



Plasticization of Submicron-Structured LOVA Propellants by a Linear Dinitramine

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Abstract: Raman spectroscopy is a powerful tool for the analysis of complex energetic materials. In this work, this technique has been used to observe the inter-molecular interactions occurring in nitrocellulose-based propellants containing 1,3,5-trinitro-1,3,5-triazinane (RDX) and plasticized with 2,4-dinitro-2,4-diazahexane (DNDA6). The plasticization mechanism of nitrocellulose by DNDA6 was observed. RDX was found to be markedly uninvolved in chemical interactions in these matrices, hinting at a potential loss of stability in compositions for LOVA (LOw Vulnerability Ammunitions).

Keywords: nitrocellulose, RDX, DNDA6, LOVA, Raman spectroscopy

1 Introduction

In the search for higher performance and better stability, propellant compositions have changed over the last two decades to include materials possessing both higher energies and lower mechanical sensitivities. A key aspect of this approach is the use of energetic plasticizers, especially those with valuable properties. In this regard, DNDA6 is particularly interesting as this compound shows an excellent plasticizing ability towards nitrocellulose, enough to ensure temperature-independent combustion of the mixture [1-3].

The structural characterization of these new propellants is a necessary step towards understanding the action of plasticizers. In particular, Raman

spectroscopy has provided insights for both the identification and the characterization of energetic materials [4-7]. Due to fewer overlaps in Raman spectra compared to the corresponding data obtained by infrared absorption, this technique is well suited for the analysis of complex energetic formulations.

By studying the Raman signature of a propellant and its pure base components, it is possible to observe changes that reveal the existence of interactions between the components. For example, the shift of a band towards a lower wavenumber, or its disappearance, hints at the attenuation of the associated vibrational mode. This reduction in energy is linked to the stabilization of the atoms involved in the interaction with another molecule.

In order to obtain insights into the chemical stabilization of modern LOVA propellants containing DNDA6, Raman spectroscopy was used to observe the intermolecular interactions taking place in samples prepared at NS3E. Particular attention was given to the study of the plasticization of nitrocellulose by this high-performance plasticizer and to the general interaction of the high explosive filler with the rest of the matrix.

2 Material and Methods

2.1 Components

Nitrocellulose with a nitrogen content of 12.62% was supplied by Nitrochemie AG. DNDA6 was synthesized at ISL with a purity of 99.6%. RDX (5 μm grade) was purchased from Eurenco. Ethyl acetate with a purity above 99.5% was obtained from Carl Roth GmbH.

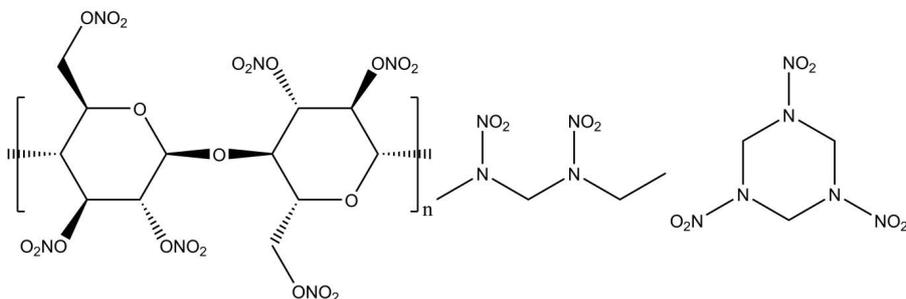


Figure 1. From left to right, structural formulas of nitrocellulose (with R = H or NO_2), DNDA6 and RDX.

2.2 Preparation of the solutions

Solutions of nitrocellulose, RDX and DNDA6 in ethyl acetate were prepared at a concentration of 1 g of energetic material per 100 g of solvent. According to the literature [8, 9], common LOVA propellants contain about ~10% nitrocellulose, ~15% plasticizers and ~75% RDX, so a similar formulation was used as starting point. To observe the influence of the various materials, other solutions were prepared by reducing the amount of RDX relative to the other compounds. The ideal nitrocellulose to plasticizer ratio has been found in former studies at ISL to be 1:2, and these relative proportions were kept constant throughout these experiments. Five formulations were prepared as shown in Table 1.

Table 1. Composition of various experimental propellant samples

Composition	Nitrocellulose [%]	Plasticizer [%]	RDX [%]
I	8	16	76
II	12	24	54
III	16	32	52
IV	20	40	40
V	24	48	28

To ensure the adequate homogeneity of these solutions, nitrocellulose was first dissolved for 24 h in ethyl acetate before the plasticizer and high explosive were added. After this latest step, each solution was magnetically stirred for 4 h making it ready for processing.

2.3 Preparation of the propellants

The solutions obtained were processed by Spray Flash Evaporation (SFE), a technique developed in the NS3E laboratory and well suited for the elaboration of nanosized and submicron-sized energetic materials [10-14]. This technique involves spraying a pressurized (40 bars) solution through a micrometric (60 μm) and heated (140 $^{\circ}\text{C}$) nozzle into a chamber under primary vacuum. The sudden drop in pressure and temperature causes the extremely fast evaporation of the solvent and the formation of nanosized and submicron-sized particles. An important advantage of this process, in the scope of this work, is its compatibility with a large range of solvents and compounds and its ability to process multiple species at once to produce composite materials.

2.4 Raman spectroscopy

A small mass of each sample was pressed into cylindrical pellets using a pressure of 16 MPa. These pellets were then leveled with a Leica RM2145 microtome by

scraping 100 μm off the surface, in steps of 10 μm to 1 μm . The resulting samples were characterized with a Renishaw InVia Raman spectroscope, using a laser with a wavelength of 514 nm and a power of 12 mW. Acquisitions were performed with 20 scans, an exposure time of 10 s per scan and a resolution of 1 cm^{-1} . Since the spectra of the reference materials, shown in Figure 2, exhibit bands in the 200-1700 cm^{-1} and 2700-3200 cm^{-1} regions, all Raman analyses were performed across a range spanning from 200 cm^{-1} to 3200 cm^{-1} . The bands observed were attributed to vibration modes according to information found in the literature [6, 7, 15, 16]. To designate vibrational modes, the following abbreviations are used: ν for stretching vibrations and δ for scissoring deformations.

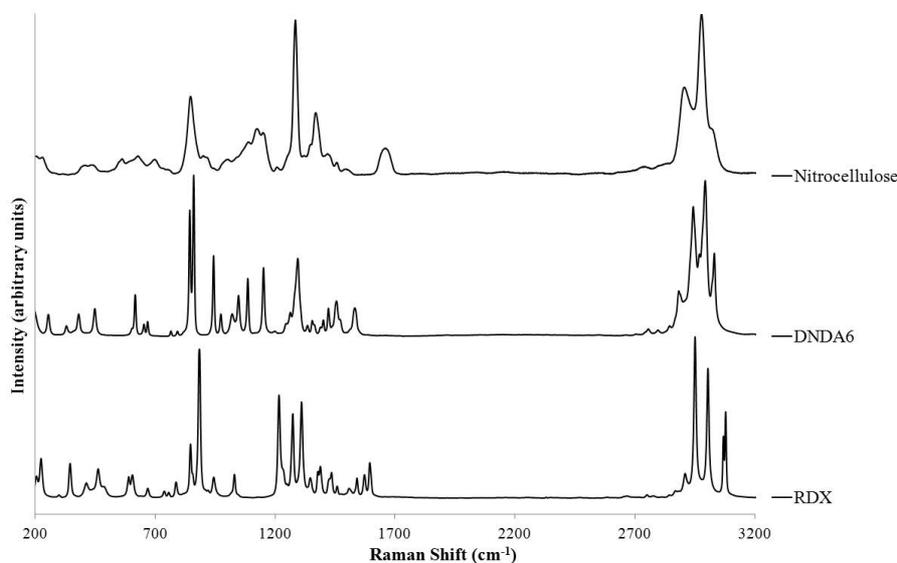


Figure 2. Raman spectra of the reference materials.

Theoretical spectra corresponding to the five compositions shown in Table 1 were calculated by adding together the reference signals, weighted by the relative concentration of each material. As these spectra do not take into account any alteration of the signal that may happen in the complete mixture, comparison with the experimental results was used to highlight these interactions. These spectra are shown in Figures 3, 4 and 5.

3 Results and Discussion

3.1 Plasticization of nitrocellulose by DNDA6

Due to the comparatively low concentration of nitrocellulose in the propellants, the characteristic bands of the binder are often masked by stronger bands of DNDA6 or RDX. While this hinders the study of the plasticization mechanism, some noteworthy observations can be made.

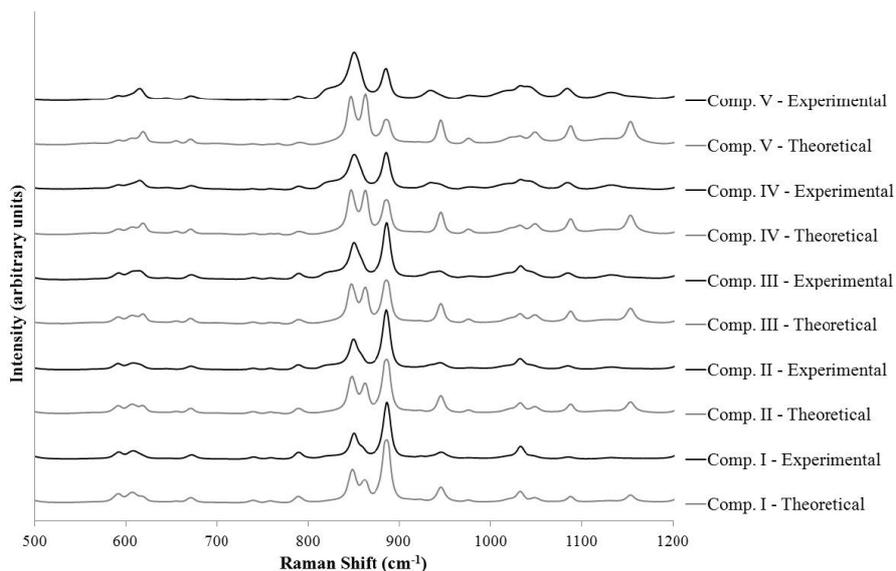


Figure 3. Theoretical and experimental Raman spectra of the samples; 500-1200 cm^{-1} range.

Evidence of the action of the plasticizer can be found in the spectra of the propellants by observing the band related to the $\nu(\text{C}-\text{O}-\text{C})$ vibrational mode at 820 cm^{-1} . This band isn't present in the spectrum of raw nitrocellulose. This is compounded by the strong shift of the band corresponding to the $\nu(\text{C}-\text{O})_{\text{Pyranose}}$ vibration at 1130 cm^{-1} by 5 cm^{-1} towards higher energies. Both results prove that the pyranose rings of the cellulosic chain gained a greater vibrational energy during the mixing process, which translates into a reduced steric hindrance. This shows that the nitrocellulose chains interact less strongly with each other in the propellants than they do in pure nitrocellulose, clear evidence of the plasticizing action of DNDA6. This also proves that the plasticizing mechanism does not involve the rings themselves but rather the outer functional groups.

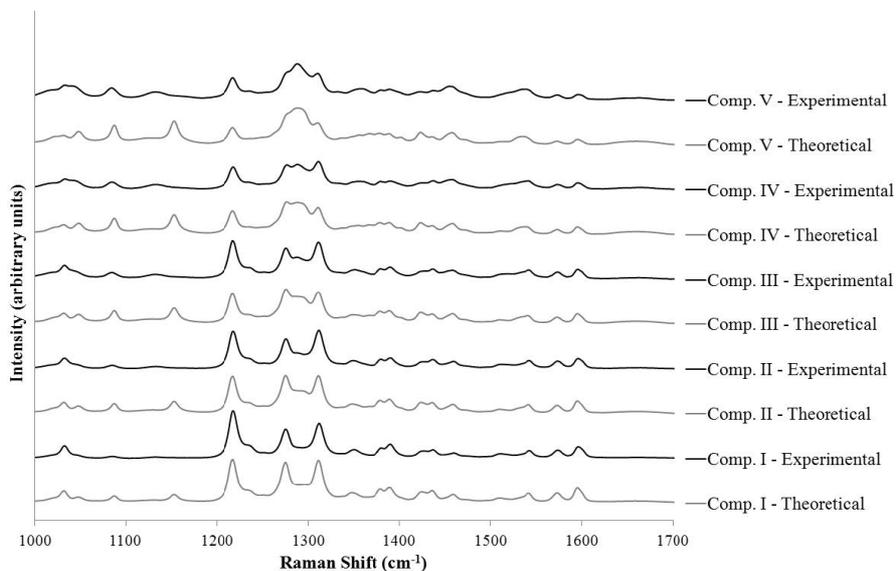


Figure 4. Theoretical and experimental Raman spectra of the samples; 1000-1700 cm^{-1} range.

Indeed, the $\delta(\text{C-OH})$ vibration found at 1427 cm^{-1} can be seen to be attenuated in the processed samples. From these results, it can be inferred that the plasticizer interacts primarily with the remaining hydroxyl groups of nitrocellulose.

Regarding the Raman spectra of pure DNDA6, it is interesting to note the appearance of the $\nu(\text{C-N-C})$ vibration mode in the form of two bands at 845 cm^{-1} and 863 cm^{-1} . This twin band is created by the asymmetry of the molecule, which gives different energy levels to the two C-N-C chains. These bands can be seen to have merged in the propellants' spectra. This is the result of an inter-molecular interaction involving a functional group participating in the two C-N-C chains equally, which would be the central methylene of DNDA6. While methylene groups are usually weak hydrogen bond donors, Gill and Naufflett [17] surmised that the central methylene of DNDA6 is activated by the presence of the two electro-attracting nitramine groups surrounding it. Indeed, the disappearance from the samples' spectra of numerous bands related to the methylenes of DNDA6 demonstrates that methylene groups take part in intermolecular interactions. These bands are related to the $\delta(\text{CH}_2)$ vibration (at 1427 cm^{-1} and 1472 cm^{-1}) and the $\nu(\text{C-H})$ vibration (at 2970 cm^{-1} , 2998 cm^{-1} and 3029 cm^{-1}).

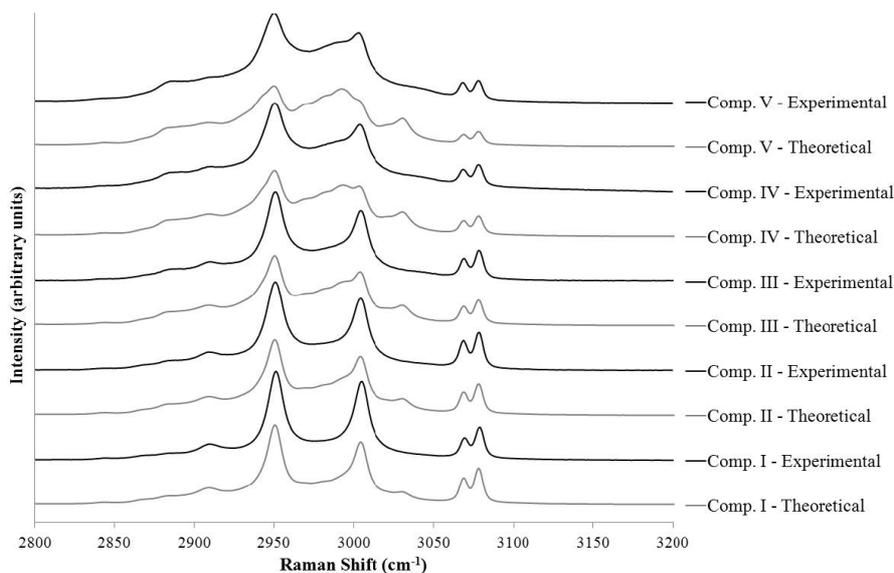


Figure 5. Theoretical and experimental Raman spectra of the samples; 2800-3200 cm^{-1} range.

In a similar fashion, the $\nu(\text{N}-\text{C}-\text{N})$ vibrational mode of DNDA6 show signs of a lowered vibrational energy. The bands associated with this vibration (situated at 1048 cm^{-1} and 1086 cm^{-1}) are shifted 5 cm^{-1} towards lower wavenumbers in the spectra of the propellants, while the band at 1150 cm^{-1} disappears entirely. Additionally, these spectra show that the band at 975 cm^{-1} is attenuated and the band at 944 cm^{-1} is strongly shifted by 10 cm^{-1} towards lower energies. Both of these changes may be attributed to the combined vibrational mode $\delta(\text{CH}_2) + \nu(\text{N}-\text{NO}_2)$ of DNDA6. From these results, it can be asserted that the plasticization of nitrocellulose by DNDA6 is due to the formation of hydrogen bonds between the two molecules. The central methylene of the plasticizer is the donor in this interaction, while residual hydroxyl groups of the nitrocellulose act as receptors.

Concerning the action of nitro groups in these interactions, two observations can be made. The first is that, for both materials, the bands corresponding to the $\nu(\text{NO}_2)$ are largely unaffected by the SFE process. This is particularly relevant for the weak but easily identified band of nitrocellulose at 1660 cm^{-1} . The second observation is that two bands related to the rocking deformation of the nitro groups of DNDA6 are heavily modified by the preparation of the propellant: the first band, at 618 cm^{-1} , is shifted 4 cm^{-1} towards lower energies while the second band, at 654 cm^{-1} , disappears from the spectra. Seeing as this

concerns only the rocking deformation of this group and not the stretch vibration, as previously said, nor the wagging deformation observable at 1335 cm^{-1} , it is unlikely to be the result of hydrogen bonding. It may therefore be concluded that an interaction not easily observable by Raman spectroscopy is specifically hindering this rocking deformation.

3.2 Interactions between RDX and the matrix

It must be noted that, despite the high visibility of RDX-related bands in the studied spectra, very few significant spectral changes concerning this material have been detected in any of the compositions studied. The only vibrational mode to be modified by processing is the in-plane bending of the RDX ring. All five associated bands (at 415 , 465 , 589 , 606 and 669 cm^{-1}) show a slight shift of 2 cm^{-1} toward higher energies. This signifies that RDX is slightly less sterically hindered in the propellant than in the reference material, which may simply be a consequence of the crystallite size reduction inherent to the SFE process. As a result of these extremely limited changes, it has to be assumed that RDX has few, if any, interactions with the other components of the samples. This is likely to be the result of crystallization of the RDX outside the plasticized nitrocellulose matrix, greatly limiting the contact surface and the visibility of any interaction taking place at grain boundaries. The presence of crystals in an otherwise amorphous propellant means the introduction of crystalline defects and grain boundaries, both conducive to the formation of hot spots. We therefore conclude that this lack of interaction between RDX and the matrix is a significant threat to the stability and reliability of the propellant, especially for applications at low temperatures.

4 Conclusion

The Raman signatures of five different propellant compositions were studied and compared to references, underlining the various interactions that occur between the components of these samples. It was shown that the plasticization mechanism involves the formation of hydrogen bonds between the activated central methylene of DNDA6 and the hydroxyl groups of nitrocellulose. It was also demonstrated that no significant interaction takes place between RDX and the other materials. This shows that there is room to further increase the stability of energetic materials by improving the plasticization of high explosive fillers.

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