

## Laser-Induced Decomposition of 2,2',4,4',6,6'-Hexanitrostillbene at 263, 527 and 1053 nm

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Investigation on laser-induced decomposition will provide important information for a better understanding of detonation mechanism of energetic materials. The effects of laser irradiation on 2,2',4,4',6,6'-hexanitrostillbene at different laser wavelengths has been studied by XPS and FT-IR. Results showed photodecomposition mechanism of 2,2',4,4',6,6'-hexanitrostillbene is wavelength-dependent. In case of 263 and 527 nm irradiated, the nitro-nitrite isomerization and the fragmentation of *trans*-C=C bond are the main decomposition steps, while in the case of 1053 nm, only the fragmentation of *trans*-C=C bond was observed.

**Key Words:** 2,2',4,4',6,6'-Hexanitrostillbene, Laser-induced decomposition, Wavelength-dependent.

### INTRODUCTION

2,2',4,4',6,6'-Hexanitrostillbene (Fig. 1) is a typical heat-resistant and insensitive explosive with the attractive characteristics of excellent thermal stability, impact and shock insensitivity along with good performance<sup>1</sup>. Laser initiation of high explosive is a complex process and the detonation mechanism that takes place during decomposition is not easily identified in chemical physics. How the energy from the laser is transferred into localized bonds is yet not well understood. Precisely to say which bonds absorb this energy and cause molecular decomposition is also of great interest<sup>2</sup>.

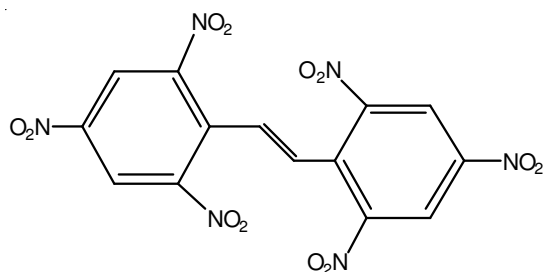


Fig. 1. Molecular structure of 2,2',4,4',6,6'-hexanitrostillbene

Several researchers have studied the laser-induced decomposition of some energetic materials, including (dimethyl nitramine) (DMNA)<sup>3-5</sup>, (1,3,5-triamino-2,4,6-trinitrobenzene) (TATB)<sup>6-10</sup>, (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane) (HMX), (1,3,5-trinitro-1,3,5-triazacyclohexane) (RDX)<sup>10-14</sup>,

(2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) (CL-20)<sup>14-17</sup>, *etc.*, but inconsistencies still existed for the photodissociation mechanism of energetic materials. C-NO<sub>2</sub> broken, O atom elimination, H atom transfer, OH formation and nitro-nitrite isomerization reaction *etc.* have been proposed as the primary process for the laser-induced decomposition under admittedly different experimental conditions, such as different phases, different temperatures and different photodissociation wavelengths.

The chemical physics response mechanisms of a photo-induced event will depend on the material, the wavelength, the energy and the duration of the light pulse *etc.* However, to our best of knowledge there have been few reports on the study of direct laser-induced photolysis of 2,2',4,4',6,6'-hexanitrostillbene. In order to understand the effects of laser irradiation on 2,2',4,4',6,6'-hexanitrostillbene, especially at the irradiation of different laser wavelengths, the chemical state changes and the element composition of the 2,2',4,4',6,6'-hexanitrostillbene surface before and after laser irradiation were studied by X-ray photoelectron spectroscopy (XPS). The chemical structure changes of explosives before and after laser irradiation was further determined by FT-IR spectroscopy.

### EXPERIMENTAL

A schematic diagram of the experimental apparatus used for this study was depicted in Fig. 2. 2,2',4,4',6,6'-Hexanitrostillbene powder (with a purity > 99.5 %) synthesized at institute of Chemical Materials was ground to a uniform grain size of

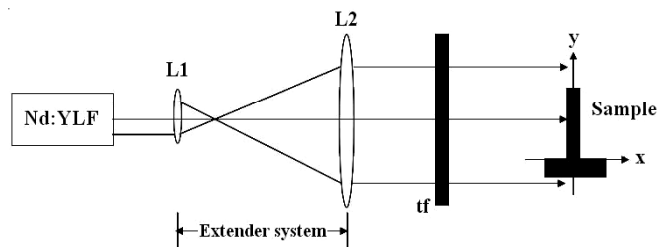


Fig. 2. Schematic diagram of the experimental apparatus used in this work. L<sub>1</sub>, L<sub>2</sub>-fused silica lens; tf-neutral filter

20 mm. For the experiment, 2,2',4,4',6,6'-hexanitrostillbene powder was sandwiched between two quartz plates. The decomposition was achieved by focusing 263, 527 and 1053 nm light output of a Nd:YLF laser normal to the surface of the samples at a repetition rate of 10 Hz. A commercial traveling optical parametric amplifier of super fluorescence (TOPAS, Light Conversion) system is used for wavelength extension. The pulse duration for this laser is 8 ps at the full width of half maximum (FWHM). The laser powder density was maintained at 1012 W/m<sup>2</sup>. Care was taken to ensure that the decomposition laser influence was low enough that ions were not produced directly at the surface.

The chemical state of 2,2',4,4',6,6'-hexanitrostillbene were obtained by a VG250 X-ray photoelectron spectroscopy (VG Scientific, UK) employing AlK<sub>α</sub> for excitation. The instrument was operated in constant analysis energy (CAE) mode with the pressure below  $2 \times 10^{-9}$  mbar. The FT-IR spectra of 2,2',4,4',6,6'-hexanitrostillbene samples were recorded on a Nicolet 6700 FT-IR spectrometer.

## RESULTS AND DISCUSSION

**XPS Characterization:** Elemental analysis of the 2,2',4,4',6,6'-hexanitrostillbene surface before and after laser irradiation by XPS shows only carbon, nitrogen and oxygen to be present; XPS does not detect hydrogen. Fig. 3a shows the XPS N 1s narrow scan spectra of 2,2',4,4',6,6'-hexanitrostillbene before and after laser irradiation at 263, 527 and 1053 nm. In 2,2',4,4',6,6'-hexanitrostillbene there is no nitrogen in the ring and only one nitrogen peak arising from -NO<sub>2</sub> group is observed in the XPS spectra at *ca.* 405 eV. After laser irradiated at 263 and 527 nm, a new peak occurs on the low binding energy of the 401 eV, which is attributed to the chemical state of N 1s of the nitrite ester derivative (-ONO) of 2,2',4,4',6,6'-hexanitrostillbene in the laser-induced decomposition process. In the case of 1053 nm irradiated samples, the N 1s spectra show no change. A similar result is observed on the O 1s narrow scan peak, as shown in Fig. 3b. The *ca.* 532 eV O 1s peak is assigned to the chemical environments of -NO<sub>2</sub>. The O 1s spectra of 2,2',4,4',6,6'-hexanitrostillbene after laser irradiated at 263 and 527 nm shows a new peak at the low binding energy of *ca.* 528 eV, which may be attributed to the chemical environments of -ONO in 2,2',4,4',6,6'-hexanitrostillbene. In case of 1053 nm irradiated samples, the O 1s spectra also show no change which is correspondence with the result of the N 1s spectra. The results indicated that the chemical structure of 2,2',4,4',6,6'-hexanitrostillbene may be dramatically influenced by the laser irradiation.

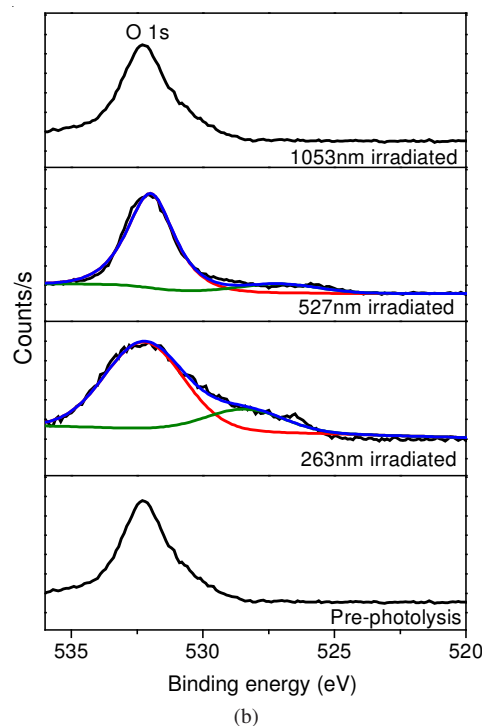
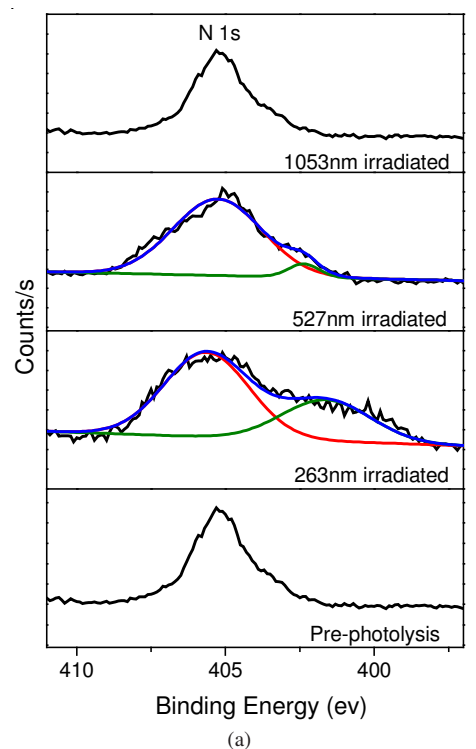


Fig. 3. XPS N 1s (a) and O 1s (b) narrow scan spectra of 2,2',4,4',6,6'-hexanitrostillbene before and after laser irradiation

**FT-IR spectra:** Photoexcitation of 2,2',4,4',6,6'-hexanitrostillbene results in the formation of a small hole where the laser impinged on the sample; visual inspection shows a dusting of residual black material on the windows. The post-photolysis spectrum indicates that there is a population of residual 2,2',4,4',6,6'-hexanitrostillbene, which is attributed to the material at the edge of the photolysis hole. Comparison of the FT-IR spectra of 2,2',4,4',6,6'-hexanitrostillbene before and after laser irradiation at 263 and 527 nm (Fig. 4), three new

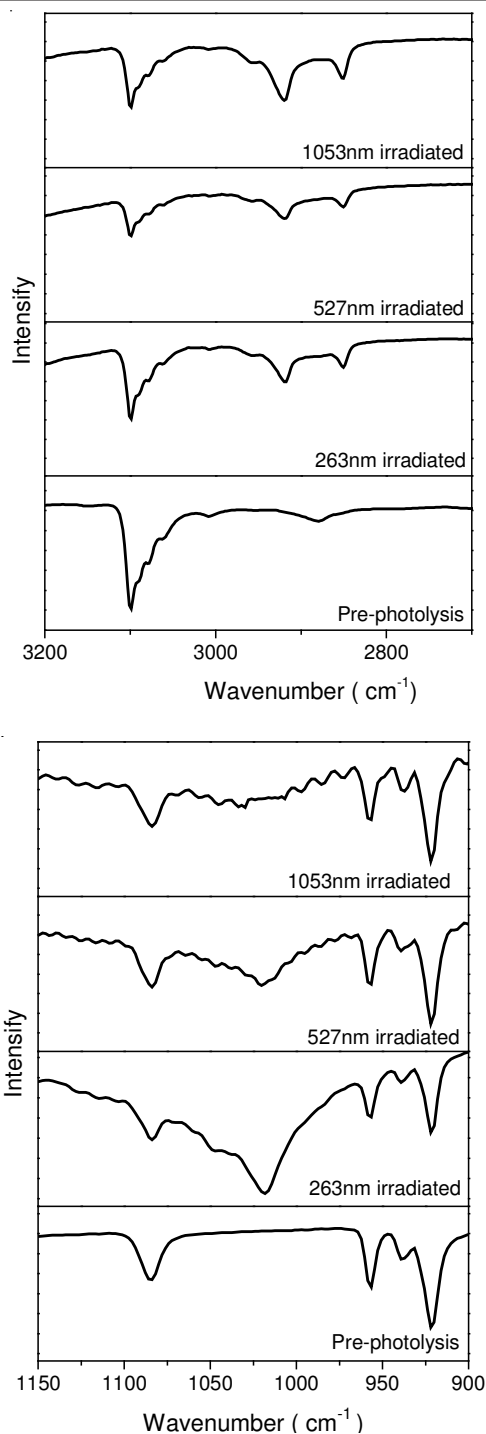


Fig. 4. FT-IR spectra of 2,2',4,4',6,6'-hexanitrostillbene before and after laser irradiation

peaks in the post-photolysis spectrum at *ca.* 2919, 2850 and 1020  $\text{cm}^{-1}$  can be observed directly. The 2919 and 2850  $\text{cm}^{-1}$  peak is assigned to the C-H stretching vibration of  $-\text{CH}_3$  or  $-\text{CH}_2$  group. The 1020  $\text{cm}^{-1}$  peak is assigned to C-O stretching vibration. In the case of 1053 nm, only 2919 and 2850  $\text{cm}^{-1}$  peak can be observed. Other products are difficult to characterize due to the spectral congestion or IR inactive vibrations.

Before discussing the decomposition channels, the mechanism of production of 2,2',4,4',6,6'-hexanitrostillbene molecules in the present experiments should be considered. In general, photoexcitation of a molecule will populate an excited state

that can typically proceed down two different pathways: (1) absorbed light energy is converted to internal and translational energy, the excited molecules rapidly undergo internal conversion to the ground state with a high degree of vibrational energy from which decomposition occurs; (2) internal conversion or intersystem crossing to another excited state from which the molecule may return to the ground state or couple to a dissociative state resulting in a chemical reaction. In first case, the molecule may be in a state that is similar to that resulting from rapid heating, it is the so-called photothermal decomposition process. In second case, it may induce a chemical mechanism that is unique and unlike the thermal pathway, it is the so-called photochemical decomposition process. In the photothermal decomposition process the number of molecules that desorbs and the translational energy of the products will depend on the number of photons whereas in a photochemical decomposition process only the number of desorbing molecules will depend on the number of photons. In the present experiment 2,2',4,4',6,6'-hexanitrostillbene molecules was considered to undergo a photochemical decomposition process for the following evidence. We have performed a calculation of the translational temperature for 2,2',4,4',6,6'-hexanitrostillbene molecules under our laser conditions according to Garland *et al.*'s investigation<sup>18</sup>. The laser powder density used was 1012  $\text{W}/\text{m}^2$ , resulting in a fluence at about  $10^{-1}$   $\text{mJ}/\text{cm}^2$ . The translational temperature of 2,2',4,4',6,6'-hexanitrostillbene following laser desorption as a function of decomposition laser fluence is less than 300 K, which is much lower than the thermal decomposition temperature of 2,2',4,4',6,6'-hexanitrostillbene. Therefore, it is confirmed that absorption of light from the 263, 527 and 1053 nm decomposition laser results in a photochemical decomposition for 2,2',4,4',6,6'-hexanitrostillbene molecules.

To characterize the laser-induced photodecomposition steps, we have used X-ray photoelectron spectroscopy and FT-IR spectroscopy to study the chemical structure changes of 2,2',4,4',6,6'-hexanitrostillbene before and after different laser wavelengths irradiation. In the XPS measurements of 263 and 527 nm irradiated samples, the appearance of the new peaks of N 1s narrow scan spectra at about *ca.* 401 eV and O 1s narrow scan spectra at *ca.* 528 eV are definitely shown to be associated with the photo-generation of the nitrite ester derivative ( $-\text{ONO}$ ) of 2,2',4,4',6,6'-hexanitrostillbene. In the FT-IR spectra, the 1020  $\text{cm}^{-1}$  peak is assigned to C-O stretching vibration. Combined with the experimental results of XPS measurements and FT-IR spectra of 2,2',4,4',6,6'-hexanitrostillbene samples irradiated at 263 and 527 nm, it is concluded that a nitro-nitrite ( $\text{NO}_2\text{-ONO}$ ) isomerization mechanism occurs in the decomposition process. Additionally, in the FT-IR spectra of 2,2',4,4',6,6'-hexanitrostillbene samples irradiated at 263 and 527 nm, another two new peaks at *ca.* 2919 and 2850  $\text{cm}^{-1}$  are also observed, which is assigned to the C-H stretching vibration of  $-\text{CH}_3$  or  $-\text{CH}_2$  group. One possible explanation consistent with the above data is that the *trans*-C=C bond in 2,2',4,4',6,6'-hexanitrostillbene molecule was broken. One could argue that the excited state populated by photoexcitation of 2,2',4,4',6,6'-hexanitrostillbene may access a facile pathway to the fragmentation of C=C bond on the

ring. However, an experimental study of the photoexcitation of some simpler aromatic systems (*i.e.*, benzene, nitrobenzene and aniline) demonstrate the stability of the aromatic ring. Ring cleavage in photoexcited benzene is a low quantum yield process (*ca.* 0.01-0.05) and photoexcitation of nitrobenzene and aniline favour reactions at the NO<sub>2</sub>/NH<sub>2</sub> moiety rather than ring cleavage<sup>10</sup>. Although we cannot rule out the possibility of ring fission as the primary decomposition step in 2,2',4,4',6,6'-hexanitrostillbene, it seems unlikely based on the stability of the aromatic ring and on the limited observations of ring fission in other energetic materials decomposition studies. The more plausible interpretation of the 2919 and 2850 cm<sup>-1</sup> peak in FT-IR spectra is attributed to the fragmentation of *trans*-C=C bond in 2,2',4,4',6,6'-hexanitrostillbene molecule. While the 2,2',4,4',6,6'-hexanitrostillbene sample was irradiated at 1053 nm, the XPS N 1s and O 1s narrow scan spectra show no change. Only two new peaks at about 2919 and 2850 cm<sup>-1</sup> are observed in the FT-IR spectra. Besides from Figs. 2 and 3, it also can be seen that the decomposition of 2,2',4,4',6,6'-hexanitrostillbene at 263 nm irradiated is much more serious than that of 527 and 1053 nm. Based on these results, it is concluded that the laser-induced photodecomposition mechanism of 2,2',4,4',6,6'-hexanitrostillbene may be dramatically influenced by the laser wavelength.

Since the decomposition reaction steps of 2,2',4,4',6,6'-hexanitrostillbene are wavelength-dependent, whether the photoinduced reactions in 2,2',4,4',6,6'-hexanitrostillbene are induced by a single photon or multiple photons in the fixed wavelength is still poorly understood. The absorption spectra of solid 2,2',4,4',6,6'-hexanitrostillbene in the ultraviolet spectra region between 240 and 430 nm shows a strong absorption at about 380 nm that tails off to *ca.* 30 % at 430 nm (measured in our laboratory). The single photon absorption cross-section at 527 and 1053 nm is expected to be weaker. Therefore, the decomposition of 2,2',4,4',6,6'-hexanitrostillbene at 263 nm irradiated is much more serious than that in 527 and 1053 nm. However, studies of other materials indicate that despite a small absorption cross section, a high power light pulse can still create a measurable population of photoproducts *via* single photon excitation. Kunz *et al.*'s investigation<sup>19</sup> showed that the single photon photo-initiation occurs at crystal dislocations and defects in an energetic material. In our experiment, the 2,2',4,4',6,6'-hexanitrostillbene powders are sandwiched between two quartz plates. It involves a grinding and compressing process. Presumably this process may dramatically increase the crystal dislocations or defects making the single photon absorption cross section increase in the visible

### Conclusion

The decomposition of 2,2',4,4',6,6'-hexanitrostillbene solid samples following irradiation with different laser wave-

length light has been investigated. In our experimental conditions, it is suggested that the laser-induced decomposition is a photochemical decomposition process. The chemical structure changes of 2,2',4,4',6,6'-hexanitrostillbene before and after laser irradiation are identified using X-ray photoelectron spectroscopy (XPS) and FT-IR spectroscopy. Results showed that the chemical structures of 2,2',4,4',6,6'-hexanitrostillbene may be dramatically influenced by the laser irradiation. In the case of 263 and 527 nm irradiated, the nitro-nitrite isomerization and the breaking of *trans*-C=C bond have been both evidenced to be occurred in the decomposition reaction step, while in the case of 1053 nm irradiated, only the fragmentation of *trans*-C=C bond was observed in the photodecomposition process. Laser wavelength clearly affects the mechanism of solid 2,2',4,4',6,6'-hexanitrostillbene decomposition.

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