SUPERSONIC MOLECULAR BEAM, RESONANCE ENHANCED MULTIPHOTON IONIZATION, TIME-OF-FLIGHT MASS SPECTROSCOPY 1. TECHNIQUE AND DETECTABILITY LIMIT.

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Abstract

An ultratrace detection method that offers exceptional selectivity has been developed based on the technique of supersonic molecular beam, resonance enhanced multiphoton ionization, time-of-flight mass spectroscopy (MB/REMPI/TOFMS). Preliminary determinations indicate near unit collection efficiency for ions produced in the excitation region as well as single ion detection sensitivity, thus giving observable detection limits of < 300 ppt. Single vibronic level REMPI of the supercooled molecules in conjunction with TOFMS provides selectivity of 10^4 against chemically similar compounds. Studies were carried out using moist air expansions for a variety of organophosphonate and sulfide chemical warfare agent (CWA) simulant molecules.

1. Introduction

We report on an ultratrace detection program based on the application of pulsed supersonic molecular beam (MB), resonance-enhanced multiphoton ionization (REMPI), time-of-flight mass spectroscopy (TOFMS). A principal objective of this program was to demonstrate highly specific real-time ultratrace detection levels in an apparatus that is potentially van-mobile. The results of this work are presented in this paper. Other objectives of the program, which include studies of the spectral, photochemical and photophysical properties of the common CWA simulant molecules, are discussed in papers II and III, which follow.

An integral part of the MB/REMPI/TOFMS technique is the rapid molecular cooling of a gas sample that occurs when it is allowed to expand into a vacuum. In a supersonic molecular beam, molecules are produced in an ultracold state consisting of just a few rovibrational states[1]. Laser excitation of the molecules therefore occurs from a very narrow range of states rather than from the broad distribution of states that is found in "thermal" (i.e. room or ambient temperature) samples. This feature accounts for excellent sensitivity and selectivity for the respective reasons that (i) the collection of cold molecules are in virtually the same energy state and can therefore be excited quantitatively using a single wavelength of light and (ii) each compound has its own characteristic set of narrow excitation wavelengths that is distinct from that of other compounds.

MPI in which some integral number of photons (usually one or two) is resonant with an allowed intermediate state is said to be resonance-enhanced[2,3]. The enhancements are typically a few orders of magnitude over non-resonant excitation and therefore well suited to trace detection since (i) ionization efficiency is high (1-100%) and (ii) selectivity is accomplished by having to excite through a specific energy state of the target molecule. The benefit of REMPI to trace detection reaches its full potential when used in conjunction with supersonic molecular beams for the reasons discussed above. To illustrate this point, we compare in Fig. 1 laser absorption spectra recorded for aniline in a room temperature vapor and in a supersonic molecular beam. One should note the dramatic decrease in the spectroscopic linewidths as well as the elimination of the broad and diffuse background in the su-

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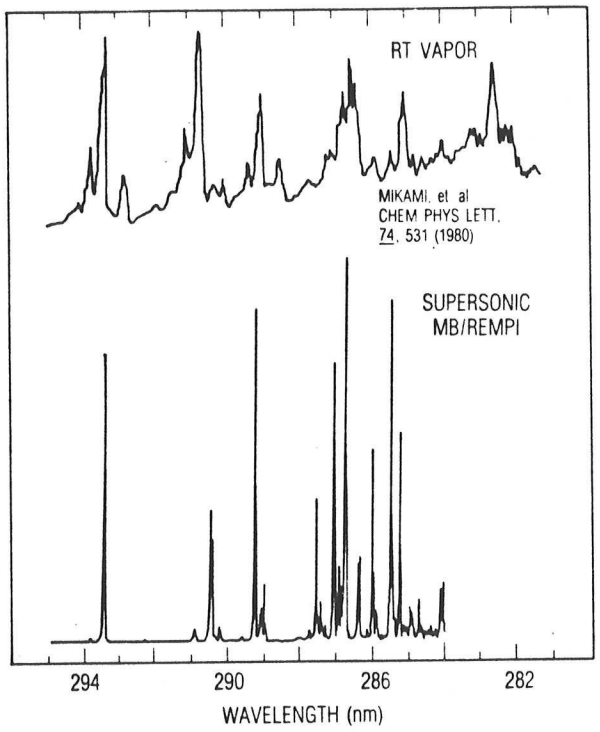

FIG. 1. (Lower trace) Ionization (REMPI) excitation spectrum of aniline in a pulsed supersonic molecular beam. Spectrum was recorded by detecting mass 93 parent ion as a function of excitation wavelength. The MPI process represents a 1 photon resonance, 2 photon ionization scheme (i.e. 1+2 REMPI). (Upper trace) Fluorescence excitation spectrum of aniline in a room temperature vapor as reported by other investigators.

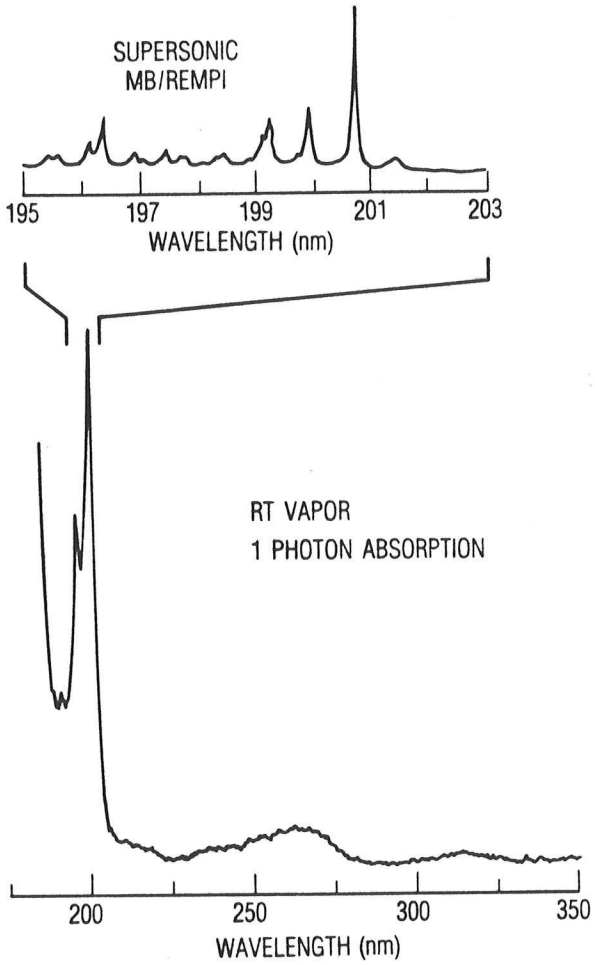

FIG. 2. (Upper trace) 2+2 REMPI excitation spectrum of the simulant DIMP recorded from a supersonic expansion by detecting fragment mass 43. (Lower trace) One photon absorption spectrum of DIMP as a room temperature vapor.

personic spectrum. This makes possible the specific excitation of the target molecule by avoiding spectral overlap with potential interferent molecules. An example of the spectral manifestations of supersonic cooling is demonstrated for the CWA simulant diisopropyl methylphosphonate (DIMP) in Fig. 2. Mass spectroscopy affords an additional level of selectivity by allowing mass descrimination. The TOFMS method has the advantage over other mass spectrometric methods in that it detects all ions simultaneously.

2. Apparatus

An ultrasensitive small frame molecular beam system, incorporating the important features of larger systems, was constructed to serve as a preprototype for a van mobile unit. A schematic of the small frame apparatus including the laser excitation and data acquisition system is illustrated in Fig. 3. The vacuum system consists of two differentially pumped chambers separated by a 1 mm skimmer. The main chamber, which contains the excitation and detection components, is 12 l in volume and pumped by a 1200 l/s turbomolecular pump (TMP) which is side mounted so as to catch the directed molecular beam throughput. An all metal conflat design was chosen to allow high temperature (up to 200 °C) bakeouts to remove internal chamber deposits that can contribute to background signals. Ambient pressure in the main chamber is 8×10^{-9} Torr, rising to $7-15 \times 10^{-8}$ Torr during operation of the pulsed molecular beam source. The main cham-

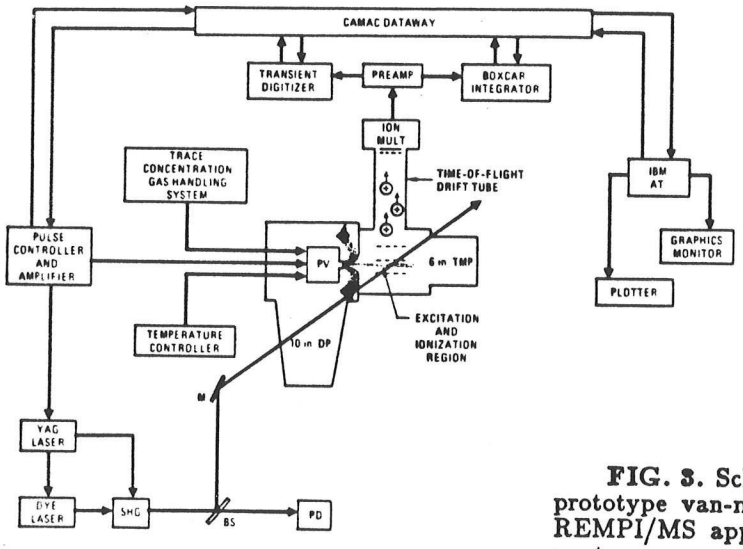

FIG. 3. Schematic of the small-frame, pre-prototype van-mobile, pulsed supersonic MB/REMPI/MS apparatus and associated components.

ber pump-down time of 10 ms, however, insures that the instantaneous pressure in the chamber at the time of a molecular beam pulse is near to the ambient pressure.

The use of pulsed nozzles for supersonic expansions is now well established with several designs available to meet specific requirements. However, the lack of a commercial high repetition rate, high temperature pulsed nozzle prompted us to construct a pulsed source in-house using a new design based on fast solenoid activation[4,5]. This design offers a unique combination of features that are important to the CWA detection program, namely, (i) high repetition rates (up to 100 Hz), (ii) temperature control (up to 200 °C), (iii) continuous gas sample flow capabilities, and (iv) internally mountable sample holder.

The second harmonic of a pulsed Nd:YAG laser at 532 nm is used to pump a tunable dye laser in all our excitation schemes. The non-linear techniques of frequency doubling, frequency mixing (i.e. summation) and Raman shifting are used in various combinations to achieve the desired range of wavelengths.

A dual microchannel plate (MCP) detector, capable of detecting single ions, is used to record ion intensities as a function of drift time. Two modes of data acquisition are employed; (i) TOF mass spectroscopy in which the intensities and drift times of the ion mass groups are recorded using a 200 MHz transient digitizer and (ii) excitation spectroscopy in which the wavelength dependence for the formation of a particular ion mass is recorded by gated boxcar integration of the ion peak as the laser wavelength is scanned. An IBM AT computer is used to handle all data acquisition and signal averaging as well as subsequent data handling involving file manipulation, analysis and plotting.

3. Detectability Limits

3.1. Definitions

We adopt a straightforward definition of sensitivity as being the concentration of a target molecule that gives a signal that exceeds the background signal (i.e. the concentration that is detectable). Detectability limit refers to the actual sensitivity in the presence of contaminants. The detectability limit, C_o, in the present case, was determined by recording the signal strength, S_{calib}, for a calibrated sample concentration, C_{calib}, and comparing it to the background fluctuation level, S_o. This leads to the simple relation for detection limit of

$$C_o = C_{calib}\frac{S_o}{S_{calib}}. \qquad (1)$$

The only assumption in Eq. (1) is that the ion count rate does not vanish at the extrapolated detection limit.

We define two response times; (i) τ_∞ being the time required for the signal to grow to within 1/e of its final value, where we assume exponential growth

of the form

$$S(t) = S(\infty)\left[1 - e^{-\frac{t}{\tau_\infty}}\right]. \qquad (2)$$

and (ii) τ_o being the time required for an actual signal to exceed the background level. We may consider τ_o to be the response time for detection and τ_∞ the response time for measurement of concentration. They can be related to each other using Eq. (2) to give

$$S(\tau_o) = S(\infty)\left[1 - e^{-\frac{\tau_o}{\tau_\infty}}\right]. \qquad (3)$$

Defining $S(\tau_o) = S_o$ and rearranging then gives

$$\frac{\tau_o}{\tau_\infty} = -\ln\left(1 - \frac{S_o}{S(\infty)}\right). \qquad (4)$$

It is not difficult to see that the response time for detection, τ_o, can be considerably smaller than τ_∞ for target molecule concentrations well above the detection limit.

3.2. Sensitivity

We used dimethyl sulfide (DMS) as a simulant for the mustard agent HD. The response of our detection system to a 60 ppb sample of DMS in water-saturated air (i.e. 100% relative humidity, 17000 ppm) is presented in Fig. 4. The low level "baseline" signal represents the background fluctuation or detection level of our molecular beam apparatus. An enlargement of the baseline region along with a detectability scale (Eq. (1)) is included for convenience. The ratio of sample signal to background signal, $\frac{S_{sample}}{S_o}$, is greater than 200, corresponding to a detection limit for DMS of less than 300 ppt. The measurement response time, τ_∞, is 6 s, however, the detection response time, τ_o, at 60 ppb is just 30 msec according to Eq. (4). Naturally, other factors (i.e. transit time of sample through delivery lines) can increase the actual "system" response time; however, the intrinsic value of τ_o can be approached with careful design.

The excitation scheme leading to the signal in Fig. 4 involves a 2 photon absorption, followed by a 1 photon ionization (i.e. 2+1 REMPI) at wavelength 390.62 nm corresponding to resonance enhancement through the vibrationless level of 3p Rydberg-like state at 195.31 nm. (c.f. paper II). The 2 photon absorption into the 3p state is not strictly allowed, the transition being far more efficient using one photon excitation at 195.31 nm. The near term development of millijoule pulse energies at 195.31 nm can be expected to lead to improvements in the detection limit by two orders of magnitude.

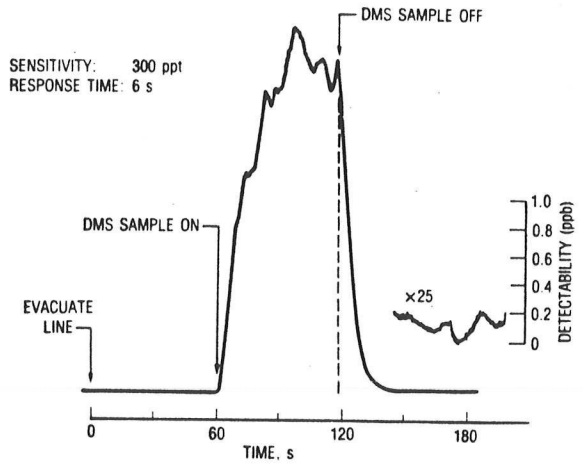

FIG. 4. Sensitivity determination for a 60 ppb sample of dimethyl sulfide (DMS) in water saturated air. The baseline signal represents the background level of our molecular beam apparatus.

Trade-offs between measurement response time, τ_∞, and detection level, C_o, can be made to enhance one parameter at the expense of the other. For instance, by applying a smoothing factor to the detected signal, the background noise fluctuations can be reduced thereby lowering the detection limit. Increasing τ_∞ to improve C_o is actually a favorable situation since the detection response time, τ_o, essentially remains unchanged by this operation. Although the growth of a signal is slowed due to the smoothing operation, it also does not have to grow as much to exceed the diminished background.

3.3. Selectivity

The usable sensitivity, (i.e. detectability), requires a high level of descrimination against contaminant molecules. We have measured the selectivity of the MB/REMPI/TOFMS technique against contaminants using a 10 ppm sample of DIMP in N_2. In Fig. 5, the response of the DIMP sample is compared to a room air sample and a room air sample saturated with water. The results show that the selectivity of DIMP to water signal is greater than 10^5. However, more importantly, it demonstrates that water vapor does not form molecular complexes with DIMP (or DMS, Fig. 4) that would degrade the signal strength due to non-resonant excitation and loss of mass identification. A test of the selectivity against chemically similar compounds was performed using a 10 ppm sample of DIMP in a

1300 ppm sample of DMMP (dimethyl methylphosphonate). The results are illustrated in Fig. 6 and show a selectivity of about 10^3-10^4. A similar level of selectivity is observed for gasoline (also displayed in Fig. 6).

Our preliminary sample delivery system makes use of premixed calibrated samples in stainless steel gas cylinders using polyflo tubing and valves to mix the various samples. This arrangement underestimates the actual performance level since the trace concentrations of target molecules in the sample cylinder tend to adsorb on the wall and delivery line surfaces before reaching the pulsed supersonic valve. Consequently, the actual concentrations delivered to the molecular beam system may be less than that in the sample cylinder. Moreover, the adsorbed target molecules give a low level signal after turning off the sampler cylinder flow. This signal accounts for a substantial share of the background signal in our selectivity determinations indicating that our selectivity ratios are actually greater than reported. We have constructed a continuous flow trace concentration sample delivery system that will prepare and deliver calibrated trace concentrations with high fidelity to the detection apparatus. Calibration of the delivery system is currently underway. Finally, our measurements have not as yet benefitted from a number of refinements (i.e. determination of the optimum excitation scheme) to be implemented.

4. Atmospheric Monitoring

We addressed several questions concerning the implementation of the MB/REMPI/TOFMS method for atmospheric monitoring; (i) Do the target molecules form complexes with water vapor thus undermining detection efforts, (ii) Do the target molecules form cluster among themselves, (iii) Does the supersonic expansion of atmospheric air give sufficient cooling of CWA simulants, and (iv) can the gas inlet system to the detection system be designed to avoid delivery lines which can adsorb trace amounts of target molecules?

A particular concern in detection systems that rely on the introduction of seeded gas samples into a vacuum system is the complexation of the target molecule with other molecules through hydrogen bonding or van der Waals forces[1]. This can be especially troublesome when water vapor is present since much higher concentrations of water compared to trace target molecules are likely to be encountered in atmospheric monitoring. The problem of water complexation with CWA molecules is often

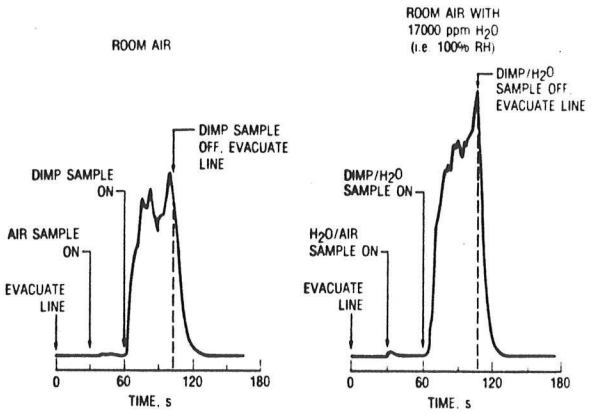

FIG. 5. Selectivity determination for a 10 ppm sample of DIMP in N_2 with a water saturated air sample.

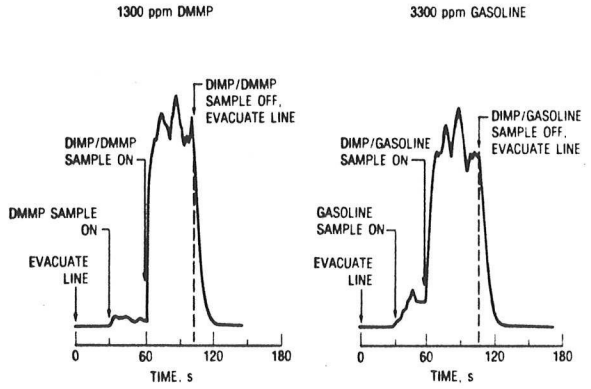

FIG. 6. Selectivity determinations for a 10 ppm sample of DIMP in N_2 with the chemically similar species DMMP and with gasoline.

observed in systems using atmospheric pressure ionization (API)[6] in which ionization is accomplished by protonating the CWA molecules thereby creating strong bonding interactions with water[7]. Our ionization approach differs in that the neutral, unprotonated CWA molecules are allowed to expand into the vacuum forming a molecular beam. The molecules are collision free when ionization occurs so that no complexation with ions is possible. The immunity to water complexes is demonstrated in Figs. 4 and 5 for DMS and DIMP, respectively.

The question of complexation of target molecules in a supersonic expansion to form homologous clusters was also investigated. DMS was particularly prone to complexation at high concentrations (10,000 ppm) Since cluster (or at least dimer) formation is a bimolecular event, the extent of clustering can be expected to decrease at lower concentration. Clustering of DMS was found to become insignificant at concentrations below 1000 ppm and should be negligible at trace concentration.

The extent of molecular cooling that occurs in a supersonic expansion is strongly dependent on the carrier gas and pressure. Without adequate cooling, the spectral lines of a sample will become rotationally broadened leading to a decrease in selectivity. We recorded the excitation spectrum of DIMP using atmospheric air as the carrier gas and found a degree of cooling that was comparable to that observed using 50 psi of He as a carrier gas (see paper II).

In Sec. 3.2. above, it was argued that trace amounts of molecules can adhere to delivery lines thereby decreasing the number of molecules that can be injected into a detection apparatus. Our pulsed supersonic molecular beam valve has two characteristics that alleviate this problem. First, the design incorporates continuous flow capabilities that insure that a fresh atmospheric sample is always present at the injection aperture. Second, the valve may alternatively be constructed using an open structure that allows the atmosphere to be in direct contact with the pulsed aperture. Both adaptations would minimize the surface interactions that can degrade detection capabilities.

5. Conclusions

The technique of supersonic molecular beam, resonance enhanced multiphoton ionization, time-of-flight mass spectroscopy (MB/REMPI/TOFMS) was demonstrated as an ultratrace detection method that offers exceptional selectivity. Studies were carried out using moist air expansions for a variety of organophosphonate and sulfide CWA simulant molecules. Preliminary determinations indicate near unit collection efficiency for ions produced in the excitation region as well as single ion detection sensitivity, thus giving observable detection limits of < 300 ppt. Single vibronic level REMPI of the supercooled molecules in conjunction with TOFMS provides selectivity of 10^4 against chemically similar compounds.

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