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Short communication

Laser photoionization of triacetone triperoxide (TATP) by femtosecond and nanosecond laser pulses

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Abstract

Laser ionization time-of-flight mass spectrometry has been applied to the study of triacetone triperoxide (TATP), an improvised explosive. Wavelength dependent mass spectra in two time regimes were acquired using nanosecond (5 ns) and femtosecond (130 fs) laser pulses. We find the major difference between the two time regimes to be the detection of the parent molecular ion when femtosecond laser pulses are employed.
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1. Introduction

In recent years there have been an increasing number of reports describing incidents involving peroxide based explosives such as triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) in conjunction with terrorist activities. Due to the simple synthesis [1] using readily available starting materials, TATP is the dominant compound involved in these cases, the most notable of which are the “shoe bomber” incident and the London Subway attacks in 2005. Surprisingly, TATP’s physical properties including sensitivity to flame, heat, impact, and friction [2] and sublimation/decomposition at 25 °C [3] precludes its use in either commercial or military applications, even though its explosive power is similar to TNT.

The chemical structure of TATP, shown in Fig. 1, differs from many of the conventional explosives because it lacks nitrogen, amino, or nitro groups. Consequently, the detection of TATP using common chemical sensors based on nitro and amino sample-and-detect techniques is not possible. To complicate matters further, TATP has a sugar-like visual appearance and X-ray spectrum, which makes it difficult to recognize with current bulk screening technologies. Likewise, UV absorption spectra measured at SRI revealed no significant structural features in the investigated wavelength range (230–340 nm).

Current analytical methods used for TATP analysis include IR and Raman spectroscopy, ion mobility spectrometry, ^{1}H and ^{13}C NMR [4], HPLC [5], GC/MS [6], and chemical ionization coupled to tandem mass spectrometry [7]. Most of these techniques are applied in a laboratory environment and are usually not applicable to field screening scenarios. However, due to its dangerous properties and wide spread use, an analytical method is needed for the identification of TATP in complex matrices and low concentrations either before or after detonation. Mass spectrometer based techniques have shown promise for field deployment in a wide variety of scenarios, and are a very powerful analytical technique, especially when used in conjunction with laser photoionization. In particular, this technique has shown a high potential for the rapid, selective and sensitive analysis of complex matrices such as monitoring waste incineration processes or the time resolved analysis of the exhaust from diesel engines [8–10].

It is the objective of the present research to explore the laser photoionization of TATP in varying temporal regimes and to evaluate their potential to extend the current analytical methodologies used to detect TATP.

2. Experimental

The TATP investigations were conducted using two separate laser photoionization time-of-flight mass spectrometer instruments, both of which are described briefly. The femtosecond

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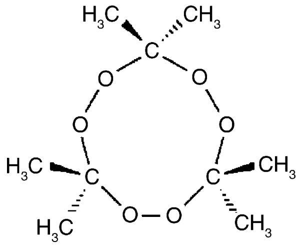

Fig. 1. Chemical structure of triacetone triperoxide (TATP).

system consists of a reflectron time-of-flight mass spectrometer (nominal $m/\Delta m \sim 1000$, Stefan Kaesdorf, Munich, Germany) with a capillary inlet system for sample introduction. The room temperature TATP vapor pressure (~52 mTorr) [11] was sufficient to generate ion signal and was entrained in UHP He to simplify spectral interpretation by removing background signals from laboratory air. The femtosecond laser system consists of a Ti:Sapphire oscillator, regenerative amplifier, and tunable OPA (Spectra Physics Tsunami, Spitfire, and OPA 800C), which produced nominally 130 fs pulses with energies of 840, 30, and 3 μJ, at wavelengths of 795, 500, and 325 nm, respectively, at a repetition rate of 1 kHz. The laser was focused into the ionization region with a 150 mm lens, and the resulting mass spectra were recorded with a 1 GHz digitizer (Acquiris AP235).

The nanosecond system is very similar in all respects, consisting of a reflectron time-of-flight mass spectrometer (nominal $m/\Delta m \sim 1000$, RM Jordan, Grass Valley, CA) and capillary inlet. The 266 and 355 nm laser wavelengths used were generated by a Nd:YAG laser (Continuum Powerlite 9010) at a repetition rate of 10 Hz producing 5 ns pulses with 30 mJ of energy, which were focused using a 270 mm lens. Ion signals were also recorded with a 1 GHz digitizer (Signatec PDA 1000). Instrument control and data acquisition were accomplished with custom software based on the Labview (National Instruments) programming environment.

The TATP sample was synthesized in-house following a scheme described in the open literature [1].

3. Results

Fig. 2a shows the mass spectrum of TATP taken at room temperature with 795 nm, 130 fs, 840 μJ laser pulses, while Fig. 2b shows the corresponding mass spectra taken with 266 nm, 5 ns, 30 mJ pulses. Expanded views of low mass and parent ion regions are shown in Figs. 3 and 4, respectively. The femtosecond mass spectra, Figs. 2a and 4a, show the parent ion signal at 222 amu, along with a significant number of TATP decomposition products, including acetyl ion $C_2H_3O^+$ (43 amu), acetone ion $C_3H_6O^+$ (58 amu), $C_3H_7O^+$ (59 amu), $C_3H_7O_2^+$ (75 amu), $C_3H_6O_4^+$ (101 amu), and $C_3H_6O_5^+$ (117 amu). In addition, no significant wavelength dependence was observed in the femtosecond regime at 330, 490, and 795 nm. However, it should be noted that isolating this dependence is difficult due to the varying power densities under which the mass spectra were acquired.

In contrast, the TATP mass spectra taken at 266 nm (Figs. 2b and 4b) lack the parent ion and high mass fragments, and are dominated by low mass species (Fig. 3b), the most prevalent of which is the acetyl ion (43 amu). The mass spectra taken at 266 and 355 nm in the nanosecond regime are qualitatively similar, and as a result the 355 nm mass spectrum is not shown. The main difference in the two nanosecond mass spectra is the degree of fragmentation observed, with the 266 nm producing more $C_3H_7O^+$ (59 amu) ion signal, while 355 nm produced more methyl ion CH_3^+ (15 amu) signal. These comparisons were made by normalizing the mass spectra to the 43 amu fragment

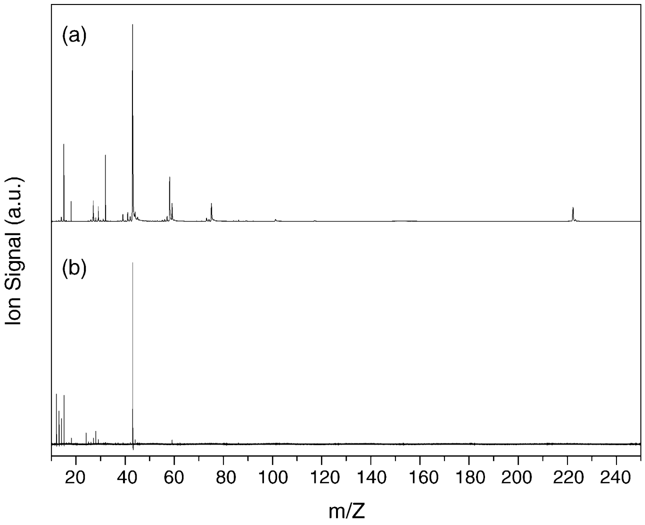

Fig. 2. Laser photoionization time-of-flight mass spectra of TATP. (a) 795 nm, 130 fs, 840 μJ pulses and (b) 266 nm, 5 ns, 30 mJ pulses.

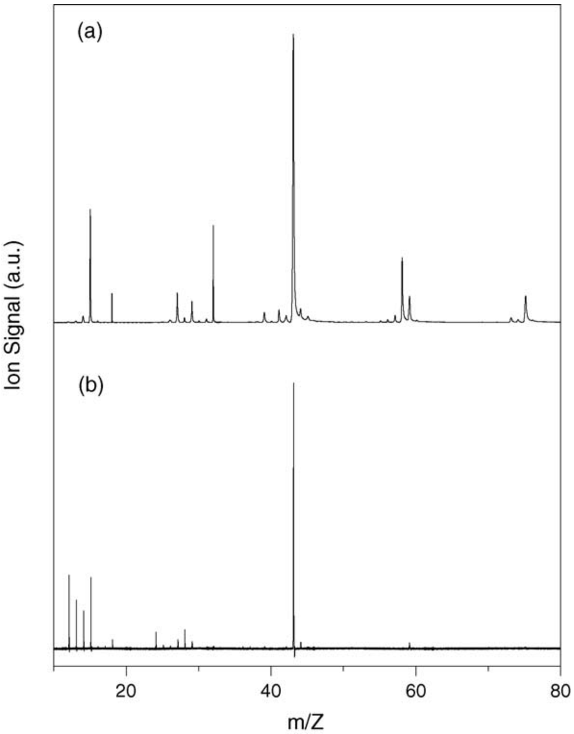

Fig. 3. Expanded view of the low mass fragments present in the TATP mass spectra between 10 and 80 amu. (a) 795 nm, 130 fs, 840 μJ pulses and (b) 266 nm, 5 ns, 30 mJ pulses.

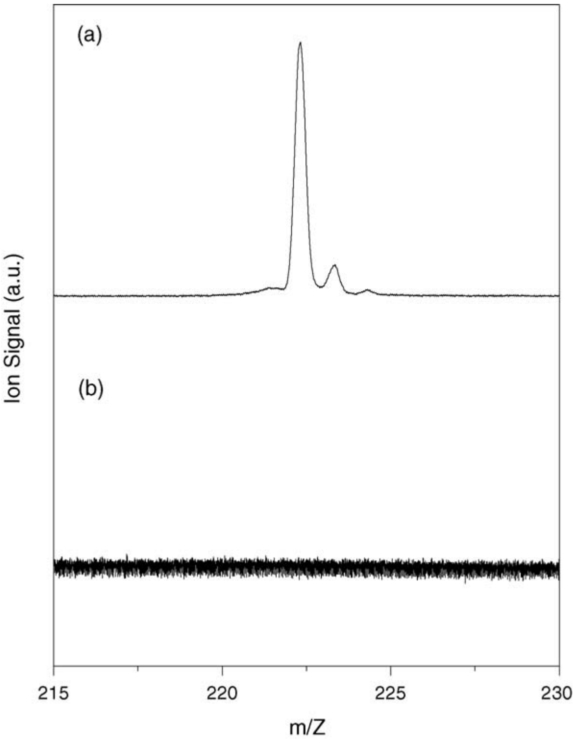

Fig. 4. Expanded view of the parent ion region in the TATP mass spectra between 215 and 230 amu. Note the lack of the parent species (TATP = 222 amu) using nanosecond laser ionization. (a) 795 nm, 130 fs, 840 μJ pulses and (b) 266 nm, 5 ns, 30 mJ pulses.

signal. It should be noted that the peak intensity at 59 amu is more than 20% of the acetone ion peak (58 amu) intensity, and thus cannot be ascribed to the 1.1% ^{13}C monoisotopically substituted acetone species.

4. Discussion

A comparison of the laser photoionization mass spectra of TATP taken in the femtosecond and nanosecond regime reveals similarities previously documented for a variety of explosive and explosive related compounds. While most of these studies have focused on aromatic species containing the nitro moiety (NO_2), they have found that the dissociative nature of the photoionization event results in a high degree of fragmentation when nanosecond approaches are employed, oftentimes yielding mass spectra without the presence of a parent ion signal. In addition, they find that the use of femtosecond laser pulses generally provides appreciable parent ion signal, with a rich fragmentation pattern that may be thought of as a fingerprint of the primary species [12,13]. The mass spectra shown in Figs. 2–4 reveal that similar photophysics is occurring in the TATP molecule.

Additionally, the UV absorption spectrum of TATP presented in Fig. 5 is qualitatively similar to H_2O_2 [14], indicating that in this wavelength region, the main absorbing species is the peroxide bond. For H_2O_2, excitation of this bond results in dissociation, while for TATP a similar dissociation or ring opening likely occurs. Therefore, the nanosecond laser ionization at 266 nm most probably proceeds through an intermediate state. This may account for the presence of the $C_3H_7O^+$ (59 amu) signal in the 266 nm nanosecond mass spectra, and its lack thereof at 355 nm. Without accurate knowledge of the ionization potential of TATP, we speculate that the observed nanosecond ionization is the result of a two or three-photon process at 266 nm, or a three-photon process at 355 nm, providing 9.3, 14, and 10.5 eV of energy, respectively. However, as is noted for the nitro containing explosives, dissociation and fragmentation of the parent molecule is occurring on a timescale shorter than the laser pulse inhibiting the detection of the parent ion.

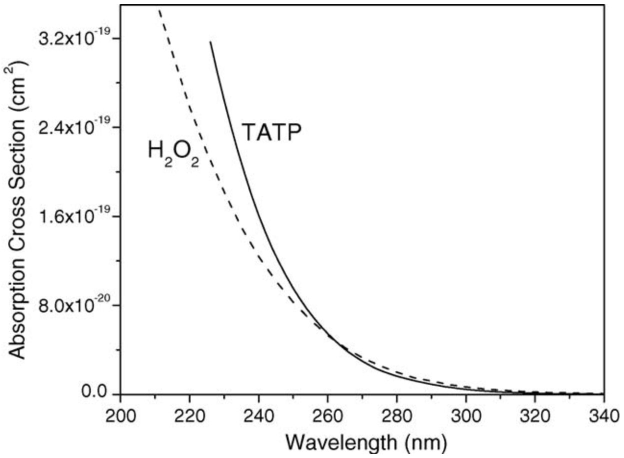

Fig. 5. Ultraviolet absorption spectrum of TATP and H_2O_2 between 210 and 340 nm. Solid line is TATP and dashed line is H_2O_2. H_2O_2 reproduced from Ref. [14].

For the femtosecond ionization, a number of mechanisms may be active and contribute to the observed TATP mass spectra. The lack of a strong wavelength dependence at 330, 490, and 795 nm suggests that energy resonance with an intermediate state is not the determining factor. At 795 nm, six or seven photons, 9.4 and 10.9 eV, respectively, could provide the energy necessary for non-resonant multiphoton ionization. However, ionization based solely on a multiphoton event may not be the appropriate picture at the high power densities employed in these experiments. The adiabaticity parameter [15] ($\gamma = 0.29$ at 795 nm and 3×10^{14} W/cm^2), a measure of the ionization regime that may be expected for a molecule in the presence of a strong laser field, was calculated using the ionization potential of acetone (9.7 eV). It indicates that the ionization regime is probably dominated by field dissociation associated with the intense electric field produced by the laser pulse. It is therefore assumed that TATP, with a larger molecular framework than acetone and a similar ionization potential, falls in this regime.

GC/MS analysis of neat TATP and TATP from post-explosion debris has also been reported [6,16]. The GC/MS studies, employing 70 eV electron impact ionization, yield mass spectra qualitatively similar to those obtained in this study employing femtosecond laser photoionization. The major differences between the two include the generation of a higher percentage of parent ion signal to the fragment species for femtosecond laser photoionization. In addition, a larger amount of the acetone ion $C_3H_6O^+$ (58 amu) is found compared to the $C_3H_7O^+$ (59 amu) when femtosecond ionization is used. The former difference is most likely the result of the “softer” ionization provided by the femtosecond laser pulses, even though the power density employed in the experiments (3.5×10^{14} W/cm^2) is relatively high, while the latter is most likely reflective of the difference in the electron impact versus femtosecond ionization process and fragmentation of the acetone molecule.

5. Conclusions

Laser ionization time-of-flight mass spectrometry is shown to be a plausible approach for the detection and identification of improvised explosive devices based on peroxides, such as TATP. Investigation of mass spectra in different pulse length regimes reveals the presence of the parent molecular ion in cases where an ultrashort laser pulse was used. Femtosecond laser ionization of TATP also provides a higher percentage of parent molecular ion signal and different fragment ratios when compared to EI-MS studies.

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