+ k^*_{dp}) is obtained from the neutral fall time and/or the anion rise time at pH 7. A complete kinetic analysis will be presented in a subsequent paper. A short summary of representative results from this analysis is given in Table I.

The most striking result revealed by this work is the contrast between the excited-state dynamics of 1-naphthol and those of 2-naphthol[18] (see Table I). For 2-naphthol, nanosecond time resolution is sufficient for direct observation of the excited-state dynamics. In 1-naphthol, excited-state proton transfer (k^*_{dp}) is ~280 times faster, and solvent quenching (as manifested by τ_0) is ~80 times faster than in 2-naphthol. Proton-induced quenching of RO^{-*} is found to be substantial in 1-naphthol, direct confirmation of the results of previous indirect studies.[7,9,18] These effects can be explained by postulating that the charge-transfer character of the lowest excited singlet state of 1-naphthol is stronger than that of 2-naphthol, due, for example, to increased ^1L_a character in the 1-naphthol excited state.[11] If this results in a decrease in the relative electron density on the oxygen, it would cause an increase in the driving force for the excited-state proton-transfer reaction, consistent with the observed increases in both the excited-state proton-transfer rate and the pK^*_a of 1-naphthol relative to 2-naphthol. The measurements reported here are currently being extended by the systematic study of excited-state dynamics in naphthols and substituted naphthols as a function of solvent, temperature, pressure, and excitation wavelength.

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Fragmentation of Oligopeptide Ions Using Ultraviolet Laser Radiation and Fourier Transform Mass Spectrometry[1]

William D. Bowers, Sherri-Sue Delbert, Richard L. Hunter, and Robert T. McIver, Jr.*

Department of Chemistry, University of California Irvine, California 92717

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Collisionally activated dissociation (CAD) has become a powerful and widely used method for the structural characterization of ions by mass spectrometry.[2] The cross section for collisional fragmentation is large, typically 10–100 Å^2 at ion energies less than 100 eV, when the mass of the parent ion is comparable to the mass of the collision gas.[3,4] But higher molecular weight ions are not efficiently fragmented because only a small fraction of the translational energy of the ion is available for internal excitation.[5] For example, in a collision between argon and a 30-eV ion of mass 1000 u, only 3.8% of the initial ion energy (1.2 eV) is available in the center of mass frame for internal excitation and subsequent fragmentation of the ion. An alternative method is to use laser radiation to fragment the ions. With an excimer laser, radiation at 193 nm (6.42 eV) can be deposited specifically into internal electronic excitation of the ion, and absorption of even one UV photon is usually sufficient to cause fragmentation.

The effective use of pulsed lasers to fragment ions in mass spectrometers has proven to be difficult. One problem is that with quadrupole and magnetic sector mass spectrometers the interaction region between the laser and the ion beam is very small. Even with a 1-nA ion beam current fewer than 1000 ions are irradiated during the 20-ns pulse of an excimer laser. Another difficulty is that a complete mass spectrum cannot be obtained for each laser pulse because the scan speed is far slower than the duration of the laser pulse.

These limitations are alleviated in ion cyclotron resonance spectrometers (ICR) because the ions are stored in an analyzer cell for up to several seconds and can be irradiated with many laser pulses.[6-9] In this paper we demonstrate that oligopeptide ions stored in an ICR analyzer cell are fragmented efficiently by ultraviolet laser radiation. In addition, a complete mass spectrum of the photofragment ions is obtained for each pulse of the laser by Fourier transform detection.[10-14]

The experiments were performed with a Fourier transform mass spectrometer (FT-MS) that has been described previously.[15] The peptides (Sigma Chemical Co.) were dissolved in methanol and then evaporated to dryness on the tip of a direct insertion probe. Since the vapor pressure of the peptide is typically less than 10^{-8} torr, low-pressure chemical ionization[16] was used to generate the protonated oligopeptide ions. In a typical FT-MS photodissociation experiment an electron beam is fired through the analyzer cell to produce gaseous reagent ions. With dimethylamine as the reagent gas, dimethylammonium ions form rapidly and are stored in the analyzer cell of the FT-MS instrument. Protonated peptide ions are generated continuously by reaction of the gaseous peptide molecules with dimethylammonium ions. At the end of a 3-s reaction period an excimer laser (Tachisto Model 800XR) is triggered a predetermined number of times to fragment the ions. Fragment ions produced by the laser radiation are trapped in the FT-MS analyzer cell and after a 2-ms delay time are accelerated by a radiofrequency (rf) pulse. Ion image current signals induced on the plates of the analyzer cell by the coherent cyclotron motion of the ions are amplified, digitized, and stored in a 16K word buffer memory. Finally, the data are transferred over a parallel interface to an IBM 9001 computer having a Sky Computer floating point array processor which calculates the fast Fourier transform to yield a mass spectrum.

When leucylalanine (Leu-Ala) is protonated by dimethylammonium ion, only the protonated molecular ion at m/z 203 is observed in the FT-MS spectrum. Dimethylamine is a good reagent gas for the peptides because it has a proton affinity comparable to that of the amino acids.[17] Previous studies of oligopeptides by chemical ionization mass spectrometry have utilized low proton affinity reagents, such as isobutane and methane, which cause such extensive fragmentation that the protonated molecular ion is low in abundance.[18,19]

When the unfocused beam of an excimer laser (one pulse at 193 nm and an energy of 42 mJ) is crossed with protonated Leu-Ala ions stored in the analyzer cell, fragment ions are produced by photodissociation. The fragmentation pattern is

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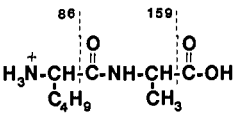
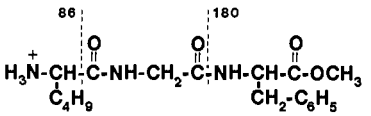


The dominant photofragmentation process is loss of CO_2 to give m/z 159. A smaller peak at m/z 86 results from cleavage of the α-C–C bond in leucine with transfer of a hydrogen and charge retention on the N-terminus. These are the A_2 and A_1 sequence ions, respectively. Weber and Levson have reported the CAD spectra of several protonated oligopeptides made by field desorption.[20] For protonated Leu-Ala they report a base peak at m/z 87, and in none of the spectra is loss of CO_2 apparent. Comparison can also be made with the electron impact mass spectrum of Leu-Ala, which has m/z 86 as the major fragment.[21] Thus, the loss of CO_2 seen in the FT-MS laser photodissociation spectrum is an unusual fragmentation that may be indicative of absorption of the photon energy specifically by the carboxyl chromophore.

We have observed that the extend of photofragmentation of protonated Leu-Ala depends strongly on the wavelength of the laser radiation. Protonated Leu-Ala readily photodissociates at 193 nm and to a smaller extent at 249 nm, but photofragment ions were not observed at 350 nm. For comparison we recorded the absorption spectrum of Leu-Ala in methanol (0.44 g/L) using a Cary 219 UV–visible spectrophotometer. The absorbance was negligible between 400 and 260 nm but increased sharply below 250 nm, in parallel with the photodissociation yields of the gaseous positive ions. A number of previous studies have shows a close correlation between solution absorption spectra and gas-phase photodissociation spectra.[6,7,22]

Loss of CO_2 from protonated Leu-Ala is not particularly desirable. One way we have circumvented this is to make the methyl ester derivative by treating the peptide with a stock solution of 0.5 N HCl in methanol for 1 h at room temperature. Photodissociation of the protonated *O*-methyl ester of Leu-Ala at 193 nm produces only m/z 86.

Photodissociation of the protonated *O*-methyl ester tripeptide Leu-Gly-Phe also proceeds efficiently at 193 nm. The fragmentation pattern is



The major photofragment peak is m/z 180, which corresponds to the Z_1 sequence ion $^+NH_3CH(CH_2C_6H_5)COOCH_3$. A small amount of the A_1 sequence ion m/z 86, $^+NH_2{=}CH(C_4H_9)$, is also seen, and its relative abundance increases as the laser power is increased. In order to confirm the structure of the m/z 180 photofragment, the C-terminus was labeled 50/50 with acidic CH_3OH/CD_3OH, so that fragment ions containing the C-terminus appear in the mass spectrum as doublets three mass units apart. From 193-nm radiation, photodissociation of protonated Leu-Gly-Phe-OCH_3/OCD_3 produces the doublet m/z 180/183, confirming that it is the C-terminus Z_1 sequence ion.

We plan to investigate the photodissociation of other oligopeptides, but their low volatility will probably limit these studies to molecular weights less than about 800 u. For high molecular weight biomolecules, we plan to utilize a tandem quadrupole–Fourier transform mass spectrometer (QFT-MS) where ions made by fast atom bombardment in the source of a quadrupole mass spectrometer are stored and mass analyzed in a separate ICR analyzer cell.[23,24] It should also be possible to use several laser pulses to sequentially fragment ions, in a manner similar to the consecutive CAD experiments (MS/MS/MS) done by FT-MS.[25,26]

Acknowledgment. Our first ion photodissociation experiments were performed with lasers loaned by the San Francisco Laser Center, and currently we are using an excimer laser on loan from F. S. Rowland. This work was supported by the National Science Foundation and a grant from the Chevron Research Co. S.S.D is grateful to the University of California for a Regents Fellowship.

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A New Environment for Water. The First Authenticated Example of Water Molecules Engaged in Twin, Three-Center Hydrogen Bonds: The Crystal and Molecular Structure of $\{[(CH_3)_2SnCl_2{\cdot}H_2O]_2{\cdot}18\text{-crown-}6\}_n$

M. M. Amini,[†] A. L. Rheingold,*[‡] R. W. Taylor,*[†] and J. J. Zuckerman*[†]

Department of Chemistry, University of Oklahoma Norman, Oklahoma 73019
Department of Chemistry, University of Delaware Newark, Delaware 19716

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A uniquely situated water molecule is found in the lattice of $\{[(CH_3)_2SnCl_2{\cdot}H_2O]_2{\cdot}18\text{-crown-}6\}_n$. While no stable binary complexes of water with 18-crown-6 have been isolated,[1,2] enhanced dipole and acidity can be brought about in water by complexation to a metal.[1] The water molecules, which are coordinated to tin in the title compound, engage in twin, three-center (bifurcated) hydrogen bonding to the crown ethers. The protons, which have been located in two X-ray structure determinations on the same data crystal, one at 23 and one at -120 °C,[3] each participate in a short contact to two oxygen atoms in two crown molecules. Thus each water molecule is five-coordinated with the geometries depicted in Figure 1 [O(5) and O(6) lie on mirror planes, so the environments of each pair of attached hydrogens are identical]. There is no authenticated precedent for such an

[†] University of Oklahoma.
[‡] University of Delaware.

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(3) Dimethyltin(IV) dichloride crystallizes with 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) as a hydrated dimer, mp 132–138 °C, $\{[(CH_3)_2SnCl_2{\cdot}H_2O]_2{\cdot}18\text{-crown-}6\}_n$, $C_{16}H_{40}Cl_4O_8Sn_2$, fw 739.683 daltons, in the monoclinic space group $C2/m$ with a = 16.348 (3) Å, b = 11.668 (2) Å, c = 15.063 (4) Å, β = 93.22 (2)°, V = 2868 (1) Å^3, Z = 4 at 23 °C. The structure was studied at 23 °C (ρ_{calcd} = 1.713 g cm^{-3}) and −120 °C (ρ_{calcd} = 1.769 g cm^{-3}) and solved by direct methods (SHELXTL-SOLV) using 2951 unique reflections (3σ cutoff) from 3459 collected (3341 unique) on an R3 Nicolet automated diffractometer (Mo K_α, μ = 21.48 cm^{-1}, $4° \le 2\theta \le 55°$; scan speed 3°/min) to a final, conventional R value of 0.0331 and R_w of 0.0371 at 23 °C and 0.0282 and 0.0269, respectively, at −120 °C. Corrections for absorption (empirical) and secondary extinction were applied. The final refinement utilized anisotropic thermal parameters for all non-hydrogen atoms and isotropic parameters for the two hydrogen atoms of interest; the remaining hydrogen atoms were treated as fixed, idealized isotropic contributions. The water molecule hydrogen atoms were not found at 23 °C but were positioned so as to minimize the hydrogen-bonded distances to the ether oxygen atoms. At −120 °C, the two independent water hydrogen atoms were located at conventional hydrogen-bonded distances in positions indistinguishable from those assigned at 23 °C. Their inclusion lowered R from 0.0291 to 0.0282. Crown C(7) and C(8) atoms are disordered in equal occupancy locations, viz., C(7′) and C(8′) about the crystallographically imposed mirror plane. No peaks on the final difference map were greater than a diffuse background (0.66 e$^-$ Å^{-3} at 23 °C; 0.87 e$^-$ Å^{-3} at −120 °C) at convergence.

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