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Investigation of Ambient and High Temperature Aging of PETN by Laser Induced Fluorescence and Ultraviolet Absorption Spectroscopies

Larry R. Dosser and Carl J. Seliskar*

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*University of Cincinnati

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Abstract

The chemical aging of pentaerythritol tetranitrate (PETN) has been and continues to be an important problem in producing and maintaining high energy compounds and components. The work done to date has identified several key concerns in evaluating the chemical and physical aging processes of PETN. These include the manner in which a particular type of PETN is prepared, the sample preparation procedure insofar as it can influence the adsorbed species on the solid PETN, and the methods of measurement and their influence on the quantitative determination on the gaseous decomposition products. In the work reported here, two noninvasive spectroscopic methods of measurement were chosen: laser induced fluorescence, which was used to monitor NO_2, and ultraviolet spectroscopy, which was used to monitor NO. A unique sample vessel design permitted both measurements to be made on the sample, and these two species could readily be measured in the presence of one another. Adsorbed NO_2, and its subsequent reaction to yield NO, was detected. Three types of PETN samples were aged at elevated temperatures, and varying amounts of NO and NO_2 were detected, depending on the sample and the method of preparation. The results indicate that an in situ experiment is necessary to further investigate PETN aging.

Introduction

The chemical aging of pentaerythritol tetranitrate (PETN) has been and continues to be an important problem in producing and maintaining high energy compounds. Historically, numerous investigations have documented the evolution of gaseous decomposition products as a result of thermally induced (i.e., accelerated) aging [1–7]. Some general agreement may be found in the results of such studies, although the disagreement among certain detailed results clearly requires that further investigations be performed.

In brief, the early work of Rideal and Robertson suggested the following overall thermal decomposition reaction for gaseous products [1]:

$$\text{PETN} = 0.52\ NO_2 + 2.11\ NO + 0.42\ N_2O + 0.28\ CO_2 + 0.93\ CO + 0.09\ H_2 + \text{formaldehyde} + \text{residue}$$

Ng, Field, and Hauser, in an important early study, examined the decomposition of a thermally aged single crystal of PETN at temperatures below the melting point (141°C) [2]. Using conventional time-of-flight mass spectrometry and a direct inlet source chamber for thermal aging, these investigators found prominent mass peaks at m/e values of 18, 28, 29, 30, 44, and 46 corresponding to parent ions of the gaseous products H_2O, N_2, CO, H_2CO, NO, CO_2, N_2O, and NO_2. These studies showed that, at aging temperatures of less than 141°C, the major mass peak (m/e = 30) is that of the NO molecule, whereas at higher temperatures the chemical decomposition reaction apparently changes substantially and produces large amounts of H_2O (mass 18) and N_2 and CO (nominal mass 28). Thus, this investigation appeared to establish a clear difference between chemical aging at near ambient temperatures and accelerated thermal aging at high temperatures.

In work done by Volltrauer, PETN (powder form) was examined over the temperature range 326–393 K (53–120°C) using a considerably different experimental procedure [3,4]. The chemiluminescent reaction of PETN product gases NO_X ($x = 1,2$) with ozone during the heating of PETN in a continuous flow system was monitored. The results of this study were conditioned by an inability to distinguish between the various nitrogen oxides released. In spite of this shortcoming, the results clearly showed that PETN samples can have significant and even large amounts of adsorbed nitrogen oxides, which are desorbed with a small activation energy (about 15 kcal/mole). Furthermore, a single activation energy of about 33–36 kcal/mole was found to describe the evolution of NO_X from the thermochemical decomposition of PETN.

Miller, Haws, and Dinegar also examined the gaseous decomposition of thermally aged PETN, and they reported a variety of activation energies for the principal decomposition products N_2O, H_2O, CO_2, N_2, CO, and ($NO + NO_2$) [5]. In brief, they reported that N_2O and H_2O release is described by an activation energy of 50–56 kcal/mole over the temperature region 363–408 K (90–135°C), whereas the activation energies for products CO_2, N_2, and CO change from low values (7.1, 7.6, 19.9, respectively) at 373 K to high values (64.9, 65.7, 71.1, respectively) for higher temperatures ($373 \text{ K} < T < 408 \text{ K}$).

Recently, Dosser reported that it was feasible to examine the evolution of NO_2 and NO in situ by recording the laser induced fluorescence (LIF) spectrum of these molecules [6]. The technique was found to be extremely sensitive for measuring trace amounts of these gases. The work described in this report is an extension of the preliminary study and further illustrates the value of spectroscopic techniques for independent analysis of gaseous decomposition products.

The reports on the aging of PETN appear to be consistent regarding the evolution of the principal gaseous products NO, NO_2, CO, N_2, N_2O, and CO_2. Nonetheless, the activation energies for the decomposition reaction(s) of PETN are in serious disagreement. The method of measurement and the method of sample preparation appear to have influenced the results obtained thus far. In the reports to date, it is not clear that each study began with measurements on equivalent material; indeed, one study began with a high vacuum pumped single crystal [2], whereas another began with a powder precipitate [5]. If, as suggested by Volltrauer [3,4], surface adsorption is significant for the nitrogen oxides, as it certainly must be for adsorbed water vapor, the method of PETN sample preparation must have been a crucial determinant in the reported results.

The complexity of multicomponent chemical systems resulting from the decomposition of nitric acid esters of organic compounds was recently reviewed by Druet and Asselin [7]. In this review, they pointed out that such chemical aging systems typically contain NO_2, which serves an autocatalytic role in the further decomposition reactions. Other principal decomposition products such as NO, CO, and CO_2 may be chemical reagents in a complex multiequilibrium network of reactions which can be changed by invasive measurements of products. In addition, the presence of water in such a system changes the chemistry dramatically by producing a complex mixture of the well-known oxyacids of nitrogen [8].

The work done to date identifies several key concerns in studying the chemical and physical aging processes of PETN. These concerns include the following:

1. The preparation, chemical and physical homogeneity, and chemical definition of the PETN samples studied.
2. The sample preparation procedure insofar as it can influence the adsorbed species on solid PETN and the decomposition of PETN vapor over the solid sample.
3. The method(s) of measurement and its (their) influence on the outcome of the attempted chemical speciation of the gaseous products of the decomposition of PETN.
4. The need for a matrix of measurement methods which together can begin to untangle the complex chemistry and physics of ambient PETN aging.

In the work reported here, the combination of LIF and ultraviolet (UV) spectroscopies permitted the quantitative, independent determination of NO and NO_2 in the presence of each other. This represents the first time these spectroscopies have been applied in such a manner to the complex PETN aging problem. The spectroscopic investigation, as well as the development of a precise sample handling protocol, is an excellent beginning for addressing the four major concerns enumerated above.

Physical Methods of Measurement

As discussed in the Introduction, two noninvasive spectroscopic methods of measurement were chosen: LIF and UV absorption spectroscopies. Both methods were applied at specified intervals to PETN samples during the aging process, as described in detail in the following sections of this report. These methods were used to unambiguously monitor the presence and time variations of selected chemical species. A brief general discussion of each is given below.

Ultraviolet Absorption Spectroscopy

PETN decomposition product molecules NO and NO_2 have characteristic sharp absorption spectra, which allows quantitative identification by simple absorption spectroscopy. To illustrate this point, Figures 1 and 2 show the spectra of NO and NO_2, respectively. Portions of these spectra were used to identify and quantify the amount of these molecules at relatively

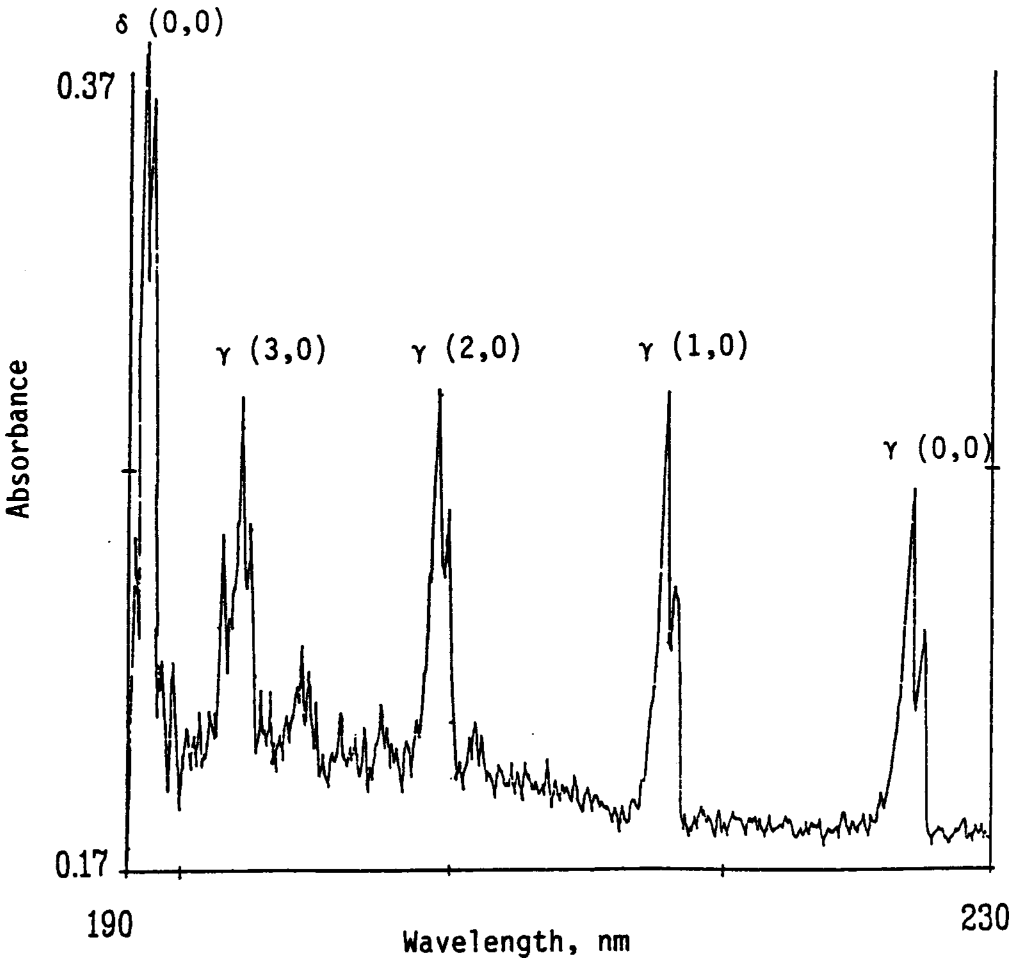


Figure 1 – Ultraviolet absorbance spectrum of 12.3 torr NO (10–mm pathlength). Spectroscopic assignments are shown in the figure for the gamma and delta systems.

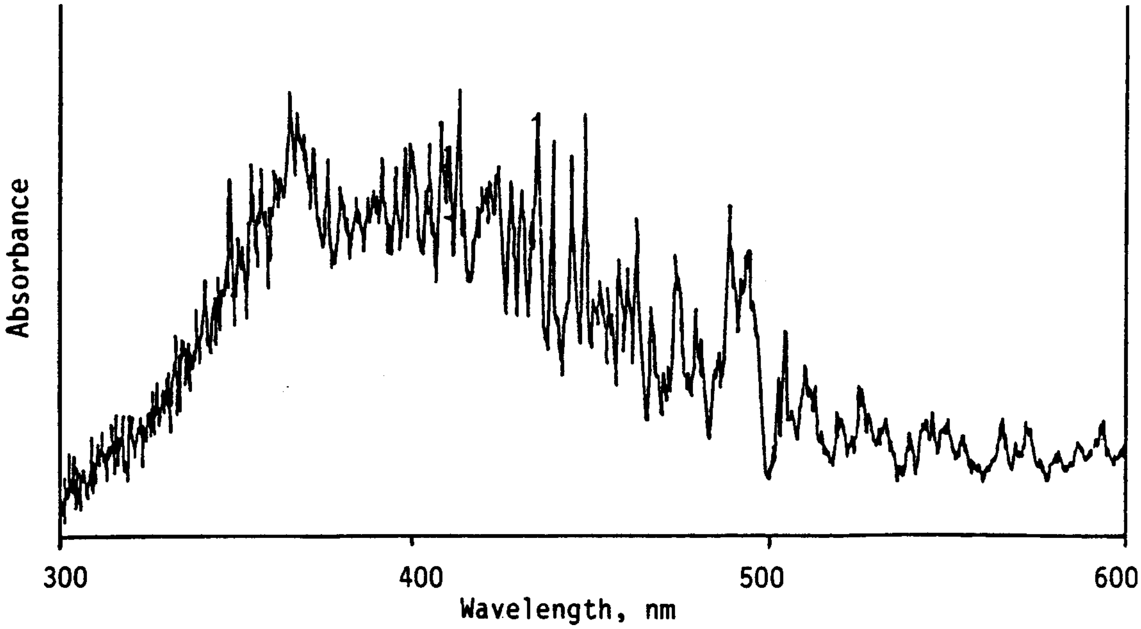


Figure 2 – Visible absorbance spectrum of NO_2 taken with a 10–mm pathlength.

high concentrations in samples of decomposing PETN. Solid PETN, or what appeared to be PETN, adsorbed to the quartz optical sample cell could also be measured by UV absorption. No attempt was made to quantify the adsorbed PETN-like materials on the quartz cell walls. However, it would be possible to do this if necessary.

LIF of NO_2

LIF of molecules in the gas phase is a sensitive technique to quantify molecules at low concentrations [9]. In the case of NO_2, the laser excitation can be easily achieved throughout the entire visible region of the spectrum [10]. Fluorescence (or, more properly, resonance fluorescence) can then be monitored at wavelengths to the red of the excitation wavelength [9,10]. It is essential to demonstrate in such an experiment that this process is a result of the absorption of one laser photon. Multiphoton processes could cause such undesirable processes as ionization or chemical fragmentation of the molecule and, therefore, a nonlinear response to laser intensity. Figure 3 shows LIF signal as a function of laser pulse energy. The plot is clearly linear and illustrates that the LIF of NO_2 is indeed a one-photon process under the experimental conditions.

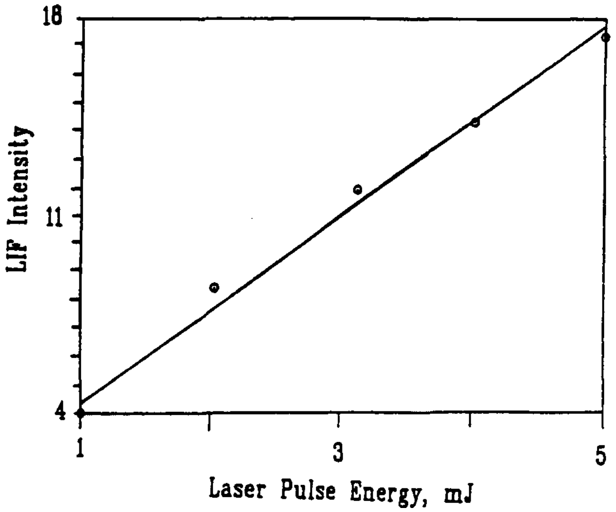


Figure 3 - LIF intensity as a function of laser pulse energy at 570.7 nm for an NO_2 pressure of 108 mtorr. The solid line represents the least squares fit ($R^2 = 0.99$).

In the experiments reported, two excitation wavelengths were chosen for the LIF of NO_2. The first was selected on the basis of convenience and consisted of using the second harmonic of the Nd:YAG laser at 532 nm, as done by Dosser [6]. The NO_2 absorption spectrum in this region is shown in Figure 4a, with the position of the laser wavelength indicated. The second laser wavelength was chosen in an attempt to minimize the "continuum component" of the fluorescence. The wavelength was generated with a tunable dye laser that was pumped with the second harmonic of the Nd:YAG laser. The dye laser was tuned to a strong isolated absorption maximum at 570.7 nm, as shown in Figure 4b. The resulting LIF dispersed fluorescence spectrum is shown in Figure 5, where the characteristic fluorescence bands of NO_2 can be clearly seen.

It is generally known that certain foreign gases can collisionally redistribute the discrete fluorescence of the NO_2 molecule even when such collisions are nonreactive. It is also known that foreign gases can modify the proportion of discrete to continuum emission in NO_2. Thus, experiments were performed to ascertain the magnitude of this effect under the present

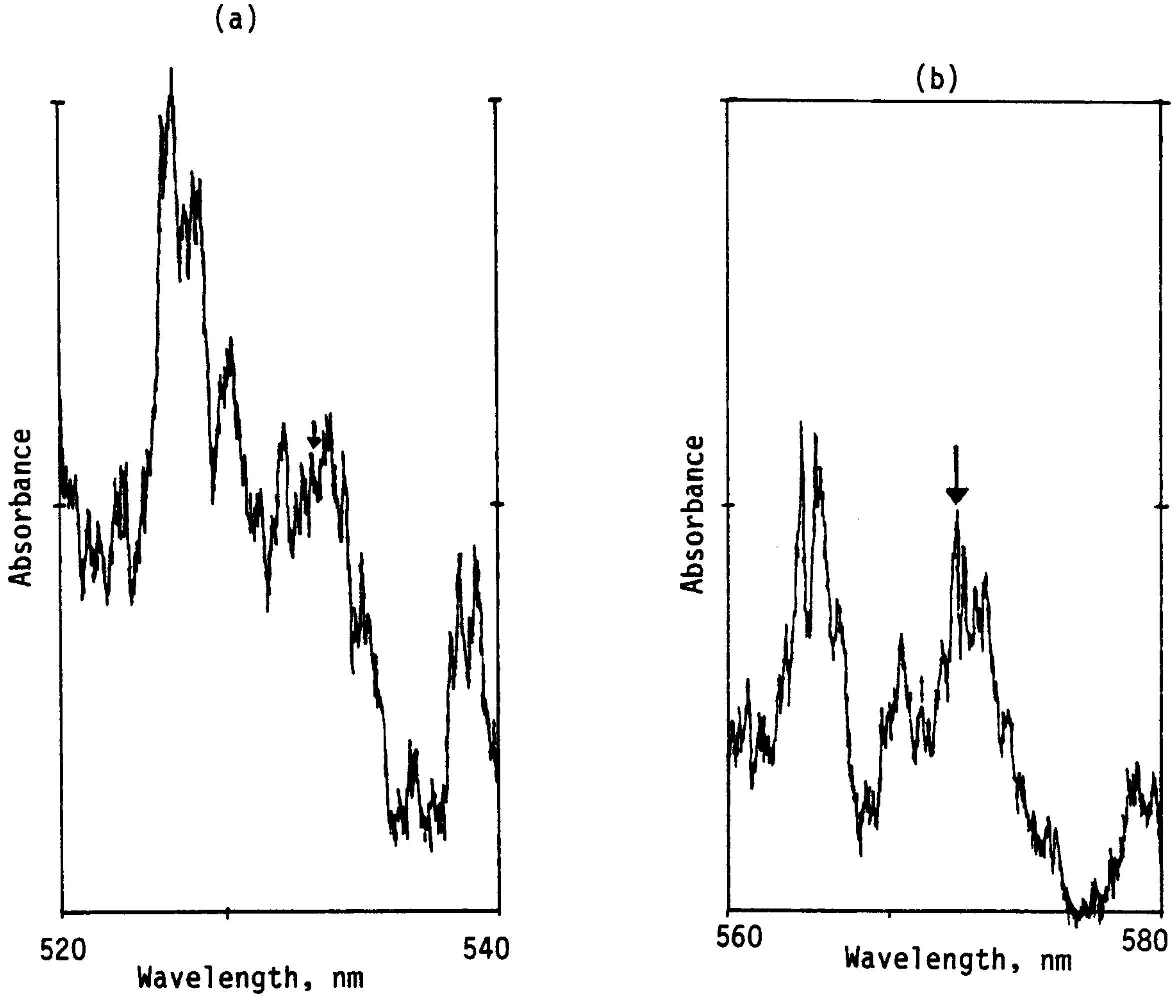


Figure 4 – Visible absorbance spectrum of NO_2 in the region of 532.0 nm (a) and 570.7 nm (b). The arrows indicate the position of the laser wavelength.

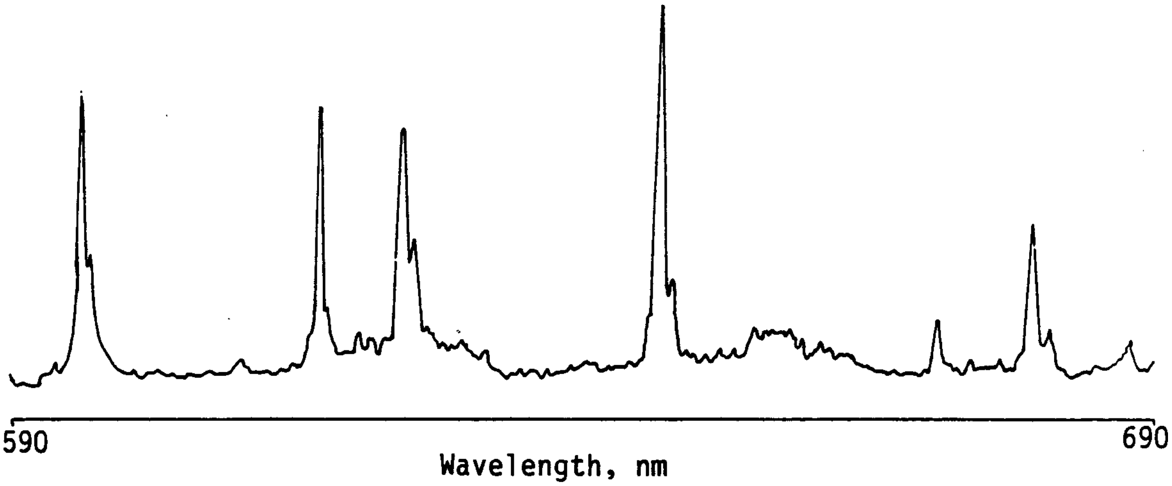


Figure 5 – LIF spectrum of 15 mtorr of NO_2 with 570.0-nm excitation.

circumstances. In the experiments, a pressure of neon gas was added to a fluorescence cell that initially contained NO_2. The LIF of NO_2 was then recorded as a function of the total pressure, and the ratio of the peak intensity to the total intensity was computed. The LIF results of adding the collision partner neon at varying pressures to NO_2 are summarized in Table 1.

Table 1 - LIF RESULTS OF ADDING NEON TO NO_2

Total Pressure (mtorr)	Discrete Fluorescence[a] (532 nm excitation) (%)
18 (pure NO_2)	49
129	32
216	32

[a] Computed as the ratio of sharp peak intensity to the total intensity at a fixed wavelength.

The results indicate that the presence of additional gaseous species can slightly, but significantly, affect the measurement of the LIF intensity if it is determined solely on the level of discrete emission. In all measurements reported, the total fluorescence is used as the primary experimental quantity. The observed effect of total pressure on the LIF makes it important to measure dispersed resonance fluorescence to allow monitoring of the ratio of discrete to continuum emission.

Calibration of Spectroscopic Measurements

The UV-visible absorption spectra of NO and NO_2 were taken in sample vessels with 10 mm x 10 mm square quartz cells attached to them. The vessels were identical to those used in the PETN studies described below. Capacitance manometers were used to measure the pressures of the commercially pure gases that were transferred to the sample vessels. Records of the absorbance spectra were made on a Shimadzu UV-260 spectrophotometer, and the extinction at specified wavelengths under the prevailing resolution was determined by simple application of the Lambert-Beer law.

The same quartz vessel construction was used for the LIF experiments. In this case, however, the range of linearity of the working curve for LIF was unknown, and this necessitated additional measurements. At the excitation wavelength of 532 nm, the NO_2 fluorescence intensity is not linear above several mtorr pressure absolute. At the excitation wavelength of 570.7 nm, the working curve is linear below 6 mtorr absolute pressure, as shown in Figure 6. The lowest pressure shown (220 μtorr) represents the lower limit of the present ability to measure pressure even though the LIF signal-to-noise ratio indicates that at least one, possibly two more orders of magnitude less NO_2 could be measured with confidence. Clearly, the LIF of NO_2 gas is an extremely sensitive technique.

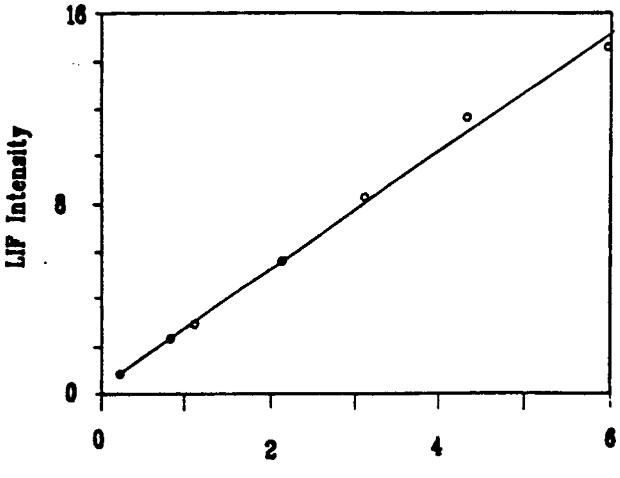


Figure 6 – LIF intensity as a function of the measured (nominal) pressure with 570.7-nm excitation. The solid line represents the least squares fit to the measured data points (R^2 = 0.99).

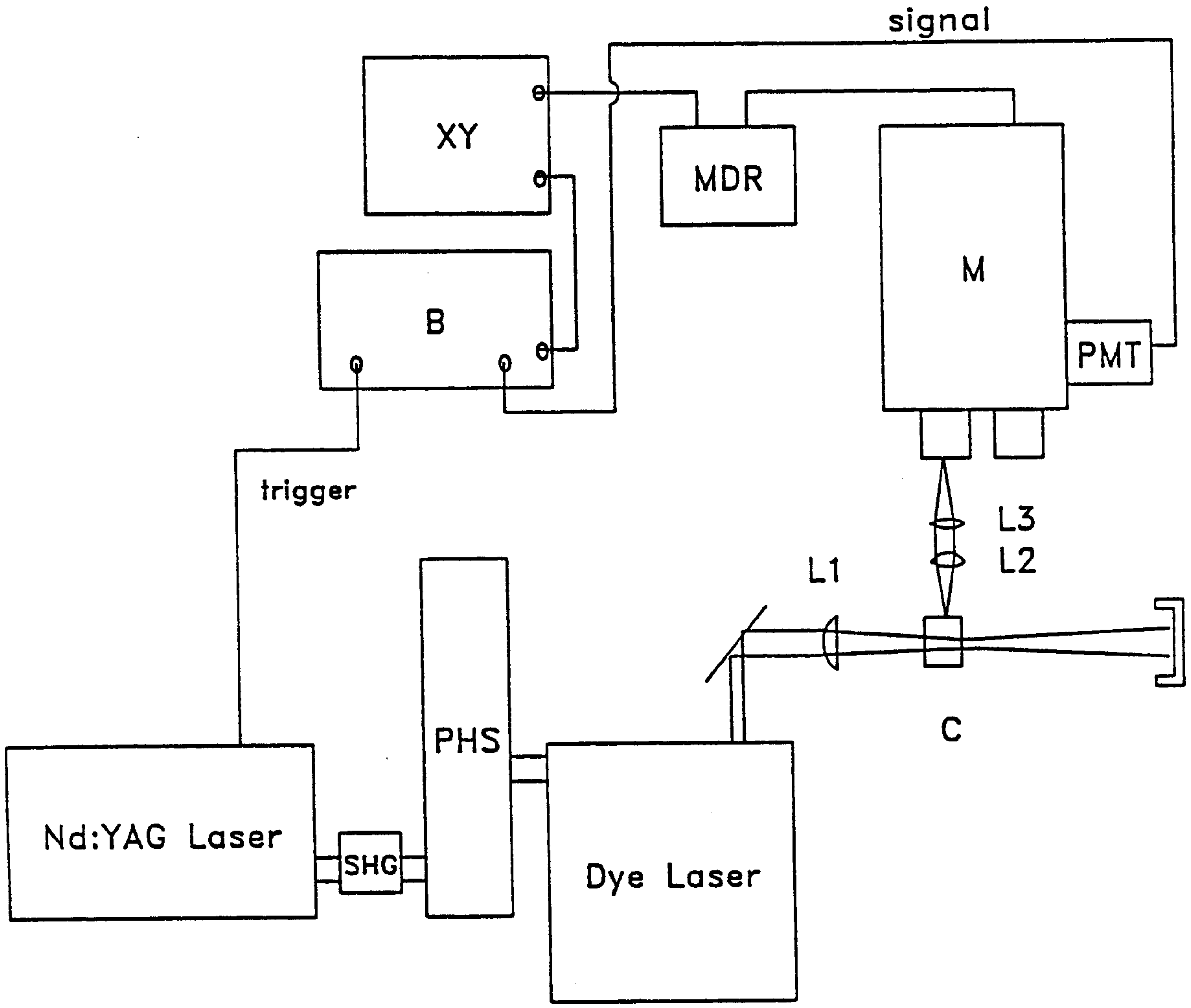
LIF Instrumentation

LIF measurements were made on an assembled group of instrument modules, as shown in Figure 7. The Nd:YAG laser was a Spectra-Physics DCR-2 pulsed YAG laser and delivered 10-ns pulses at a rate of 10 Hz. The second harmonic of the laser was generated with a nonlinear crystal and used either for LIF experiments or for pumping the dye laser. As discussed earlier, the dye laser was selected as the best pump source for the LIF experiments. As shown in Figure 7, the beam was weakly focused in the fluorescence cell. In fact, it was necessary to have the actual focus outside the cell to prevent laser-induced damage to the quartz walls of the cell. The fluorescence signal was collected and sent to a 0.64-m JY monochromator, where it was dispersed and detected with a Hammatsu R928 photomultiplier tube. A Stanford boxcar integrator, which was triggered from the DCR-2, was modified for a long integration time to better measure the dispersed fluorescence. The fluorescence spectrum was scanned with the monochromator which supplied the x-axis drive for the XY plotter. The signal from the boxcar averager drove the y-axis of the plotter to produce the LIF spectrum. Calibration standard samples of pure NO_2 were run before each series of measurements on PETN samples.

Sample Preparation and Measurements

The PETN sample vessels shown in Figure 8 were constructed from Pyrex and Suprasil quartz and charged with the solid sample using a microfunnel. The total mass of a vessel without a sample was typically 21 g, including the ball joint. This compact size permitted the vessel to be weighed directly before and after sample addition. Vessels containing PETN were placed on a vacuum line consisting of standard stainless steel and Pyrex connections. The line was pumped with a small turbomolecular pump backed by a forepump. Pressures in the line were monitored by thermocouple, ion, and capacitance manometer gauges at various points in the line. Sample vessels were sealed off under high vacuum and aged under a variety of thermal conditions as indicated below.

Several samples of PETN were used in this study, and their physical properties are summarized in Table 2. The samples studied were ER-17129A, ER-17129B, and ER-17129C. In the following



XY = x-y recorder
B = boxcar averager
MDR = monochromator driver
M = 0.64-m monochromator
L = lens
C = cell
PHS = prism
SHG = second harmonic generator
PMT = photomultiplier tube

Figure 7 – Experimental LIF apparatus.

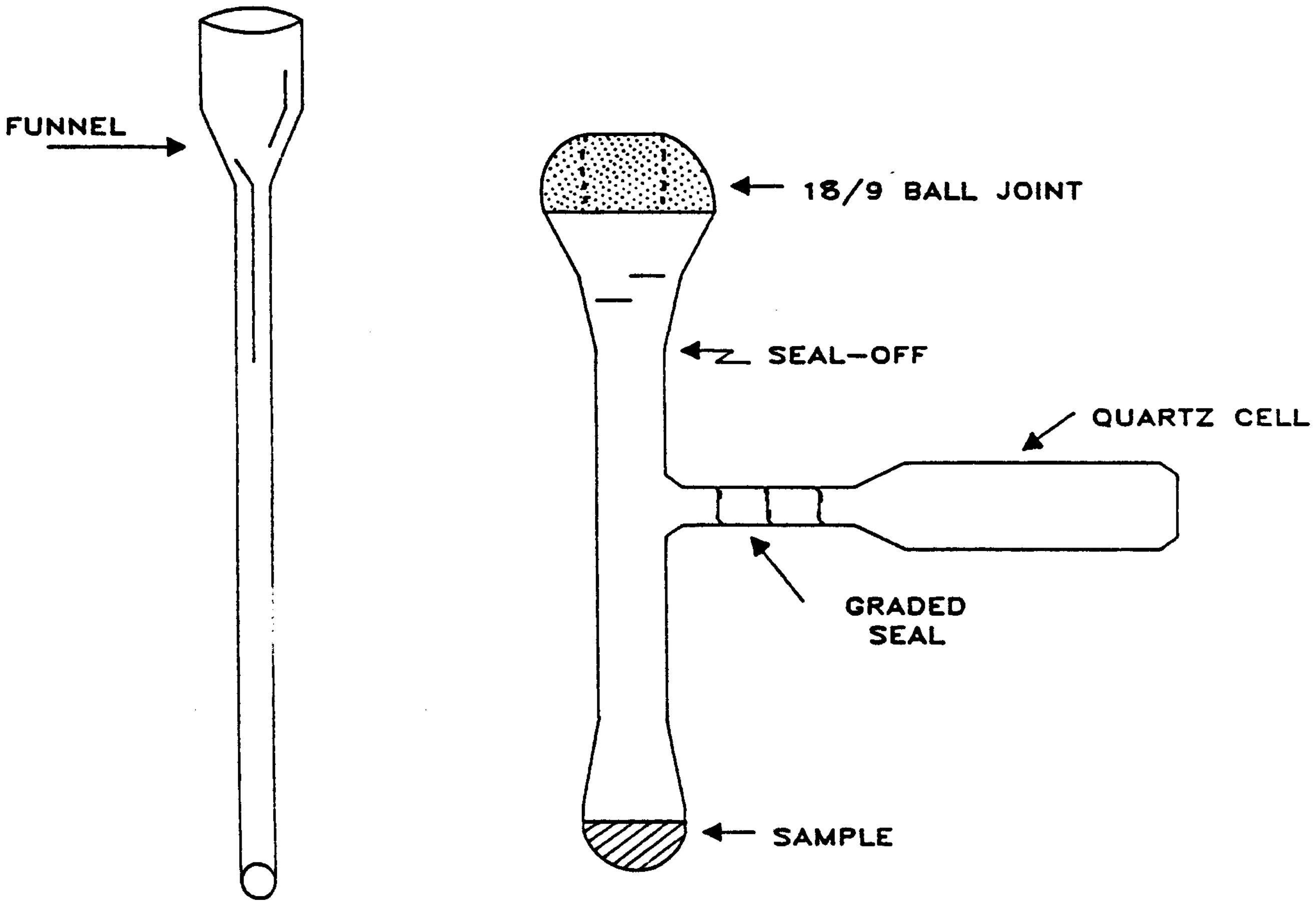


Figure 8 – PETN sample vessel and microfunnel.

Table 2 - SAMPLES STUDIED

Sample	Description	Fisher	Moisture (%)	Solvent (%)	Melting Point[a] (°C)
ER-17129A	Composite	7650	0.013	0.47	139.5-141.5
ER-17129B	Before Bake	7190	0.019	0.49	138.9-141.5
ER-17129C	After Bake	5840	0.017	0.28	140.8-142.0

[a] Differential thermal analysis.

discussion, the samples will be referred to as A, B, and C, respectively. Sample A was a composite sample made up of several batches prepared in the same manner and then blended together. Sample B was prepared by putting sample A through an additional processing step and drying it. Sample C was prepared by baking sample B at 100°C for 100 hr.

Several vessels were prepared with each sample of PETN. These vessels went through different vacuum line preparation and different heating cycles. All elevated temperature aging was done in convection ovens, and the ambient temperature was approximately 22°C. The vessels were examined for the presence of NO_2 and NO at various stages in these cycles.

Two methods of vacuum line preparation were performed on the vessels. In one method, the vessels were pumped under high vacuum overnight (approximately 16 hr) before they were sealed off. The seal-off was made under vacuum, and the vessel was pumped during the procedure. This was done to ensure that any decomposition products created by the seal-off would be pumped out of the vessel. In the second method, the portion of the vessel containing the powder was first cooled to liquid nitrogen temperature (-179°C). The air was then pumped out of the vessel using the capacitance manometers to indicate when "zero" pressure was attained. At this time, the vessel was sealed off while it remained at liquid nitrogen temperature. When vessels were prepared in this manner, water, solvent, adsorbed gases, and other products remained behind. Only the high volatility components of air were pumped out.

At least one vessel containing each sample of PETN was retained as an ambient standard. The remainder of the vessels were subjected to elevated temperatures of 90, 100, and 119°C over several time intervals. The presence of NO during the thermal cycling was determined by measuring the absorbance of the NO (1,0) gamma band relative to the background. All measurements were normalized to a 0.2-mm slit width on the spectrophotometer. The presence of NO_2 was determined by recording the LIF spectrum using 570.7-nm excitation from the dye laser.

The effect of vacuum line preparation on the experimental results was dramatic. A vessel containing sample A was cooled to liquid nitrogen temperature, evacuated, and sealed off. This sample (sample 081688-2) was then allowed to warm to room temperature and remain at ambient temperature for approximately 2 hr. At this time the LIF spectrum of NO_2 shown in Figure 9a was recorded, and the characteristic bands of NO_2 are unmistakable. This detection of NO_2 is in stark contrast to a vessel that contained PETN from the same sample that was pumped on overnight. This vessel showed no NO_2 even after heating to 100°C. The presence of NO_2 in the first vessel was apparently from NO_2 that had been adsorbed on the surface. This result supports the work of Volltrauer [3,4], who also observed NO_2 on the surface of PETN. It is also interesting to note that the NO_2 of sample 081688-2 was all but gone approximately

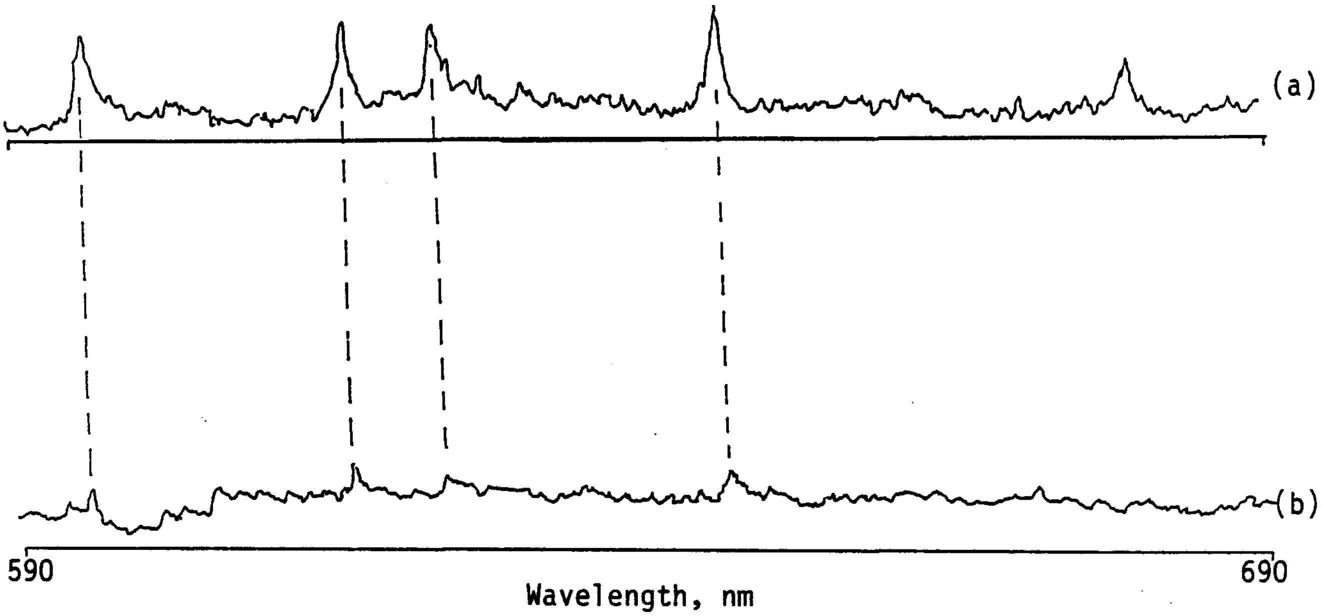


Figure 9 – LIF spectra of PETN samples with excitation at 570.7 nm. Figure 9a represents sample 081688–2 2 hr after seal–off; 9b represents sample 081688–2 22 hr after seal–off.

22 hr later, with only a trace showing up in the LIF spectrum, as shown in Figure 9b. Furthermore, as the NO_2 disappeared in the LIF spectrum, NO began to appear in the UV spectrum. Given the behavior observed, it seems inescapable that initially evolved NO_2, in fact probably surface–adsorbed NO_2, was transformed to the product molecule NO by some unidentified chemical reaction.

The ambient standards of samples A and C produced small amounts of NO (absorbance was 0.008 (A) and 0.004 (C)), but the ambient standard for sample B did not. As the other vessels containing these samples were thermally cycled, NO measurements were made on them. The results of the measurements on samples A, B, and C are shown in Figures 10a, 10b, and 10c, respectively. Samples A and C showed similar behavior with a slight increase in NO production as the temperature and time were increased. There was a large increase in NO production at the highest temperature of 119°C. Sample A showed the greatest NO production at this temperature, and sample C produced about two–thirds as much. It is interesting to note that sample B produced no detectable NO even at 119°C. NO was also found in a 3–yr–old sample prepared by Dosser using high vacuum techniques similar to those reported here [6].

Two ambient standard vessels of sample A were prepared using the vacuum line technique of cooling the vessels to liquid nitrogen temperature, evacuating them, and sealing them off. One of these vessels contained twice as much material as the other, and this vessel was kept in the dark as much as possible. Less NO was observed by UV spectroscopy in this sample even though there was more starting material. This result indicates that

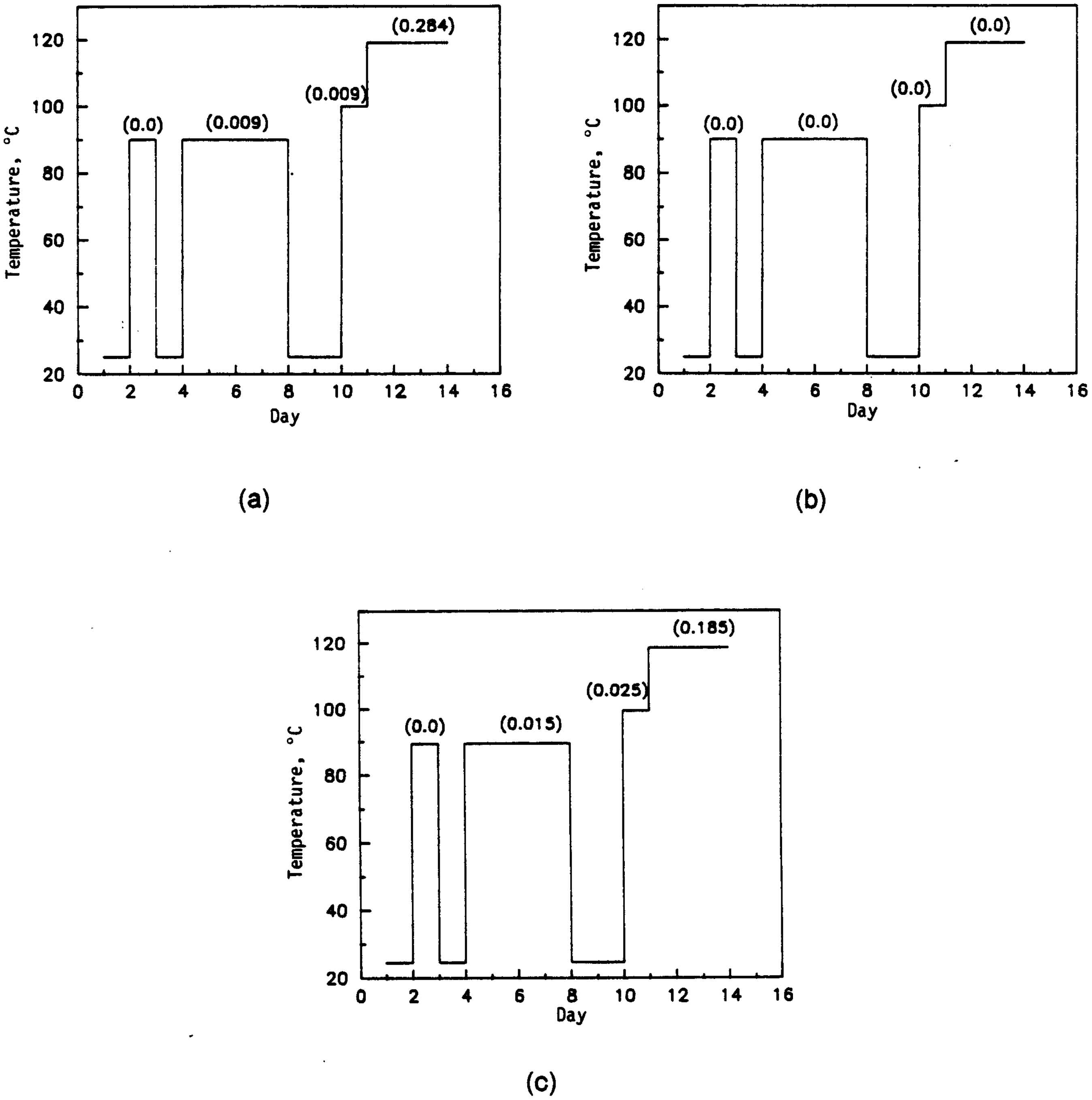


Figure 10 – NO production as a function of time and temperature for samples A (10a), B (10b), and C (10c). The NO absorption is shown in parentheses.

light may play a role in the decomposition of PETN or the chemistry of its decomposition products and that light is clearly a facet of the chemistry that must be investigated.

In addition to the surface NO_2 that was detected by LIF, NO_2 was also produced by thermal decomposition at 119°C. However, this was only observed in sample B. When this sample was removed from the 119°C oven, NO_2 was visually detected because of its characteristic ocher color. However, this color had nearly disappeared by the time the sample was transported to the laser diagnostic laboratory for the LIF experiment. Sufficient NO_2 was present, however, to be observed by both LIF and visible absorption spectroscopy. This visible decrease in NO_2 concentration in the vessel during the transportation time of approximately 30 min raises the question as to whether NO_2 was also present in the vessels containing samples A and C but was reduced by either adsorption or reaction to a level too low to detect.

Summary

A technique for uniformly preparing PETN samples under precise conditions was developed and evaluated. The importance of such sample handling techniques was clearly demonstrated, particularly with respect to NO_2 production. The design of the sample vessels proved to be particularly useful because the LIF and UV-visible spectra could be taken in the same vessel. The procedure for loading the powder into the sample vessel worked quite well, and the vacuum line procedures, including sealing off the vessels, could be easily performed.

The LIF spectrometer was an improved design over that used by Dosser in his previous study [6]. The monochromator was a 0.64-m instrument and was a considerable improvement over the 0.2-m monochromator previously used in terms of resolution and stray light rejection. The sensitivity of the LIF measurements to NO_2 was determined to be at least 2 μtorr with this system. This corresponds to approximately $5x10^{-13}$ moles of gas in the sample vessel. This sensitivity is four orders of magnitude better than that obtained using gas chromatography/mass spectrometry methods currently employed at Mound. The technique for recording LIF spectra was also firmly established. A better laser wavelength for taking the LIF spectrum of NO_2 was determined, and the linear pressure region for taking the measurements was determined. LIF was found to be capable of easily detecting NO_2 at pressures below the detectability level of present pressure sensors.

One factor that can affect the measurement of fluorescence and the quantitative evaluation of the signal is quenching of the fluorescing species by other gases. This effect was demonstrated on the LIF of NO_2 by introducing pressures of the inert gas neon into the cell containing the NO_2. Further experiments to determine the effect of quenching on the NO_2 LIF spectrum by suspected decomposition products such as NO, CO, and CO_2 are needed.

The UV-visible spectrometer also proved to be a valuable tool in this spectroscopic investigation. Not only did it allow the determination of the best wavelength to laser pump NO_2, but it also provided a method of measuring NO in the same sample vessel used for the LIF measurement. NO has a characteristic band structure in the UV, and it can unambiguously be identified. Although the sensitivity of absorption spectroscopy is not equivalent to that of LIF, sufficient NO was produced to be readily detected. The detection limit of the UV-visible spectrometer to NO was approximately 3 x 10^{-8} moles in the sample vessels.

The combination of LIF and UV-visible spectroscopies proved to be a valuable combination in investigating the decomposition of PETN. The two techniques permit the independent, noninvasive determination of NO and NO_2 in the presence of each other. This could not be done in previous studies where all NO_2 was converted to NO before a measurement was made [3,4]. Measuring the two gases separately and in the presence of each other removed ambiguities in the measurement. The need for an in situ experiment was demonstrated in the results obtained in this work. The fact that NO_2 was visually observed to disappear in less that 30 min indicates that the both the LIF and UV absorption experiments need to be performed in the vessel as the temperature is raised. This disappearance of NO_2 also raises the question as to whether the NO_2 reduction is the result of reaction or adsorption. The answer to the question could have a significant effect on thermal cycling experiments. Specific gas mixtures of proposed decomposition products should be made to determine whether gas phase reactions occur.

The LIF technique can also be applied to the detection of NO. Dosser recorded fluorescence excitation spectra of NO and determined the technique had excellent sensitivity [6]. The new LIF spectrometer should have even better sensitivity. However, using one photon UV excitation to obtain fluorescence excitation spectra of NO should be done with caution because photochemistry on PETN vapor or PETN solid on the vessel walls might occur. If this happens, then a two-photon process for detecting NO using visible light should be used to eliminate the problem.

There is clearly a need for more work to be done using these techniques. Many more samples need to be prepared, including some with high purity PETN. The effects of particle size, additives, and other variables need to be investigated, as do pressed pellets that are used in components. The LIF and UV-visible analytical spectroscopic techniques were shown to be valuable tools. Other laser spectroscopic techniques, such as multiphoton and photoacoustic spectroscopies, are complementary techniques that hold considerable promise as well in determining the nature of the chemical aging of PETN.

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