# Lasers and Mass Spectrometry

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# New Developments in Molecular Detection by Supersonic Molecular Beam, Laser Mass Spectrometry

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Sensitive methods of detection serve a wide variety of applications.[1] Chemical analysis, for instance, often involves determining the composition of a given sample (i.e., assays) or the extent of contamination. Particular requirements might include the separation of isomers or isotopic substituents in molecules. These applications usually require high levels of sensitivity and selectivity, but not necessarily rapid analysis times (at least on a real-time basis). Another important area requiring trace detection methods is atmospheric monitoring. Applications are great in situations that have high environmental impact, such as toxic waste sites, space launch facilities, and nuclear power plants. Here, rapid analysis is more important. This statement is particularly true in situations involving toxic and hazardous compounds that might endanger life (i.e., chemical warfare agents).

As sensitivity continues to improve, the problem of interference from more abundant compounds becomes a greater concern. This awareness has motivated work to develop methods capable of realizing greater selectivity. Our approach to this problem has centered on the use of multiphoton ionization (MPI). This process relies on the sequential absorption of photons until the total energy of the molecule exceeds the ionization potential. If the photon wavelength is chosen to match an absorbing state of the molecule, the process is called resonance enhanced (i.e., REMPI). The resonance step not only improves sensitivity substantially, but it also provides a means for selectively ionizing molecules. In some of the earlier MPI applications, additional selectivity was introduced by tandem arrangements that included stages such as gas chromatography (GC) to separate the constituents of a mixed gas sample before ionization. Optical selectivity, though not adequate by itself for thermal samples, was used to augment the GC selectivity by taking advantage of the different absorption properties and ionization potentials. Klimcak and Wessel demonstrated high levels of sensitivity and selectivity using such an arrangement for the isomers phenanthrene and anthracene.[2] More recently, Reilly and co-workers demonstrated selective detection using an arrangement based on the combination of GC and time-of-flight (TOF) mass spectrometry.[3] This method

provides mass selectivity; however, they opted for a fixed wavelength excimer laser for ionization, thus sacrificing some optical selectivity for simplicity of operation.

Some form of mass spectrometry is now used by most detection methods based on MPI. Preparation of gaseous samples by supersonic expansion offers enormous benefits with regard to selectivity and will be discussed at length shortly. However, it can be argued that this improvement comes at the expense of sensitivity since the gaseous sample, on expansion in the vacuum chamber, is at a significantly lower density in the region of detection. In response to this concern, Kolaitis and Lubman have demonstrated the advantages of atmospheric pressure MPI mass spectrometry in conjunction with an ion mobility drift tube apparatus.[4] Exceptional levels of sensitivity are possible at atmospheric pressures, in which part-per-billion (ppb) concentrations correspond to greater than $10^{10}$ molecules/cm$^3$. The optical selectivity of REMPI, however, is reduced in atmospheric samples, and the separability of the ion drift times is limited by diffusion-controlled broadening; hence the major source of selectivity is provided by the quadrupole mass spectrometer.[4]

Another approach to improving sensitivity involves accumulating trace molecules on a cooled substrate. After adequate coverage has been achieved, the molecules can then be desorbed by a pulsed laser and photoionized above the surface.[5] Pulsed desorption and MPI has also been applied extensively to surface analysis of materials[6] and is motivated to a large extent by the semiconductor community. The technique is likewise gaining popularity as a means for introducing nonvolatile or thermally unstable molecules into the gas phase or vacuum[7].

Efforts to improve selectivity have often centered on advancing the mass spectrometer performance. Mass resolution can be improved by simply operating two spectrometers in tandem (MS/MS).[8] However, the most important development for obtaining ultrahigh mass resolution is Fourier transform mass spectrometry (FTMS), which has recently been reviewed by Marshall.[9] The basis for this technique is the use of an ion trap cell that derives from ion cyclotron resonance (ICR) spectrometers, hence the technique is often referred to as FTICR. The resolution depends on the residence time of the ions in the ion trap cell, and can reach levels exceeding 100,000. This capability permits separation of compounds of the same nominal molecular weight, but of different molecular structure.

Detection methods that improve optical selectivity are understandably based on techniques originally developed for high-resolution spectroscopy. Foremost among these is the use of supersonic molecular beams. For detection applications, supersonic cooling accounts for excellent sensitivity and selectivity because (1) the cold molecules are in virtually the same energy state and can therefore be nearly completely ionized by resonance excitation using a single wavelength of light, and (2) each molecule typically has its own characteristic set of narrow excitation wavelengths (i.e., spectral fingerprints) that is distinct from that of other molecules. In the following sections, recent work will be reviewed that demonstrates the enormous enhancement in optical selectivity that becomes possible by supersonic molecular beam detection. However, it is emphasized that sensitivity is likewise considerable. The loss in sensitivity due to the dilution in molecular density that occurs upon expansion is largely compensated by the benefit that results from the very narrow distribution of initial energy states.

## EXPERIMENTAL TECHNIQUE

### Supersonic Molecular Beam

The expansion of a high pressure of gas into a vacuum through an aperture is termed a supersonic expansion and can lead to substantial cooling of molecular internal energy. The method is well established and extensively reviewed.[10] The very narrow distribution of initial rovibrational states in conjunction with laser excitation has many valuable benefits. From a detection and sensitivity standpoint, nearly complete molecular excitation can be achieved using a single wavelength of light. For selective excitation, it is possible to populate single vibronic levels in excited electronic states and to form rovibrationally cold ions.

Most molecular beam photoionization experiments employ some form of mass resolved detection, usually using either a quadrupole or TOF mass spectrometer. A schematic of our molecular beam system[11] is illustrated in Fig. 21.1. The compact apparatus consists of two differentially pumped chambers, the first containing the molecular beam source and the second the excitation and detection components. A 1-mm-diameter skimmer, situated at the interface of the two chambers, allows a narrow collimated portion of the supersonic jet to enter the second chamber. This arrangement directs the majority of the gas pumping load to the first (source) chamber, allowing the second (detection) chamber to operate at higher vacuum. The source chamber is pumped by a liquid nitrogen trapped 2000 L/sec diffusion pump. The detection chamber is pumped by a 1200 L/sec turbomolecular pump that is mounted on the side to catch the direct output of the molecular beam. An all metal conflat design was chosen for the overall system 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 detection chamber is about $1 \times 10^{-8}$ torr, rising to about $2 \times 10^{-7}$ torr during operation of the pulsed molecular beam source under typical conditions (e.g., 10 Hz, 50 psi He, 500-$\mu$m-diameter nozzle, 400-$\mu$sec gas pulse width, 2.5-cm nozzle–skimmer distance). The detection chamber pumpdown time of 10 msec, however, ensures that the instantaneous pressure in the chamber at the time of a molecular beam pulse is close to the base 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 an in-house pulsed source using a design based on fast solenoid activation.[12] This design offers a unique combination of features important to the detection method: (1) high repetition rates (up to 100 Hz), (2) temperature control (up to 200°C), (3) continuous gas sample flow capabilities, and (4) internally mountable sample holder.

The TOF mass spectrometer employs a configuration of three parallel grids,[13] spaced 1 cm apart, to direct the ions toward the detector. This is accomplished by applying different voltages to the grids (the final grid is held at ground), thereby creating the necessary electric fields for accelerating the ions. A relatively small field of about 100–200 V/cm is applied across the first two grids. This region encom-

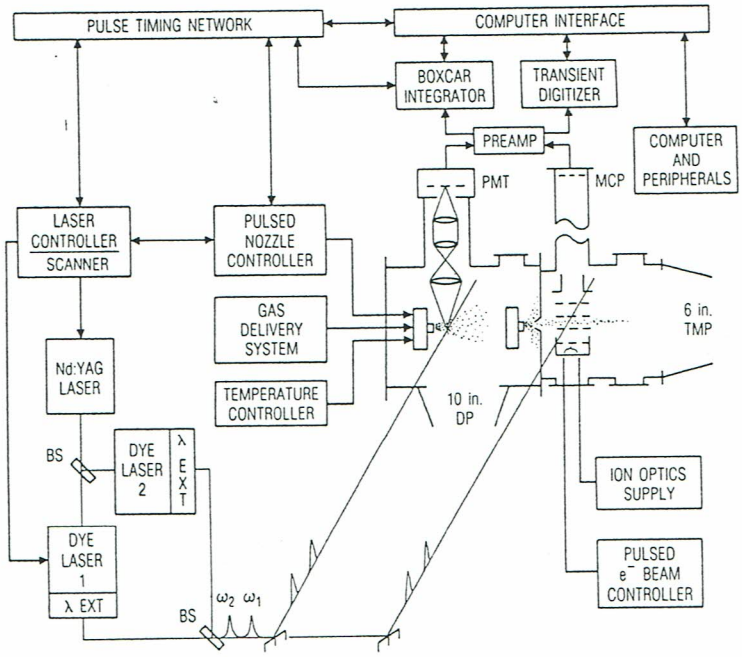


**Fig. 21.1.** Schematic of the supersonic molecular beam TOF mass spectrometer apparatus and associated components: PMT, photomultiplier tube; MCP, microchannel plate; DP, diffusion pump; TMP, turbomolecular pump; BS, beamsplitter; λ EXT, wavelength extension components.

passes the volume where the molecular beam and the laser intersect. The ions that are formed then move into the region between the second and third grids where they encounter a much greater field (about 1500–2000 V/cm). The ions are accelerated to high energy in this region. They then enter a 1-m field-free TOF drift region that allows the slower heavy ions to separate from the faster light ions. A time-resolved microchannel plate detector monitors the intensity and arrival time of each ion mass. The recorded TOF signals are then routinely converted to a mass spectrum. Most of the experiments described here use MPI to form ions. A fourth grid and a tungsten filament are used to generate a pulsed electron beam for applications requiring electron impact ionization.[14]

## Laser Excitation and Detection

Laser excitation is provided by a tunable dye laser pumped by an 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 obtain a tuning range of 275–440 nm (10–20 mJ/pulse). Frequency doubling followed by mixing with 1064 nm extends the tuning range to 222 nm (1–3 mJ/pulse). Shorter

wavelengths to 195 nm (10–100 μJ) are generated using anti-Stokes Raman shifting in an $H_2$ pressure cell. A spherical lens is used to focus the light into the molecular beam.

TOF mass spectra are recorded using a 200-MHz transient digitizer. Ionization-detected excitation spectra are recorded by scanning the ionizing laser wavelength and detecting a specific mass, using a time-gated boxcar integrator (channel A). A second boxcar integrator (channel B) is used to record the laser pulse intensity. The recorded spectrum is normalized approximately by storing the ratio $A/B^2$ or, more precisely, by storing the pulse-to-pulse values of $A$ and $B$ for subsequent analysis using an appropriate model for the MPI.

### Sample Preparation

The trace concentrations reported in this review were prepared by evacuating a 2-L 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 ensure a linear dependence of signal with concentration. Dilution of dimethyl sulfide followed this dependence reasonably well 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).

## TANDEM OPTICAL/MASS DETECTION

Sensitive detection relies on finding photoionization processes that are efficient. Aromatic molecules are ideally suited as they involve strong absorption cross sections at convenient wavelengths, require just two photons to ionize, and form relatively stable parent ions. Aromatic molecules have therefore been employed extensively as model compounds for evaluating detection capabilities by REMPI. Other classes of molecules pose more serious detection challenges. Ionization efficiency may be reduced by competitive neutral pathways (e.g., dissociation, internal conversion), inconvenient lasing wavelengths, or large ionization potentials (IP) requiring more than two photons to ionize. Mass selectivity may also be compromised by extensive ion fragmentation. Finally, many molecules of interest are nonvolatile (i.e., biological molecules), thereby making the introduction of sufficient material into a photoionization source difficult.

The following sections focus primarily on recent work from our laboratories, with reference to related work by other researchers. We shall refer to specific excitation pathways as $m + n$ REMPI, where $m$ refers to the number of photons absorbed to excite a resonance state, and $n$ the additional absorbed photons necessary to ionize the molecule. An REMPI excitation spectrum can be recorded by measuring the ionization signal for the parent ion or some characteristic fragment ion as a function of excitation wavelength. This provides a sensitive analog to a one-photon absorption spectrum.

## Aromatic Molecules

Lubman and co-workers have made contributions in demonstrating the detection capabilities of supersonic molecular beam MPI mass spectometry.[15–18] In a series of experiments, they determined the extent of separability attainable by molecular beam MPI mass spectrometry for (1) structural isomers,[16] (2) molecules of similar mass,[17] and (3) isotopic substituents.[18] For instance, they demonstrated that the 1 + 1 REMPI (sometimes referred to a R2PI) excitation spectra for structural isomers of dichlorobenzene are dramatically different, allowing a sensitive optical means for separation that is not available by mass detection alone. A similar study was conducted for the *o*-, *m*-, and *p*-cresol isomers.[18] These experiments were notable as they actually considered the separability of the isomers in supersonic expansions of air samples, in which cooling is not as effective. Nonetheless, discrimination limits between $10^2$ and $10^3$ were achieved, and a theoretical detection limit of 20 ppb was reported.[16]

Other groups have demonstrated optical selectivity for isomers without the aid of molecular beams. These include the selective ionization of either anthracene or phenanthrene using excitation at either 285 or 310 nm.[2] Another example is the selective ionization of chrysene over triphenylene using XeCl excimer excitation at 308 nm in which the two-photon energy exceeds the IP of chrysene (7.8 eV), but not triphenylene (8.1 eV).[3] Although optically selective excitation has been emphasized in the above studies of isomers, it is also possible to obtain mass selectivity by identifying different fragmentation patterns as a function of ionizing wavelength. The related challenge of separating molecules of similar or of the same nominal mass is less demanding than the isomer problem, since the parent masses can often be separated, and the optical and fragmentation properties tend to be more different for less similar molecules.

We have used aromatic molecules as models for establishing enhanced two-stage optical selectivity by using double resonance excitation in the detection process. This work is described later in the chapter.

## Challenging Applications

Many molecules present special challenges or sensitive detection. Often, the most hazardous molecules, which demand the greatest levels of detection sensitivity, are poorly understood spectroscopically. We have been engaged in studies to establish the detectability of more "troublesome" classes of molecules by the supersonic molecular beam MPI mass spectrometry technique. Good examples are the organophosphates and phosphonates that represent groups of insecticides and pesticides, as well as chemical nerve agents. Vacuum UV absorption spectra indicate that strong single-photon absorptions occur only at relatively high energies (i.e., wavelengths of about 200 nm and shorter).[19] This situation also characterizes many organosulfide molecules.[11,19–21] The spectroscopy of these compounds poses problems for sensitive detection, as adequate pulse energies are difficult to generate at these wavelengths using conventional pulsed dye lasers and nonlinear frequency generation methods. Hydrazines are an important class of toxic molecules that are used as rocket fuels, but whose physical properties are a challenge to laser-based

detection methods. We consider each of these groups of compounds in the following sections.

Sensitive and selective laser detection requires specific excitation processes that uniquely probe the molecule of interest. The high-resolution spectroscopic data necessary for this task, however, were not available for the classes of compounds previously mentioned. Therefore significant experimental effort was directed toward fundamental spectroscopic studies to provide the so-called spectral data base or signatures. This was accomplished by first recording room temperature vapor phase absorption spectra using a home-built UV and vacuum UV spectrometer. Once absorptive wavelength regions were defined, high-resolution REMPI excitation spectra were recorded using a scanning laser in the supersonic molecular beam mass spectrometer apparatus.

### *Organophosphonates*

A variety of excitation processes through different electronic states were investigated for diisopropyl methylphosphonate (DIMP). These excitation schemes, which are diagramed in Fig. 21.2, invariably lead to ion fragmentation with no evidence for a parent ion at mass 180. However, characteristic fragment ions are evident in the mass spectra in Fig. 21.3 that afford mass selective detection unique for DIMP. The 2 + 2 REMPI excitation spectrum of DIMP in Fig. 21.4 shows a highly resolved vibrational structure for the resonance electronic state transition. In this case, the absorptions were detected by recording the predominant isopropyl ion fragment at mass 43 (see Fig. 21.3c). The spectrum in Fig. 21.4 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 reduced rotational broadening and hot band intensity (due to rotational and vibrational energy, respectively, in the nascent molecule) compares favorably 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.

Because sufficient tunable pulse energy at 200 nm was not available, it was necessary to drive the formally allowed one-photon transition by using two photons at half the transition energy. Although this is not a favorable excitation mechanism for sensitivity purposes, a detection limit on the order to 50 ppb was nonetheless obtained. The other excitation mechanisms shown in Fig. 21.2 were examined in an attempt to improve the detection efficiency. A 1 + 2 REMPI excitation via a lower energy state at about 266 nm was also studied. However, the resonance transition was very weak and diffuse and, hence, sensitivity was not improved by this route. Interestingly, there was no resemblance in the mass spectra when exciting by these two different routes, as illustrated in Fig. 21.3. There is some evidence that the 200-nm state may dissociate, thereby altering the fragmentation pattern in addition to reducing the ionization efficiency.[11,19]

The molecule dimethyl methylphosphonate (DMMP) exhibits rather different spectroscopic and photochemical behavior than the structurally related molecule DIMP. Broadband UV/VUV absorption spectra of room temperature vapor-phase samples showed no evidence for any strong absorption bands ($\epsilon > 500$) at wave-

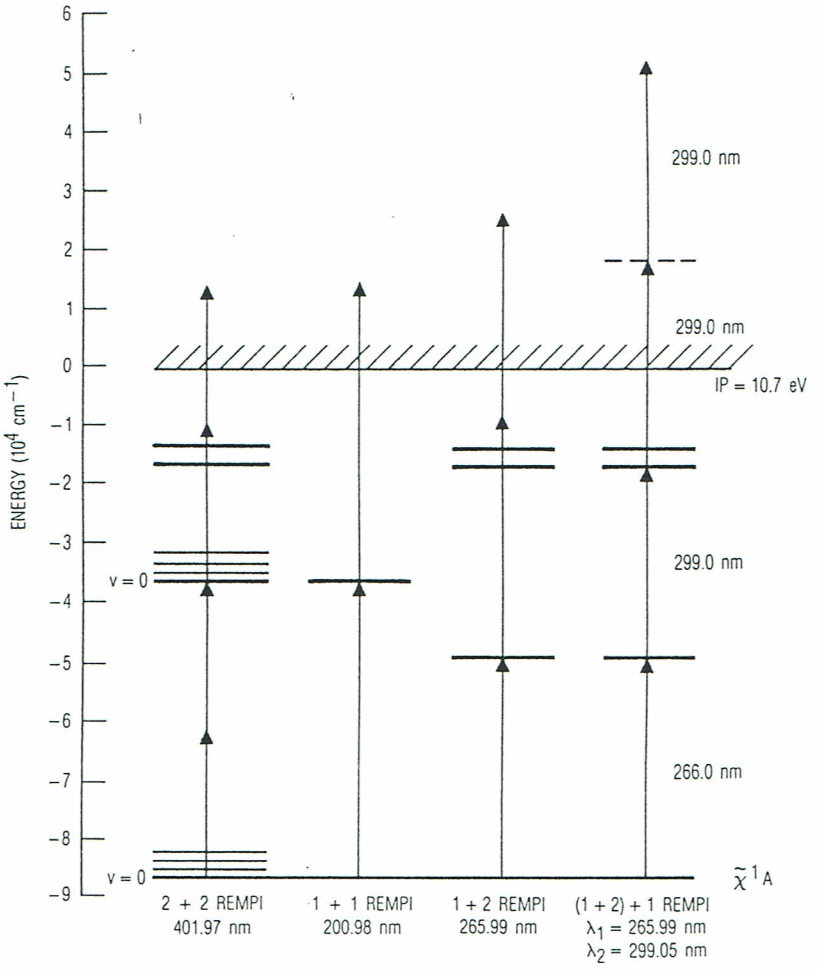


**Fig. 21.2.** REMPI excitation schemes used in the study of DIMP.

lengths longer than 140 nm, nor were any vibrationally resolved electronic state features revealed.[19] Since optical selectivity by discrete resonance excitation was apparently not available for DMMP, we sought to obtain optical selectivity by REMPI excitation of a major photofragment of DIMP. Other investigators have reported the efficient production of PO radical from DMMP by a variety of excitation sources that include ArF and KrF excimer laser excitation,[22] $CO_2$ laser excitation,[23] and microwave discharge.[24] We therefore used the narrow PO vibrationless transtion $\tilde{A}\,^2\Sigma^+ \leftarrow \tilde{X}^2\Pi$ at 247.7 nm to ionize the fragment by 1 + 1 REMPI. Fortuitously, this wavelength also proved effective for photodissociating DMMP to give the characteristic fragment PO, thereby avoiding the need for a second wavelength of light. A more selective example of the use of photofragment spectroscopy that used two-color excitation is described later in this chapter.

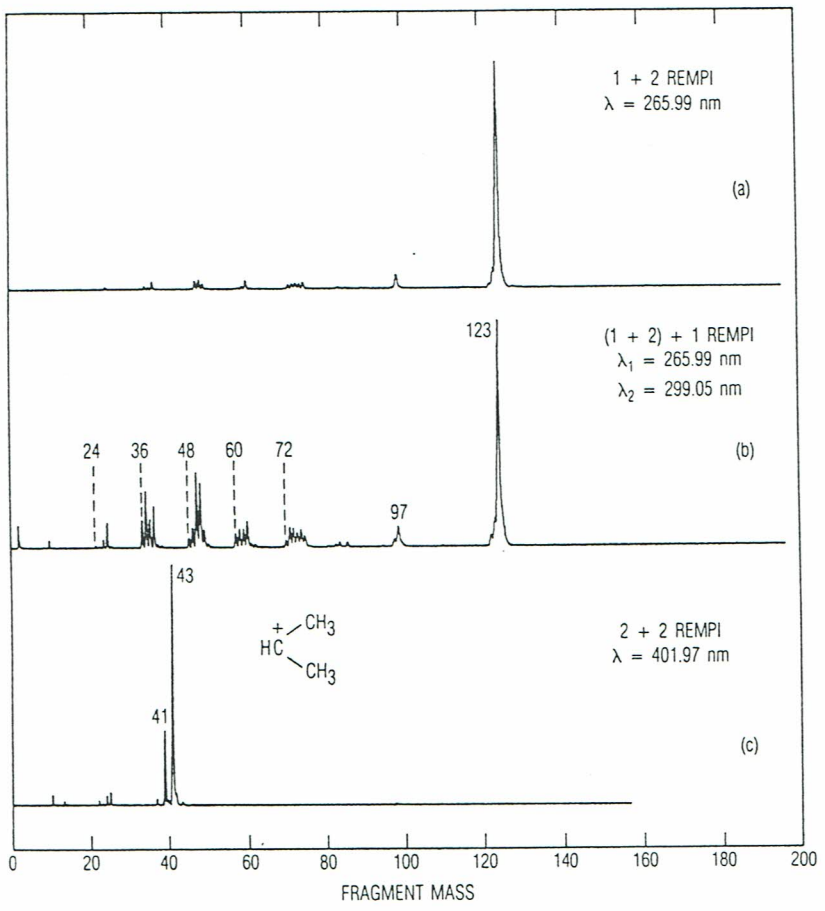


**Fig. 21.3.** REMPI/TOF mass spectra of DIMP in a supersonic beam: (a) 1 + 2 REMPI using 265.99 nm; (b) 1 + 2 REMPI using resonant 265.99 nm, followed by 299.05 nm to ionize and further fragment the ions; (c) 2 + 2 REMPI at 401.97 nm.

### *Organosulfides*

The REMPI detection efficiency of dimethyl sulfide (DMS) was, likewise, hindered by the necessity of driving an otherwise single-photon transition (at 195 nm) using two photons in a 2 + 2 REMPI excitation. The molecular beam excitation spectrum, for an electronic transition assigned as a $3p$ Rydberg state, is shown in Fig. 21.5. Although vibrationally well resolved, the linewidths ($\sim$15 cm$^{-1}$) are considerably broader than those observed for DIMP ($\sim$7 cm$^{-1}$) in Fig. 21.4. 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 (see, for example, the discussion under Excitation to Higher Electronic and Rydberg States). However, predissociation, which can compete with ionization, also seemed possi-

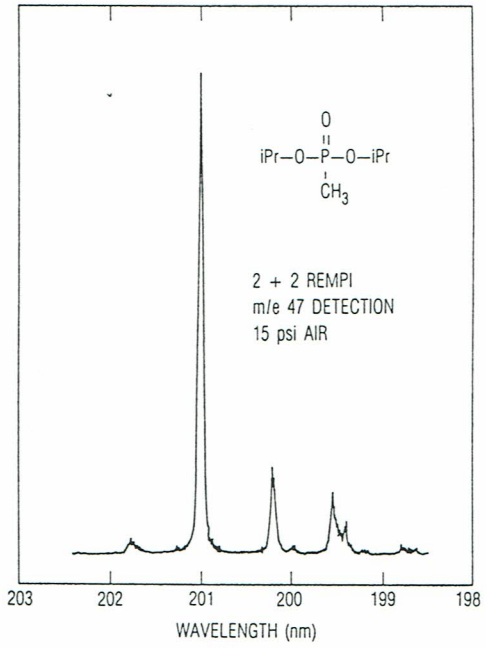


**Fig. 21.4.** 2 + 2 REMPI molecular beam excitation spectrum of DIMP using atmospheric room air as the carrier gas (0.5% DIMP in 15 psi air). The isopropyl fragment ion at mass 43 was monitored in recording the spectrum.

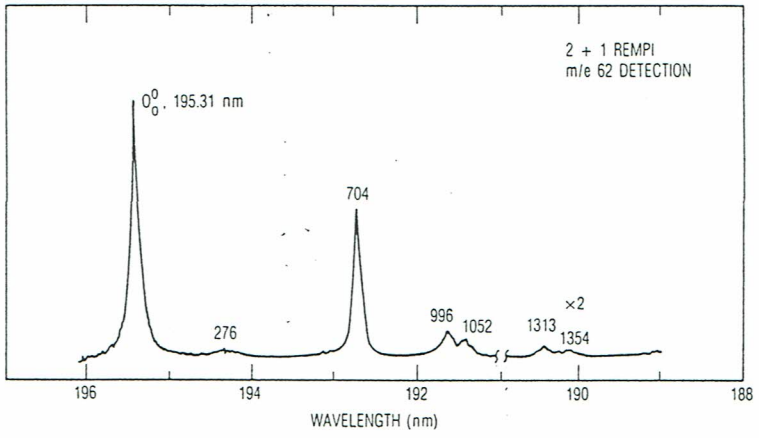


**Fig. 21.5.** 2 + 1 REMPI molecular beam excitation spectrum of the 3*p* Rydberg state of DMS (0.1% DMS in 50 psi He). The spectrum was recorded by detecting the parent ion at mass 62. Vibrational intervals are reported in $cm^{-1}$.

ble. For instance, DMS has been reported to undergo dissociation to form $CH_3S\cdot$ radicals following 193-nm excitation.[20]

We investigated the extent of photodissociation of DMS following excitation into the $3p$ Rydberg state, as well as into a lower energy Rydberg and valence state. In each case, the major signal was the parent ion.[11] This result is evidence not only for stable electronically excited neutral states (at least over the duration of the 5-nsec laser pulse), but for stable ions to energies as high as 16000 $cm^{-1}$ (corresponding to the excess absorbed photon energy above the IP of DMS). The stability of DMS made possible a detection limit on the order of 1 ppb (see the section on Detection Levels) for the 2 + 1 REMPI excitation through the $3p$ state in spite of the two-photon absorption step. Unfortunately, the lower energy $3s$ transition at 227.9 nm that allowed a more favorable 1 + 1 REMPI excitation did not improve on this figure because of a weak absorption cross section.[11]

The molecular stability, and hence detection sensitivity, can be seriously compromised by the introduction of a weakly bound substituent. The substituted analog chloro-DMS demonstrates this quite well. The VUV absorption spectrum shows a very long Franck–Condon progression[19] in what is presumed to be the corresponding $3p$ state previously discussed for DMS. The vibrational frequency of

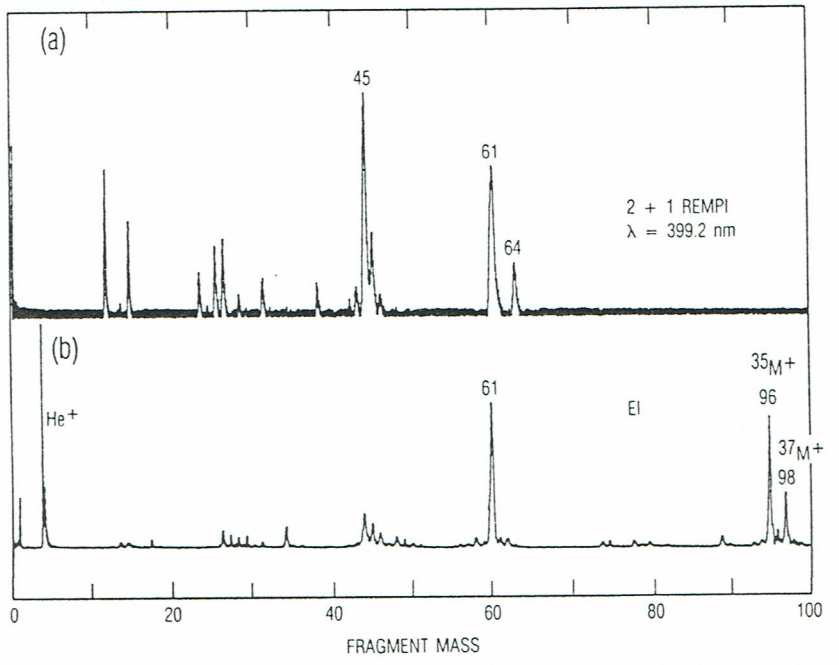


**Fig. 21.6.** Molecular beam TOF mass spectra of chloro-DMS: (a) 2 + 1 REMPI (399.2 nm) excitation showing the absence of parent ion and poor sensitivity (low signal-to-noise ratio); (b) 70-eV EI excitation showing the presence of parent ion and much better signal-to-noise ratio.

405 $cm^{-1}$ is consistent with an S−C−Cl deformation or bending motion. The 2 + 1 REMPI molecular beam mass spectrum via the $v = 4$ overtone vibration at 199.6 nm is shown in Fig. 21.6. This excitation was chosen so that the three-photon energy exceeded the IP. The REMPI mass spectrum is compared to the spectrum recorded, using 70-eV electron impact (EI) ionization. EI excitation leads to direct ionization, thereby avoiding dissociative intermediate states in the neutral molecule. EI ionization of chloro-DMS proved to be efficient, and the resulting mass spectrum shown in Fig. 21.6 exhibits significant parent ion formation. This is in marked contrast to the REMPI results, which suffer from extremely weak ionization efficiency and the absence of parent ion. Instead, the prominent ion signal occurs at fragment mass 61, resulting from loss of Cl. These results are suggestive of a rapid C−Cl dissociation in the neutral excited state, followed by nonresonant MPI of the neutral mass 61 fragment.[19] For detection purposes, the method of photofragment excitation, which we employed for DMMP detection, would be more appropriate for monitoring dissociative molecules such as chloro-DMS.

The cases described for the organophosphonates and organosulfides represent detection difficulties as a result of unfavorable spectroscopic properties. These limitations will mostly be overcome by new developments in laser and crystal technology (e.g., broadly tunable ultrafast dye lasers, solid-state lasers, $\beta$-barium borate crystals) as well as additional spectroscopic studies to identify more efficient excitation methods. Nonetheless, the detection efficiency (see the section on Detection Levels) by the the molecular beam MPI method for these rather unfavorable molecules compares well with other techniques. Also, the present technique offers real-time detection.

### *Hydrazine*

The molecule hydrazine ($N_2H_4$) and the methylated analogs, methyl hydrazine and 1,1′-dimethyl hydrazine, are most commonly noted for their use as propellant fuels for launch vehicles and satellite thrusters. They are also quite toxic, and hence methods are sought to detect their presence in environments in which the fuel is handled. The initial phase of our laser/molecular beam studies on hydrazine detection required basic electronic state spectroscopic information to be obtained. Published spectra were limited to a single, vibrationally unresolved ambient vapor-phase UV absorption spectrum, which showed an onset to absorption at about 260 nm.[25] The source of the broadening was at first believed to be due to either very rapid photodissociation or thermal congestion. However, preliminary work in our laboratory using molecular beam expansions rules out the latter possibility. Other possible sources of broadening include large geometry changes in the excitation process, as well as strong interactions of the excited electronic state with the dense vibrational level spacing in a lower electronic state.[26] We have been pursuing this problem along two directions. Experimentally, direct absorption spectra are being recorded in a supersonic expansion using a monochromatized broad band light source for medium resolution, but wide tunability extending into the VUV. Theoretically, *ab initio* calculations are in progress to calculate lower electronic state energies and absorption strengths.

## Detection Levels

A major objective in our molecular detection effort is to establish the limits of sensitivity and selectivity by molecular beam MPI mass spectrometry. To judge the performance levels for different classes of molecules, we have adopted the following simple model for detection levels.

### *A Working Model*

For simplicity, we define sensitivity as 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 at concentration $C_{ref}$, and comparing it to the background fluctuation level $S_0$. This leads to a simple relation for detection limit given by

$$C_0 = C_{ref} \frac{S_0}{S_{ref}} \tag{21.1}$$

The only assumption in Eq. (21.1) is that the ion count rate does not vanish at the extrapolated detection limit.

We define two response times: (1) $\tau_e$ 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

$$S(t) = S(\tau_e)[1 - e^{-t/\tau_e}] \tag{21.2}$$

and (2) $\tau_0$ being the time required for the detected signal to exceed the background fluctuation level $S_0$. We may consider $\tau_0$ to be the response time for detection and $\tau_e$ the response time for measurement of concentration. They can be related to each other using Eq. (21.2) to give

$$S(\tau_0) = S(\tau_e)[1 - e^{-\tau_0/\tau_e}] \tag{21.3}$$

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

$$\frac{\tau_0}{\tau_e} = -\ln\left[1 - \frac{S_0}{S(\tau_e)}\right] \tag{21.4}$$

It is not difficult to see that the response time for detection, $\tau_0$, can be considerably shorter than $\tau_e$ for target molecule concentrations well above the detection limit.

### *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) is presented in Fig. 21.7. An enlargement of the baseline region, along with a detectability scale, is included for convenience. The ratio of the reference sample signal to background signal $S_{ref}/S_0$ is greater than 200. This corresponds to a detection limit for DMS of less than 300 ppt. The measurement response time $\tau_e$, based on the signal strength vs time in Fig. 21.7, is 8 sec; however, the detection response time $\tau_0$ at 60 ppb is on the order of 100 msec. Naturally, other factors (i.e., transit time of sample through delivery

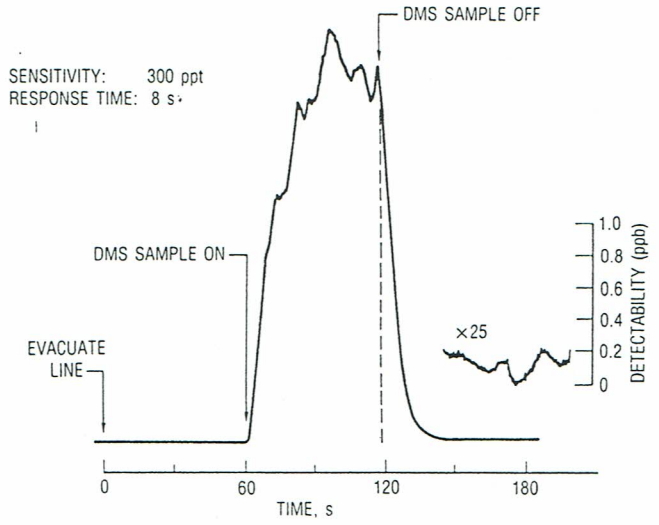


**Fig. 21.7.** Sensitivity determination for a 60 ppb sample of dimethyl sulfide (DMS) in water-saturated air. The baseline signal represents the background level of our molecular beam apparatus. The sample signal represents the response to turning the sample flow on and off at specified times.

lines, laser repetition rate, etc.) can increase the actual "system" response time; however, the intrinsic value of $\tau_0$ can be approached with careful design. Finally, it is noted that by varying experimental conditions (e.g., smoothing factors), tradeoffs between measurement response time $\tau_e$ 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. 21.7 involved 2 + 1 REMPI at a wavelength of 390.62 nm. This corresponds to resonance excitation through the vibrationless level of the $3p$ Rydberg-like state at 195.31 nm. As discussed earlier, 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. New developments are now making possible the generation of high-power far-UV laser pulses. This will soon enable one-photon resonance excitation of the organosulfides; thus, an appreciable improvement in sensitivity can be expected.

### *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 sample. Excitation of DIMP was by 2 + 2 REMPI via the 200.98-nm electronic state (Figs. 21.2–21.4). Detection was for the $m/e = 43$ fragment ion (Fig. 21.3c). 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 resulted in a selectivity of about $10^4$. A similar level of selectivity was observed using gasoline as an interferent. In a related experiment the response of the DIMP sample was compared to a room air sample saturated with water. The results, which were obtained in the same manner as previously described, indicate that the selectivity of DIMP to water is greater than $10^5$. However, more importantly, it demonstrates that water vapor does not form molecular complexes with DIMP (or DMS) that would degrade the signal strength due to nonresonant excitation and loss of mass identification.

### Atmospheric Monitoring

The value of supersonic molecular beam mass spectroscopy for trace detection was recognized from the start. The molecular cooling accounts for narrow excitation linewidths, which contributes to an appreciable optical selectivity. For MPI excitation, the selectivity is further augmented by single mass detection. Sensitivity is considerable, largely because of the ability to detect single ions using modern ion lenses and detectors. Detection is very rapid in the sense that the total trip, from the time the neutral molecules exit the molecular beam source to the time the ionized particles reach the detector, is well under a millisecond. For chemical analysis, which allows the preparation of samples in convenient carrier gases, impressive detection capabilities have been reported for a variety of applications. The more challenging application is in atmospheric monitoring in which the carrier gas is 1 atm of air. Several potential concerns were investigated in our laboratories, including the following questions: (1) Does the supersonic expansion of atmospheric air provide adequate molecular cooling? (2) Do the target molecules form complexes with water vapor, thus undermining detection efforts? (3) Do the target molecules form clusters among themselves? (4) Can the gas inlet system to the detection apparatus be designed to avoid delivery lines that can adsorb trace amounts of target molecules?

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. The cooling efficiency of atmospheric air is usually less than ideal and, hence, a reduction in the realizable selectivity may be expected. For the organophosphonates, considerable supersonic cooling was achieved for atmospheric expansions, as evident by the REMPI excitation spectrum of DIMP in Fig. 21.4.[11] The extent of cooling was judged to be comparable to that observed using 50 psi of He as a carrier gas. This is a rigorous test, as large "floppy" molecules with many low-frequency vibrations are difficult to cool using diatomic carrier gases.[12]

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.[10] This can be particularly troublesome when water vapor is present, as much higher concentrations of water compared to trace target molecules are likely to be encountered in atmospheric monitoring. The possibility for complexation between water

and the target molecule under humid conditions can cause a loss of wavelength and mass identity. Problems with complexation are often encountered in atmospheric pressure ionization (API),[6] in which molecules are ionized by protonation, thus increasing their propensity to undergo hydrogen bonding. This problem is amplified since the ionization occurs at atmospheric pressures and not under the collisionless conditions of a molecular beam. Our ionization approach differs in that the neutral, unprotonated 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 complexation was demonstrated for DIMP and DMS, in which it was found that the excitation/detection signal described earlier was insensitive to whether the carrier gas was dry or entrained with room temperature water vapor.

The question of complexation of target molecules in a supersonic expansion to form homologous clusters was also investigated using electron-impact ionization. DMS was particularly prone to complexation at high concentrations (10,000 ppm). Because 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 became insignificant at concentrations below 1000 ppm and should, therefore, be negligible at trace concentration.

During our work it became obvious (to no great surprise) that for very low premixed concentrations, a large proportion of the target molecules were adhering to the delivery lines, thereby decreasing the number of molecules that reached the pulsed molecular beam valve. Our pulsed valve has two characteristics that can alleviate this problem. First, the design incorporates continuous flow capabilities that ensure 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.

## DOUBLE RESONANCE ENHANCED SELECTIVITY

As detection limits improve, the requirements for selectivity become greater. We have been exploring the potential for an additional level of optical selectivity by using two-color double resonance excitation augmented by TOF mass detection.[27–31] Several variations have been examined involving a second resonance excitation from the intermediate neutral state to discrete vibronic states below[27,30] and above[28,30] the ionization potential (IP). The method of ion dip detection[32,33] figures prominently in these experiments. In this technique, the first dye laser generates a constant ion signal by 1 + 1 REMPI through an intermediate state at the one-photon level. In one scheme, a second dye laser is used to excite from the intermediate state to another state, which competes with the ionization step and depletes the ion signal (see Fig. 21.8a). In another scheme, the second dye laser is used to photofragment, and therefore deplete, the parent ion signal, which in turn causes a concomitant increase in the fragment ion signal.[29]

The appeal of the two-color detection schemes to be described is that they do

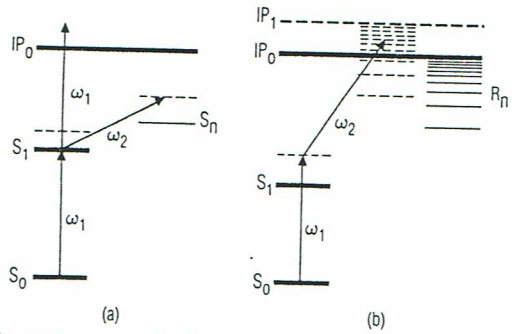


**Fig. 21.8.** Double resonance excitation scheme for higher excited electronic state and Rydberg detection: (a) excitation to final states below the IP, using ion dip detection; (b) excitation to final states above IP that undergo autoionization.

not require both colors for successful detection. As discussed in the preceding sections, the one-color REMPI method provides exceptional sensitivity and selectivity of its own accord when used in conjunction with molecular beam cooling and mass detection. The role of the second color is to serve as a desirable step for obtaining a greater level of selectivity. The use of two-color excitation may be viewed as providing detection by the first color and verification by the second color.

## Excitation to Higher Electronic and Rydberg States

Discrete higher excited electronic states can offer very specific conditions for molecular detection by double resonance excitation. This is particularly true of Rydberg states, which tend to have narrow excitation linewidths. We consider excitation to final resonant states below and above the first ionization threshold. The excitation schemes, which involve ion dip and autoionization detection, respectively, are portrayed in Fig. 21.8.

### *Below Threshold Excitation—Ion Dip Detection*

Detection of a higher excited state, $S_n$, in aniline and aniline-$d_5$ is illustrated in Fig. 21.9 for an ion dip excitation/detection scheme similar to Fig. 21.8a. The aniline $S_n$ spectra were recorded by first generating an ion signal by 1 + 1 REMPI via the vibrationless ($v = 0$) $S_1(\tilde{A}\,^1B_2) \leftarrow S_0(\tilde{X}\,^1A_1)$ transition using the first tunable laser pulse $\omega_1$. The second tunable pulse $\omega_2$, overlapped spatially and temporally with the first pulse, was tuned through the $S_n(v) \leftarrow S_1(0)$ resonances.[27,30] These absorptions compete with ionization, thereby creating the ion dip signals. The excitation spectra were mass-selected by detecting only the aniline parent ion signal $M^+$, using the boxcar gated integrator.

Spectroscopically, the two-color ion dip technique is important for detecting higher excited electronic states that are too short lived to be detected by conventional ionization or fluorescence detection methods. In fact, the lifetime of the final state determines in part the strength of the ion dip signal and, hence, the sensitivity for that particular excitation. For example, saturation of a long-lived state under intense laser power would depopulate the intermediate state by no more than 50%,

hence the ion dip signal could not exceed 50%. However, if the upper state decays at a rate greater than the $\omega_2$ pumping rate (i.e., the up-pumping process is irreversible), then the lower state can be nearly completely depleted, leading to ion dip signals greater than 50%. This holds the potential for very sensitive detection. Ion dip signals exceeding 50% could be obtained for nearly all the observed $S_n(v) \leftarrow S_1(0)$ transitions in aniline and aniline-$d_5$ by decreasing the $\omega_1$ and increasing the $\omega_2$ intensity. Apparently, the $S_n$ state undergoes rapid decay,[27,34] either by dissociation or radiationless decay, to a set of states that is not easily ionized by $\omega_1$ or $\omega_2$.

It is interesting to note in Fig. 21.9 that the spectral linewidths for aniline-$d_5$ are significantly narrower than for the protiated molecule. This behavior is due to the reduction in vibrational frequencies that occurs upon deuteration. Vibrational interactions between initially excited states and underlying vibrations from lower electronic states are made weaker because of the larger differences in vibrational quantum number. This Franck–Condon effect outweighs the effects of an increased density of states. Finally, we have recently obtained evidence for narrower electronic transitions at higher energy, which may prove promising from the viewpoint of selective detection.

### *Above Threshold Excitation—Autoionization*

Rydberg series, which are excited electronic states, are commonly known to converge to ionization thresholds. However, in molecules in which internal energy

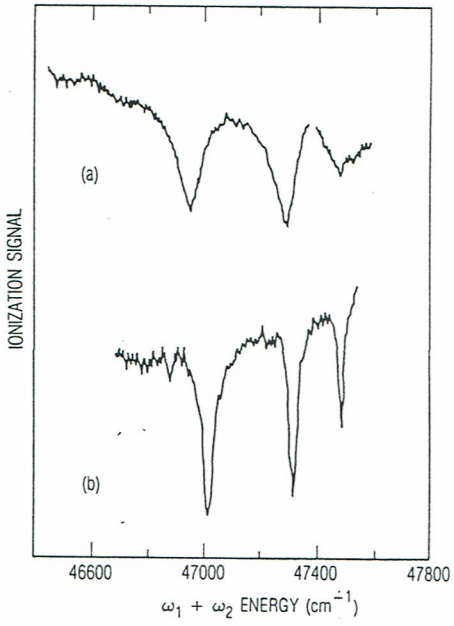


**Fig. 21.9.** Ion dip spectrum for the $S_n(v) \leftarrow S_1(v = 0)$ absorption of (a) aniline and (b) aniline-$d_5$. Ion dip intensities are plotted relative to the ion signal level in the absence of the $\omega_2$ beam.

(i.e., vibrations and rotations) is possible, the total molecular energy in excited Rydberg states can exceed the IP. Excitation to vibrationally excited Rydberg states represents narrow transitions, which can spontaneously ionize for facile detection by mass spectrometry. An important mechanism for ionization is called vibrational autoionization, and is due to the interaction of a vibration with the ionization continua. The interactions are often sufficiently weak that transitions to these states can be rather sharp. In our experiments,[28] $\omega_1$ is used to excite a specific vibrational level in $S_1$; $\omega_2$ is then used to excite to a Rydberg state in an efficient step that preserves the vibrational excitation (Fig. 21.8b). Often many members of an autoionizing Rydberg series can be identified,[28,30] providing additional possibilities for selective detection. The observed linewidths for the autoionizing transitions are significantly narrower upon deuteration of naphthalene, a trend also observed for the ion dip transitions in aniline previously discussed.

### Resonance Ion Dissociation in Naphthalene Ions

We have been investigating new methods for obtaining double mass selectivity along with the usual double optical selectivity made possible by two-color excitation. A promising excitation technique, which we refer to as resonance ion dissociation (RID), is illustrated in Fig. 21.10a. In this scheme, the first laser populates a single vibrational level of the ion by 1 + 1 REMPI and the second scanning laser dissociates the ion by resonance-enhanced multiphoton dissociation. The dissociation process is evident by observing a decrease in the parent ion $M^+$ signal (i.e., ion dip) and a corresponding increase in the fragment ion, $[M - m]^+$ signal. Detection of both the parent ion and the characteristic fragment ion, therefore, may hold promise as a very selective detection method.

Singly charged cations of aromatics have been studied in a variety of low-temperature matrices.[35] The vibrationally resolved ion spectra are distinctive, showing strong red absorption bands corresponding to transitions between normally filled molecular orbitals in the neutral. Low-pressure vapor phase studies of the spec-

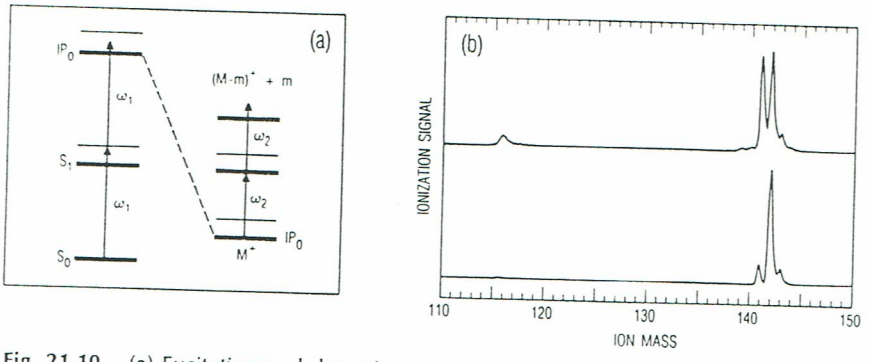


**Fig. 21.10.** (a) Excitation and detection sequence for resonance ion dissociation. (b) Mass spectrum of 2-methylnaphthalene showing resonance ion dissociation: (lower trace) 1 + 1 REMPI by $\omega_1$ only at 308.3 nm; (upper trace) 1 + 1 REMPI by $\omega_1$ and RID by $\omega_2$ at 662 nm, revealing an efficient and specific H-atom dissociation.

troscopy of ions formed by electron impact in an ICR spectrometer[36] and by MPI in a mass spectrometer,[37] however, failed to reveal the vibrational structure that was evident in the low-temperature matrix spectra.[35] This may be attributed to the thermal energy content of the precursor neutral molecules. Cooling the precursor molecules by supersonic expansion may lead to the formation of cold ions by 1 + 1 REMPI.

We have observed vibrationally resolved resonances in naphthalene and 2-methylnaphthalene (2-MeN) by recording RID spectra following selective vibronic preparation of the molecular cation.[29,30] These studies relied on the detection of the low-energy H-atom photodissociation channel of naphthalene and 2-MeN cations as $\omega_2$ was scanned through resonant absorptions of the molecular ion (Fig. 21.10a). For the 2-MeN cation, vibrational structure was observed for a visible and a UV state; for naphthalene, only a UV state was observed. The UV vibrationless electronic transition was observed to occur at 304.7 nm (naphthalene) and 308.9 nm (2-MeN). The origin of the 2-MeN cation absorption in the visible region occurred at 662 nm. The $\omega_1$ 1 + 1 REMPI mass spectrum of 2-MeN in the absence and presence of the $\omega_2$ RID pulse is presented in Fig. 21.10b. The H-atom dissociation at the $\omega_2$ wavelength of 662 nm is very distinctive and specific. Only a small yield of the next lowest energy dissociation channel, loss of $C_2H_2$, is evident.

The linewidths in the RID spectra of the cations are rather broad for both the visible ($\sim$200 $cm^{-1}$) and the UV resonances ($\sim$150 $cm^{-1}$), although they are comparable to the matrix absorption spectra.[25] However, a pronounced power broadening was evident in which the visible transitions of the cooled 2-MeN ions were saturated, even relatively far from resonance. This behavior can be explained[29] by the presence of a strong continuum background absorption to longer wavelengths, which is believed to be associated with a lower excited electronic state.

For selective detection, the broadness of the ion transitions is somewhat discouraging. However, the decreased optical selectivity in the $\omega_2$ excitation step is compensated by the increased mass selectivity resulting from parent/fragment detection. Furthermore, the visible absorptions in the aromatic ions are very selective in that they are typically inactive in neutral molecules. Finally, the dissociation process is very efficient (Fig. 21.10); consequently, the detection efficiency is favorable by this scheme. The important point to consider is that molecular beam excitation and detection using a single color has proved to be a very powerful means for sensitive and selective detection; hence the second color should be viewed as having a nonessential, but still a very enhancing, role in sensitive and selective detection. In this context, the $\omega_2$ RID pulse aptly serves that purpose.

## SUMMARY AND CONCLUSIONS

Multiphoton ionization in molecular beam systems has advanced into a remarkably diverse tool since its infancy about a decade ago. Creative adaptations of the MPI/molecular beam method have contributed enormously to our fundamental understanding of the spectroscopy and dynamics of excited state molecules. It is only natural that the benefits of high resolution and sensitive detection would be recognized and applied toward molecular detection. The nature of this chapter lim-

its us to reporting on recent and ongoing efforts in our laboratory; however, this represents only a small part of a very active field. We hope that our reference to other work will present the reader with a broader view of the subject matter.

The molecular detection work reviewed here should provide a glimpse of the potential performance obtainable by molecular beam MPI mass spectrometry in terms of speed, sensitivity, and selectivity of detection. There are many classes of compounds that are favorably disposed to detection by laser techniques such as REMPI. Our attempt here is to show that it is possible to overcome the challenges of spectroscopically and physically more demanding classes of molecules. It seems reasonable to expect further refinements of experimental methods in this area. The maturing of molecular beam, laser mass spectrometry as a viable broad-based analytical tool only awaits the imminent development of rugged, compact, and widely tunable sources of laser pulses.

## ACKNOWLEDGMENTS

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