

Monitoring of Vapor-Phase Nitro Compounds Using 226-nm Radiation: Fragmentation with Subsequent NO Resonance-Enhanced Multiphoton Ionization Detection

G. W. Lemire,[†] J. B. Simeonsson,[†] and R. C. Sausa*

US Army Research Laboratory, AMSRL-WT-PC, Aberdeen Proving Ground, Maryland 21005-5066

The development of a novel technique for sensing trace vapors of NO₂-containing compounds is reported. This technique is based on the use of one laser operating at 226 nm to both photofragment the target molecule and detect the characteristic NO fragment, formed from a rapid predissociation of NO₂, by resonance-enhanced multiphoton ionization (REMPI) and/or laser-induced fluorescence (LIF) via its A²Σ⁺-X²Π (0,0) band origin. The analytical utility of this technique is demonstrated on a number of compounds, including dimethylnitramine, nitromethane, nitrobenzene, trinitrotoluene (TNT), and 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX), employing molecular beam sampling with time-of-flight mass spectrometric analysis of the jet-cooled analyte seeded in an atmosphere of buffer gas. With the present system, limits of detection of 8 and 24 parts per billion (ppb) are obtained for RDX and TNT, respectively, using only ~100 μJ/pulse of laser energy. The limits of detection of the other compounds studied are also presented and discussed.

INTRODUCTION

The development of laser-based, analytical sensors for the rapid detection and monitoring of trace atmospheric vapors in real time has been of great interest in recent years.¹⁻⁴ Environmental issues pertaining to pollution prevention and compliance have been important driving forces behind this development. Another important related issue deals with the detection of trace atmospheric vapors of energetic materials such as explosives and propellants. This is not surprising given the potential civilian and military applications for these developing technologies in aviation security, as well as antiterrorist and demilitarization actions.

Ultraviolet-visible (UV-vis) spectroscopic techniques can at times provide very specific and sensitive methods of detection for many atomic and molecular systems. However, larger molecules are in general more difficult to detect spectroscopically in the UV-vis spectral region due to the lack of distinguishing structure or absence of any features in their absorption or emission spectra. One approach to circumventing this lack of specificity in the UV-vis spectral region has been to combine spectroscopic and mass spectrometric techniques. A common approach involves the ionization of the target molecule for mass spectrometric detection by a multiphoton process usually involving a single resonance. In general, this method of ionization can result in a soft ionization process with a minimum amount of

fragmentation. (See ref 1 and references therein for a partial list of representative studies.) However, soft ionization is frequently difficult to achieve for large fragile molecules which tend to predissociate when irradiated with UV radiation. In order to prevent or minimize the fragmentation of these fragile molecules, unique conditions must be employed. In a recent study of nitro aromatic compounds by Zhu and co-workers,¹ the laser ionization process was performed under atmospheric conditions in a buffer gas and the resulting ions injected into a mass spectrometer. These experiments demonstrated that the fragmentation process could be strongly moderated but not completely quenched.

An alternate approach to detecting large fragile molecules is based on the use of UV laser radiation to photodissociate the parent molecules into characteristic fragments (see ref 5-13 for a partial list of representative studies). The photofragments typically include di- and triatomics, as well as atoms, which generally have structured, readily identifiable transitions in the UV-vis spectral region. These fragments may be detected either by their prompt emission, if electronically excited during the photolysis, by laser-induced fluorescence (LIF), or by resonance-enhanced multiphoton ionization (REMPI).

Characteristic of many propellants and explosives is the presence of one or more NO₂ functional groups bonded to either a carbon or nitrogen atom. This functional group is weakly bound to the main skeletal portion of the molecule by approximately 40-50 kcal/mol, depending on the molecule, and is responsible for the weak and structureless absorption feature observed in the UV near 230 nm.^{14,15} A perusal of the literature reveals that the UV laser photodissociation of energetic molecules, such as RDX,¹⁶ and model compounds,^{11,12,17} under collision-free conditions, results in the production of NO₂ in the initial step in the photolysis. Two common laser-based spectroscopic methods of detecting NO₂

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* To whom correspondence should be addressed.

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are by LIF and from its prompt emission.^{11,16,17} However, both of these methods are very inefficient since the absorbed radiation is radiated over a large spectral region, visible to near infrared. The radiative lifetime for these transitions is also very large, typically $\sim 50\text{--}120\ \mu\text{s}$,¹⁸ and is indicative of a weak oscillator strength. Moreover, predissociation to $\text{NO} + \text{O}$ predominates over fluorescence at wavelengths less than 400 nm. The NO fragment is better suited for detection since it is readily formed from the predissociation^{19,20} of NO_2 and its radiative lifetime²¹ ($\sim 200\ \text{ns}$) is significantly shorter than the NO_2 states excited in the visible region. The NO fragment can be detected with a high degree of sensitivity and selectivity by (1 + 1) REMPI and/or LIF via its $\text{A}^2\Sigma^+ \text{--} \text{X}^2\Pi$ transition near 226 nm. Thus, one laser tuned to 226 nm can be used for both parent photofragmentation through its structureless UV absorption feature and fragment detection.

The laser photodissociation/fragment detection technique is most effective when coupled with pulsed molecular beam (MB) sampling and time-of-flight (TOF) mass spectrometric analysis. A TOF mass spectrometer of modest design and optimization can detect a packet of ions of up to 500 amu in less than 100 μs with resolution ($m/\Delta m$) greater than 500, while pulsed molecular beam sampling can greatly improve the selectivity over ambient sampling and the sensitivity over CW sampling. The molecules in the beam are colder than those at ambient conditions since they are subject to a supersonic expansion. Thus, they are produced in a few distinct ro-vibrational states, and as a result, their absorption spectrum is considerably less congested, although the NO fragment is certainly no longer colder. Spectral interference from other molecular systems is therefore minimized, if not eliminated. The application of a pulsed nozzle also greatly reduces the total gas throughput entering the analysis chamber while still maintaining a high density of the sample.

In this paper, we report on the sensitive detection of nitro compound vapors using a one-laser photofragmentation/fragment detection technique. A laser tuned to 226 nm is used for both the photolysis of target molecule and subsequent detection of the NO fragment by REMPI and/or LIF via its $\text{A}^2\Sigma^+ \text{--} \text{X}^2\Pi$ transition. The analytical utility is demonstrated using trace energetic materials and model compounds in a MB/TOF apparatus. Limits of detection for various compounds such as NO_2 , dimethylnitramine (DMNA), nitromethane, nitrobenzene, trinitrotoluene (TNT), and 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX) are reported and discussed.

EXPERIMENTAL SECTION

A schematic diagram of the molecular beam apparatus equipped for laser spectroscopy and time-of-flight mass spectrometry is depicted in Figure 1. The apparatus has been constructed for both laser-induced fluorescence and resonance-enhanced multiphoton ionization studies. The body of the apparatus consists of two main chambers. The first chamber consists of an 8-in. tee with smaller ports added for laser excitation and fluorescence collection. This chamber is pumped out through the bottom of the tee by a 1000 L/s turbo molecular pump (Leybold-Heraeus, TurboVac 1000). To the left of the tee is a pulsed supersonic valve (R. M. Jordan Co., PSV) modified so that it can be translated the length of the chamber and can be positioned for either LIF or REMPI experiments. To the right of the tee is mounted an 8-in. 4-way cross serving as the second

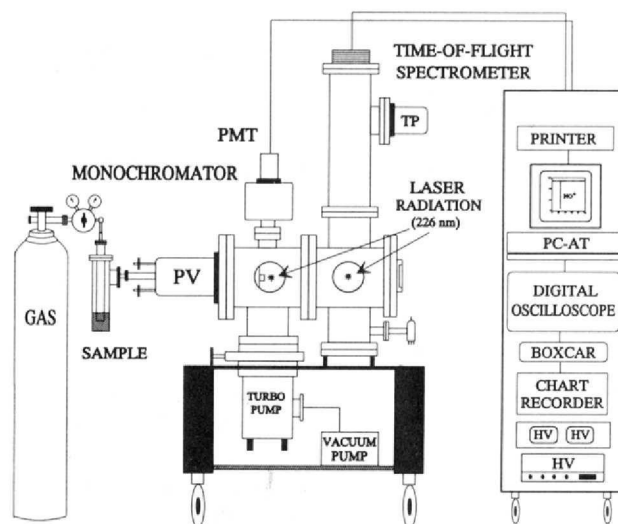


Figure 1. Schematic of the experimental apparatus.

chamber. These two chambers are differentially pumped and are separated by a skimmer with a 3-mm orifice (Beam Dynamics, Inc., Model 2). Mounted on the top of the cross chamber is a 1-m commercial time-of-flight mass spectrometer (R. M. Jordan Co.) with reflectron.

The TOF mass spectrometer distinguishes ions of different masses by their different arrival times to the detector located at the end of the flight tube. Although the time of arrival of the ions depends on the sum of the transit times through various regions of the mass spectrometer, it is proportional to the square root of the mass-to-charge ratio of each ion.^{22,23} Therefore, the time of arrival, t_1 , of mass m_1 is related to the time of arrival, t_2 , of mass m_2 by the equation

$$m_1/m_2 = t_1^2/t_2^2 \quad (1)$$

The determination of any mass, m_2 , may be made with an accurate measurement of t_1 for a known mass, m_1 . In this study NO was used for the calibration of the mass spectra. For a typical set of operating conditions, an acceleration voltage of approximately 2000 V ($1\ \text{eV} = 1.60 \times 10^{-12}\ \text{g}\cdot\text{cm}^2/\text{s}^2$) and a flight length of 2 m, a complete mass spectrum up to a mass of 500 amu ($1\ \text{amu} = 1.67 \times 10^{-24}\ \text{g}$) could be recorded in approximately 72 μs .

Samples of nitromethane (Aldrich), nitrobenzene and trinitrotoluene (Eastman-Kodak), and DMNA and RDX (ARDEC) were selected for this study. For safety precautions, samples of TNT and RDX were handled in aliquots of less than 10 mg in a static and shock-free environment. All the samples were used without further purification. They were introduced into the analysis chamber either in an effusive flow, so that the gas in the sampled volume was replenished at a rate sufficient to avoid accumulation of photolysis products, or in a pulsed molecular beam. All reported data is from the latter, where the vapors of the analytes were seeded in an atmospheric pressure of air (Potomac), nitrogen (Matheson), or argon (ARL) gas, and the mixture was expanded into the analysis chamber using a pulsed valve (10 Hz) with a 0.5-mm-diameter nozzle. Although the valve has the capability of being heated to temperatures as high as 150 °C, it was operated at room temperature for all the samples studied, except RDX and TNT. In the case of RDX and TNT, the samples were heated to approximately 100 °C during analysis. A temperature difference of $\pm 10\ ^\circ\text{C}$ results in an uncertainty in the vapor pressure determination which would effect the sensitivity measurements by a factor of 2. Standard mixtures used to determine the sensitivity were prepared by serial dilution of 0.1% NO_2/Ar (Matheson), 570 ppm $\text{CH}_3\text{NO}_2/\text{Ar}$, and 131 ppm DMNA/Ar. The NO_2 sensitivity was determined using a 6.2 ppm NO_2/air (Scott-Marrin). Sensitivity measurements for nitrobenzene at room temperature, as well as TNT and RDX at 100 °C,

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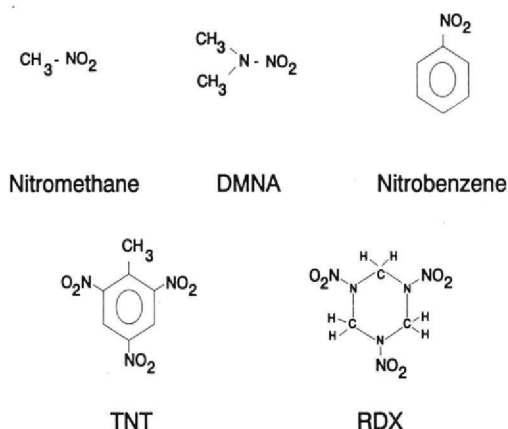
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Chart I. Structural Formulas and Names of Nitro Compounds Used in This Study



were obtained by using standard Ar mixtures containing the analytes at their respective vapor pressures.^{24,25}

The pulse pressure was calculated by employing the following equation:

$$P_{\text{pulse}} = P(r/R)^2(1 - \cos^3 \theta) \quad (2)$$

adapted from ref 3. In the above equation, P is the backing pressure, r is the radius of the nozzle, R is the radius of the skimmer orifice, and θ is the skimmer transmission angle. This angle is equal to the arctangent of the ratio of the radius of skimmer orifice (R) to the distance from the skimmer to the nozzle (D). A pulse pressure of 180 mTorr was obtained when using a backing pressure of 770 Torr, a nozzle diameter of 0.5 mm, a skimmer diameter of 3.0 mm, and a skimmer to nozzle distance of 2.0 cm.

The samples were photolyzed and the NO fragment subsequently ionized using focused ($f = 250$ - or 500 -mm lenses) UV radiation at or near 226 nm. An excimer pumped dye laser (Lumonics Hyper EX-400 and Hyper DYE-300) with second harmonic generator (Lumonics TRAK-1000) operated at 10 Hz was used to generate the tunable UV radiation. Pulsed energies of the order of 10–150 μJ with duration of 15–20 ns were employed for detection. The line width of the tunable UV radiation is approximately 0.16 cm^{-1} (fwhm).

The LIF technique was also employed for comparison to the REMPI technique. The fluorescence signal, whether prompt or induced, was collected 90° to the photolysis beam and focused onto the entrance slit of a 0.25-m monochromator (McPherson, Model 218) acting as a broad-band filter (≈ 8 -nm fwhm). The monochromator was tuned to approximately 237 and 500 nm for the detection of NO and NO_2 , respectively. Schott filters UG-11 and GG-435 were also used in place of the monochromator. The signals were detected with a photomultiplier tube (EMI 9789QA) and directed into a gated integrator (Stanford Research Systems). Both fluorescence and ion signals were displayed and monitored in real time on a 125-MHz digital oscilloscope (LeCroy 9400). A PC-AT computer was employed for data acquisition and analysis. The NO_2 prompt emission signal from DMNA was considerably less than that obtained from the NO LIF, as expected. Thus, studies involving NO_2 prompt emission from other precursors were not pursued.

RESULTS AND DISCUSSION

Presented in Chart I are the names and structural formulas of molecules used in this study. A cursory inspection of the chart reveals that these nitro compounds, as well as other energetic materials, contain one or more weakly bound NO_2 functional groups. The physical processes underlying our approach to the detection of nitro compounds may be

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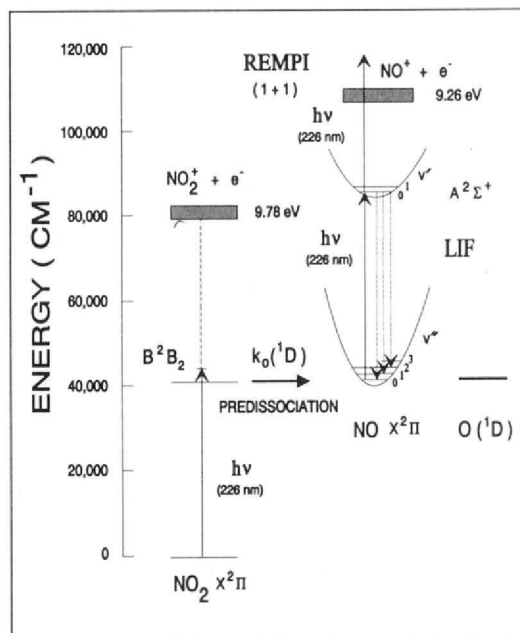


Figure 2. Potential energy diagram of NO_2 and NO showing the multiphoton scheme employed for the REMPI and LIF detection of the NO photofragment at 266 nm.

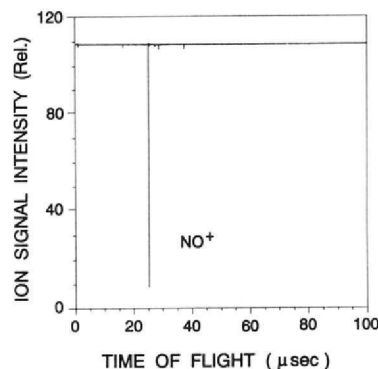
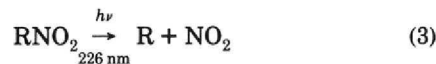


Figure 3. Time-of-flight REMPI spectrum of NO^+ generated from DMNA. The sample was introduced into the analysis chamber in molecular beam using Ar as the carrier gas, and the mixture was irradiated with approximately 100 μJ of 226-nm radiation.

understood by referring to Figure 2 which shows potential level diagrams of NO_2 and NO. In our approach, the target molecule (RNO_2) is first photolyzed to NO_2 , along with its corresponding companion radical (R), via the process



The NO_2 fragment is then detected by monitoring its predissociative product NO using (1 + 1) REMPI or LIF employing its $\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi$ (0,0) band at 226 nm. This mechanism is similar to that described by Moss and co-workers¹² in a recent paper on the photodissociation dynamics of nitromethane using a two-laser pump-and-probe technique. However, in the present results the photolysis wavelength was chosen to coincide with the maximum signal associated with the A–X (0,0) transition in NO and is generalized to all NO_2 -containing compounds.

Presented in Figure 3 is a typical mass spectrum obtained when photolyzing a molecular beam of DMNA seeded in argon using 226-nm radiation. DMNA was studied since it is a simple analogue of cyclic nitramines such as RDX (see Chart I). The spectrum shown in Figure 3 is characteristic of all the compounds studied. It reveals a prominent peak whose arrival time to the detector is measured as 23.2 μs . This time

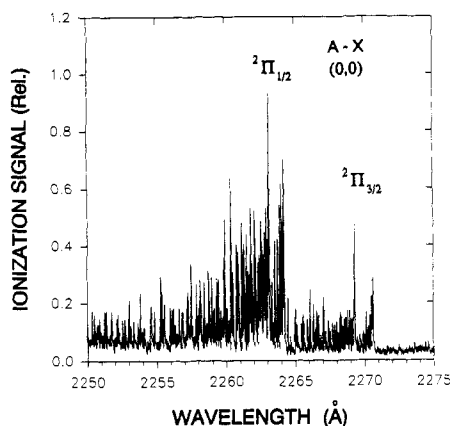


Figure 4. REMPI excitation spectrum of NO^+ in the region of 226 nm. The NO^+ was generated from a molecular beam of DMNA.

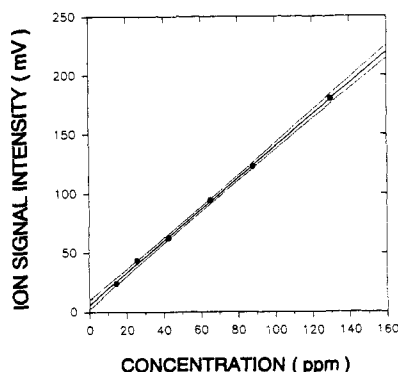


Figure 5. Concentration dependence of the REMPI NO^+ ion signal obtained from a molecular beam of DMNA. The solid line is a least squares fit of the data (●) with 95% confidence (---). The slope yields a value of 1.34 ± 0.04 mV/ppm (2 SD).

corresponds to a mass-to-charge ratio (m/z) of 30 and is attributed to the NO^+ ion. Similar results were obtained when using air or nitrogen as the carrier gas. No such peak was observed, however, when the laser was tuned off-resonance. The observed peak is void of any interference and is clearly a result of a REMPI process. To maximize the signal intensity and verify the mass spectral assignment, an excitation spectrum was obtained by scanning the tunable UV radiation while monitoring the $m/z = 30$ peak. This spectrum is shown in Figure 4. It reveals numerous rotational lines which are attributed unequivocally to electronic transitions of the $\text{NO } A^2\Sigma^+ - X^2\Pi (0,0)$ band.

A plot of the NO REMPI signal intensity as a function of concentration of the precursor molecule, DMNA, is shown in Figure 5. The plot is linear and has a slope of 1.34 ± 0.04 mV/ppm (2 SD). A limit of detection of 450 ppb is obtained when using a background noise value of 200 μV . Detection limits are defined in this study as the concentration, C_L (ppb), that produces a signal (mV) equal to three times the standard deviation, σ (mV), of the background divided by the sensitivity, S (mV/ppb), of the method to the compound. The linearity of the plot implies that the NO is formed in a collision-free environment, as expected in a molecular beam, and that this technique is suitable for quantification purposes. The dynamic range of measurements in these studies is limited to about 2 orders of magnitude due to the limited accuracy of the flow meters used for dilution at low concentration and low vapor pressures of the compounds at high concentrations. However, it is reasonable to anticipate that the method is linear in its response all the way to the detection limit. Indeed, similar studies of NO by REMPI methods have shown the capacity for single-ion detection in combination with a large

Table I. Limits of Detection for Various Nitro Compounds Studied Using the Technique of Laser Photofragmentation/NO Fragment Detection by REMPI-TOF

compound	limit of detection (ppb)	compound	limit of detection (ppb)
NO	8	RDX	8
NO_2	240	TNT	24
CH_3NO_2	1000	nitrobenzene	2400
DMNA	450 (2000) ^a		

^a Limit of detection obtained by laser-induced fluorescence of NO via its $A^2\Sigma^+ - X^2\Pi (0,0)$ transition.

dynamic range of sensitivities.²⁶

Presented in Table I are limits of detection for several compounds studied employing the fragmentation/REMPI technique using 226-nm radiation. As seen from Table I, detection limits have been obtained in the ppb to ppm range. The limits of detection refer to the gas concentration of the analyte prior to introduction into the analysis chamber. Vapor pressures of the compounds were obtained from refs 24 and 25 and used to estimate the initial concentrations. For 1 atm of backing pressure, the calculated gas volume throughput of the supersonic nozzle (per pulse) is 6.8 Torr/ cm^3 . This corresponds to absolute detection limits of 1 and 3 pg for RDX and TNT, respectively, and compares favorably with absolute detection limits reported for TNT which are on the order of 200 pg.²⁷ For nitromethane, Schendel and co-workers¹⁰ reported a concentration detection limit of $4.2 \times 10^9/\text{cm}^3$ by monitoring the prompt emission resulting from approximately 30 mJ/pulse of ArF laser excitation. A detection limit of 1 ppm in this study corresponds to a concentration of approximately $6 \times 10^9/\text{cm}^3$ in the probe region of the laser.

The limits of detection for the precursors depend on a number of factors such as the efficiency of sample introduction, the laser pulse energy, the efficiency in the photodissociative pathways leading to the formation of NO in its $X^2\Pi (v'' = 0)$ vibronic state, and the voltage settings of the ion optics and detector. Although the experimental system used for these studies was optimized with respect to these factors in order to obtain the maximum sensitivity possible, the current design of the experimental system could be improved for performing trace analysis. Significant improvements in the sensitivity can be expected with higher laser energies and with a supersonic valve/sampling device whose design increases the sample throughput into the photolysis region. The ability to operate the valve at a higher repetition rate (>50 Hz) and at elevated temperatures, in order to eliminate condensation of the precursor, would also be desirable. A supersonic nozzle meeting some of these criteria has been designed and demonstrated by Imasaka and co-workers²⁸ as part of an ionization detector apparatus for gas chromatography.

In the present studies, the experimental conditions were identical for all of the compounds. Thus, any differences shown in Table I are indicative of different absorption cross sections that the target molecules have at 226 nm and the photodissociation efficiency. It is clear from Table I that RDX, TNT, and NO_2 are particularly efficient in generating REMPI signals. In the case of NO_2 , this was not too surprising since Morrison and co-workers^{19,20} observed that by far the most prominent ion fragment generated by the multiphoton excitation of NO_2 at wavelengths in the region from 425 to

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455 nm was the NO^+ . Their data suggest that the course of excitation in this system is dominated by predissociation into $\text{NO}(^2\Pi) + \text{O}(^1\text{D})$ at the level of the second photon within the $\text{B}(^2\text{B}_2)$ state. They contend that this high energy dissociation pathway becomes important soon after this channel becomes energetically accessible. With 226-nm excitation, this pathway is in fact available by a single photon absorption.

As noted earlier, the measured REMPI signals depend on several factors. One compound, DMNA, was chosen to investigate the dependence of the signal on the laser pulse energy. The dependence of ion signal intensity on laser energy was determined using the equation

$$S = C(I_{226})^n \quad (4)$$

where S is the ion signal intensity, I_{226} is the laser beam fluence, C is a system-dependent constant, and n the number of photons required to produce the NO^+ signal. The value of n was determined from the slope of a log-log plot of the variables in eq 4. A priori, one might expect the value of n to be as high as 4, two photons required to generate NO in its $\text{X}^2\Pi$ state and two photons to ionize it (see Figure 2). However, the slope of the plot yielded a value of $n = 1.62 \pm 0.01$ (2 SD) indicating that the formation of the ion requires at least two photons. This near quadratic dependence suggests that one or more of the intermediate photochemical steps necessary to generate NO^+ from RNO_2 is saturated. It also suggests that a significant enhancement in the signal can be achieved at higher laser intensities.

The proposed laser photodissociation/fragment detection technique is intended to identify nitro compounds as a class or group by detecting the presence of the specific NO fragment, not the parent molecule. One advantage of this technique is its high degree of selectivity for NO since it combines the REMPI method with TOF mass spectrometry. The overall selectivity of induced ionization methods is a multiplicative combination of the selectivity achieved by the laser excitation process(es) and the selectivity achieved by the mass spectral device.²⁹⁻³¹ As shown in Figure 3, a high degree of selectivity is obtained by the REMPI method. When the laser excitation wavelength is tuned to a strong NO transition, the ionization of NO occurs virtually at the exclusion of any other species. The selectivity for the NO fragment is further enhanced by the use of a TOF mass spectrometer, which prevents detection

of any spectral ionization interferences, except those which are also isobaric.

For the purposes of comparing the methods of REMPI and LIF photofragment detection, the NO fragment was monitored by LIF via its $\text{A}^2\Sigma^+ - \text{X}^2\Pi$ (0,0) band following the photolysis of DMNA with 226-nm radiation. As shown in Table I, the limit of detection was estimated to be 2 ppm, a factor of approximately 4 worse than that obtained with the REMPI technique. This difference in sensitivity results primarily from a high background inherent in this LIF measurement. The selectivity can also be compared for the two methods, since they share a common wavelength of excitation at 226 nm. In this study, the selectivity of the LIF measurement is lower due to the relatively larger bandwidth of the monochromator and interference filter used and is not necessarily characteristic of the LIF technique. The large bandwidth is necessary, however, in order to collect the broadband fluorescence emission of NO and maintain a sufficient level of sensitivity.

SUMMARY AND CONCLUSION

A novel technique for the detection of trace NO_2 -containing compounds has been developed for the purpose of detecting energetic materials such as propellants and explosives. It employs one laser operating at 226 nm and is based on the photofragmentation of the target molecule with subsequent detection of NO by REMPI and/or LIF via its $\text{A}^2\Sigma^+ - \text{X}^2\Pi$ (0,0) band origin. The analytical utility has been demonstrated on a number of compounds, including NO_2 , DMNA, TNT, and RDX, using a molecular beam, time-of-flight apparatus. Detection limits in the ppb were achieved for RDX and TNT with extremely low laser energies, $\sim 100 \mu\text{J}$ /pulse. Lower limits of detection are, however, projected by employing an improved system design and higher laser energies.

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