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Laser-Induced Photofragmentation/ Fragment Detection Spectrometry of Brominated Compounds

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13. ABSTRACT (Maximum 200 words) Studies have been performed to evaluate the analytical capabilities of a novel, one-color, laser-induced photofragmentation/fragment detection technique for the detection of ambient brominated compounds. Laser radiation at 260.634 nm is used to both fragment the brominated compounds and excite the characteristic Br atom photofragment via its two-photon $4p^4 5p^4 D^{\circ}_{3/2} \leftarrow 4p^5 2P^{\circ}_{3/2}$ transition. Detection is accomplished by either (2+1) resonance-enhanced multiphoton ionization (REMPI), or by laser-induced fluorescence (LIF) or stimulated emission (SE) from the $4p^4 5p^4 D^{\circ}_{3/2} \rightarrow 4p^4 5s^4 P_{5/2,3/2}$ transitions at 844 and 751 nm, respectively. The SE signal is coaxial to the laser beam and is approximately two orders of magnitude greater than the LIF signal at 844 nm. Measurements are performed in a photolysis cell at total pressures of 1-760 Torr. For REMPI detection, total (nonselective) ion collection is employed using a miniature pair of electrodes. The absorption cross section of the two-photon $4p^4 5p^4 D^{\circ}_{3/2} \leftarrow 4p^5 2P^{\circ}_{3/2}$ transition is estimated to be $1.8 \times 10^{-45} \text{ cm}^4 \text{ s}$, and limits of detection in the ppb are obtained for CH_3Br , CHBr_3 , and CHClBr_2 . Results are discussed and compared to those obtained by other techniques.			
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1. INTRODUCTION

Volatile halogenated organic compounds, particularly those containing Cl or Br, are of considerable environmental importance because of their stratospheric ozone depletion capabilities, their contributions to the global greenhouse effect, and their utility as indicators of biological inputs in biogeochemical studies of marine and atmospheric systems [1-3]. Concerns are also growing that chlorinated organics are causing cancer in adults and adverse health and reproductive effects in the offspring of both humans and wildlife [4]. As a result, the development of monitoring methods for halogenated species has received increased attention.

A common method presently used to determine halogenated species under ambient conditions is cryogenic preconcentration of the sample followed by gas chromatography with electron capture detection (GC-ECD) [3,5,6]. Reifenhäuser and Heumann have reported parts-per-trillion (ppt) level sensitivities for CHBr_3 and other Br-containing compounds using this approach [3,5]. Absolute limits of detection (LODs) using GC-ECD are on the order of 1-100 pg of Br, depending on the compound [5,6]. Despite high sensitivity, the GC-ECD technique requires extensive sample manipulation and a long measurement cycle (approximately 1 hr).

Laser-based methods offer the advantages of high sensitivity and speed for the real-time monitoring of halogenated species *in situ* or remote. Cool and coworkers have reported the study of a resonance-enhanced multiphoton ionization time-of-flight mass spectrometry (REMPI-TOFMS) technique for the monitoring of C_2Cl_4 (TCE) in combustion environments [7]. Brewer and coworkers employed a pump-probe scheme to measure the quantum yields for atomic iodine production for a number of alkyl halides and HI [8]. One laser operating at 248 nm was used for photolysis while another tuned at 304.7 or 306.7 nm was used for a two-photon excitation involving the $5p^4 6p \ ^2D^{\circ}_{5/2} \leftarrow 5p^5 \ ^2P^{\circ}_{3/2}$ and $5p^4 6p \ ^2D^{\circ}_{3/2} \leftarrow 5p^5 \ ^2P^{\circ}_{1/2}$ transitions, respectively. The excited atoms decay to the ground state first by emission of an infrared photon, $^2D^{\circ}_{5/2} \leftarrow ^2P_{3/2}$ or $^2D^{\circ}_{3/2} \leftarrow ^2P_{1/2,3/2}$, and then by emission of a vacuum ultraviolet (VUV) photon which is detected. Using a similar pump/probe technique, Jeffries, Raiche, and Jusinski have described a two-laser atomization/laser-induced fluorescence (LA/LIF) technique suitable for measuring total chlorine in, for example, incinerator effluent [9]. Jeffries and Sappey have also employed two-photon LIF and stimulated emission (SE) to monitor ground state Cl atoms in an rf plasma etching environment [10]. Their excitation scheme was similar to Selwyn, Batson, and Sawin [11] and

employed excitation of the $3p^4 4p \ ^4S^{\circ}_{3/2} \leftarrow 3p^5 \ ^2P^{\circ}_{3/2,1/2}$ at 233 nm. Fluorescence to the $3p^4 4s(^4P)$ multiplet was then monitored near 750 nm.

Methods employing a one-color laser photofragmentation/REMPI or LIF fragment detection (PF/FD) scheme are an effective means for detecting a common substituent from a class of precursor species, and have been employed to detect various functionalities, including Cl [7,9,12], Br [3], and NO_2 [14–16]. Arepalli and coworkers employed tunable radiation ranging from 230 to 245 nm for the (2+1) REMPI detection of Cl $3p^5 \ ^2P^{\circ}_{3/2}$ and Cl $3p^5 \ ^2P^{\circ}_{1/2}$ atoms from photolysis of various chlorinated precursors in a low-pressure environment (approximately 2 Torr) [12]. For HCl and DCl, a detection sensitivity of better than 10^{10} molecules/cm³ was achieved. Using the same technique, Arepalli and coworkers also detected Br $4p^5 \ ^2P^{\circ}_{3/2}$ and Br $4p^5 \ ^2P^{\circ}_{1/2}$ atoms in the wavelength region of 240–285 nm [13].

Recently, we have shown that laser photofragmentation with subsequent REMPI detection when coupled with molecular beam TOF mass spectrometry can be used to detect atmospheric NO and nitro-containing vapors with both high sensitivity and selectivity [14]. A single laser operating at 226 or 193 nm was employed for both the photolysis of the parent molecule and exciting the resulting NO fragment. NO was detected by both (1+1) REMPI or LIF via its $A^2\Sigma^+ - X^2\Pi(0,0)$ band near 226 nm, or by (1+1) REMPI via its $A^2\Sigma^+ - X^2\Pi(3,0)$, $B^2\Pi - X^2\Pi(7,0)$ and/or $D^2\Sigma^+ - X^2\Pi(0,1)$ bands near 193 nm. At 226 nm, NO^+ ions were produced almost at the exclusion of any other ions such that mass spectrometric detection was virtually unnecessary. More recently, we reported the development of a laser-induced photofragmentation/photoionization (PF/PI) technique employing a miniature pair of electrodes for the real-time measurement of ambient nitrogen oxides [15]. Similar studies on NO/ NO_2 have been performed by Ledingham and coworkers [16]. While only a single laser operating near 226 nm was used as both the photolysis and photoionization source, our studies demonstrated high sensitivity for several compounds, even with only 10- μJ laser pulse energies.

In this report, we describe the extension of the PF/(LIF, REMPI) techniques and a novel laser photofragmentation with subsequent stimulated emission technique (PF/SE) to the detection of volatile brominated compounds. The three techniques have been investigated for their utility in measuring trace levels of volatile brominated species under ambient conditions. The output of a single laser is tuned to a strong two-photon $4p^4 5p \ ^4D^{\circ}_{3/2} \leftarrow 4p^5 \ ^2P^{\circ}_{3/2}$ transition of Br at 260.634 nm. The Br atoms are subsequently detected by either (2+1) REMPI, or by LIF or SE by monitoring the $4p^4 5p \ ^4D^{\circ}_{3/2} \rightarrow 4p^4 5s \ ^4P_{3/2,5/2}$ transitions at 844 and 751 nm, respectively. For REMPI, nonselective (total) ion detection is

employed. The REMPI, LIF, or SE signals observed at the two-photon resonance wavelength are used to quantify the total Br content of the sample vapor. To our knowledge, this is the first time that ionization, fluorescence, and SE methods have been applied to the detection of Br atoms and brominated species in the same study. It is also the first time that SE of Br atoms has been reported.

2. EXPERIMENTAL

Presented in Figure 1 is a schematic of the experimental apparatus. The sample cell utilized was a six-way stainless steel cross with 2.75-in conflat flanges. MgF_2 windows mounted on the cell provided optical access for photolysis, REMPI, LIF, and SE. An excimer-pumped dye laser system (Lumonics, HYPER EX-400, HYPER DYE-300, and HYPER TRAK-1000) operating with coumarin 500 dye and with a beta barium borate frequency doubling crystal was used to provide up to 200- μJ pulses near 260 nm. At this wavelength, the frequency doubled laser linewidth is estimated to be 0.11 cm^{-1} from the reported value of 0.076 cm^{-1} for the fundamental (Lumonics). Pulse energies were monitored between measurements using a Joulemeter (Molelectron Detector Inc., J4-05). The laser output was directed by prisms to the sampling cell. Focusing of the laser beam was accomplished using a 150-mm lens (suprasil) external to the cell.

For the REMPI studies, two planar stainless steel electrodes served as ion/electron detectors. Each is approximately 1.5 cm^2 in area and separated by 0.63 cm. Electrical contact to the electrodes (used for biasing and for signal collection) was accomplished through a plate mounted to one of the arms on the cell. The collection voltages ranged from 0 to 400 V. The laser beam passed between the electrodes and was focused in the center of the electrode length to optimize ion/electron collection. For the LIF studies, the fluorescence was viewed normal to the photolysis laser axis and was monitored with a photomultiplier tube (PMT) (Hamamatsu, R955) equipped with band pass filters centered at either 844 or 750 nm (fwhm $\sim 10 \text{ nm}$). The PMT voltage ranged from $-1,000$ to $-1,200 \text{ V}$. For the SE studies, the emission was viewed coaxial and in the forward direction of the laser beam, and was detected 1 m from the cell with either a monochromator (ISA-H1061)/PMT combination or filtered PMT. The PMT and filters were the same as those used for LIF detection. The beam waist in the focal region is estimated to be $40 \mu\text{m}$ in diameter (three times the diffraction limit) resulting in a maximum fluence of $6 \times 10^8 \text{ W/cm}^2$. An estimation of the effective volume probed by the laser is approximately $2.5 \times 10^{-6} \text{ cm}^3$ (equal to 2-mm path length and $1.3 \times 10^{-5} \text{-cm}^2$ focal area).

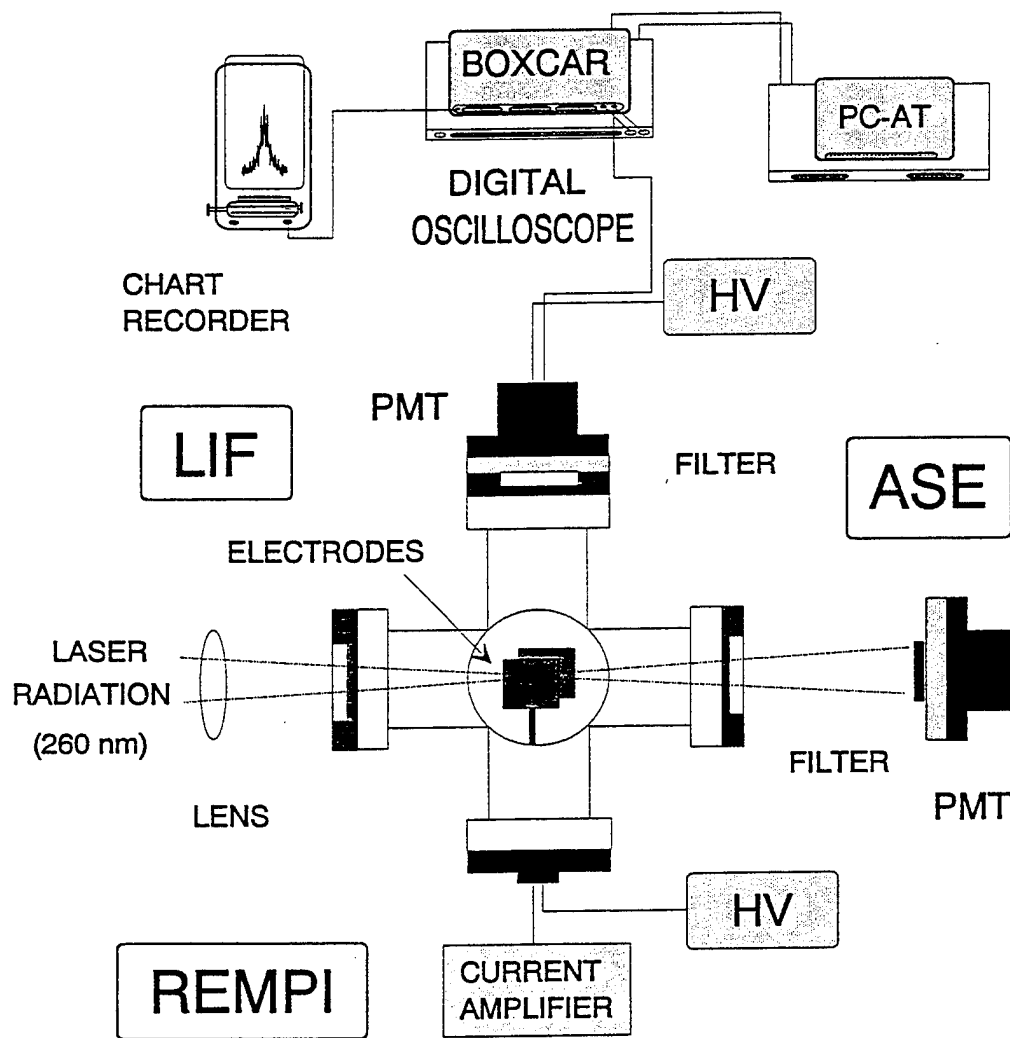


Figure 1. Schematic of experimental apparatus.

Samples were prepared by serial dilution of standard gases (CH_3Br) or were sampled at their room temperature vapor pressures (CHBr_3 , CHBr_2Cl) as trace species in buffer gases (air, N_2). Pressures were measured with a barocel pressure sensor (Edwards/Datametrics 600A-1000T) interfaced to a recorder (Edwards/Datametrics 1500). They ranged from 1 to 760 Torr total pressure in the measurement cell. The samples were flowed through the photolysis cell at $500 \text{ cm}^3/\text{min}$ nominally to prevent build-up of photolysis products. The photolysis cell volume was estimated to be 350 cm^3 .

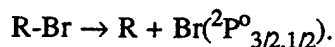
At high concentrations, a sustained period of flushing with N_2 between samples was necessary to minimize both ionization and fluorescence signals resulting from adsorbed molecules from previous runs

on the cell walls. The background was generally more of a problem in the ionization measurements and may be due to ionization of either the parent molecule or a fragment other than Br. Experimentally, it was observed that the magnitude of the background near 260 nm represented as much as 50% of the total ionization signal when the laser is resonance with the Br transition, indicating that alternate ionization processes originating from the parent molecule and/or other daughter fragments are operative. Such high background signals were limited to relatively low laser pulse energies.

The PF/REMPI measurements were performed using +400 V on the collection electrodes, the same as that used for PF/REMPI studies of nitrogen oxide species [15]. REMPI signals from the detection electrodes were amplified using a current amplifier (Keithley 427, gain 10^5 – 10^7 V/A, time constant 0.01 ms) and then sampled by a boxcar averager. The amplifier was connected as closely as possible to the collection electrode output to minimize radio-frequency pick-up along the signal cable. The REMPI, LIF, and SE signals were viewed in real-time on a 125-MHz digital oscilloscope (LeCroy 9400). The boxcar output was acquired by a personal computer for storage and subsequent data analysis. Analytical sensitivity determinations were performed at 10-Hz laser repetition rate using a boxcar gate of 15 μ s for REMPI and 30 ns for LIF and SE with 100-shot averaging. The noise in this study was defined as the standard deviation of 16 independent measurements of the background signal off resonance when N_2 was flowed through the cell.

3. RESULTS/DISCUSSION

The physical process underlying our approach for the detection of brominated compounds may be understood by referring to Figure 2, which shows a partial potential energy level diagram for the Br atom. In our approach, the precursor molecule is first photofragmented yielding the Br atom in its ground ($^2P^o_{3/2}$) and/or first excited ($^2P^o_{1/2}$) state, and its corresponding companion radical (R), via the process



The Br atoms are then detected by (2+1) REMPI via the $4p^45p\ ^4D^o_{3/2}$ energy level, or by LIF or SE involving the $4p^45p\ ^4D^o_{3/2} \rightarrow 4p^45s\ (^4P_{3/2},\ ^4P_{5/2})$ transitions near 844 and 751 nm, respectively. For brominated compounds, the characteristic absorption spectrum in the 230–280-nm region is ascribed to the $n \rightarrow \sigma^*$ transition localized on the Br atom. The Br atom is bound to the main skeletal portion of the molecule with a bond energy ranging from 46.34 Kcal/mole for Br-Br to 87.4 Kcal/mole for H-Br

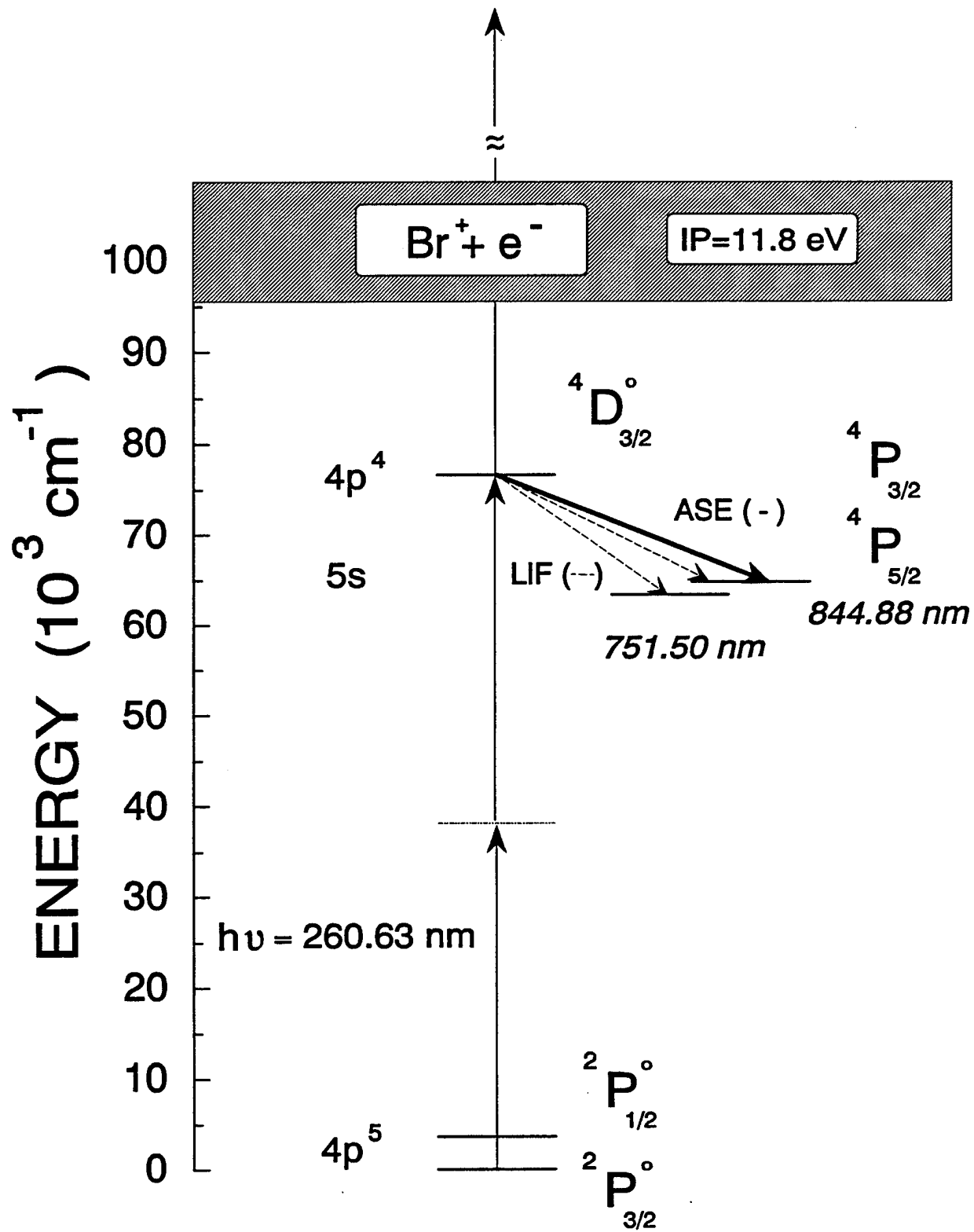


Figure 2. Partial energy level diagram showing pertinent states and two-photon transitions of Br atom.

(1 Kcal/mole = 349.76 cm⁻¹) [17]. For CF₃Br and RH_xBr_{4-x} (x = 1,2), the Br atom is bound to the carbon atom by approximately 70 Kcal/mole. Thus, the parent (analyte) molecules are photofragmented and Br atoms are generated in this wavelength region.

Presented in Table 1 are the two-photon allowed transitions of Br in the range of 231.40–281.77 nm, calculated using energies and term symbols reported by Moore [18]. By investigating this spectral region, we observed a strong Br atom signal at 260.634 nm, which corresponds to the spin-forbidden 4p⁴5p ⁴D_{3/2}^o ← 4p⁵ ²P_{3/2}^o transition (see Figure 2). Arepalli et al. [13] also found this transition to be one of the most sensitive in the 240–285-nm spectral region. Although other Br excitation wavelengths were observed, the transition at 260.634 nm proved to be the best for analytical measurements, primarily because of the combined efficiencies of the dye and doubling crystal near 260 nm. It is interesting to note that for analogous PF/LIF studies of chlorinated compounds, Jeffries et al. [9] employed a similar transition at 233.290 nm, which corresponds to the spin-forbidden 3p⁴4p ⁴S_{3/2}^o ← 3p⁵ ²P_{3/2}^o transition of Cl [9].

An estimate of the magnitude of the two-photon absorption cross section for the Br 4p⁴5p ⁴D_{3/2}^o ← 4p⁵ ²P_{3/2}^o transition is obtained by the following expression given by McIlrath et al. [19]:

$$\sigma_0^{(2)}(\omega) = \frac{\pi e^4 \omega_i^2 f_1 f_2}{8 \epsilon_0^2 m^2 c^2 \omega_1 \omega_2 (\omega_1 - \omega_2)^2}, \quad (1)$$

where e is the electronic charge (C), m is the mass of the electron (kg), ϵ_0 is the permittivity of free space (C²/(N m²)), c is the speed of light (m/s), ω_i ($i = 1,2,l$) is the angular frequency of the radiation (s⁻¹), and f_i ($i = 1,2$) is the absorption oscillator strength of the strongest transitions between the appropriate states. Substitution of the appropriate energies and oscillator strengths ($f_1 = 0.199$, $f_2 = 0.513$) into equation (1) yields a value of 3.8×10^{-43} m⁴. For comparison, McIlrath et al. [9] have estimated the two-photon cross section for O atoms at 226 nm as 7.0×10^{-44} m⁴. This value agrees well with those predicted by more rigorous quantum mechanical methods, which include contributions from multiple intermediate states [20,21]. Thus, the previous expression is an approximation that is effective when the two-photon cross section is dominated by a single intermediate state. Lesser contributions by additional intermediate states

Table 1. Two-Photon Allowed Transitions of Br Atom

TRANSITION	λ (nm)	TRANSITION	λ (nm)
$4P^{\circ}_{5/2} \leftarrow 2P^{\circ}_{1/2}$	281.77	$4P^{\circ}_{1/2} \leftarrow 2P^{\circ}_{1/2}$	243.58
$4P^{\circ}_{3/2} \leftarrow 2P^{\circ}_{1/2}$	280.44	$4D^{\circ}_{5/2} \leftarrow 2P^{\circ}_{1/2}$	243.52
$4D^{\circ}_{5/2} \leftarrow 2P^{\circ}_{1/2}$	277.76	$4D^{\circ}_{3/2} \leftarrow 2P^{\circ}_{1/2}$	243.15
$4P^{\circ}_{5/2} \leftarrow 2P^{\circ}_{1/2}$	277.31	$4D^{\circ}_{1/2} \leftarrow 2P^{\circ}_{1/2}$	241.71
$4D^{\circ}_{3/2} \leftarrow 2P^{\circ}_{1/2}$	273.78	$2P^{\circ}_{3/2} \leftarrow 2P^{\circ}_{1/2}$	239.33
$4D^{\circ}_{1/2} \leftarrow 2P^{\circ}_{1/2}$	268.87	$2P^{\circ}_{1/2} \leftarrow 2P^{\circ}_{1/2}$	238.64
$4P^{\circ}_{5/2} \leftarrow 2P^{\circ}_{3/2}$	267.86	$2P^{\circ}_{3/2} \leftarrow 2P^{\circ}_{1/2}$	235.87
$2D^{\circ}_{5/2} \leftarrow 2P^{\circ}_{1/2}$	267.31	$2P^{\circ}_{1/2} \leftarrow 2P^{\circ}_{1/2}$	235.66
$4S^{\circ}_{3/2} \leftarrow 2P^{\circ}_{1/2}$	266.72	$2F^{\circ}_{5/2} \leftarrow 2P^{\circ}_{1/2}$	235.32
$4P^{\circ}_{3/2} \leftarrow 2P^{\circ}_{3/2}$	266.66	$2D^{\circ}_{3/2} \leftarrow 2P^{\circ}_{1/2}$	234.86
$2P^{\circ}_{3/2} \leftarrow 2P^{\circ}_{3/2}$	266.05	$4S^{\circ}_{3/2} \leftarrow 2P^{\circ}_{1/2}$	234.57
$2P^{\circ}_{1/2} \leftarrow 2P^{\circ}_{1/2}$	264.95	$2D^{\circ}_{5/2} \leftarrow 2P^{\circ}_{1/2}$	234.36
$4D^{\circ}_{3/2} \leftarrow 2P^{\circ}_{1/2}$	264.85	$2S^{\circ}_{5/2} \leftarrow 2P^{\circ}_{1/2}$	234.04
$4D^{\circ}_{7/2} \leftarrow 2P^{\circ}_{3/2}$	264.23	$4P^{\circ}_{1/2} \leftarrow 2P^{\circ}_{1/2}$	233.86
$4P^{\circ}_{5/2} \leftarrow 2P^{\circ}_{3/2}$	263.83	$4P^{\circ}_{5/2} \leftarrow 2P^{\circ}_{3/2}$	233.70
$2D^{\circ}_{1/2} \leftarrow 2P^{\circ}_{3/2}$	263.14	$4D^{\circ}_{3/2} \leftarrow 2P^{\circ}_{3/2}$	233.22
$2S^{\circ}_{3/2} \leftarrow 2P^{\circ}_{1/2}$	262.55	$4P^{\circ}_{7/2} \leftarrow 2P^{\circ}_{3/2}$	233.12
$4D^{\circ}_{1/2} \leftarrow 2P^{\circ}_{1/2}$	260.63	$4P^{\circ}_{1/2} \leftarrow 2P^{\circ}_{3/2}$	233.06
$4D^{\circ}_{3/2} \leftarrow 2P^{\circ}_{3/2}$	256.18	$4D^{\circ}_{5/2} \leftarrow 2P^{\circ}_{3/2}$	232.95
$4D^{\circ}_{1/2} \leftarrow 2P^{\circ}_{3/2}$	254.76	$4P^{\circ}_{5/2} \leftarrow 2P^{\circ}_{1/2}$	232.73
$2D^{\circ}_{5/2} \leftarrow 2P^{\circ}_{3/2}$	254.23	$2P^{\circ}_{3/2} \leftarrow 2P^{\circ}_{3/2}$	232.36
$4S^{\circ}_{3/2} \leftarrow 2P^{\circ}_{3/2}$	253.62	$4P^{\circ}_{1/2} \leftarrow 2P^{\circ}_{1/2}$	232.30
$2P^{\circ}_{1/2} \leftarrow 2P^{\circ}_{3/2}$	252.62	$2D^{\circ}_{3/2} \leftarrow 2P^{\circ}_{1/2}$	232.28
$2D^{\circ}_{3/2} \leftarrow 2P^{\circ}_{3/2}$	250.98	$2D^{\circ}_{5/2} \leftarrow 2P^{\circ}_{1/2}$	232.10
$2S^{\circ}_{3/2} \leftarrow 2P^{\circ}_{3/2}$	250.43	$2P^{\circ}_{3/2} \leftarrow 2P^{\circ}_{1/2}$	231.98
$4P^{\circ}_{1/2} \leftarrow 2P^{\circ}_{3/2}$	244.39	$4P^{\circ}_{3/2} \leftarrow 2P^{\circ}_{1/2}$	231.87
$4P^{\circ}_{5/2} \leftarrow 2P^{\circ}_{1/2}$	244.22	$4D^{\circ}_{1/2} \leftarrow 2P^{\circ}_{1/2}$	231.40
$4P^{\circ}_{3/2} \leftarrow 2P^{\circ}_{1/2}$		$4D^{\circ}_{1/2} \leftarrow 2P^{\circ}_{3/2}$	

are best accounted for by explicit quantum mechanical approaches, although such calculations require extensive computational capabilities.

The units of $\sigma_0^{(2)}(\omega)$ is in m^4 and are related to the generalized cross section by a normalized lineshape function, δ [19,20]. In the limit of a relatively broad laser profile, the line shape function is dominated by the laser bandwidth and is simply $1/(\delta\omega_{\text{laser}})$ [19]. For our system, the frequency doubled bandwidth (fwhm) of the laser is approximately 0.11 cm^{-1} ($1 \text{ cm}^{-1} = 2.998 \times 10^{10} \text{ s}^{-1}$), yielding a value of the generalized cross section, $\sigma^{(2)}(\omega)$, of $1.8 \times 10^{-45} \text{ cm}^4\text{s}$ at 260.634 nm.

The two-photon absorption transition rate, $R_{tp} \text{ (s}^{-1}\text{)}$, is given by the following expression:

$$R_{tp} \text{ (s}^{-1}\text{)} = \sigma^{(2)}(\omega) \cdot I^2, \quad (2)$$

where $\sigma^{(2)}(\omega)$ is the generalized two-photon absorption cross section (cm^4s), and I is the laser intensity (photons/ (cm^2s)). Using typical values of laser energy (100 μJ) and pulsewidth (10 ns), we estimate that the photon flux in the probe region at 260 nm is 1.0×10^{27} photons/ cm^2s . For a cross section of 1.8×10^{-45} cm^4s and a photoionization cross section of approximately 10^{-18} cm^2 , the estimated two-photon excitation rate and photoionization rate are both on the order of 10^9 s^{-1} , which is also the order of the radiative and nonradiative decay rates for Br atoms at 100 Torr (current experimental conditions). While neither the absorption or photoionization processes is likely to be completely saturated at this laser intensity, the rates should be sufficient to realize good sensitivity for ionization and fluorescence detection approaches.

Employing two-photon excitation of Br atoms at 260.634 nm, a comparison study of ionization, fluorescence and SE detection techniques has been performed. This is the first time these three methods have been applied to the detection of Br atoms in the same study. It is also the first time that SE of Br has been reported. We verified that the observed emission was SE by the fact that the emission appeared to have an intensity threshold, was coherent in its propagation (as determined by its constant measured intensity both close to and away from the cell), and was much stronger than the isotropically emitted LIF (nearly two orders of magnitude greater when normalized for the observed solid angle). Further evidence that the observed emission was SE was the negligible emission observed at 751 nm, as compared to 844 nm. While both transitions originate from the same $5p\ ^4D_{3/2}^o$ state, only the 844-nm line showed significant SE emission. As the lower state of the transition at 751 nm is the lowest of the 4P multiplet, establishing and maintaining a population inversion with this state is less probable due to collisional decay to the state from other states, which spoils the gain. Similar effects have been observed in the SE profile of Cl [10]. SE to the $5s\ ^4P_{1/2}$ state of Br at 1014.3 nm was not verified due to the limited response of the PMT.

Figure 3 shows several spectral scans of the transition at 260.634 nm as observed when using CH_3Br as the precursor species for Br and PF/REMPI detection. The dependence of the signal magnitude on the laser intensity is nonlinear suggesting that increases in the laser intensity could lead to significant increases in the Br ionization signal. As the excitation of the Br atoms is a 2+1 REMPI process, the power dependence might be expected to be as high as 4. A plot of the Br ion signal (generated from CH_3Br) as a function of the laser intensity at 260.634 nm reveals a power dependence of 1.5, indicating the possible saturation of at least one of the photoexcitations of the precursor molecule and/or the Br fragment. Partial saturation of the ionization is consistent with our estimations of the excitation rates, as the

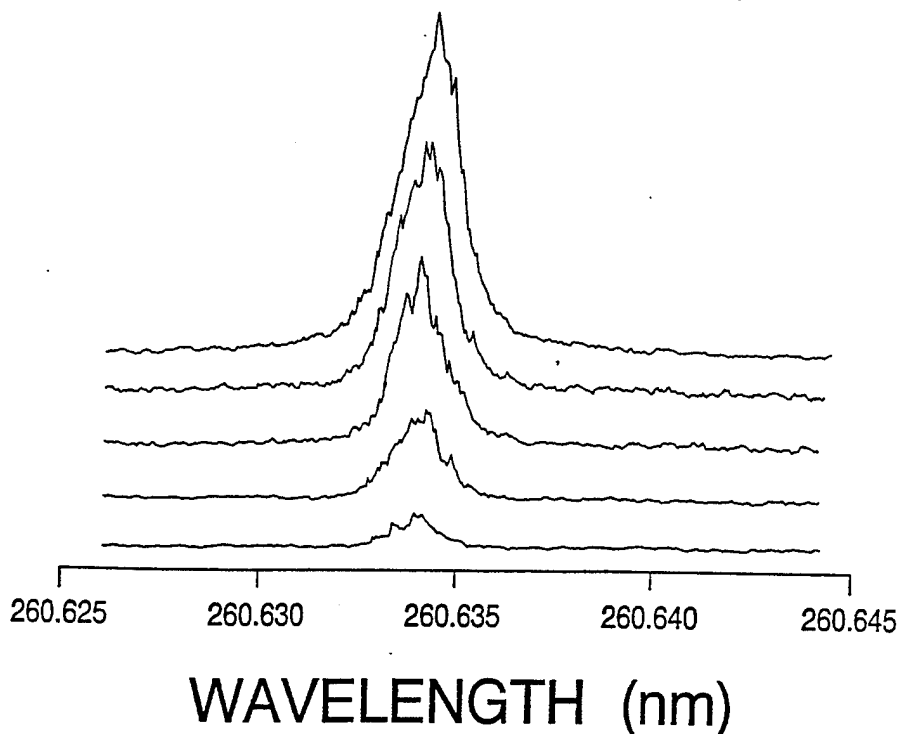


Figure 3. Fragmentation ionization spectra of CH_3Br near 260.6 nm showing the spin-forbidden $4p^45p^4D^{\circ}_{3/2} \leftarrow 4p^52P^{\circ}_{3/2}$ transition of Br. The spectra (from bottom to top) correspond to incident laser intensities of 1.2, 1.9, 3, 4.1 and $4.9 \times 10^8 \text{ W/cm}^2$. The baseline of the spectra are offset for clarity.

excitation and radiative deexcitation rates are comparable. A power dependence study of 1.5 was also observed by PF/LIF, which similarly indicates partial saturation of one of the photoexcitations of the PF/LIF processes.

Close inspection of the spectra in Figure 3 does not reveal significant broadening of the excitation profile lineshape with laser intensity. The linewidth at the highest laser energy is approximately 0.0016 nm (when corrected for the laser bandwidth) and is relatively constant over the intensities employed. Lack of broadening indicates that saturation of the two-photon absorption is not significant and that modest increases in the laser intensity could lead to enhanced sensitivities, although higher laser intensities will only be advantageous if they result in an enhanced signal-to-noise ratio.

A study of the pressure dependence of the excitation profiles observed using REMPI, LIF, and SE is shown in Figure 4. Profiles were obtained at pressures of 100 Torr and 1 atm. In the case of each technique, the profile is broadened at 1 atm. The broadening is greatest for the ionization and least for

the SE profiles. The narrowness of the SE profile relative to the LIF and ionization is expected due to the exponential gain of the medium, which leads to a spectral narrowing of the profile [22]. The reason for the difference in the widths of the LIF and ionization profiles is as yet unknown.

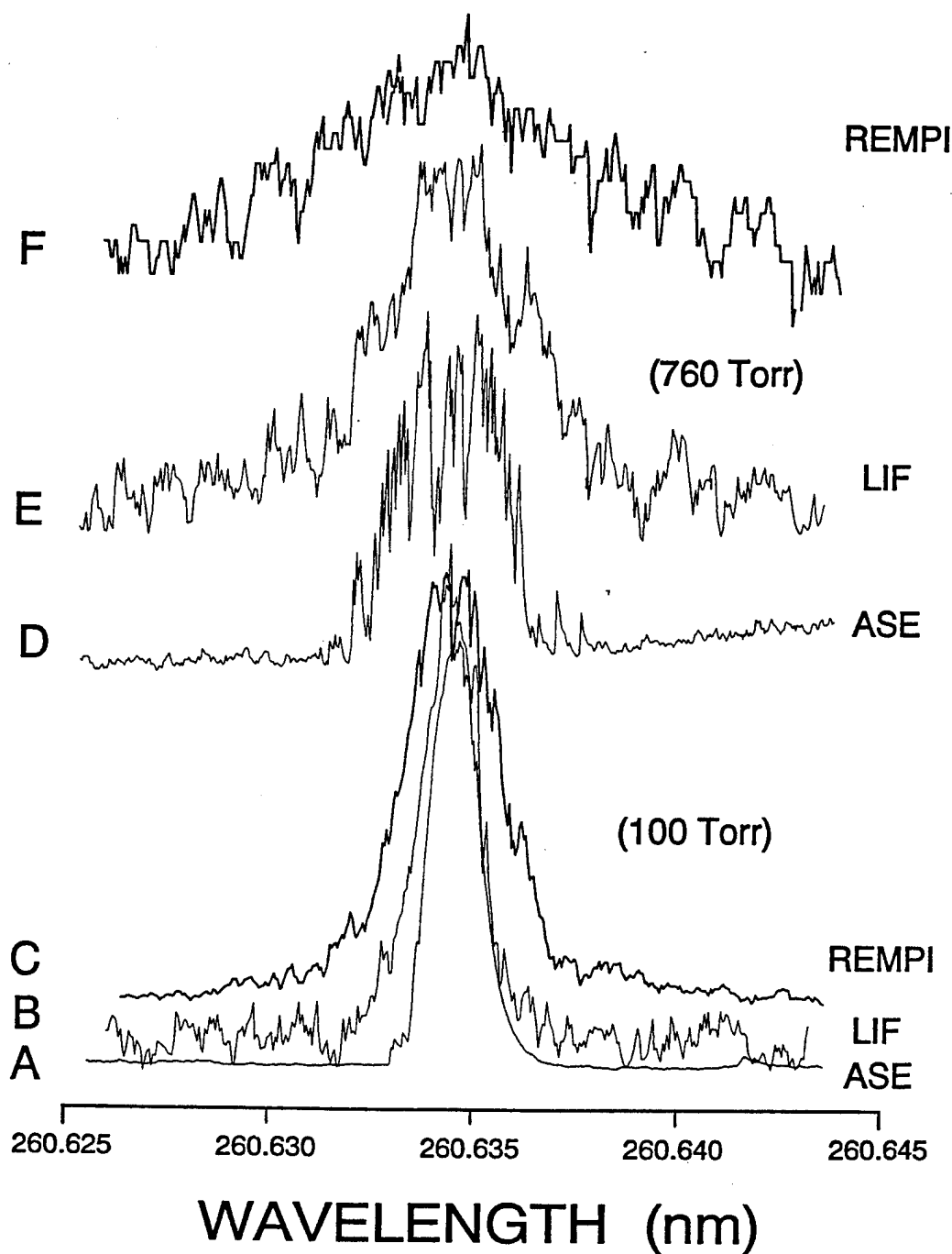


Figure 4. Normalized excitation profiles of Br atom (generated from CHClBr_2) at 100 Torr and 760 Torr for PF/REMPI (heavy line), PF/LIF (medium line), and PF/SE (light line).

Shown in Figure 5 are the signal dependencies for the SE, LIF, and ionization techniques as functions of the total cell pressure. It is important to note that for each pressure indicated in the figure, the mixing ratio of sample is constant, that is, the sample (analyte) density changes with the pressure. It is observed that increased pressures reduce the sensitivities, although pressure influences the individual techniques differently. In the case of ionization, the signal is at a maximum at relatively low pressures (near 50 Torr) and then falls rapidly at higher pressures. This behavior is believed to be due to combined effects of quenching and transfer losses of the ions/electrons to the collection electrodes at higher pressures [15]. In the cases of LIF and SE, it is seen that the pressure dependencies of these two techniques are similar, although the SE signal shows a steeper rise at lower pressures and faster decay at higher pressure than the LIF. The different pressure dependencies for LIF and SE are related to the effects of collisions on the SE lineshape, where increased collisions broaden the linewidth and reduce the gain [22].

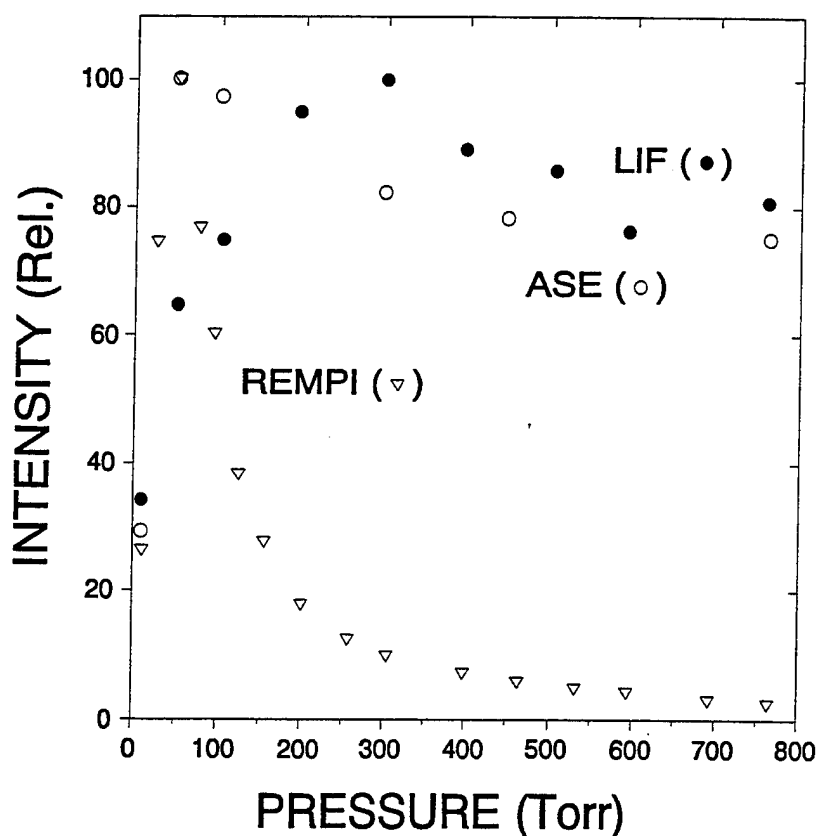


Figure 5. Pressure dependence of normalized signals for PF/REMPI (open inverted triangles), PF/LIF (filled circles) and PF/SE (open circles) techniques.

Further studies were performed to evaluate the analytical capabilities of the REMPI, LIF, and SE techniques for detecting brominated compounds in the gas phase. Measurement conditions were 100 Torr

total pressure and laser energies ranging from 75 to 200 μJ at 260 nm. Estimates of the limits of detection (equal to 3σ) were determined for CH_3Br , CHBr_3 , and CHClBr_2 and are given in Table 2. Noise (σ) in this study is defined as the standard deviation of 16 independent measurements of the background signal in N_2 measured off resonance at 260.64 nm. Sensitivities were inferred from signals measured for a single concentration using mixtures containing approximately 10 ppm of the specified compound in N_2 , except for the SE where approximately 500 ppm mixtures were used. As the sensitivity was evaluated from a single concentration, considerable uncertainty may be associated with the absolute values given in Table 2. However, since the REMPI, LIF, and SE techniques were evaluated in the same study under the same conditions, the data in Table 2 are very useful for making relative comparisons of the three techniques.

Table 2. Estimated Limits of Detection for Brominated Compounds

	PF/REMPI (ppb)	PF/LIF (ppb)	PF/SE (ppm)
CH_3Br	130	—	—
CHBr_3	2.5	350	20
CHClBr_2	2.2	250	10

As shown in Table 2, high sensitivities (LODs in the ppb) were observed using the PF/REMPI technique for CHClBr_2 , CHBr_3 , and CH_3Br , with the first two compounds having a sensitivity of approximately 60 times greater than the last. Apparently, the efficiency in the photodissociation pathways leading to the formation of Br is higher for CH_3Br and CHClBr_2 than for CHBr_3 . In addition, the stoichiometry favors the production of more Br atoms on a per mole-atom basis for CHClBr_2 and CHBr_3 than the singly substituted CH_3Br . As a comparison of our PF/REMPI results, Arepalli et al. [13] have also used this technique and estimated an LOD of 0.4 ppb for Br atoms as generated from HBr and other compounds. It should be noted, however, that the HBr (and other species) was sampled in pure form and at much lower pressures (mTorr) than were used in the present studies and extrapolation of their results to dilute samples in a buffer gas matrix is difficult. Nonetheless, in both studies the absolute number of Br atoms detected at the LOD are very similar (on the order of 10^4 – 10^6).

Table 2 also reveals that the sensitivities obtained from the PF/REMPI approach are two and four orders of magnitude greater than the LIF and SE techniques, respectively. The high sensitivity achieved

using the PF/REMPI approach demonstrates the strong potential of the method, and suggests the approach will be most effective when efficient fragmentation of the parent molecule is assured. This may only be possible by using a separate fragmentation source, that is, a dual laser approach [9]. The REMPI approach is, however, susceptible to high background noise as well as the highest degree of interference (due to nonresonant multiphoton ionization). It should be possible to eliminate all the ionization interferences by employing mass spectrometric detection, except those which are also isobaric. Laser photoionization/mass spectrometry has already been demonstrated by Cool and coworkers [7] as an effective method for monitoring complex sample environments. However, due to the limited sample throughput of most mass spectrometers, these systems may suffer lower sensitivity, which would limit their applicability to sample environments that require mass selectivity.

The PF/LIF approach as implemented here has lower sensitivity relative to PF/REMPI, as shown in Table 2. This difference in sensitivity results primarily from the high background and laser scatter inherent in these PF/LIF measurements, and is not necessarily characteristic of the technique. The analytical capability of this approach can be improved, however, by better system design. For example, the use of a PMT with greater sensitivity in the near IR, the addition of light baffles, signal collection optics, and/or spectrometers.

As shown in Table 2, the PF/SE technique has the lowest sensitivity, yet it also has a strong analytical potential. Unlike REMPI and LIF, the background noise of the SE approach is low and can be made even lower with appropriate shielding of the detector. Furthermore, since the signal is coherent and the background emission is incoherent, increasing the laser intensity to saturation conditions should greatly enhance the sensitivity without compromising the signal-to-noise ratio. This is an important contrast between the SE and LIF-REMPI techniques. LIF and REMPI already suffer from significantly higher background signals at the laser intensities used in these studies; thus, any further increases in the intensity are not likely to improve the signal-to-noise ratio for either of the two techniques. The sensitivity of the SE technique may be enhanced by using a longer focal length lens to increase the gain length. In addition to also providing strong optical signals, the SE technique has other attributes that are unique due to its coherent nature [22]. Even though the SE signal is coaxial with the laser, it can be easily separated with filters or prisms, and, since it is bidirectional, it only requires "one-window access" to the sample environment [10,22]. This has important implications for accessing remote or hostile environments and also for coupling to fiber optic probes. For these reasons, it is believed that the SE technique has great potential utility for Br atom monitoring applications.

4. CONCLUSIONS

Laser-induced photofragmentation/fragment spectrometry at 260.634 nm using ionization, fluorescence and stimulated emission techniques have been employed to detect brominated compounds under ambient conditions. These techniques have been evaluated as to their relative analytical capabilities for trace level determinations. SE of Br atoms at 844 nm is reported for the first time and its merits as an analytical technique have been considered. It is anticipated that SE will have several advantages over conventional methods for rapid and convenient measurements of ppm levels of Br atoms in gaseous environments. In the present studies, the PF/REMPI technique is demonstrated as having the highest sensitivity with estimated LODs for CHBr_3 and CHClBr_2 in the low ppb range. Limits of detection for the LIF and SE approaches are somewhat higher and in the ppm range for the same compounds.

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* In reference (13), the wavelength of the $4D^{\circ}_{3/2} \leftarrow 2P^{\circ}_{3/2}$ transition was reported as 260.622 nm rather than the value of 260.634 nm which we calculate. This appears to be a transcription error since other values reported are in good agreement to those we calculate.

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