Reprinted from Analytical Chemistry, 1990, *62*.

REAL-TIME DETECTION of Chemical Agents Using Molecular Beam Laser Mass Spectrometry

Jack A. Syage
Aerophysics Laboratory
The Aerospace Corporation
P.O. Box 92957
Los Angeles, CA 90009

The alleged production and use of chemical warfare agents are causes for great concern. When these agents are unleashed into the atmosphere, the physiological response is quick and dramatic. Short-term exposure can be lethal at parts-per-million levels, and even at parts-per-billion concentrations chemical warfare agents can cause serious, irreversible injury. These concerns prompted our efforts to develop a detector as a warning system for chemical warfare agents. For obvious reasons, the detector must be sensitive and have a rapid response time. Less obvious is the fact that the system must be selective and able to distinguish between poisonous molecules and those that normally exist in the atmosphere. In other words, anyone can find a needle, but finding one in a haystack poses a more challenging problem.

Our molecular detection work centers on the use of multiphoton ionization (MPI) and mass spectrometry (MS) (*1*). By enhancing MPI-MS with supersonic molecular beam expansion (*2*), resonance-enhanced excitation, and time-of-flight (TOF) mass detection, we have been able to design a suitable detection system.

MPI-MS

MPI occurs when a molecule sequentially absorbs photons until the total energy of the molecule exceeds the ionization potential. Resonance-enhanced MPI occurs when the photon wavelength chosen matches an absorbing state of the molecule. The resonance step not only substantially improves sensitivity but also provides a means for selectively ionizing molecules. If the intermediate resonance absorption lineshapes are narrow, then the likelihood of excitation frequencies overlapping for different molecules diminishes dramatically. Selective ionization for a particular molecule would occur despite the abundance of other molecules in the sample. Hence high-resolution spectroscopic techniques translate into highly selective detection (*3–6*).

In high-resolution supersonic molecular beam spectroscopy (Figure 1), the most important element is the expansion of gas at high pressure (atmospheric gas in this case) into a vacuum. Because of the dynamics of the expansion, the sample undergoes substantial cooling of the internal rotational and

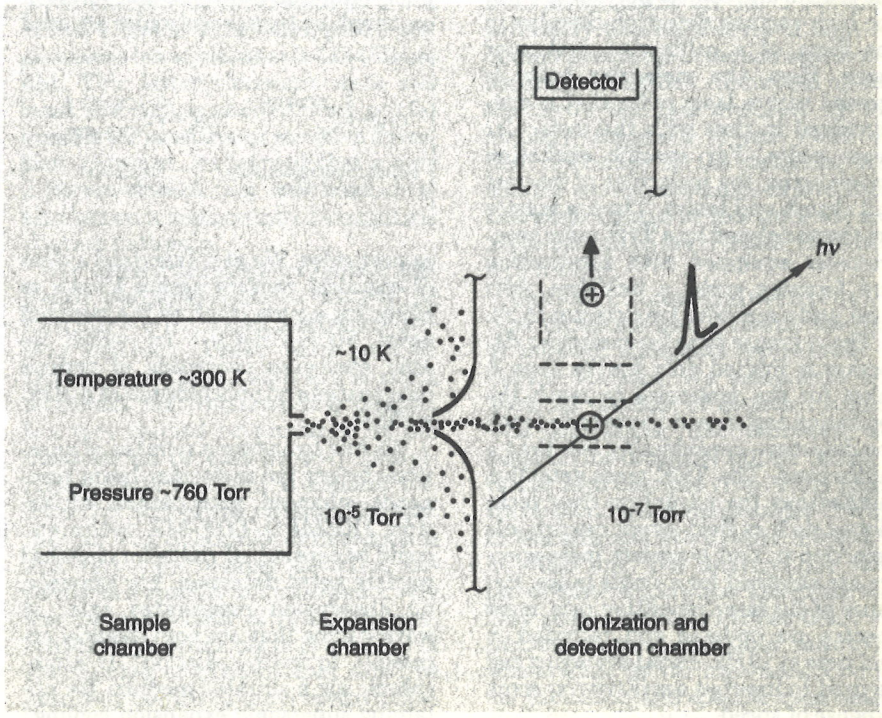


Figure 1. Pictorial view of the molecular beam laser MS technique.

0003-2700/90/0362-505A/$02.50/0

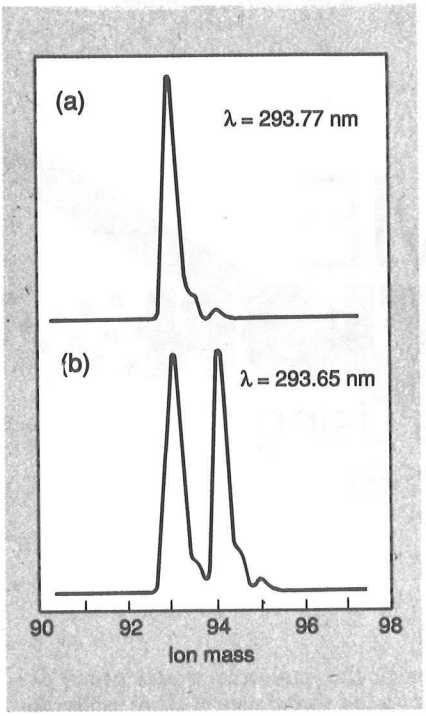


Figure 2. 1 + 1 resonance-enhanced multiphoton ionization mass spectra of aniline: (a) excitation of the nominal aniline absorption maximum and (b) enhancement of the ion signal for natural abundance aniline ^{13}C.

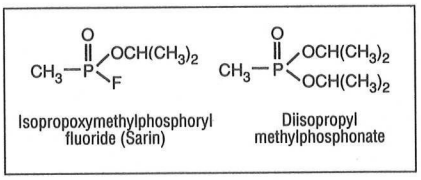
vibrational degrees of freedom. At a distance into the expansion chamber, when no further cooling occurs, the expanding gas pulse is skimmed to allow the central and coldest portion to enter the high-vacuum detection chamber in the form of a collimated molecular beam. Here, the molecular beam is crossed with a laser pulse that is synchronized in time with the molecular beam pulse. For specific excitation wavelengths, the molecules of interest will absorb and ionize. The ion masses are then analyzed by a TOF mass spectrometer equipped with acceleration and focusing grids, a field-free drift tube, and a sensitive ion detector (*5*, *6*).

The response time for molecular detection is limited only by the time it takes for the molecules to reach the ionization region and the ions to reach the detector—considerably less than a millisecond. The TOF mass detection method has the advantage over techniques such as field-swept quadrupole detection in that complete mass spectra are obtained for a single pulse. Because of the laser repetition rate, mass spectra are updated and recorded in real time at 10 Hz. Signal averaging can be used to improve sensitivity at some expense of speed.

The selectivity of mass spectrometric detection is not always adequate for ultratrace detection at parts-per-billion levels. For this reason, high-resolution optical excitation was applied to enhance performance. A good example of optical selectivity is illustrated by using aniline and natural abundance aniline containing a single ^{13}C (Figure 2). The absorption spectra for these two species are essentially indistinguishable except for a nearly imperceptible shift in the line positions (293.77 nm vs. 293.65 nm, respectively, for the origin transition). By conventional electron impact or MPI-MS, the mass intensities would reflect the natural abundance of both species (Figure 2a). However, in the presence of a molecular beam, where high-resolution conditions prevail, it is possible to preferentially excite the less abundant species, thereby enhancing the ion signal for that mass (Figure 2b) (*7*, *8*). Despite the stringent conditions imposed by the exceptionally close-lying absorption wavelengths ($\Delta\lambda$ = 0.12 nm), an optical enhancement of nearly 20 was obtained.

Detection

Chemical warfare agent detection was addressed in our labs by using molecules that have nearly identical structural and spectroscopic properties as actual agent molecules, but without the lethality. For example, we used the molecule diisopropyl methylphosphonate as an analogue for the nerve agent isopropoxymethylphosphoryl fluoride (Sarin). Other forms of organophosphonate molecules are used as pesticides. We also examined a class of chemical warfare agents known as blistering agents (such as the mustard agent $S(CH_2CH_2Cl)_2$) for which we used analogues consisting of various chlorinated and nonchlorinated dialkyl sulfides.



We had to answer a number of questions before the molecular beam resonance-enhanced multiphoton ionization (REMPI)/TOF-MS technique could be considered viable for chemical warfare agent detection. For example, do absorption resonances exist at wavelengths that are conveniently accessible to laser radiation? Is atmospheric air a suitable medium for obtaining supersonic expansion cooling? Are the intermediate resonance states sufficiently stable to allow further photon absorption, leading to ionization?

Little spectroscopic information existed for chemical warfare agent analogue molecules prior to this study. Therefore we began by constructing a medium-resolution, gas-phase absorption spectrometer to record survey spectra in the ultraviolet (UV) and the vacuum-UV regions. This provided the necessary database for high-resolution detection measurements. It became evident that it would be difficult to detect the organophosphonate and the organosulfide molecules by laser ionization because of the lack of strong one-photon absorptions in the near-UV region of the spectrum where adequate laser pulse energy is most readily available (i.e., $\lambda > 220$ nm). The lowest energy strong bands for both classes of molecules occur at ~200 nm. This made it necessary to resonantly ionize by the less efficient process of two-photon absorption using 400-nm laser pulses. (Recent advances in crystal technology now permit us to generate 200-nm laser pulses conveniently.) We reached our first milestone when highly resolved spectra were recorded for diisopropyl methylphosphonate by 2 + 2 REMPI excitation and for dimethyl sulfide by 2 + 1 REMPI under optimized expansion conditions (*6*).

Our second concern was whether atmospheric air would act as an effective medium for supersonic expansion cooling. The cooling of seed molecules expanded in a high-pressure carrier gas improves with increased pressure and

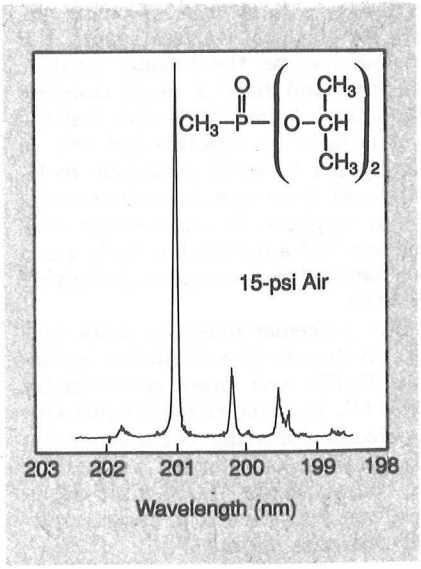


Figure 3. 2 + 2 REMPI excitation spectrum of diisopropyl methylphosphonate (0.5% diisopropyl methylphosphonate in 15-psi air).

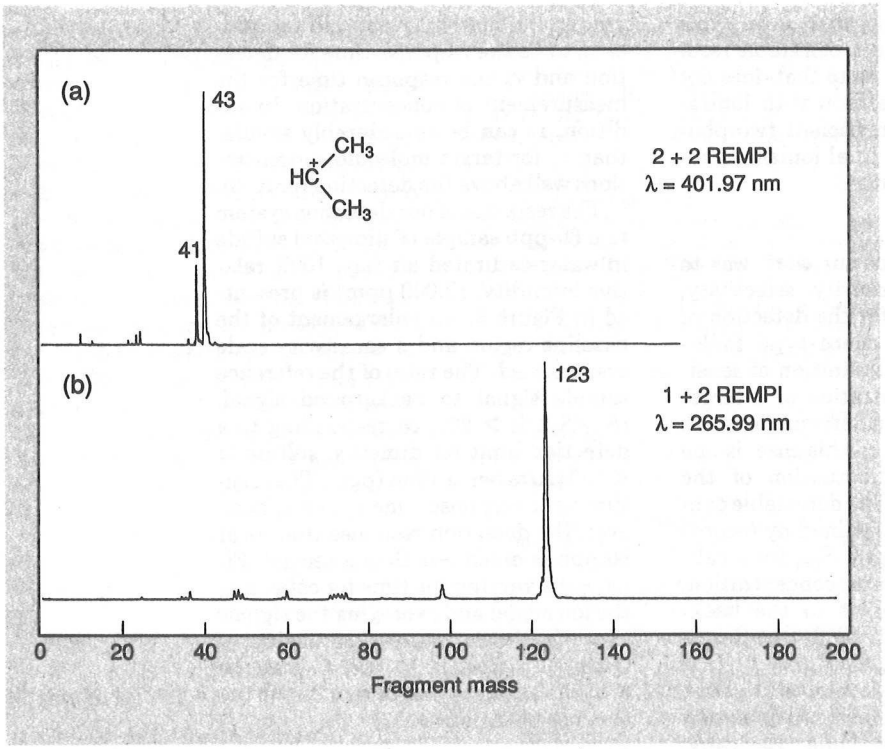


Figure 4. REMPI mass spectra of diisopropyl methylphosphonate in a supersonic beam recorded for two different excitation conditions.
(a) Predominant peak at *m/z* 43 and (b) predominant ion signal at *m/z* 123.

is most efficient for carrier gases that lack internal energy, such as the monoatomic rare gases. The suitability of atmospheric air as a carrier gas was found to compare favorably with more optimum expansion conditions (e.g., 50 psi He). The narrow-line resonance absorption ionization spectrum of diisopropyl methylphosphonate in air (Figure 3) attests to the highly selective excitation conditions obtainable for atmospheric samples. Thus supersonic molecular beam spectroscopy can be used for atmospheric sampling.

Finally, a lengthy study was undertaken to investigate the photochemical and photophysical properties of the intermediate vibronic (*vib*rational–elec*tronic*) states that serve to resonantly enhance the ionization step. Our most serious concern was that short-lived states that dissociate or decay would compete with the ionization step to diminish the ion signal (*5*, *6*, *9*). We explored several methods to overcome such problems: exciting and ionizing with laser pulses that are short (i.e., picosecond) (*10*) compared with the dissociative lifetime, ionizing and detecting a known fragment of the dissociation, and exciting through a different resonance intermediate state that is long lived.

The detection of diisopropyl methylphosphonate is an example in which the REMPI mass spectrum did not reveal a significant amount of molecular ion at 180 amu. The 2 + 2 REMPI excitation for the strong origin transition in Figure 3 gave a predominant peak at *m/z* 43 (Figure 4a). Ionization from a lower energy electronic state by 1 + 2 REMPI, on the other hand, gave a predominant ion signal at *m/z* 123 (Figure 4b). This latter electronic state was weak and diffuse and therefore not favorable for sensitive or selective detection. However, we learned that a very different dissociation and fragmentation behavior can occur by different excitation pathways.

We carried out electron impact ionization studies to establish that the 123 amu ion is a molecular ion fragmentation product. These same studies showed that the 43 amu ion is not a molecular ion fragmentation product but may instead be produced by the dissociation of diisopropyl methylphosphonate before it is ionized, followed by MPI of the neutral isopropyl radical. The selectivity of detection is still very high because detection depends on a specific ion mass and a very narrow wavelength of light; however, sensitivity is relatively poor because of the number of photons that must be absorbed per diisopropyl methylphosphonate molecule (at least four) to obtain a signal. A detection limit of 50 ppb was measured with a time response of 6 s by this excitation scheme. Recent research to extend laser wavelength ranges now makes it possible to apply direct 200-nm excitation by using a much more efficient 1 + 1 REMPI scheme.

The related organophosphonate molecule, dimethyl methylphosphonate, exhibits somewhat different spectroscopic and photochemical behavior than the structurally related molecule diisopropyl methylphosphonate. Broadband UV/vacuum-UV absorption spectra of room-temperature vapor-phase samples showed no evidence for any strong absorption bands ($\epsilon < 500$) at wavelengths longer than 140 nm, nor were any vibrationally resolved electronic state features revealed. Because optical selectivity by discrete resonance excitation was apparently not available for dimethyl methylphosphonate, we sought to obtain optical selectivity by REMPI excitation of a major photofragment.

Other investigators have reported the efficient production of PO radicals from dimethyl methylphosphonate by a variety of excitation sources (*9*). We therefore used the sharp PO vibrationless transition $\tilde{A}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$ at 247.7 to ionize the fragment by 1 + 1 REMPI. This wavelength also proved effective for photodissociating dimethyl methylphosphonate to give the characteristic fragment PO, thereby avoiding the need for a second wavelength of light (*6b*). In a related program, we have been investigating the use of two independently tunable sources of light for double-resonance detection schemes of aromatic molecules. Additional optical selectivity becomes available by this strategy, especially if one views the first resonance as the detection step and the second resonance as a verification step. Details of this work for aromatic molecules are reported elsewhere (*5*, *11*, *12*).

Our study of chemical warfare agent-type molecules also included the class of mustard simulants represented by dialkyl sulfides. We summarize this work for the case of dimethyl sulfide. The first strong electronic-state absorption for dimethyl sulfide occurs at rather high energies (195.31 nm origin transition), which necessitated the use of less efficient two-photon absorption at ~390 nm. The intermediate resonance-state absorption spectrum was very sharp in the molecular beam expansion; hence, enormous selectivity was evident by the high-resolution laser excitation and specific mass detection. The overall ionization described by 2 + 1 REMPI resulted in a predomi-

nantly molecular ion at 62 amu. This observation is evidence of a stable resonance intermediate state that does not dissociate in competition with ionization. Despite the inefficient two-photon absorption, the final ionizing photon was very efficient.

Performance

A major objective of our work was to quantitate the sensitivity, selectivity, and response time for the detection of chemical warfare agent-type molecules. Our working definition of sensitivity is the concentration of a target molecule that gives a detectable signal. A detectable signal, in this case, is one that exceeds the fluctuation of the background signal. The detectable concentration C_0 is determined by recording the signal strength, S_{ref}, for a calibrated reference sample concentration, C_{ref}, and comparing it to the background fluctuation level S_0 (the detection limit is $C_0 = C_{ref}S_0/S_{ref}$).

A model was also developed to relate the experimentally measured detection levels and response time. Basically, there is the usual trade-off in which sensitivity improves the longer one collects signals. We define τ_e as the response time required for the signal to grow to within $1/e$ of its final value and τ_0 as the response time required for the detected signal to exceed the background fluctuation level S_0. We consider τ_0 to be the response time for detection and τ_e the response time for the measurement of concentration. In addition, τ_0 can be considerably smaller than τ_e for target molecule concentrations well above the detection limit (*6*).

The response of our detection system to a 60-ppb sample of dimethyl sulfide in water-saturated air (i.e., 100% relative humidity, 17,000 ppm) is presented in Figure 5. An enlargement of the baseline region and a sensitivity scale are included. The ratio of the reference sample signal to background signal, (S_{ref}/S_0), is > 200, corresponding to a detection limit for dimethyl sulfide of < 300 parts per trillion (ppt). The measurement response time τ_e is 8 s; however, the detection response time τ_0 at 60 ppb is much less than a second. Finally, by varying the time for collecting the ion signal and averaging the signals over the background fluctuation, a trade-off between τ_e and C_0 can be made to enhance one parameter at the expense of the other.

Summary

Molecular beam MPI is a powerful research tool that has contributed enormously to our fundamental understanding of the spectroscopy and dynamics of excited-state molecules. It is only natural that the benefits of high

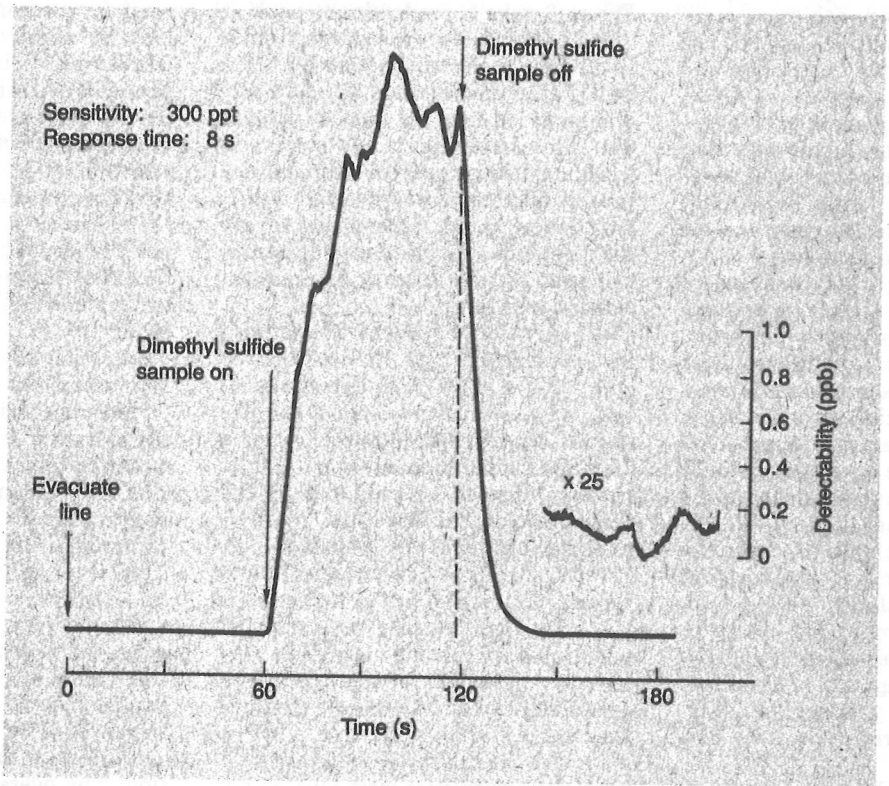


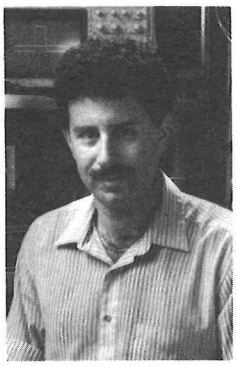
Figure 5. Sensitivity determination for a 60-ppb sample of dimethyl sulfide in water-saturated air.

resolution and sensitive detection would be recognized and applied toward molecular detection. The work reviewed here demonstrates the potential performance of molecular beam MPI-MS in terms of speed, sensitivity, and selectivity of detection. Many classes of compounds are favorable candidates for detection by REMPI. We have attempted to show that it is possible to overcome the challenges presented by complex molecules such as chemical warfare agents and pesticides. The maturing of molecular beam laser MS as a viable broad-based analytical tool depends only on the development of rugged, compact, and widely tunable sources of laser pulses.

I am indebted to my collaborators, James E. Pollard, Ronald B. Cohen, and John E. Wessel, who contributed substantially to various projects relating to laser molecular beam MS.

References

(1) *Lasers and Mass Spectrometry;* Lubman, D. M., Ed.; Oxford University Press: New York, 1990.
(2) a. Levy, D. H.; Wharton, L.; Smalley, R. E. In *Chemical and Biological Applications of Lasers;* Moore, C. B., Ed.; Academic Press: New York, 1977; Vol. 2, p. 1. b. Smalley, R. E.; Wharton, L.; Levy, D. H. *Acc. Chem. Res.* **1977,** *10,* 139.
(3) Lubman, D. M. *Anal. Chem.* **1987,** *59,* 31 A.
(4) Syage, J. A.; Wessel, J. E. *Appl. Spectrosc. Rev.* **1988,** *24,* 1.
(5) Syage, J. A. In *Lasers and Mass Spectrometry;* Lubman, D. M., Ed.; Oxford University Press: New York, 1990; p. 468.
(6) a. Syage, J. A.; Pollard, J. E.; Cohen, R. B. *Appl. Opt.* **1987,** *26,* 3516. b. Syage, J. A.; Pollard, J. E.; Cohen, R. B. Technical Report No. SD-TR-88-13, 1988; U.S. Air Force Systems Command (Space Division).
(7) Sin, C. H.; Tembreull, R.; Lubman, D. M. *Anal. Chem.* **1984,** *56,* 2776.
(8) Leutwyler, S.; Even, U. *Chem. Phys. Lett.* **1981,** *81,* 578.
(9) a. Long, S. R.; Christesen, S. D. *J. Phys. Chem.* **1989,** *93,* 6625. b. Sausa, R. C.; Miziolek, A. W.; Long, S. R. *J. Phys. Chem.* **1986,** *90,* 3994.
(10) a. Syage, J. A. *J. Chem. Phys.,* **1990,** *92,* 1804. b. Syage, J. A.; Steadman, J. *Chem. Phys. Lett.,* **1990,** *166,* 159. c. Steadman, J.; Syage, J. A. *J. Chem. Phys.,* in press.
(11) a. Syage, J. A.; Wessel, J. E. *J. Chem. Phys.* **1986,** *85,* 6806. b. Syage, J. A.; Wessel, J. E. *J. Chem. Phys.* **1987,** *87,* 3313. c. Syage, J. A.; Wessel, J. E. *J. Chem. Phys.* **1987,** *87,* 6207.
(12) Syage, J. A.; Wessel, J. E. *Appl. Opt.* **1987,** *26,* 3573.



Jack A. Syage received a B.A. degree from Hamilton College (1976) and a Ph.D. in physical chemistry from Brown University (1982). He accepted a postdoctoral position at Caltech under the guidance of Ahmed Zewail in 1982 and conducted studies in high-resolution and time-resolved picosecond molecular beam spectroscopy. He joined the Aerospace Corporation in 1984. His research interests, besides trace detection, include combustion kinetics, ultrafast phenomena, molecular cluster dynamics, transition-state spectroscopy, and reactions in intense laser fields.