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Enhancement of Rhodamine 6G and Crystal Violet Raman Spectrum Peaks by Graphene-Enhanced Raman Spectroscopy

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ABSTRACT— Due to the unique properties of graphene, since its discovery, many applications in different fields from chemical sensors to transistors have been proposed for it. One of the most important applications of graphene is in the enhancement of Raman spectroscopy, which has recently attracted the attention of scientists. This article investigates its potential as a substrate for Raman enhancement called graphene-enhanced Raman spectroscopy (GERS). We use rhodamine 6G (R6G) and crystal violet (CV) to illustrate the effect of graphene oxide on Raman enhancement. It was shown that Raman peaks of rhodamine 6G and crystal violet solutions deposited by solution soaking on the graphene-based substrate have significantly increased compared to those deposited on the bare glass substrate. Using a Raman spectrometer, The Raman spectra of these materials were taken and their graphs were compared. It is shown that this method can enhance the Raman signals of molecules of rhodamine 6G and crystal violet.

KEYWORDS: Crystal violet, Graphene, Graphene-enhanced Raman spectroscopy, Rhodamine 6G

I. INTRODUCTION

Raman spectroscopy is a technique for measuring the frequency shift of inelastically scattered light from the sample when the photon from incident light strikes a molecule and produces a scattered photon [1]. Raman spectroscopy had a limited application for many decades because of the very low efficiency of the normal Raman scattering [2]. There are over 25 types of Raman spectroscopy techniques [3]. For example, Surface-Enhanced Raman Spectroscopy (SERS), Tip-Enhanced Raman Spectroscopy (TERS), and Graphene-Enhanced Raman Spectroscopy (GERS).

Graphene is a two-dimensional material of sp2 hybridized carbon atoms arranged in a hexagonal honeycomb lattice [4]. Since its discovery in 2004, graphene has been used in various fields due to its special properties such as excellent mechanical capacities, good biocompatibility, high stability, and unique and tunable electronic and optical properties [5].

Raman signal enhancement for various molecules adsorbed on graphene called graphene-based enhanced Raman spectroscopy (GERS), is a new method that has attracted much attention today [6]. For the first time, the experimental enhancement of the Raman signal using graphene was reported by Ling and his colleagues in 2010. They deposited the organic molecules on the surface of graphene using standard thermal evaporation. Then, Raman spectroscopy was obtained [7]. After that, more research was done on this issue. Pinyun Ren and his colleagues provided a technique to deposit N-doped graphene on Si/SiO2 substrates, resulting in a greater chemical mechanism-based Raman enhancement of R6G molecules than pristine graphene [8].

The fluorescent dyes have been used as an ingredient in products such as biotechnology, food, etc. Rhodamine 6G and crystal violet are the most important dyes. Their use leads to polluting the environment and their residues in food pose potential health risks [10], [22]. Most dyes have complex properties such as aromatic structure and high stability [10]. Therefore, the identification and elimination of R6G and CV from wastewater streams is important.

There have been many reports of various techniques applied to identify dye molecules However, each of these referred techniques has its limitations. Among the available techniques, graphene-enhanced Raman spectroscopy (GERS) has advantages that include rapidity, non-destructivity, lower cost, and simpler operation [5].

The microscopic mechanism of GERS is still under debate. However, in most articles, the reason for the enhancement is the chemical mechanism (CM), rather than the electromagnetic mechanism (EM) observed in noble metal particles (e.g. Ag, Au, …) for surface-enhanced Raman scattering (SERS). Graphene and its derivatives such as graphene oxide exhibit surface plasmons and its characteristics make the EM absent. Therefore, CM is responsible for GERS enhancement where the analyte and substrate exchange charges through π-π interactions [8], [9].

In this article, we report the fabrication of a graphene-based substrate produced by depositing graphene oxide on a glass slide. Then, it shows improved enhancement for Raman spectra of absorbed rhodamine 6G and crystal violet molecules compared to the bare glass.

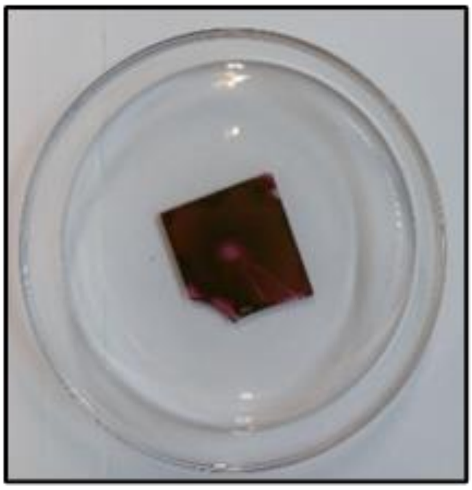
II. EXPERIMENTAL METHOD

A. *Sample preparation*

2cc of graphene oxide suspension was deposited on each glass slide, which was cut to approximately 20 mm×20 mm. The graphene-based layers were prepared using the spin-coating method. For spin-coating, the graphene oxide suspension was placed onto the glass and rotated with a speed of 1500 rpm for 50 seconds and then at 500 rpm for 20 seconds so that the substrates have a uniform coating. Then the prepared substrates were placed in the oven at 80°C for 5 hours. A sensing molecule is needed to investigate the enhancement of enhanced Raman spectroscopy using graphene oxide. In this paper rhodamine 6G and crystal violet are used for this purpose, placed on an empty glass slide and a substrate covered with graphene oxide. Rhodamine 6G and crystal violet solutions were prepared at concentrations of 5×10^{-5} M and 8×10^{-8} M respectively.

B. *Deposition of R6G and CV over the graphene-based substrate*

Rhodamine 6G and crystal violet solutions with specific concentrations were deposited on the graphene-based substrates and bare glass slides. using solution soaking. We used the solution soaking method to deposit the R6G and CV on the surface of the substrates, which has been widely used by researchers in similar studies. For solution soaking, the substrates were placed in the R6G and CV solutions for 1 hour. Then, they heated in the oven at a temperature of ~ 60° C for 16 hours to evaporate the water. Figure (1) shows the substrates after depositing the solutions of R6G and CV on them.



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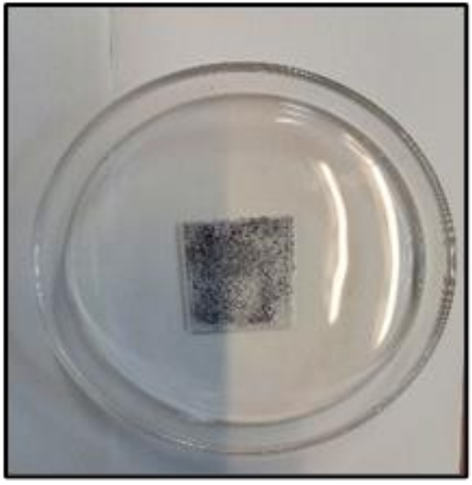

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Fig. 1. The image of (a) rhodamine 6G solution and (b) crystal violet solution, deposited on the graphene-based substrate by solution soaking.

C. *Equipment*

Raman spectroscopy was performed using the Technooran Micro-Raman instrument (Microspectrophotometer-ram-532-004) equipped with a CCD camera detector. This device has an Nd: YAG laser with a wavelength of 532 nm and a maximum power of 200 mW. This microspectrophotometer has four microscopic objective lenses for magnification (4X, 10X, 40, and 60X) and its spectral resolution is 10 cm-1. Figure 2 shows the image of the Technooran Miro-Raman instrument and Fig. 3 shows the schematic diagram of the Raman spectrometer.

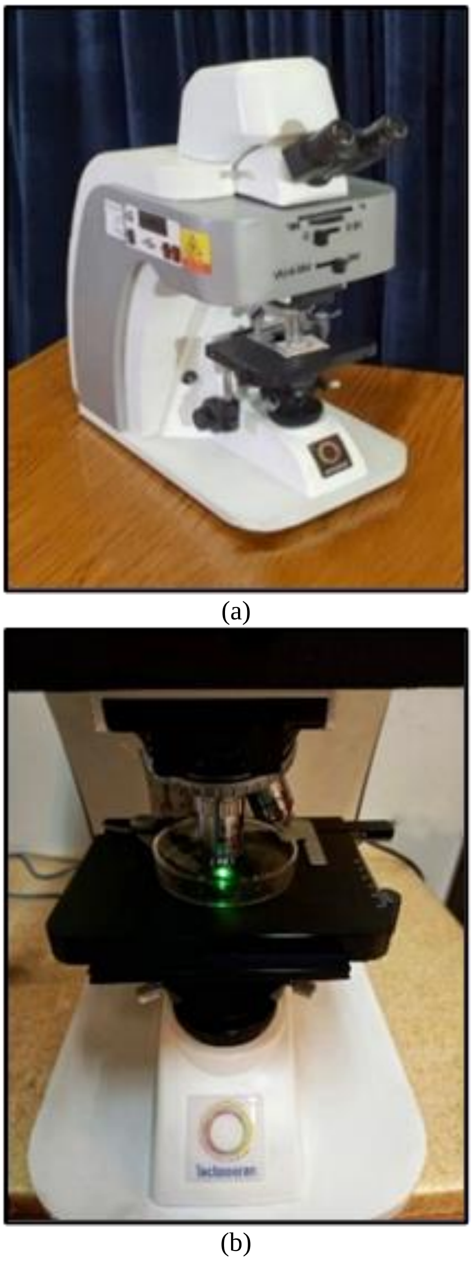
(a)

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Fig. 2. Photo of (a) Technooran Miro-Raman instrument and (b) during experiment.

To measure the Raman spectrum of the samples, a laser intensity of 40 mW laser (at magnification 40X) was utilized with an exposure time of 4 s. Then, the obtained spectra were plotted using OriginPro software.

We subtracted baselines and smoothed Raman spectrums with OriginPro software. To deal with the noise of the spectrometer we did spectroscopy in the dark space to avoid excess light, and only the laser light was irradiated to the samples. We removed the noise of the spectrometer by smoothing it.

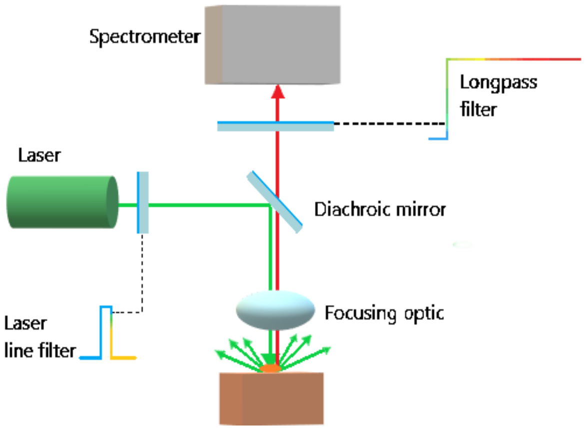


Fig. 3. Schematic diagram of the Raman spectrometer

Visible light of 532 nm from a laser source is delivered through a lens and a filter. The light is then reflected by a mirror and a holographic notch filter (function like a mirror in this path) and focused onto the sample through a microscope objective lens. The backscattered light from the sample is collected by the same objective and passed through the same notch filter, which now filters out the dominating Rayleigh component and transmits the Raman-shifted wavelengths. The Raman scattered light is transported to the spectrometer, and the beam is deflected onto the diffraction grating, which separates the beam into its constituent wavelengths. Then light through a lens is directed onto a CCD detector, which converts the distribution of light intensity as the function of wavelength to a digital signal to produce a two-dimensional plot of spectral intensity vs wavenumber position (Raman shift from laser wavelength, in cm^{-1}) [11].

III. RESULTS AND DISCUSSION

After preparing the graphene-based substrate using graphene oxide spin-coating on the glass slide, Raman spectroscopy was used to check that the coating of the substrate was done well. Raman spectra were taken from five points on the surface of the fabricated substrate and averaged. Figure 4 shows the typical Raman spectrum of graphene oxide materials, which has three main bands D, G, and 2D at 1349, 1604, and 2939 cm^{-1}, respectively [12], [13].

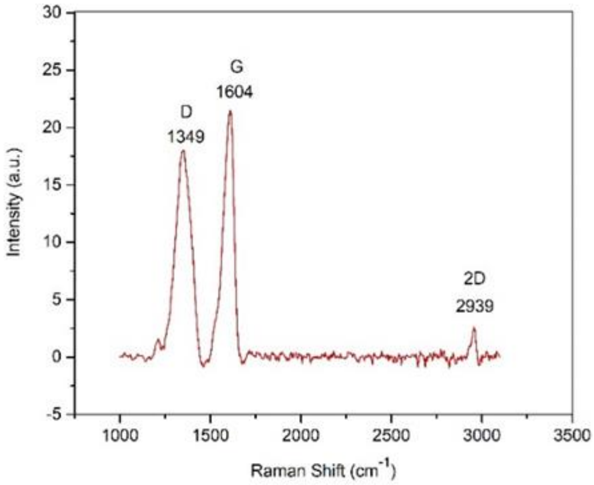
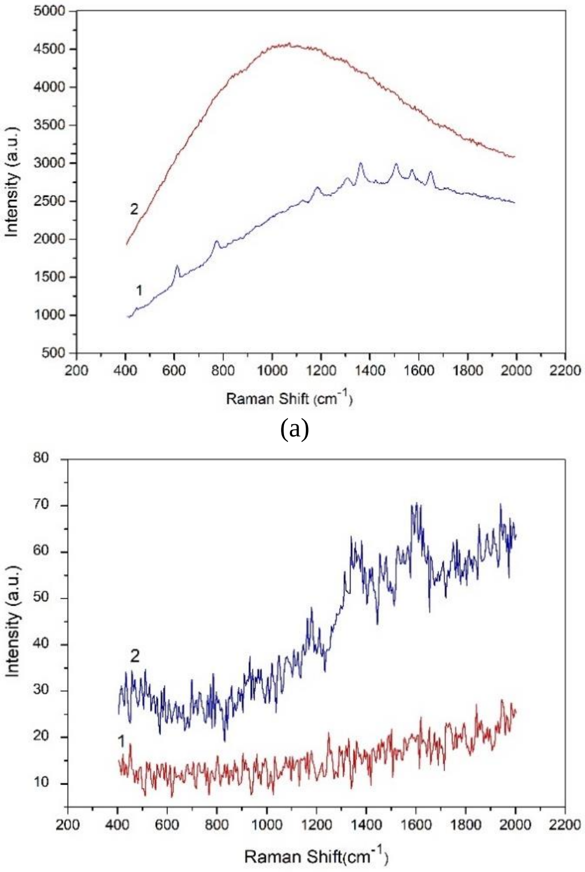


Fig. 4. Raman spectrum of graphene oxide suspension coated on a glass slide.

Rhodamine 6G and crystal violet were used as probe molecules to investigate the GERS effect. To demonstrate the effect of the graphene-based substrate on the enhancement of Raman signals, the Raman spectrum was taken from rhodamine 6G and crystal violet solutions, which were placed on an empty glass slide, and the substrates were prepared with graphene oxide. Figure 5 shows the comparison of Raman spectra. It is observed according to the form of amplification of Raman signals with the GERS method.

Graphene and its derivatives such as graphene oxide are very outstanding materials as substrates for Raman enhancement. By utilizing its large surface area and superior adsorption capabilities, graphene can be used to quench the photoluminescence of fluorescent dyes and drastically eliminate the fluorescence background [14]. The photoluminescence suppression effect is due to electron transfer and energy transfer between the graphene and the R6G and CV dye molecules. By taking advantage of the increased probability of the Raman transition when the analyte is absorbed, this technique is known as chemical enhancement [14].



(a)

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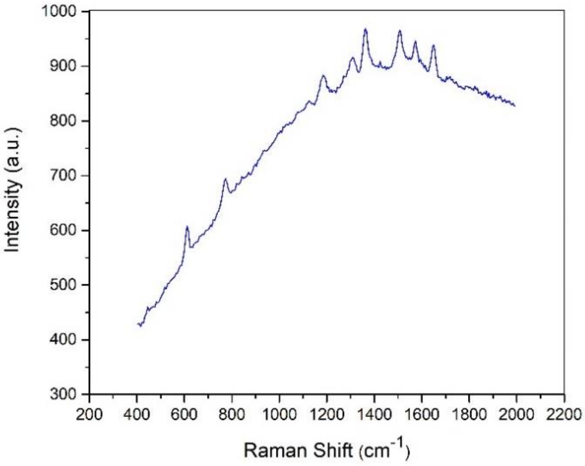
Fig. 5. Raman spectrum of (a) R6G solution placed 1- on a graphene-based substrate. and 2- on a bare glass slide and (b) CV solution is placed 1- on a bare glass slide. and 2- on a graphene-based substrate.



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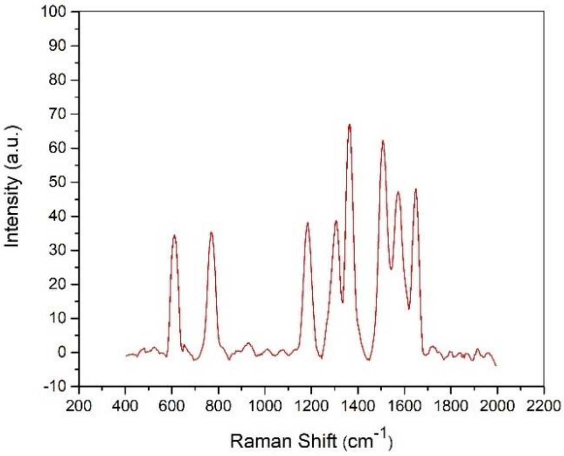

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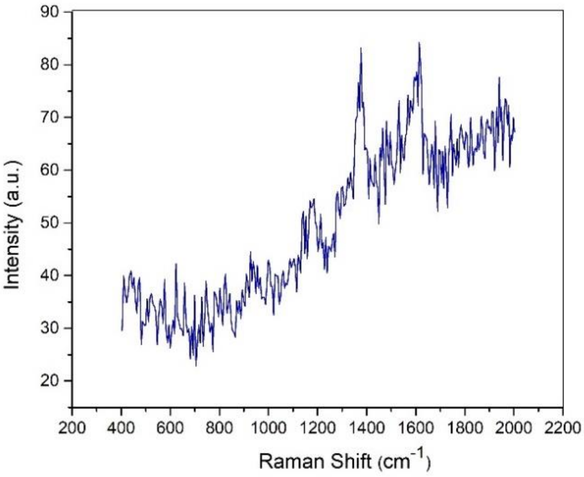
Fig. 6. (a) Primary unsmoothed Raman spectrum and (b) baseline subtracted Raman spectrum of R6G solution placed on a graphene-based substrate.

We subtracted baselines and smoothed Raman spectrums with OriginPro software. Fig. 6 and Fig. 7 show the primary unsmoothed and baseline subtracted Raman spectra of R6G and CV solutions, which were placed on the graphene-based substrate.

In general, 8 bands in rhodamine 6G and 8 bands in crystal violet were identified with this method. The bands detected by this method agree with the references [19], [20].

Figure 8 shows the baseline smoothed Raman spectrum of rhodamine 6G and crystal violet solutions deposited on the substrates which were manufactured using graphene oxide.



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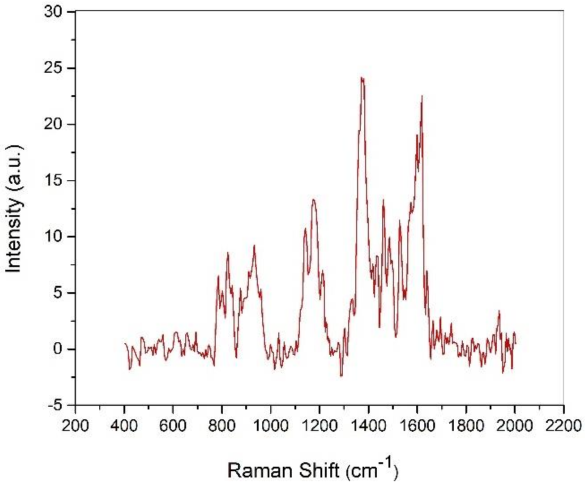

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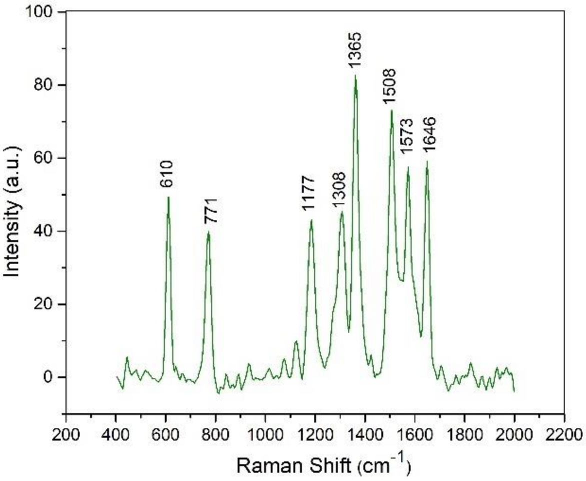
Fig. 7. (a) Primary unsmoothed Raman spectrum and (b) baseline subtracted Raman spectrum of CV solution placed on a graphene-based substrate.

Table 1. Vibrational bands related to different peaks in the Raman spectrum of rhodamine 6G on graphene-based substrate [15]-[18].

Tentative assignments	**Wavenumber (cm^{-1})**
C-C-C ring in-plane vibration	610
C-H out-of-plane bending	771
C-H in-plane bending	1177
N-H in-plane bending	1308
C-C stretching	1646,1508,1365
C-O-C stretching vibration	1573

Tables 1 and 2 show the vibrational bands corresponding to the rhodamine 6G [15]-[18] and crystal violet peaks [19]-[23].



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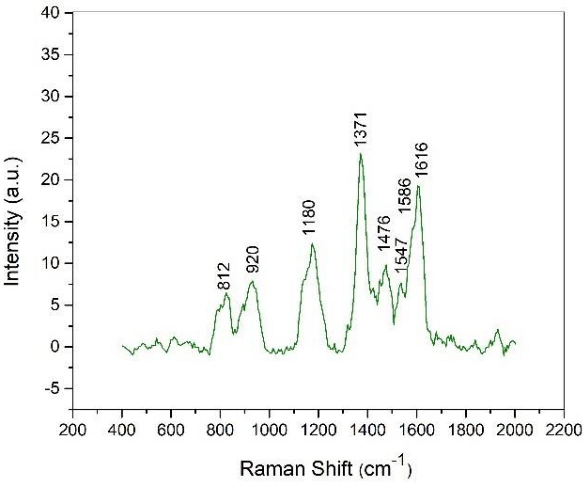

(b)

Fig. 8. (a) Raman spectrum of R6G solution on a graphene-based substrate. (b) Raman spectrum of CV solution on a graphene-based substrate.

Table **2** Vibrational bands related to different peaks in the Raman spectrum of crystal violet on graphene-based substrate [19]-[23].

Tentative assignments	**Wavenumber (cm^{-1})**
C-H ring in-plain bending	812
C-H out-of-plain bending	920
C-H ring bending	1180
C-H bending/ CH3 symmetric bending / C-C-C ring bending	1371
CH3 asymmetric bending	1476
C-N ring stretching / CH3 symmetric bending	1547
C-C ring stretching	1586
In-plane aromatic C–C	1616

IV. CONCLUSION

Since graphene-enhanced Raman spectroscopy (GERS) increases the intensity of Raman signals well, a lot of information can be extracted from the structure and properties of the material by analyzing the vibrational bands. Due to the many capabilities of this method, many applications in different fields such as drug discovery, diagnosis, food safety, and security are predicted for it. In this article, we use a new spin-coating method to produce a substrate based on graphene. This method has many advantages. The substrate produced in this way is cheaper, available, renewable, and repeatable.

For investigation of the effect of enhancing Raman spectroscopy using graphene for rhodamine 6G and crystal violet, it was shown that the intensity of Raman signals on prepared graphene-based substrates is completely increased compared to bare glass. With this method, all their Raman peaks can be identified.

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