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Photoacoustic spectroscopy of standard explosives in the MIR region

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ABSTRACT

An emerging and important topic of interest in the field of homeland security is the identification and quantification of explosives. This paper brings new elements in the Laser Photoacoustic Spectroscopy (LPAS) based characterisation of some classical explosives (2,4-DNT; 2,6-DNT; HMX; TATP; PETN) in solid phase at CO_2 laser wavelengths, not yet reported in the literature to our knowledge. Moreover, we report our LPAS analysis of TNT and RDX, already previously studied with the same technique in the same spectral interval by different authors. The reported photoacoustic signals from standard commercial samples of the classical explosive substances were recorded in the 9–11 μm region, by a CO_2 laser based homemade optical apparatus. The underlying experimental activity was performed in the molecular spectroscopy laboratory of the ENEA Research Centre in Frascati.

1. Introduction

In the field of homeland security, the identification and quantification of explosives is a highly significant task, both for the fight against illegal use of these compounds in the terrorist activity and for eliminating the health risks associated with the release of explosives in the environment from military sites and ammunition plants. Beyond their dangerous aspect as highly energetic materials, being nitro-aromatic chemical compounds, they also possess a strong toxic effect at very low doses. A characteristic of nitro-aromatic compounds is their ability to rapidly penetrate the skin. They can cause local irritation, anaemia on chronic exposures, liver damage and bladder tumours. The United States Environmental Protection Agency (US EPA) included the dinitrotoluene (DNT) molecule in the health advisory (HA) regulations, in which it was established that the reference dose (RfD) for 2,4-DNT is 0.002 mg/kg/day, and equivalent level in the drinking water (DWEL) is 0.1 mg/L as it presents harmful effects and may induce ischemic heart disease, hepatobiliary cancer and urothelial and renal cell cancers [1]. These threats demand for the fast development of innovative and effective detection systems able to monitor explosives in trace. Different methods (i.e. optical sensors, electrochemical sensors, biosensors) that can compete with the canine sensorial system have been developed during the last decade. Searching in the ISI database in the topic "explosive detection", it can be found that in the last 10 years, more than 550 papers (articles, proceeding papers and reviews) were published in this subject area. In the present paper we bring new elements in the photoacoustic (PA) based spectroscopic characterisation and identification of some classical explosives in solid phase (2,4-DNT; 2,6-DNT; HMX; TATP; PETN), at CO_2 laser wavelengths (9.2–10.8 μm), which till now, were not reported in the literature to our knowledge. Moreover, we report on our Laser Photoacoustic Spectroscopy (LPAS) analysis of TNT and RDX, previously studied with the same technique in the same spectral interval by Prasad et al. [2] and Chaudhry et al. [3]. LPAS is well employable for the qualitative and quantitative analysis of substances in trace, irrespective of whether they are gaseous, liquids or solids [4]. Trace detection based on LPAS technique is especially convenient for gas sensing at the ppb level, but since the explosives have extremely low vapour pressures (ranging from less than 1 ppt for HMX to more than 1 ppm for EGDN), their vapour detection is a very complicated task. We focused on the detection and identification of solid energetic compounds. LPAS has many advantages over optical spectroscopy such as high signal to noise ratio, direct measurement of nonradiative transitions, it does not require a pretreatment of the sample and it has the possibility to analyse any kind of sample, transparent or opaque.

2. Photoacoustic method

2.1. The photoacoustic effect

In 1880, Bell discovered the photoacoustic (PA) effect in solids [5]. He observed that an audible sound is produced when chopped sunlight is incident on optically absorbing materials. For many

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decades, PA effect was forgotten, but in the 1960s, an important achievement was reached: the realisation of the first laser (ruby laser) followed by the realisation of the CO_2 laser in 1968. The first use of laser in PA gas detection was made by Kerr and Atwood in 1968 [6]. This was a great improvement for PA detection due to the superior beam quality, spectral purity and high power radiation of laser with respect to the conventional light sources for spectroscopy. Because CO_2 laser has high output powers (order of watts) and is tuneable on strong fundamental vibrational transition lines, it turned out to be an ideal source to push the sensitivity of PA detection in the ppb range or even below.

2.2. Indirect wave generation

PA generation can be the consequence of a direct or indirect effect [7]. In the direct effect, the acoustic wave is produced directly in the sample where the radiation beam is absorbed, while in the indirect PA generation, the acoustic wave is produced in a coupling medium adjacent to the sample, mainly due to the heat dispersion and to acoustic transmission from the sample (Fig. 1). Here, the sample is a solid or liquid and the coupling medium is gaseous or liquid. The indirect PA generation makes our case. We used micrograms of solid explosive samples closed in the PA cell at atmospheric pressure with ambient air as adjacent medium.

The Rosencwaig-Gersho theory [4] indicates that the PA effect is primarily dependent on the relationship between three parameters: the thickness of the sample l, the optical absorption length $l_\beta=1/\beta$ and the thermal diffusion length $\mu=(2\alpha/\omega)^{1/2}$, where β is the absorption coefficient, α is the thermal diffusion coefficient and ω is the chopping frequency of the incident light. If we consider the case of a strongly absorbing material, we are dealing with the situation of an optically opaque solid ($l_\beta \ll l$) as most of the light is absorbed within a distance that is small compared to l, and essentially no light is transmitted. For thermally opaque thin solids ($l_\beta \ll \mu \ll l$), the signal is quite strong (it is $1/\beta l$ times stronger than thermally thin solids: $\mu \gg l$, $\mu > l_\beta$) and depends on the thermal properties of the backing material (aluminium in our case) and varies as ω^{-1}.

2.3. Saturation effects

In order to avoid saturation effects due to the sample concentration as well as due to the laser power, we characterised the PA cell by using a strong absorber. The saturation of the PA signal theoretically occurs in optically opaque materials when μ becomes larger than l_β. For example, in the case of carbon black powder that exhibits a high value of β in the IR region from 1.5 to 12 μm, the saturation was reached essentially for sample quantities over 0.7 mg (Fig. 2).

For the explosives analysis, quantities lower than 300 μg were used, so no saturation due to the sample concentration was expected. Regarding the saturation due to the power density of the laser, the linear response of the PA cell containing carbon black is reported in Fig. 3 as a function of the increasing laser power. It has been observed that for a fixed amount of carbon black the PA cell response is linear (2.31 mV/mW slope) both for low level laser powers (2–20 mW) as well as for high level laser powers (300–800 mW).

It is known that the PA signal increases directly as the power of the incident beam increases. Thus, it appears that the sensitivity of the PA systems could be improved by employing more powerful laser sources. Unfortunately, at sufficiently high levels of radiation intensities, optical saturation effects come into play. For this reason, in achieving higher detectability with LPAS it is preferable to reduce the noise level, rather than using more powerful laser sources.

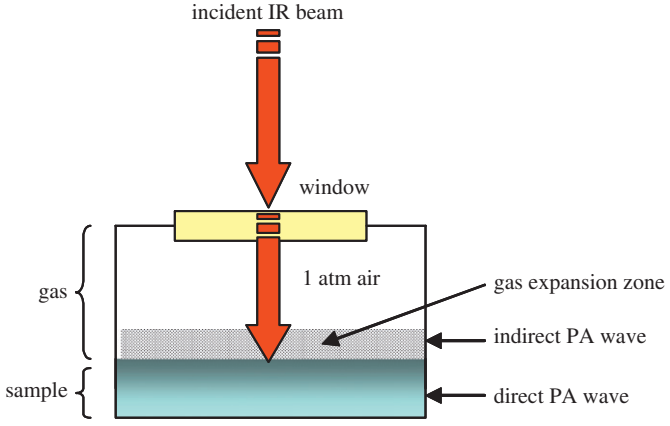

Fig. 1. Generation of direct and indirect PA waves in the PA cell.

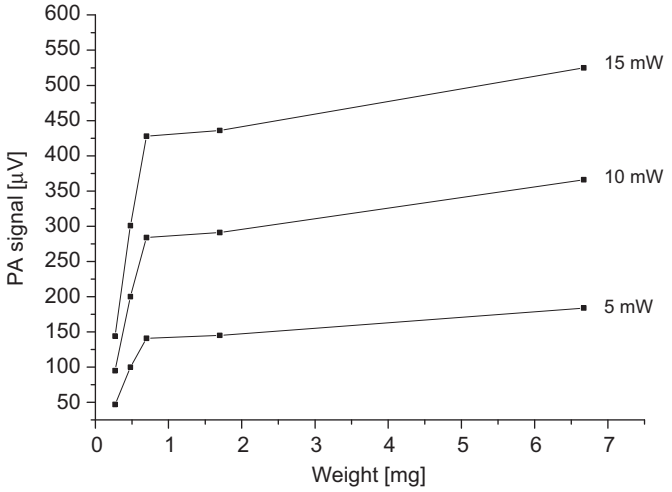

Fig. 2. PA signals for carbon black powder in different quantities at three different laser powers.

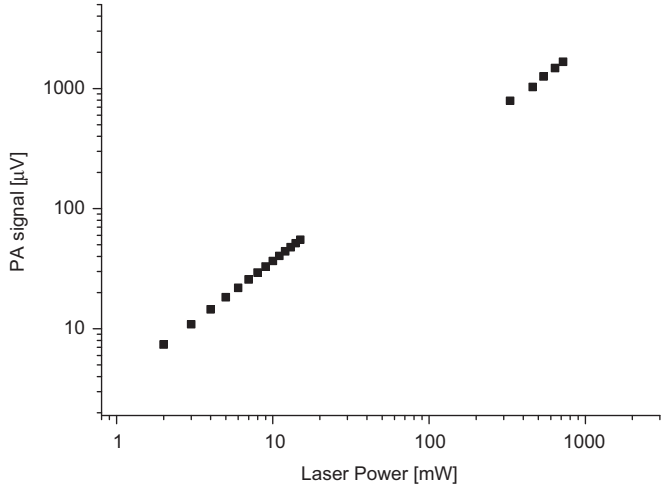

Fig. 3. A log–log plot of the PA cell response at low level and high level laser powers.