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ULTRATRACE DETECTION OF ATMOSPHERIC CONTAMINANTS BY SUPERSONIC MOLECULAR BEAM, MULTIPHOTON IONIZATION, MASS SPECTROSCOPY

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An ultratrace detection method that offers < 300 ppt and selectivity of $\sim 10^4$ is demonstrated for organophosphonate and sulfide chemical agent simulant molecules.

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. An integral part of the MB/REMPI/TOFMS technique is the extensive molecular cooling that occurs in a supersonic expansion in which nearly all molecules are relaxed to the vibrationless level and to just a few rotational states[1]. This condition 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.

Our ultrasensitive compact molecular beam 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 chamber 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.

A pulsed nozzle design based on fast solenoid activation[2] was constructed since it offers a unique combination of features that are important to the detection method, 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.

A 2-photon absorption, 2-photon ionization (i.e. 2+2) REMPI excitation spectrum of diisopropyl methylphosphonate was recorded using room air as the carrier gas to demonstrate the potential of supersonic molecular beam spectroscopy for atmospheric monitoring (Fig. 1). The extent of molecular cooling in terms of rotational broadening and hot band intensity is nearly equal to that obtained using 50 psi He as a carrier gas. Hence, considerable optical selectivity is made possible by supersonic expansion of atmospheric samples. An additional stage of selectivity is of course provided by the TOF mass spectrometer.

We adopt a straightforward definition of sensitivity as being the concentration of a target molecule that gives a signal that exceeds the background signal fluctuation (i.e. the concentration that is detectable). The detectable concentration, C_o, 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. We also define two response times; (i) τ_∞ being the time required for the signal to grow to within 1/e of its final value and (ii) τ_o being the time required for an actual signal to exceed the background fluctuation level. We may consider τ_o to be the response time for detection and τ_∞ the response time for measurement of concentration.

The response of our detection system to a 60 ppb sample of DMS in water-saturated air (i.e.

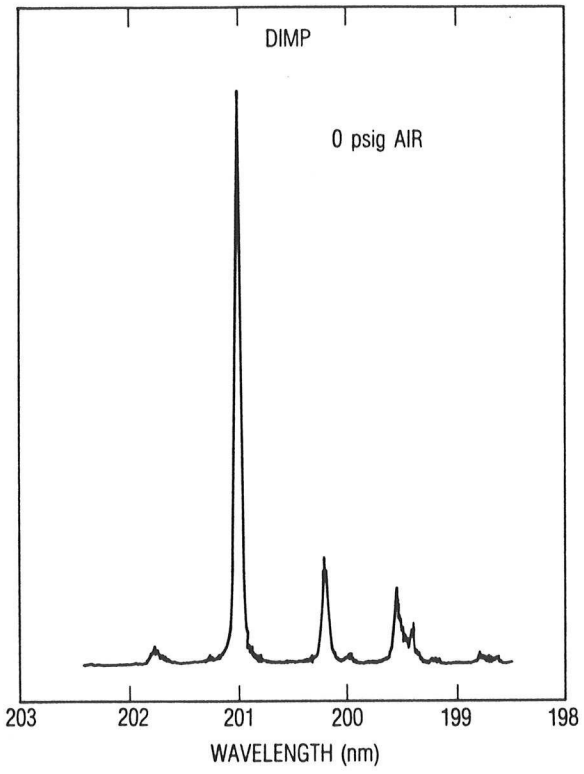

FIG. 1. 2+2 REMPI excitation spectrum of DIMP in a supersonic molecular beam using atmospheric room air (0 psig = 15 psi) as the carrier gas (0.5% DIMP in 15psi air). The fragment ion at m/e=43 was monitored in recording the spectrum.

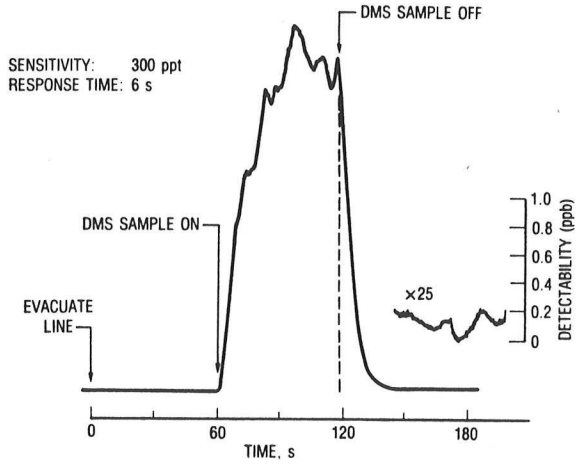

FIG. 2. Sensitivity determination for a 60 ppb sample of dimethyl sulfide (DMS) in water-saturated air. The baseline signal represents the background level of our molecular beam apparatus. The sample signal represents the response to turning the sample flow on and off at specified times.

100% relative humidity, 17000 ppm) is presented in Fig. 2. An enlargement of the baseline region along with a detectability scale is included for convenience. The ratio of sample signal to background signal, $\frac{S_{split}}{S_o}$, 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 on the order of 100 msec. Naturally, other factors (i.e. transit time of sample through delivery lines, laser repetition rate, etc.) can increase the actual "system" response time; however, the intrinsic value of τ_o can be approached with careful design. By varying experimental conditions (e.g. smoothing factors), tradeoffs between measurement response time, τ_∞, and detection level, C_o, can be made to enhance one parameter at the expense of the other.

The usable sensitivity, (i.e. detectability), requires a high level of descrimination against contaminant molecules. A test of the selectivity of the MB/REMPI/TOFMS technique against chemically similar compounds was performed using a 10 ppm sample of DIMP and a 1300 ppm sample of DMMP (dimethyl methylphosphonate) in N_2. This determination resulted in a selectivity of about $\sim 10^4$. A similar level of selectivity is observed for gasoline. In summary, the MB/REMPI/TOFMS technique is capable of exceptional sensitivity and selectivity for atmospheric monitoring.

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