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Initiation of chemistry in molecular solids by processes involving electronic excited states

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Abstract

This article presents a description of the initiation of chemistry in molecular solids by laser excitation under high-pressure conditions. An experimental and theoretical study on the initiation of cyclotrimethylene triamine (RDX) suggests that the initiation process involve electronically excited states. Ab initio calculations on RDX crystals including vacancies and edge dislocations are used to provide an interpretation of the measured RDX initiation properties at pressures up to 5.0 GPa and laser fluences between 1.0 and 10 J/cm^2. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Laser initiation of chemical reactions in molecular solids at a high pressure is a complex process important in studies of high-pressure chemistry and physics. A clear understanding of the energy transfer process does not exist. Classically, an excitation is presented to occur by either a single- or a two-photon absorption. However, most organic molecular solids do not absorb the energy in the visible excitation region. Therefore, molecular solids are described to absorb energy by the two-photon mechanism without any fundamental understanding of the excitation process. This article attempts to provide a description and a possible interpretation of the laser initiation of molecular solids with visible excitation and the effect of pressure on the initiation process.

Cyclotrimethylene triamine (RDX) was selected to study laser initiation of molecular solids as a function of pressure. RDX is an energetic molecular solid (molecular formula $C_3H_6N_6O_6$) with the Pbca structure containing eight molecules per unit cell and is relatively sensitive to initiation by external forces, such as impact or shock. RDX reaction propagates once a critical amount of energy is absorbed. The initiation mechanisms of RDX and other energetic materials are relevant to the materials' stability and safety. The exact nature of the RDX initiation mechanism (as in most energetic compounds) is unclear. There are several popular ideas describing initiation beyond simple thermal chemistry. The oldest is the concept of hot spot initiation. Several mechanisms for hot spot initiation have been described over the last couple of decades [1–7]. A hot spot is presumed to be a local region in a crystal where energy is trapped. The hot spot size is important. If the hot spot is very small, no reaction propagation will occur. However, if the hot spot size is large enough, thermal decomposition is possible [8–15]. Sharma and Coffey [16] argue that such hot spots are associated with regions in a crystal that have high shear stress. A high density of disloca-

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[*] The publisher regrets to announce the death of Dr. A. Barry Kunz in 2001 since submission of this paper.

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tions normally accompanies such regions [17]. In other studies, hot spots are thought to include voids in the solid, or regions of significant electric charge [18]. Additionally, several mechanisms involving excited electronic states are proposed [3,19]. The most prominent mechanism involving excited electronic states is that of metallization proposed by Gilman [12,20]. RDX and TATB metallization has been estimated to be from 2 to 2.5 Mbar region. This value is inconsistent with a concept of metallization as the initiation process, as peak pressures for RDX and TATB initiation are reported to be far less than the metallization pressures [21]. The idea of the involvement of excited electronic states was buttressed by studies on RDX and TATB, among other systems, in which initiation sensitivity was found to correlate with details of the electronic structure [22,23].

This article presents a description of the initiation of RDX by laser excitation under modest pressure conditions (up to 5.0 GPa). This combined experimental and theoretical study on the initiation of RDX suggests that the initiation involves electronically excited states at moderate pressures. We believe that the laser initiation mechanism suggested earlier [23] with application to RDX, can be used as a model description for the initiation mechanism of most molecular solid under high-pressure conditions during pulsed laser heating.

2. Theoretical

The theoretical methods employed here are largely standard. The initial calculations are made for the pure, perfect crystal using the CRYSTAL95 code [24] in its Hartree-Fock (HF) limit. The HF limit is well known to substantially overestimate band gaps. Correlation corrections are incorporated by methods developed earlier [25] to improve the HF estimate. This correlation correction, which is largely due to polarization effects reduces the computed pure, perfect RDX gap by 8.42 eV to a value of 5.25 eV.

Theoretical calculations are presented for RDX including isotropic compression. These are given for pure, perfect RDX and RDX molecular vacancies, edge dislocations, and vacancies associated with edge dislocations. Other defect structures such as nanocracks and free surfaces have been studied but do not modify the results and conclusions found here and are not further described. These results indicate that the band gap in pure, perfect RDX is greater than 5 eV, and exhibits a weak sensitivity to isotropic distortion. The pressure needed to eliminate the band gap is estimated to lie between 2 and 2.5 Mbar. The inclusion of dislocations and also vacancies associated with dislocation changes the picture dramatically. Vacancies were introduced into the lattices using a super-cell method. In the case of solid RDX, the unit cell contains eight RDX molecules. In the present case, one RDX molecule in either eight or 16 was removed. The effect of the defect on the band structure calculation was found to be small. The net result is that the band gap is continuously reduced by about 0.7 eV in response to the vacancy. Next, an edge dislocation is introduced both with and without a vacancy. Again, this is done in a super-cell approach in which the dislocation core is studied along with any included vacancy. The super-cell is periodic along the dislocation line only and dislocation–dislocation interactions are not included. The dislocation edge introduces occupied and virtual states in the band gap, which are well separated from the band states. The edge dislocations reduced the RDX gap to approximately 3.3 eV. Finally, these studies are repeated as a function of isotropic distortion to mimic the effect of pressure. Unlike the direct band gap for pure perfect RDX, the gap levels introduced by the dislocation within the band gap are found to be far more sensitive to distortion than are the band states. These gap states have the excitation energies of 2–3 eV for pressure in the few tens of kbar range. The results of this study are presented graphically in Fig. 1. The states introduced in the gap are associated with the N–NO_2 bonding (anti-bonding) orbitals. The large effect of the edge dislocation may be easily predicted if one considers a simple picture of such a dislocation. Here, one inserts an extra half plane of molecules into a lattice. At the tip of the dislocation (the region studied here) the density of molecules is greater than in the bulk and orbital overlaps are greater than in the bulk. This accounts for the enhanced effect on the gap with and without pressure. The absence of such overlap enhancement also accounts for the relatively small effect of vacancies and nano-cracks under static pressure conditions.

Assuming that optical absorption to the conduction band or to the gap levels can trigger initiation, the

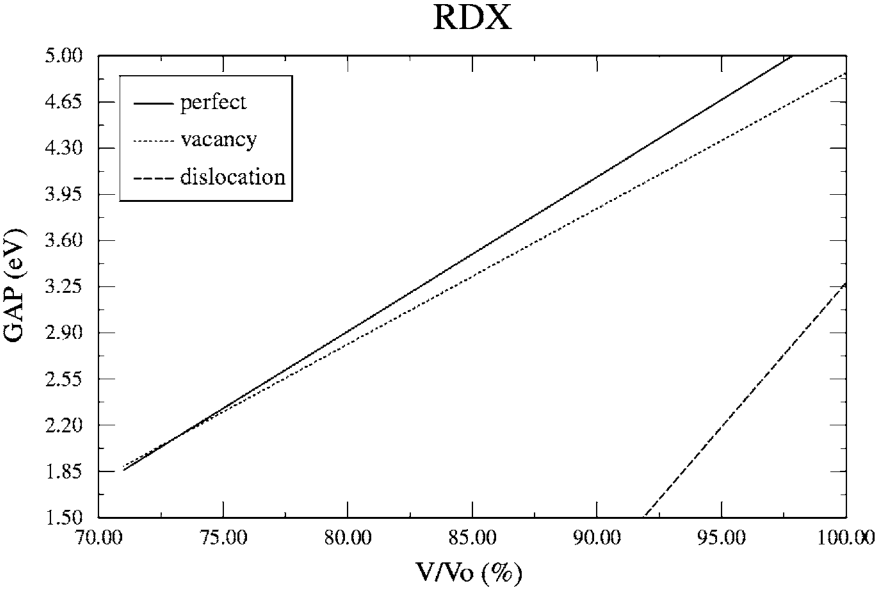

Fig. 1. Summary of the results of quantum chemical simulation of the optical gap for RDX with different defects as a function of volumetric contraction.

probability of optical absorption to initiate a material (RDX) would increase with pressure as indicated by the calculations mentioned earlier (Fig. 1). Therefore, the pressure dependent band structure changes will improve the absorption efficiency, thus enabling initiation at lower laser fluences as a function of pressure.

3. Experimental

In a system of strongly absorbing sites in a non-absorbing matrix, total absorption is increased by (1) increasing the number of absorbing sites, (2) increasing the absorptivity of the absorbing particles (i.e. pressure tuning the wavelength of the incident beam to the maximum absorbance), or (3) increasing the number incident photons (fluence). In our experiments, the number of absorbing sites (1) as discussed later is related to reaction propagation more than initiation. Qualitatively, the effect of pressure in initiation (2) and (3) has similar effects. Threshold absorption of light is necessary to observe initiation. In (2), the wavelength of light required for initiation at a constant fluence would decrease with pressure. In (3), the fluence required for initiation at a constant wavelength would decrease with pressure. We selected method three primarily due to the simple nature of the experiment.

Experimental results are presented on the laser fluence (532 nm, pulse duration 8 ns) required to initiate RDX as a function of pressure in Fig. 2. Samples were pressurized to a desired pressure in a Merrill Bassett anvil cell and initiated by a single pulse from a Nd:YAG laser operating at 532 nm. The reported initiation energy is the energy required to induce a detectable amount of a reaction, either by infrared spectroscopy or through optical inspection of the recovered sample. Localized initiation is observed in all RDX samples during initiation.

Single crystals of RDX (note: the HMX free process produced the RDX used in this work) of the appropriate dimensions were grown from solution. From these crystals a selection of high quality crystals was made. Only crystals with a single extension under crossed polarized light were selected. The crystals were free of voids, solvent inclusions, and internal surfaces and are quite clear. All samples were prepared from these hand-selected crystals. The sample arrangements studied are a single crystal in a hydrostaic pressure medium of liquid 1:1 pentane:isopentane, a crushed crystal pressed between two NaCl plates, and a powder compaction of RDX between

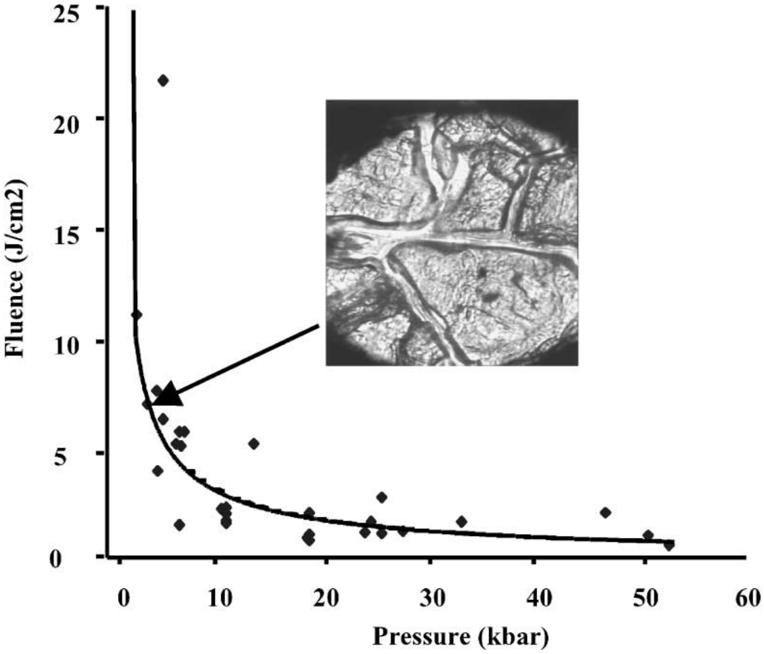

Fig. 2. Laser fluence as a function of pressure required to initiate RDX. The data shown represent a combination of data collected from the three different sample arrangements. The sample configuration did not influence the energy required for initiation. However, the extent of reaction increased as the defect density in the material increased. Inset shows the recovered sample of a pressed crystal of RDX at 0.3 GPa initiated with 7 J/cm^2 of 532 nm radiation. Notice that the sample did not initiate uniformly but shows localized regions of initiation along several grain boundaries in the sample.

two NaCl plates. In all three cases, the samples were optically transparent under pressure with no detectable interfaces or defects by optical methods. In all three-sample arrangements, the material is transparent to visible excitation. Specifically, the excitation wavelength (2.35 eV or 532 nm) is in a spectral region for which RDX is transparent. In all pressures studied, no measurable absorption of light at the excitation wavelength was observed.

As expected, defects and grain boundaries are present in all the sample arrangements. The sample geometries selected for these studies permitted a wide range of defect centers to be present in the samples. The smallest defect density will occur in the single crystals and the largest occurs in the compacted powders. (It is important to reemphasize that the single crystal is compressed in a hydrostatic medium of liquid 1:1 pentane:isopentane and that the compacted samples are pressed in NaCl. Therefore, the single crystals are under uniform compression and the compacted powders are in a quasi-hydrostatic environment with a non-measurable pressure gradient.) A single crystal of RDX has a rather high concentration of defects, typically 5×10^{12} defects per cm [2,16]. These defects are typically located around a localized region called a dislocation. Dislocation tips are normally evenly distributed across the RDX crystal but the dislocations are present as planes and screws within the crystal, therefore, giving localized defect densities within the crystal. Typically, the concentration of dislocations are 5×10^6. This gives a density of approximately 8.5×10^{16} molecules in a 1 mm^3 sample. Of course, the concentration of defects (dislocations, interfaces, and grain boundaries) for the crushed crystals and powders compacted to transparency at high pressure would be substantially higher. Unfortunately, the defect densities of these samples cannot be measured at this time. However, qualitatively the number of defects increases in the following order:

$$\text{single crystals} < \text{compacted crystals} < \text{pressed powders} \quad (1)$$

All samples were pressurized to the desired starting pressure before laser excitation. A single excitation pulse (8 ns at 532 nm) was used to identify the initiation energy as a function of pressure. Although the samples absorbed no measurable light, initiation is observed. This indicates that very little external energy was needed to create initiation if properly introduced. Initiation occurred in local reaction zones within the crystal. The laser fluence required to initiate a reaction for different pressures is independent of the sample arrangement as shown in Fig. 2. Samples from single crystals and pressed crystals initiated at pressure were recovered (at pressures <4.0 GPa for single crystals and <0.5 GPa for pressed crystals). Cracks originating from the local reaction zones along different RDX crystallographic planes were detected in single crystals while initiation was observed at scattered local regions along cracks and grain boundaries in compacted crystal (see inset in Fig. 2). Compacted samples produced from dispersed powders were never recovered.

Although the critical initiation energy is independent of the sample arrangement, it was observed that the extent of reaction observed, once initiated, was strongly dependent on the sample arrangement. The reaction did not progress fully in single crystals but was quenched. This is likely due to the scarcity of the active initiation centers. The reaction in samples pressed to transparency from single crystals was never quenched at pressures above 0.5 GPa, while compacted powders were never quenched. Therefore, the number of dislocations and grain boundaries was not critical for initiation but strongly influenced the extent of reaction because of the increased surface of initiation centers.

4. Discussion and conclusions

This article has examined the role of electronic excitations in the initiation of chemical reactions in solid RDX. It has been seen that direct excitation at 2.35 eV is sufficient to cause initiation under modest pressure. Normally, RDX is transparent to green light, and seems to be almost so in the present case. Nonetheless, a presumed weak absorption is sufficient to cause initiation. Two processes come to mind when a weak absorption is present. The first is a two-quantum absorption across the band gap, and might be facilitated by the intensity of the present laser light. This effect would induce a uniform absorption across the sample. We tend to discount this concept because upon excitation of the crystal after the fact, initiation seems to have occurred at scattered discrete regions, rather than uniformly as might be anticipated for a two-quantum event. The second possibility is associated with absorption at defects. The dislocation planes and cores would be randomly distributed but localized so that initiation would occur in discrete regions of the sample. In one of the present studies, crystals were selected that had no discernible voids or internal surfaces. Sample initiation occurred in discrete region of the crystals and not uniformly across the sample. Therefore, absorption must have occurred at undetected point or line defects. In this study, theory favors absorption at a vacancy associated with a dislocation core. The absorption does not require a two-quantum effect as one might initially expect. Energetically, the dislocation core is found to attract RDX molecular vacancies, and this complex is seen at ambient pressure to have defect band gap of 2.73 eV. This gap is very sensitive to pressure and reduces to less than 2.25 eV with pressure in the few tens of kbar range. Thus the energy associated with this defect is consistent with the absorption of the green excitation wavelength observed experimentally. We would like to mention here that there are at least three additional possibilities, that could yield the results we found: (1) the energy transfer process leading to reaction are modified by the addition of pressure (not likely), (2) there is a lowering of the reaction barrier with pressure (particularly in the region of a defect), or (3) there is a change in mechanism with pressure (particularly in the region of defect). Strictly speaking, it is difficult for the moment to completely rule out these reasons. After an optical absorptivity of RDX is measured as a function of pressure and the dislocation density, the final conclusion can be made and an excitonic mechanism will be refined. However, a recent study on metal azides provides an additional support in favor of the interpretation presented here [26]. A dislocation-induced effect on early stages of slow decomposition in the electric field has been experimentally studied for AgN_3 whiskers. The results obtained imply that the gas emission (product of the chemical reaction) takes place only in the dislocation emergence sites. Next, studied kinetics of the pre-explosion conductivity, optical absorption, and luminescence of AgN_3 crystals using YAG:Nd^{3+} laser pulse initiation (1064 nm, 10 mJ, 30 ps) suggests that chemical decomposition in crystals with low density of dislocations develops noticeably slower than in the highly defective samples, showing a strong correlation between density of dislocation in the crystal and chemical reactivity [26].

The essential conclusion is that here is seen an initiation process that is conclusively associated with an electronic excited state. This process involves relatively few excited states, and is certainly not in accord with the metallization hypotheses.

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