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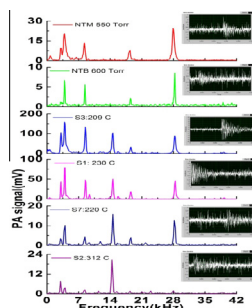
Study of acoustic fingerprinting of nitromethane and some triazole derivatives using UV 266 nm pulsed photoacoustic pyrolysis technique

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HIGHLIGHTS

- Study of UV based photo and thermal dissociation mechanism of nitromethane and HEMs.
- Recording of acoustic thermal finger print spectrum of HEMs.
- Discussion of thermal stability of HEMs on the basis C-NO₂ rupture of chemical bonds.

GRAPHICAL ABSTRACT



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ABSTRACT

We report a comparative study of acoustic fingerprints of nitromethane, nitrobenzene and some nitro rich triazole derivatives using pulsed photoacoustic technique. UV 266 nm wavelength i.e. Fourth harmonic of Q-switched Nd: YAG laser having pulse duration 7 ns and 10 Hz repetition rate is employed to record the time resolved PA spectrum. The PA fingerprint is produced due to absorption of incident UV light by molecule itself and photo dissociation of nitromethane and nitrobenzene at room temperature while in case of triazole it is attributed to the combination of thermal and photo-dissociation process. The entire dissociation process follows the route of cleavage of C-NO₂ bond to produce free NO, NO₂ and other by product gases due to $\pi^* \leftarrow n$ excitation. In addition, we have studied the thermal stability criteria of nitro rich triazoles based on the quality factor of acoustic resonance frequencies of the PA cavity. We have also studied the effect of data acquisition time to ascertain the decay behavior of HEMs samples.

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Introduction

Nitromethane, nitrobenzene, trinitrotoluene and triazoles are having common NO₂ moiety in their structure. Except nitrobenzene, the remaining other compounds are treated as high energy materials (HEMs). These molecules are widely used in defense, industry and pharmaceuticals applications [1,2].

Nitromethane (NM) is a volatile organic compound which is explosive in nature and available in liquid form at room temperature. It is widely used as a laboratory solvent, synthetic reagent and fuel [3–5]. The absorption range of nitromethane gas molecules lies between 190 and 355 nm. In addition, nitromethane also contains HNO₃ vapor which also has absorption in 105 and 350 nm range. It has several low lying electronic states which can be seen by means of optical absorption and photo dissociation techniques [6–9]. Several groups have reported the decomposition pathways of nitromethane using 266 nm wavelength. Yue et al. have reported

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the photo dissociation dynamics of gaseous nitromethane using single photon laser induced fluorescence technique and shown that the rotational state of $2\pi_{3/2}$, $2\pi_{1/2}$ distribution of nitromethane follows the Boltzmann distribution law [10]. Nitromethane has two absorption bands in UV region, the strong band is located around 198 nm while the second weak band is located at 270 nm [11–13]. Park et al. have reported the formation of oxygen atom due to photolysis of nitromethane molecule at 248 nm and 266 nm wavelengths, respectively. It is obtained from pulsed laser based (LP/VUV) LIF pump and probe technique. In case of photo dissociation of CH_3NO_2 which occurs between 240 and 270 nm range is attributed to $\pi^* \leftarrow \pi$ transition localized in NO_2 moiety. Several groups have reported NO_2 as a major product of dissociation formed due to photolysis of molecules. NO_2 is formed due to rupture of C–N bond due to $\pi^* \leftarrow n$ excitation by 266 nm at room temperature. The nitromethane follows two different types of photo dissociation mechanism based on their excitation wavelength. Nanoseconds pulses at 226 nm initiate the $\pi^* \leftarrow \pi$ photolysis and produced free CH_3 , NO radicals while selection of 266 nm follows the $\pi^* \leftarrow n$ excitation process. The second channel opens the formation of CH_3 , NO_2 , CH_3O and OH ion fragments [8].

The detection of gas/vapor molecules in terms of high selectivity and sensitivity are achieved by means of laser based photoacoustic technique [14–17]. Marius et al. have shown the photoacoustic spectra of some of the nitro compounds including NM and NB using two optical parametric oscillators (OPO) systems which covers from 0.7–1.9 μm and 5–11 μm , wavelength range respectively [18]. Nitrobenzene (NB) is an aromatic compound which has only one NO_2 functional group attached to the benzene ring. It is mainly used as a laboratory reagent and solvent. However, triazole derivatives are having high nitrogen content and newly synthesized thermally stable HEMs. They can also be treated as an eco friendly HEMs which has high detonation velocity and heat of formation. These compounds can be widely used as a gun propellants and rocket fuel [19]. We have chosen four numbers of laboratory made nitro rich triazole derivatives named 1-(2,4-dinitrobenzyl)-1H-1,2,3-triazole (S1), 1-(3,5-dinitrobenzyl)-1H-1,2,3-triazole (S2), 1-(2-methoxy-3,5-dinitrobenzyl)-1H-1,2,3-triazole (S3), 1-(3,4-dinitro benzyl)-1H 1,2,3 triazole (S7). The structures of NM, NB and triazole derivatives are shown in Fig. S1 (Supplementary part).

The UV–Visible absorption range of some of the gas molecules are based on HITRAN data base which is listed below. There is a series of some intermediate byproduct gases which is released by high energy materials during the decomposition process. The entire process take place in multiple steps: NO : 6.5–207 nm, NO_2 : 230–930 nm, N_2 : 6.2–113 nm, N_2O : 100–240 nm, NO_3 : 403–794 nm, N_2O_4 : 185–430 nm, CO : 6.2–177 nm, HNO_3 : 105–350 nm, HCN : 64–195, NH_3 : 10–230 nm, CO_2 : 0–205 nm, Oxygen O_2 : 0–245, 242.3–294.1 and 333–666 nm.

Several research groups have used different mathematical modeling and instrumental techniques to study the thermal stability and decomposition mechanisms of HEMs compounds [20–25]. These compounds are having strong electronic transitions due to presence of nitro functional group. In our previous report, we have used 532 nm wavelength to study the thermal decomposition and stability of S1, S2, S3 molecules in the indigenously designed PA pyrolysis system. The entire studies were based on the detection of freely released NO_2 at different temperature range. However, it has been realized that majority of HEMs molecules are having their own fingerprint spectra between deep to near UV-region. It is important to be noted that when these molecules are excited by wavelength of 266 nm then entire molecules give characteristic signature in terms of radiative and nonradiative transitions. As 266 nm wavelength initiate the photo-dissociation in nitromethane and produces free NO_2 and NO including some other

types of byproduct gases. Recent theoretical calculation reported by Arneas et al. have clearly shown that the vibrational transition in NO_2 from the major and minor channels should be assigned as (1^2B_1) and (1^2A_2) which appears in form of PA signal [26]. The process of dissociation is attributed to cessation of C– NO_2 bonds. The similar analogy can be adopted for the dissociation of nitro rich triazole derivatives in their vapor phase. In addition, some of the principal functional groups of HEMs also have strong absorption in deep UV region as mentioned above. The vapor of solid HEMs sample is produced by heating small quantity of solid compound between 30 and 350 °C temperature range. Similarly, theoretical and experimental approach for the photo dissociation of nitrobenzene at 266 nm is studied by Li et al. [27]. Some of the important radicals formed during the photo dissociation process of nitromethane at 266 nm is shown by several groups, Nicholson has shown the formation of NO_2 and CH_3 through the following root $\text{CH}_3\text{NO}_2 + h\nu \rightarrow \text{CH}_3 + \text{NO}_2$ [28]. McKee reported the formation of NO radical $\text{CH}_3\text{ONO} + h\nu \rightarrow \text{CH}_3\text{O} + \text{NO}$ [29], while, Zabarnick reported the formation of OH radical $\text{CH}_3\text{NO}_2 + h\nu \rightarrow \text{CH}_2\text{NO} + \text{OH}$ [30], whereas Park et al. documented the formation of oxygen atom $\text{CH}_3\text{NO}_2 + h\nu \rightarrow \text{CH}_2\text{NO} + \text{O}$ [11]. But Wen-Fan Hu et al. revealed the formation HNO molecule $\text{CH}_3\text{ONO} + h\nu \rightarrow \text{C}_2\text{H}_2\text{O} + \text{HNO}$ [31].

The PA technique works on the principle of detection of acoustic signal produced by different types of gaseous molecules after absorption of incident laser radiation of suitable wavelength. These molecules follow different dissociation path which produces different types of gases such as NO_2 , NO , N_2O , O_2 , CO , CO_2 , HCN , HONO , etc. Most of these molecules have strong absorption in 266 nm wavelength range. Therefore, the resultant PA signal represents the acoustic fingerprint of the particular type of molecule in terms of the intensity and acoustic modes of the given PA cell. This may also be understood in following manner. Since each of the released gaseous product has its own density and moreover they are the integrated part of the actual density of the compound in the vapor phase. Therefore, their collective contribution towards the PA signal can be treated as acoustic fingerprints of these molecules.

Experimental details

The experimental set up for recording of pressure dependent (non thermal) and temperature dependent (thermal) fingerprint spectra of liquid and solid HEMs is shown in the Fig. S2 (Supplementary part). The PA cell used in the experiment is made of stainless steel. It has internal diameter of 1.5 cm and length of 7.5 cm and used to record the PA spectrum. The quartz windows are placed in both sides of the cell to allow the laser radiation. The cell is designed to study the samples in the vapor form therefore the vapors of NM and NB which is already available in liquid form and can easily be collected by evacuating the PA cell at room temperature. But for the solid HEMs of nitro rich triazoles derivatives S1, S2, S3 and S7 require continuous heating under controlled condition. Therefore, we have used a round bottom flask which is housed in a temperature controlled oven to convert solid samples into vapor form at different temperature range. The solid HEMs compounds are placed in a round bottom flask for controlled pyrolysis between 30 and 350 °C range. A needle valve is used to control the flow rate of vapor through the inlet. The photoacoustic signal (PA signal) produced by vapor is detected by a pre-polarized microphone of responsivity 50 mV/Pa (BSWA, China). The microphone is placed in the center of the cell to record the excited longitudinal and radial modes of the cavity in very efficient manner. The output signal of the microphone has been fed to the preamplifier which is coupled to the 200 MHz oscilloscope (Tektronix,

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