

Research Article

Vibrational Spectrum of HMX at CO₂ Laser Wavelengths: A Combined DRIFT and LPAS Study

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The vibrational spectrum of solid standard HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) was investigated. Two spectroscopic techniques were adopted for their different sensitivity and resolution. A preliminary survey of the absorption bands of the compound was performed in the 8000–400 cm⁻¹ spectral range by employing the diffuse reflectance infrared Fourier transform (DRIFT) technique at room temperature. The high-resolution line spectrum of HMX was obtained in the 9.2–10.8 μm spectral range by laser photoacoustic spectroscopy (LPAS) method, using a line tuneable 10 W stabilised cw CO₂ laser light source. By comparing the data collected with the two techniques in the common frequency range, a very good agreement was observed.

1. Introduction

Nowadays the joined efforts at different levels from national and international authorities and governments to increase the homeland security are devoted to fight against the new threats arising from terror and organized crime. Here we take into account threats based on use of explosive materials where the detection capability is fundamental. The identification of hidden explosives is a very difficult task, mostly due to their very low vapour pressure at normal conditions, as well as due to the existence of a wide variety of energetic species with similar spectral features. Consequently, the identification and quantification of explosive traces require very sensitive instrumentation and the development of fast screening sensors which are not invasive and not destructive. Optical methods operating in the middle infrared (MIR) region have the potential capability to detect the fingerprint signatures of organic molecules. In principle, they can detect explosive species with high specificity.

A high number of explosives contain –NO₂ groups, having quite intense infrared active absorption bands whose vibration frequency strictly depends on the molecular structure and consequently constitutes a fingerprint [1]. This

datum is particularly important when dealing with solid materials, since bandwidths are much more sharp than in vapour state. A further difficulty of the detection of gaseous molecules is due to the decomposition of the considered molecules at the temperature required to gain the sufficient vapour pressure for obtaining a readable spectrum, which would contain traces of the decomposition products.

In the frame of a systematic study of solid energetic materials we combined two noninvasive infrared spectroscopic techniques not requiring manipulation of the sample: the diffuse reflectance infrared Fourier transform (DRIFT) and the Laser Photo-Acoustic IR Absorption Spectroscopy (LPAS) with the aim of putting in evidence the diagnostic power of the latter method. The octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine molecule, also known as Octogen (HMX), was considered a very good test case for solid hazardous material detection because of its very low vapour pressure at standard condition and high melting point [2, 3]. Until present, for its quite expensive synthetic process, HMX was mostly employed in military warheads, often in combination with organic media. Recently, a new preparation method has been published presenting the advantages of higher yield and lower cost [4], and HMX is

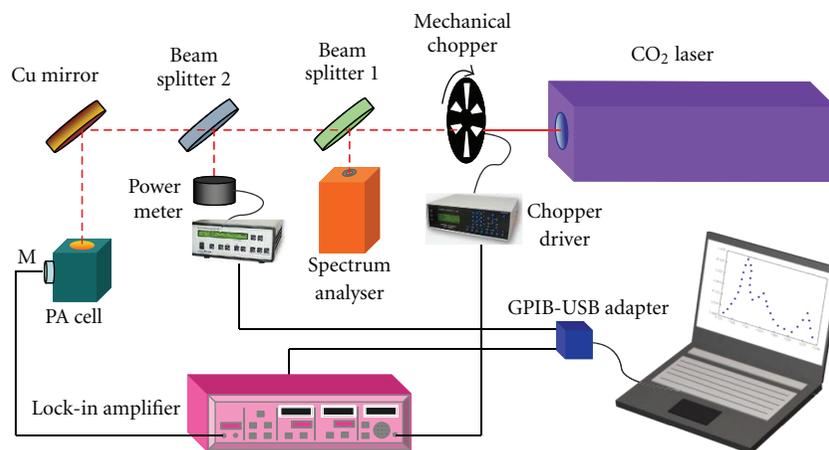


FIGURE 1: Schematic of LPAS experimental setup.

receiving renewed interest. In the following, the results of the integrated approach aimed to the detection of traces of solid HMX are reported.

2. Materials and Methods

HMX is known to occur in three polymorphic forms: α , β , and δ . Both α and β polymorphs are stable at standard conditions, while the δ phase can be produced by heating the β form over 140 Celsius degrees [5, 6]. For the present study the high-purity α polymorph (Restek) was employed. For safety reasons, the sample was highly diluted (1 mg/1 mL) in acetonitrile (AcCN).

The evaporation rate of HMX at room temperature is negligible with respect to that of solvents [7]. Therefore, for DRIFT spectra a controlled amount of the solution was dispersed in a weighted amount of KBr (Sigma-Aldrich, FT-IR grade of purity) and the solvent was completely extracted under low vacuum. This procedure allowed the determination of sample/KBr ratio. In all cases, at least two concentrations (1 : 100 and 1 : 1000) were analyzed. Reference spectra were obtained on weighted KBr in which the same amount of solvent was added and then extracted. In all the measurements, no absorption bands of the solvent were detected.

The experimental apparatus consisted in an FTIR spectrometer (IFS66 Bruker) equipped with a Praying Mantis (Harrick) DRIFT accessory located in the sample chamber under rotary vacuum. Spectra were recorded in the 8000–400 cm^{-1} range at a resolution of 2 cm^{-1} or better, cumulating 1024 scans. Both Globar and quartz lamps were used as sources since the latter is more efficient in the high-frequency region.

High-resolution measurements on HMX were obtained by the laser photoacoustic spectroscopy (LPAS). Details about the LPAS technique and about our homemade experimental layout were given previously [8, 9]. The block diagram of the LPAS apparatus is illustrated in Figure 1. The adopted laser source was a frequency stabilised 10 W cw grating tuneable $^{12}\text{C}^{16}\text{O}_2$ laser, emitting single mode IR radiation in the range 9.2–10.8 μm with $\Delta\nu = 75 \text{ MHz}$ ($\approx 0.0025 \text{ cm}^{-1}$

line spectral width). The intervals between lines are 0.01 and 0.02 μm , for R and P branches, respectively.

The home-built PA cell, with about 3 cm^3 inner volume, was equipped with a sensitive miniature microphone (mod. EK3033 Knowles). The unfocused laser beam (6 mm diameter) wavelength, incident on the sample, was monitored by an online CO_2 spectrum analyser (mod. 16A, Optical Engineering, USA). A very small amount ($<100 \mu\text{g}$) of pure HMX holding inside the PA cell resulted to be enough to produce a measurable photoacoustic signal. The PA cell was operated with ambient air, so no pure nitrogen and no synthetic air bottles were necessary as buffering gas. The PA absorption of the sample measured at a given wavelength was the mean value evaluated over 50 different automatic records of the PA signal; the procedure was repeated for each one of the emitted laser lines. Because the CO_2 laser emits high power (order of watts) IR radiation, and it is tuneable on strong fundamental vibrational transition lines, it resulted to be an ideal source able to push the sensitivity of LPAS down to trace levels, making it suitable for explosives analysis.

3. Results and Discussion

The spectroscopic behaviour of HMX has been the subject of many studies in the past [10, 11]. More recently, a theoretical and experimental treatment of HMX has been published giving an accurate assignment of all fundamental vibrations [12]. A few information about overtones and/or combination bands is reported in the paper of Mattos et al. [13], which extended the investigated spectral range up to 5200 cm^{-1} . The DRIFT data presented in this paper (Figures 2 and 3) furnishes a further extension to 8000 cm^{-1} evidencing the existence of two more peaks at 5972 and 5263 cm^{-1} of very low intensity, attributable to combination of very strong modes such as NCN or NO_2 with CH-stretching modes. The comparison of the data existing in the literature with the present results showed an excellent agreement and a perfect equivalence of two different experimental processes: diffuse reflectance spectroscopy used in our experiment and pellets transmission. It is important to stress that DRIFT

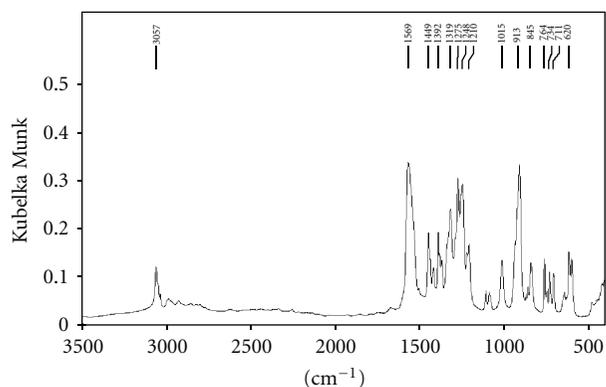


FIGURE 2: DRIFT spectrum of HMX: fundamental levels.

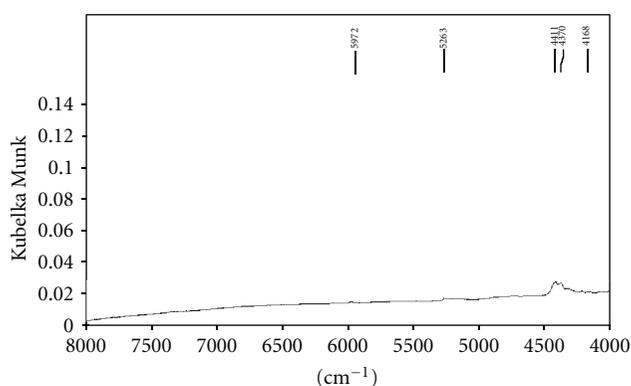


FIGURE 3: DRIFT spectrum of HMX: overtones and combination bands.

method represents a very good and fast simplification of the experimental procedure. Vibrational modes detected in this work are collected in Table 1 together with the proposed assignment in agreement with those reported by Brand et al. [12] in the investigated common range.

No previous CO₂-LPAS study on HMX from different authors was reported in literature at our knowledge; the first one was obtained from our experiments [8]. By using our homemade apparatus, we obtained strong PA signals from the HMX sample along each one of the sixty laser lines emitted by the adopted coherent source. This resulted in the rich line spectrum reported in Figure 4, where the wavelength-depending evolution of the PA signal was also compared to the portion of FTIR-DRIFT spectrum falling in the same spectral range. As it appears from the shown diagram, the continuous spectrum fits very well the spectral line representation. Following the assignment summarized in Table 1, the LPAS signals detected at 9–11 μm may be mainly attributable to t CH₂ and r NNO₂ movements, active in the probed range. The peak evidenced by FTIR at 9.9 μm falls outside the range covered by the laser emission. Nevertheless, the absorption line set detectable by the LPAS apparatus was enough for the HMX characterization and identification, as previously shown [8].

TABLE 1: HMX observed active modes and proposed assignment (vwv: very very weak, vw: very weak, w: weak, m: medium, s: strong, vs: very strong, br: broad, st: stretch, b: bend, t: torsion, def: deformation, sc: scissors, r: rock).

Observed frequencies (cm ⁻¹)	Assignment
5972 vwv	2 × st CH
5263 vwv	2 × st CH
4411 vw	CH st, st NNO ₂
4370 vw	CH st, st NNO ₂
4169 vwv	CH st, st NNO ₂
3057 m	st CH
3030 mw	st CH
2987 mw	st CH
2924 mw	st CH
2857 w	
2806 w, br	
1569 vs	st NO ₂
1449 ms	
1439 m	sc CH ₂
1421 m	sc CH ₂
1392 s	wag CH ₂
1386 m	st NNO ₂
1372 m	st NNO ₂
1319 s	st NNO ₂
1275 vs	r NNO ₂ , b CH ₂
1248 vs	st NCN
1225 s	st NCN
1210 s	st NCN
1110 w	
1091 w	
1015 m	t CH ₂ , r NNO ₂
913 vs	t CH ₂
877 w	Ring breathing
863 mw	st NCN
845 m	
764 m	st NCN
752 mw	
734 m	
711 m	
649 w	Ring def
620 m	
603 m	
485 w	Ring def

4. Conclusion

HMX was adopted as test compound for a combined FTIR-DRIFT and LPAS analysis.

Spectroscopic results here reported in the medium infrared region are in good agreement with literature IR data, even if obtained through different techniques. For the first time, the spectroscopic investigation has been extended to

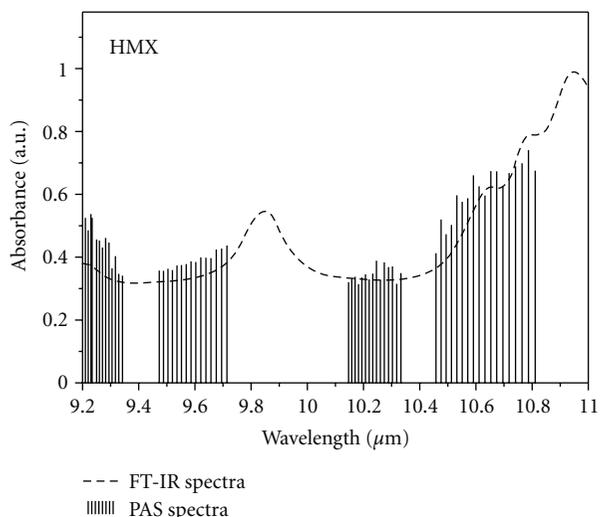


FIGURE 4: LPAS and FTIR absorption spectra of HMX in the 9–11 μm range.

the region where weak bands assigned to combination modes and/or overtones are expected.

As infrared spectroscopy is helpful in assessing the feasibility of different detection techniques for trace amount of explosive compounds, the spectral extension here reported seems quite important. In fact, very recently, few explosive compounds have been studied using Cavity Ring Down Spectroscopy (CRDS) in the spectral region around 6000 cm^{-1} [14].

Concerning the LPAS signals, HMX exhibited measurable photoacoustic absorptions obtained with less than $100\text{ }\mu\text{g}$ sample amount, making it possible to record a rich line spectrum in the 9–11 μm infrared spectral range. The LPAS high selectivity is mainly based both on the high-resolution features, given by the narrow (75 MHz) line width of the adopted laser source, and on the laser capability to be line tuneable on strong fundamental vibrational transition lines in the IR fingerprint region. This consents in principle to probe a single rotovibrational transition, specific of the analyzed species. Moreover, the high output power of the CO_2 laser beam contributes to push the sensitivity of PA detection in the trace range. Finally, apart from its intrinsic simplicity and ruggedness, LPAS has many advantages over other optical spectroscopy methods: high signal-to-noise ratio, direct measurement of nonradiative transitions, no pretreatment of the sample is required, being non-destructive, and it has the possibility to analyse any kind of sample, transparent or opaque.

The agreement between FTIR and LPAS data was excellent.

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