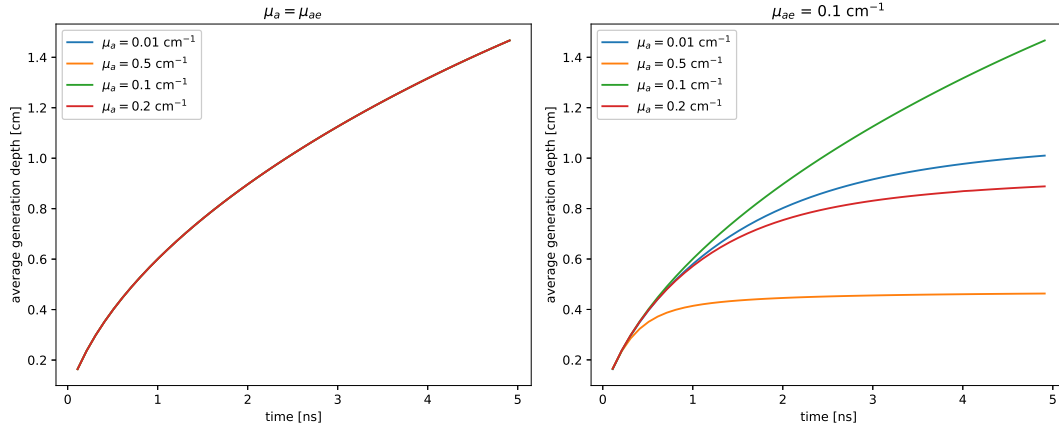


Fig. 2. Average generation depth of Raman photons, varying the absorption and assuming $\mu_a = \mu_{ae}$ (left), varying μ_a and assuming fixed at $\mu_{ae} = 0.1 \text{ cm}^{-1}$ with $\mu'_s = \mu_{se} = 10 \text{ cm}^{-1}$.

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