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Raman and time-resolved pulsed photoacoustic spectroscopy of solid trinitrotoluene in graphite mixture: For identification of double resonant optical phonon signatures

K.S. Rao[a,b], A.K. Chaudhary[a,*]

[a] Advanced Center for Research in High Energy Materials (ACRHEM), University of Hyderabad, 500046, India
[b] The Guo China-US Photonics Laboratory, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, China

HIGHLIGHTS

- Graphite as a sensor for identification of TNT using 1064 nm wavelength.
- The PA study with respect to different weight percentage of graphite in TNT matrix.
- Identification of acoustic and optical phonons waves transfer mechanism between GP and TNT using 785 nm wavelength.
- Development of a new tool for detection and identification of explosive molecules using commercially available laser systems.

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ABSTRACT

The optical phonon waves transfer mechanism between pure graphite (GP) and trinitrotoluene (TNT) using 1064 nm as an excitation wavelength based on the double resonant Raman effect and the pulsed photoacoustic (PA) technique has been investigated. The study was carried out at a different weight percentage of GP within TNT with respect to the two excitation wavelengths of 532 nm and 1064 nm (30 ps, 10 Hz, Q-switched Nd: YAG laser). The equal and double proportional matrix of the GP and TNT (solid samples) generate a strong PA signal with high quality factor (Q-factor) due to the interaction of optical phonons of GP and TNT in the same phase. The Raman spectra, recorded at 785 nm wavelength provides an insight on the pi-electron coupling between the GP and TNT. The obtained experimental results confirm that the pure GP and its derivatives, which have a SP^2/SP^3 hybridization, can be used to develop a new sensing optode for the detection and identification of explosive molecules in the visible and near-IR wavelengths range.

1. Introduction

The detection of solid high energy materials (HEMs) or explosives in visible and NIR region using photoacoustic (PA) spectroscopy is still a challenging task due to the absence of absorption bands in this region. Many optical and chemical analytical techniques for the detection of explosives are reported by different groups [1–6]. These analytical techniques were demonstrated on the basis of the absorption or emission of incident radiation from the analysts. Among all, PA spectroscopy is one of the most versatile and potent absorption-based technique because it can identify molecules in the solid, liquid, and gaseous phase in trace level using deep UV, IR, and THz radiation [7–16]. High power pulsed and CW lasers of 532 nm and 1064 nm wavelengths are easily available, therefore, several researchers have demonstrated the wide range of applications in the field of laser spectroscopy for different materials at these wavelengths [17–23]. In present report, we have demonstrated the new mechanism of detection of the explosive using graphite (GP) as a sensing medium at 532 and 1064 nm wavelength range.

Recently, Sharkaway et al. have reported the laser-induced PA spectroscopy for trace detection of explosives using 1064 nm obtained from Nd: YAG laser, which is used in a combination of optical interferometry technique [17]. However, the strength of the generated acoustic signals was quite low. Similarly, TNT is detected by Haibo Zhou et al. using ultra-high Raman scattering of off-resonated p-amino benzenethiol (PABT) through the formation of TNT-PABT complex, where silver nanotubes arrays were used for enhancing the Raman signal [18]. On the other hand, a double resonant Raman spectroscopy

* Corresponding author.
E-mail addresses: akcphys@gmail.com, anilphys@yahoo.com (A.K. Chaudhary).

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is one of the attractive technique, which is widely used to investigate the disorder and defects in the graphite-based system [19]. In addition, the detection and characterization of TNT using different optical techniques have been reported [16,20–23]. Mcnesby et al. have reported the Raman spectra of TNT and some other high-energetic materials using Fourier transform Raman (FTR) spectroscopy by employing near-IR laser radiation with a scattering source of 1060 nm [20]. M. Snels et al. have detected the solid explosive TNT in the near infrared spectral range between 1560 nm and 1680 nm using CW cavity ring down (CRD) spectroscopy [16]. Pushkarsky et al. demonstrated the detection of TNT using laser-based photoacoustic technique [21]. They have explored continuous-wave high-power quantum cascade laser in external grating cavity geometry tunable up to 400 nm and extended up to 7300 nm. They have also used the flash heater to evaporate solid TNT in a CRD absorption cell. Deshmukh et al. have investigated the TNT in water samples collected from nearby military training center using solid phase microextraction technique coupled with Fourier transform Raman spectroscopy [22]. Idros et al. demonstrated the colorimetric-based detection of TNT explosives using functionalized silica nanoparticles [23].

In our previous report the promising use of 532 nm wavelength to identify the TNT in GP mixture using pulsed PA technique combined with double resonant Raman effect has been reported [24]. In the present study, we have introduced the use of fundamental wavelength (i.e. 1064 nm) of Nd: YAG laser system of pulse duration of 30 ps and 10 Hz repetition rate for recording of characteristic PA spectra of TNT in different weight percentage of GP. In addition, the Raman spectra of GP, TNT, and GP + TNT at 785 nm wavelength have been recorded. The generation of PA signal from TNT in GP matrix is going to open a new channel of research in explosive detection.

Pure GP does not emit any light photons because there is no transition between the conduction and valence energy bands. But it strongly emits thermal radiation, which falls in the far infrared region. Therefore, source medium GP plays an important role in interaction with the carbon in C—H—O group of TNT molecules. In the case of TNT, two energy bands (Raman bands) are generated due to NO_2 and cyclic aromatic ring, while for GP it is attributed to D-band. The carbon atoms of GP are arranged in a hexagonal structure, where one carbon atom forms a covalent bond with three surrounding atoms [25]. It is well-known that carbon has valence of 4 and it can make four bonds. In the case of GP three electrons of carbon form three bonds among themselves, and the other free electron floats freely between two layers of carbon plates as shown in Fig. 1(a). This free electron is delocalized and mobile by nature. Thus, it can conduct the electricity and give the GP the property of an electric conductor despite being a non-metal. A force created between these two layers of carbon with the aid of the electrons is known as Van Der Waal force [26,27]. Graphene is a two-dimensional (2D) building block for carbon allotropes of every other dimensionality.

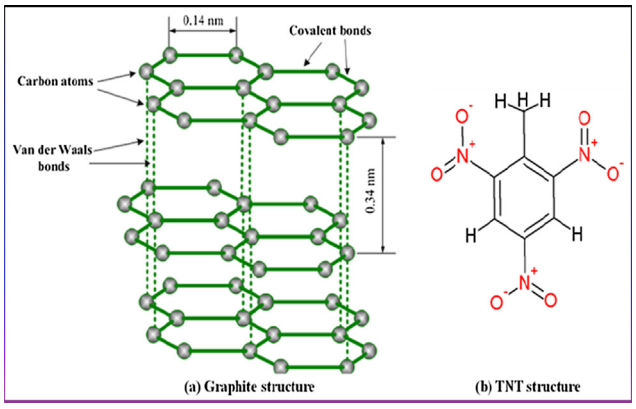

Fig. 1. The structure of (a) graphite and (b) trinitrotoluene (TNT).

It can be stacked into 3D graphite, rolled into 1D nanotube, or wrapped into 0D fullerenes. The G and 2D Raman peaks change their shape, position, and relative intensity with respect to the number of graphene layers. Also, it reflects the evolution of the electronic structure and electron-phonon interactions. The origin of the D and G bands along with second-order D peak of graphene has been studied in [28].

The broad range of excitation energy of GP lies between 1.91 eV (649 nm) and 2.52 eV (488 nm) that shows the first and second-order Raman spectra of the GP respectively [28–33]. Raman spectroscopy is a well-established tool for vibration spectroscopic analysis and is employed for the identification and detection of explosives [20,34–37]. Wang et al. [29] have analyzed the Raman spectra of industrial TNT dissolved in acetone and reported seven major bands. They have used 1064 nm wavelength obtained from the diode-pumped Nd: YVO_4 solid laser as an excitation source. The 2D GP structure consists of two carbon atoms per unit cell, which are associated with six numbers of phonon modes. Among them, three belong to acoustic (A), and the other three to optic (O) phonon modes. The optic phonon modes are further divided into out of plane (OT) phonon mode, one longitudinal (L), and the other one transverse (iTO) [19].

The optical/acoustic phonons are responsible for transferring the vibrational energy and momentum from GP to TNT. This phenomenon was also perceived in the Raman spectra of samples. In this case, the shift in D and G bands of GP, as well as TNT bands in the GP + TNT mixture was observed. This is the indication of coupling of pi-electrons between GP and TNT (due to electron-phonon or phonon-phonon interactions) that leads to transfer the phonon waves momentum from GP to TNT. As a result, TNT can absorb the incident radiation that leads to generation of strong PA signal. The present study revealed that near-IR wavelengths could also be useful to identify solid TNT and other HEMs in the presence of GP using pulsed PA spectroscopy.

2. Experimental arrangements

The experiment was performed in three steps. In the first step, the mixture of TNT and GP were prepared in different weight proportions. The powder samples were converted into a circular disk of variable thickness in the form of pellets using two tons of pressure. In the second step, the mixture was placed in an aluminum cubic shaped PA cell of length 5 cm, width 5 cm, and height 6 cm. The fundamental and the second harmonic wavelengths, i.e. 1064 nm and 532 nm, obtained from Q-switched Nd: YAG laser of 30 ps duration at 10 Hz (PL-2250 Ekspla, Lithuania) were employed to excite the mixture of TNT and GP. The generated PA signal was recorded using a pre-polarized microphone (BSW, China), which was housed in a teflon (PTFE) jacket and placed at a distance of 1.0 cm from the sample cavity. The distance between the center of the sample and the microphone head was 2.2 cm. An aluminum plate had a window of one-inch diameter glass/quartz covered with a neoprene washer, which was used to cover the cavity. The generated PA signal was amplified using a preamplifier and fed to the digital storage oscilloscope (Tektronix, 200 MHz) for the recording of the time domain signal. The oscilloscope was connected to the personal computer, which has a data acquisition program developed using LabView software. In the third step pure TNT & GP and their mixtures were subjected to portable Raman spectrometer, λ = 785 nm (B &W Tek, USA) for the recording of Raman spectra.

3. Results and discussion

3.1. 1064 nm based photoacoustic spectra of TNT with GP

Fig. 2(a and b) shows the PA spectra of a pure GP (2 mg) and composite (GP + TNT, 1:1 ratio by weight) respectively. The PA spectra are recorded at data acquisition time t = 1 ms and at incident laser energy E_{in} = 2.0 mJ. The excited acoustic modes for the matrix of GP and TNT (GP + TNT) show the shift in the frequency with respect to the