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Characterization of Raman Spectral Changes in Energetic Materials and Propellants During Heating

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Abstract

Raman spectroscopy has been shown to be a useful tool for characterizing neat crystalline explosive samples and for identifying principle components in many propellant and explosive formulations. Herein, we report recent measurements of Raman spectra of explosives and propellant formulations during bulk heating and recent measurements of laser heating of the samples during measurement of Raman spectra. The results of these measurements are important to investigators using Raman spectroscopy to measure vibrational spectra of burning propellant samples.

Acknowledgments

The authors would like to thank Dr. Jeffrey Morris (U.S. Army Research Laboratory [ARL]) for providing the RDX crystals used in this study, Dr. Richard Kranze for assistance in propellant sample preparation, and Drs. Betsy Rice and Cary Chabalowski for the normal-mode analysis of RDX. This work was performed while Dr. Nicholas F. Fell, Jr., held a National Research Council (NRC) ARL Research Associateship.

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1. Introduction

Raman spectroscopy has been demonstrated to be useful for the identification of energetic materials and the characterization of propellants [1–3]. Since the Raman spectrum of most solid materials exhibits less spectral overlap than for the corresponding infrared (IR) absorption spectrum, Raman spectroscopy is the method of choice for the characterization of structural changes in these materials during slow heating to the melting point. In addition, the lower sensitivity of Raman spectroscopy, relative to IR absorption spectroscopy, minimizes interference from gas-phase species generated during thermal decomposition. For RDX (cyclo-1,3,5-trimethylene-2,4,6-trinitramine) and RDX-based propellants, thermal decomposition begins below the melting point [4].

Raman spectra yield information about the lattice and internal vibrational modes of the sample. Changes in the Raman shifts of peaks measured during heating of the sample can be used to determine the effects of heating on the lattice and internal molecular vibrational parameters. For example, in a molecular crystal such as RDX, a Raman shift of a peak moving to lower frequency with heating may indicate that the vibrational motion giving rise to this spectral feature is less hindered sterically because of increases in the crystal lattice spacings.

In this paper, we describe the effects of slow, step-wise heating on Raman spectra of a crystal of RDX, a slice of XM39 gun propellant (76% RDX, 24% plasticizers and binders), and a small amount of the explosive C4 (94% RDX, 6% hydrocarbons) over the temperature range from 300 K to 453 K. The energetic materials literature contains many studies of heating to high temperatures, designed to simulate the conditions experienced during combustion events ranging from atmospheric pressure deflagration to weapons firing and explosion [5–12].

Typically, measurements of vibrational spectra of energetic materials during heating are undertaken to obtain experimental confirmation of the initial reactions and reaction products hypothesized to occur during thermal decomposition. We have chosen to investigate the changes in vibrational spectra, in both the peak positions and intensities, at temperatures below the decomposition point to obtain insight into physical changes occurring prior to thermal decomposition.

2. Experimental

The Raman spectra for this study were measured using three different systems. System one measured spectra using a Bomem DA-8.02 Fourier transform spectrometer with a backscattering Raman accessory. The incident, unpolarized (1,064 nm, 9,394 cm^{-1}) radiation was provided by a Quantronix Series 100 continuous wave Nd: YAG laser. Two holographic, Rayleigh rejection filters (Kaiser Optical) were placed in the optical train to reduce the amount of Rayleigh scattered radiation reaching the liquid-N_2-cooled InGaAs detector. The detector sensitivity range was from 6,500 cm^{-1} to 10,000 cm^{-1}. Because of using this system, we were unable to measure spectral features with a Raman shift greater than approximately 2,900 cm^{-1}. All spectra were collected using 400 mW of incident laser power for 256 scans at 4-cm^{-1} resolution.

System two used a visible laser with an output wavelength of 785 nm as the scattering source (SDL, Inc.). Laser radiation was delivered to and collected from the sample using a lens-coupled fiber optic probe, filtered after scattering using a holographic rejection filter (Kaiser Optical), spectrally resolved using a monochromator (ISA, Inc.), and detected using a charge coupled device (CCD) camera (Princeton Instruments). Effective resolution was approximately 8 cm^{-1}. System three used a visible laser (Lexel Model 95 Argon ion laser) with an output wavelength of 514.5 nm. A linear diode array detector (EG&G Model 1455 intensified linear diode array) was used to detect the Raman-shifted radiation. The diode array detector consisted of 1,024 elements, of which the center 700 were intensified. A holographic Rayleigh rejection filter (Kaiser Optical) was also used with this system. The Raman scattered light was collected in a backscattering geometry. All spectra collected with this system were the result of averaging 100 one-second integrations on the array using 500 mW of incident, unpolarized 514.5-nm radiation as the scattering source. The use of a 150-µ entrance slit on the monochromator resulted in a spectral resolution of 12–18 cm^{-1}. The diode array was calibrated for Raman shift from previously reported values for RDX at room temperature [13, 14]. All spectra displayed here were used without further correction.

For the experiments reported here using systems one and three, samples were placed in a heated aluminum cell, which was designed and built in-house. The cell (Figure 1) was conductively heated using a resistive cartridge heater embedded in the cell body. A Pt/Pt-10% Rh thermocouple was used to monitor the temperature and provided feedback to one of the two controllers used in these experiments (Omega Model CN2002 K-A-AT or Valco Instrument Co., Inc. Model ITC).

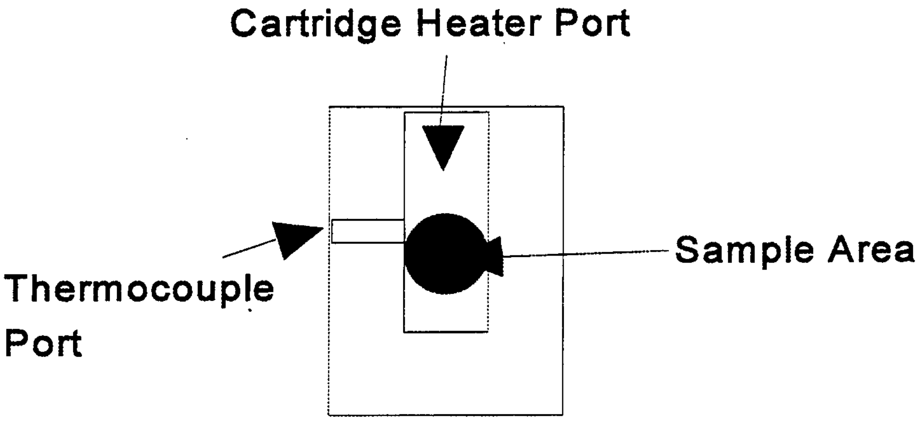


Figure 1. Heatable Aluminum Sample Cell.

The energetic materials examined included an RDX crystal (the RDX crystals were recrystallized from an acetone/ethanol solution), a thin slice of XM39 (a solid gun propellant), and a small (several milligram) sample of C4 explosive. XM39 contains 76% RDX, 12% cellulose acetate butyrate, 4% nitrocellulose, 7.6% acetyl triethyl citrate, and 0.4% ethyl centralite. C4 is a plastic explosive composed of 94% RDX and 6% oil/polymer binder. All energetic materials and compositions used in this study were obtained from in-house sources.

The experimental procedure was as follows. The sample was placed in the heatable cell. The heatable cell position was optimized by maximizing the Raman signal at room temperature. The sample cell temperature was then increased in steps of 10–20 K up to the onset of sample melting (usually evidenced by large increases in detector output voltage, since RDX melts with decomposition and heat release swamps the detector). After the temperature equilibrated at each step value (~60-s soak), a Raman spectrum was collected. The process was continued until the sample melted or began to decompose prior to melting (usually evidenced by discoloration).

3. Results

A room temperature Raman spectrum (100 cm^{-1} to 1,600 cm^{-1}) of a single crystal of RDX (typical size 2 × 3 × 1 mm), with general band assignments, is shown in Figure 2. The inset shows the chemical structure of a single molecule of RDX. A normal-mode analysis [15] employing the density functional theory on an isolated RDX molecule yields frequencies in close agreement with the values observed in the room-temperature spectrum of the crystal, indicating that over the Raman-shift frequency range studied here, measured spectral features are attributable to internal molecular vibrations. Raman spectra of an RDX crystal, RDX powder, XM39, and C4, measured as a function of temperature, are shown in Figures 3 and 4. From these figures, two effects may be noticed. First, as temperature is increased, the intensity of Raman-shifted radiation decreases. Second, less apparent, is the dependence on temperature of the Raman shift of some spectral features.

Figure 5 shows the changes in Raman shifts of individual peaks as a function of temperature for a single crystal of RDX. As has been shown previously [1, 2], Raman spectra of nitramine-based energetic materials are dominated by features due to molecular vibrations of the crystalline components. Therefore, measured peak shifts are similar in all four samples; so, only changes for the RDX crystal are shown here. The Raman peak observed to change frequency with increasing temperature to an extent significantly greater than others is the peak near a shift of 150 cm^{-1}. This peak was not predicted by a normal-mode analysis of a single RDX molecule [15]. Because of the significant temperature dependence of the Raman shift and because this vibrational frequency was not predicted by the single RDX molecule normal-mode analysis, we believe this peak is due to a lattice vibration or combination of lower frequency internal and lattice vibrations. Significant temperature dependence of lattice-type modes in RDX have been measured by previous

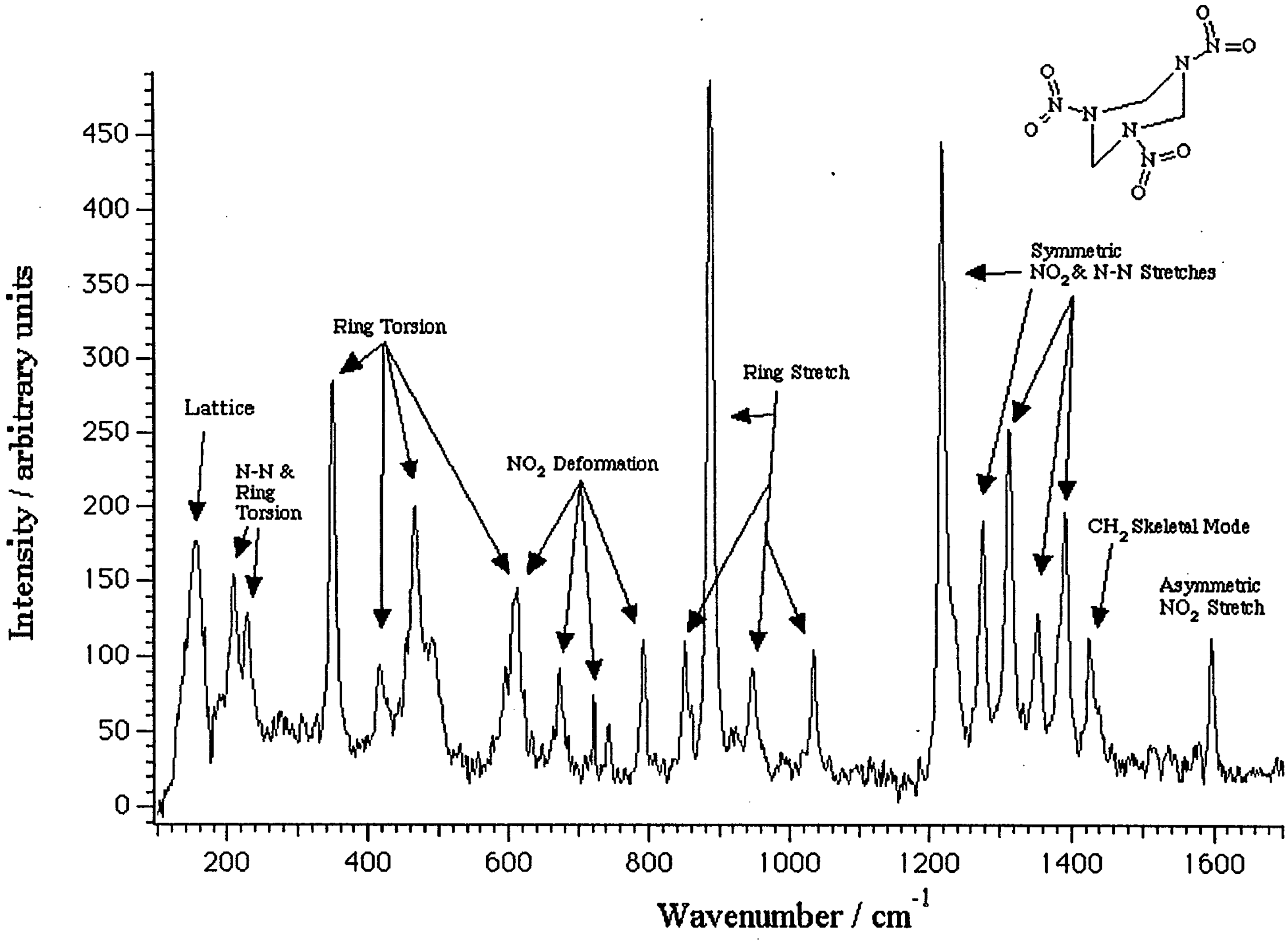
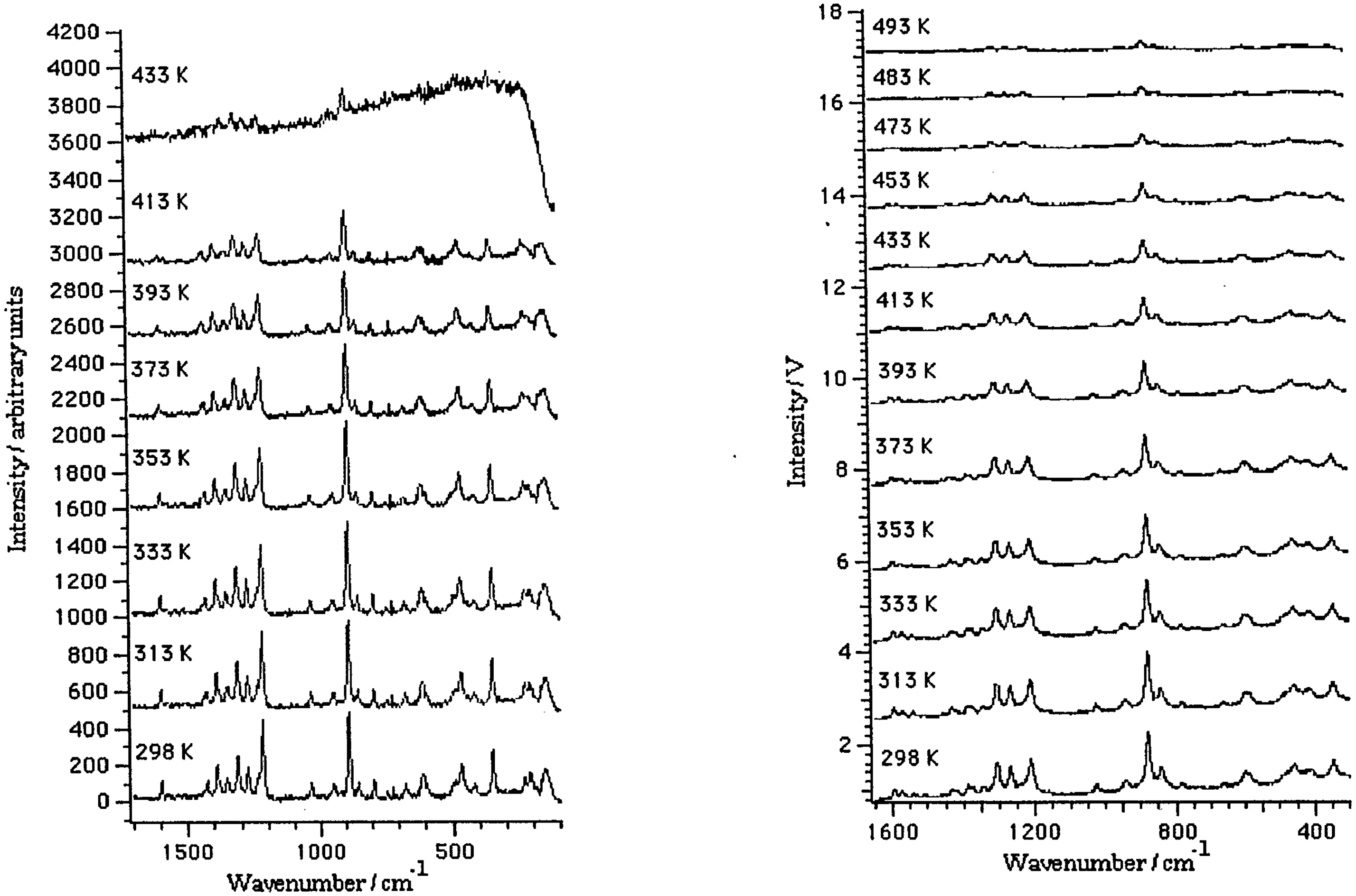


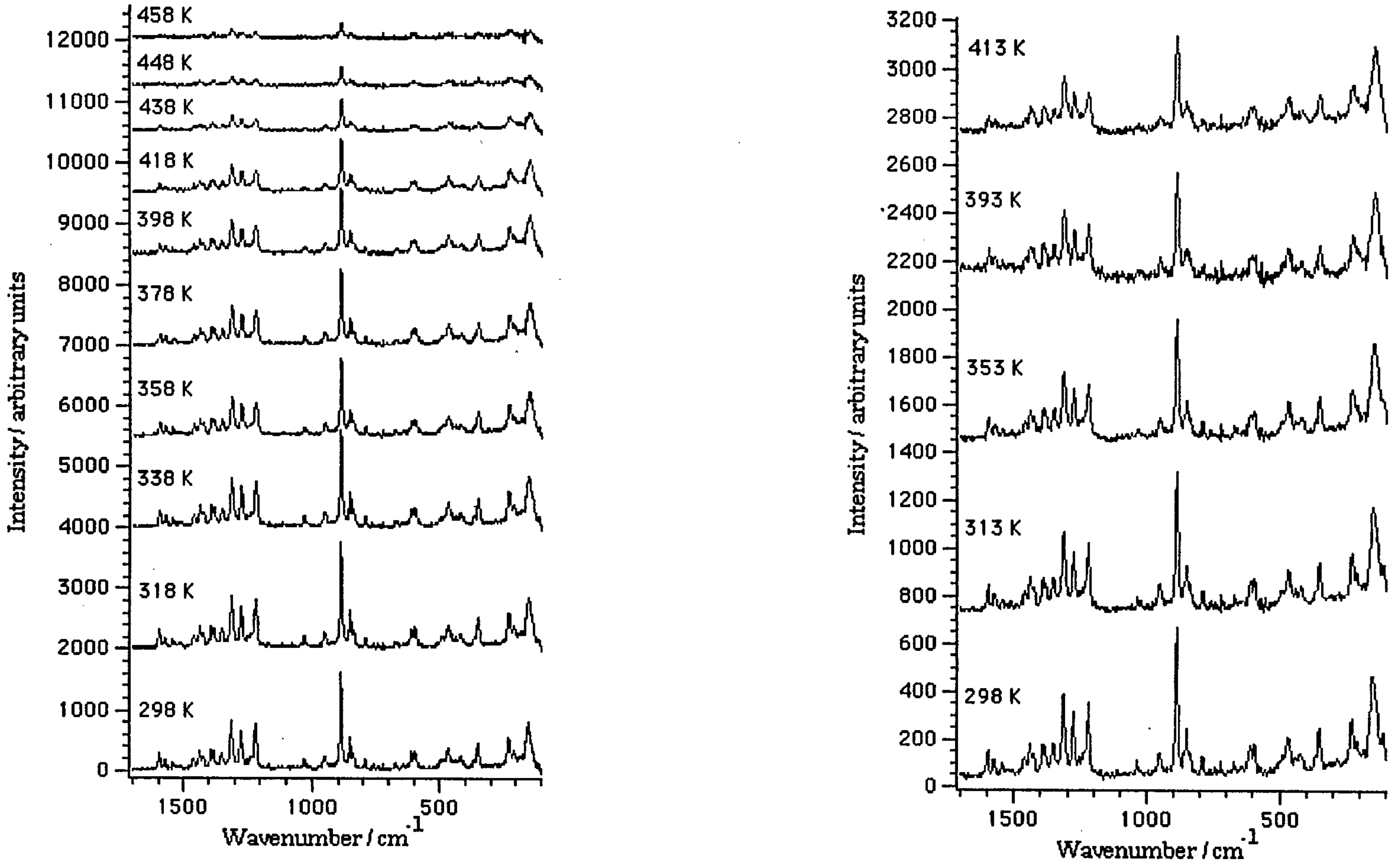
Figure 2. Raman Spectrum of RDX Crystal at 298 K. Inset: Structure of RDX Molecule.



A) RDX Crystal

B) RDX Powder

Figure 3. Raman Spectra as a Function of Temperature.



A) XM39

B) C4

Figure 4. Raman Spectra as a Function of Temperature: (a) XM39 Propellant and (b) C4 Explosive, NIR FTR System.

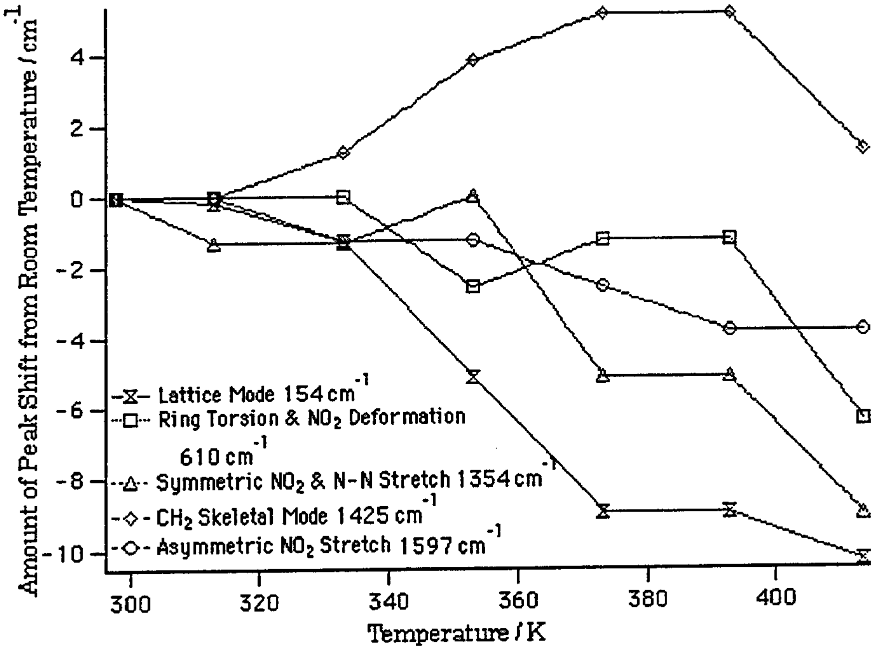


Figure 5. Raman Peak Shifts With Heating for RDX Crystal.

investigators [16]. Spectra of the four samples from 2,800 to 3,500 cm^{-1} show no significant changes in Raman shifts of individual peaks with increasing temperature and are not displayed here.

The most apparent change in the elevated temperature spectra shown in Figures 3 and 4 is a general decrease in Raman intensity as the temperature is increased. In addition to the general decrease in Raman intensity with increasing temperature, there is also a noticeable variation in relative Raman peak intensity with increasing temperature. This may be indicative of a loss of order in the crystal [13]. When the samples were allowed to return to room temperature following heating and the Raman spectrum was remeasured, overall Raman signal and relative peak intensity were similar to spectra measured prior to heating; although, for all samples measured, the final (after heating) Raman signal level was slightly less than the Raman signal level measured prior to heating.

Because reported temperatures are those of the sample holder, several measurements were made to ascertain whether the sample was being heated by the probe laser to temperatures higher than that of the sample holder. Two different experiments were conducted to measure heating in the vicinity of the laser spot. In the first experiment, the Raman spectrum of a 0.3-mm-thick by 6.5-mm-diameter slice of unperforated XM39 propellant (76% RDX) was measured using system two (laser radiation at 785 nm as the scattering source). For this experiment, the sample was not resistively heated. The incident power was approximately 0.2 W. A K-type thermocouple, coated with heat-conducting paste, was positioned at various locations on the slice of propellant. Observed temperature increases ranged from 6 K when the thermocouple was positioned on the side opposite of the laser spot to 11 K when the thermocouple was positioned directly in the laser spot.

A second experiment used an RDX crystal placed in the heated sample holder (see Figure 3) and a Pt/Pt-10%Rh thermocouple (diameter = 0.1 mm) was placed on the surface of the crystal. A microscope cover slide was then placed on top of this assembly, pressing the thermocouple junction against the face of the crystal, and secured using a cover plate designed for this purpose. The Raman spectrum of the single crystal was then measured using 400 mW of continuous laser radiation at 1.06 µ. During these experiments, the temperature of the cell holding the RDX crystal was slowly increased. The measured temperature increases due to laser heating ranged from 6 K to 19 K. As with the experiments using visible radiation as the scattering source, the greatest temperature increase from laser heating was measured when the thermocouple was placed directly in the laser spot. Also, it was observed that as the bulk (sample holder) temperature was increased; for a given laser power, the magnitude of laser heating increased. For samples heated within 30 K of the melting point of RDX (478K), exposure to laser radiation usually caused melting/decomposition. Formulated RDX (i.e., C4, XM39) typically melted/decomposed at a lower bulk temperature than neat RDX, presumably because the formulation ingredients bring about a melting-point depression of RDX.

4. Discussion

Since the change in Raman shift frequency with temperature has been reported previously [16], the discussion section focuses on the observed changes in Raman intensity. There are a number of possible explanations for the observed decrease of Raman signal intensity with increasing temperature. Several of these are discussed.

4.1 Laser Heating. Laser heating of RDX can result in sample sublimation, melting, and chemical decomposition. Any of these will cause less sample to be available for scattering and result in decreased Raman signal intensity. The temperature increase at the sample surface due to laser heating may be approximated by [17]:

$$T_{surface} = E_0\, \alpha(1 - R)/\rho AC, \tag{1}$$

where E_0 is the incident laser energy, R is the reflectivity of RDX at the laser frequency, α is the absorption coefficient of RDX at the laser frequency, ρ is density of RDX, A is the area of the laser spot, and C is the heat capacity of RDX. For incident radiation at a wavelength of 1,064 nm (9394 cm^{-1}), α is approximately 20 cm^{-1}, and R is approximately 0.90 [18]. For a 1-s exposure, laser spot size approximately 0.5 mm in diameter, using a 400-mW incident beam, this corresponds to a temperature increase of approximately 4.5 K. Longer sample exposure, smaller laser spot size, and/or increased laser power will cause greater heating.

For the experiments reported here, in which the sample is continuously exposed to the scattering laser radiation, laser heating effects may be an important contributor to decreases in measured Raman signal intensity with increasing temperature. To determine if sample in the laser-scattering volume was removed by sublimation or melting, or by decomposition, measurements of Raman spectra of each of the samples were made after the sample had returned to room temperature. In each case studied, the Raman signal intensity returned to near preheating levels when the sample was allowed to cool. This indicates that removal of material from the scattering volume by laser heating is not entirely responsible for the observed signal decrease.

Additionally, the temperature of the sample holder for a set of experiments was compared to the temperature calculated from the Raman anti-Stokes/Stokes intensity ratio of the peak near 345 cm^{-1} for Raman spectra of a single crystal of RDX measured using radiation at a wavelength of 1064 nm as the scattering source. The temperature of the sample can be determined from the ratio of the anti-Stokes Raman intensity, I_{as}, and the Raman Stokes intensity, I_s, as described in equation (2):

$$I_{as}/I_s = (\nu_L + \nu_i)^4/(\nu_L - \nu_i)^4 \exp(-hc\nu/kT). \tag{2}$$

Here, ν_L is the laser frequency, ν_i is the frequency of the vibration, h is Planck's constant, c is the speed of light, k is the Boltzman constant, and T is the temperature [19]. The results of these calculations are shown in Table 1. The sudden jump in calculated temperature above 393 K is interesting because it may suggest the bulk temperature, for this experimental setup, at which laser heating becomes important.

Table 1. Measured Temperatures and Temperatures Calculated From the Raman Anti-Stokes/Stokes Intensity Ratio From Equation (2) (Error Is Estimated at ±10%)

Thermocouple Temperature (K)	Anti-Stokes/Stokes Intensity Ratio	Calculated Temperature	Percent Difference From Measured (%)
298.0	0.2091	267.2	-10.34
313.0	0.2354	285.3	-8.850
333.0	0.2472	293.6	-11.83
353.0	0.2641	305.5	-13.46
373.0	0.2696	309.4	-17.05
393.0	0.3763	390.6	0.6107
413.0	0.4166	424.5	2.785
433.0	0.4176	425.5	-1.732

4.2 Laser Damage. Laser radiation may cause sample surface ablation and sample cracking that can result in decreased signal intensity. To check for laser damage to the sample, single crystals of RDX were examined after several series of experiments conducted at room temperature. No visible damage (checked with an optical microscope) could be detected. Additionally, spectra of single crystals exposed to 400 mW of laser radiation at 1.06 μ for several hours at room temperature exhibited no change in Raman intensity.

4.3 Increased Rayleigh Scatter. An increase in Rayleigh scatter, brought about by temperature-induced changes in sample surface morphology (e.g., increase in the reflectivity of the sample surface) will result in decreased Raman signal intensity. An increase in the Rayleigh scatter reduces the amount of laser light available for the inelastic scattering process. No attempts were made to measure changes in Rayleigh scatter with increasing temperature.

4.4 Density Changes. Since a possible explanation for the change in frequency with increasing temperature of the Raman peak near 150 cm^{-1} is an increase in the crystal lattice spacing, a decrease in the density of the scattering material may contribute to the decrease in overall signal intensity with increasing temperature. This decrease in the number density of scattering molecules would decrease the Raman intensity. In the case of naphthalene [20], a molecular crystal, the density decreases from 1.0253 g/cm^3 at 293 K to 0.9625 g/cm^3 at 373 K or 6.125%. A similar degree of density change might be expected for RDX and RDX-containing compositions. Equation (3) describes the Raman intensity (I) as a function of laser power (E^2) and scatterer density (N). Laser power and scatterer density are functions of depth (z) within the sample.

$$I = \int_0^d K\, E^2(z)\, N(z)\, d. \qquad (3)$$

The constant K includes the Raman cross section and geometric and instrumental factors. Figure 6 shows the Raman spectrum of naphthalene measured from room temperature to 358 K. The observed decrease in Raman signal intensity for naphthalene heated from room temperature to 358 K is larger than that predicted using equation (3).

4.5 Population Change. As temperature is increased, the population of higher vibrational states increases, thus decreasing the population of the $v = 0$ state from which most Stokes Raman scattering is generated. This would be seen experimentally by an increase in the ratio of the anti-Stokes Raman intensity (I_{as}) to the Stokes Raman intensity (I_s). From Table 1, over the temperature range studied, the I_{as}/I_s ratio increased for the 345-cm^{-1} line in the RDX crystal by a factor of 2. The Stokes signal intensity decreased continuously while the anti-Stokes Raman signal intensity initially increased, but later decreased along with the Stokes signal. If an increase in the population of higher vibrational

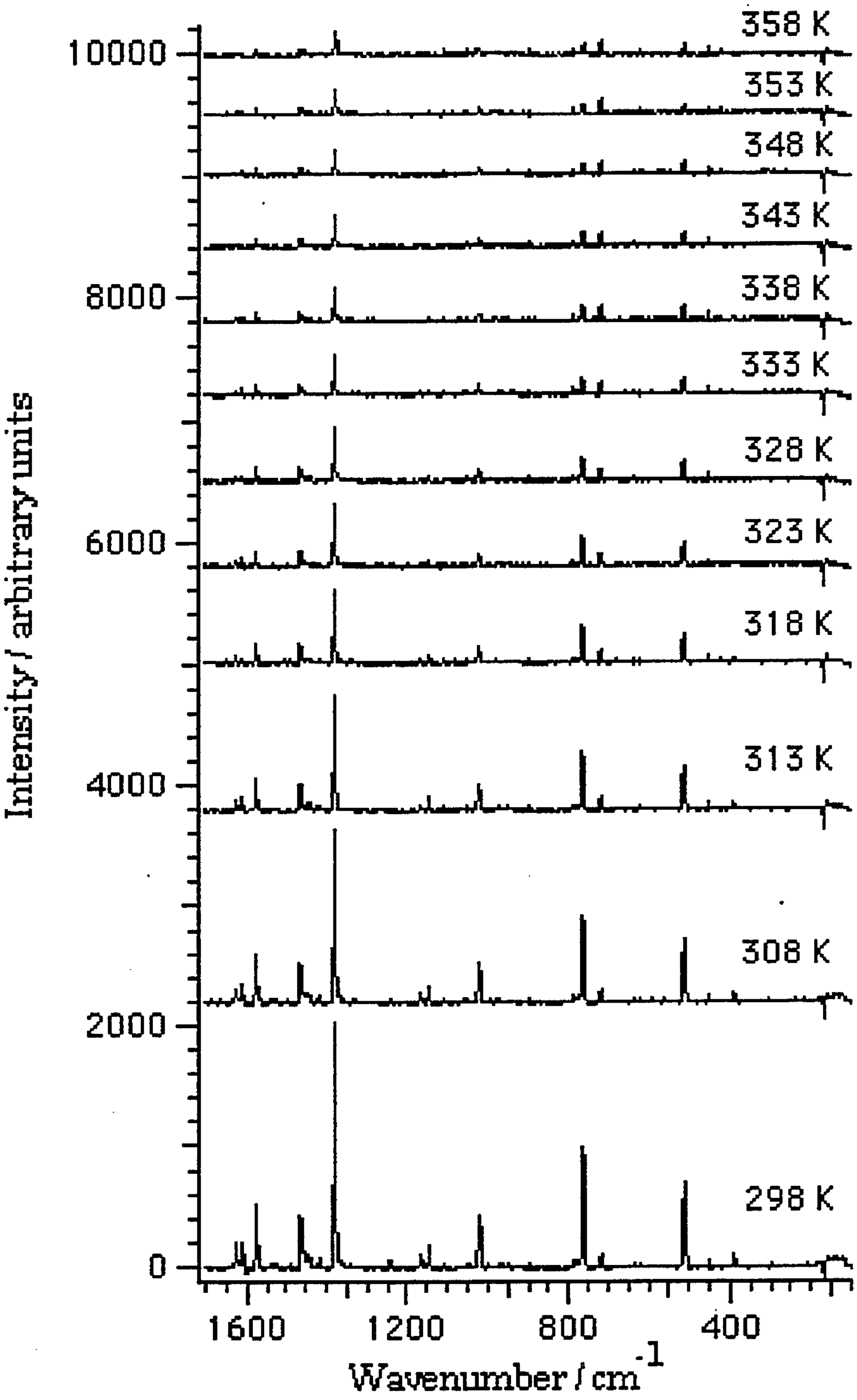


Figure 6. Raman Spectra of Naphthalene at Elevated Temperatures.

states was solely responsible for the decreased Stokes signal intensity, the anti-Stokes signal should not decrease over the temperature range studied.

4.6 Changes in Refractive Index. A change in the refractive index and transparency with increasing temperature may change the focal point of the laser radiation incident on the sample and thus move the source of the Raman signal out of focus with the entrance slit of the monochromator or the interferometer. To investigate this, at each temperature at which spectra were measured, a Raman spectrum of naphthalene was measured, then the sample position was reoptimized to obtain the maximum Raman signal, and a second Raman spectrum was collected. The results of this experiment for a range of temperatures from 313 to 373 K and only showing the Raman spectra of naphthalene after the refocusing of the sample position are shown in Figure 7. The repositioning of the sample improves, but does not restore the signal intensity to its previous level.

4.7 Premelt-Phase Transition. A premelt-phase transition may give rise to a decrease in observed Raman signal intensity with heating. Hexahydro-1,3,5-trinitroso-s-triazine (TRDX), the nitroso analog of RDX, exhibits a premelt-phase transition [21]. This type of transition may be accompanied by a decrease in the density and therefore the Raman signal. Measurements using a differential scanning calorimeter (DSC) of RDX from 300 K to 477 K did not detect such a premelt-phase transition.

4.8 Fluorescence. No measurable fluorescence signal was observed for any experiments using laser radiation at 1.06 μ as the scattering source. When laser radiation at 532 nm was used as the scattering source, a small fluorescence signal was always observed. The intensity of the fluorescence signal did not exhibit a noticeable temperature dependence.

4.9 Incandescence. For the temperature range studied in these experiments, measurable incandescence should occur only when laser heating causes the sample to combust. Since RDX melts with decomposition, there is considerable heating and gas evolution when the sample temperature reaches 477 K. Spectra of single crystals of RDX measured at the melting point using laser radiation

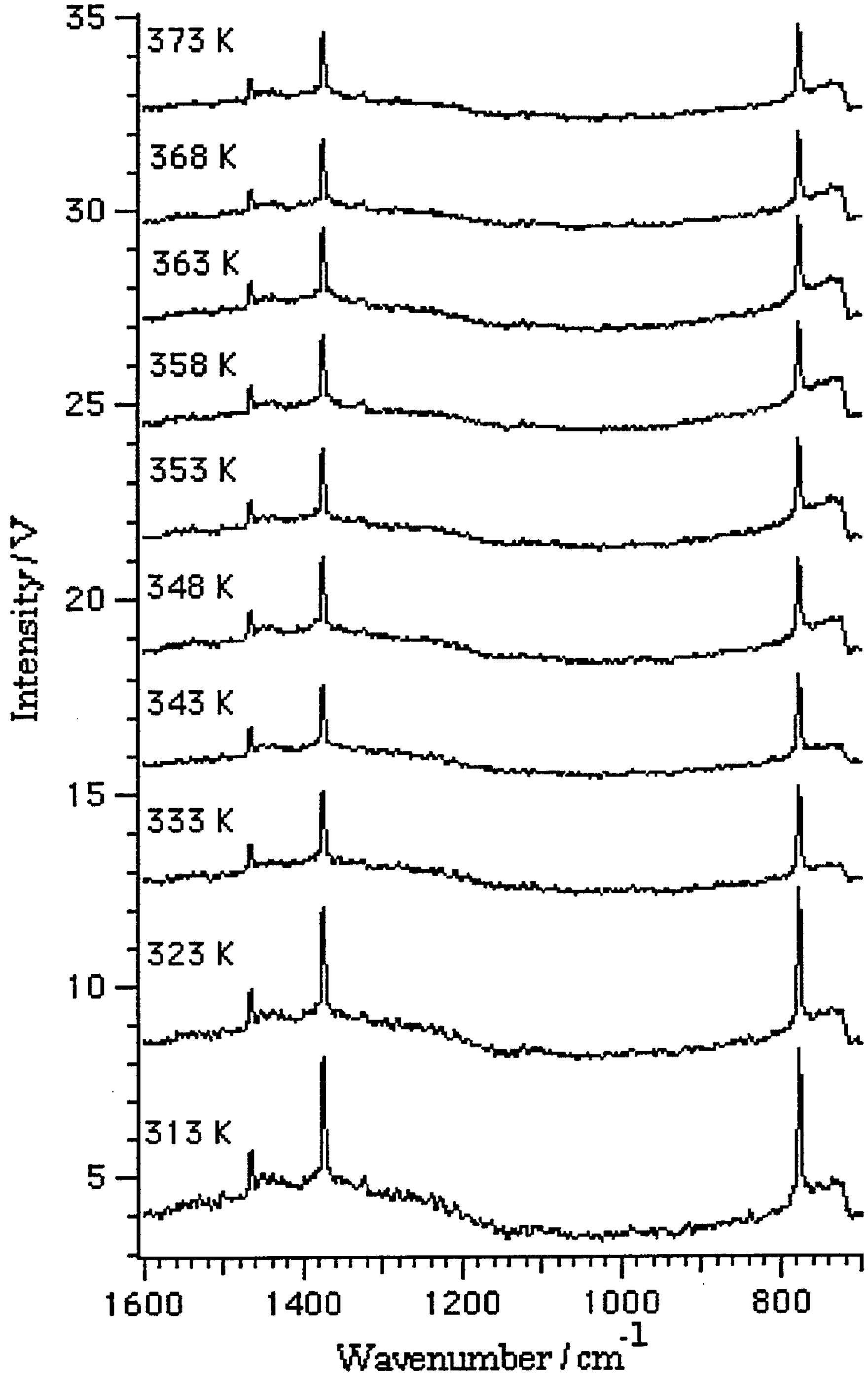


Figure 7. Raman Spectra of Naphthalene From 313 K to 373 K. Each Spectrum Shown Was Collected After the Sample Position Was Optimized After the Temperature Equilibrated at the Elevated Temperature.

at 1064 nm as the scattering source show increased background intensity beginning near a shift of 2700 cm^{-1} and increasing in the direction of greater Raman shift.

Incandescence intensity may be approximated as radiation from a blackbody. The peak in incandescence intensity near the melting point of RDX occurs at a wavelength of approximately 5,800 nm. So, when using 1,064-nm laser radiation as the scattering source, it is possible to have incandescence interferences at wavelengths corresponding to large Raman shifts typical of the C-H vibration (~3,000 cm^{-1}). However, we saw no indication of intensity from incandescence at Raman shifts between 100 cm^{-1} and 1,600 cm^{-1}. Potential interferences from incandescence may be almost entirely avoided by use of visible laser radiation as the scattering source.

5. Conclusions

The changes in Raman peak intensities and frequencies with increasing temperature have been examined to determine if any insight may be gained into the physical changes in RDX prior to the onset of thermal decomposition. The measured peak shifts are indicative of an increase in the lattice spacing in RDX during heating, eventually leading to loss of crystallinity (melting). These experiments have also shown a decrease in the Raman intensity as the temperature increases. It is not clear if the observed decrease in Raman intensity is due to the measuring method (laser vaporization/sublimation of sample from the scattering volume) or is caused in part by changes in the scattering cross section with increasing temperature. Results from experiments presented here indicate that sample heating by the probe laser may be an important contributor to the observed decrease in signal intensity. For RDX, sample heating is greater for laser-scattering radiation at a wavelength of 1,064 nm than for laser-scattering radiation at 514 nm. The sample heating becomes more important as the bulk sample temperature is increased. At bulk sample temperatures near the melting point of RDX, laser heating can cause the sample to undergo sublimation, melting, and/or chemical reaction. Because temperatures calculated using the Stokes/anti-Stokes ratio are in reasonable agreement with bulk temperatures, and because most of the Raman signal intensity returns when the sample is cooled, laser heating alone does not seem to be responsible for the observed decrease in Raman signal intensity with increasing temperature.

Several other factors that contribute to the decrease in observed Raman signal intensity with increasing temperature have been discussed. The decrease in Raman signal intensity with increasing temperature probably has contributions from each of these factors. In rough order of decreasing importance for experiments described in this report, the factors contributing to the decrease in Raman signal intensity with increasing sample temperature are laser sample heating, density changes, population changes, and changes in refractive index and reflectivity. To minimize problems associated with laser heating, the use of a low-power visible scattering source is recommended. Finally, to minimize sample exposure to scattering radiation for spectra of burning or elevated temperature samples, a pulsed-laser source should minimize many of the factors affecting Raman signal decrease with increasing sample temperature.

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Raman spectroscopy has been shown to be a useful tool for characterizing neat crystalline explosive samples and for identifying principle components in many propellant and explosive formulations. Herein, we report recent measurements of Raman spectra of explosives and propellant formulations during bulk heating and recent measurements of laser heating of the samples during measurement of Raman spectra. The results of these measurements are important to investigators using Raman spectroscopy to measure vibrational spectra of burning propellant samples.

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