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Spectrometric Studies of Selected Nitrocompounds Using Laser-Induced Photofragmentation/Photoionization at 193 nm

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13. ABSTRACT *(Maximum 200 words)*

A new method for detecting trace vapors of NO$_2$-containing compounds near atmospheric conditions has been demonstrated using one color laser photofragmentation/fragment ionization spectrometry. An ArF laser is employed to both photolytically fragment the target molecules in a collision-free environment and ionize the characteristic NO fragments. The production of NO is hypothesized to result from a combination of two NO$_2$ unimolecular fragmentation pathways, one yielding NO in its $X^2\Pi$ electronic ground state and the other in its $A^2\Sigma^+$ excited state. Ionization of ground state NO molecules is accomplished by resonance-enhanced multiphoton ionization processes via their $A^2\Sigma^+ <- X^2\Pi$ (3,0), $B^2\Pi <- X^2\Pi$ (7,0), and/or $D^2\Sigma^+ <- X^2\Pi$ (0,1) bands at 193 nm. The analytical utility of this method is demonstrated in a molecular beam time-of-flight apparatus. Limits of detection range from the parts-per-million (ppm) to parts-per-billion (ppb) level for NO, NO$_2$, CH$_3$NO$_2$, dimethylnitramine (DMNA), *ortho-* and *meta*-nitrotoluene, nitrobenzene, and trinitrotoluene (TNT). Under effusive beam experimental conditions, discrimination between structural isomers, *ortho*-nitrotoluene and *meta*-nitrotoluene, has been demonstrated with the use of their characteristic photofragmentation/photoionization mass spectra.

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1. INTRODUCTION

Trace detection of energetic materials (EMs) is a difficult analytical problem that has important applications in aviation security, forensics, and military mine countermeasures (Fainberg 1992; Reutter, Buechele, and Rudolph 1983; and Haung, Kolaitis, and Lubman 1987). The challenge is to develop a vapor phase detector for these compounds that has sufficiently high levels of sensitivity and selectivity, and can operate in real time. This is a formidable challenge since most EMs are low in volatility and thermally labile. Methods that are currently used to detect EMs in the vapor phase include ion mobility spectrometry (IMS) and mass spectrometry coupled with gas chromatography (Fainberg 1992). By comparison, optical detection is difficult to accomplish because of weak and featureless absorptions, and the susceptibility of large molecules to undergo nonradiative relaxation processes including fragmentation. An alternative approach to direct spectroscopic detection is photofragmentation/photoionization (PF/PI) spectroscopy. In this technique, characteristic fragments generated from the photolysis of the parent molecule are probed spectroscopically. For representative studies, see Rodgers, Asai, and Davis (1980); Schendel, Hohmann, and Wehry (1987); Lee et al. (1992); Sausa, Alfano, and Miziolek (1987); Clark et al. (1992); Marshall et al. (1992); Oldenborg and Baughcum (1986); Schendel et al. (1990); and Schendel and Wehry (1988); and references therein. These smaller fragments include atoms, diatomics, and triatomics, which have relatively sharp and strong spectral features, and can readily be detected by prompt emission, laser-induced fluorescence (LIF), or multiphoton ionization (MPI) spectrometry techniques.

Common to most EMs is the NO_2 functionality which is easily removed by excitation in the 190–250 nm region of the ultraviolet (UV) spectrum (Smit 1991). The NO2 molecule can itself be detected or further fragmented to form NO, which is detected by LIF or resonance-enhanced multiphoton ionization (REMPI) using the strong $A^2\Sigma^+$ (v′=0) <- $X^2\Pi$ (v″=0) transition at 226 nm for excitation. Recently, we reported the demonstration of a new method of detecting NO_2–containing compounds based on the photolysis of the parent molecule and subsequent REMPI of the NO fragment using one laser tuned to 226 nm (Lemire, Simeonsson, and Sausa 1993). This method is both sensitive and selective, and achieves gas phase concentration limits of detection (LOD) in the parts per billion (ppb) to parts per million (ppm) range for selected compounds, including trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5,-triazine (RDX).

A significant drawback of the method used in our previous work is the complexity of the instrumentation which includes an excimer-pumped dye laser system with second harmonic generation.

Instead of a dye laser, it would be preferable to use a nontunable laser source which can both photofragment and ionize the NO fragment. The ArF laser operating at 193 nm is a good candidate for this approach since it is an efficient photolysis source useful for generating the NO_2 fragment (Schendel, Hohmann, and Wehry 1987), and can also operate as a REMPI source for NO molecules exciting several transitions in the $A^2\Sigma^+$ <- $X^2\Pi$ (3,0) and $B^2\Pi$ <- $X^2\Pi$ (7,0) bands near 193 nm (Robie, Buck, and Bischel 1990) through higher rotational levels. In addition to ground state resonances, the ArF laser output can excite transitions in the $D^2\Sigma$ ($v'=0$) <- $X^2\Pi$ ($v''=1$) band ($J''=19.5$-44.5) (Robie, Buck, and Bishel 1990; Wodtke et al. 1988).

In the current study, selected nitrocompounds are detected with the use of an ArF laser as the photofragmention source for target molecules and also as the REMPI source for NO fragments. The analytical utility of this method is demonstrated on a number of compounds including NO, NO_2, dimethylnitramine (DMNA), nitromethane, nitrobenzene, *ortho-* and *meta*-nitrotoluene, and TNT employing molecular beam sampling with mass spectrometric detection. Limits of detection are reported and compared to those obtained previously by other methods. The photodissociation and ionization mechanisms at 193 nm are also discussed. Discrimination between different NO_2-containing compounds is demonstrated using two structural isomers under effusive beam conditions. Mass spectra containing characteristic fragmentation is observed for each isomer.

2. EXPERIMENTAL

The molecular beam/time-of-flight mass spectrometer system used in this study has been described in a previous publication (Lemire, Simeonsson, and Sausa 1993). A schematic diagram of the salient features is shown in Figure 1. Briefly, sample vapors were introduced as minor species in Ar (99.995%, Potomac Gases), nitrogen, or air (ARL Post Gases) which served as the expansion gas. Gas phase concentrations were calculated using the vapor pressures of the compounds at room temperature. The mixtures were expanded from a pulsed supersonic valve (R. M. Jordan and Associates) into a vacuum chamber, pumped by a turbomolecular pump, which maintained an average pressure of 10^{-4} Torr. A skimmer placed 2 cm from the nozzle transmitted a molecular beam into a second high-vacuum chamber (10^{-6} Torr). The molecular beam traversed the ionization region of a reflectron-type (Wiley-McLaren design) time-of-flight mass spectrometer (R. M. Jordan and Associates) whose flight tube was oriented perpendicular to the direction of the molecular beam. Ions produced in the ionization region were transmitted into the flight tube by acceleration plates biased at 1,500 V. Effusive beam sampling was

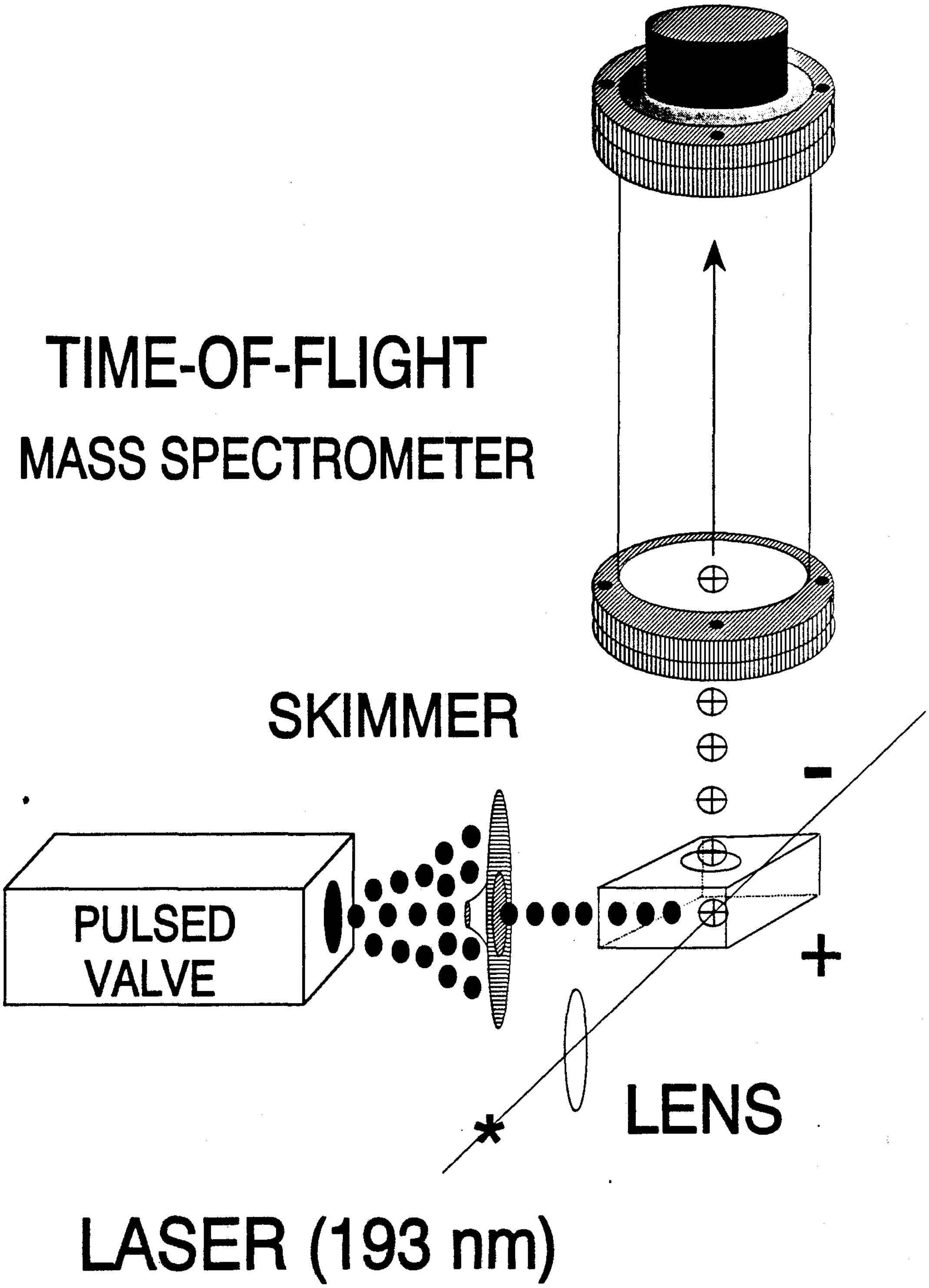

Figure 1. Schematic diagram of the salient features of the experimental apparatus.

accomplished by placing a small amount of the compound of interest in a quartz tube connected by a Cajon fitting to a needle valve on the ionization chamber. Sample vapor pressures in the chamber were regulated by the needle valve.

An excimer laser (Lambda Physik EMG 150C) operating at 193 nm with ArF was used for photolysis and ionization. The laser beam was aperatured to 10 mm in diameter, and transmitted into the vacuum chamber through MgF_2 windows into the center of the ionization region. In this region, the laser beam was both perpendicular to the molecular beam and the flight tube. A quartz lens (250 mm) external to the vacuum chamber was used for focusing to increase the laser fluence in the sample ionization region. Pulse energies of the ArF laser were nominally 1 to 1.5 mJ in the photolysis region for all of the measurements. A maximum laser fluence of 10^{22} photons/cm^2 was calculated using a focal spot area estimated to be 1×10^{-7} cm^2.

Operation of the pulsed supersonic valve and the laser was synchronized and controlled by a precision delay generator (Stanford Research Systems #DG535). Time-of-flight mass spectra were acquired by a 125-MHz digital oscilloscope (LeCroy 9400) that was interfaced to a PC-AT for storage. Quantitative measurements were performed by collecting the NO^+ signal with a boxcar (Stanford Research Systems 255) whose gate was adjusted to the time of arrival of the NO^+ fragment. The boxcar was also interfaced through an A/D converter to the PC-AT for data storage and analysis.

Calibration of the time-of-flight mass spectrometer response was accomplished using a standard NO in Ar mixture. The times-of-arrival NO^+ and Ar^+ ion signals allowed the determination of unknown masses through the following relationship (Wiley and McLaren 1955; Karataev, Mamyrin, and Shmikk 1972).

$$\frac{m_1}{m_2} = \left(\frac{t_1}{t_2}\right)^2 \tag{1}$$

Samples of DMNA were obtained from ARDEC, *ortho-* and *meta*-nitrotoluenes from ARL, and nitrobenzene and TNT from Eastman-Kodak. Nitromethane (spectrophotometric grade) was obtained from Mallinckrodt. NO was obtained from Union Carbide at 0.1% in Ar. NO_2 was obtained from Matheson at 6.20 ppm in air.

3. RESULTS/DISCUSSION

Selected nitrocompounds have been studied using the one laser photofragmentation/photoionization method. Shown in Figure 2 is a typical time-of-flight ion spectrum obtained at 193 nm for a molecular beam of DMNA in Ar. DMNA is a simulant molecule for the primary explosives RDX and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). In results similar to those for excitation at 226 nm (Lemire, Simeonsson, and Sausa 1993), the ion spectra of all the compounds at 193 nm are characterized by a strong ion signal whose time-of-arrival corresponds to a mass-to-charge ratio of 30. The molecular weight of NO^+, and the high intensity of the NO^+ signal and near exclusion of all other ion signals are indicative of a resonant enhancement of the fragmentation and/or ionization processes, and demonstrate the high selectivity of the method when 193-nm excitation is used. As a result of the higher laser fluences used at 193 nm, buffer gases such as Ar, N_2, and air-produced Ar^+, N_2^+, and other ion signals necessitating mass spectrometric detection. It is interesting to note that no ion signal was observed for NO_2^+. The absence of NO_2^+ signals is consistent with our previous studies, and is indicative of the rapid predissociation of excited NO_2 which prevents detectable ionization of the molecule.

Concentration limits of detection (LODs) measured for each compound studied are reported in Table 1. They are based on the measurement of the NO^+ ion signal and range from the ppb to ppm levels in 1 atm of Ar prior to introduction into the sampling apparatus. The analytical sensitivity is dependent on a number of parameters including: (1) the absorption cross section of the parent molecule at 193 nm, (2) the efficiency of photofragmentation of the parent molecule at 193 nm to yield NO in both its ground ($X^2\Pi$) and electronically excited ($A^2\Sigma^+$) states, and (3) the ionization cross section at 193 nm for NO in the above-mentioned states. Shown for comparison are LODs for the same compounds using the same apparatus with 226-nm excitation. The linear dynamic range at 193 nm extends three orders of magnitude for the detection of NO and over two orders for the detection of nitromethane. For most compounds, the upper bound of the linear dynamic range was limited by the vapor pressure of the compound.

It is useful to compare the results obtained in this study with those of similar studies. Employing photfragmentation/fluorescence spectrometry (PFFS), Schendel, Hohmann, and Wehry (1987) have reported an LOD for nitromethane of 4.2×10^9 molecules/cm^3 and similar order of magnitude values for nitriles, amines, and alkenes. Wodtke et al. (1988) estimated an LOD of 1 ppb for LIF measurements of NO in a flame using an ArF laser which corresponds to a number density of 4×10^9 molecules/cm^3. With an estimated gas throughput of 0.041 Torr-cm^3, the LOD of 180 ppb for nitromethane in this study

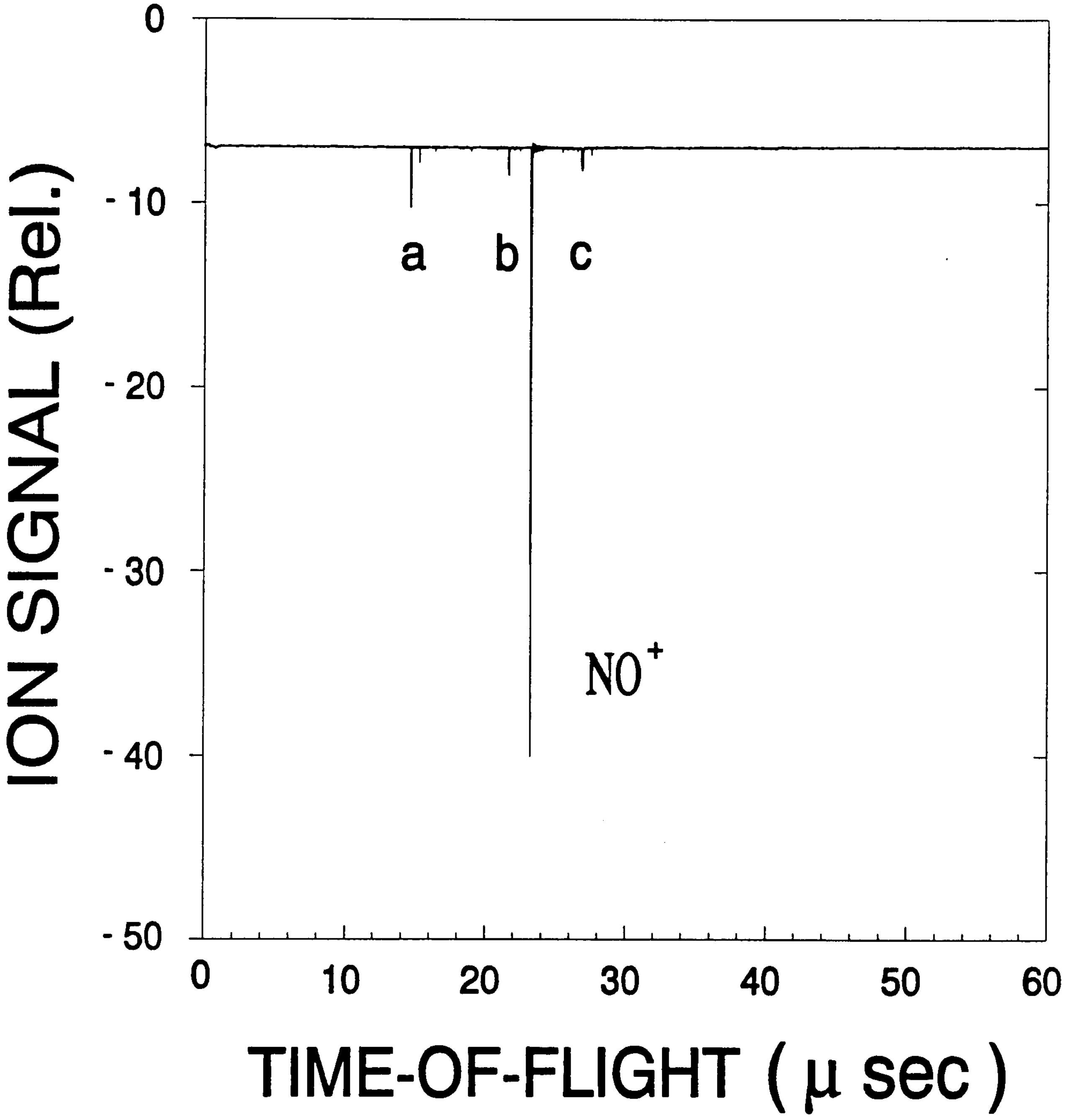

Figure 2. Time-of flight spectrum of a molecular beam of DMNA sampled from and atmosphere of argon. This spectrum is an average of ten spectra collected in 1 second using 193-nm radiation as the photolysis source. Features A, B, and C are assigned to C^+, C_2^+, and Ar^+, respectively.

Table 1. Limits of Detection of Selected Nitrocompounds Using ArF Laser Photofragmentation/Ionization Spectrometry

Compound	Limits of Detection (ppm[a] in Ar) 193 nm	Limits of Detection (ppm[a] in Ar) 226 nm
NO	1.2	0.008[b]
NO_2	0.50	0.24[b]
CH_3NO_2	0.18	1.0[b]
DMNA	0.51	0.45[b]
Nitrobenzene	0.49	2.4[b]
Ortho-nitrotoluene	0.12	15
Meta-nitrotoluene	0.10	36
TNT[c]	0.21	1.7

[a] Concentrations of species based on vapor pressures reported in Dobratz (1981) and CRC Handbook of Chemistry and Physics (1986).

[b] Reported previously in Lemire, Simeonsson, and Sausa (1993).

[c] Results for TNT obtained using an effusive sample source.

corresponds to a number density of 1×10^9 molecules/cm^3 in the probe region. Clark et al. (1993) have estimated an LOD of 1.1×10^9 molecules/cm^3 for nitrobenzene using a similar photofragmentation ionization at 226.3 nm. In the present study, an LOD of 0.49 ppm for nitrobenzene corresponds to a number density of 3×10^9 molecules/cm^3.

Further inspection of the results in Table 1 shows important differences in the trends of the detection limits at 193 nm and 226 nm. In particular, the LODs for individual compounds at different wavelengths suggest differences in the photofragmentation and/or photoionization mechanisms. For example, the LOD for NO is 8 ppb at 226 nm, and 1.2 ppm at 193 nm. At 226 nm, the laser excitation wavelength is resonant with the strong $A^2\Sigma^+$ (v'=0) <- $X^2\Pi$ (v''=0) transition, which is a highly efficient means of ionizing ground state NO molecules. In a supersonic expansion of NO, the vast majority of molecules are in low rotational energy levels of the vibrational ground state and, as a result, the REMPI of NO at this wavelength is highly sensitive. In contrast, the LOD for NO is over two orders of magnitude greater at 193 nm than at 226 nm, even despite higher laser energies (1 to 1.5 mJ at 193 nm vs. 100 μJ at 226 nm). This observation is due to the fact that the 193-nm excitation is resonant with transitions from weakly populated rotational states in the vibrational ground state in the A<-X and B<-X bands of NO. Furthermore, the spectral energy density of the ArF laser, which has a relatively large spectral bandwidth (100 cm^{-1}), is approximately 60 times less than the dye laser radiation. Both of these factors contribute to a low overall photoionization rate; thus, a lower sensitivity for NO detection.

By contrast, the relative sensitivities for large molecules at 193 nm are in general higher than those at 226 nm, as shown in Table 1. The increased sensitivity may be explained in terms of two factors: (1) the photofragmentation efficiency for the larger molecules is usually higher at shorter wavelengths, and (2) following photofragmentation, a larger fraction of the nascent NO fragment population distribution is resonant with the 193 nm radiation as compared to the 226 nm radiation. The latter factor is supported by studies of the population distributions of the photofragments of nitromethane at 193 nm (Butler et al. 1983; and Moss, Trentelman, and Houston 1992), which indicate that up to 10% of the NO produced by unimolecular dissociation of the NO_2 photofragment may be in v=1 in the $X^2\Pi$ state. As noted earlier, high sensitivity LIF measurements of vibrationally excited NO have been reported at 193 nm (Wodtke et al. 1988) by way of the $D^2\Sigma$ (v'=0)<- $X^2\Pi$ (v"=1) band. Presumably these transitions are also effective as first steps in a 1+1 REMPI mechanism for the production of NO^+.

The enhanced sensitivity for the NO photofragment at 193 nm also indicates that the photofragmentation and ionization mechanisms may be different at 193 nm and 226 nm. In order to understand the dynamics of the fragmentation and ionization processes at 193 nm, it is useful to consider the potential energy level diagrams of NO and NO_2 shown in Figure 3. Ground state NO molecules have several absorption resonances with the output of the ArF excimer laser (Robie, Buck, and Bishel 1990; Wodtke et al. 1988), which correspond to high rotational lines of the A<-X and B<-X bands. The multiphoton ionization of NO by a 1+1 REMPI mechanism is possible by these transitions; however, it is inefficient since these high rotational energy levels are unlikely to be significantly populated in a supersonically cooled expansion. Following absorption at 193 nm, NO_2 molecules have sufficient energy to predissociate primarily into NO($X^2\Pi$) and O(^1D) atoms (Butler et al. 1983; Moss, Trentelman and Houston 1992). The nascent NO fragments have a range of internal energies compared to the jet-cooled NO molecules and, as a result, more will be ionized by the 1+1 REMPI processes. This observation is manifested in the measured LOD's for NO and NO_2 which are 1.2 and 0.5 ppm, respectively (see Table 1).

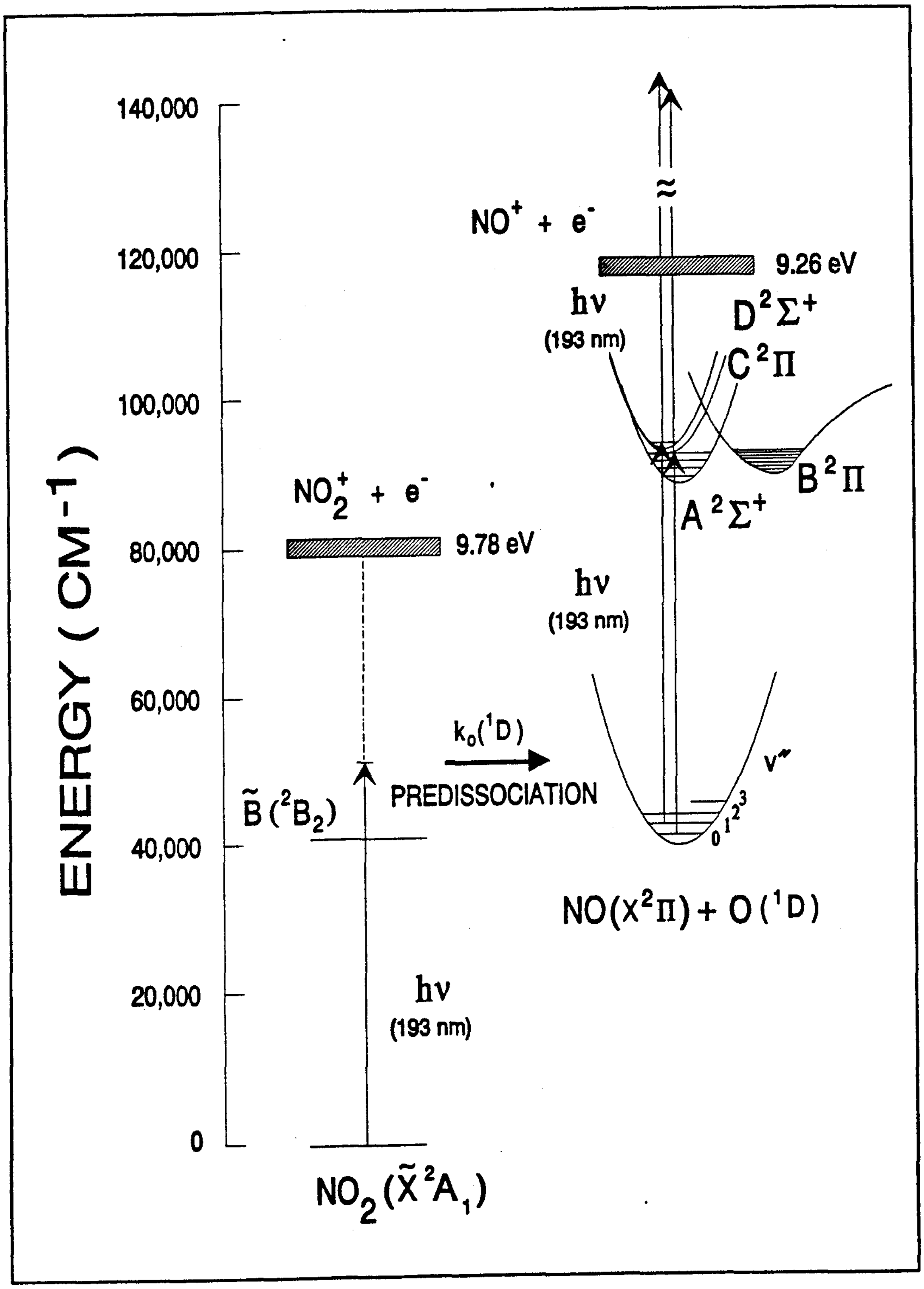

Figure 3. Potential energy diagram of NO_2 and NO revealing the resonance-enhanced multiphoton ionization scheme for detection of NO at 193 nm.

The mechanism by which NO^+ is produced from the ArF photofragmentation of R-NO_2 has not been yet determined. However, its formation is believed to result from both ground and electronically excited NO_2, produced from the 193-nm excitation of R-NO_2. This mechanism is inferred from previous studies on the photofragmentation dynamics of nitromethane at 193 nm (Butler et al. 1983; Moss, Trentelman, and Houston 1992). In one of these studies, Moss and co-workers employed multiphoton ionization spectroscopy and time-of-flight mass spectrometry to determine the nascent photofragment energy distributions of several of the products. Their study reveals that both NO(X) and NO(A) are produced from the parent molecule by a two-channel dissociation. The major channel produces CH_3 and its companion photoproduct NO_2, formed in its electronically excited $\tilde{A}\,^2B_2$ state. The electronically excited NO_2 has sufficient internal excitation to further dissociate to NO(X) and O as follows:

$$NO_2\ (\tilde{A}\,^2B_2) \dashrightarrow NO\ (X\,^2\Pi) + O\ (^1D)\ . \tag{2}$$

Under our experimental conditions, multiphoton ionization of the ground state NO is then possible by transitions in the A, B and D <-X bands. In the minor channel, the NO_2 photofragment is produced in its excited $\tilde{B}\,^2B_2$ state. The subsequent absorption of an additional 193 nm photon results in its photodissociation yielding $NO(A^2\Sigma^+)$ and $O(^3P)$. This channel is represented by the following reaction:

$$NO_2(\tilde{B}\,^2B_2) \xrightarrow[193nm]{h\nu} NO(A\,^2\Sigma) + O(^3P)\ . \tag{3}$$

Photoionization of the NO at 193 nm is direct from this state and requires one less photon than the ionization of ground state NO molecules. If these two channels are viable for the other nitrocompounds studied, then the sum of the contributions from the these two channels and that from ground state NO_2 photofragments accounts for the enhanced sensitivity observed for NO fragments at 193 nm.

In addition to the sensitivity of the photofragmentation/photoionization approach, it is interesting to note that ArF laser excitation and effusive source sampling have been used to distinguish structural isomers of nitrotoluene by their mass spectral fragmentation patterns. In this study, it was observed that the relative intensity of the various ions in a given spectrum were highly dependent on the focusing characteristics of the laser excitation. The largest ion signals for the NO photofragment were observed when the laser fluence was the highest. The only other ion signal of similar intensity was attributed to

C^+, which results from a two photon resonance-enhanced excitation process of the metastable carbon atom via its well-known (Sausa, Alfano, and Miziolek 1987; Döbele and Rückle 1982, 1992) (2p3s $^1P_1$<-2p^2 $^1D_2$) transition at 193.1 nm. As the laser fluence was reduced, the NO^+ and C^+ signals decreased dramatically, and other ion signals appeared. These signals corresponded to the parent ions and larger fragments characteristic of the parent molecules. Previous studies of the ultraviolet photofragmentation and ionization of nitrobenzene using effusive sampling and a tunable dye laser in the 245–260 nm range have shown similar intensity-dependent results (Clark et al. 1992).

Shown in Figures 4a and 4b are time-of-flight mass spectra of ortho-nitrotoluene (ONT) and meta-nitrotoluene (MNT), respectively, which illustrate the fragmentation and ionization of the molecules using an unfocused ArF laser as the excitation source and effusive sampling. These two molecules produce similar fragments but in different intensity ratios. The ArF excited spectra are similar to electron impact (EI) spectra, with the exception of enhanced signals for the NO^+ species, and can be used to identify and differentiate these two isomers. Relative fragment peak intensities for ONT and MNT are given in Table 2. Readily identifiable masses include m/z=77 (phenyl group), 91/92 (tropylium or benzyl ion and the protonated forms) and 137 (nitrotoluene parent ion).

The ion peaks at m/z=77 and m/z=107 are noticeably more intense in the case of MNT. The m/z=107 is attributed to CH_3-C_6H_4-O, which is the result of a rearrangement of the parent molecule followed by the loss of NO. This rearrangement is well-known for nitro-containing aliphatic and aromatic hydrocarbons (Silverstein, Bassler, and Morrill 1991). This rearrangement is also rationalized by the different peak intensities for the two isomers. Steric effects by the adjacent methyl group can hinder the rearrangement in the case of ONT but are less important in the case of MNT. This same trend is observed in the electron impact mass spectra, m/z=107 ion intensity being of the lowest intensity for the *ortho*-isomer, of moderate intensity for the *meta*-isomer, and of greatest intensity for the *para*-isomer where the methyl and nitro groups are farthest apart.

The above results demonstrate that, under effusive conditions, identification of isomeric compounds may be accomplished by adjustment of the laser fluence to produce characteristic mass fragments. The potential for compound discrimination or even identification by this method is a significant prospect for the photofragmentation/photoionization approach. The current example of structural isomer differentiation illustrates how, in this case, sensitivity can be compromised in order to obtain enhanced selectivity. A similar trend was expected under atmospheric molecular beam conditions, but was not observed. At present, this difference is not well understood, and is under investigation.

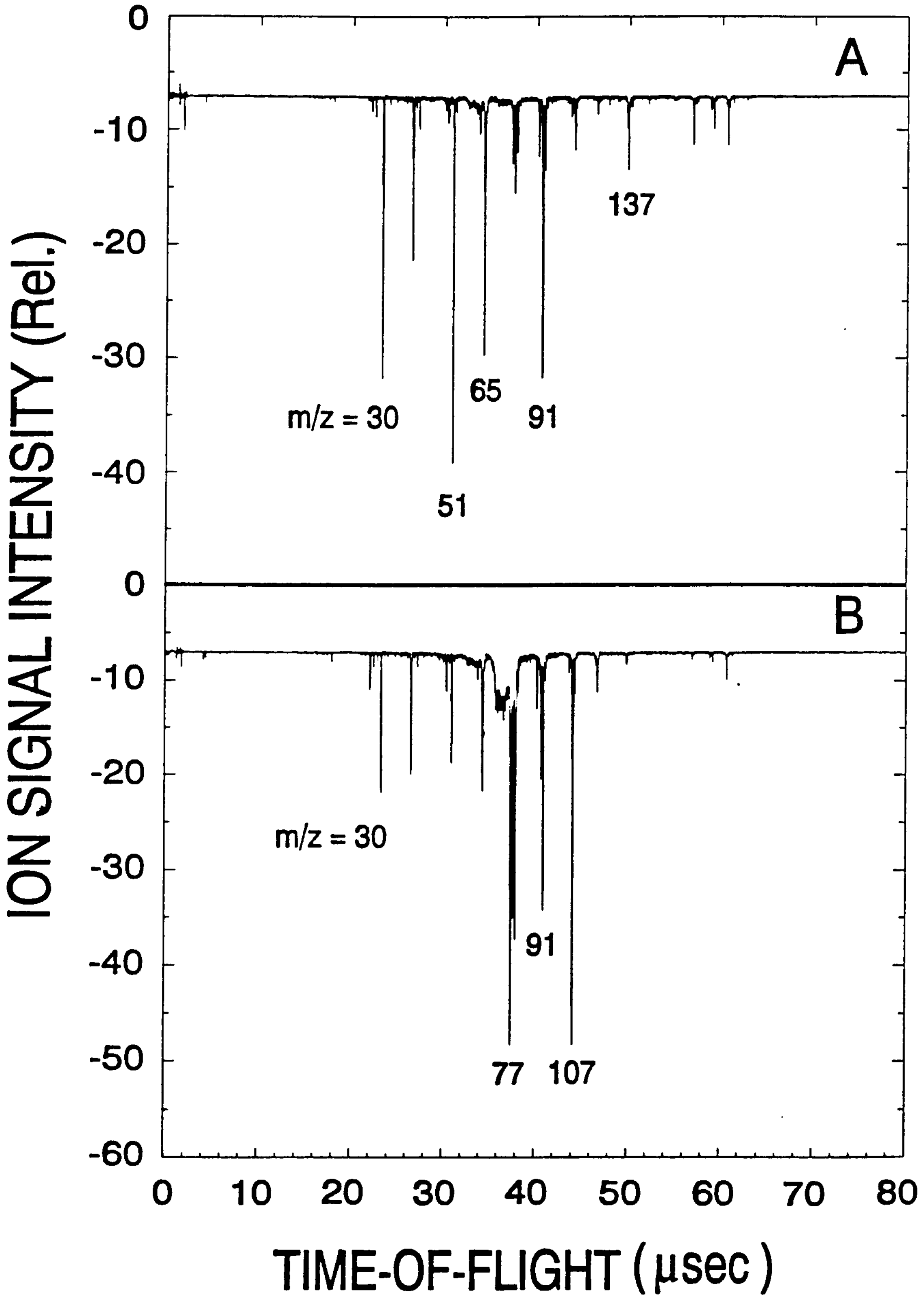

Figure 4. Time-of-flight spectra of *ortho*-nitrotoluene (A), and *meta*-nitrotoluene (B) obtained under effusive sampling using 193-nm radiation.

Table 2. Relative Intensities of Ions for *Ortho*- and *Meta*-Nitrotoluene

m/z	*Ortho*-nitrotoluene (%)[a]	*Meta*-nitrotoluene (%)[a]
30	36	77
39	31	45
50	10	—
51	28	100
65	36	71
77	100	26
91	13	77
92	66	—
107	100	15
120	9	—
137	3	21

[a] Intensities normalized to most intense mass peak.

Under atmospheric molecular beam conditions, significant improvement in the performance of the system could be achieved with changes in the sampling apparatus, whose current design is not optimal for trace analytical determinations. Improvements in the sample transmission efficiency from atmosphere into the photolysis/ionization region, estimated to be 0.02% in this study, could enhance the sensitivity greatly. Adsorption on the nozzle surface also lowers the sampling efficiency by removing a fraction of the sampled species. The ability to heat the nozzle to 150–200° C in order to avoid adsorption/ condensation would be beneficial.

Temperature control of the nozzle would also reduce the amount of time spent flushing between samples, which was necessary to reduce background ion signals. A high temperature nozzle meeting this criterion has been designed and demonstrated previously for supersonic jet spectroscopy of polyaromatic hydrocarbons (PAHs) and would be ideal for this application (Imasaka, Okamura, and Ishibashi 1986). Another improvement to the system would be to increase the laser intensity to improve the signal-to-noise characteristics. The ArF laser intensity was insufficient to saturate the measured ion signal in this study and could be increased to saturation to increase the sensitivity and reduce pulse-to-pulse fluctuations in the measured ion signals. Higher laser intensities would increase the sensitivity of the focal volume by increasing the number of species probed.

As these studies suggest, there are practical advantages to using an ArF laser rather than a dye laser for photofragment detection of NO_2-containing compounds. An ArF laser can deliver up to several hundred millijoules per pulse at 193 nm, making it a much more effective photolysis source than any dye laser currently available. By having several spectral resonances with the NO molecule, the ArF laser is an effective REMPI source. In broadband operation, the ArF laser can simultaneously excite several transitions from the $X^2\Pi$ ($v''=0,1$) states which enhances photofragment detection. It can also produce electronically excited NO fragments in the $A^2\Sigma^+$ state which are readily photoionized. In contrast, a narrow bandwidth (<0.1 cm^{-1}) dye laser generally restricts excitation to a single transition and rovibrational state. Other advantages of the ArF laser are that it is nontunable, rugged, and compact since it does not require laser dyes, dye cells, or delicate optical components. Although standard excimer laser technology does usually require gas handling equipment and the use of corrosive gases, excimer lasers can incorporate sealed discharge chambers allowing simplified operation. Thus, it is believed that excimer lasers have better potential for remote and/or *in situ* applications of the photofragmentation/fragment ionization technique.

4. CONCLUSIONS

A new method for the trace detection of nitrocompounds has been demonstrated at atmospheric conditions. This method uses an ArF excimer laser to both photofragment the parent molecule and ionize the characteristic NO fragment, and a time-of-flight mass spectrometer for detection. The photolysis yields significant nascent population of NO in rotationally and possibly vibrationally excited ground states resonant with 193-nm radiation, resulting in efficient ionization of the NO photofragment species by REMPI processes. ArF excitation can also ionize NO, which is produced in its electronically excited $A^2\Sigma^+$ state from the photolysis of the NO_2 fragment, and thus enhance the observed ionization signals for NO photofragments. The analytical utility of this method has been demonstrated on a number of compounds including NO, NO_2, nitromethane, DMNA, *ortho-* and *meta*-nitrotoluenes, and TNT. The limits of detection range from 100 ppb for meta-nitrotoluene to 1.2 ppm for NO and compare favorably with those reported by other spectroscopic methods. Under effusive sampling conditions, the selectivity of the method has been demonstrated to be enhanced by reducing the laser fluence to increase the ionization of other fragments.

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