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ABSTRACT: We examined the deep UV 229 nm photochemistry of NaNO₃ in solution and in the solid state. In aqueous solution excitation within the deep UV NO₃ strong π → π* transition causes the photochemical reaction NO₃ → NO₂ + O·. We used UV resonance Raman spectroscopy to examine the photon dose dependence of the NO₂ band intensities and measure a photochemical quantum yield of 0.04 at pH 6.5. We also examined the response of solid NaNO₃ samples to 229 nm excitation and also observe formation of NO₂. The quantum yield is much smaller at ∼10⁻⁸. The solid state NaNO₃ photochemistry phenomena appear complex by showing a significant dependence on the UV excitation flux and dose. At low flux/dose conditions NO₂ resonance Raman bands appear, accompanied by perturbed NO₃ bands, indicating stress in the NaNO₃ lattice. Higher flux/dose conditions show less lattice perturbation but SEM shows surface eruptions that alleviate the stress induced by the photochemistry. Higher flux/dose measurements cause crating and destruction of the NaNO₃ surface as the surface layers are converted to NO₂. Modest laser excitation UV beams excavate surface layers in the solid NaNO₃ samples. At the lowest incident fluxes a pressure buildup competes with effusion to reach a steady state giving rise to perturbed NO₃ bands. Increased fluxes result in pressures that cause the sample to erupt, relieving the pressure.

INTRODUCTION

NaNO₃ is utilized in many chemical and industrial processes, and also utilized as an energetic material in explosives. It is important to understand the factors that enable NaNO₃ to function as an explosive and to develop methods to easily, remotely detect it.¹⁻³ In the work here we utilize deep UV resonance Raman spectroscopy (UVRRS) to probe the nature of the NaNO₃ electronic excited states and their complex photochemistry.⁴⁻⁵ We find strong RR enhancement of the NO₃ stretching fundamentals, as well as overtones, indicating that the excited state is displaced relative to the ground state.⁶⁻¹⁰ The large deep UV Raman cross sections and the large number of intense overtones and combinations indicate that NaNO₃ can be spectroscopically detected easily with deep UV excitation.¹¹⁻¹³ UVRR may prove a useful technique for stand off monitoring of NO₃ species.

We find that the displaced NO₃ excited state correlates with a facile NO₃ photochemistry in aqueous solution with 229 nm light;¹⁴⁻²² we measure a quantum yield, φ ≈ 0.04 for the photolysis: NO₃ → NO₂ + O·. We demonstrate that this photochemistry also occurs in the solid state, but that the lattice constraints dramatically decrease the quantum yield. This monophotonic photochemistry at individual lattice sites perturb NO₃ molecules at adjacent lattice sites, shifting the NO₃ Raman bands. The perturbations of the NO₃ lattice sites depend upon not only the photon dose but also on the laser flux. Higher doses and fluxes give rise to photochemistry that degrade and excavate the solid NaNO₃ surfaces.

We carefully examined the evolution of the lattice as the photochemistry progressed. We also examined the photochemical quantum yield for photolysis in the solid state of NaNO₃ to examine the dependence of the activation barriers for photochemistry on the lattice geometry.

The work here also characterizes the evolution of the deep UV Raman spectra of NaNO₃ with deep UV excitation. This information will prove valuable for defining the time and flux varying Raman signature of these types of compounds upon deep UV excitation, that might be used, for example, for standoff detection. These studies also examine the dependence of photochemistry on solid state molecular constraints.

EXPERIMENTAL SECTION

UV Raman measurements were obtained by using the instrumentation previously described.²³⁻²⁴ Briefly, excitation utilized a Coherent Industries Innova 300 FreD frequency doubled Ar⁺ laser to generate CW 229 nm excitation. We utilized a modified Spex Triplemate spectograph and a Princeton Instruments CCD camera (Spec-10 System, Model 735–0001). Aqueous solution NaNO₃ and NaNO₂ molar absorptivities were obtained from Ianoul et al.²⁵

SEM measurements were obtained by using a Phillips FEG XL-30 FESEM. The NaNO₃ solid sample was translated across the 20 μm diameter spot size 229 nm laser beam at a rate of ∼0.25 cm/min during which the UV Raman spectra were measured.
The sample was then sputter coated with Pd for subsequent SEM studies.

**X-ray Powder Diffraction.** X-ray powder diffraction patterns were collected using a Bruker AXS D8 Discover powder diffractometer at 40 kV, 40 mA for Cu Kα, (λ = 1.5406 Å) radiation with a scan speed of 0.20 s/step and a step size of 0.02018°. Samples were prepared by finely grinding the sample with a mortar and pestle and then evenly dispersing the powder on a vaseline-coated glass slide. The data were analyzed for d-spacings by using the Bruker Powder Analysis Software package EVA program.

We compared our powder diffraction data to that of the Inorganic Crystal Structure database and the American Mineralogist Database to search for comparable literature powder patterns. The NaNO₃ directly obtained from JT Baker (Analyzed Inorganic Crystal Structure database and the American Mineralogist Database) showed a very good correlation with NaNO₃ crystallized in the trigonal R̅-3c space group (a = b = 5.077 Å, c = 16.82 Å) with the five largest peaks at d-spacings of 3.07, 2.85, 2.32, 1.92, and 1.90 Å.

We studied a solid sample that we prepared to be fully dense in order to ensure high thermal conductivity. These solid samples were prepared by melting an anhydrous crystalline sample of NaNO₃ (J. T. Baker Analyzed Reagent) in a oven (Tmax = 360 °C). The melted sample was allowed to cool over a period of 16 h. The NaNO₃ sample cooled from the melt gave some powder diffraction peaks identical to those above, but the diffraction from the two samples clearly differ. A search of the database found another NaNO₃ polymorph that crystallizes in the trigonal R̅-3c space group (a = b = 5.084 Å, c = 8.175 Å) whose diffraction closely matches the melt sample (largest d-spacings at 3.88, 3.00, 2.73, 1.86, and 1.85 Å). The differences observed between the relative diffraction intensities for the melt compared to the literature compound attribute to a somewhat lower melt sample crystallinity.

The R̅3c structure contains alternating layers of Na⁺ and NO₃⁻ groups, with NO₃⁻ anions in alternating layers rotated 60° relative to one another. Paul and Pryor report a phase transition to a R̅3m structure at 275 °C where the c-axis spacing is halved and two Na⁺ orientations are disordered (each N⁻ atom has 6 half-occupancy O atoms coordinated).

**Solution UV Raman Measurements.** A 1.5 mL aqueous solution containing 0.0387 mg/mL NaNO₃ was placed in a 1 cm path length fused silica cuvette that was continuously stirred by using a small magnetic stir bar. The stirred samples were illuminated for extended time periods and UV Raman spectra were measured during short time accumulations during and after sample illumination periods. The 20 μm beam waist (measured in air) was focused just inside the cuvette window.

**Solid UV Raman Measurements.** We prepared fully dense samples of NaNO₃ to avoid any uncertainty concerning thermal conductivity in our solid samples, such as that which would occur for small packed crystallites where thermal conductivity could be inhibited by the presence of air pockets between packed crystals.

We heated the reagent NaNO₃ powder in an oven to 360 °C where it melted. We allowed it to slowly cool over 16 h to room temperature. During cooling it formed a monolith consisting of multiple grains. The stationary solid NaNO₃ measurements were obtained from static samples by attaching thin ~0.2 cm² pieces onto a sample holder in the spectrometer with double stick tape. The laser beam was focused onto the sample surfaces by using a 10 cm focal length fused silica lens. The focal spot was measured at the sample to have a 1/e diameter of 20 μm.

We decreased the average laser flux onto the solid samples by utilizing a spinning cell where flat solid sample pieces were wedged into circular grooves in the flat surface of a cylindrical spinning metal sample holder. To avoid movements of the beam on the sample as we varied the illumination power we altered the laser power by swapping metallic film neutral density filters in the beam.

### RESULTS AND DISCUSSION

Figure 1 shows the 229 nm aqueous solution and solid state UVRR of NaNO₃. This excitation occurs within the very strong 205 nm lowest energy allowed π → π⁺ transition.

There is also a lower energy very weak absorption centered around 310 nm.

The solution and solid state UVRR spectra are strikingly similar showing dominating enhancements of the NO₃⁻ ν₁ symmetric stretching vibrations at ~1047 and 1065 cm⁻¹ for the solution and solid state samples, respectively. The first and second overtones of ν₁ also show significant intensities. The NO₃⁻ ν₃ antisymmetric stretch between 1336 and 1401 cm⁻¹ shows significant intensities, and is interestingly split in water. The first overtones are also clearly observed for this vibration.

The out-of-phase ν₂ 830 cm⁻¹ vibration is not evident in either the solution or solid state spectrum, but its overtones are clearly evident as bands at ~1666 cm⁻¹. Other combinations and overtones are also clearly present.

We showed previously that the strong 205 nm NO₃⁻ π → π⁺ transition dominates the resonance Raman enhancement of the solution spectra. The similar aqueous solution and solid spectra clearly indicate very similar resonant transitions. The strong resonance enhancement and the overtone scattering clearly indicates that the resonant excited state is displaced along the N—O bonds. Indeed, Waterland and Myers extensively examined resonance enhancement of KNO₃ in aqueous solution and observed essentially identical spectra. They analyzed the excitation profiles in detail using the time dependent wave packet formalism and concluded that the N—O bond lengths were expanded by ~7 pm in the excited state. Gaff and co-workers have developed a method for calculating resonance Raman cross sections through ab initio calculations based upon the optimization of ground and excited state geometries. For the case of the nitrate anion, they found a difference of ~8 pm between the ground and excited state bond lengths. We are presently...
analyzing the overtone patterns to get further information on the excited state displacement.

Interestingly, we see significant photochemistry for the solution and solid phase samples of NaNO₃ as shown below. However, the quantum yields dramatically differ between the two phases. It is large for the solution phase and very small for the solid state. This suggests that the solid state photochemical reaction coordinate involves additional constraints that limit the quantum yield from that in water.

**Solution Phase Photochemistry.** Figure 2A examines the illumination time dependence of the 229 nm Raman spectra of an aqueous NaNO₃ solution. As noted by Narayanswamy, the UV illumination of nitrate salts results in the formation of nitrites and molecular oxygen: NO₃⁻ + hν → NO₂⁻ + O₂. The resulting photolysis decreases the NO₃⁻ symmetric stretching band intensity at 1045 cm⁻¹ and generates an increasing intensity for the broad NO₂⁻ peak at 1330 cm⁻¹. Figure 2B shows the difference spectrum between the 48 min illumination and the initial spectrum.

For low conversion conditions the photolysis quantum yield can be determined from:

\[ \phi \sim \frac{\left( \frac{I_{NO_2}}{I_{NO_3}} \right) \cdot \left( \frac{\sigma_{NO_2}}{\sigma_{NO_3}} \right) \cdot C_{NO_3} \cdot V \cdot N_{AV}}{\int_0^\infty \text{photons}(t) \cdot dt} \]

The relative number of nitrite molecules produced was determined from the relative peak intensities normalized to the relative Raman cross section values which we measured to be \( \left( \frac{\sigma_{NO_2}}{\sigma_{NO_3}} = 0.65 \right) \). The illumination photon dose was determined from the measured intensity of the laser and corrected for reflection losses from the cuvette surfaces using the Fresnel equation with an interior refractive index of water. \( V \) is the sample volume and \( N_{AV} \) is the Avogadro’s number. We find \( \phi = 0.04 \) for the aqueous solution quantum yield.

**Solid Phase Photochemistry.** The photochemical response of solid NaNO₃ samples to 229 nm excitation is highly dependent on both the light flux (power/area) and dose (photons/area). Thus, we will discuss the laser illumination response phenomena starting from low flux and dose conditions. We simultaneously achieved low excitation flux conditions and high UVRR S/N ratios by spinning the solid NaNO₃ samples. The lowest flux illuminated solid samples were packed within a 1.5 cm diameter, ~2 mm wide groove in a spinning cell. The solid sample fragments were packed into the groove such that the flat fragment sample surfaces were approximately at the same height from the groove surface bottom. The spinning cell was mounted with its axis of rotation parallel to the optical axis of the collection lens and the cell was spun at >600 rpm. The 229 nm laser excitation beam excited the spinning sample approximately in a backscattering geometry with the laser beam focused to a ~20 μm diameter spot. The CW incident, 229 nm, ~0.5 mW beam resulted in a flux of ~48 mW/cm² within the illuminated sample annulus.

Figure 3A examines the UVRR of the illuminated spinning sample of solid NaNO₃ to a spinning solid sample of NaNO₂. At the earliest times the NaNO₃ sample shows the NO₃⁻ → NO₂⁻ as evident in the formation of the 1331 and 1654 cm⁻¹ peaks that derive from the NO₂⁻ → ν1 stretch and its overtone band that dominates the spectrum of NaNO₂. The intensity of the NO₂⁻ peaks increase as the illumination times increase as evident in Figure 3B that expands the ν3 band region. We are, as yet, uncertain of the origin of the growing 1766 cm⁻¹ peak.

In addition to the increasing intensity of the NO₂⁻ bands, we see an upshift in the frequency of the ν1 symmetric stretching band from 1068 to 1077 cm⁻¹ (Figure 3C). Accompanying this NO₃⁻ band upshift with increasing illumination time, there is a loss of intensity in the ν3 antisymmetric stretching band at 1385 cm⁻¹ accompanied by the formation of a new band at 1425 cm⁻¹. This band is assigned to an upshifted perturbed ν3 antisymmetric stretching band; the frequency sensitivity of the ν3 band is ~4 times that of the ν1 band.

This NO₃⁻ band upshift obviously results from perturbations of the NaNO₃ lattice due to the photochemical formation of NO₂⁻ and O²⁻. One possibility (consistent with results below) is that pressure in the lattice increases with photolysis and that the stress induces frequency upshifts due to mechanical compression of the NO₃⁻ groups (see below).

This spectral response to laser illumination does not result from laser heating. As shown below the high heat conductivity of fully dense solid NaNO₃ sample results in a negligible sample temperature increase of <5 °C from our 229 nm excitation beam.

Figure 4 shows the time dependence (in units of dose) of the increasing intensity of the photochemically produced NO₂⁻.
band and the time dependence of the intensity of the upshifted NO$_3^-$/$\nu_1$ and $\nu_3$ bands. Figure 4a shows that the NO$_2^-$/$\nu_1$ band intensity initially linearly increases and then levels off as the solid NaNO$_3$ surface layer converts to NO$_2^-$ in contrast, the appearance of the upshifted $\nu_1$ and $\nu_3$ bands show a short initial time delay, after which their intensities linearly increase (Figure 4b and c).

A distinctly different behavior is observed in Figure 5 that shows UVRR spectra which utilized an increase in flux and dose to illuminate a spinning solid NaNO$_3$ sample where the groove diameter was decreased to 2.5 mm (average flux = 465 mW/cm$^2$). The photochemical formation of the NO$_2^-$ peaks is more extensive than in Figure 3, and the NO$_2^-$ peak bandwidth increases at the higher dose values.

The NO$_3^-$ $\nu_1$ and $\nu_3$ bands show distinctly different behaviors than those in Figure 3. The $\nu_1$ band upshifts less and a lower frequency $\nu_1$ band shoulder grows in at $\sim$1050 cm$^{-1}$. The $\nu_3$ band does not show the upshifted subband as observed at the lower dose flux conditions of Figure 3.

Figure 6 shows the dosage dependence of the NO$_2^-$ $\nu_1$ band intensity for this increased dose/flux condition. The intensity of the NO$_2^-$ peak does not saturate at a dose of 0.01 mW sec $\mu$m$^{-2}$, but continues to increase up to the highest doses of 0.1 mW sec $\mu$m$^{-2}$.

Figure 7 shows the UVRR spectra of a stationary solid NaNO$_3$ sample at a constant, but higher fixed dose excitation 0.091 mW sec $\mu$m$^{-2}$, but where the incident power increases from 0.175 mW to 0.605 mW at the sample, while the illumination time decreases from 165 to 47 s.

Here we find that the observed NO$_2^-$ $\nu_1$ band intensity and the extent of photolysis are independent of flux but remain the same for constant dose. Each spectrum was measured at different regions of the sample. Each UVRR spectral measurement spanned the entire illumination period and the spectra were identically scaled.

The spectra are similar to one another indicating that the spectra are independent of the power flux and are sensitive mainly to the dose. Surprisingly, the extent of photolysis is similar to that observed in Figure 3, even though the dose is >1000-fold higher. Figure 8 shows that for this case the $\nu_1$ band and 2$\nu_1$ band frequencies downshift in clear contradiction to the observed behaviors above.

The different behaviors observed for these different flux and dose conditions can be understood by examining the impact of illumination on the morphology of the solid NaNO$_3$ samples. Figure 9 shows the SEM and UVRR spectra of a solid NaNO$_3$ sample that was translated through the laser beam by using a translation stage while monitoring the sample UVRR. The sample was then sputter coated with Pd and its SEM measured.
The NaNO₃ sample was translated across the 20 μm diameter laser beam by hand rotating the translation stage micrometer at a rate of ∼0.25 cm/min (with a time averaged flux of 54 W/cm²). The Figure 9A SEM image shows the surface of a sample where the beam initially illuminates the bottom of the sample that was lowered vertically along the line L–K. The less evident part of the line around position L shows where the sample was translated at a rate of 0.25 cm/min during which the UVRR spectrum was collected. This translation resulted in a dose of ∼5.4 × 10⁻⁴ mW·sec μm⁻², just below the lowest dose used in the Figure 4 data. The sample was stopped to measure the spectrum at point K in the sample, where it accumulated a dose of 8.5 × 10⁻² mW·sec μm⁻². The Figure 9B and C SEM photographs show expanded views of the K and L regions. Further expanded views are shown in Figure 10.

Excitation with doses of 8.5 × 10⁻² mW·sec μm⁻² clearly disrupts the NaNO₃ solid sample. For the Figure 9 and 10 sample L regions we see surface eruptions as dots on the low dose edges of the illuminated lines. Closer to the middle of the line where the illumination intensity is a maximum these dots appear to coalesce to form crevice lines. The expanded SEM regions in Figure 10 show that in the center of the line, the higher dose intensities cause formation of connected regions of dots. In the case of the much higher doses in region K we see large craters and crevices where the surface material looks spongy.

The lowest dose measurements result in partial conversion of NaNO₃ to NaNO₂ + O₂⁻. It is possible that the atomic oxygen formed quickly reacts to form O₂. Whatever the case, the increase in molecular species in the solid results in pressure induced stresses. For stress levels below the material failure threshold, the non-photolyzed NaNO₃ lattice sites will be compressed, resulting in an increase bond order and ν₁ and ν₃ vibration frequency increases, as observed in the Figure 3 UVRR spectra obtained at the low fluxes and doses that result in modest conversions to NO₂⁻.
Higher flux and dose measurements result in failure of the material that relieves the stress. In this case, the upshifted $\nu_3$ band does not appear, while the $\nu_1$ band upshift decreases. Significant photochemical conversion to NO$_2^-$ occurs which perturbs the NO$_3^-$ frequency.

Figure 8. Expanded UVRR of the stationary solid NaNO$_3$ sample shown in Figure 7. The $\nu_1$ and 2$\nu_1$ bands show spectral changes due to low frequency bandshifts.

Figure 9. SEM and UVRR of illuminated solid NaNO$_3$ sample. The sample was illuminated with a 229 nm, 20 $\mu$m diameter $\sim$0.5 mW beam (with an average flux of 6 W/cm$^2$). (A) Palladium coated NaNO$_3$ sample surface showing surface damage line along the L$-$K direction formed by translating the sample at a rate of 0.25 cm/min. Additional illumination lines are also evident. (B) Expanded SEM of K region where sample was stationary for a period of 1 min while measuring its UVRR. (C) Expanded SEM of L region where sample translated at a rate of $\sim$0.25 cm/min through the beam while measuring the UVRR. (D) 229 nm UVRR of regions K showing extensive photochemistry, and region L with modest photochemistry due to translation of sample through the beam.

Figure 10. SEM expanded view of regions K and L of Figure 9.
At the highest doses there is significant conversion to NO$_2^-$ and the NaNO$_3^-$ lattice crumbles, forming a spongy looking material with craters that indicate that material is sloughed off. This is the reason that the sample surface layers never fully convert to NO$_2^-$; the NO$_3^-$ product falls from the surface, exposing fresh NaNO$_3$. In this case the NO$_3^-$ bands downshift as shown in Figure 8.

The increased pressure induced by the photolysis is concentrated at the sample surface and in a thin layer below where the photolysis is localized. The stressed NaNO$_3$ lies below layers of essentially pure NaNO$_2$. The outside surface NaNO$_3$ layers contain significant NO$_2^-$ at the surface but the concentration of NO$_3^-$ decreases with depth due to attenuation of the beam. The maximum pressure occurs in layers significantly photolyzed to NO$_2^-$. It is likely that the NO$_2^-$ is not well ordered in the lattice and is brittle.

We can very roughly calculate the effective pressure if the photolysis simply results in conversion to only NO$_2^-$ and O$_2$. Assuming full conversion to O$_2$ that expands into the total volume of the NaNO$_3$ the ideal gas law calculates a pressure of >300 atm assuming no excluded volume exists from the NO$_2^-$ formed. The true pressure, thus, will be much higher and sufficient to cause the brittle NO$_2^-$ overlayer to erupt.

Only in the lowest flux/dose measurements do we observe simple photolysis of the NaNO$_3$ sample. For this condition, we can use the rate of the NO$_2^-$ v1 band intensity increase to calculate the photolysis quantum yield.

**Solid State Photolysis Theory.** It is easy to model the expected UVRR spectra that result from the photochemical conversion of NaNO$_3$ to NaNO$_2$ in the lattice if we assume photolysis subsequent to photon absorption at a constant quantum yield. Intrinsically to this calculation is the assumption that there is no diffusion of species within the ionic lattice and that there are no interactions between lattice sites. The photochemistry involved is: NO$_3^-$ + hv $\rightarrow$ NO$_2^-$. Only the 229 nm molar extinction coefficient (3400 (mol/L)$^{-1}$ cm$^{-1}$) for NO$_3^-$ is from the surface ($r=0$) to $\infty$, and over the measurement time interval, $t_F$. The ratio of Raman intensities of NO$_2^-$ to NO$_3^-$ Raman intensities:

$$ R = \frac{\alpha_R}{\alpha_R^0} = \frac{\int_0^{t_F} \phi(t) I_0(t) e^{-3\gamma t} \, dt}{\int_0^{t_F} \phi(t) I_0(t) e^{-3\gamma t} \, dt} $$

where $\phi_0 = 1.6 \times 10^{-25}$ cm$^2$ and $\alpha_R = 7.4 \times 10^{-26}$ cm$^2$ are the 229 nm Raman cross sections of NO$_2^-$ and NO$_3^-$, respectively, estimated from spectra of these ions in aqueous solution. The integration over $r$ is from the surface ($r = 0$) to $\infty$, and over the measurement time interval, $t_F$.

We can calculate the photochemical quantum yield from the power and time dependence of the relative NO$_2^-$ to NO$_3^-$ Raman intensities, $R$. Figure 11 shows the flux dependence of the value of $R$, the ratio of NO$_2^-$ to NO$_3^-$ for a solid NaNO$_3$ sample as in Figure 3 in a 1.5 cm diameter annular spinning cell, for a beam diameter of 20 $\mu$m we observe $R \approx 0.1$ after 25 min illumination. Figure 11 shows $R$ for a 25 min illumination time and for quantum yields of $\phi = 10^{-8}$ and $\phi = 10^{-9}$. A quantum yield of $\phi = 10^{-8}$ calculates an $R \approx 0.1$ value, close to that experimentally observed.

Although these quantum yields are very small, these $\sim 0.5$ mW excitation powers focused to small rotating cell annular excitation areas ($\sim 3 \times 10^{-5}$ cm$^2$) result in large photon fluxes and
The Journal of Physical Chemistry A

The maximum temperature calculated by Lax is as follows:

$$T_{\text{max}} = \frac{P}{2\pi K} \left( \frac{1}{r} \right)$$

where

$$\left( \frac{1}{\gamma} \right) = \frac{1}{w} \left( \int_{0}^{\infty} f(R)dR \right)^{-1} \approx \frac{1}{w} \pi^{1/2}$$

where $P$ is the incident power $(P = 1 \, \text{mW})$, and $K$ is the thermal conductivity. We estimate $K = 30 \, \text{mW/cm·K}$ based upon values given for similar inorganic nitrates. $w$ is the beam diameter, and $(1/r)$ is the mean inverse distance from a point on the surface at the beam center to the remaining points on the surface using a weight factor $f(R)R$ proportional to the intensity incident (weighted by area) on the surface.37

We measured a beam full width at half-maximum of 20 μm. We, thus, calculated a maximum temperature rise of 5 °C for the incident power of 1 mW absorbed by an infinitesimally thin layer at the surface. Therefore, we conclude that laser heating does not contribute to any phase transitions or additional chemistry converting NaNO3 to NaN02.

The situation, however, could significantly differ for the photochemically degraded sample which shows spongy surface structures that must have much smaller thermal conductivities. These damaged porous sample volumes may show additional thermally induced phenomena due to laser beam illumination.

**CONCLUSIONS**

Deep 229 nm excitation UVRR spectra of NaNO3 in solution and the solid state show strong resonance enhancement of the NO3− fundamentals, overtones, and combination bands. These results indicate that the excited state is placed relative to the ground state. If the excited state is not dissociative, then transfer to another excited state surface is required to generate the observed photochemistry. It appears unlikely that the vertically excited ππ* state is dissociative given the previous theoretical UVRR excitation profile studies that find a bound ππ* excited state somewhat expanded along the N–O bonds.5,11,12

We measure a quantum yield for a NaN03 neutral aqueous solution of 0.04. In contrast, in solid state NaN04 we measure a quantum yield of ~10−8 that is dramatically decreased, probably due to the additional constraints by the lattice on the photochemical reaction coordinate(s). We estimate an increased activation barrier of ~40 kJ/mol. The resonant π → π* transitions seem very similar for the aqueous solution and solid state nitrates in view of their very similar UVRR spectra.

Low photon flux/dose conditions result in pressurization of the lattice resulting in upshifts in the NO3− bands. Higher flux/dose conditions that significantly photolyze the sample surface result in high internal pressure that fracture the NO3− surface layer causing eruptions alleviating the pressure. Higher flux/dose measurements fracture the sample causing cratering and removal of the NO3− surface layers. In this case, although extensive photolysis occurs, the ratio of NO2−/NO3− UVRR intensities becomes constant as the laser beam penetrates the sample. The perturbed NO3− frequencies downshift due to the disorder caused by the photolysis.

The NaNO3 UVRR spectral time dependence results from a competition between different dynamics occurring during the deep UV excitation. The photochemistry to NO2− is very fast...
yielding atomic oxygen. For low excitation fluxes, pressure builds up in the converting sample to shift the NO$_3^-$ vibrational modes. The pressure buildup competes with effusion of the photochemically generated gases which include molecular oxygen. When the pressure exceeds the material failure threshold the sample erupts to release the gases. In this regime, the NO$_3^-$ vibrational band frequencies shift due to perturbation of the environment due to exchange of adjacent NO$_3^-$ lattice sites with NO$_2$.

The deep UVRR spectra measured are very intense and the UVRR spectra shows a time-dependent evolution that is characteristic of solid state NaNO$_3$. The bright UVRR of NaNO$_3$ in addition to its temporal spectra dependence makes it an excellent candidate for UVRR standoff detection. The laser flux/dose dependence of the UVRR can be used as a reliable confirming signature for the presence of this material.

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