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Commentary

Detection of Polycyclic Aromatic Hydrocarbons by Raman Technique

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Commentary

Polycyclic aromatic hydrocarbons or polynuclear aromatic hydrocarbons (PAHs) are a group of ubiquitous organic compounds that contain two or more fused benzene rings (Figure 1) in a linear or clustered fashion (Nagy et al., 2013). The worldwide distribution of PAHs has attracted a significant concern for their adverse effects on living organisms. PAHs are present in the air, water, sediments, and even in solid-liquid interfaces. The principal source of PAHs is believed to be either petrogenic or pyrolytic. Large amounts of PAHs are being released into the environment via incomplete combustion of fossil fuels, oil spills, petrochemicals, motor vehicles, wood burning, pyrolysis of organic matter, and incinerations (Du and Jing, 2011; Nagy et al., 2013). In the sedimentary rocks and marine environments, high levels of PAHs are distributed by the diagenetic and epigenetic transformations of small organic matter (Alajtal et al., 2010). PAHs are toxic to all biota and exhibit strong affinity to lipids. The compounds show little tendency to undergo biodegradation and possess relatively long lifetimes. Though there are hundreds of individual PAH species are available, the US EPA has identified sixteen compounds as priority pollutants (Augusto et al., 2013). These hydrophobic compounds are extremely hazardous and can cause mutagenic, carcinogenic, and teratogenic effects on the human body (Guerrini et al., 2009).

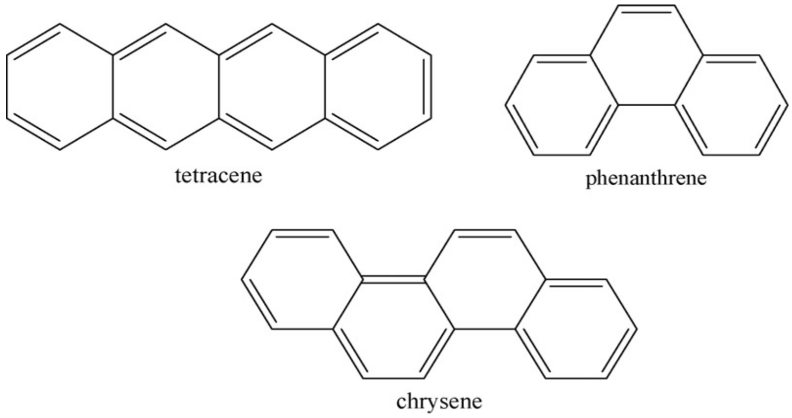

Figure 1: Structures of some PAHs (Alajtal et al., 2010).

Generally, the distribution of PAHs in the environment occurs in a mixture; therefore, the detection of the individual compound is a challenging job (Du and Jing, 2011). The conventional techniques

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used for the detection of trace amounts of PAHs include capillary electrophoresis, mass spectrometry, quartz crystal microbalance (QCM), liquid chromatography, electrochemiluminescence, synchronous luminescence, room temperature phosphorescence, fibre optic-based laser sensors, fluorescent spectrometry, and Raman scattering technique (Asher, 1984; Sheng et al., 2012). However, mass spectrometric methods require laborious matrix preparation. The fluorescence-based liquid chromatography is an excellent tool for the identification of individual PAH, but the method requires expensive instrumentation and time-consuming sample preparation. The fluorescence technique is also affected by the matrix problem, like spectral interferences from other luminescent materials (Asher, 1984). Moreover, the broad fluorescence bands from a mixture of PAHs overlap many small peaks, making the detection even more complicated. Raman technique, on the other hand, is currently recognised as one the most effective spectroscopic tools for the unambiguous detection of PAHs in broad spectra of environmental samples (Muniz-Miranda et al., 2011; Otto et al., 1992).

The Raman technique, complementary to infrared (IR) spectroscopy (Figure 2), the non-polar molecules, like PAHs are more sensitive than polar compounds, is a versatile, sensitive, and selective method compared to other spectroscopic techniques, which allows providing a level-free and quick sample characterisation (Robinson et al., 2012).

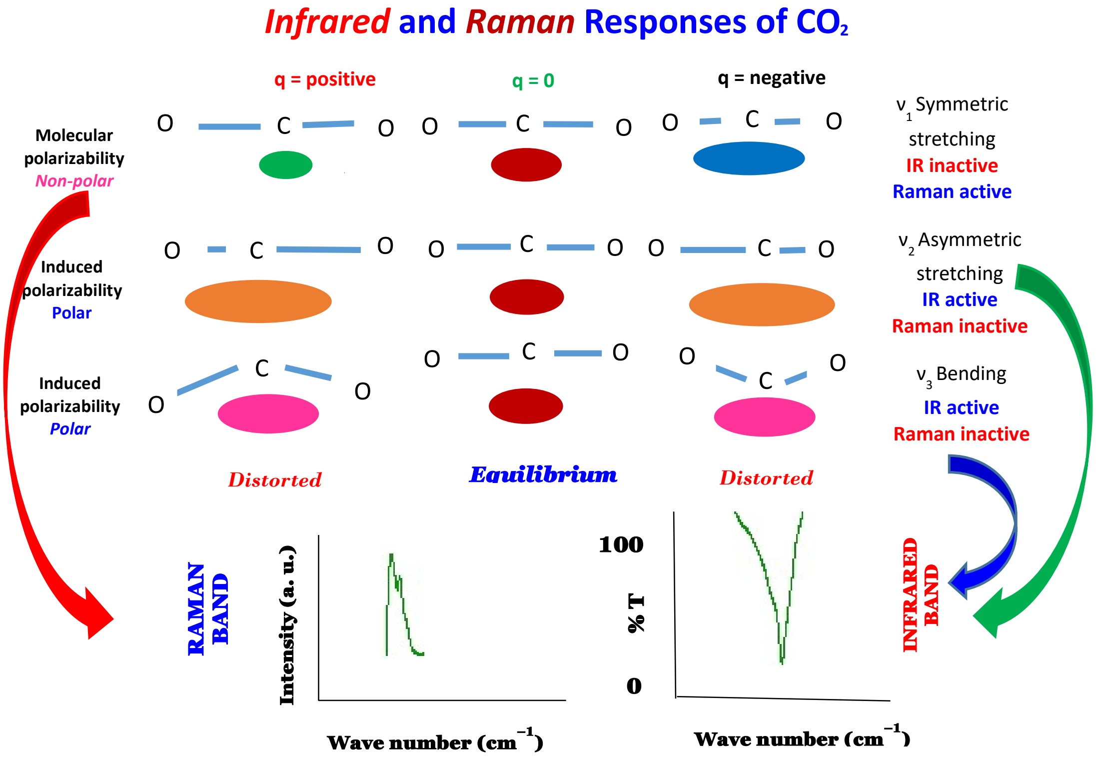

Figure 2: The figure demonstrates the complementary nature of IR and Raman.

A substance must possess some sorts of dipole moments to be an IR active. Though CO_2 has no permanent dipole moment, it is IR active. Why? The CO_2 molecule may undergo symmetric stretching (ν_1 vibration, simultaneous elongation and contraction of both C–O bonds) or asymmetric stretching (ν_2 vibration, one C–O bond undergoes an elongation, while the other receives a contraction and vice versa). The ν_1 vibrational mode causes no dipole change, and hence it is IR inactive. However, this vibrational mode is Raman active. How? The inelastic scattering of transduction Raman beam pushes the molecular electron cloud aside and cause to develop an induced polarisation on CO_2. Thus, the combined effect of the electromagnetic field and rovibronic coupling make the CO_2 molecule a little bit polar. The Raman response is proportional to the magnitude of this polarisability change concerning the rovibronic state; the more is the induced polarisability; the strongest in the Raman signal. Since PAHs are mostly non-polar, a similar mechanism applies to these compounds. The induced polarisability of the electric dipole-electric dipole of PAHs molecules makes them a suitable candidate to be detected by the Raman technique. The asymmetric stretching (ν_2) and bending (ν_3) vibrations of CO_2 could also develop some dipole moments on the molecule; therefore, these two vibrations cause the CO_2 molecule to be IR active, but Raman inactive. It is worth mention, the ν_2 and ν_3 vibrations of CO_2 molecule make it a strong greenhouse gas!

The Raman spectroscopy, a non-destructive tool that produces sharp molecular ‘fingerprints’, requires minimum matrix preparation. The Raman measurement is based on transduction mechanism, the inelastic scattering of monochromatic laser beam striking on metal surfaces causes a big signal enhancement (Ferrari and Basko, 2013). The Raman intensity varies with the fourth power of the local electromagnetic field and gives a fast sample identification. Raman signals are usually 10–100 times narrower than fluorescence bands, and hence offers multiple detecting opportunities, which experiences very little or no scattering interferences from the surroundings (Xu et al., 2010). In addition, the Raman bands are not affected by humidity or the presence of oxygen (Li et al., 2010). One of the essential applications of Raman technique is the detection of PAHs in complex environmental samples. Figure 3 shows the Raman spectrum of a typical PAH.

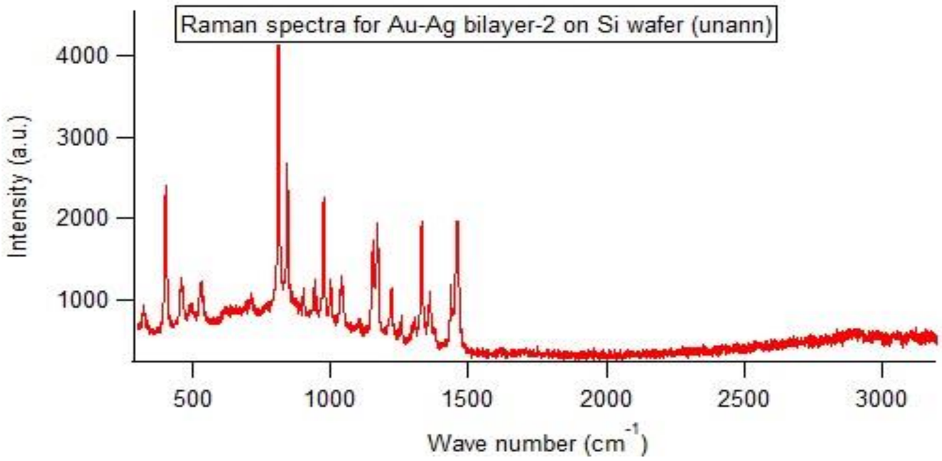

Figure 3: Surface-Enhanced Raman Scattering (SERS) from a typical PAH carried out with a dispersive Raman instrument. The sample was placed on the gold-silver (Au-Ag) bilayer deposited on a silicon wafer (figure credit belongs to the author).

For screening real samples in the laboratory set up as well as in field levels, many Raman devices are now available (Sharma et al., 2012). For instance, the palm-size portable Surface-Enhanced Raman Scattering (SERS, Figure 4) offers an excellent promise to quantify environmental pollutants in real-life conditions with a sound sensitivity.

Figure 4: A palm-size SERS device capable of screening samples in the field level (Sharma et al., 2012).

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