

Ultrafast photodissociation dynamics of HMX and RDX from their excited electronic states via femtosecond laser pump–probe techniques

M. Greenfield, Y.Q. Guo, E.R. Bernstein *

Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872, USA

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Abstract

Femtosecond laser pump–probe techniques are employed to investigate the mechanisms and dynamics of the photodissociation of HMX and RDX from their excited electronic states at three wavelengths (230 nm, 228 nm, and 226 nm). The only observed product is the NO molecule. Parent HMX and RDX ions are not observed. The NO molecule has a resonant $A^2\Sigma \leftarrow X^2\Pi$ (0,0) transition at 226 nm and off-resonance two-photon absorption at 228 nm and 230 nm. Pump–probe transients of the NO product at both off-resonance and resonance absorption wavelengths indicate the decomposition dynamics of HMX and RDX falls into the timescale of our laser pulse duration (180 fs).

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1. Introduction

Energetic materials such as HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) and RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) have broad applications as explosives and fuels. In order to understand how the chemical energy in these materials converts into mechanical energy and improve the efficiency of using them in explosion and combustion applications, much effort has been expended on the elucidation of the decomposition mechanisms and dynamics of HMX and RDX both experimentally and theoretically in the past decades [1–8]. The following initial steps in the decomposition mechanism for the ground electronic states have been proposed: N–N bond fission to generate the NO₂ molecule [9]; formation of a five-membered ring to generate an HONO intermediate which then decomposes to NO and OH [10,11]; and concerted symmetric ring fission to form three CH₂NNO₂ [12]. Although the decomposition of energetic materials from their excited electronic states plays a very important role in the detonation of these materials [13–16], only a few studies of these

excited state processes have been pursued. We have done several useful and informative experiments to investigate the initial steps in the photodissociation of both HMX and RDX from their first excited electronic states using ns laser pulses [17,18]. Results, for both energetic materials, show that the NO molecule is one of the initial decomposition products, while NO₂ and HONO have been ruled out as potential intermediates of the initial NO product. Two possible mechanisms for the NO product are N–N bond fission of the unstable nitrosamine intermediate [(CH₂NNO₂)₃CH₂NNO or (CH₂NNO₂)₂CH₂NNO] which occurs after an O atom loss from the HMX or RDX molecule, and isomerization of the RNNO₂ intermediate to RNONO with subsequent NO release.

Detonation of energetic materials is an ultrafast process, therefore, not only the mechanisms, but also the dynamics of the decomposition of these materials are important. As mentioned above, mechanistic studies have been widely performed, but currently the dynamics of the decomposition of both HMX and RDX have not been directly measured due, in part, to the limitation of the time resolution of the experimental techniques. A few hundred femtoseconds is a proposed time regime for the initial decomposition step of these energetic materials [19]. With the rapid

* Corresponding author. Fax.: +1 970 491 1801.

E-mail address: erb@lamar.colostate.edu (E.R. Bernstein).

development of femtosecond laser technology, one can measure the ultrafast dynamics of interesting systems using pump–probe techniques [20]. In this work, femtosecond pump–probe techniques are employed to investigate the decomposition dynamics of HMX and RDX. Single UV femtosecond laser beam detection shows the NO molecule is the only observed product from the excited electronic state decomposition of either HMX or RDX. Parent ions are not observed. Femtosecond laser pump–probe experiments at three wavelengths (226 nm, 228 nm, and 230 nm) are carried out to monitor the time evolution of the NO product appearance in an effort to determine the dynamics of the decomposition of both HMX and RDX. The NO molecule has a resonant $A^2\Sigma \leftarrow X^2\Pi(0,0)$ transition at 226 nm and off-resonance two-photon absorption at 228 nm and 230 nm. The pump–probe transients for the NO product at both resonance and off-resonance absorption wavelengths show that the dynamics of the decomposition of HMX and RDX falls into the time scale of our laser pulse duration (180 fs).

2. Experimental procedures

The experimental set-up consists of a femtosecond laser pump–probe system, a laser desorption supersonic jet expansion nozzle, and a time of flight mass spectrometer (TOFMS). The intact, gas phase, and isolated HMX or RDX molecules are produced through the combination of matrix assisted laser desorption (MALD) and supersonic jet expansion. The MALD method has been proven to be a good technique for placing non-volatile, thermally unstable samples into the gas phase in a vacuum chamber [21,22]. The laser desorption supersonic jet expansion nozzle and the TOFMS have been described in detail in our previous publications [17,18]. The femtosecond laser system consists of a self-mode-locked Ti:sapphire oscillator (KM Labs) that is pumped by a 4.75 W diode laser (Coherent, Verdi) at 532 nm and generates femtosecond laser pulses with center wavelength of 805 nm, output power of 430 mW and repetition rate of 91 MHz. A home-made ring cavity Ti:sapphire amplifier, which is pumped by the second harmonic of a 10 Hz Nd:YAG laser (Quanta Ray GCR), is employed for pulse amplification. The amplified pulse has an energy of 1.5 mJ with a 10 Hz repetition rate and a temporal width of <30 fs. A commercial traveling optical parametric amplifier of super fluorescence (TOPAS, Light Conversion) system is used for wavelength extension. The three wavelengths (226 nm, 228 nm, and 230 nm) used in this work are deep UV outputs from the TOPAS and are used as the fragmentation/ionization source for the time resolved TOFMS experiments. To avoid absorption saturation, the power density is maintained at $1.3 \times 10^{13} \text{ W cm}^{-2}$.

The pulse duration of the UV laser pulses has been measured to be ~ 180 fs using a self-diffraction (SD) autocorrelator [23] and the off-resonance two-photon absorption of the furan molecule. The two methods use the same pump–probe

optical system as the femtosecond laser pump–probe experiments in which both pump and probe beams have the same wavelength. The autocorrelation trace is obtained by recording the signal intensity versus the delay time between the two beams. A self-diffraction signal appears when two beams are overlapped both spatially and temporally on a thin quartz diffraction medium. The maximum signal position is determined to be the zero delay time for the pump–probe system. Fig. 1a is a typical SD autocorrelation trace (circles) with a Gaussian shape fitting (solid line) that shows a width (FWHM) of 254 fs, which yields a laser pulse duration of 180 fs. The off-resonance two-photon absorption of the furan molecule shows an absorption signal enhancement when the two beams are overlapped in the ionization region of the TOFMS. The enhanced absorption signal (Fig. 1b) displays similar laser pulse duration to that measured by SD autocorrelation. In the femtosecond UV/UV pump–probe experiments on HMX and RDX, the sample molecules are excited by the pump beam, and fall apart according to their photodissociation dynamics. Photodissociation products are further photoionized by the delayed probe beam and detected via the TOFMS. By delaying the probe beam with respect to the pump beam, product appearance time can be determined.

The experiment is run at a repetition rate of 10 Hz. The 10 Hz trigger source derives from the 91 MHz pulse train. The timing sequence for the pulsed nozzle and the ablation laser is controlled by a time delay generator (SRS DG535). Ion signals are detected by a microchannel plate detector (MCP). Signals are recorded and processed on a PC using an ADC card (Analog Devices RTI-800) and a box car averager (SRS SR 250). The delay time between the pump and probe beam is controlled by a micro translation stage (Thorlabs: LNR50SEK1) and a step size of 13 fs is used. Each point on the pump–probe transient corresponds to an average intensity resulting from 100 laser shots.

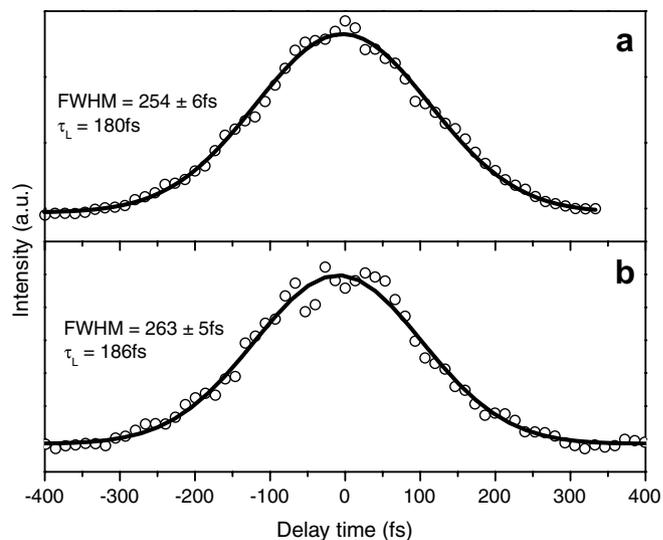


Fig. 1. Measurements of the femtosecond laser pulse duration at 226 nm using a self-diffraction autocorrelator (a) and off-resonance two photon absorption of the furan molecule (b).

3. Computational procedures

The theoretical ion state calculation of RDX molecule is based on the optimized ground state geometry of its AAA conformer, which is suggested as a possible structure for RDX in the vapor phase and has been calculated by Rice and Chabalowski [24]. Single point energy calculations and ion state geometry optimizations are performed via the GAUSSIAN 98 program [25] at the B3LYP density functional level [26,27] with a 6-31G* basis set [28–30].

4. Results and discussion

Fig. 2 shows mass spectra obtained from the photodissociation of HMX, RDX, and NO₂ gas. Spectra were taken using a single femtosecond laser beam at 226 nm. The NO molecule is the only observed product from the UV photodissociation of not only the HMX molecule but also the RDX molecule. Although the MALD technique is a good method to place easily fragmented, fragile molecules in the gas phase without fragmentation, great efforts are taken in our previous work to ensure that HMX or RDX are not fragmented in the ablation process [17,18]. Three different methods have been employed to explore this issue: comparison of NO velocity distributions from the nozzle; determination of arrival time for the NO signal intensity as a function of nozzle/pump laser timing; and NO rotational and vibrational temperature determinations as a function of source of NO. These methods demonstrate that NO from HMX and RDX is generated at the decomposition/ionization region rather than in the ablation nozzle.

Neither the HMX and RDX parent ion is observed even though femtosecond laser pulses are employed for ionization. This suggests that HMX and RDX do not have a stable ion state when excited by UV light. X-ray laser (25.6 eV) single photon ionization experiments have proven to be an excellent method to prevent fragmentation due to multi-photon absorption even for weakly bound van der

Waals clusters [31], and therefore this X-ray laser is also employed to photoionize HMX and RDX molecules. The parent ions of these molecules are not observed by either fs or X-ray laser ionization.

In order to further confirm our unstable ion state observation, non-local density functional calculations have been performed using a B3LYP method and the 6-31G* basis set. Single point energy calculation and geometry optimization of RDX ion state give vertical and adiabatic ionization energies of 10.28 and 9.89 eV, respectively; however, the optimized geometry of the RDX ion state shows that two NO₂ (i.e., NO + O) fragments are separated from the parent, illustrating that the RDX ion state is not stable at this level of theory. Therefore, our experimental observation is in good agreement with the calculational result.

For NO₂ gas fs ionization TOFM spectrum, both NO and NO₂ ions are observed indicating that two different processes occur simultaneously on the femtosecond time scale: one is NO₂ photodissociation into NO and O, and the other is direct NO₂ ionization. This is different from energy resolved (nanosecond) laser experiments, for which only the NO ion signal is observed [17]. Ledingham et al. have done a comparison of femto-, pico-, and nanosecond multi-photon ionization and dissociation of NO₂ at 248 nm and 496 nm [32]. At 248 nm, they observed the NO₂/NO ion ratio varied from 1% using nanosecond laser pulses to about 60% for 300 fs laser pulses. Both ours and Ledingham's observations for NO₂ gas show a strong competition between NO₂ ionization and NO₂ photodissociation into the NO molecule if femtosecond laser pulses are used. Since the NO₂ ion has not been observed from the photodissociation of HMX or RDX, we conclude that the NO₂ molecule is not the intermediate for the initial decomposition product, the NO molecule, of either HMX or RDX even in femtosecond temporal regime.

Femtosecond pump–probe experiments on the decomposition of HMX and RDX are carried out at three different wavelengths (230 nm, 228 nm, and 226 nm). For each wavelength, the laser beam is split into pump and probe beams. The gas phase HMX or RDX molecule is pumped to its first excited electronic state by the pump beam, it then dissociates into products according to corresponding mechanisms and dynamics. The probe beam is used to excite and ionize the initial products so that the dissociation dynamics can be monitored. Assuming the decomposition of HMX and RDX takes a much longer time than the laser pulse duration, we should be able to observe the buildup of the product signal as the delay time between the pump and probe beams is varied. The NO product is selected to monitor the dynamics of the decomposition process. The pump–probe transients for both molecules are obtained by recording the NO ion signal versus the delay time between the pump and probe beams and have been found to be equivalent. Fig. 3a,b show the pump–probe transients for the NO product of HMX at 228 nm and 230 nm, respectively. Circles correspond to experimental measurements, and the solid lines are the Gaussian-fitted results.

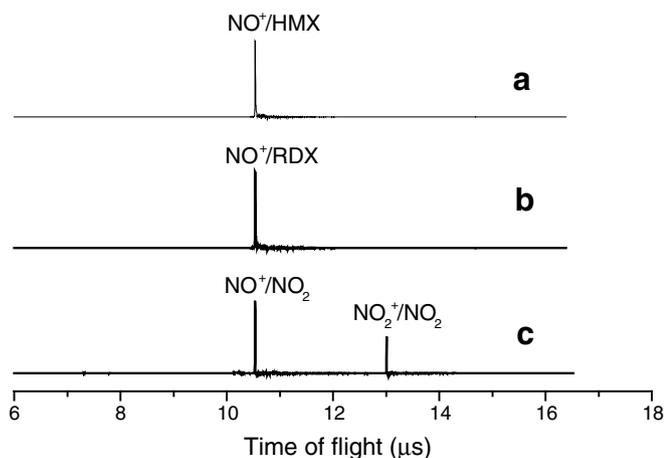


Fig. 2. Mass spectra of NO from the photodissociation of HMX (a), the photodissociation of RDX (b), and NO₂ gas (c) using femtosecond laser pulses at 226 nm.

Instead of a buildup of NO signal, an enhancement of signal intensity is observed around zero delay time. The transients display a symmetric Gaussian shape because both pump and probe beams are identical in these experiments. These two wavelengths (228 nm and 230 nm) are off-resonance for the NO molecular transition and ionization of the NO molecule requires two photons; therefore, off-resonance two-photon absorption enhancement occurs when the pump and probe beams are overlapped both temporally and spatially. The Gaussian full widths at half maximum for the transients at 228 nm and 230 nm are 240 fs and 250 fs, respectively. Both results are consistent, within the experimental uncertainty, with the autocorrelation recorded for the time duration of the UV femtosecond laser pulses. Thus, we conclude that the dynamics of the decomposition of HMX as well as RDX fall into the time scale of the present pulse duration of our UV femtosecond laser, and the off-resonant two-photon absorption of the NO product becomes equivalent to the measurement of the time duration of the laser pulses.

The pump–probe transients for NO gas (a) and the NO product of RDX (b) at 226 nm are shown in Fig. 4 and are illustrated as a fluctuating flat line. The NO $A^2\Sigma \leftarrow X^2\Pi$ (0,0) transition has a resonance single-photon absorption occurring at 226 nm; therefore, if the decomposition of either HMX or RDX occurs much faster than the laser pulse duration, measurements will show the life time of the first excited state of the NO molecule rather than the onset dynamics of the decomposition process. From the fluorescence life time measurement of the first excited state of the NO molecule, we know the life time of this state is in the hundreds of ns range, so the NO ion signal should remain almost constant within the scanned delay time range (± 1 ps). This is consistent with our observation, which indicates the dynamics of the decomposition of both HMX and RDX is faster than our laser pulse. In brief sum-

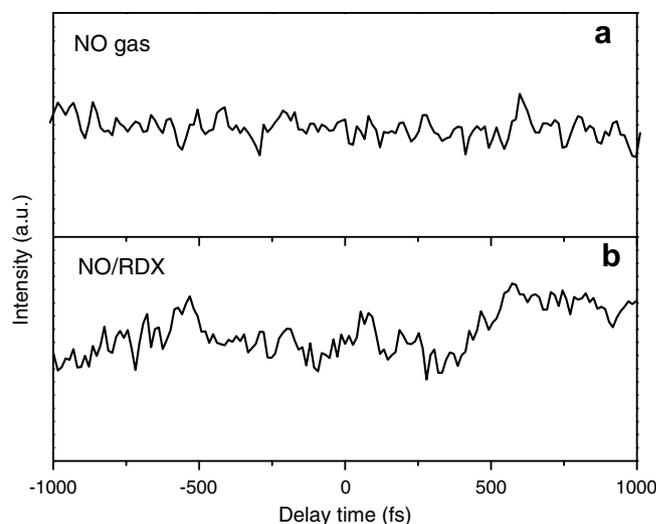


Fig. 4. Femtosecond pump–probe transients for the NO molecule from NO gas (a) and the photodissociation of RDX (b) at 226 nm. The NO $A^2\Sigma \leftarrow X^2\Pi$ (0,0) transition has a single-photon resonance absorption at 226 nm. Equivalent transients have been recorded for HMX.

mary, both on-resonance and off-resonance wavelengths measurements illustrate that the decomposition of HMX and RDX falls within the time scale of our femtosecond laser pulse duration (180 fs). Note that shorter fs laser pulses may not resolve this time scale because of uncertainty principle constraints and coherence/wavepacket dynamics for dissociative states.

5. Conclusions

The NO molecule is the only observed product from the UV femtosecond laser photodissociation of HMX and RDX using both off-resonant and resonant absorption wavelengths for the NO transition. NO_2 is ruled out as the intermediate for the NO product even in the femtosecond temporal regime. HMX and RDX parent ions are not observed. This suggests these molecules do not have stable ion states when excited by UV light. The pump–probe transients for the NO product at both off-resonant and resonant wavelengths indicate that the decomposition dynamics of either HMX or RDX falls within the time scale of our femtosecond laser pulse duration (180 fs).

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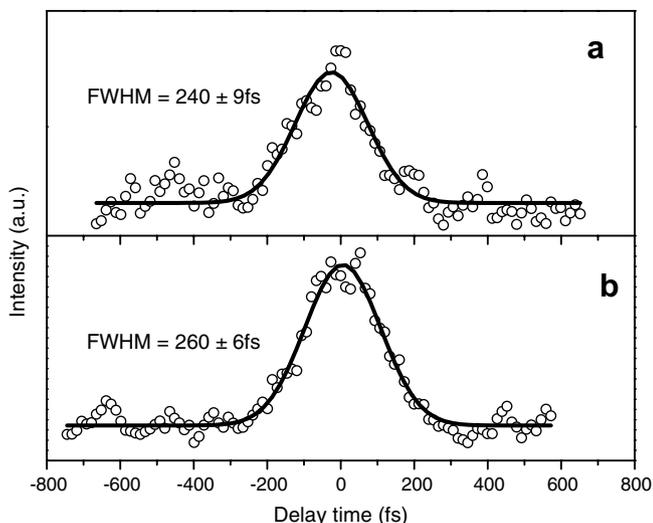


Fig. 3. Femtosecond pump–probe transients for the NO molecule from the photodissociation of HMX at 228 nm (a) and 230 nm (b). At both wavelengths, off-resonance two photon absorption occurs. Similar results have been observed for RDX.

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