Sensitive Mass Spectrometry of Molecular Adsorbates by Stimulated Desorption and Single-Photon Ionization

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We report the extension of the general method of photoionization mass spectrometry (PI-MS),[1-3] with its well-known advantages in generality (nonselectivity of ionization) and relatively low fragmentation rates (which further decrease with increasing molecular weight[4]) to the study of organic compounds of negligible vapor pressure in an extremely sensitive manner (subfemtomole limits). The experimental technique consists of stimulated desorption, single-photon ionization of the desorbed neutral molecular component using coherent vacuum ultraviolet (VUV) light, and reflection time-of-flight mass spectrometry.

The current challenges of the MS of nonvolatile, thermally labile molecules and molecules of extremely low volatility are the *desorption* and *ionization* processes. Major progress in the development of several techniques[5] (secondary ion MS, plasma desorption MS, and laser desorption MS) has been made where desorption and ionization occur in one step. However there are distinct advantages to be found in decoupling the two processes.

Because the neutral yields during stimulated desorption are typically orders of magnitude higher than secondary ion yields,[6] by sampling the neutral emission one can expect to gain greater flexibility and control over both processes and avoid so-called matrix effects and unpredictable secondary ion yields, leading to improved quantitation and more uniform detection probabilities.

This two-step separation has been clearly realized recently with multiphoton ionization (MPI) of inorganic compounds[7,8] and also organic compounds.[9-12] However, the use of one-photon ionization reported here avoids two significant problems associated with MPI. First, the MPI usually is highly selective in ionization probability of organic compounds leading to very nonuniform detection sensitivities; this places severe limits on the ability to quantify relative abundances in mixed compounds especially for unknowns. Second, MPI often leads to uncontrollable fragmentation especially when applied under efficient (sensitive) ionization conditions.[13-15] Single-photon ionization avoids these major difficulties and can be considered as a "universal" detector. Its implementation in a high efficiency regime though has required a very high brightness VUV photon source.

The SALI experimental technique has been described in detail in ref 8. Briefly, a pulsed Ar^+ ion beam at 7 keV from a duoplasmatron ion gun incident at 60° from normal was used for
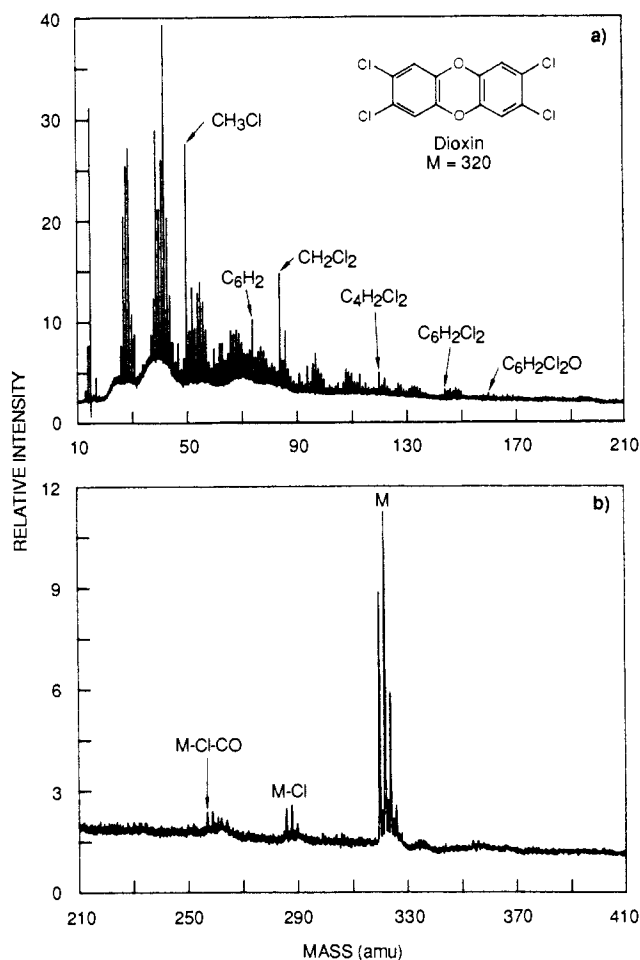

Figure 1. Photoionization time-of-flight mass spectrum of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. The spectrum was obtained from 200 pulses of Ar^+ bombardment for desorption and 118-nm radiation for ionization.

desorption, though laser desorption may be a very good alternative in future studies. The Ar^+ dose was $<3 \times 10^9/cm^2$ per pulse over 0.02 cm^2. The VUV radiation (118 nm, 10.5 eV) was obtained by frequency tripling of the third harmonic of a Nd:YAG laser (355 nm) in a phase-matched mixture of xenon and argon.[16,17] By using an input energy of 20 mJ per pulse we obtained 1.3 × 10^{12} photons/pulse corresponding to 220 W (10^{-4} conversion efficiency) as measured by an acetone cell absolute photoionization detector.[18] The VUV radiation was focused into the UHV chamber by a LiF lens which also served as a window. The laser beam was directed off the center axis of the lens so that the 355-nm light was dispersed by ∼3 mm from the VUV beam near the sample which was sufficient so that only the 118-nm light contributed to the signal given our experimental geometry. A reflection time-of-flight mass spectrometer was used to analyze the photoions. Any secondary ions were electrostatically rejected (transmitted) by the reflector; this is accomplished[8] by setting the back reflector grid to an electric potential between the surface potential (ground) where any secondary ions are formed and the potential at the region of photoionization (approximately −300 V).

For the present examples, samples of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and the purine 7-methylguanine were placed on a clean silicon wafer allowing for the solvent (nonane

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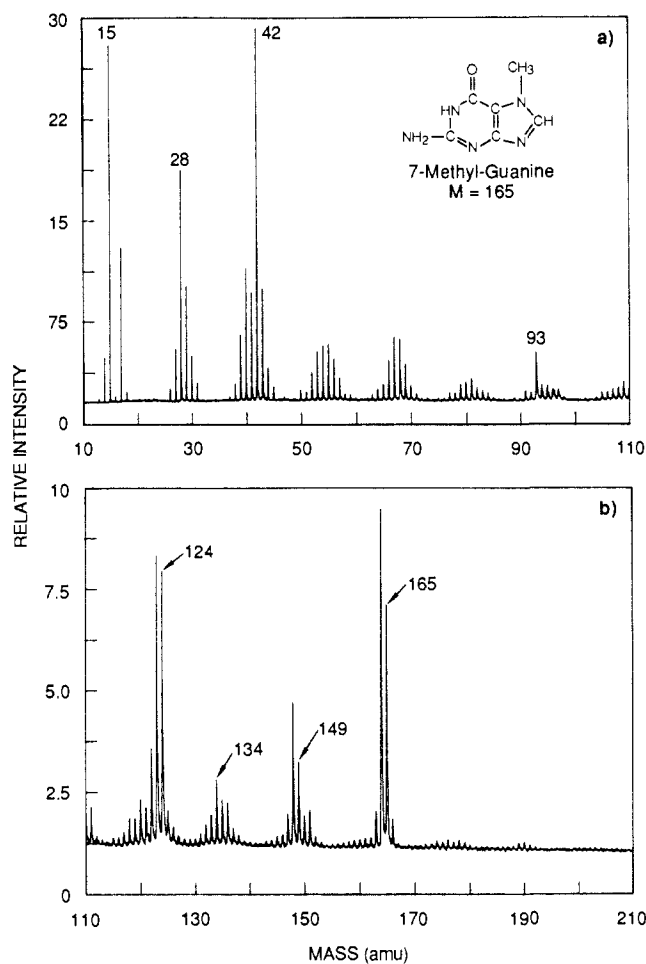
Figure 2. Mass spectrum of 7-methylguanine. The spectrum was accumulated over 1000 pulses. Main fragment peaks referred to in the text are indicated.

and water, respectively) to dry before introduction into the UHV chamber; small crystallites were observed.

Figure 1 displays the mass spectrum of TCDD taken with 200 pulses of Ar^+ bombardment and VUV laser ionization. While characteristic fragments are seen in the low mass region, notably m/e = 50 amu (CH_3Cl) and 84 amu (CH_2Cl_2), the high mass part of the spectrum shows parent molecules (m/e 320–328) in a clear fashion with the characteristic isotope pattern. Decomposition by loss of Cl and COCl is evidenced to be a minor process by the low intensity of the mass peaks at 286–292 and 257–264 amu, respectively. The signal of the parent molecule obtained with one single pulse had S/N of 10. Assuming a desorption yield of 1–10 molecules per incident ion, a detection limit of 3×10^{-17}–3 $\times 10^{-16}$ mol is estimated corresponding to the amount of compound removed in a single pulse; a much larger amount of material was on the sample mount for these initial experiments. Thus this is an extrapolated limit. Note this sensitivity can be improved with better spatial dispersion of the sample on the substrate and with a higher intensity VUV source. For the current 1-mm diameter focus of the light (passing about 1 mm above the sample), the estimated ionization efficiency is about 1%; an efficiency too high would lead to multiple absorption and excessive fragmentation. We also note that with multiphoton ionization at 248 and 308 nm no parent molecular ion or even structurally significant fragment were observed.

The spectrum of the purine 7-methylguanine shown in Figure 2 also exhibits a strong parent ion signal (165 amu) as well as with the loss of hydrogen (164 amu) and highly characteristic fragment peaks at m/e = 149 and 134 amu due to the loss of the NH_2 and CH_3 groups. The fairly strong feature at m/e = 124 amu is likely due to the decomposition of the imidazole ring leaving a pyrimidine ring with an NH group attached; the peak at 93 amu

then corresponds to the further loss of NH_2 and NH groups. The sensitivity here is the same as for the dioxin, that is, S/N of about 10 for a single pulse.

The extent of fragmentation from the ion bombardment versus the photoionization is not presently known though future comparative studies with laser desorption and photoionization at slightly longer wavelengths will help to clarify this issue. Additional structural information for unknown molecules can be obtained by photofragmentation with the addition of variable amounts of a second laser beam.[19] The approach reported here is also being applied to the surface analysis of bulk structural polymers.[14]

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Accelerating Symmetry Forbidden Reactions: The Vinylcyclopropane → Cyclopentene Cation Radical Rearrangement

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Woodward–Hoffmann forbidden reactions represent perhaps the most general class of organic transformations which remain unrealized. Thus the discovery of general ways to accelerate these reactions is an important experimental goal. One-electron oxidation may be a simple and useful strategy for this purpose.[1] We describe herein the successful application of this idea to the [1,3] sigmatropic rearrangement of vinylcyclopropanes to cyclopentenes.

The accelerating effect of one-electron oxidation on the rate of a symmetry-forbidden reaction has been most clearly demonstrated for the dimerization of substituted ethylenes to cyclobutanes.[2] In one instance, for the cation radical dimerization of *trans*-4-propenylanisole, the activation enthalpy for the cycloaddition reaction has been reported to be only 0.7 kcal/mol.[3]

It remains unclear, however, whether one-electron oxidation will have a similarly dramatic effect for other symmetry-forbidden reactions. For example, recent calculations on the degenerate [1,3] sigmatropic rearrangement of the propene cation radical predict a rather substantial barrier, ca. 30 kcal/mol.[4] We decided to test the viability of the cation radical [1,3] sigmatropic rearrangement by using the vinylcyclopropane → cyclopentene rearrangement as a model reaction.[5]

Our initial attempt at the cation radical ring expansion reaction utilized *cis*-1-*p*-anisyl-2-vinylcyclopropane (1) as a substrate and

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