RESONANCE IONIZATION SPECTROSCOPY

Ninth International Symposium

Manchester, United Kingdom June 1998

EDITORS

John C. Vickerman
The University of Manchester Institute of Science and Technology

Ian Lyon
The University of Manchester

Nick P. Lockyer
The University of Manchester Institute of Science and Technology

James E. Parks
The University of Tennessee, Knoxville

AIP

AIP CONFERENCE PROCEEDINGS 454

American Institute of Physics **Woodbury, New York**

Photoionization Studies of Small Biological Molecules Using Femtosecond Laser Pulses

V. Vorsa, K. F. Willey, T. Kono, N. Winograd

Department of Chemistry, The Pennsylvania State University
184 Materials Research Institute Building, University Park, PA 16802, USA

Abstract. We report on the fs photoionization and dissociation dynamics of small biological molecules sputtered from surfaces and in the gas phase. Femtosecond postionization studies of ion-beam desorbed dopamine at 800, 400, 267, and 200 nm are presented and compared to the fragmentation patterns observed for gas phase dopamine under similar laser conditions. Differences in the amount of fragment ions originating from the molecular ion suggest that dopamine undergoes extensive fragmentation during the sputtering process. We also present fs postionization data for the amino acid alanine at 267 and 200 nm along with its positive SIMS mass spectrum.

INTRODUCTION

Laser postionization of surface-desorbed neutral species has emerged as a highly sensitive surface analysis technique (1) that is particularly well suited for secondary ion mass spectrometry (SIMS) experiments. Most of the studies, thus far, have concentrated on resonance enhanced multiphoton ionization (REMPI) of the desorbed neutral species with nanosecond lasers. Although this REMPI has proven to be successful in the detection of atomic species (2), molecular species have proven to be more challenging. This is mainly due to a high degree of fragmentation particularly for larger organic and biological molecules.

Femtosecond postionization has shown great potential for producing large ionization efficiencies while at the same time keeping fragmentation to a minimum (3). In this paper we present the fs photoionization studies of the neurotransmitter dopamine at 800, 400, 267, and 200 nm and amino acid alanine at 267and 200 nm.

EXPERIMENTAL METHOD

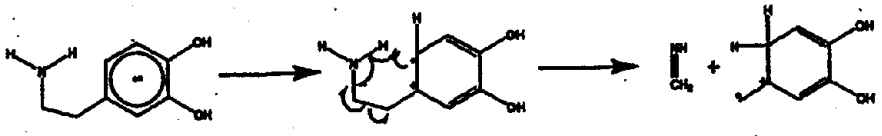
All experiments are carried out using a TOF-SIMS apparatus in conjunction with a Ti:sapphire-based laser system. The sample is desorbed from the surface with a pulsed 25 keV Ga^+ ion beam. The desorbed species are intersected with a laser beam in the extraction region of the mass spectrometer where they are pulse-extracted into the reflectron-based TOF mass spectrometer. The 1 kHz Ti:sapphire femtosecond laser system (3,4) (Clark-MXR, Inc.) produces 100 fs pulses centered on 800 nm containing 3.5 mJ of energy per pulse. This output is directed into a

CP454, *Resonance Ionization Spectroscopy*
edited by J. C. Vickerman, I. Lyon, N. P. Lockyer, and J. E. Parks
 1-56396-810-X/98/$15.00

harmonic generator to produce 400, 267, and 200 nm wavelengths. The pulse widths for these wavelengths are ~200, 250, and 400 fs, respectively.

RESULTS AND DISCUSSION

Shown in Fig. 1(a-d) (top) are the gas phase mass spectra of dopamine following fs photoionization at the four wavelengths taken at near threshold laser conditions. Three major and one minor species are observed including the molecular ion M^+ at m/z 153, a fragment ion McL^+ at m/z 124 (see below), and a side chain fragment $CH_2NH_2^+$ at m/z 30. The aminomethyl side chain fragment has a particularly low ionization potential of 6.2 eV. A much weaker fragment ion channel M^+-CH_2NH_2 is also observed at m/z 123. The m/z 124 product ion appears to arise from a radical site rearrangement reaction. This type of rearrangement fragment (McL^+) is frequently observed in the electron impact mass spectra of phenylalkanes where the side chain is propyl or larger (5) and is commonly referred to as a McLafferty rearrangement Eq. (1). Note, this reaction takes place in the ion-state rather than in the neutral.



(1)

The minimum number of photons required to ionize dopamine (IP = 8.18 eV (6)) at 800, 400, 267, and 200 nm is 6, 3, 2, and 2, respectively. Energetically, this leads to an excess of 1.1 eV for the three longer wavelengths and 4.2 eV for 200 nm. From power dependence studies, we believe the 800 nm mass spectra results in more than 6 photons being deposited into the molecule. This extra energy, therefore, results in a mass spectrum that more closely resembles the 200 nm spectrum.

Figure 1(a-d) (bottom) displays the postionization spectra of dopamine taken at threshold laser intensities. A much higher degree of fragmentation and spectral congestion (particularly at lower masses) is observed for 800 and 400 nm postionization. The 267 nm data exhibits simpler a spectrum containing the characteristic dopamine fragments as seen in the gas phase data while 200 nm postionization produces mostly $CH_2NH_2^+$. The dominant peak at all excitation wavelengths and laser intensities is $CH_2NH_2^+$. The m/z 123 and 124 fragments are both present, however, the yield of the m/z 123 fragment is much greater than the McL^+ fragment. In the gas phase experiments the McL^+ fragment is one to two orders of magnitude greater. Gas phase power dependence studies show identical photon orders for the M^+ and McL^+ ions, while postionization power dependence studies show the M^+ ion exhibiting a substantially lower photon order than the McL^+ ion. This suggests that extensive fragmentation of dopamine is occurring prior to postionization. Moreover, the molecular ion yield is very low (<1% of the characteristic fragments). Power dependence studies of the fragments exhibit strikingly low photon orders (~3 for 800 nm and ~2 for 400 nm) suggesting that the

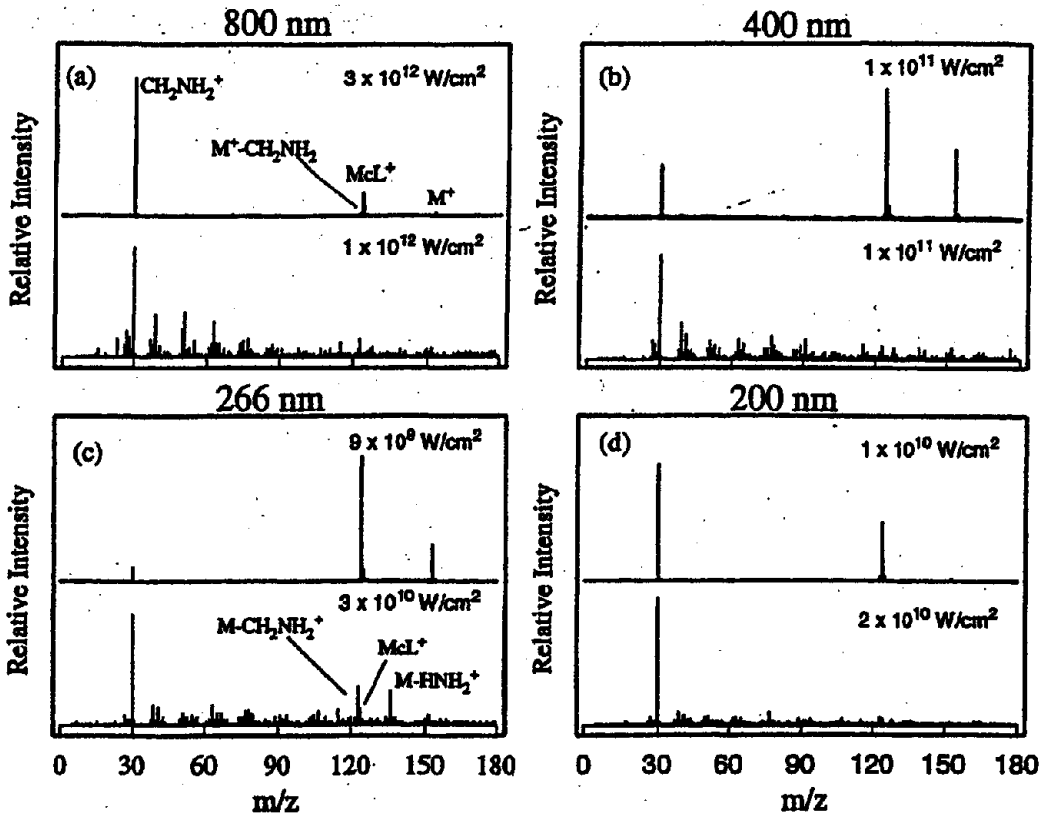


FIGURE 1. Femtosecond ionization-dissociation mass spectra of gas-phase dopamine (a) - (d) (top) and ion desorbed dopamine (a) - (d) (bottom) following 800, 400, 267, and 200 nm excitation.

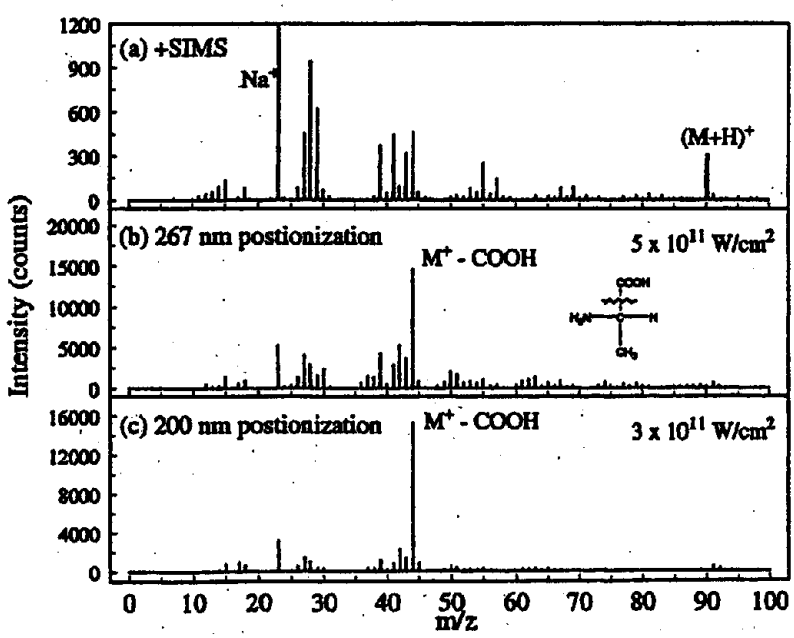


FIGURE 2. Mass spectrum of alanine (IP = 8.9 eV) under identical sputtering conditions. (a) +SIMS, (b) fs postionization at 267 nm, and (c) fs postionization at 200 nm.

desorbed species contain a high degree of internal excitation. A comparison of ion yields between postionization at 267 nm and SIMS was made. With a laser intensity of ~7×10^{11} W/cm^2 we measured up to a 20-fold increase in the amount of characteristic ions produced with postionization over SIMS under identical ion sputtering conditions.

Positive SIMS and postionization spectra (267 and 200 nm) of alanine recorded under identical sputtering conditions are shown Fig. 2. The protonated molecular ion $(M+H)^+$ can clearly be seen in the SIMS spectra at m/z 90. The postionization spectra, on the other hand, show a characteristic fragment at m/z 44 corresponding to the loss of the carboxylic acid group, but very little molecular ion. Comparing the molecular ion yield for SIMS to the M^+-COOH ion yield for postionization we find 1-2 orders of magnitude increase in signal. We observe a loss of carboxylic acid in other amino acids with alkyl side chains with 200 nm excitation, but only in certain cases for 267 nm excitation. This loss appears to be correlated with the removal of an electron from the nitrogen lone pair orbital of the amine group which corresponds to the first IP for amino acids with alkyl side chains.

CONCLUSIONS

We have carried out femtosecond photoionization studies on gas phase and ion-beam desorbed dopamine at 800, 400, 267, and 200 nm. Ion-desorbed dopamine is found to undergo extensive fragmentation and the fragments are found to contain a high degree of internal excitation. We find up to a 20-fold increase in ion yield with 267 nm postionization over SIMS. Postionization at 267 and 200 nm produces large yields of M^+-COOH in alkyl amino acids. We are currently investigating the fs postionization of other amino acids and biologically important molecules.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support of the National Institutes of Health and the National Science Foundation.

REFERENCES

1. Winograd, N., *Anal. Chem.* 65, 622 A (1993).
2. Parks, J. E., *Lasers and Mass Spectrometry*; Lubman, D. M., Ed., Oxford : Oxford University Press, 1990, ch. 2 pp. 37-64.
3. Brummel, C. L., Willey, K. F., Vickerman, J. C., Winograd, N., *Int. J. Mass Spectrom. Ion Processes* 143, 257 (1995).
4. Willey, K. F., Vorsa, V., Braun, R. M., Winograd N., *Rap. Commun. Mass Spectrom.*, (in press).
5. McLafferty, F. W., Turecek, F., *Interpretation of Mass Spectra*, 4th ed., Sausalito, California: University Science Books, 1993, Ch. 9 pp. 238-240.
6. Choi, Y., Lubman, D. M., *Anal. Chem.* 64, 2726 (1992).