

229 nm UV Photochemical Degradation of Energetic Molecules

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ABSTRACT

We examined photochemical degradation of energetic molecules upon UV resonance Raman (UVRR) excitation of the 229 nm UVRR spectra of solid HMX, TNT and RDX. Comparisons of the UVRR spectra of these photodegraded samples to those of different carbon samples indicate some features similar to carbon compounds with sp^2 bonding, vaguely reminiscent of graphitic carbon as well as amorphous carbon. Spinning the energetic material samples minimizes the per molecule photon flux which decreases the photochemistry. We very roughly estimated photochemical degradation quantum yields of $<10^{-6}$.

Keywords: UV resonance Raman, photodegradation, explosive detection, standoff detection

1. INTRODUCTION

Absorbing materials subject to laser irradiation in the course of UV Resonance Raman (UVRR) spectral acquisitions cycle through their excited states multiple times and may undergo photolysis. We recently demonstrated a clear example of this type of process, for nitrate which undergoes photolysis with 229 nm excitation to nitrite.¹ Any applications of UVRR for remote detection must be based on an understanding of the ground state UVRR spectra and the temporal evolution of the sample components to photodegraded species.

We recently studied the photochemistry of solid and solution sodium nitrate by using 229 nm UVRR spectroscopy.¹ In these studies we were able to monitor purely ground state $NaNO_3$ by minimizing the photon flux per $NaNO_3$ during the Raman excitation by using a spinning cell in which the powder sample was pressed into a 2 mm wide circular groove of approximately 1.5 cm diameter.

In the work here, we studied the photon dose dependence of the 229 nm UVRR spectra of HMX, TNT and RDX by using spinning and stationary sample cells. We also compared the extensively photodegraded samples to those of carbon.

2. EXPERIMENTAL

The 229 nm excitation wavelength used here was from a CW Coherent FreD laser. The power at the sample was approximately 1.0 to 1.8 mW. The laser beam diameter is $\sim 25 \mu m$ at the sample. All spectra were acquired with the SPEX Triplemate Spectrograph as described before.^{2, 3} The prefilter entrance slit was set to $250 \mu m$ and the spectrograph entrance slit set to $150 \mu m$. Acquisition times ranged from 0.5 s in the "focus" mode to 20 s/read for a total of 3 reads (60 s) in the "acquire spectrum" mode. All spectra presented are the accumulation of 3 reads.

All samples were mounted on a brass cell with a 2 mm wide circular groove of diameter 1.5 cm, and the rotation speed was maintained by a SPEX 1445A controller. The cell was either stationary or rotated at the controller's minimum speed.

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3. RESULTS AND DISCUSSION

Fig. 1 shows that photodegradation occurs for stationary HMX samples over a period of 4 min. The HMX was mixed with NaF powder for these samples to form a powder that could pack tightly in the spinning cell. The initial spectrum most closely resembles previously acquired spectra of HMX in acetonitrile solution.³ The HMX photodegradation is indicated by the changes observed with increasing illumination. The attenuation of all the HMX bands initially observed indicates the photochemical conversion of HMX and the emergence of new chemical species. The difference spectrum shows that the new features appearing have two broad bands at 1418 and 1680 cm^{-1} . In addition, the sharp band at 1043 cm^{-1} may indicate formation of a nitrate-like species.

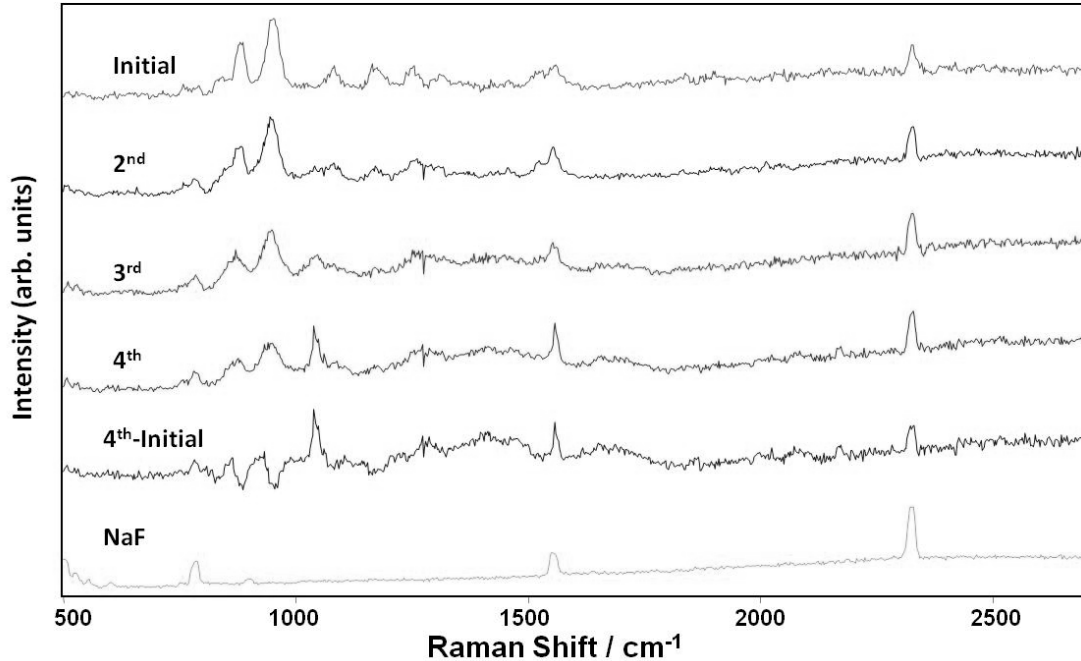


Figure 1. Spectra of blend of HMX and NaF stationary sample. Photodegradation occurs progressively from the initial through the 4th spectrum obtained in this sequence. Photodegradation is also shown in the difference spectrum of 4th -initial.

The use of a spinning cell dramatically decreased the photolysis evident for HMX. Rotating the sample during laser illumination allows the energy to be distributed over a much larger volume than when the sample is stationary during the spectral acquisition. A typical spectrum (60 s accumulation) of HMX acquired with the cell rotating at the minimum speed is shown in Fig. 2. We observed no changes in the spectrum during acquisition with the cell spinning. Peculiarly, we only see the 1044 cm^{-1} band in spinning HMX and stationary solid HMX and NaF after 3 min illumination.

The HMX spectra can be observed to be changing within seconds. A spectrum of stationary pure HMX with a significantly increased photodegradation is shown in Fig. 2. This spectrum differs from those in Fig. 1 that showed the appearance of two broad bands at 1418 and 1680 cm^{-1} and the 1044 cm^{-1} band. Instead, the more extensively degraded HMX spectrum is weaker and consists of a broad feature centered around 1550 cm^{-1} somewhat similar to that observed in spectra of amorphous carbon.^{4,5} In addition, two new, much narrower bands appear at 693 and 985 cm^{-1} .

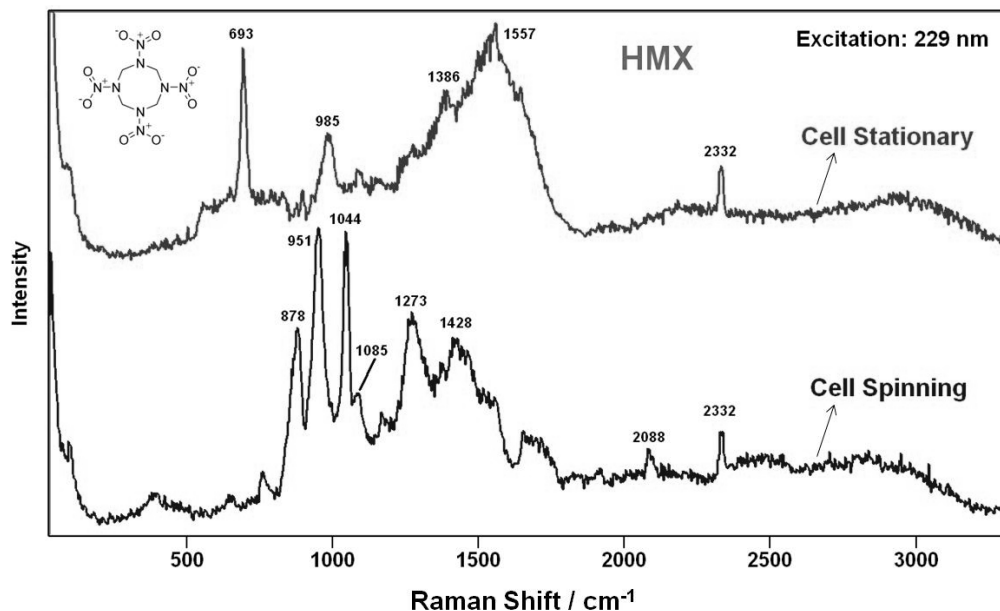


Figure 2. Spectra of solid HMX in the absence of NaF obtained with the sample stationary and with the cell spinning. Both spectra were acquired under the same conditions. Photodegradation is more extensive and shows a somewhat different spectrum than that in the presence of NaF.

We also examined the UVRR of solid RDX in a spinning cell as well as a stationary sample. As shown in Fig. 3, RDX is structurally similar to HMX. Thus, their spinning Raman spectra are similar but with sufficient differences to distinguish between RDX and HMX. The spinning solid sample of RDX shows no evidence of photochemical degradation. The spectrum is close to that of RDX dissolved in acetonitrile.³ The stationary 229 nm UVRR spectra of RDX and HMX appear similar (Fig. 4). The UVRR of photodegraded RDX also shows one broad, degraded feature at $\sim 1550\text{ cm}^{-1}$. In addition, there are two narrower bands at 694 and 984 cm^{-1} .

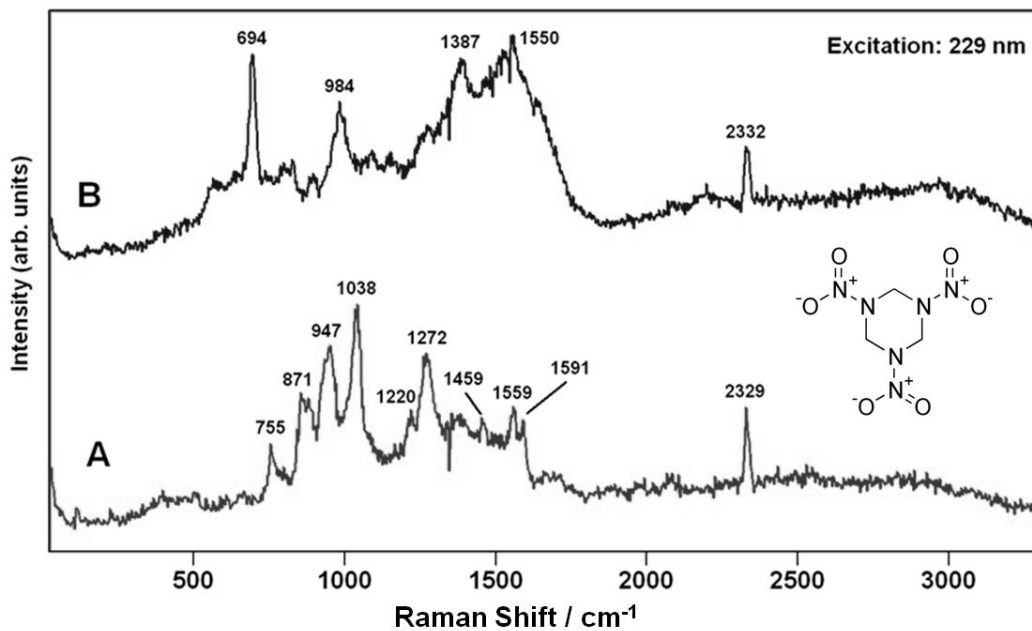


Figure 3. Raman spectra of RDX acquired with A) in cell spinning, and B) cell stationary.

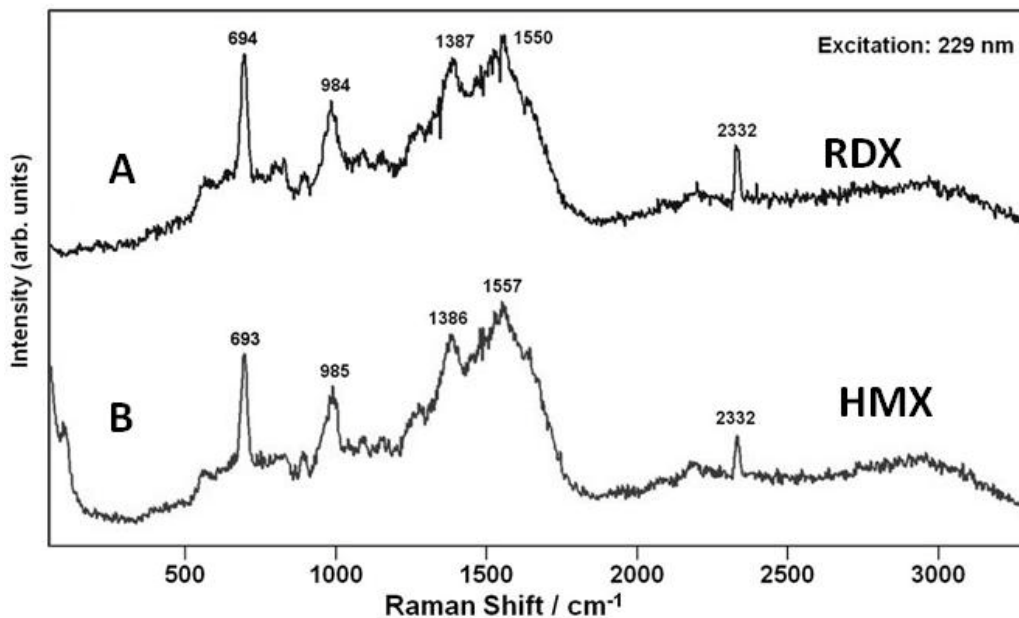


Figure 4. Raman spectra of photodegraded A) RDX and B) HMX.

We also see a similar behavior for TNT. The UVRR of the spinning solid TNT sample resembles that of TNT in acetonitrile³ with no sign of photodegradation (See Fig. 5A.). However, the spectrum acquired for the stationary TNT (Fig. 5B) somewhat resembles that from graphitic carbon^{4, 6} and charcoal⁷, suggesting that the TNT has been photolyzed to a graphitic carbon type species.

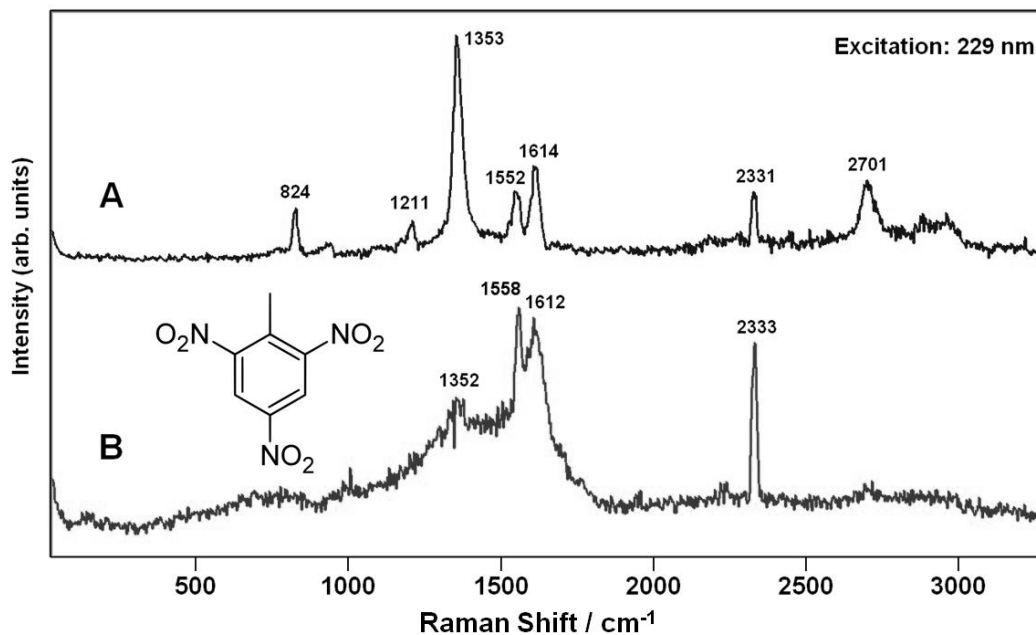


Figure 5. Raman spectra of solid TNT acquired with A) the cell spinning, and B) stationary.

We examined the 229 nm photodegradation of acetaminophen, a simple aromatic compound with amide and hydroxyl ring substituents (Fig. 6). The UVRR acquired with the spinning sample (Fig. 6) shows the bands previously identified for this material with excitation out of resonance.⁸ The stationary photolyzed UVRR is also very different from that of the spinning sample and shows two broad bands centered at 1330 and 1615 cm^{-1} . This stationary spectrum of acetaminophen appears somewhat similar to spectra of graphitic carbon^{4,6} and charcoal⁷.

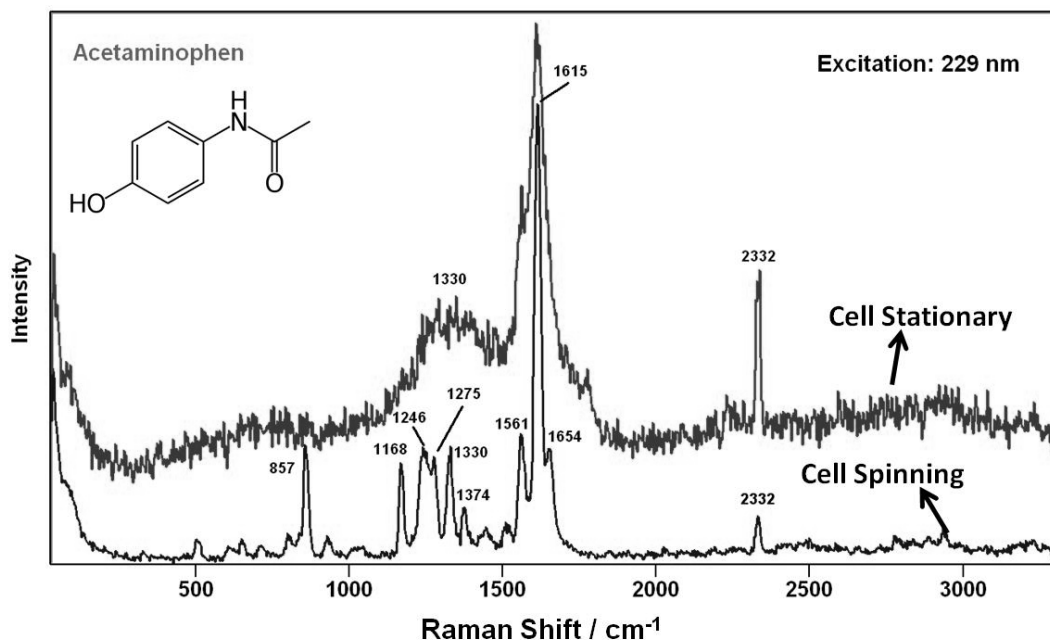


Figure 6. Raman spectra of acetaminophen acquired with the cell spinning and stationary.

It is difficult to imagine the photodegraded species resulting from the UVRR excitation. It probably mostly involves carbon since the functional groups have photolyzed into gaseous species. The most likely possibility is that the photochemical residue contains aromatic species with some sp^2 bonding. The Raman spectra of graphitic carbon species (mainly sp^2 bonded) show a strong dependence on factors such as the excitation wavelength and sample disorder.⁶ For graphitic carbon there are two characteristic bands, the G band at ~ 1630 and the D band at 1350 cm^{-1} .⁶ The intensity of the D band is known to vary dramatically with excitation wavelength and the amount of disorder.⁶ The D band also shows a significant frequency dependence on excitation wavelength.⁶ The strongest Raman bands of PAH such as pyrene and related molecules are observed at these frequencies.⁹ The fact that we see features approximately at the frequency regions of the D and G bands for HMX in Fig. 1 and TNT in Fig. 5 suggests structural similarities. We see a further evolution of HMX and RDX UVRR to a single broad feature similar to that of amorphous carbon^{4,5}.

The photochemistry results from cycling of these molecules through their excited states. From the solution absorption spectra³ we calculate 229 nm absorption cross sections of $\sim 10^{-16} \text{ cm}^2$ for HMX, RDX and TNT. Given the the illumination times and the excitation conditions used we can very, very roughly estimate that $\sim 5 \times 10^6$ photons are absorbed for every surface molecule of the solid samples. This indicates a photodegradation quantum yield of $< 10^{-6}$ (estimated, at best to within an order of magnitude).

4. CONCLUSIONS

We studied 229 nm UVRR and characterized the photodegradation of HMX, RDX, TNT and acetaminophen.

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