

THE 248 nm PHOTODECOMPOSITION OF HEXAHYDRO-1,3,5-TRINITRO-1,3,5-TRIAZINE

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Electronically excited $\text{NO}_2(^2\text{B}_2)$ and $\text{OH}(\text{A } ^2\Sigma)$ were detected following 248 nm photolysis of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). $\text{NO}_2(^2\text{B}_2)$ was formed via a one-photon process, while $\text{OH}(\text{A } ^2\Sigma)$ was probably formed via a two-photon process. Emission spectra and lifetimes were determined for both emitting species, and $\text{NO}_2(^2\text{B}_2)$ quenching rate constants were measured for RDX, NO_2 and NH_3 , and compared with calculated values using hard sphere and multipole interaction models. Possible formation mechanisms for $\text{NO}_2(^2\text{B}_2)$ and $\text{OH}(\text{A } ^2\Sigma)$ are discussed.

1. Introduction

RDX is one of the most powerful military secondary explosives. Nevertheless, the initial steps of the rapid decomposition of solid RDX, following exposure to initiating stimuli such as thermal, shock, infrared or ultraviolet laser pulses, have not yet been determined, even though products from the slow thermal decomposition of gaseous and solid RDX have been studied extensively [1–6]. An X-ray photoelectron spectroscopy study of shock-induced decomposition of powdered RDX showed that N–N bond scission occurred in such samples [7], and more recently, gaseous decomposition products have been detected using UV–visible and IR absorption spectroscopies, as well as mass spectroscopy, following the irradiation of powdered RDX samples using CO_2 laser pulses [8].

In addition, there have been two molecular beam studies involving the direct observation of transient species generated via primary dissociation channels of highly vibrationally excited RDX (hereafter referred to as RDX^+) under collision-free conditions [9,10]. In both cases, RDX^+ was prepared using a pulsed CO_2 laser. In the first study, $\text{OH}(\text{X } ^2\Pi)$ was

observed using laser-induced fluorescence; the most likely mechanism for its production was deemed unimolecular decomposition via a five-membered ring [9]. In the second study, decomposition products were detected using time-of-flight and angle-resolved mass spectroscopy. These experiments indicated at least two primary dissociative channels for RDX^+ [10]. The first, accounting for almost $\frac{2}{3}$ of the overall decomposition, was a concerted triple dissociation leading to $\text{CH}_2=\text{N}-\text{NO}_2$, while the other involved N–N bond scission, forming NO_2 .

This Letter reports the first direct observations of (i) $\text{NO}_2(^2\text{B}_2)$, resulting from primary N–N bond scission in electronically excited RDX and (ii) $\text{OH}(\text{A } ^2\Sigma)$, possibly a secondary photoproduct with hot HONO as the immediate precursor. RDX was excited electronically using 248 nm radiation (KrF laser, 15 ns pulse), and emission spectra and decay kinetics were measured using a nanosecond kinetic fluorescence spectrometer.

2. Experimental

The experimental arrangement is shown schematically in fig. 1. Unfocused 248 nm radiation from a KrF excimer laser (Questek 2840) passed through a 7 mm diameter aperture before traversing a 6.3 cm diameter quartz sample cell. The sample cell was located in an oven having three quartz windows, two

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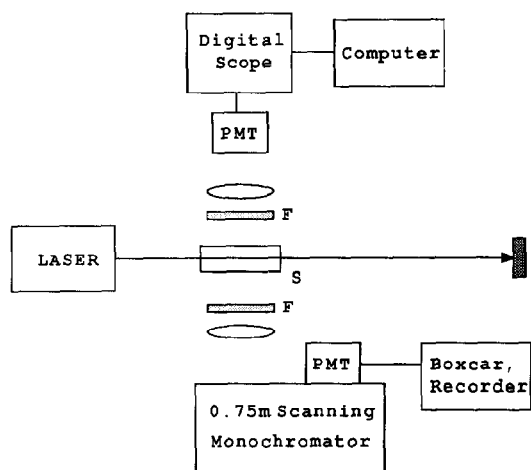


Fig. 1. Schematic drawing of the experimental arrangement used for spectral and decay rate measurements (F=filter, PMT=photomultiplier tube, S=sample).

for transmitting the laser beam and one for fluorescence observation. The laser energy was 10 mJ at the sample. The cell contained RDX crystals, and was typically heated to 460 K and pumped continuously in order to minimize product buildup. Temperatures were monitored using a thermocouple and pressures were measured using a capacitance manometer (MKS). Photofragment fluorescence was monitored at right angles to the laser beam using a short focal length lens and a 0.75 m scanning monochromator (Jarrell-Ash 78-496, 1180 lines mm^{-1} grating, 4 Å resolution with 400 μm slits), equipped with a photomultiplier tube having a flat response in the 400–800 nm region (Hamamatsu R928). Signals were averaged using a boxcar integrator (PAR 162/165), whose output was sent to an XY plotter.

The experimental arrangement used for the emission lifetime and quenching measurements was similar to the one described above, except that fluorescence was monitored directly with the photomultiplier tube through a set of long-pass filters (Corning 3-71 and 3-75 for $\text{NO}_2(^2\text{B}_2)$ emission, and Hoya U-340 and UV-28 for $\text{OH}(A^2\Sigma \rightarrow X^2\Pi)$ emission). Signal decays were averaged for 30 laser shots using a digital oscilloscope (Nicolet 4094A) set at appropriate channel widths, interfaced to an HP-86A microcomputer, where the kinetics and statistical analyses were done.

RDX crystals, twice recrystallized from acetone, were degassed at room temperature, while NO_2 and NH_3 were degassed at 77 K prior to use. As mentioned above, in most cases, the sample vapor was pumped continuously through the cell to avoid product buildup. However, for quenching measurements with added gases, static samples were used and temperatures were kept below 423 K in order to minimize RDX decomposition.

3. Results

Photolysis of RDX vapor (428 K) at 248 nm resulted in intense visible fluorescence. As shown in fig. 2, the emission extends from 420 nm to the near infrared, with a maximum near 608 nm, and is without apparent structure. Similar broad, featureless spectra, characteristic of $\text{NO}_2(^2\text{B}_2)$, have been observed previously in the 248 nm photodissociation of tetranitromethane (TNM) [11] and in the 193 nm photodissociation of nitroalkanes [12]. For RDX and TNM, the emission spectra are identical, indicating that $\text{NO}_2(^2\text{B}_2)$ is formed with similar vibrational excitation, independent of the species to which it was originally attached, suggesting that bond scission may be faster than randomization of the initially implanted energy.

Total fluorescence decay rates were obtained at different RDX vapor pressures in order to determine the quenching rate constant, $k_Q(\text{RDX})$, and the $\text{NO}_2(^2\text{B}_2)$ emission lifetime. The RDX vapor pres-

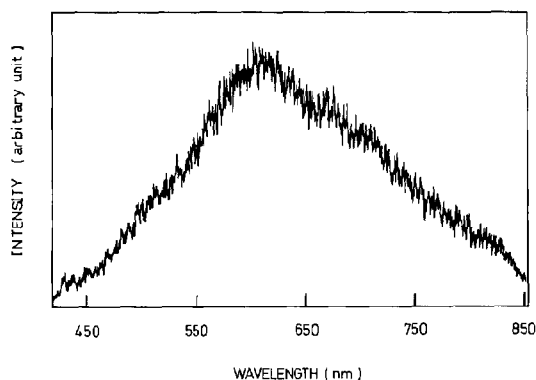
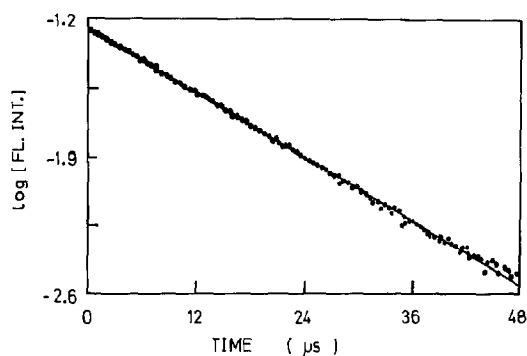
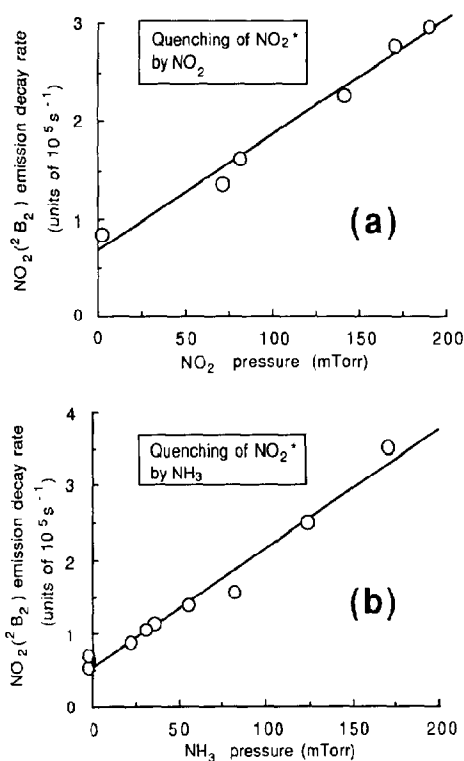


Fig. 2. Dispersed $\text{NO}_2(^2\text{B}_2)$ emission spectrum following 248 nm RDX photodissociation (428 K).

Fig. 3. Typical decay of NO₂(²B₂) emission (425 K).Fig. 4. NO₂(²B₂) emission decay rate versus pressures of (a) NO₂ and (b) NH₃ (426 K).

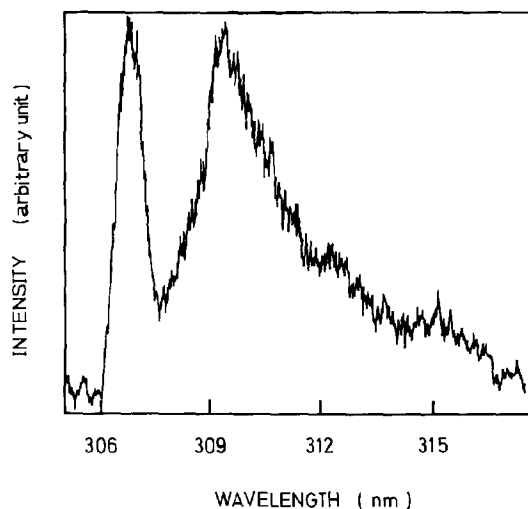
sure was varied by changing the sample temperature (393–459 K); a typical decay trace is shown in fig. 3. The decay rate was calculated using 200 points of the fluorescence decay between 10 and 90% of the maximum signal, spanning almost three lifetimes.

Decays were single-exponential for all temperatures (i.e. up to 460 K). Plots of decay rate versus RDX vapor pressure, to obtain the slope and intercept, yield $k_Q(\text{RDX}) = (3.54 \pm 0.14) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and an NO₂(²B₂) radiative lifetime of $26 \pm 1 \text{ μs}$, respectively. Similarly, $k_Q(\text{NO}_2)$ and $k_Q(\text{NH}_3)$ were obtained by plotting fluorescence decay rates versus quencher pressure at $426 \pm 1 \text{ K}$ (see fig. 4). The obtained k_Q 's along with those found in the literature are listed in table 1.

In addition to the fluorescence discussed above, KrF-laser photolysis of 425 K RDX vapor also resulted in intense emission in the range 305–320 nm, as shown in fig. 5. This emission is characteristic of the (0,0) band of the OH(A²Σ→X²Π) system. Furthermore, this OH emission intensity was found to increase quadratically with laser fluence over the range 50–150 mJ cm⁻², indicating that OH(A²Σ)

Table 1
NO₂(²B₂) quenching rate constants (k_Q 's)

Quenching species	k_Q (10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹)		
	426 K	300 K [13]	300 K [14]
RDX	3.54 ± 0.14	—	—
NO ₂	4.26 ± 0.40	5.0 ± 0.5	3.52
NH ₃	5.15 ± 0.50	15.7 ± 1.5	8.35

Fig. 5. Dispersed OH(A²Σ→X²Π) fluorescence spectrum excited via KrF-laser-induced photodissociation of RDX (425 K).

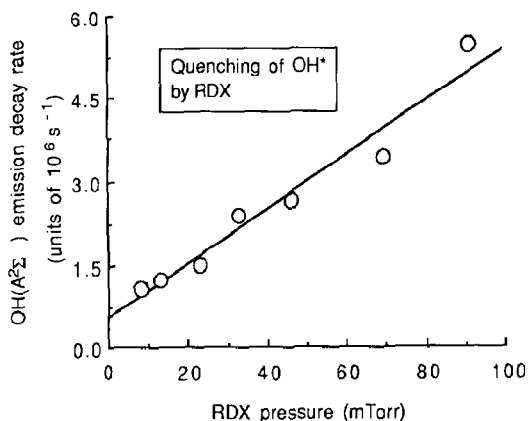


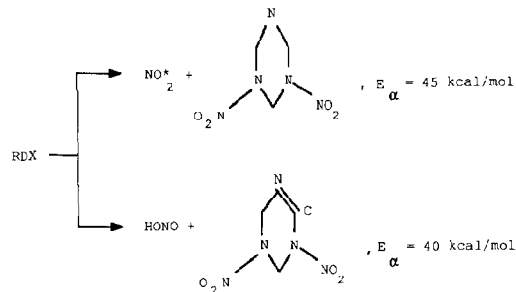
Fig. 6. $\text{OH}(\text{A}^2\Sigma \rightarrow \text{X}^2\Pi)$ emission decay rate versus RDX pressure.

formation is due to two-photon absorption, in contrast to the one-photon process producing $\text{NO}_2(^2\text{B}_2)$. The total fluorescence decay rates were also examined at various RDX pressures to determine the quenching rate constant and the emission lifetime. Decays were single exponential and the lifetime varied from 800 to 200 ns with increasing RDX pressure. Observed decay rates versus RDX pressure are plotted in fig. 6; the resulting rate constant is $1.2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

4. Discussion

The UV absorption spectrum of RDX contains two overlapping bands at 235 and 202 nm. The former has been attributed to a ${}^1\text{B}_2 \leftarrow {}^1\text{A}_1$ transition and is mainly of $\pi^* \leftarrow \pi$ nature, localized in the NO_2 groups [15]. The broad feature, spectral range and long lifetime (26 μs) of the observed visible emission indicates the formation of electronically excited $\text{NO}_2(^2\text{B}_2)$ photofragments [16]. The spectral range, rotational structure and lifetime of the UV emission, on the other hand, indicates electronically excited $\text{OH}(\text{A}^2\Sigma)$. The quadratic fluence dependence of this emission further suggests that the production of $\text{OH}(\text{A}^2\Sigma)$ is via a two-photon process. The prompt production (i.e. within the laser pulse) of electronically excited $\text{NO}_2(^2\text{B}_2)$ and $\text{OH}(\text{A}^2\Sigma)$ upon irradiation of gaseous RDX suggests that dissociation

may include the following two channels [17]:

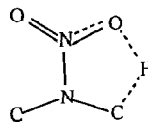


That is, N–N bond scission and five-center HONO elimination, which can be followed by: $\text{HONO} + h\nu (248 \text{ nm}) \rightarrow \text{OH}(\text{A}^2\Sigma) + \text{NO}$. The presence of $\text{NO}_2(^2\text{B}_2)$ emission near 420 nm ($\approx 68 \text{ kcal mol}^{-1}$) indicates that NO_2 is internally excited up to the maximum energy available (70 kcal mol^{-1}). Since $\text{NO}_2(^2\text{B}_2)$ has an estimated electronic energy of 28 kcal mol^{-1} [18], $\text{NO}_2(^2\text{B}_2)$ was thus formed with very high rovibrational energy. At such high energies, the density of states can be very high and this can contribute to the broad nature of the observed spectrum. This is consistent with a very rapid dissociation, in which N–N bond rupture is fast compared to vibrational energy randomization in RDX prior to fragmentation. Indeed, the formation time of NO_2 from the closely related molecule dimethyl nitramine (DMNA) excited at 266 nm was found to be $\leq 6 \text{ ps}$ [19].

The experimentally determined k_Q 's of $\text{NO}_2(^2\text{B}_2)$ by RDX, NO_2 and NH_3 at 426 K, listed in table 1, are similar to those obtained at room temperature by Donnelly et al. [13], Renlund and Trott [14] and our group [11]. The values of the k_Q 's are rather large and indicate that multipole attractive forces can be important in the quenching process, as in the collisional quenching of electronically excited diatomic radicals $\text{OH}(\text{A}^2\Sigma)$ [20], $\text{CH}(\text{A}^2\Delta)$ [21] and $\text{NH}(\text{A}^3\Pi)$ [22]. A multipole interaction model was suggested by Crosley and coworkers [23] to calculate quenching rate constants. This model has been applied to the quenching of these diatomic radicals [24]. The quenching of $\text{NO}_2(^2\text{B}_2)$ by NO_2 , and its temperature dependence can be substantially accounted for with the model. In fact, when the experimental quenching rate constants of various quenchers (CO , N_2 , CH_4 , C_2H_4 , Cl_2 , NO_2 , HCl ,

CH₃CN, H₂O, NH₃ and CH₂O) are plotted against those from this multipole interaction model [11], the quenchers are grouped automatically into four classes of nonpolar, polar, hydrogen bonding prone and chemical activity prone, respectively, as expected^{#1}. This indicates the likely validity of the model for the collisional quenching of NO₂ emission, in contrast to the hard sphere model, from which no trend can be discerned. However, for the strongly polar quencher, NH₃, the experimentally determined quenching rate constants decrease with increasing temperature to an extent which is much larger than that predicted by the multipole interaction model. Specifically, the model predicts an increase of about 10% in the quenching rate of NO₂ by NH₃ in the temperature range of 300 to 426 K, while the experimental results show decrease of at least a factor of two over the same temperature range. For the model to produce this large decrease the temperature would have to change from 300 to 1100 K. Although the intermolecular multipole attraction forces may assist the approach of the collision partners and control the geometry of the intermediate collision complex, the presence of a hydrogen bond between oxygen of NO₂ and hydrogen of collider can be very crucial to the formation of a weakly bonded collision complex and, therefore, to the whole process of collisional quenching. However, this work will not attempt to provide a detailed mechanism describing the collisional quenching of NO₂(²B₂) molecules. This problem will be addressed in a future work.

Energy conservation insures that OH(A²Σ) formation requires at least two 248 nm photons, and the experiment bears this out. Some postulates have been proposed concerning the formation of HONO and OH in the decomposition of vibrationally excited RDX [9,17], but no solid conclusion can be drawn yet. The formation from excited RDX of the transient five membered ring, T,



however, was deemed to be the most logical [9]. OH(A²Σ) can possibly arise via one of the four routes following this most logical transient, T. (1) OH(X²Π) could be formed directly from T and subsequently absorbed another photon to form OH(A²Σ). However, this is highly unlikely due to the extremely low absorption coefficient of OH(X²Π) at 248 nm. (2) T could be formed by RDX and was energetic enough to give rise to OH(A²Σ) directly. For a large molecule like RDX in such highly excited state it is hard to imagine the large extent of energy localization at OH. Another problem is that the two-photon absorption cross-section of RDX may not be high enough to give the observed similar order of magnitude in intensities of OH and NO₂ emission, barring the unlikely event of very low quantum yield for the single photon induced N-N bond fission. (3) T could be formed by singly excited RDX, absorbed another photon and dissociated into OH(A²Σ). Objections to this route are similar to that of (2). (4) T, which could be resulted from singly excited RDX, promptly gave rise to vibrationally hot HONO through concerted dissociation. The hot HONO then absorbed one photon and dissociated into OH(A²Σ) and NO.

Although it cannot be ascertained which of the four routes listed above are operative, based on the present experimental results, it seems likely that route (4) is dominant in view of a recent report [25] on the involvement of HONO as an intermediate in the photodissociation of HNO₃. Future experiments involving two lasers similar to that described in ref. [25] may shed light on whether an intermediate, like HONO, of substantial lifetime is involved in the 248 nm photodissociation of RDX.

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^{#1} Due to the unknown initial velocity distribution of nascent NO₂, *k_Q*'s are compared here instead of the more conventional quenching cross-sections. If ambient temperatures are employed in converting *k_Q*'s to *σ_Q*'s (*σ_Q* = *k_Q* / *⟨v⟩*, where *⟨v⟩* is the average relative speed), the conclusion regarding the grouping of classes of quenchers will still be the same albeit an error in scaling factor.

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