The current results are evidence that a hopping (dephasing) rather than overlapping absorption bands is the origin of some of the decrease in P_{max} for the tris vs. the mono bpy complex. Consistent with this result for the tris complex is the time-resolved P_{max} of the $[Ru(bpy)py_4]^{2+}$ for which no change in P_{max} as a function of T can be measured at even the shortest time possible. This result verifies that the data for $[Ru(bpy)_3]^{2+}$ are not instrumental artifacts. Relative rates of exciton hopping as a function of solvent are obtained (Table I). Qualitative analysis shows there to be a dependence of hopping rate upon solvent.

In addition to exciton hopping of the emitting state, the TR photoselection experiment provides detail relating to nonradiative relaxation. For information on the original excitation to be retained, the original excitation must be into a localized state and a relaxation pathway must exist between absorbing and emitting states that does not cause the loss of the polarization properties of the absorption. Therefore, in addition to the emitting state, the absorbing singlet state must possess spatially isolated orbitals. This is in agreement with absorption studies performed by Meyer and co-workers.[21]

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Subfemtomole Quantitation of Molecular Adsorbates by Two-Step Laser Mass Spectrometry

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We report the quantitative analysis of molecules adsorbed on a surface using a two-step laser methodology. Here the first laser pulse causes virtually complete desorption of the molecules by rapid heating of the substrate surface. Then a second laser pulse, suitably delayed in time so as to intercept the maximum number of desorbed molecules, causes selective multiphoton ionization of the molecules in a time-of-flight (TOF) mass spectrometer. The difficulty in analyzing nonvolatile and thermally labile molecules by conventional mass spectrometry is mainly caused either by thermal decomposition during evaporation or by strong fragmentation accompanying ionization. Several methods using laser desorption[1-12] have been developed to obtain mass spectra without significant fragmentation. These techniques are celebrated for their powers of identifying complex molecules but not for their ability to measure relative or absolute molecular concentrations.[13] To achieve quantitation of molecular substances, mass spectrometry usually has to be interfaced with a quantitative analytical method, e.g., gas chromatography or liquid chromatography.[14,15]

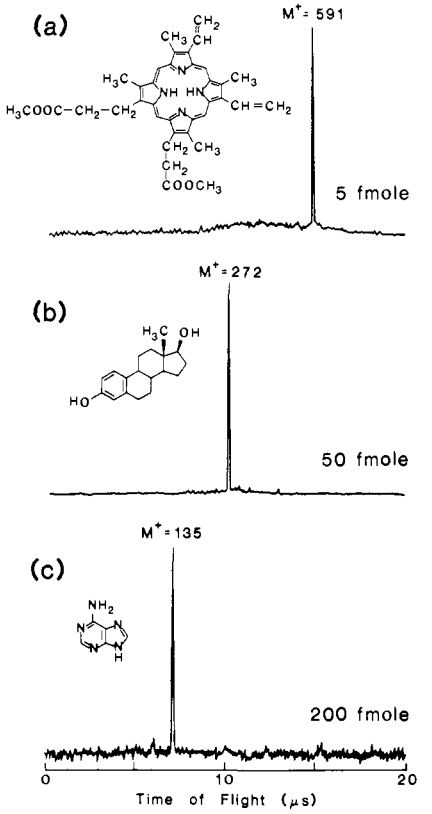

Figure 1. Laser desorption/multiphoton ionization mass spectra of (a) protoporphyrin IX dimethyl ester, (b) β-estradiol, and (c) adenine. The amount of each sample desorbed by a CO_2 laser pulse is 5, 50, and 200 fmol, respectively. Operating conditions: CO_2 laser fluence ~400 mJ/cm², Nd:YAG laser fluence ~3 mJ/cm², duty cycle = 10 Hz, and signal averaging time = 20 s.

Our two-step laser methodology is intended to overcome the problems mentioned above. For a number of molecules studied, e.g., protoporphyrin IX dimethyl ester, β-estradiol, and the four bases of DNA, the mass spectra obtained are dominated by the parent ion peak. Moreover, the ion signal is found to be linear with surface coverage over more than 5 orders of magnitude from nanomole to subfemtomole amounts per new target area exposed by consecutive laser shots. A detection limit (S/N = 2) of 4×10^{-17} mol of protoporphyrin IX dimethyl ester, corresponding to $\sim 10^{-5}$ of a monolayer, is obtained.

In our previous work the two-step laser methodology has been described and applied to the quantitation of the 20 phenylthiohydantoin (PTH) amino acids.[16] Improvements in the reduction of chemical and electrical interference permit the sensitivity to be increased by at least 3 orders of magnitude while maintaining linear response. In the first step of our methodology, the pulsed output of a CO_2 laser (10.6 μm; ~10 mJ/pulse; 10-μs pulse width; 10-Hz repetition rate) is directed onto a thin film of the sample deposited on the inner surface of a rotating glass cup or tube. Neutral molecules escape from the surface in a rapid laser-induced thermal desorption process. It has been argued[17-19] that the heating rate is so rapid (10^8 K/s) that internally lukewarm intact molecules are desorbed, even though more traditional heating rates (10 K/s or less) cause extensive molecular decomposition on the surface. After an appropriate time delay (70-90 μs) the fourth harmonic (266 nm) of a Nd:YAG laser (~1 mJ/pulse; 10-ns pulse width; 10-Hz repetition rate) causes 1 + 1 resonance-enhanced multiphoton ionization (REMPI) of the desorbed molecules in an interaction region located about 1 cm from the surface. The

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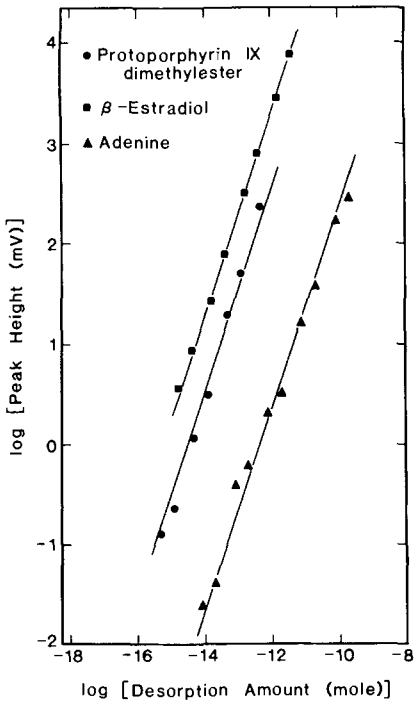

Figure 2. Parent ion signal for protoporphyrin IX dimethyl ester, β-estradiol, and adenine vs. amount desorbed per laser pulse.

glass cup or tube forms part of the first electrode (repeller plate) of a linear (30 cm) time-of-flight mass spectrometer. The ions are detected by an electron multiplier with two preamplifiers (EG&G ORTEC Model 9301 and 474) which feed a transient digitizer (LeCroy 9400) so that the entire mass spectrum can be recorded from a single laser shot. Typically, an average over 200 laser shots is taken. From the spectrum is subtracted a "gas-phase background spectrum" obtained with the desorption laser off. The sample container can be rapidly introduced (~1 min) into the time-of-flight mass spectrometer (pressure $\sim 10^{-7}$ torr) through a vacuum interlock.

Protoporphyrin IX dimethyl ester, β-estradiol, and adenine were obtained from Sigma Chemical Co. and were used without further purification. Chloroform solutions are placed inside the spinning glass cup or tube and the solvent is removed under a rough vacuum (10^{-1} torr) to produce a nearly uniform film.

Typical laser desorption/multiphoton ionization mass spectra of protoporphyrin IX dimethyl ester, β-estradiol, and adenine are shown in Figure 1. Note that in each case the spectrum shows almost exclusively the parent ion, indicating that fragmentation is negligible. A calculated detection limit (S/N = 2) of 4×10^{-17} mol is obtained for protoporphyrin IX dimethyl ester. These results demonstrate ultrahigh sensitivity of our methodology, which is comparable to that of TOF secondary ion mass spectrometry (SIMS).[20-22] In contrast to this work in which the desorption step is separated from the ionization step,[23] the ionization process in other techniques, such as SIMS, fast atom bombardment (FAB), plasma desorption, field desorption (FD), and direct laser desorption/ionization, depends sensitively on the nature of the matrix.[21]

The linear dependence of signal on sample concentration is investigated with fixed CO_2 laser power (50 kW/cm^2), fixed Nd:YAG laser power (300 kW/cm^2), and fixed time delay (70–90 μs, depending on the molecule) between CO_2 laser pulse and Nd:YAG laser pulse. The results for protoporphyrin IX dimethyl ester, β-estradiol, and adenine are shown in Figure 2 where the parent ion peak height is plotted against the desorption amount per CO_2 laser pulse. The desorption amount is calculated on the basis of the amount deposited on the substrate, the new area exposed per laser shot, and the assumption that all irradiated molecules are desorbed. The sample concentration ranges from nanomoles to subfemtomoles. It should be noted that the linearity covers more than 5 orders of magnitude of sample concentration. The complete desorption by the CO_2 laser has been demonstrated within the concentration range given in the figure. In contrast to other mass spectrometric methods for the analysis of molecular adsorbates,[24,25] the ability of the present two-step laser method to cover so wide a dynamic range of quantitation appears to be unprecedented.

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Synthesis and X-ray Crystal Structure of $(\mu_3\text{-}COCH_3)(\mu_2\text{-}CH_2)(Cp)(MeCp)Fe_2Mn(CO)_5$, the First Carbyne–Methylene Cluster. Carbon–Carbon Coupling To Give a Methoxyvinyl Cluster

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The study of transition-metal cluster compounds that incorporate two different σ-bound organic fragments, compounds that we call difunctional clusters, is attracting increasing attention.[1,2] This work is important with respect to both uncovering new modes

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