

Study of the laser-induced decomposition of energetic materials at static high-pressure by time-resolved absorption spectroscopy

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Abstract. The reactivity of laser-initiated energetic materials has been studied at high-pressure using time-resolved absorption spectroscopy in a diamond anvil cell (DAC). The results obtained for nitromethane (NM) are presented in this paper. A change in reactivity is clearly seen around 25 GPa. Below this pressure, a one-step reaction is found to occur. The decomposition products formed behind the combustion front are essentially carbon residues as shown by Raman spectroscopy. At higher pressure, a two-step mechanism is observed. The first step, which is similar to the reaction observed below 25 GPa, leads to the formation of carbonaceous products. It is followed by a slower step which leads to the formation of a transparent amorphous product. This product remains stable in the DAC after reaction.

1. Introduction

A detailed description of the reaction rates and mechanisms occurring in shock-induced decomposition of condensed explosives is very important to improve the predictive capabilities of shock-to-detonation transition models. However, direct measurements of such experimental data are difficult to perform during detonation experiments. A new approach has been developed enabling the study of energetic materials (homogeneous and heterogeneous) in the time scale of real reaction chemistry, at high pressure and high temperature, without the difficulties associated to detonation experiments. It combines the advantage of the Diamond Anvil Cell (DAC) and the heating capacity of the laser. By coupling pulsed laser ignition of the sample in the DAC with time-resolved streak camera recording of transmitted light, it is possible to make direct observations of deflagration phenomena at detonation pressure [1-4]. Measurements of combustion front propagation rates (CFPR) can be performed as a function of pressure, giving data that can be introduced in shock to detonation transition models. The addition of time-resolved absorption spectroscopy can give direct information on the global reaction kinetics which can be studied as a function of initial pressure and temperature [3, 5-8].

This paper presents the results of time-resolved absorption spectroscopy measurements of the high-pressure laser-induced decomposition of NM, an explosive which has one of the simplest chemical structures. Experiments were performed up to 27 GPa and the results were compared to previous high-pressure experimental studies [1, 9].

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2. Experimental details

Experiments were performed using a membrane DAC. Liquid NM samples were loaded into a 200 μm hole drilled in a stainless steel gasket. A ruby sphere was added for pressure determination by fluorescence spectroscopy. All experiments were conducted at ambient temperature. In these conditions, NM crystallizes at 0.4 GPa, leading to the formation of a poly-crystalline sample. The crystal structure is orthorhombic, space group $P2_12_12_1$ [10].

The experimental set-up is shown in figure 1. A single pulse from a Nd:YAG laser (532 nm, 5 ns pulse duration, 10 μJ) was focused on the sample down to a 10 μm diameter in order to initiate a fast decomposition reaction. For CFPR measurements, the sample was fully illuminated with the output of a dye laser (603 nm, 40 μs pulse duration). Transmitted light from the sample was magnified and focused on the 100 μm slit of a streak camera. The image of the initiating laser was also centered on the camera slit and used to select the one-dimensional cross-section of the illuminated sample to be monitored during reaction. After this alignment procedure, an interference filter at 603 nm was placed in front of the streak camera to attenuate the intensity of the initiation laser.

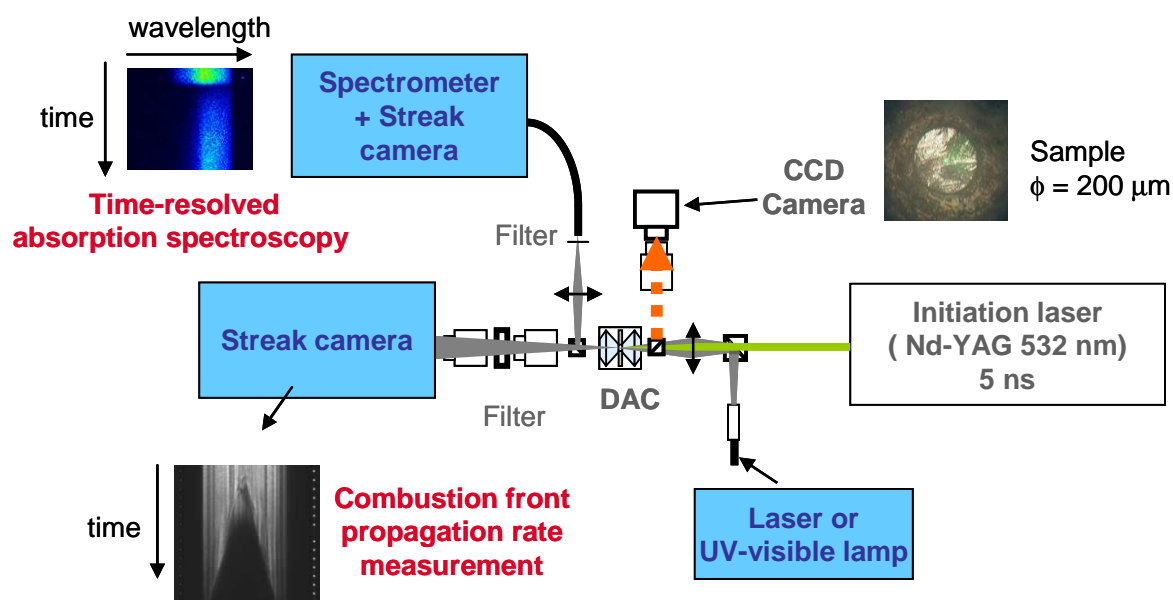


Figure 1. Experimental set-up for combustion front propagation rate measurements and UV-visible time-resolved absorption spectroscopy.

The absorption spectroscopy experiments were carried out using a pulsed UV-visible Xe arc lamp, delivering light between 300 and 650 nm with a 400 μs intensity plateau. The light transmitted through the sample was dispersed in wavelength by a spectrometer and streaked in time by a streak camera. The resulting images $I(\lambda, t)$ were recorded by a CCD detector. The light coming from the initiating laser was filtered using a low-pass filter, which reduced the wavelength range transmitted to 300 - 500 nm. For each experiment, an image was recorded before initiation in order to measure the intensity transmitted through the pressurized sample, $I_0(\lambda, t)$ which was taken as a reference. Then a transmitted image $I(\lambda, t)$ was recorded during reaction. The data were further manipulated to get the change in absorbance with respect to the reference intensity $\Delta A(\lambda, t) = \log_{10}(I_0(\lambda, t)/I(\lambda, t))$. From that image, two sets of data were extracted. The change in absorbance at a certain time t_i was obtained by averaging ΔA over 500 ns around t_i . This allowed the determination of the evolution of the differential absorbance as a function of time, which can give information on the formation of any transient species. Similarly, the change in absorbance at a certain wavelength λ_i was obtained by averaging

ΔA over 10 nm around λ_r . This gives information on the reaction profile, assuming that the change in absorbance is proportional to the quantity of reacted explosive. In all experiments, a small fraction of the light coming from the initiation laser was visible on the images and was assigned to zero time.

After each experiment, a final transmission image was recorded in order to get the long term absorption spectrum. Raman spectra were also recorded to characterize the final products remaining in the DAC after reaction.

3. Results and discussion

CFPR measurements of NM have already been performed by Rice and Foltz who observed a dramatic change in reactivity around 25 GPa [1]. Below this pressure, the reaction yielded to the formation of a black opaque residue whereas above this pressure, the reaction product was found to be transparent. In order to confirm the ability of our experimental set-up to give valuable data, we first performed similar CFPR measurements and found the same results as Rice and Foltz. To gain further insights on the change of reactivity of NM occurring around 25 GPa, we performed UV-visible absorption spectroscopy experiments at 10 GPa and 27 GPa, two pressures which are representative of the two reactivity regimes previously identified. Reaction rates were first measured and found to be 20 m/s at 10 GPa and 60 m/s at 27 GPa, which is in good agreement with previously reported data [1].

Figure 2 shows typical transmitted light images taken during reaction at 10 GPa (a) and 27 GPa (b). The color scale is arbitrary. On both images, the initiation laser can be seen at 532 nm and is used to determine zero time. At 10 GPa, after an initiation delay of 1 μ s, the transmission drops down to zero at all wavelengths in about 5 μ s, which is the time required for the reaction front to propagate at 20 m/s over the 100 μ m of the sample radius. As previously observed by Rice and Foltz, the reaction product formed behind the combustion front is an opaque residue. At 27 GPa, the evolution of the transmission as a function of time and wavelength shows a very different behaviour. After a short initiation delay (200 ns), a fast drop in intensity is first observed and is followed by a much slower increase in intensity. This indicates a two-steps reaction mechanism. The first step yields to the formation of an opaque product in 2 μ s, which corresponds to the front propagation rate measured at 27 GPa. This step is similar to the reaction observed at 10 GPa. The second step is much slower than the first step; it is completed in about 20 μ s. After reaction, the remaining product is more transparent than the NM initially present in the DAC.

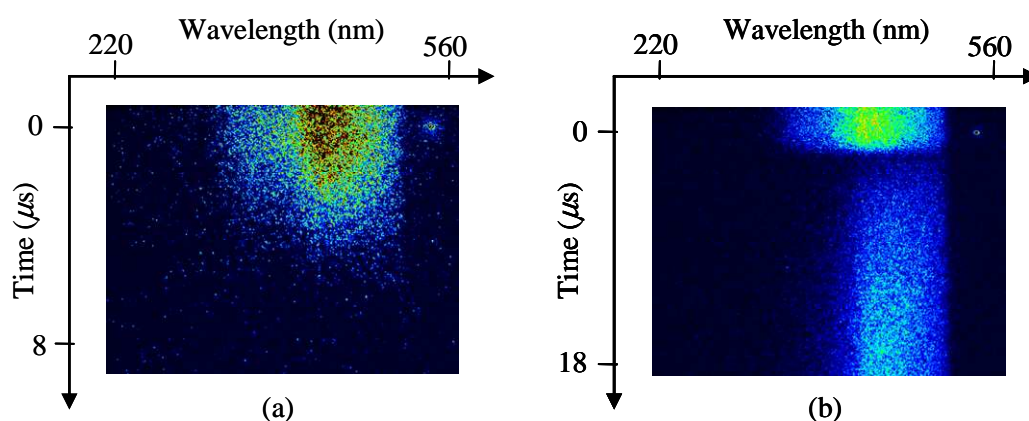


Figure 2. Transmission streak images recorded during reaction of nitromethane at 10 GPa (a) and 27 GPa (b). The color scale is arbitrary.

Figure 3 shows the Raman spectra NM at 10 GPa (a) and 27 GPa (b) together with that of the recovered compound taken after reaction at 10 GPa (c) and 27 GPa (d). On all spectra, the first and

second order Raman modes of diamond can be seen [11]. At ambient pressure, they are located at 1332 and around 2500 cm^{-1} respectively and shift to higher wavenumbers with pressure. At 10 GPa, the only band that can be attributed to the remaining product is located at 1580 cm^{-1} . This band is assigned to the E_{2g} mode of graphite [12]. At 27 GPa, no vibrational mode is observable on the Raman spectrum, except that of diamond. This indicates that the remaining compound is amorphous. This amorphous character explains the higher transmission observed for this product compared to that of NM. Indeed, the microcrystalline nature of the initial NM sample leads to a higher diffusivity which is responsible for the loss of transmission.

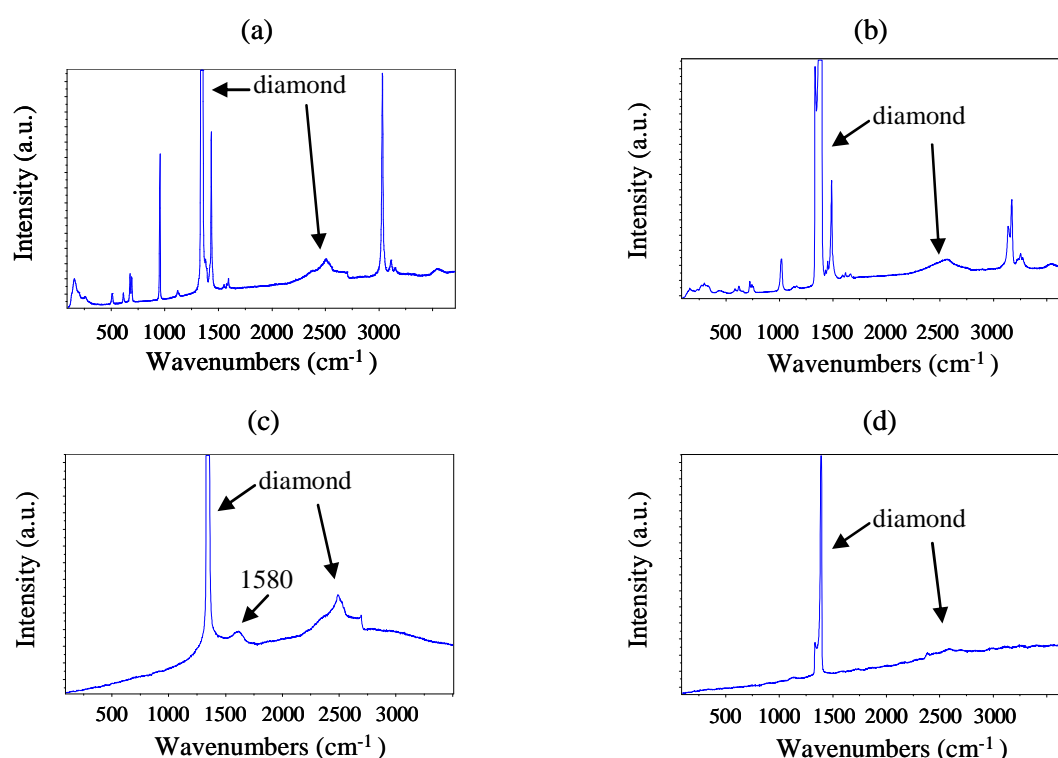


Figure 3. Raman spectra of nitromethane at 10 GPa (a) and 27 GPa(b) and of the remaining sample after reaction at 10 GPa (c) and 27 GPa (d).

Figure 4 shows the change in absorption as a function of time recorded during reaction of NM at 10 GPa (a) and 27 GPa (b). At 10 GPa, the spectra recorded at different times between 1 and 5 μs do not show any feature that could reveal the presence of a transient species. Only a broad band due to the progressive opacity of the sample is observed. At 27 GPa, the change in absorbance as a function of time shows the formation of a broad band in 2 μs , which is due to a carbonaceous product. At longer times, a transient absorption band is observed at 375 nm. This band remains at least for 15 μs and then disappears progressively. It is not present on the spectrum of the recovered sample after reaction. This spectrum shows a negative change in absorbance at all wavelengths, which is due to the fact that the product is amorphous and is thus less scattering than the poly-crystalline initial NM. It also shows a negative band below 350 nm which is due to the consumption of NM which absorbs in this wavelength range.

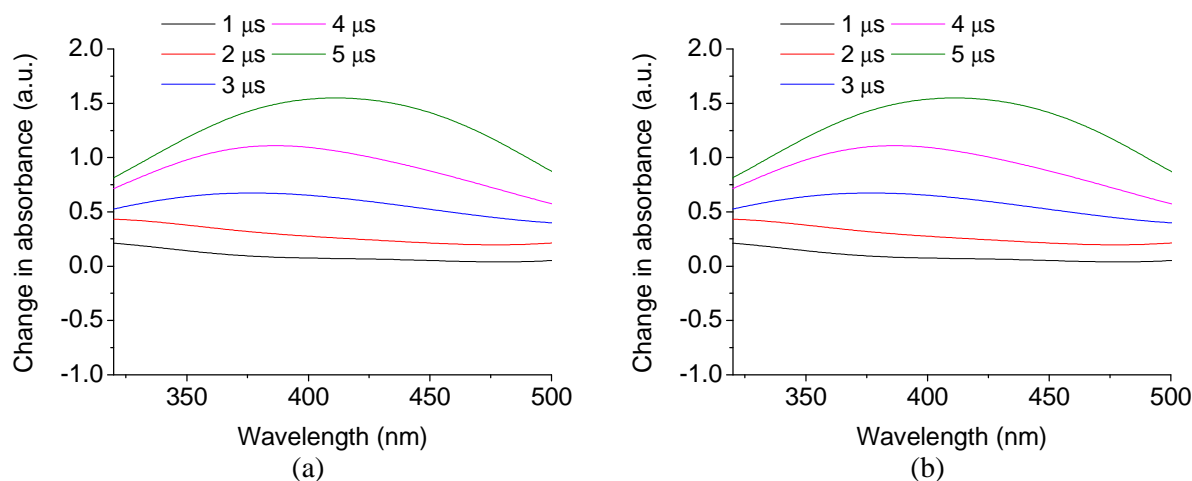


Figure 4. Change in absorbance as a function of time recorded during reaction of NM at 10 GPa (a) and 27 GPa (b).

Our absorption spectroscopy measurements performed at 10 GPa and 27 GPa show two different reactivity regimes which is in agreement with our CFPR measurements and with those of Rice and Foltz [1]. At 10 GPa, the reaction profile has a sigmoid shape which is characteristic of the decomposition of a solid energetic material. After an initiation delay of 1 μ s, during which the reaction interface is established, the reaction starts to propagate through the sample at constant speed and finally decelerates when most of the initial NM has been consumed. The final product is here a graphitic residue which is formed just behind the combustion front. At 27 GPa, two steps are observed in the reaction profile. The formation of a carbon residue is found to occur in a first step after a shorter initiation delay than at 10 GPa. The rate of this first step is equivalent to the front propagation rate. Then a much slower second step starts to compete with the first one and leads to the final transparent product. In their study of the high pressure and temperature phase diagram of NM, Courtecuisse *et al.* have already observed the irreversible transformation of NM into a transparent amorphous compound (named CI in their work) when NM was compressed above 34 GPa at room temperature [9]. They also found that this compound was formed at lower pressure when NM was heated. Upon further heating, CI was found to transform into an opaque compound CII with a faster reaction rate. CII is formed at 280 °C at 10 GPa and at 340 °C at 27 GPa. In our experiment, at 27 GPa, it is possible that the first step which takes place behind the combustion front where the highest temperatures are found yields to CII. Then CI could be formed later on in a second step, when the sample has cooled down. At 10 GPa, the reaction product that we observed is graphitic and is thus different from CI which did not give any Raman signal [9].

Our absorption spectra also reveal the presence of a transient absorption band located around 375 nm which precedes the formation of the final product. This band has not been assigned yet, but it could be due to the formation of one of the intermediate species described in the bimolecular reaction mechanism proposed by Bardo on the basis of theoretical calculations [13] and confirmed experimentally by Piermarini *et al.* [14]. The first two species proposed in their mechanism are nitrosomethane (H_3CNO) and nitromethanol (HOCH_2NO_2) which have quite similar electronic structure as nitromethane and are thus likely to have a close UV-visible absorption spectrum such as the one observed in our results.

4. Conclusion

CFPR and time-resolved absorption spectroscopy measurements of laser-initiated samples of NM have been performed at high pressure. Our results show that different reactivity regimes take place at 10

and 27 GPa. At 10 GPa, a one-step decomposition reaction is observed which leads to the formation of a carbon residue. At 27 GPa, a more complex mechanism is observed. A fast first step leads to the formation of a carbonaceous product and a slower second step leads to the formation of a transparent amorphous product. A transient absorption band which appears during the reaction development could be due to the formation of one of the species described in the bimolecular mechanism proposed previously. Time-resolved Raman spectroscopy experiments could help in determining unambiguously the nature of the transient species.

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Corrigendum

Study of the laser-induced decomposition of energetic materials at static high-pressure by time-resolved absorption spectroscopy - CORRIGENDUM

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Figure 4(b) has been updated because it was originally the same as figure 4(a).

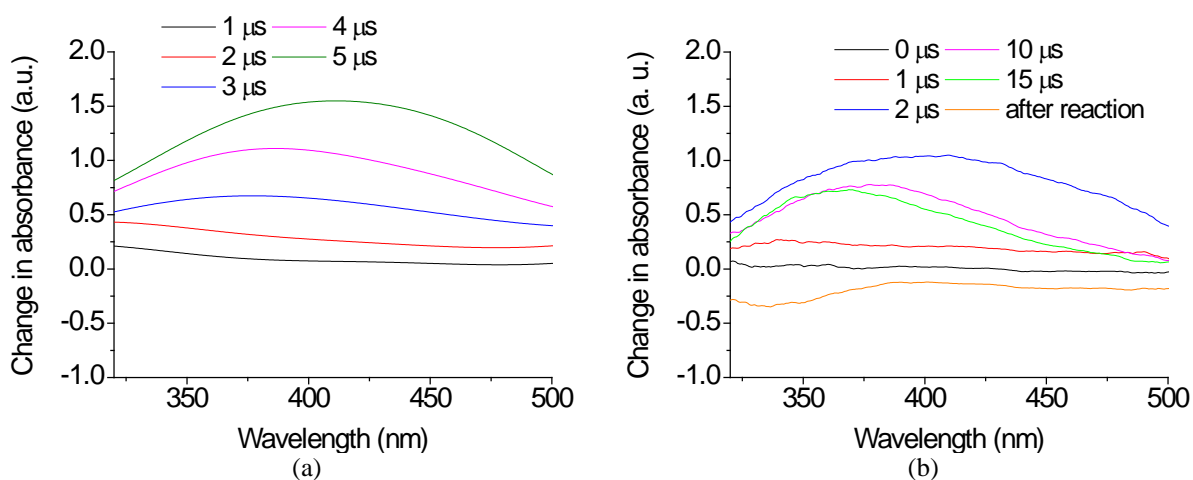


Figure 4. Change in absorbance as a function of time recorded during reaction of NM at 10 GPa (a) and 27 GPa (b).