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Photo-fragmentation cross-section of gaseous 2,4,6-trinitrotoluene at different ultraviolet wavelengths

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ABSTRACT

The photo-fragmentation cross-section of 2,4,6-trinitrotoluene (TNT) vapor at room temperature was determined at different ultraviolet wavelengths (254, 300, 340, and 400 nm) by measuring the concentration of NO molecule with cavity ring down spectroscopy and correcting for the photo-fragmentation cross-section of NO_2 . Nitric oxide (NO) molecules are produced by the TNT photo-fragmentation processes via an intermediate production of NO_2 . Our results reveal that the photo-fragmentation cross-section of TNT changes appreciably with change in wavelength with xenon arc lamp illumination, increasing with decreasing excitation wavelength. The maximum value of cross-section was observed at the shortest photo-fragmentation wavelength studied (254 nm), which is closest to the wavelength of an absorption peak of TNT near 220 nm.

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1. Introduction

The optical characteristics of toxic energetic materials (EMs) is of scientific interest because of possible health hazards as these materials can easily penetrate the soil and then migrate into ground water. 2,4,6-Trinitrotoluene, commonly known as TNT, is a yellow, odorless solid that does not occur naturally in the environment. It enters the environment in waste waters and solid waste resulting from the manufacture of the compound, the processing and destruction of bombs and grenades, and recycling of explosives. Exposure to TNT occurs through eating, drinking, touching, or inhaling contaminated soil, water, or air containing TNT. The health effects in people exposed to TNT include anemia, abnormal liver function, skin irritation, and cataracts. This substance has been found in at least 20 of the 1430 (1.4%) National Priorities list sites identified by the U.S. Environmental Protection Agency (EPA). The EPA has determined that this substance is a possible human carcinogen. In recent years, worldwide attention has been drawn to efforts to detect it by several analytical methods. To decrease the detection limit, there is a need for improved analytical performance in terms of sensitivity, selectivity, and temporal response that are beyond the scope of conventional methods of analysis. TNT vapor and explosive material have been studied by several techniques

* Corresponding author. Tel.: +44 161 306 3963. *E-mail address*: Ramesh.Sharma@manchester.ac.uk (R.C. Sharma). [1-7]. Spectroscopic methods can provide high selectivity and sensitivity for explosive detection [7]. An alternative approach to direct spectroscopic detection is photo-fragmentation (PF) spectroscopy. In this technique, characteristic fragments generated from the photolysis of the parent molecule are monitored spectroscopic ally [8–11]. To develop a quantitative description of the PF process, it is necessary to know the absorption cross-section of the corresponding explosive materials in the gas phase. Because of their low vapor pressures and pronounced tendency to decompose at elevated temperatures, the available ultraviolet (UV) spectra of these compounds have primarily been recorded either in solution [12-14] in the solid phase; [14,15] gas phase spectra are [16-20]. Cavity ring down spectroscopy (CRDS) is the most suitable technique for study of the optical properties of these specific nitro compounds [18]. By means of CRDS, we can measure the vapor density of TNT in real time, while conventional methods require many hours for vapor mass collection [19]. As a part of our efforts [18] to study the optical properties of gaseous TNT in the ultraviolet region, the photo-fragmentation cross-section of TNT vapor at room temperature (300 K) was evaluated at different wavelengths by using CRDS to measure the concentration of nitric oxide (NO) molecules produced.

2. Experimental

Fig. 1 illustrates the experimental arrangement. A dye laser (Continuum ND60) was pumped by the third harmonic (355 nm)

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Fig. 1. Experimental arrangement for TNT photo-fragmentation and UV-CRDS to measure the resulting NO concentration.

of a pulsed Nd:YAG laser (Continuum NY82S-10) with a 10-Hz repetition rate. The pulse duration was about 7–8 ns. The dye laser was operated with Coumarin 460 dye and generated 5-mJ pulses with 0.04 cm⁻¹ spectral width in the 445–485 nm spectral range. To achieve proper spatial beam quality, a 1×-Galilean telescope with two 200-mm focal length lenses and a 100- μ m pinhole were used together with two iris apertures.

The dye laser was frequency doubled by an INRAD AT-II Auto tracker II and the output was frequency selected using an INRAD 752-104 four-prism filter (labeled "wavelength separator" in Fig. 1). Mode matching was achieved with the help of a 5×-Galilean telescope that consisted of two quartz lenses of 20- and 100-mm focal lengths and a 10- μ m pinhole. The 227-nm laser beam entering the ring down cavity had 0.3 mJ energy, 0.3 cm⁻¹ spectral width, 1-mm diameter, and 0.75 m⁻¹ beam convergence. We modified the resonance cavity used in previous work [18] and it is shown in Fig. 1.

The laser radiation and radiation from a 100-W xenon arc lamp (Oriel, Model 66187) entered the cavity in mutually perpendicular directions. The cell, with a length of 52.6 cm and a radius of 1.75 cm, was constructed from stainless steel high vacuum components (MDC Vacuum Products). The TNT sample used was added to the cell by dissolving 0.3 g of it in 2 mL of acetone. It was spread on the walls of the PMT end of the cell. The walls were coated with the solution and then the solvent was evaporated. The cell was then evacuated and filled with argon to a pressure of one atmosphere. Instead of higher temperatures (92 °C) [18] the present experiment was performed at room temperature. To avoid mirror condensation, the viewports were always kept 10 °C above room temperature was mea-

Table 1	
Experimental paramete	rs.

sured using thermocouples that have an accuracy of ± 0.1 °C. The radiation of the xenon arc lamp, which entered from a direction perpendicular to that of the laser radiation, was used to photo-fragment TNT. The photo-fragmentation cross-section of TNT by the xenon arc lamp was evaluated by monitoring the concentration of NO using CRDS.

To perform CRDS, the ring down resonator was built from two mirrors, M1 and M2 (MLD Technologies), each with a 6-m radius of curvature. The maximum reflection of the mirrors was 99.7% at 230 nm; the minimum was 99.1% as the wavelength varied ± 2.5 nm. A photomultiplier tube (Hamamatsu R166UH) was used to record the CRDS decay waveform. Special attention was paid to the acquisition mode of the photomultiplier tube (PMT) to avoid signal saturation. To make the receiver system less sensitive to the ring down resonator alignment, a converging lens (labeled "collection lens" in Fig. 1) and a quartz diffuser plate were placed before the PMT. Signals were digitized by a digital oscilloscope (Tektronix TDS 410A) and transmitted to a data acquisition computer through a GPIB interface. Finally, photo-fragmentation of TNT was evaluated by using appropriate selected filter wavelengths (centered at 254, 300, 340, 400 nm with bandwidths of ~20 nm).

3. Results and discussion

To decrease the detection limit of the energetic material using the PF technique, the following two criteria must be fulfilled. (1) The molecular species to be detected must have an appreciable PF crosssection at a wavelength λ that is accessible with existing lasers/light sources. (2) Absorption of this parent molecule at λ must result in bond dissociation.

Filter (nm)	Power (mW)	Exposure time (min)	E_t (J)	$[NO]_{con} = \alpha / \sigma (per cm^3)$	[TNT] _{con} (per cm ³)	$[N]_{hv}$
254	0.1	154	0.924	7.5E10	6.2E11	1.18E18
300	0.115	145	1.0005	7.25E10	6.2E11	1.51E18
340	0.12	168	1.21	6.2E10	6.2E11	2.06E18
400	0.25	332	14.94	7.15E10	6.2E11	1.05E19

Table 2

Ν

Wavelength (nm)	$\sigma_{\rm TNT-NO}$ at RT ^a (cm ² /molecule)	$\sigma_{ m NO_2-NO}$ at 21 $^\circ m C^b$ (cm²/molecule)	$\sigma_{ m PF-TNT}$ at RT ^a (cm ² /molecule)	$\sigma_{ m Ab-TNT}$ at 92 $^\circ m C^c$ (c
254	9.85E-19	1.05E-20	9.75E-18	4.E-17
300	7.44E-19	1.32E-19	6.13E-19	1.E-17
340	4.75E-19	2.02E-19	2.73E-19	
400	1.05E-19	-	9.50E-20	

Photo-fragmentation and absorption cross-sections as a function of wavelength.

^a This work.

^b NO₂ + $h\nu \rightarrow$ NO + O: data from Ref. [21].

^c TNT absorption cross-section at 92 °C reported in Ref. [18].

Keeping these facts in mind, the present work was devoted to estimating the maximum PF cross-section of TNT at room temperature by determining its PF cross-section at different wavelengths. We used a 100-W xenon arc lamp along with different filters to obtain appropriate wavelengths for photo-fragmentation of TNT into NO. The photochemical processes involved in the present PF of TNT are:

 $C_6H_2CH_3(NO_2)_3 + h\nu_{(xenonarclamp)} \rightarrow$

$$C_6H_2CH_3(NO_2)_2 + NO_2(X^2A_1)$$
 (1)

$$NO_2(X^2A_1) + h\nu_{(\text{xenonarclamp})} \rightarrow NO(X^2\Pi) + O(^1D)/O(^3P)$$
(2)

The presence of the resulting NO concentration is detected by sensitive ring down laser spectroscopy by recording its absorption signal:

$$NO(X^{2}\Pi) + h\nu_{(dvelaser)} \rightarrow NO(A^{2}\Sigma^{+})$$
(3)

The total photo-fragmentation cross-section of TNT to NO, $\sigma_{\text{TNT-NO}}$, was then calculated by using the following formula:

$$\sigma_{\text{TNT-NO}} = \frac{[\text{NO}]_{\text{con}} \times Volume}{[\text{TNT}]_{\text{con}} \times L_{\text{TNT}} \times [N]_{hv}}, \text{ cm}^2$$
(4)

where [NO]con is the concentration of NO produced by PF of TNT by the xenon arc lamp, Volume is the total volume of the cell, [TNT]con is the concentration of TNT in the cell at temperature T (in the present experiment at room temperature), L_{TNT} is the total length of the cell, and $[N]_{hv}$ is the number of photons having a frequency v. [TNT]con is calculated by first calculating its partial pressure using the relationship given by Dionne et al. [19].

$$\log_{10} P(\text{ppb}) = \frac{-5481}{T(\text{K})} + 19.37$$
(5)

The [TNT]_{con} in Eq. (4) was then estimated by using

$$p = [\text{TNT}]_{\text{con}} kT \tag{6}$$

where k is Boltzmann constant and T is the temperature (in Kelvin). The concentration of nitric oxide [NO]_{con}, was evaluated as described in our previous experiment [18]. We first determined the absorption coefficient of NO molecule by measuring the CRDS decay time (τ) and using the equation

$$k(\lambda) = \frac{L}{cl} \left(\frac{1}{\tau(\lambda)} - \frac{1}{\tau_0(\lambda)} \right)$$
(7)

where *L* is the resonator cavity length, *l* is the absorption cell length; τ_0 and τ are the CRDS decay times of the waveforms measured for an empty cell and a filled cell, respectively. The concentration of nitric oxide was evaluated using

$$[NO]_{con} = \frac{k(\lambda)}{\sigma}$$
(8)

where σ is the absorption cross-section of NO molecule determined earlier [18]. To calculate $N_{h\nu}$, we first estimated the energy (E_t) of the xenon lamp using the equation:

$$E_t = P \times t \tag{9}$$

m²/molecule)

where *P* is the power of the photolysis wavelengths from the xenon arc lamp, which are selected by optical filters, and t is the exposure time of these photolysis wavelengths to the cell. Finally, N_{hv} was obtained by using:

$$J_{h\nu} = \frac{(Power)(time)}{hc/\lambda}$$
(10)

where h is Planck's constant, c is the speed of light in vacuum, and λ is the photolysis wavelength from the Xe lamp as selected using the optical filters. The values of E_t and $N_{h\nu}$ are calculated using Eqs. (9) and (10) and are tabulated in Table 1. Table 1 lists the different experimental parameters used for these measurements. Table 2 lists the total photo-fragmentation cross-sections $\sigma_{\text{TNT-NO}}$ for photo-fragmentation of TNT resulting in NO, the photo-fragmentation cross-sections σTNT_{NO-NO_2} for photo-fragmentation of NO₂ resulting in NO [21], and the photo-fragmentation cross-sections σ_{PF-TNT} of TNT at different excitation wavelengths of the xenon arc lamp. The different photofragmentation cross-sections are related by

$$\sigma_{\text{PF-TNT}}(\lambda) = \sigma_{\text{TNT-NO}}(\lambda) - \sigma_{\text{NO}_2 - \text{NO}}(\lambda)$$
(11)

The various photo-fragmentation cross-sections are plotted as a function of the excitation wavelength in Fig. 2. It is clear from the graph that the TNT photo-fragmentation cross-section $\sigma_{\text{PF-TNT}}$ increases with decrease in PF wavelength. Our result is in accordance with the result reported by Simeonsson et al. [22] that the PF efficiency of energetic molecules is usually higher



Fig. 2. Change in photo-fragmentation cross-section of TNT, NO2, and total TNT to NO with wavelength. RT = room temperature.

at shorter wavelengths. The increasing σ_{PF-TNT} with decreasing photo-fragmentation wavelength may be also explained (1) by the fact that our previous study [18] has demonstrated that the absorption cross-section of TNT vapor increases with decreasing wavelength and (2) by the fact that the NO_2 functionality of TNT is easily removed by excitation in the 190-250 nm region of the ultraviolet spectrum [15] and that this NO₂ molecule is further photo-fragmented to form NO. As Fig. 2 shows the photo-fragmentation cross-section of TNT is much larger than the photo-fragmentation cross-section of NO₂. This suggests that in the overall $TNT \rightarrow NO_2 \rightarrow NO$ photo-fragmentation process, that the photo-fragmentation of NO₂ to NO is the rate-limiting step. The vapor-phase TNT absorption cross-sections [18] at two wavelengths are also given in Table 2 for comparison. The absorption cross-section data in Ref. [18] was determined at 92° while the photo-fragmentation cross-section measurements in this work were performed at room temperature. Although the absorption and photo-fragmentation cross-sections have very similar magnitudes, comparison between the two results is not simple because the effect of temperature on the rate of photo-fragmentation is not known in this case. Our results reveal that the detection limit of TNT may be increased at shorter wavelengths due to an increase in $\sigma_{\text{PF-TNT}}$ at shorter wavelengths This is supported by previous experiments where the limits of detection of TNT were found to be 0.21 ppm at 193 nm and 1.7 ppm at 226 nm [22].

4. Conclusions

We have demonstrated a simple spectroscopic method for determining the PF cross-section of TNT vapor at room temperature. This study will be helpful in improving the detection limit of TNT using the photo-fragmentation technique. Based on this technique, the PF cross-section may be determined for other energetic materials.

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