Ultrasensitive detection of atmospheric constituents by supersonic molecular beam, multiphoton ionization, mass spectroscopy

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An ultrasensitive detection method for atmospheric monitoring has been developed based on the technique of supersonic molecular beam, resonance enhanced multiphoton ionization, and time-of-flight mass spectroscopy (MB/REMPI/TOFMS). Several organophosphonate and organosulfide compounds, representing simulants to a class of toxic compounds, were studied. Detection levels as low as 300 ppt (dimethyl sulfide) were obtained. Single-vibronic-level REMPI of the cooled molecules in conjunction with TOFMS provided selectivity of $\sim 10^4$ against chemically similar compounds in humid air expansions. The fragment ions formed by REMPI excitation are shown for diisopropyl methylphosphonate to depend strongly on the resonant intermediate state of the neutral molecule.

I. Introduction

We report on an ultrasensitive detection method based on the application of a pulsed supersonic molecular beam (MB), resonance enhanced multiphoton ionization (REMPI), time-of-flight mass spectrometer (TOFMS). A principal objective of this work was to demonstrate highly specific real-time ultrasensitive detection levels in a reasonably compact apparatus. An integral part of the MB/REMPI/MS 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 (1) the cooled molecules are in virtually the same energy state and can, therefore, be excited quantitatively using a single wavelength of light and (2) each compound has its own characteristic set of narrow excitation wavelengths that is distinct from that of other compounds.

A large number of compounds that are considered hazardous when present in the atmosphere have strong optical transitions at wavelengths that are conveniently accessible to commercial lasers. Aromatic molecules, for example, have been reported to undergo very efficient REMPI[2] and are, therefore, ideal candidates for detection by MB/REMPI/MS. We chose to study a class of compound that is known to be a difficult candidate for trace detection to examine the generality of the MB/REMPI/MS technique. The organophosphonates are a class of compound that includes pesticides and chemical nerve agents. They are particularly difficult to detect owing to their photoinstability and lack of strong optical transitions at available laser wavelengths. The organosulfides are simulants to toxic compounds and exhibit detection difficulties similar to the organophosphonates.

II. Experimental

A schematic of our MB/REMPI/TOFMS system is illustrated in Fig. 1. The compact molecular beam system consists of two differentially pumped chambers separated by a 1-mm diam skimmer. The main chamber, which contains the excitation and detection components, is 12 liters in volume and pumped by a 1200 liter/s turbomolecular pump, 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 base 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 close to the base pressure.

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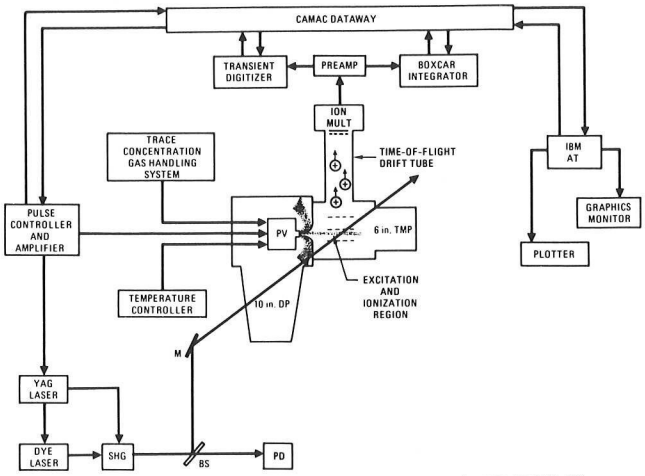

Fig. 1. Schematic of the pulsed supersonic MB/REMPI/MS apparatus and associated components. The components are defined as follows: SHG, single harmonic generator; BS, beam splitter; PD, photodiode; *M*, mirror; DP, diffusion pump; TMP, turbomolecular pump; PV, pulsed valve.

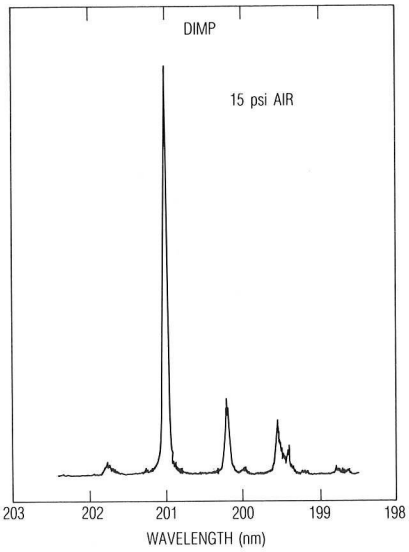

Fig. 2. 2 + 2 REMPI excitation spectrum of DIMP in a supersonic molecular beam using atmospheric room air (0 psig = 15 psi) as the carrier gas (0.5% DIMP in 15-psi air). The fragment ion m/e = 43 was monitored in recording the spectrum.

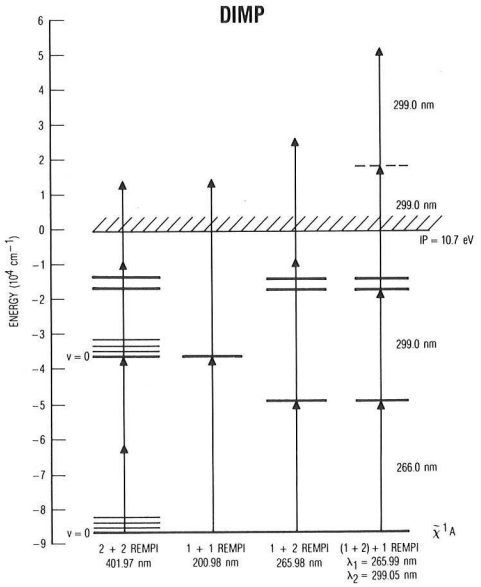

Fig. 3. REMPI excitation schemes used in the study of DIMP.

A pulsed nozzle design based on fast solenoid activation[3] was constructed that offers a unique combination of features important to the detection method, namely, (1) high repetition rates (up to 100Hz), (2) temperature control (up to 200°C), (3) continuous gas sample flow capabilities, and (4) internally mountable sample holder.

Laser excitation was provided by a tunable dye laser pumped by a Nd:YAG laser operating at 532 nm (500 mJ/pulse). By frequency doubling the visible dye output or by frequency mixing the visible with the Nd:YAG 1064-nm output, we obtained a tuning range of 275–440 nm (10–20 mJ/pulse). Frequency doubling followed by mixing with 1064 nm extended the tuning to 222 nm (1–3 mJ/pulse). Shorter wavelengths to 195 nm (10–150 μJ) were generated using anti-Stokes Raman shifting in an H_2 pressure cell. A 350-mm focal length spherical lens was used to focus the light into the molecular beam.

Time-of-flight mass spectra were recorded using a 200-MHz transient digitizer. Ionization excitation spectra were recorded by scanning the ionizing laser wavelength and detecting a specific mass using a time-gated boxcar integrator *A*. A second boxcar integrator *B* was used to record the laser pulse intensity. The recorded spectrum was normalized approximately by storing the ratio A/B^2.

Trace concentrations were prepared by evacuating a 2 liter stainless steel cylinder, introducing the target molecules to low pressure (typically 1 Torr as measured using a digital capacitance manometer), and backfilling to high pressure (typically 400 psi) with the carrier gas. The resulting mixture (~50 ppm) was diluted further by releasing the pressure and backfilling to attain the desired concentration. For concentrations below 1 ppm, successive dilutions were prepared and the signal levels monitored to insure a linear dependence of signal with concentration. For dimethyl sulfide, this relationship was approximately maintained to 60 ppb, below which the signal decreased faster than the concentration (presumably due to wall adsorption on the polyethylene and stainless steel delivery line).

III. Spectroscopy and Excitation Conditions

An ionization excitation spectrum of diisopropyl methylphosphonate (DIMP) is illustrated in Fig. 2. Excitation was by two-photon absorption, two-photon ionization (i.e. 2 + 2 REMPI) and is illustrated in Fig. 3. Detection involved the predominant m/e = 43 ion mass (corresponding to the isopropyl fragment), which is evident in the TOF mass spectrum in Fig. 4(c). The

excitation spectrum in Fig. 2 was recorded using room air as the carrier gas to demonstrate the potential of supersonic molecular beam spectroscopy for atmospheric monitoring. The extent of molecular cooling in terms of rotational broadening and hot band intensity compares favorably with 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.

Sensitive detection of molecules by laser excitation requires detailed knowledge of the spectroscopic and photochemical properties of the molecule of interest to determine the best excitation schemes for achieving optimum detection limits. Consequently, four different excitation schemes were studied for DIMP to access different excited electronic states and deposit various amounts of energy into the parent and fragment ions (see energy level diagram, Fig. 3). The TOF mass spectra are given in Fig. 4. In no case was the parent ion M^+ observed, even though ions were formed with as little as 13,000 cm^{-1} internal energy. This is consistent with electron impact (EI) ionization studies of DIMP[4,5] which show M^+ is unstable at thermalized vibrational energies.

The fragment ions at m/e = 97 and 123, which are formed by EI ionization,[4] are also formed when exciting through the weak and structureless neutral electronic state at 266.0 nm [Fig. 4(a)]. Introducing a second wavelength for ionization and ion absorption leads to further fragmentation [Fig. 4(b)], but again the stable m/e = 97 and 123 ion fragment signals remain strong. Interestingly, the ion absorption by the second color induces a fragmentation that allows formation of C_6 alkyl fragments (background hydrocarbon contamination can be ruled out; see Sec. II). A possible pathway is elimination of the central PO_3 moiety followed by a combination of the isopropyl groups.

Ionization through the resonant higher excited electronic state at 200.98 nm shows a very different behavior [Fig. 4(c)]. The absence of the M^+ ion may be considered consistent with evidence suggesting a thermally unstable parent ion. However, there is also no evidence for the stable m/e = 97 and 123 ion fragments that are formed in high yield by EI ionization and REMPI via the 266.0-nm neutral state. Instead, for 2 + 2 REMPI via the 0_0^0 transition at 200.98 nm, a prominent m/e = 43 ion fragment attributable to the isopropyl group occurs. Furthermore, attempts to observe 1 + 1 REMPI using low laser power (30 μJ) gave a negligible ion signal. These results are consistent with excitation to a resonance state whose dissociation competes with ionization. The observed ion signal is, therefore, believed to occur via nonresonant ionization of the neural isopropyl fragment. Other evidence for the dissociative nature of neutral excited state DIMP[6] and DMMP (dimethyl methylophosphonate)[4,6,7] has been reported. The argument for the neutral excited state dissociation of DIMP to give isopropyl is further

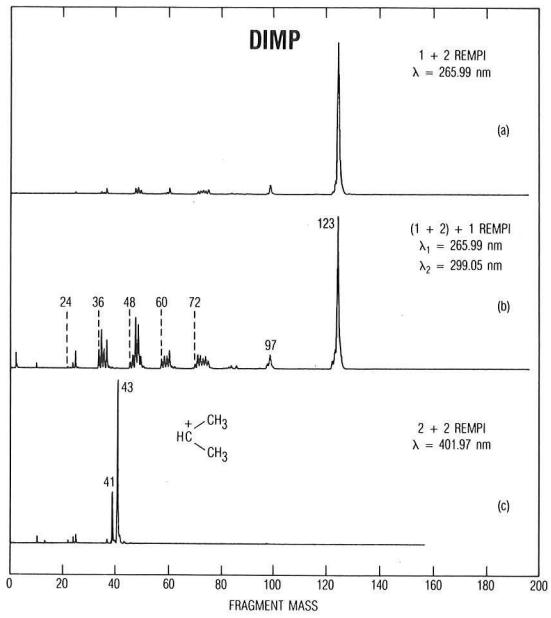

Fig. 4. REMPI/TOF mass spectra of DIMP in a supersonic beam: (a) 1 + 2 REMPI using 265.99 nm (0.4 mJ); (b) 1 + 2 REMPI using resonant 265.99 nm (0.4 mJ, first anti-Stokes Raman) and 299.05 nm (2.5 mJ, UV fundamental) to ionize with further absorption of 299.05 nm by ions leading to fragmentation; (c) 2 + 2 REMPI at 401.97 nm (2 mJ/pulse).

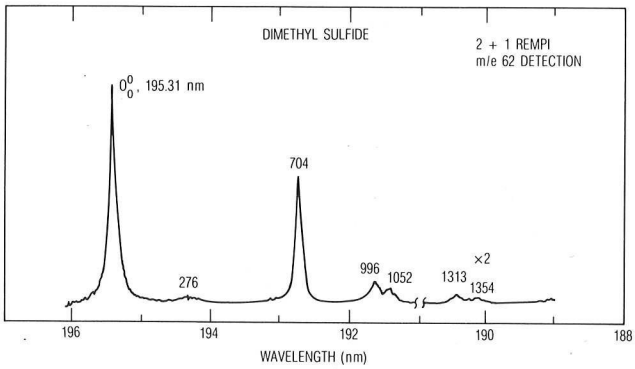

Fig. 5. 2 + 1 REMPI excitation spectrum of the *3p* Rydberg state of DMS in a supersonic molecular beam (0.1% DMS in 50-psi He). Spectrum was recorded by detecting the parent ion at m/e = 62. Vibrational intervals are reported in cm^{-1}.

supported by the absence of this species by ion fragmentation induced by either photon excitation [compare Fig. 4(c) with (b)] or electron impact excitation.[4,5]

Spectroscopic studies for ultrasensitive detection of a class of sulfide molecules was also undertaken. Dimethyl sulfide (DMS) was observed to have a resolved 2 + 1 REMPI excitation spectrum (Fig. 5) for an electronic state assigned as a *3p* Rydberg state.[8] The linewidths of the 2 + 1 excitation lines are relatively broad (~ 15 cm^{-1}). This property is not unusual for transitions to higher excited vibronic levels due to the greater density of states as well as interactions with many nearby electronic states.[9] However, predissociation, which can compete with ionization, also seemed possible. For example, DMS has been report-

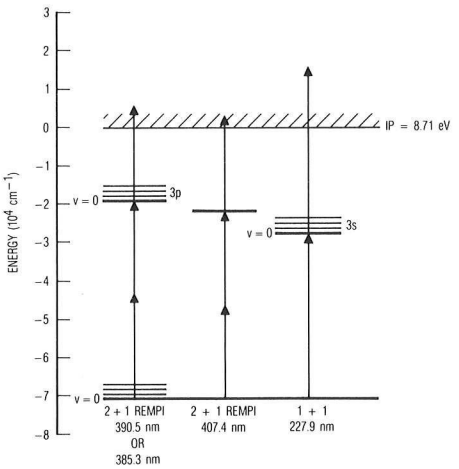

Fig. 6. REMPI excitation schemes used in the study of DMS.

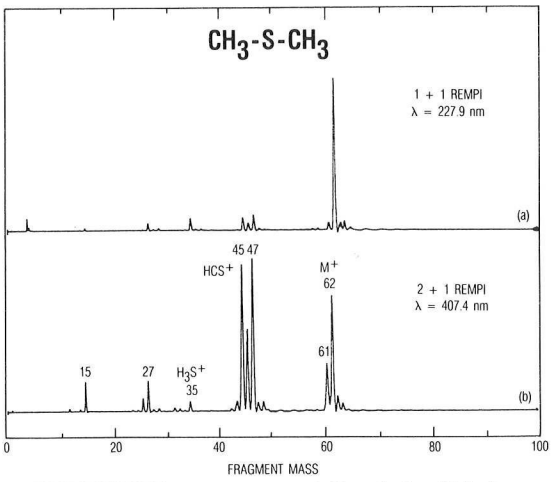

Fig. 7. REMPI TOF mass spectra of dimethyl sulfide in a supersonic molecular beam: (a) 1 + 1 REMPI via the 3*s* Rydberg state at 227.9 nm; (b) 2 + 1 REMPI via the featureless valence state at 203.7 nm.

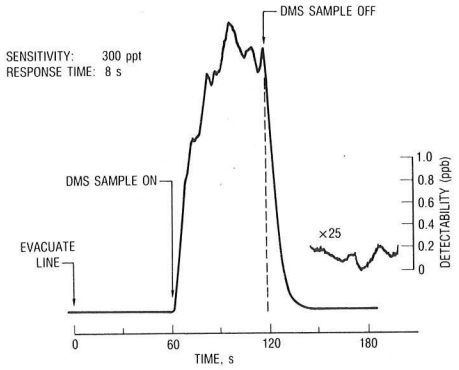

Fig. 8. Sensitivity determination for a 60-ppb sample of dimethyl sulfide (DMS) in water-saturated air. The base line signal represents the background level of our molecular beam apparatus. The sample signal represents the response to turning the sample flow on and off at specified times.

ed to undergo dissociation to form CH_3S · radicals following 193-nm excitation.[10]

We investigated the extent of photodissociation of DMS following excitation into Rydberg valence states. The candidate electronic states and excitation schemes are illustrated in Fig. 6. The REMPI mass spectra, illustrated in Fig. 7, are evidence for significant M^+ formation regardless of whether the valence state or the *3s* Rydberg state (Fig. 6) is excited. A similar result was obtained when exciting through the *3p* Rydberg state. The predominance of the parent ion M^+ signal is evidence not only for stable electronically excited neutral states (at least over the duration of the 5 ns laser pulse) but for stable ions to energies as high as 16,000 cm^{-1} (Fig. 6).

IV. Detectability Limits

A. Working Model

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_0 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_0. This leads to the simple relation for detection limit of

$$C_0 = C_{\text{calib}} \frac{S_0}{S_{\text{calib}}} . \tag{1}$$

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: (1) 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

$$S(t) = S(\infty)\left[1 - \exp\left(-\frac{t}{\tau_\infty}\right)\right], \tag{2}$$

and (2) τ_0 being the time required for an actual signal to exceed the background fluctuation level. We may consider τ_0 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

$$S(\tau_0) = S(\infty)\left[1 - \exp\left(-\frac{\tau_0}{\tau_\infty}\right)\right]. \tag{3}$$

Defining $S(\tau_0) = S_0$ and rearranging then gives

$$\frac{\tau_0}{\tau_\infty} = -\ln\left[1 - \frac{S_0}{S(\infty)}\right]. \tag{4}$$

It is not difficult to see that the response time for detection τ_0 can be considerably smaller than τ_∞ for target molecule concentrations well above the detection limit.

B. Sensitivity

The response of our detection system to a 60-ppb sample of DMS in water-saturated air (i.e., 100% relative humidity, 17,000 ppm H_2O) is presented in Fig. 8. An enlargement of the base line region along with a detectability scale is included for convenience. The ratio of sample signal to background signal $(S_{\text{calib}})/S_0$ is > 200, corresponding to a detection limit for DMS of $<$

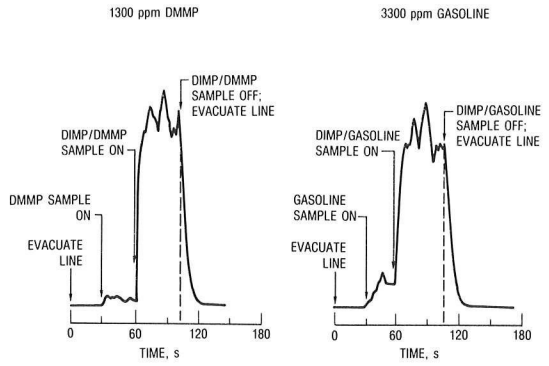

Fig. 9. Selectivity determinations for a 10-ppm sample of DIMP in N_2 with the chemically similar species DMMP and with gasoline.

300 ppt. The measurement response time τ_∞ is 8 s. However, the detection response time τ_0 at 60 ppb is of the order of 100 ms. Naturally, other factors (i.e., transit time of sample through delivery lines and laser repetition rate) can increase the actual system time; however, the intrinsic value of τ_0 can be approached with careful design. Finally, it is noted that by varying experimental conditions (e.g., smoothing factors), trade-offs between measurement response time τ_∞ and detection level C_0 can be made to enhance one parameter at the expense of the other.

The excitation scheme leading to the signal in Fig. 8 involves 2 + 1 REMPI at a wavelength of 390.62 nm corresponding to resonance enhancement through the vibrationless level of the *3p* Rydberglike state at 195.31 nm (Fig. 5). The transition to the *3p* state is formally allowed by one-photon excitation but symmetry forbidden by two-photon excitation. Hence the two-photon absorption cross section is very small and not favorable from the standpoint of ionization efficiency. The near term development of millijoule pulse energies at 195.31 nm can be expected to lead to improvements in the detection limit by 2 orders of magnitude.

C. Selectivity

The usable sensitivity (i.e., detectability) requires a high level of discrimination against contaminant molecules. A test of the selectivity of the MB/REMPI/MS technique against chemically similar compounds was performed by mixing a flowing 10-ppm DIMP sample (in N_2) with a 1300-ppm DMMP (dimethyl methylphosphonate) sample. Excitation of DIMP was by 2 + 2 REMPI via the 200.98-nm electronic state (Figs. 2 and 3). Detection was for the m/e = 43 fragment ion (Fig. 4(c). The selectivity was determined by recording the signal intensity in the absence and presence of the target DIMP sample and taking account of the ratio of the DIMP and DMMP concentrations. This determination, displayed in Fig. 9, resulted in a selectivity of $\sim 10^4$. A similar level of selectivity is observed using gasoline as an interferent. In a related experiment the response of the DIMP sample is compared to a room air sample saturated with water. The results, which were obtained in the same manner as described above, indicate that the selectivity of DIMP to water is $> 10^5$. However, more important, it demonstrates that water vapor does not form molecular complexes with DIMP (or DMS, Fig. 8) that would degrade the signal strength due to nonresonant excitation and loss of mass identification.

V. Conclusions

The technique of supersonic molecular beam, resonance enhanced multiphoton ionization, time-of-flight mass spectroscopy (MB/REMPI/TOFMS) was demonstrated as an ultrasensitive detection method that offers exceptional selectivity. Studies were carried out using humid air expansions for a variety of organophosphonate and sulfide molecules. Detection limits to <300 ppt have been determined. Single-vibronic-level REMPI of the cold molecules in conjunction with TOFMS provides selectivity of $\sim 10^4$ against chemically similar compounds. Efficient supersonic molecular cooling and lack of water–molecule complexation were demonstrated for humid atmospheric air expansions thereby attesting to the applicability of the MB/REMPI/TOFMS technique for atmospheric monitoring.

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