

# Raman spectra of powders of aromatic compounds

*Ilyos Rakhmatullaev*<sup>1,5\*</sup>, *Nikolay Bunkin*<sup>2</sup>, *Isakul Urunov*<sup>3</sup>, *Tulkin Nurmurodov*<sup>4</sup>, and *Hayotjon Botirov*<sup>4</sup>

<sup>1</sup>Department of Natural Sciences, Branch of National Research Nuclear University MEPhI in Tashkent, Tashkent, 100214, Uzbekistan

<sup>2</sup>Department of Physics, Moscow State Technical University named after N.E. Bauman, Moscow, 105005, Russia

<sup>3</sup>Department of General Physics, Navoi State University of Mining and Technologies, Navoi, 210100 Uzbekistan

<sup>4</sup>Department of Chemical Technology, Navoi State University of Mining and Technologies, Navoi, 210100, Uzbekistan

<sup>5</sup>Department of Exact Sciences, University of Science and Technology, Tashkent, 100208, Uzbekistan

**Abstract.** A method for fiber-optic recording of Raman spectra has been developed based on the use of fiber-optic cells, photon traps, a copper vapor laser, a small-sized spectrometer, and a data processing system. The Raman spectra of micropowders of a number of aromatic compounds and pharmaceuticals (C<sub>15</sub>H<sub>11</sub>NO, C<sub>14</sub>H<sub>12</sub>, C<sub>9</sub>H<sub>8</sub>O<sub>4</sub>) were studied. It was established that by using resonator cells and fiber optics technology in micropowders of the studied compounds at room temperature, a Raman opalescence regime can be realised, consisting of a significant increase in the intensity of Raman scattering. It was found that, under the recording conditions used, the intensity of the Raman lines of the compounds studied was comparable to the intensity of the excitation line. Subsequently, such studies will open up broad opportunities for recording and studying weak Raman signals.

## 1 Introduction

In recent years, Raman spectroscopy has emerged as a powerful analytical tool for investigating the composition and structure of diverse inorganic and organic substances. This advancement has been facilitated by the widespread availability of laser excitation sources and highly sensitive spectrometers capable of detecting low-intensity scattered light signals [1-4]. Despite the significant progress in modern laser Raman spectroscopy, challenges persist in optimizing laser light sources and enhancing the efficiency of converting excited radiation into Raman scattering signals [5]. These challenges are particularly pronounced in dispersed media, which are characterized by strong scattering of excitation radiation at unshifted frequencies [6].

---

\* Corresponding author: [JARakhmatullaev@mephi.ru](mailto:JARakhmatullaev@mephi.ru)

The inherent limitations of Raman spectroscopy stem from the extremely small effective cross-section for Raman scattering in molecular media (approximately  $10^{-28} \text{ cm}^2$ ). Furthermore, Raman scattering can be obscured by fluorescence, which typically exhibits an intensity several orders of magnitude greater than Raman scattering. This interference is especially problematic for aromatic compounds containing fluorophores, particularly when examined using visible excitation wavelengths.

Conventional techniques for recording Raman spectra in dispersed media involve focusing laser radiation within the medium. However, at sufficiently high laser intensities, this approach can alter the initial characteristics of the substance under investigation, leading to photodestruction, localized heating, and photoinduced phase transformations. Consequently, there is an active pursuit of novel approaches to develop highly sensitive and selective methods for recording and studying both spontaneous Raman scattering spectra and their nonlinear analogues.

Recent advancements in Raman spectroscopy have focused on enhancing signal collection efficiency and reducing interference. One approach involves the use of aberration-free spectrograph designs, which can significantly improve data quality and resolution<sup>5</sup>. For instance, the IsoPlane 81 integrated imaging spectrograph system has demonstrated a 3x signal improvement when using a fiber bundle compared to a single-core fiber for coupling Raman scattering into the spectrometer<sup>5</sup>.

Another promising development is the concept of remote plasmonic-like enhancement (RPE), which utilizes a dense random array of Ag nanoislands coated with a column-structured silica overlayer<sup>4</sup>. This technique has shown significant enhancement of both Raman scattering and fluorescence, even without direct proximity between analyte molecules and metal nanostructures. Enhancement factors of up to  $10^6$  have been reported for certain compounds<sup>4</sup>.

These innovations in spectrometer design and signal enhancement techniques are paving the way for more sensitive and versatile Raman spectroscopy applications, potentially overcoming some of the inherent limitations of the technique and expanding its utility in various fields of scientific research and industrial applications.

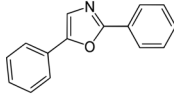
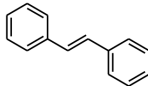
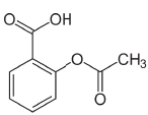
This study presents an innovative technique for exciting Raman spectra in dispersed media. The proposed method employs a repetitively pulsed laser source, fiber-optic cells, a compact spectrometer, and a data processing system. This approach aims to address the aforementioned challenges and enhance the capabilities of Raman spectroscopy in analyzing complex dispersed systems.

## 2 Materials and methods

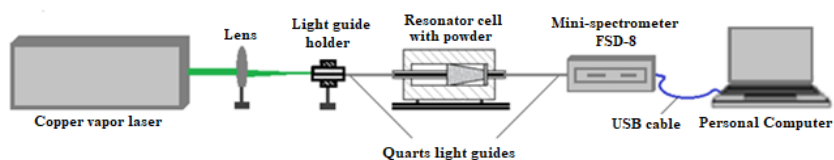
The work examined micropowders of aromatic compounds and pharmaceuticals: C<sub>15</sub>H<sub>11</sub>NO (PPO), C<sub>14</sub>H<sub>12</sub> (stilbene) and C<sub>9</sub>H<sub>8</sub>O<sub>4</sub> (aspirin) from Sigma Aldrich with a purity of 98%. To obtain Raman spectra, the substances under study were placed in photon traps. The studies were carried out at room temperature. Sample chemical and structural formulas are given in Table 1.

To capture Raman spectra, a fiber-optic approach was employed, as illustrated in Figure 1. The excitation source was a copper vapor laser (CVL), which emits radiation in the visible spectrum at wavelengths of 510.6 nm and 578.2 nm. For the experiments, the green line of the CVL ( $\lambda = 510.6 \text{ nm}$ ) was utilized, while the yellow line ( $\lambda = 578.2 \text{ nm}$ ) was effectively suppressed using a filter. The CVL is notable for its compact size, high monochromaticity, stable radiation output, and low power consumption (approximately 1 kW). It operates in a pulse-periodic mode, delivering short generation pulses (20 ns) at a high repetition rate of  $10^4 \text{ Hz}$ , with peak power reaching  $10^5 \text{ W}$ .

**Table 1.** Chemical and structural formulas of PPO, stilbene and aspirin.

Substance name	Chemical formula	Structural formula
PPO	$C_{15}H_{11}NO$	
Stilbene	$C_{14}H_{12}$	
Aspirin	$C_9H_8O_4$	

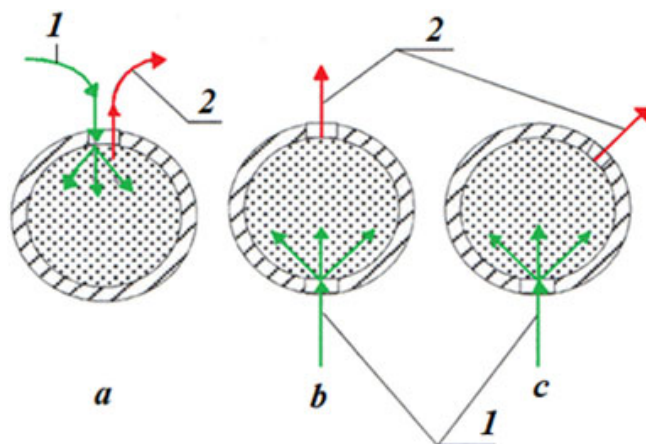
The laser radiation was directed into the sample cuvette via a light guide. The scattered radiation was collected by another light guide with a diameter of 100  $\mu\text{m}$  and directed to the slit of a fiber-optic minispectrometer. The minispectrometer then transmitted digital information about the Raman spectrum to a computer through a USB connection. This setup facilitates efficient and precise measurement of Raman spectra, leveraging the advantages of fiber-optic technology for enhanced data acquisition and analysis.



**Fig. 1.** Experimental setup diagram.



**Fig. 2.** Various designs of resonator cells with test samples.



**Fig. 3.** Schematic diagrams of resonator cells: a – “back scattering” (“reflection”) scheme; b – “through the light” scheme; c - “scattering at an angle” scheme. 1 – exciting (primary) radiation, 2 – secondary radiation.

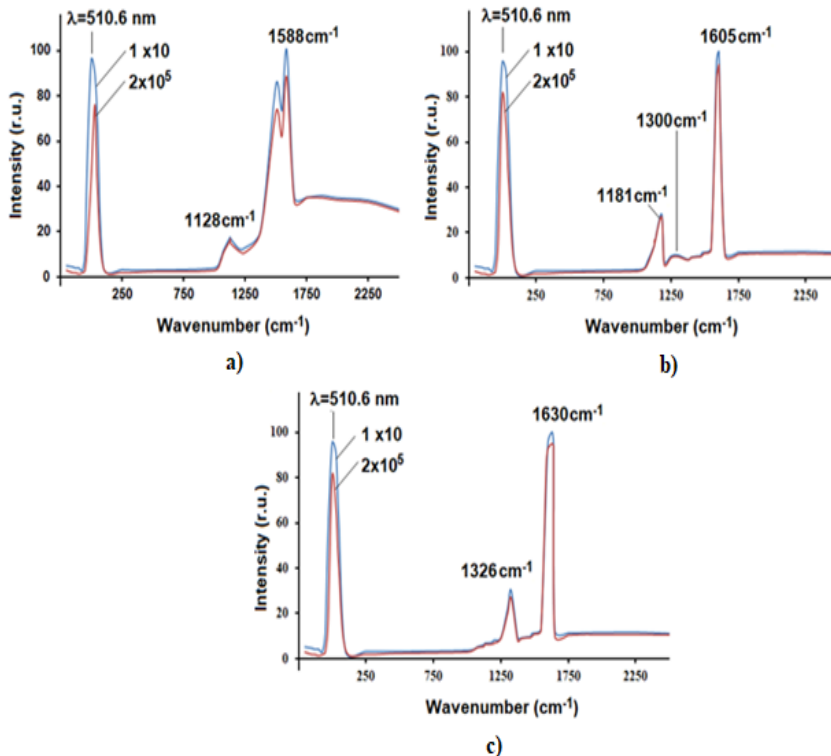
To enhance the signal of secondary radiation (in particular, Raman scattering) in powders, we manufactured special designs of resonator cells–photon traps (Figure 2). The cuvettes had a capillary diameter of 1.5–3 mm and a length of 20–50 mm. The edges of the cuvette holes can be made of metals (copper, duralumin, etc.), for which the effect of a gigantic increase in the probability of excitation of processes is realized. These cuvettes are made of duralumin. The cuvette is made in the form of a closed cavity with two holes for the input of primary (laser) radiation and the output of secondary radiation arising in the sample (Figure 3). Teflon adapters ensure the seal of the cuvette. A cavity was cut out in the body of the photon trap, which is the working volume and is filled with the powder under study. If necessary, an absorption filter 2 mm thick was inserted into the resonator housing to further increase the Raman contrast. By using light filters, the intensity of the laser excitation line in the secondary radiation spectrum could be reduced by almost 100 times with full transmission of the Raman signal. Light filters were used mainly when using the “reflection” method. For the “transmission” method, it turned out to be possible to record Raman radiation without using any filters, since in this case the laser radiation was greatly attenuated at the exit from the cuvette due to the processes of repeated scattering in the powder [3,5]. It was found that a cone-shaped cavity turned out to be the most optimal option for amplifying Raman signals. Figure 1 shows the design of the cuvette used in our experiments.

Thus, when using photon traps, it was possible to realize conditions under which a multiple increase in the intensity of Raman signals is observed at the exit from the cell. The main advantages of this method are the possibility of rapid non-contact analysis of extremely small amounts of a substance (~1–10 µg).

### 3 Results and discussion

Many polycyclic aromatic compounds are good phosphors and are used as active media for dye lasers [7]. In addition, most aromatic compounds are biologically active and are used in the pharmaceutical industry [8]. Aromatic compounds have a flat, rigid structure, which contributes to the manifestation of the vibrational structure of the bands. The vibrational structure of the bands of this class of compounds is due predominantly to fully symmetrical vibrations of the carbon skeleton of the molecule (C-C). In these cases, it is possible to apply a classification based on the symmetry of energy states and establish selection rules for the

molecule in question. The molecular structure of such compounds contains one or more benzene rings, as well as a number of elements (S, N, O) connecting to the benzene ring [9].



**Fig. 4.** Raman spectra of micropowders of PPO (a), stilbene (b) and aspirin (c) under excitation by the green line of a copper vapor laser ( $\lambda=510.6$  nm). Curve 1 corresponds to a resonator cell with a capillary diameter of 3 mm; curve 2 to a typical cylindrical cuvette with a diameter of 18 mm.

Figure 4 shows the Raman spectra of the studied micropowders of PPO, stilbene, aspirin and paracetamol, under excitation by CVL ( $\lambda=510.6$  nm). The Raman intensity is comparable to the intensity of the laser excitation line in all samples, as shown in this figure: as a result of using the developed photon trap, the Raman contrast at the output of the cuvette for the substances studied increases by four to six orders of magnitude compared to conventional typical cuvettes. The Raman opalescence effect [5,8] is observed, i.e. the Raman signal is comparable in intensity to the excitation radiation.

As known, the ratio of Raman scattering intensity  $I_{Raman}$  to excitation intensity  $I_{exc}$  in a homogeneous medium is given by [5]:

$$\frac{I_{Raman}}{I_{exc}} = \sigma \cdot N \cdot L \cdot \delta\Omega, \tag{1}$$

where  $\sigma$  is the effective Raman cross section ( $\sigma \sim 10-28$  cm<sup>2</sup>),  $\delta\Omega$  is the solid angle at which the radiation to be studied is detected (collection angle),  $N$  is the concentration of particles,  $L$  is the path covered by one photon of excitation radiation in the substance. For the investigation of a substance in ordinary cells  $\sim 1$  cm long, the ratio of the Raman intensity  $I_{Raman}$  to the intensity of the excitation radiation  $I_{exc}$  at a particle concentration  $N \approx 10^{22}$  cm<sup>-3</sup> and a scattered radiation collection angle  $\delta\Omega \approx 1$  steradian is

$$\frac{I_{Raman}}{I_{exc}} = 10^{-6}, \tag{2}$$

Thus, at the exit from the cell with a homogeneous medium, the Raman intensity is a million times weaker than the intensity of the exciting radiation.

The approximation of the Brownian motion has been used to determine the path travelled by a photon of the excitation radiation in an ultradisperse medium. To describe the chaotic thermal motion of tiny particles in a fluid, the Brownian thermal motion of tiny particles in a fluid. In this article, photons traversing a diffuse medium as a result of multiple scattering at medium inhomogeneities [5] are considered as Brownian particles. The free path length  $\Delta x_i = \Delta x$  of the photon is used as the characteristic size of optical inhomogeneities in the dispersed medium. If we assume that for some time interval  $\Delta t_i = \Delta t$  the photon travels a distance  $\Delta x$  in some arbitrary direction, we can write the value of the square of the final distance ( $l^2$ ) of the photon from the initial position for  $n$  time intervals  $\Delta t$ :

$$l^2 = \sum_{i=1}^n (\Delta x_i^2) + \sum_{i=2}^n (2\Delta x_i l_{i-1} \cos \alpha_i) \quad (3)$$

The following values are introduced here:  $\alpha_i$  – is the angle between  $\Delta x_i$  and the extension  $l_{i-1}$ ;  $l_{i-1}$  – is the total displacement of the photon for  $i$  time intervals  $\Delta t$ . The same calculations have been made in work [5] for a number of inorganic and organic substances. Given that a photon will travel approximately the same distance  $\Delta x$  (free path length) in any direction for a given time  $\Delta t$ , and that  $\cos \alpha_i$  is equally likely to have both positive and negative signs, since the values of  $\alpha_i$  are equally likely, we obtain for the mean value of the square of the final distance ( $\langle l^2 \rangle$ )

$$\langle l^2 \rangle = n(\Delta x)^2, \quad (4)$$

Given the values  $n = \frac{t}{\Delta t}$ ,  $\langle l^2 \rangle = \frac{(\Delta x)^2}{\Delta t} t$  (where  $n$  are the displacements  $\Delta x$  measured over time intervals  $\Delta t$ ), we obtain the photon displacement value for time  $t$ :

$$l_0 = \sqrt{\frac{(\Delta x)^2}{\Delta t}} \sqrt{t}, \quad (5)$$

The displacement  $l_0$  can be in any direction in space with an equal probability of being.

Therefore, when considering this model, we can assume that the photon that was at a certain point at the initial moment of time will, after  $t$  seconds, be near the surface of the sphere with radius  $R = l_0$ :

$$R = \sqrt{\frac{(\Delta x)^2}{\Delta t}} \sqrt{t}, \quad (6)$$

Therefore, the distance a photon travels in matter is

$$L = tc = \frac{R^2 \Delta t}{(\Delta x)^2} \frac{\Delta x}{\Delta t} = \frac{R^2}{\Delta x}, \quad (7)$$

where  $c$  is the speed of light in matter.

For the resonator cell used in the experiment, the distance between the entrance and exit ends of the optical fibre, i.e. the photon displacement in the photon trap, was  $R = 1$  cm. The free photon path length in an ultradisperse medium can be considered comparable to the size of the particles, i.e.,  $\Delta x \approx 10^{-4}$  cm. In this case, the total distance travelled by a photon of the excitation radiation in the photon trap is  $L \approx 10^4$  cm. Simultaneously, when using the photon trap, the solid angle of scattered radiation is  $\delta\Omega \approx 4\pi$ . This selection of  $\delta\Omega$  is due to the fact that the excitation radiation entering the resonator cell is reflected many times by its walls and by the surfaces of the particles of the ultradisperse medium.

Substituting the obtained values into (1), we obtain:

$$\frac{I_{Raman}}{I_{exc}} = 10^{-1}, \quad (8)$$

As a result of using the developed resonator cell, the Raman intensity contrast at the output of the cell for substances in dispersed form with micrometer dimensions increases by five orders of magnitude compared to typical cells (see formula (2)): the Raman signal is comparable in intensity to the excitation radiation - the Raman opalescence effect is observed (Figure 4).

A six-atom cyclic group (C6) is present in the structure of the organic substances studied (PPO, stilbene, aspirin). Stilbene and PPO contain two such groups, aspirin contains one. The cyclic groups in the PPO are bound by a C3NO group and in the stilbene by two CH groups.

From the spectra (Figure 4), it is clearly seen that each compound is characterised by distinct peaks at 1128 and 1588  $\text{cm}^{-1}$  for PPO, 1181, 1300 and 1605  $\text{cm}^{-1}$  for stilbene and 1326 and 1630  $\text{cm}^{-1}$  for aspirin. The observed peaks at 1128 and 1300-1326  $\text{cm}^{-1}$  in the samples are due to C-N valence vibrations.

## 4 Conclusion

Thus, it was found that when using the developed resonator cells and fiber-optic technology in powders of aromatic compounds, a Raman opalescence regime can be realized, consisting of an anomalous increase in the Raman intensity. The high efficiency of the conversion of the excitation radiation into a Raman signal is explained by the large value of the total distance covered by the photons of the excitation radiation in the dispersed medium inside the resonator cell. This also makes it possible to observe the Raman lines that are located in the resonator cell. The proposed method of Raman spectroscopy offers the possibility of building miniaturized laser chemical analysis devices, which are needed to solve many practical problems.

## References

1. O.E. Eremina, *Determination of Polycyclic Aromatic Compounds and Biogenic Amines in Objects of Complex Composition Using Giant Raman Spectroscopy* (Moscow, Moscow State University Press, 2018).
2. A.N. Spitsyn, D.V. Utkin, O.S. Kuznetsov, P.S. Erokhin, N.A. Osina, V.I. Kochubei, *Optics and Spectr* **129(1)**, 135-148 (2021).
3. A. Saletnik, B. Saletnik, C. Puchalski, *Molecules* **26**, 1537 (2021).
4. A.H. Kuptsov, G.N. Zhizhin, *Handbook of fourier transform Raman and infrared spectra of polymers vol 45* (Amsterdam, Elsevier, 1998).
5. A.P. Goncharov, V.S. Gorelik, A.V. Krawtsow, *Technical Physics* **52(11)**, 1466-1470 (2007).
6. D. Bi, *Raman Scattering of Light in Micro-Structured Media*, PhD dissertation (Moscow, Lebedev Physical Institute, 2020).
7. M. Jahn et al., *Analyst* **141**, 752-793 (2016).
8. V.S. Gorelik, I.A. Rakhmatullaev, *Jour. Russ. Laser Res.* **26(1)**, 66-82 (2005).
9. S. Kawata, T. Ichimura, A. Taguchi, Y. Kumamoto, *Chem. Rev.* **117**, 4983-5001 (2017).