EFFECT OF PHOTOCHEMICAL REACTIONS ON LUMINESCENCE OF CRYSTALLINE RDX

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Abstract — Luminscence spectra and decay of crystalline hexahydro-1,3,5-trinitro-1,3,5-s-tetrazine (RDX) are observed at 90 K and the effects of photochemical reaction on the luminescence of RDX are investigated. The uv light from high power Hg lamp is used for the photochemical reaction of RDX. While no significant changes are observed in the luminescence spectra after the photochemical reaction, the intensity profile of the spectra changes with the progress of chemical reactions. The biexponential decay of luminescence is modified by chemical reactions. Features of the electronic states of crystalline RDX are discussed in relation to the luminescence.

INTRODUCTION

The luminescence spectra in the uv/vis region are related to electronic states. The spectral band positions correspond to the energy levels of the electronic states and the decay dynamics of luminescence results from various interactions of electronic and other molecular motions.[1] There exist a lot of perturbation effects which affect the characteristics of luminescence of molecular solid systems. Changes of temperature or pressure and introduction of physical or chemical defects are examples of such perturbations. Lattice vibrations so called phonons are especially sensitive to temperature and pressure of the system; phonon energy is small enough to be activated at room temperature and phonon energy levels are easily modified by external pressure. Scattering processes of phonons and other molecular motions are greatly affected by defects of lattice. Chemical reactions of crystalline solids not only produce physical and/or chemical defects in the lattice but also generate high internal pressure due to the reaction products inside the solid.[2] Modifications of potential functions involved in the intermolecular interactions by perturbations, which accelerate intermolecular energy transfer, are considered to play important roles in the initiation of explosive chemical reactions of energetic materials.[3] Effects of external pressure on the characteristics of luminescence have been studied for a long time.[4] Red shift of luminescence spectra observed at high pressure is mainly due to the large polarizabilitiy of the excited states and the lifetime of luminescence reduces at high pressure. X-ray spectroscopic studies of solid explosives show that even core electrons of the solid materials are affected by a shock wave,[5] which is a kind of a dynamic pressure. The IR spectra of the photochemical reaction products embedded in the crystalline lattice indicate that the internal pressure exerted for the fragments corresponds to a few tens of kbar.[6]

Hexahydro-1,3,5-trinitro-1,3,5-s-triazine (RDX) is one of best characterized energetic materials.[7] While extensive studies of physicochemical properties and chemical reactions of RDX have been carried out, the optical properties of RDX have not been well investigated due to weak absorption in the UV region.[8] Thus, in this work, the effect of photochemical reactions on the luminescence of crystalline RDX is studied. The UV photolysis of crystalline RDX at liquid nitrogen temperature produces small stable fragment molecules such as N_2O, CO_2 and NO_2, which exert high internal pressure.[9]

MATERIALS AND METHODS

RDX, supplied by Hanwha Corp., is purified by recrystalization in spectrograde acetone several times.

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RDX single crystals of a few mm dimension are grown by slow evaporation of saturated acetone solution at room temperature. Lattice parameters of the grown crystals were confirmed by x-ray diffraction and consistent with the reported ones.[10] A low temperature dewar cooled with liquid nitrogen as shown in Figure 1 was employed for the photochemical reactions and the luminescence study of RDX. The whole beam of high power Hg lamp (300 W, Oriel) was used for photochemical reactions of RDX and the usual intensity irradiated at the sample is about 200 W/cm². The IR from the light source was reduced with a water filter. The luminescence of the sample at liquid nitrogen temperature was observed upon UV irradiation for a certain period. The luminescence spectra were taken with SLM 4800 fluorometer and luminescence decay was measured with a fluorescence lifetime spectrometer (Edinburgh, FL-900 CD).

RESULTS AND DISCUSSION

The absorption spectra of RDX reveal interesting features.[5] In solution, the lowest excited singlet state is observed at 236 nm, which is assigned to an n $\rightarrow$ π^* transition of the nitramine (>N-NO₂) moiety of RDX. The crystalline RDX shows a weak absorption band at 365 nm, which is not observed for the RDX in solution. The charge-transfer self-complex seems reasonable for the band of the crystalline RDX.[11]
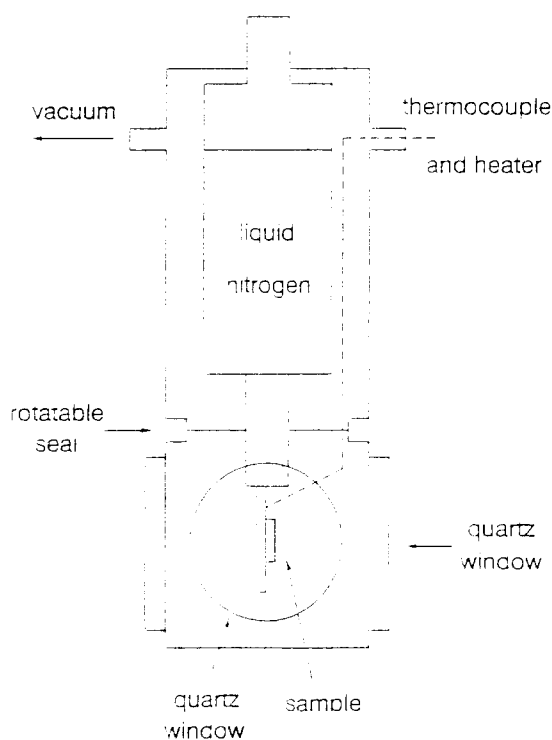
Anomalously large heat of sublimation of RDX (31.1 kcal/mole) and molecular orbital calculations of RDX molecule[12] support the charge-transfer complex. Heat of sublimation of RDX larger than that of aromatic hydrocarbon crystals indicates that the intermolecular force of RDX crystal is stronger than van der Waals force, which may suggest that the intermolecular force of RDX crystal is rather a electrostatic force. Molecular orbital calculations reveal that there exist the highly charged sites in RDX molecule which may be the binding sites in the crystalline phase.

Figure 2 shows changes of the luminescence spectra of single crystalline RDX at 90 K with photochemical reaction. Luminescence of crystalline RDX in the near UV region originates from the excited state of the charge-transfer comoplex. The samples used in the experiments are lange single crystals (about 4 MM × 4MM × 1MM). The excitation wavelength is 380 nm which is longer than the decomposition threshold of 340 nm. Although observation of weak fluorescence with maximum at 465 nm for the powdered RDX at room temperature is reported[14], luminescence of measurable intensity from single crystals of RDX is not detected at room temperature in this work. The reported luminescence spectra at 77 K are somewhat different from the spectra of Figure

Figure 1. Low temperature dewar cooled with liquid nitrogen. Head compartment with quartz windows is rotatable under vacuum.
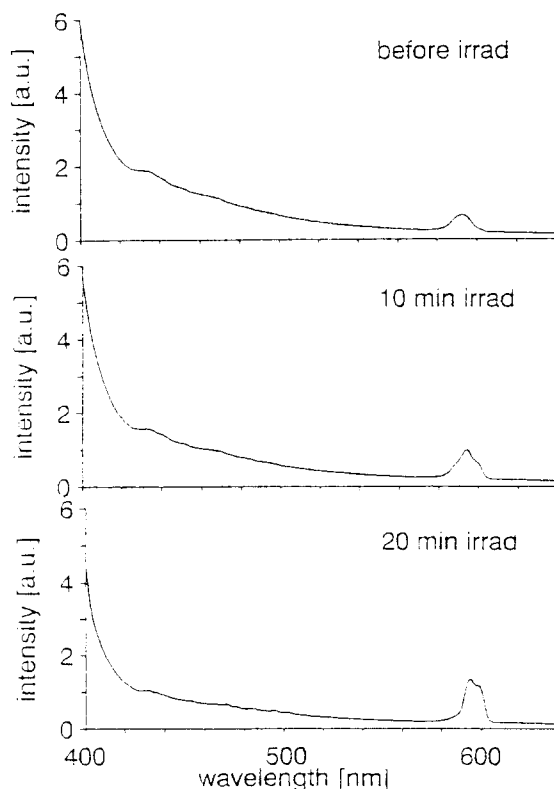

Figure 2. Luminescence spectra of crystalline RDX at 90 K at different irradiation time of Hg lamp at the intensity of about 200 W/cm². The excitation wavelength is 380 nm.

2. While the emission spectra of RDX taken before the UV irradration show the band maximum around 430 nm, the emission spectra of polycrystalline RDX are reported to show the band maximum near 500 nm at 77 K.[13] The luminescence at 77 K was assigned as the phosphorescence from the triplet state of the charge transfer complex.

The spectral differences between ref. 13 and this work at low temperature cannot be attributed to temperature difference. Morphological difference of the samples might be responsible for the spectral differences. Powdered polycrystalline samples of RDX reveal different physical properties from large single crystals. Another factor related to the morphology of the samples is the possibility of sample contamination. Impurities are one of the main causes to prevent the growth of a large single crystal. XRD data of the grown crystals and good reproducibility of the luminescence spectra from different single crystals of large size support high purity of the sample used in this work.

The band around 590 nm of Figure 2 is considered to originate from NO_2 molecules produced by room light. This band is quite shape compared with the emission around 430 nm and its energy is too low to be assigned as the triplet state of the charge-transfer complex of RDX. Growth of the 590 nm band with the progress of photochemical reaction supports that the band is due to the reaction products. Among the fragments produced by UV photolysis of crystalline RDX, nitrogen dioxide is the only species which gives emission in the visible region.[9] Gaseous NO_2 molecules of orange-brown color are known to give very complicated fluorescence spectra in the region 570 - 670 nm and the band around 590 nm is very strong.[14] The NO_2 molecules is excited by reabsorption of emitted light from RDX not by direct energy transfer from the excited RDX. The absorption cross section of NO_2 is negligible at 380 nm. Overlap of the electronic states of the donor and the acceptor should be large for the effective energy transfer. However, the overlap of the singlet electronic states of RDX and NO_2 is very small. Thus, the luminescence from the low energy triplet state of RDX, which is not clear in the spectra of Figure 2, is responsible for the excitation of NO_2.

Figure 3 shows the spectral changes photolysis induced more clearly. The spectrum before the irradiation is subtracted from the spectrum after UV irradiation. Emission intensity of the region 420 - 560 nm decreases and the band around 590 nm grows with the progress of photochemical reaction. Asymmetric growth of the red side in the 590 nm band indicates that the internal pressure on the NO_2

molecules increases with the photochemical reactions. Small negative peak around 580 nm of the difference spectra after 20 min irradiation reveals the decrease of the peak in the blue side. The change of the relative intensites of two peaks in the difference spectrais considered to be due to the increase of the internal pressure by the photochemical reaction of the RDX crystal. It may be possible to estimate the internal pressure via the spectral analysis, however, the pressure dependence of the luminescence of condensed NO_2 molecules has not been investigated to our knowledge.
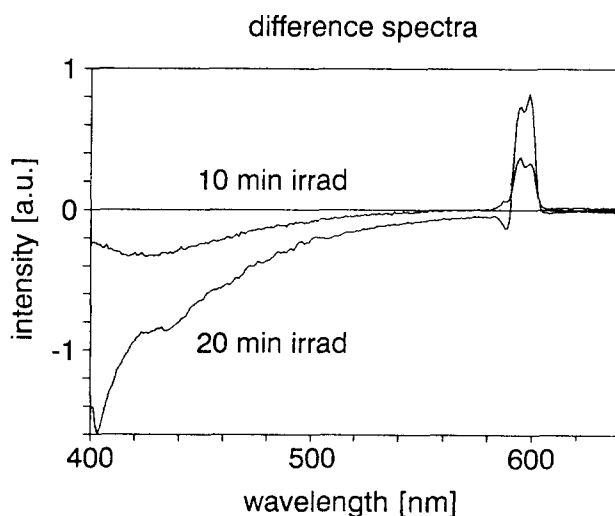

Figure 3. The difference of the spectra of Figure 2. The negative intensity indicates the intensity before the UV irradiation is larger than after irradiation. The intensity of the growing band increases with the chemical reactions.

Several aspects can be considered for the decrease of the emission intensity near 430 nm: decomposition of RDX molecules, scattering by the rough reacted crystal surface and absorption of the emitted light by the reaction product, NO_2. The inverted profile of the difference spectrum after 20 min irradiation, which is similar to the emission spectra in the UV region, indicates that the intensity decrease of the spectrum after 20 min irradiation is largely due to scattering by the reacted crystal surface. The rough surface reduces the absorption efficiency of the incident light and interrupts the effective collection of the emitted light. Of course, intensity decrease due to decomposition of RDX is also included in the spectrum after 20 min irradiation as seen in the difference spectra after 10 min irradiation. It is difficult to estimate quantitatively the degree of the decomposition of RDX from the emission intensity of the UV region since the reaction product absorlos the RDX luminescence. FT-IR studies of RDX photoreaction

show that about one third of RDX decomposes when the UV is irradiated for 20 min at the intensity of about 200W/cm^2.[9] However, the complexity of the photochemical reactions prevents even approximate evaluation of the RDX amounts: the number of NO_2 molecules produced from one molecule of RDX and the conversion efficiency of the RDX luminescence into the emission of NO_2 are not known. Since a weak emission spreads over a wide range of wavelength, the background level of the spectra and the position of the dewar may give critical effects on the measured intensity.

Various radiative and non-radiative processes are involved in the relaxation of the electronic states of solid molecules.[15] Since the excitation wavelength is longer than the decomposition threshold, of RDX relaxation via photochemical reaction can be ignored in this case. Energetic molecules containing NO_2 groups are known to reveal fast non-radiative relaxation process, that is, internal conversion to the ground state. The decay of the luminescence is usually given by a single exponential function and the rate constants of all involved relaxation processes from the prepared excited state are included in the observed relaxation time, $\tau (= [\Sigma \ k_i]^{-1})$. However, multi-exponential decay of luminescence appears when the dynamics of the excited state are complex.[16] In order to study the detailed mechanism of the multi-exponential dynamics, more information such as temperature dependence of the dynamics is required.

Figure 4 shows the decay profile of the RDX luminescence at 90 K measured by time-correlated single photon counting method. The excitation
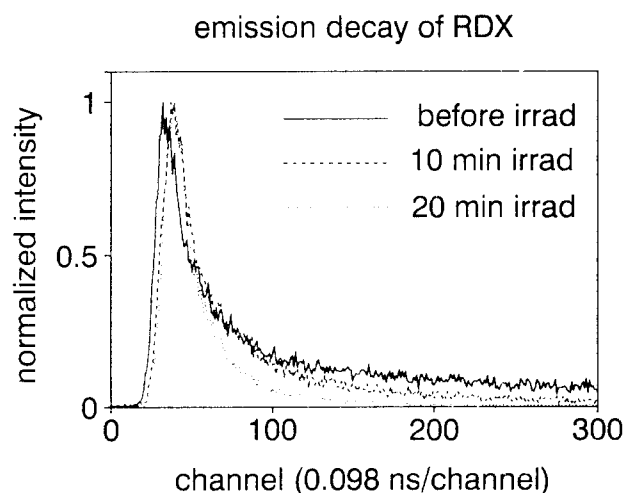
wavelength is 380 nm and the emission is observed at 430 nm as in Figure 2. Two sets of data are collected in different series of experiments. The decay data are accumulated over 30 min. The decay profiles are well fit by biexponential functions and the analysis results are given in Table 1. In this work, further investigation of the detailed dynamics was not attempted to explain the biexponential decay of the luminescence. However, it is noted from Table 1 that the photochemical reactions of the solid materials reduce the decay time constants and that the quantum yield of the fast process increases with the progress of the reaction. Decrease of the decay time constants is related the activation of non-radiative relaxation of the excited state. Defects produced by photochemical reactions and internal pressure by the photofragments modify the intermolecular potential to increase the anharmonicity involved in the phonon scatterings. The enhanced phono scattering processes contribute to non-radiative relaxation.

Table 1. Fitting parameters for luminescence decay: $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$

irradiation time	A_1	τ_1(nsec)	n_1[a]	A_2	τ_2 (nsec)	n_2[a]
0 min	33	1.4	0.02	67	43.5	0.98
10 min	44	1.1	0.10	56	7.4	0.90
20 min	65	0.4	0.21	35	2.8	0.79

[a]fraction of the total photons emitted, $n_1 = A_1 \tau_1 /(A_1 \tau_1 + A_2 \tau_2)$ and $n_2 = A_2 \tau_2 /(A_1 \tau_1 + A_2 \tau_2)$.

emission decay of RDX

Figure 4. Luminescence decay of crystalline RDX at 90 K with the uv irradiation. The excitation wavelength is 380 nm and the luminescence is observed at 430 nm. The analysis results of the decay profile are given in Table 1.

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