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Experimentally validated Raman Monte Carlo Simulation for a cuboid object to obtain Raman Spectroscopic Signatures for hidden material

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Abstract

In conventional Raman spectroscopic measurements of liquids or surfaces the preferred geometry for detection of the Raman signal is the backscattering (or reflection) mode. For non-transparent layered materials, sub-surface Raman signals have been retrieved using spatially offset Raman spectroscopy (SORS), usually with light collection in the same plane as the point of excitation. However, as a result of multiple scattering in a turbid medium, Raman photons will be emitted in all directions. In this study, Monte Carlo simulations for a three-dimensional layered sample with finite geometry have been performed to confirm the detectability of Raman signals at all angles and at all sides of the object. We considered a non-transparent cuboid container (high density polyethylene) with explosive material (ammonium nitrate) inside. The simulation results were validated with experimental Raman intensities. Monte Carlo simulation results reveal that the ratio of sub-surface to surface signals improves at geometries other than backscattering. In addition, we demonstrate through simulations the effects of the absorption and scattering coefficients of the layers, and that of the diameter of the excitation beam. The advantage of collecting light from all possible 4π angles, over other collection modes is that this technique is not geometry specific and molecular identification of layers underneath non-transparent surfaces can be obtained with minimal interference from the surface layer. To what extent all sides of the object will contribute to the total signal will depend on the absorption and scattering coefficients and the physical dimensions.

Keywords: Monte Carlo simulation; Raman spectroscopy; Photon Migration; Multiple Scattering; Explosives detection

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Introduction

The study of light-matter interactions has opened up an entire vista for researchers in the field of photonics. Understanding the propagation of light in a strongly scattering medium, such as biological tissue, and finding the analytical solution is of great interest.^[1-3] Most optical techniques used, including several imaging modalities, are based on the Rayleigh scattering phenomenon. Multiple Rayleigh scattering has also been utilized in non-invasive depth profiling and infant brain imaging studies.^[4-5] The multiple scattered light from a turbid media contains both Rayleigh and Raman scattered photons.^[6] At every scattering site, a fraction of the photons (roughly 10^{-6}) undergoes secondary inelastic (Raman) scattering which has a shifted wavelength. Paths traced by the Raman photons depend on the optical properties of the medium at the new shifted wavelength. Due to multiple scattering, there is a finite probability that the photons (Rayleigh scattered photons as well as Raman scattered photons) will come out of the medium in all directions. Conventional Raman spectroscopy involves detecting Raman signals from the illumination side (i.e. 180 degree or back scattering mode) of the sample; this forms the backbone of Raman micro spectroscopy.^[7-9] Although the backscattering mode is the most popular mode for the commercial Raman confocal microscopes used for routine Raman spectroscopy as well as for Raman imaging, it has a limited penetration depth of a few hundred microns.^[10] This hampers probing a volume lying deep inside a turbid sample, such as biological tissues, using backscattering mode. This highlights the necessity of developing new Raman-based methods to probe the sub-surface volume of such materials.

Time resolved Raman spectroscopy (TRRS) and spatially offset Raman spectroscopy (SORS) have been applied to retrieve sub-surface information of layered substances and suppress the signal from the surface layer. In TRRS,^[11,12] the collection of Raman signals after a delay (picosecond range) in the excitation allows the selective detection of photons that have migrated deeper into the medium and thus provides information about the embedded material, for instance a polyethylene terephthalate layer that was underneath a Teflon layer.^[12] In SORS, an offset between the point of excitation and the point of collection enhances the Raman intensity ratio of sub-surface vs. surface layers.^[13] For example, mouse bones under layers of tissue have been probed *in vivo* through SORS where a bundle of collection fibers was placed up to a few mm away from the point of excitation.^[14] So far, most SORS applications employed a geometry with the point of excitation and the point(s) of collection in the same plane. Ring collection or a set of fibers can be used to increase the light collection efficiency. Few researchers have reported the collection of light at other locations than the back-scattering plane. Okagbare *et al.* placed a set of 19 excitation and 50 collection fibers at various positions around a rat leg (*ex vivo* as well as a phantom construct) to further improve the bone Raman signal quality.^[15] Srinivasan *et al.* reported how light collection through a fiber bundle in transmission geometry resulted in a better sub-surface/surface signal ratio than using a back scattering geometry.^[16] Everall *et al.* compared backscattering and transmission Raman for the analysis of pharmaceutical tablets.^[17] Cylindrically-shaped samples were studied from several angles in a two-dimensional plane to localize sub-surface material. Demers *et al.* studied Teflon rod hidden inside gelatin for 2D Raman tomography,^[18] and Zandbergen *et al.* studied interior vs. exterior distributions within a catalytic extrudate.^[19]

A close study of these reports reveals that the collection of the Raman scattered photons have always been carried out with the excitation fibers and collection fibers kept in the same planes or

axes, albeit, signals in depths up to 22 mm and 2D tomography have been observed. Interestingly, the Raman scattered light from strongly scattering media undergoes multiple scattering events, leading to randomization of the photon directions, and detecting such Raman photons from multiple angles allows one to identify substances lying deeper within such media. Thus one can, in principle, record Raman spectra of diffusely scattering samples (both solids and colloidal liquids) at all 4π angles.^[20] In this case, the collection need not be restricted to the same plane as the excitation. The collection of signals at different angles has been widely applied in other medical imaging modalities like computed tomography (CT) of X-ray,^[21] photoacoustic tomography,^[22] optical coherence tomography (OCT),^[23] positron emission tomography,^[24] diffuse optical tomography.^[25] Obtaining Raman signals using various experimental geometries ensures collection of Raman signals from sample volumes lying within other multiple scattering media using either conventional lenses or optical fibers placed at different positions around the sample.^[20] This would indicate a possibility of developing frequency specific Raman imaging of turbid media such as biological tissues, similar to infra-red imaging.^[26-27] Imaging of sub-surface chemical information, such as tissues for cancer detection, probing bones lying deep under the skin (currently done in reflection or transmission mode), can probably be done more effectively using 4π angle collection from all sides and planes. Another advantage of 4π angle collection over other prevailing Raman techniques is that one can obtain three-dimensional information of the concealed object. Here, we present the results of Monte Carlo simulations for 4π angle collection of Raman signal of a packed material of a finite geometry and validated with experimental data. One aim of the study was to compare the signal intensities and sub-surface/surface ratios at the backscattering plane, sides and back side (transmission plane) of the sample.

Photon energies inside a multiple scattering medium can be quantitatively calculated using radiative transfer equation (RTE). The RTE deals with specifying energy balance between the incident, outgoing, absorbing, and the scattering radiation. However, RTE involves six different independent variables to define the radiance at a given point. Owing to the complex nature of RTE, one has to resort to some approximations. The dimensionality is reduced in the case of diffusion theory for photon propagation in a turbid medium.^[3-5] Monte Carlo modeling of photon migration in multi-layered tissue (MCML)^[28] has been useful to analyze turbid media such as biological tissue. It is computationally much more efficient than solving RTE, but giving much more accurate results compared to diffusion approximation. However, there have been fewer reports on the finite bounded surfaces, especially in the field of Raman spectroscopy. MC simulations for geometry specific application for embedded objects within a semi-infinite multilayered medium were reported.^[29-30] Although it incorporated a finite geometry within a semi-infinite medium, it precluded the finite geometry within a finite medium solution. Mesh-based MC, due to its computational complexity is used in situations where an accurate fluence map is required.^[31] Several other groups have developed Raman Monte Carlo (RMC) for their analysis. For instance, Reble *et al.*^[32] have worked on RMC simulations to study the effect of absorption and scattering coefficient of non-melanoma skin cancer and normal skin with respect to the geometry of Raman signal collection. They also studied the effect of the absorption coefficient of β -carotene on Raman measurement geometry.^[33] The influence of turbidity and scattering anisotropy of the sample on collection geometry have been simulated by Shih *et al.*^[34] Everall *et al.*^[35] simulated the photon migration in *trans*-stilbene and showed the difference in spatial distribution between Tyndall and Raman photons. Matousek *et al.*^[36] validated their

experimental results of Raman analysis of pharmaceutical tablets along with the reflection of exiting photons back into the medium through RMC simulations. Photon propagation in breast tissue was simulated by Keller *et al.*^[37] to study the application of SORS in mastectomy to monitor the tumor margin. Hokr *et al.*^[38] have also used RMC to show that increasing the number of scattering events in the medium enhances the Raman signal. Enejder *et al.*^[39] designed Raman spectroscopy for blood, based on the simulation results of RMC.

In this work, we have carried out RMC simulations for a cuboid, validated with experimental data obtained at multiple angles with respect to the excitation fiber. We have also done simulations for various excitation light beam diameters and optical properties of the sample. A few RMC models restricted the step-size of the photon and the number of steps it takes, as they were developed for semi-infinite media.^[35] Since our model is for a finite object, it is not difficult to trace the photons until they emerge from any one of the six faces of the cuboid. Our Raman Monte Carlo model can be applied in both biological as well as material applications with finite surfaces. We have modified the original MCML model by Wang *et al.*^[28] to incorporate Raman scattering. Modifications were also made to incorporate the finite object (cuboid) instead of a semi-infinite (layered) medium.

Experimental Setup

Ammonium nitrate crystals tightly packed in a commercial high density polyethylene (HDPE) container of dimension 5x 4 x 2.5 cm [height (X) * width (Y) * depth (Z)] and 0.1 cm wall thickness was the sample used for the 4π angle collection experiments and RMC simulations. Fig. 1 shows the schematic diagram of the experimental setup with details of the cuboid object used for RMC. Collection of Raman signals from the plane where the sample is illuminated is called back scattering mode (or reflection mode). When the signal collection is from the plane parallel to the excitation plane (launch surface), it is called transmission mode. The distance between launch surface and transmission surface is the depth of the cuboid. Signals are also collected from the XZ and YZ-planes, which are perpendicular to the launch surface. The laser beam was launched at the origin (0, 0, 0) of the cuboid, which is the center of the XY backscattering plane. The Raman experiment was carried out using an 830 nm continuous wave laser diode (TEC-200-0830-1000, Sacher Lasertechnik) with 0.4 cm beam diameter and 140 mW power. The *p*-polarized laser beam irradiates the sample (at normal incidence) using a free beam. The launch medium is air. The collection fibers with a core diameter of 400 μm were terminated at the other end in a linear array placed in front of a telescopic arrangement and fixed to the entrance slit of the spectrometer (Horiba, JobinYvon) equipped with a liquid nitrogen (LN_2) cooled CCD camera (Symphony, Horiba, JobinYvon, 1024 $\times$ 256 pixels, pixel size 26 $\times$ 26 μm). To eliminate Rayleigh scattered light, a notch filter (Iridian, Canada) was used in front of the entrance slit to the spectrometer. The Raman signals were collected from the sample using a bundle of three optical fibers whose intensities were summed to get a single measurement. Measurements were taken at five positions in back scattering and transmission mode. The same was repeated for XZ and YZ-planes as well. In case of the backscattering mode the fibers were positioned as close to the excitation beam as physically possible for the center measurement point (zero offset). Experimental Raman intensities are quantitated on the basis of the 1040 cm^{-1}

peak of the material, *i.e.*, ammonium nitrate and the 1294 cm^{-1} peak of the container *i.e.*, high density polyethylene.

Raman Monte Carlo simulations

Fig. 2 shows the flow chart for the algorithm used to simulate the Raman scattering in a turbid, multi-layered medium. The original MCML code^[28] written in C language was modified to incorporate Raman scattering as well as the finite cuboid object; the modifications are shown as colored blocks. The cuboid object used for the simulations has the same dimensions as the one used for the experimental work as shown in Fig. 1. The dimensionless step-size is s , the total interaction coefficient μ_t is $\mu_a + \mu_s$ (absorption + scattering coefficient), d_b is the distance of the photon to the layer boundary, g is the anisotropic scattering coefficient, and ζ is a computer generated pseudo-random number ranging from 0 to 1 used for each call of this function to determine the step size of a photon after each scattering event. The photon launched is scattered along the path traced. At each scattering site there is a check for conversion of a Rayleigh photon to a Raman photon with a probability of 10^{-6} and the layer in which this happens is tagged.^[35] After conversion the photon undergoes isotropic scattering ($g = 0$), subsequently, it undergoes further anisotropic scattering inside the medium depending on the Henyey-Greenstein phase function. Since the Raman photons are of a different wavelength than the excitation light, the optical properties of the medium could be different. However, this effect was neglected, since the shift in wavelength is in the order of 100 nm only and the optical properties will change to a negligible extent in white salts (material used in our study).^[40] If the Raman conversion criterion is not satisfied, the photon continues with absorption (dropping weight), Rayleigh scattering (re-computing direction cosines) and checks for boundary crossovers. Refractive index mismatches between the media are ignored, so the photons are transmitted at all surfaces.

The recording grid element size was 0.005 cm. Due to the cylindrical symmetry of the problem the negative XZ and YZ planes were not recorded separately, as they will have similar output as those of their positive counterparts. Burger *et al.*^[41] gave a range of reduced scattering coefficients for powders. For the initial simulation, the scattering coefficient (μ_s) of container and material were taken as 250 cm^{-1} and 500 cm^{-1} . Initially the absorption coefficient (μ_a) was set to zero, $g = 0.9$, and the Raman probability was 10^{-6} . A pencil beam was considered for the incident laser beam. The refractive indices of all media were set to 1.3.

Table 1 lists the optical properties of the media for various trials. In the first three runs, different combinations of μ_s for container and embedded material were simulated. To check if the Raman signal can be detected at the sides even in an absorbing medium, the μ_a of material and container was assumed 0.2 cm^{-1} , keeping the other parameters the same as for the first run. Since a point source is generally difficult to achieve during experiment, a simulation was also performed considering an excitation laser beam diameter of 1 cm with a ‘top-hat’ intensity profile, keeping the number of photons in the simulations the same. Rayleigh photons leaving the four planes were also simulated (only for the first trial) to study the differences in spatial distribution with that of the Raman signals.

Simulations were run for 4×10^8 photons for five times except for the absorbing model (trial 4), for which runs were carried out for eight times due to the low probability of photons reaching the boundary. All simulations were done on a 2.6 GHz, 8-core/16-thread Intel Xeon cluster (2650

V2 processors). Recorded Raman photons from the container or material were normalized by the total number of photons used to obtain the probability of emitted Raman photons (PRP). For each element of the recording grid, in all four planes, the PRP of container and material was recorded. For planes with axes XY and XZ, the PRP was integrated over the Y-axis and Z-axis, respectively, and over the Z-axis for the YZ plane to get one-dimensional distributions. The ratio of material PRP to container PRP (MCR) was computed for each one-dimensional data.

Results and discussion

All simulations were done in a Xeon cluster machine. All the trials (as listed in Table 1) together took ~61 hours to run. Percentages of total number (container + inner material) of incident photons converted to Raman photons (total Raman photons generated * 100 / number of incident photons) per run in trial 1 to trial 4 are 0.25%, 0.13%, 0.14%, and 0.018%, respectively. The total Raman photon generation is independent of the beam diameter, since the Raman photon generation percentage for trial 5 was the same as for trial 1, i.e., 0.25%.

Assuming a scattering coefficient of the container as 250 cm^{-1} and of the material as 500 cm^{-1} (first trial), the material PRP (simulation output) was compared with the experimental output (Raman signal intensity) as shown in Fig. 3. The experimental Raman signal intensities were measured at five locations per plane; three fibers covered the axis and we integrated the intensities, ignoring the dead space between the three fibers. Figs. 3(a-d) present the cumulative normalized PRP with the normalized experimental Raman signal intensity for the four planes - backscattering, transmission, XZ, and YZ planes, respectively. The experimental data correlate very well with the simulation data.

The pattern of Rayleigh photons emitted from the surfaces of the cuboidal object during Trial 1 is shown in Fig. 4. 99.1% of the Rayleigh photons (Rayleigh photons that come through the back scattering plane * 100/ sum of Rayleigh photons that come out in all six planes) exited the object through back scattering mode. 0.39%, 0.19%, and 0.07% escaped from the transmission, each XZ, and each YZ planes, respectively. However, the distribution of container and material PRP (sum of both) over the various surfaces (Raman photons that come through the particular plane * 100/ sum of Raman photons that come out in all six planes) are 58.4%, 18.1%, twice 7.9% and twice 3.9%. The distribution variation is related to the low Raman conversion probability, which leads to Raman conversion happening predominantly deep inside the medium, from where they can come out at all planes and not only the back scatter (launch) plane.

Figs. 5(a-l) depict the container and material cumulated PRP for trials 1, 2, and 3 from the back scattering, transmission, XZ, and YZ planes. At a first glance, it appears that the pattern of the output (nature of curve) does not change with the change in scattering coefficient of the container or the material. However, the PRP of the material from all the planes is highest [Figs. 5(a,d,g,j)] for trial 1, where the μ_s of container and material are 250 cm^{-1} and 500 cm^{-1} , respectively. This is intuitive because the thickness of the material is effectively more than that of the container and the μ_s is also high. Container PRP is highest from all the surfaces for trial 3 [Figs. 5(c,f,i,l)], where the μ_s of container and material are 500 cm^{-1} and 250 cm^{-1} , respectively. The reason for this increase in container PRP is that the higher the scattering coefficient, the larger the number of steps taken by a photon in that layer, so there is a higher probability of

generation of Raman photons. Although the μ_s of the material is less, due to greater depth (thickness) most of the Raman conversion still takes place in that layer. In trial 2, μ_s for the container as well as material were kept equal (both 250 cm^{-1}); the PRPs of container and material lie between that of trial 1 and trial 3 as shown in Figs. 5(b,e,h,k).

Practically zero absorbance material is a rare occurrence, therefore a trial 4 was done with an absorption coefficient of 0.2 cm^{-1} for both container and material. In an absorbing medium, the Raman photons generated in the container layer have a high probability of being absorbed in the material. This is valid only if the container thickness is much less than that of material, as is the case here. Even in the absorbing medium, the Raman signals are detectable at the perpendicular planes as seen in Fig. 6. Detectability of Raman photons from the surfaces other than back scattering plane is reduced by 5-6 orders of magnitude compared to trial 1, where all the other parameters were the same ($\mu_a = 0.0 \text{ cm}^{-1}$). The container PRP becomes very noisy in transmission, XZ, and YZ planes [Figs. 6(b-d)] due to the low number of container Raman photons exiting from those surfaces. Also the material Raman intensities at those planes were much weaker, due to a lower number of Raman photons generated (as photons were lost due to the absorbing media) and also the absorption of the generated Raman photons.

Fig. 7 shows the simulation results for a broad incident laser beam of diameter 1 cm without changing the illumination energy (Trial 5). This trial gives us an indication on how the incident light beam spread would affect the proposed technique. There is not much effect on MCR in transmission, XZ, and YZ planes [Figs. 7(b-d)]. However, in the reflection plane (Fig. 7a), especially the container Raman signal shows a clear broadening in comparison with Fig. 5a.

Fig. 8 shows a three-dimensional representation of material PRP (log of the PRPs are plotted). Values of each grid are averaged over the five runs of trial 1. Backscattering, XZ, YZ and transmission planes are represented. The color distribution depicts how the Raman signals for a three dimensional object can be collected at all angles, which is the concept of this presented method.

Table 2 summarizes the total container PRP, total material PRP, and total MCR ratio for five trials across four planes. We observed that the MCR is lowest in backscattering mode for all combinations of optical properties and excitation beam diameter. In other words, in backscattering mode the container signal dominates. In fact, the data in table 2 are cumulative of the whole back scattering plane, and the value of MCR would be much worse if measured at the point of excitation *i.e.* in a confocal geometry. Provided there is sufficient signal, measuring in transmission mode or at the perpendicular planes gives more information about the inner material than the container. The percentages of Raman photons leaving the XZ and YZ planes are 7.9% (twice) and 3.9% (twice), but the MCR of YZ is more than that of XZ in our model. This is in line with the X dimension being larger than the Y dimension: fewer photons will reach the farthest boundary, but the ones that do are more likely to be sub-surface Raman photons.

Conclusion

In this work, Monte Carlo simulations have been performed for a cuboid container with a different material inside, and the simulation results were validated with experimental data. The data show that for a hidden object in a non-transparent 3D sample the Raman signal acquisition

need not be confined to the reflection surface only, where the signal of the sub-surface material is often swamped by the surface signal.^[10] We have shown that with the multiple angle collection technique light collection at all surfaces and angles (4π angle collection geometry) gives better sub-surface to surface ratios than conventional signal acquisition techniques.^[20] Hence, it can be concluded that multiple angle collection is the next generation Raman technique for non-invasive investigations of samples that provide deeper penetration than so far being demonstrated.^[42]

With the present technique the chemical signatures of diffusely scattering turbid samples, solid explosives (but also explosives in layers, and liquid explosives concealed in different containers) can be identified. There is a finite probability of diffusely scattered Raman photons from the material coming out in all directions and at all surfaces, and depending on the dimensions and scattering and absorption properties one can choose different signal collection modes accordingly.

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Table Captions:

Table 1: Parameters used in the simulation model for the five trials.

Table 2: Summary of the simulation results of 5 trials. Cumulative probability of container Raman photons (cPRP), cumulative probability of material Raman photons (mPRP) and material to container ratio (MCR) for back scattering (BS), transmission (TT), XZ and YZ planes.

Figure Captions:

FIG. 1: Schematic diagram of the experimental setup. A cuboid container of thickness 0.1 cm with XYZ dimensions 5 x 4 x 2.5 cm filled with ammonium nitrate. Optical properties of container and material for simulations: refractive index (n) = 1.3, $\mu_a = 0.0 \text{ cm}^{-1}$ or 0.2 cm^{-1} , and $\mu_s = 250 \text{ cm}^{-1}$ or 500 cm^{-1} and $g = 0.9$ for both the layers. Light illumination at the origin. The XY-plane with $z = 0$ is the reflection plane, the XY-plane with $z = 2.5$ is the transmission plane (parallel to launch surface), the XZ-plane where $y = +2$ (surface to the side of the launch surface) and the YZ plane where $x = +2.5$ (surface upwards from the launch surface) are also shown in the figure.

FIG. 2: Modified MCML flow chart for Raman scattering in cuboidal object. s is dimensionless step-size; ξ is random number; d_b is distance between current location of the photon and the layer; μ_t is total interaction (extinction) coefficient.

FIG. 3: Comparison of simulation with experiments: Normalized cumulative probability of Raman photons of material from simulation (Trial 1) and experimentally measured Raman signal intensity (normalized) of ammonium nitrate for (a) Backscattering, (b) Transmission, (c) XZ, and (d) YZ planes.

FIG. 4: Cumulative probability of Rayleigh photons coming out of the four planes of the cuboid for $\mu_a = 0.0 \text{ cm}^{-1}$ and μ_s of container and material as 250 cm^{-1} and 500 cm^{-1} , respectively. (a) Backscattering, (b) Transmission, (c) XZ, and (d) YZ plane.

FIG. 5: Influence of scattering coefficient: Cumulative probability of container and material Raman photons from 4 surfaces of the cuboid for 3 combinations (trials 1-3) of scattering coefficients. μ_a of container and material was 0.0 cm^{-1} . (a, d, g, j) are for trial 1 across 4 planes, (b, e, h, k) are for trial 2, and (c, f, i, and l) are for trial 3. In each graph, the lower broken black line shows the container Raman photons and the upper solid red line the material Raman photons.

FIG. 6: Effect of added absorption: Cumulative probability of container and material Raman photons from 4 planes of the cuboid when absorption coefficient is 0.2 cm^{-1} . μ_s of container and material were 250 cm^{-1} and 500 cm^{-1} , respectively. (a) Backscattering, (b) Transmission, (c) XZ, and (d) YZ plane. The broken black lines show the container Raman photons and solid red lines show material Raman photons.

FIG.7: Effect of excitation beam diameter: Cumulative probability of container and material Raman photons coming out of the 4 surfaces of the cuboid for broad beam excitation with the same energy as point excitation. μ_s of the container and material were 250 cm^{-1} and 500 cm^{-1} , respectively. μ_a of container and material was 0.0 cm^{-1} . (a) Backscattering, (b) Transmission, (c) XZ, and (d) YZ plane. In each graph, the lower broken black line shows the container Raman photons and the upper solid red line shows the material Raman photons.

FIG. 8: Surface plot of normalized logarithmic of the probabilities of Raman photons coming out of the surfaces of the cuboid. Axes are in cm.

Table 1

Trial #	Absorption coefficient of container and material (cm⁻¹)	Scattering coefficient of container (cm⁻¹)	Scattering coefficient of material (cm⁻¹)	Beam diameter (cm)
1	0.0	250	500	0
2	0.0	250	250	0
3	0.0	500	250	0
4	0.2	250	500	0
5	0.0	250	500	1

Table 1: Parameters used in the simulation model for the five trials.

Table 2

	Trial 1	Trial2	Trial 3	Trial4	Trial 5
BS-cPRP	1.18E-04	1.13E-04	2.22E-04	7.42E-05	1.19E-04
BS-mPRP	1.37E-03	6.45E-04	5.87E-04	1.06E-04	1.36E-03
BS-MCR	11.61	5.71	2.64	1.42	11.49
TT-cPRP	2.31E-06	4.44E-06	1.28E-05	9.52E-11	2.31E-06
TT-mPRP	4.58E-04	2.43E-04	2.42E-04	5.78E-09	4.50E-04
TT-MCR	198.75	54.79	18.86	60.67	195.20
XZ-cPRP	1.13E-06	2.26E-06	7.04E-06	2.60E-10	1.17E-06
XZ-mPRP	2.00E-04	1.08E-04	1.15E-04	9.53E-09	2.01E-04
XZ-MCR	177.00	47.74	16.27	36.61	171.79
YZ-cPRP	4.80E-07	9.65E-07	3.17E-06	7.32E-12	5.07E-07
YZ-mPRP	9.83E-05	5.48E-05	6.03E-05	6.25E-10	9.93E-05
YZ-MCR	204.83	56.82	18.99	85.44	196.05

Table2: Summary of the simulation results of 5 trials. Cumulative probability of container Raman photons (cPRP), cumulative probability of material Raman photons (mPRP) and material to container ratio (MCR) for back scattering (BS), transmission (TT), XZ and YZ planes.

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FIG. 4: Cumulative probability of Rayleigh photons coming out of the four planes of the cuboid for $\mu_a = 0.0 \text{ cm}^{-1}$ and μ_s of container and material as 250 cm^{-1} and 500 cm^{-1} , respectively. (a) Backscattering, (b) Transmission, (c) XZ, and (d) YZ plane.

Figure 5

FIG. 5: Influence of scattering coefficient: Cumulative probability of container and material Raman photons from 4 surfaces of the cuboid for 3 combinations (trials 1-3) of scattering coefficients. μ_a of container and material was 0.0 cm^{-1} . (a, d, g, j) are for trial 1 across 4 planes, (b, e, h, k) are for trial 2, and (c, f, i, and l) are for trial 3. In each graph, the lower broken black line shows the container Raman photons and the upper solid red line the material Raman photons.

Figure 6

FIG. 6: Effect of added absorption: Cumulative probability of container and material Raman photons from 4 planes of the cuboid when absorption coefficient is 0.2 cm^{-1} . μ_s of container and material were 250 cm^{-1} and 500 cm^{-1} , respectively. (a) Backscattering, (b) Transmission, (c) XZ, and (d) YZ plane. The broken black lines show the container Raman photons and solid red lines show material Raman photons.

Figure 7

FIG.7: Effect of excitation beam diameter: Cumulative probability of container and material Raman photons coming out of the 4 surfaces of the cuboid for broad beam excitation with the same energy as point excitation. μ_s of the container and material were 250 cm^{-1} and 500 cm^{-1} , respectively. μ_a of container and material was 0.0 cm^{-1} . (a) Backscattering, (b) Transmission, (c) XZ, and (d) YZ plane. In each graph, the lower broken black line shows the container Raman photons and the upper solid red line shows the material Raman photons.

Figure 8

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