ELSEVIER

International Journal of Mass Spectrometry 176 (1998) 77–86

Multiphoton ionization mass spectrometry of small biomolecules with nanosecond and femtosecond laser pulses

N.P. Lockyer*, J.C. Vickerman

[a]*Surface Analysis Research Centre, Department of Chemistry, University of Manchester Institute of Science and Technology, P.O. Box 88, Manchester M60 1QD, UK*

Received 11 November 1997; accepted 23 January 1998

Abstract

This paper reports on the multiphoton ionization and dissociation (MPID) processes that occur in gas phase dipeptides excited with femtosecond and nanosecond laser pulses. The MPID products of the compounds tyrosyl-tyrosine, tyrosyl-leucine, and valyl-valine resulting from excitation with 5 ns and 250 fs laser pulses at 266 nm have been analysed by time-of-flight mass spectrometry. There are two important conclusions from this study. First, ion fragmentation patterns depend on the pulse length of laser radiation used to excite the neutral molecule. Photofragmentation is generally less extensive and more tuneable with femtosecond pulses compared with nanosecond pulses. Second, the efficiency of the ionization with femtosecond pulses seems relatively insensitive to the presence or absence of a chromophore in the systems we have studied; this is not true for nanosecond pulses. This suggests that although coherent processes clearly play little part in ionization with nanosecond pulses, these effects become significantly more important as the time scale of the ionization reaches the subpicosecond regime. (Int J Mass Spectrom 176 (1998) 77–86) © 1998 Elsevier Science B.V.

Keywords: Ionization; Dissociation; Femtosecond pulses; Dipeptides; Postionization

1. Introduction

Resonance-enhanced multiphoton ionization has been successfully applied to the mass spectrometry of a wide range of biomolecules [1,2]. The development of two-step desorption/ionization methods has enabled nonvolatile and thermally labile molecules to be desorbed and subsequently postionized without extensive fragmentation [3,4]. By entraining the desorbed species in an expanding gas jet, they can be vibrationally cooled and by carefully tuning the ionization laser wavelength, fragmentation can be further reduced [5]. However, the use of jet-cooling significantly reduces the amount of desorbed neutral species fragments entering the ionization region, and the added selectivity introduced by wavelength selection make the technique less appropriate for routine analysis of unknown samples. A further disadvantage of jet-cooling is that it requires experimental geometries that are incompatible with single-step desorption/ionization techniques such as secondary ion mass spectrometry. In addition, the use of nanosecond laser pulses may mean that the rate of dissociation at the 1-photon level exceeds the rate of absorption of the subsequent photon(s) required for multiphoton ionization (MPI). In this case, it may prove impossible to form intact molecular ions at any wavelength.

One possibility for overcoming fast dissociation

* Corresponding author.

PII S1387-3806(98)14005-8

rates is to increase the pumping rate by using ultrahigh intensity laser pulses. Increasing the energy of nanosecond laser pulses simply leads to excessive photon absorption by the molecular ion and more fragmentation [6,7]. The advent of picosecond and femtosecond pulsed lasers has provided a means of achieving very high photon absorption rates using low energy pulses, thereby defeating dissociation pathways and maintaining control over energy deposition. Femtosecond laser ionization mass spectrometry has recently proven very useful in minimizing fragmentation in several chromophore-containing organic systems such as nitro-compounds, benzene, aminoacids, and larger biomolecules [8–15]. Ledingham et al. [16] have recently published an excellent review of high intensity (picosecond and subpicosecond) laser mass spectrometry.

Current research in our group aims to develop the optimum postionization method for ion beam-sputtered neutral molecules. In this work we report on a comparative investigation of the application of nanosecond and femtosecond MPI to small biomolecules thermally desorbed without subsequent jet-cooling. The thermal desorption method used in this is expected to result in much less fragmentation than ion beam desorption, allowing the photofragmentation processes to be studied in greater depth [17].

2. Experimental

The work reported here was carried out at two sites. The nanosecond MPI work was performed at University of Manchester Institute of Science and Technology (UMIST) and the femtosecond MPI work at Pennsylvania State University (PSU). At both sites, experiments were performed on a dual-stage reflectron-type time-of-flight mass spectrometer (K Prism Series, Kratos Analytical Ltd., Manchester, UK) of almost identical design. The experimental set-up is shown schematically in Fig. 1.

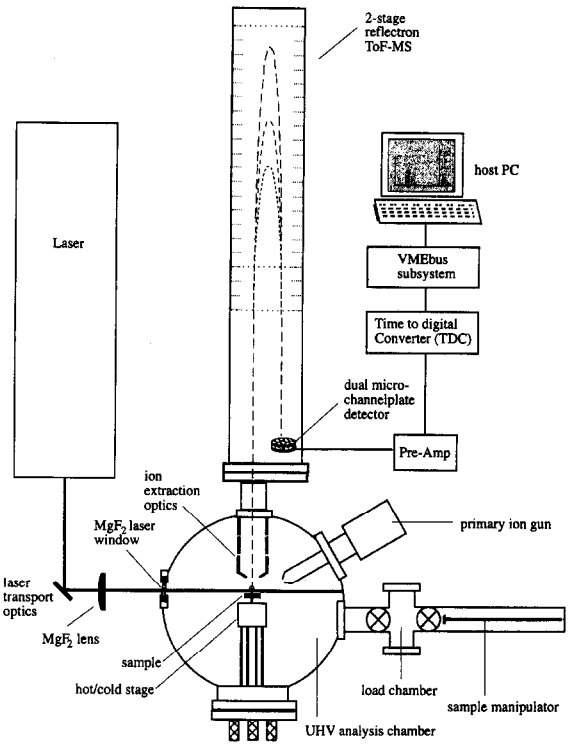


Fig. 1. Diagram of the laser ionization mass spectrometer.

2.1. Thermal desorption

The dipeptides were purchased from Sigma Chemical Company, Poole, UK and used as received. Samples were prepared by depositing thin layers in methanolic solution on clean copper stubs and air dried before loading into the mass spectrometer. Because of the low volatility of the samples at room temperature it is necessary to heat the sample stub to obtain a sufficient gas phase concentration of analyte in the ion source region. Heating is accomplished by passing electrical current through a tungsten filament located next to the sample stub or by passing heated nitrogen gas through the sample stage. A thermocouple mounted in the stub enables the sample temperature to be monitored during the experiment. The dipeptides tyrosyltyrosine, tyrosyl-leucine and valyl-valine were thermally desorbed into the gas phase at ~430 K, raising the chamber pressure from approximately 5×10^{-9} to 5×10^{-8} mb. The sample stub is

held at a potential of 2.7 kV, establishing an electric field in the region where photoions are formed.

2.2. Laser ionization

For nanosecond excitation at UMIST, we used an Nd:YAG laser (DCR-11, Spectra-Physics, Mountain View, CA) frequency-quadrupled to 266 nm with an output energy of up to 30 mJ in a 5-ns pulse. For femtosecond excitation at PSU, a regeneratively amplified, frequency-tripled, Ti:sapphire based system (Clark-MXR, Dexter, MI) giving 250-fs pulses of up to 150 μJ at 266 nm was used. The femtosecond laser is described in detail elsewhere [10].

The laser beam is focused with a 30-cm focal length MgF_2 planoconvex lens mounted outside the vacuum system and directed parallel to and a few hundred microns above the sample surface. The laser beam cross sectional area above the sample was typically of the order 10^{-3} cm^2. The laser is synchronized with the timing system of the mass spectrometer and determines the maximum repitition rate of each experiment. The Nd:YAG laser operates at 10 Hz and the Ti:sapphire laser at 1 kHz.

The first ionization energies of dipeptides are in the region 8.3 to 8.6 eV [18]. Therefore, absorption of two photons at 266 nm (4.66 eV) is sufficient to ionize ground state neutral dipeptide molecules desorbed into the laser beam. Subsequent photon absorption will deposit excess energy in the ionized species and may lead to additional photofragmentation. The rate of photon absorption will depend on the power density of the laser in the ionization volume, which in turn is a function of the pulse energy and the pulse duration. Once formed, ions are accelerated to kinetic energies in the region of 2.5 keV by the electric field, which exists between the sample and the entrance of the time-of-flight mass spectrometer (ToFMS).

2.3. Mass spectrometry and detection

An electrostatic lens serves to collimate the ions as they are extracted, producing a narrow beam of ions in the field-free drift region of the analyzer where their transit time is proportional to the square root of their mass-to-charge ratio *(m/z)*. The dual-stage reflectron incorporates an electrostatic mirror in which the ions are first decelerated from drift velocity by a steep field gradient then reflected back through the drift region to the detector by a shallower field gradient, which can more accurately achieve energy refocusing over a shorter path length. Energy refocusing is of particular importance in gas phase laser ionization mass spectrometry because significant kinetic energy differences can exist between ions formed at different potential energy regions within a loosely focused laser beam. For example, an extraction field of 2700 V cm^{-1} will result in a potential energy difference of 27 eV between ions formed at either side of a 100-μm diameter laser beam. The total path length of an ion from source to detector is about 3.6 m.

A chevron design dual microchannel plate assembly is used as an ion detector. Ion arrival signals are sent via a pre-amplifier to a VMEbus computer system containing a time-to-digital converter card. Histograms of ion flight times can then be assembled over several thousand laser pulses and converted to mass spectra by a host PC using a simple calibration routine.

3. Results and Discussion

3.1. Nanosecond versus femtosecond ionization

The content of the aromatic chromophore tyrosine (Tyr) in the sample molecules was varied intentionally to enable us to study the effect of resonant enhancement by a (π–π^*) transition at the 1-photon level. The tyrosine absorption maximum is at 273 nm [1]. We therefore expect to excite neutral species into high vibrational levels of the S_1 manifold using 266-nm photons.

Ionization of tyrosyl-leucine (Tyr-Leu) and tyrosyl-tyrosine (Tyr-Tyr) was facile with 5-ns pulses (10^8–10^9 W cm^{-2}) but no significant ion current was observed from valyl-valine (Val-Val). It has been reported previously that molecules without a chromophore are difficult to ionize using nanosecond laser pulses in the near-UV region [19]. The available

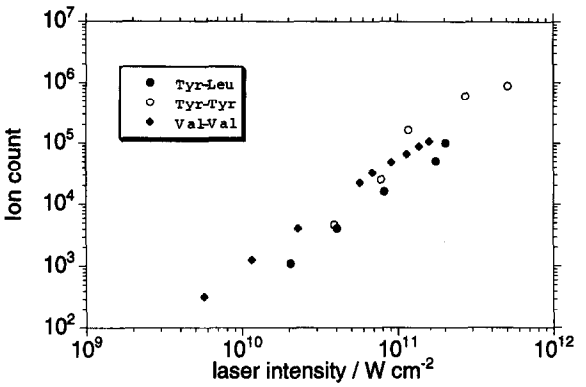


Fig. 2. Power plots of Tyr-Leu, Tyr-Tyr, and Val-Val, illustrating the effect of chromophoric groups on femtosecond MPI efficiency.

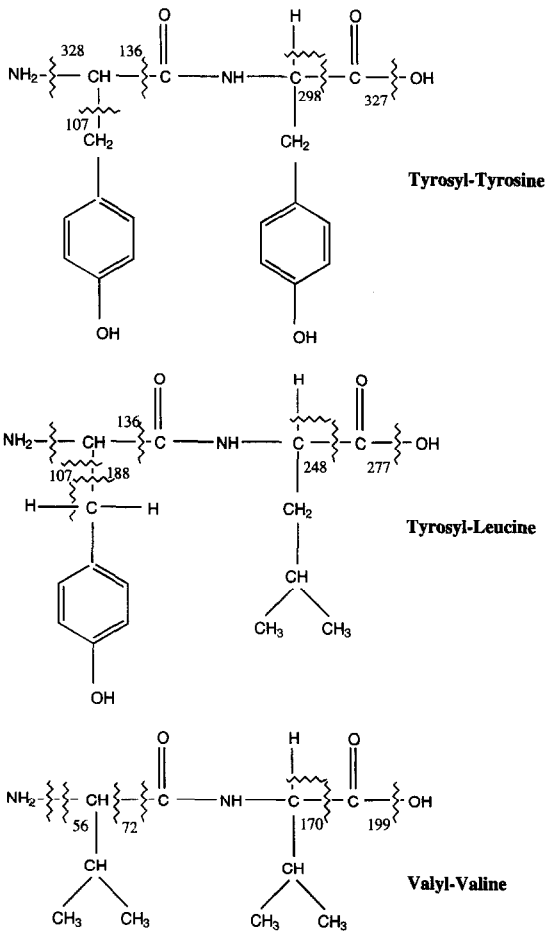
power density from the nanosecond laser is insufficient to bring about a 2-photon nonresonant ionization of Val-Val via a laser-induced virtual state. At these power densities, coherent, nonresonant processes are very inefficient and the presence of a chromophore seems to be important in providing a real intermediate state sufficiently long-lived for a given molecule to absorb a second photon. Analogues of the amino acid tryptophan are reported to have S_1 lifetimes of the order 10 ns [20] and similar values are expected for peptides [21]. Thermal desorption is expected to result in a broad vibrational and rotational state distribution in the neutral molecules so that the absorption band is significantly broadened compared with cold molecules. This may shorten the intermediate state lifetimes to the subnanosecond time scale and hence reduce the ionization efficiency of nanosecond excitation compared with cold molecules [22].

Excitation with 250-fs pulses (10^{10}–10^{12} W cm^{-2}) produces total ion currents of comparable magnitude for all three dipeptides, independent of their chromophore content. Fig. 2 shows a power plot of the total integrated ion current from Tyr-Leu, Tyr-Tyr, and Val-Val using the Ti:sapphire laser and an approximately equal number of neutral molecules. The three sets of data are within a factor of two in ion count. It is particularly noteworthy and intriguing that the data for Val-Val, a molecule with no chromophore, show very similar ionization efficiency to the aromatic ring-containing molecules. As far as we are aware, this is the first time this observation has been reported. We propose that the role of coherent absorption has increased at these ultrahigh laser intensities to a level whereby it may dominate the ionization process, at the expense of resonant, sequential absorption. This may in part be caused by a rapid AC Stark shift of resonant levels in chromophores. The data sets display a quadratic dependence on the laser intensity at the focus, suggesting we are neither optically saturating an intermediate level (real or virtual) or hole-burning in the neutral cloud. At the power densities used in these experiments optical saturation is not expected where both photons are absorbed with similar cross-sections, which is the case if intermediate state lifetimes are sufficiently long.

The threshold energy density observed for femtosecond MPI (5 mJ cm^{-2}) is significantly less than that for nanosecond MPI (2 J cm^{-2}), implying that for these thermally desorbed dipeptides femtosecond MPI is by far the more efficient process. This is in agreement with the findings of other groups working with sputtered molecules of this type [8,10]. In our experiments no ion yield was observed with the nanosecond laser at pulse energies equal to the maximum output of the femtosecond laser, so a comparison of nanosecond versus femtosecond ionization efficiency at equal pulse energy was not possible. In studying the effect of pulse duration on ionization efficiency the bandwidths of the two lasers must also be considered. The Ti:sapphire laser has a much wider bandwidth (>500 cm^{-1}) than the Nd:YAG laser (<1.0 cm^{-1}) and therefore the possibility exists of resonantly exciting a greater proportion of the vibrational distribution of the neutral ensemble. This will enhance the ionization efficiency of femtosecond MPI relative to nanosecond MPI for thermally desorbed or sputtered molecules.

3.2. Nanosecond versus femtosecond fragmentation

Molecular ions ($M^{+\cdot}$) are observed in the femtosecond spectra even at the highest laser intensity. In general, the most intense fragments in the low power femtosecond spectra arise from losses of small groups



Scheme 1. Simple bond cleavages arising from MPI of the dipeptides studied.

such as OH, NH_3, NH_2COOH, and HCOOH. Simple bond cleavages adjacent to the carbonyl group of the peptide chain to form N-terminal acyl-iminium (immonium) and, 28 mass units higher, acylium ions are also apparent, although both these fragments are less intense. No C-terminus containing fragments are seen in either the nanosecond or femtosecond MPI mass spectra. This is in agreement with other MPI studies on dipeptides where a few C-terminal fragments were only detected from much larger peptides [23].

The loss of small groups such as OH and NH_3 from the molecular ion is not observed in the nanosecond MPI mass spectra. The degree of fragmentation observed at threshold laser powers in the nanosecond MPI spectra is much greater than in the femtosecond spectra.

Scheme 1 illustrates the simple bond cleavages leading to the formation of some of the high mass fragments observed in the MPI mass spectra. The relative abundances of the higher mass multiphoton ionization and dissociation (MPID) products obtained from the dipeptides under the softest conditions using 5-ns (2 J cm^{-2}) and 250-fs (5 mJ cm^{-2}) laser pulses are shown in Table 1.

Differences in the mass spectra obtained with either nanosecond or femtosecond laser pulses are also observed at the highest laser power densities. At 1×10^{12} W cm^{-2} the femtosecond laser is capable of

Table 1
Relative abundances of dipeptide multiphoton ionization products resulting from 5-ns and 250-fs laser pulses at threshold power density

	Fragment						
	M	M-NH_2	M-OH or M-NH_3	M-H_2O	M-HCOOH	M-NH_2COOH	Immonium
Tyr-Tyr							
m/z	344	328	327	326	298	283	136
ns	—	—	—	—	—	—	91
fs	1	4	33	99	100	74	12
Tyr-Leu							
m/z	294	278	277	276	248	233	136
ns	—	—	—	—	—	—	21
fs	8	16	100	82	28	85	48
Val-Val							
m/z	216	200	199	198	170	155	72
fs	7	—	10	—	100	28	70

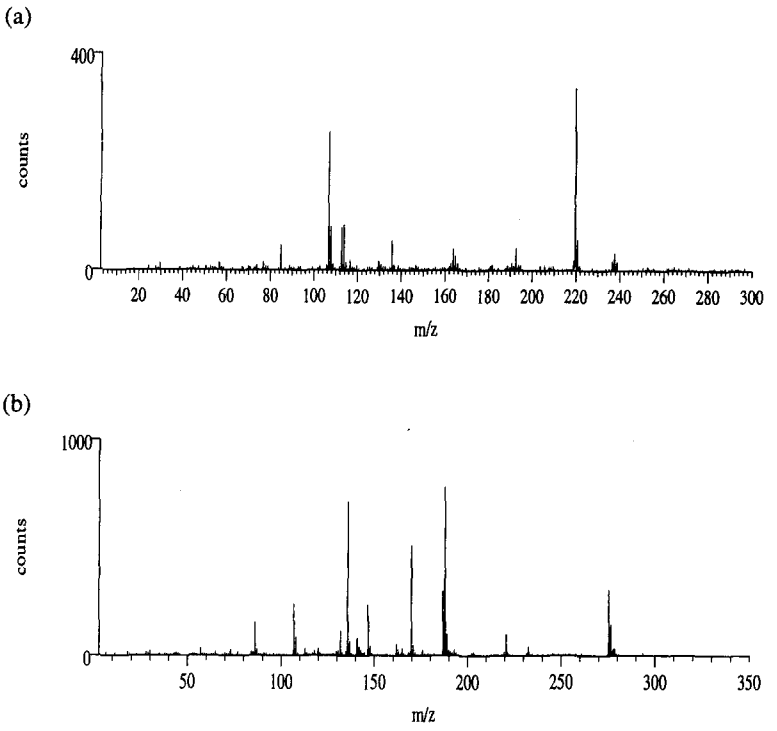
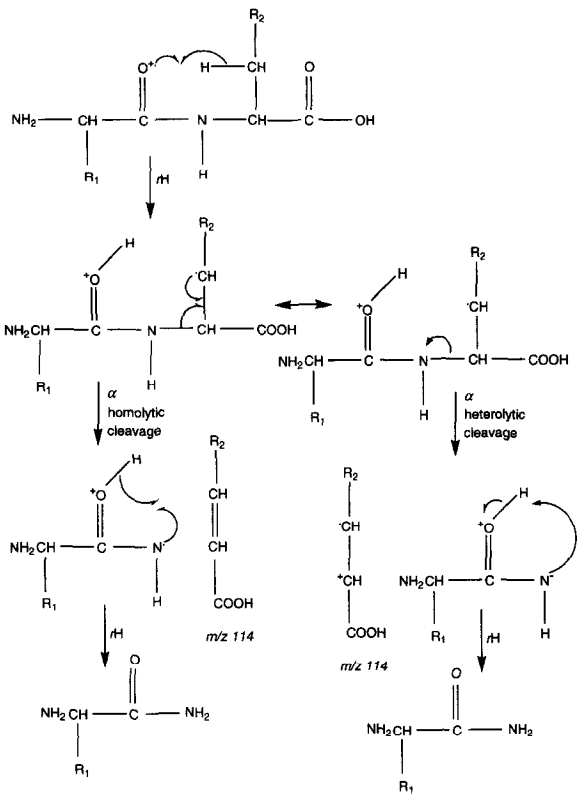


Fig. 3. Nanosecond MPI mass spectra at threshold laser power density (2 J cm^{-2}). (a) Tyr-Leu and (b) Tyr-Tyr.

producing relatively large ion signals from atomic carbon (1st IE = 11.26 eV) and hydrogen (1st IE = 13.60 eV) in these dipeptides. At the highest available power density (1×10^9 W cm^{-2}), the smallest fragment detected with the nanosecond laser is C_2H_3. This implies that although the maximum energy density obtained from the femtosecond laser under our conditions (0.3 J cm^{-2}) was of a factor 50 less than that obtained with the nanosecond laser (15 J cm^{-2}), the average energy deposited in a target molecule by a femtosecond pulse could far exceed that of the nanosecond pulse. This can be rationalized by considering the relative power densities in the femtosecond and the nanosecond laser pulse. In femtosecond MPI energy deposition is more efficient than in nanosecond MPI because of the increased absorption rate at the very high peak power density. With femtosecond MPI capable of producing a wider range of fragmentation levels (i.e. softer or harder ionization), it can be said that it is a more tuneable photodissociation method than nanosecond MPI.

There are a number of fragment ions observed only in either the nanosecond or femtosecond MPID spectra. This suggests that the fragmentation mechanism may be dependent on the time scale of the laser pulse.

The nanosecond MPID mass spectrum of Tyr-Leu (Fig. 3(a)) contains ions that result from fragmentations at sites removed from the chromophoric tyrosyl residue. For example, the highest mass observed is *m/z* 237 ($M\text{-}C_4H_9$) because of the loss of the leucyl side chain. Further loss of OH or NH_3 results in the base peak of the nanosecond MPID mass spectrum at *m/z* 220. This implies that the energy deposited in the chromophore by the absorption of the first photon is redistributed throughout the molecule before the second photon is absorbed. This conclusion is supported by the lack of *m/z* 188 from loss of the chromophoric tyrosyl (C_7H_7O) group. There are two routes by which the ($M\text{-}C_4H_9$) ion can be formed. Either the excited neutral parent (M*) can fragment at the 1-photon level to give a neutral fragment that subsequently absorbs a second photon and ionizes or dissociative ionization



Scheme 2. Type H elimination of an amide group from a dipeptide. Tyr-Leu: $R_1 = C_7H_7O$, $R_2 = C_3H_7$.

of M* occurs at the 2-photon level. No intact molecular ions are observed in the nanosecond mass spectra at any power density, so a 3-photon process involving photoionization followed by photolysis of $M^{+\cdot}$ to form the $(M\text{-}C_4H_9)^+$ ion is thought unlikely. As the power density is reduced to a threshold level for ion production, the absorption of excess photons can be neglected, according to the rules governing multiphoton excitation. Under these conditions therefore the observed fragments can be assumed to originate from processes of the same photon-order as the ionization.

The fragment ion at *m/z* 114 in the nanosecond MPID mass spectrum is thought to arise from a charge site-initiated rearrangement mechanism (Scheme 2). A positive charge located on the oxygen of the amide bond promotes migration of a γ-hydrogen (as in the McLafferty rearrangement). The N–C bond then undergoes α-cleavage to produce an amide and a carboxylic acid. If the N–C bond cleaves via a heterolytic mechanism, a radical cation at *m/z* 114 is formed directly. If the cleavage is homolytic, a neutral carboxylic acid is produced that could then absorb subsequent photon(s) and ionize. The *m/z* 114 fragment in the nanosecond mass spectrum may be formed from either of these ionization–dissociation mechanisms. Alternatively, the *m/z* 114 ion could arise from a dissociation–ionization mechanism involving M*.

The femtosecond mass spectrum (Fig. 4(a)) does not contain the *m/z* 114 ion. This implies that an $M^{+\cdot}$ species in which the charge is located on the carbonyl oxygen is not formed by the femtosecond laser pulse, because this would lead to radical ions at *m/z* 114 via rearrangement and homolytic cleavage even if the timescale of the process meant that additional photons were not available from the 250-fs pulse. An alternative site for the positive charge is within the aromatic ring of the tyrosyl chromophore. This situation would be favored if the ionization rate exceeded the rate of intramolecular vibrational redistribution (IVR). A mechanism whereby the photon energy was concentrated in the immediate vicinity of the chromophore would most likely lead to fragmentations adjacent to that site. The femtosecond spectrum of Tyr-Leu provides evidence to support this mechanism. For example, the appearance of $(M\text{-}NH_2)^{+\cdot}$, $(M\text{-}OH)^{+\cdot}$, $(M\text{-}NH_3)^{+\cdot}$, and $(M\text{-}H_2O)^{+\cdot}$ can all arise from fragmentations near the tyrosyl residue. The loss of the entire chromophore gives rise to a fragment at *m/z* 188 $(M\text{-}C_7H_6O)^{+\cdot}$. These ions are among the most intense fragments in the femtosecond MPI mass spectra of Tyr-Leu but are not observed with the nanosecond laser pulse at any available power density. The femtosecond mass spectrum of Tyr-Leu does not contain the $(M\text{-}C_4H_9)^+$ fragment ion because of the loss of the leucyl side chain or the *m/z* 220 ion, which is again consistent with a more localized energy distribution at the tyrosyl end of the molecule.

The appearance of immonium and acyl-iminium ions in the femtosecond MPID spectra suggests that there may be partial IVR from the tyrosyl ring even with these extremely fast photon pumping rates, or that the carbonyl group itself may also display some

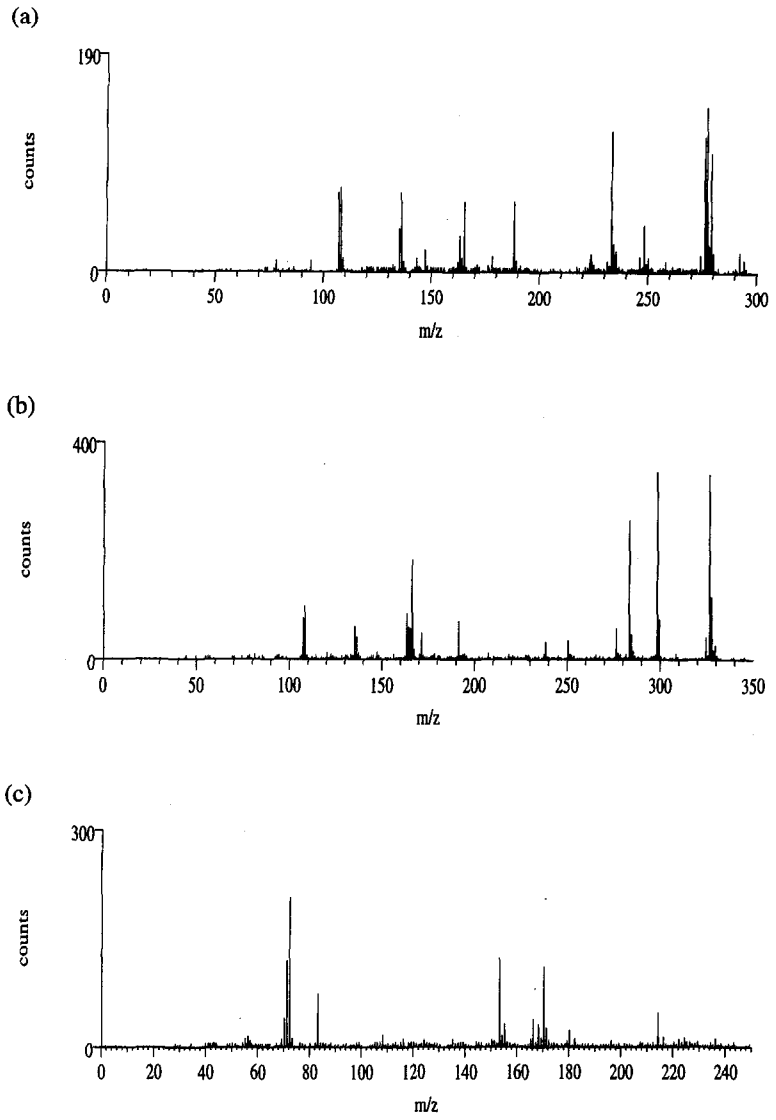
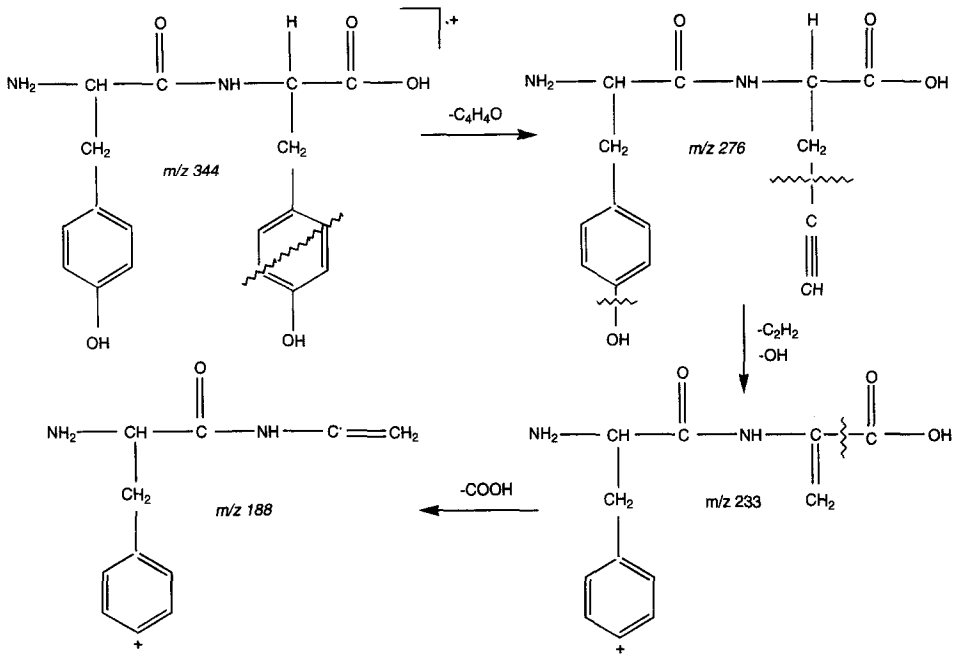


Fig. 4. Femtosecond MPI mass spectra at threshold laser power density (5 mJ cm^{-2}). (a) Tyr-Leu, (b) Tyr-Tyr, and (c) Val-Val.

chromophoric character toward the applied wavelength.

In the case of Tyr-Tyr, the loss of the tyrosyl side chain and an OH or NH_3 group leads to the formation of the *m/z* 220 fragment. This fragment has been observed with either 5 ns or 250 fs excitation, implying that the rate of the required energy redistribution can compete even with the pumping rate of the femtosecond laser pulse. This is not surprising considering that the fragmentation required to form *m/z* 220 is adjacent to one of the chromophoric groups. Another fragment apparent in both nanosecond and femtosecond MPID mass spectra of Tyr-Tyr is seen at *m/z* 276 [Figs. 3(b) and 4(b)]. The structure of this $(M\text{-}68)^+$ species is not certain, but we suggest that this fragment may arise from a ring cleavage and subsequent loss of C_4H_4O from the molecular ion (Scheme 3). Once one of the rings is cleaved the molecule is left with only one chromophore, and the competition between the rate of energy migration and



Scheme 3. Proposed MPI fragmentation pathway for Tyr-Tyr using 5-ns and 250-fs laser pulses at 266 nm.

the rate of photon absorption can again determine the fragmentation pattern. Assuming *m/z* 276 is represented correctly by the structure in Scheme 3, the further loss of C_2H_2 and OH and then COOH yield fragments with *m/z* 233 and *m/z* 188, which are seen in the nanosecond mass spectra only. Indeed, *m/z* 188 forms the base peak in the nanosecond spectrum [Fig. 3(b)]. Additional evidence for the mechanism suggested in Scheme 3 comes from the observation of fragments at *m/z* 170 and *m/z* 147, which are observed with significant intensity only in the nanosecond mass spectra. These ions may be formed from the *m/z* 188 fragment, by loss of H_2O, or the end group NHC = CH_2, respectively. These fragmentations leading to the structures proposed for *m/z* 233 and *m/z* 188 occur at sites removed from the remaining chromophore and probably involve subsequent photon absorption(s) to be energetically favorable. This is consistent with efficient IVR within the timescale of the 5-ns laser pulse. The fragments that are specific to the femtosecond spectra such as $(M\text{-}NH_2)^{+\cdot}$, $(M\text{-}OH)^{+\cdot}$, $(M\text{-}NH_3)^{+\cdot}$, and $(M\text{-}H_2O)^{+\cdot}$ are considered most likely to arise from dissociative photoionization in the immediate vicinity of the chromophores.

It is interesting to observe that having successfully ionized Val-Val, the nonresonant femtosecond MPI mass spectrum shows a similar degree of fragmentation as those of the chromophore-containing molecules [Fig. 4(c)]. The immonium ion (*m/z* 72) forms the base peak of the spectrum, but, unlike the tyrosyl-containing compounds, no acyl-iminium ion (*m/z* 100) is observed in the Val-Val spectra. Fragmentation reactions leading to acyl-iminium ions are particularly intense in the vicinity of aromatic residues [23]. The lack of aromaticity in Val-Val may explain why the *m/z* 100 fragment is not seen from this molecule.

4. Conclusions

This work further illustrates that multiphoton excitation of neutral molecules and ions with ultrashort, high intensity, laser pulses can lead to reduced fragmentation and increased molecular information relative to nanosecond multiphoton excitation. This suggests that many photodissociation pathways are effectively bypassed by the application of femtosec-

ond excitation. No molecular ions could be produced from any of the dipeptides using nanosecond pulses at any power density. Using the femtosecond laser molecular ions were observed over the full range of available power densities (10^{10}–10^{12} W cm^{-2}). Some fragmentation channels, however, are still open even when using 250-fs ionization pulses. It is unclear whether these fragmentation channels originate from the excited neutrals or molecular ions. However, it has been shown that several fragmentation mechanisms depend on the duration of the excitation pulse. This observation may be rationalized by considering the competition between intramolecular vibrational energy redistribution and ionization. Assuming that the preferred site for photon absorption in these systems is the tyrosyl ring, vibrational energy migrates through the molecule and, provided the ionization rate is not too large, fragmentation can result at sites far removed from the chromophore. As the laser power density and the ionization rate increase, slow fragmentation pathways involving atomic transfer or energy migration over relatively long distances will no longer be able to compete and fragmentation local to the chromophore is more likely. Our results suggest that the timescale for vibrational energy redistribution within the Tyr-Leu system is between 5 ns and 250 fs, and in the Tyr-Tyr system it is <250 fs.

From the differences in the observed threshold energy density we conclude that femtosecond MPI is significantly more efficient at producing ions from these thermally desorbed dipeptides than nanosecond MPI.

New evidence, presented here, suggests a reduced importance of resonance-enhancement for femtosecond MPI compared with nanosecond MPI in this series of molecules, implying that the ionization efficiency of ultrashort pulses depends to a much lesser degree on molecular structure. This may be due to a growth in coherent photon absorption rates and shifts in resonant levels at laser intensities >10^{10} W cm^{-2}.

Acknowledgements

The authors would like to thank Professor Nick Winograd of the Pennsylvania State University for use of the Ti:sapphire system and Chris Brummel and Ken Willey for assistance in acquiring the femtosecond data. The financial support of the EPSRC is gratefully acknowledged.

References

[1] J. Grotemeyer, K. Walter, U. Boesl, E.W. Schlag, Int. J. Mass Spectrom. Ion Processes 78 (1987) 69.
[2] R. Trembreull, D.M. Lubman, Anal. Chem. 59 (1987) 1003.
[3] D.M. Hrubowchak, M.H. Ervin, N. Winograd, Anal. Chem. 63 (1991) 225.
[4] M. Terhorst, G. Kampwerth, E. Niehuis, A. Benninghoven, J. Vac. Sci. Technol. A10 (1992) 3210.
[5] L. Li, D.M. Lubman, Appl. Spectrosc. 43 (1989) 543.
[6] F. Rebentrost, K.L. Kompa, A. Ben-Shaul, Chem. Phys. Lett. 77 (1981) 394.
[7] J. Silberstein, R.D. Levine, J. Chem. Phys. 75 (1981) 5735.
[8] R. Möllers, M. Terhorst, E. Niehuis, A. Benninghoven, Org. Mass Spectrom. 27 (1992) 1393.
[9] S. Wei, J. Puernell, S.A. Buzza, R.J. Stanley, A.W. Castleman, J. Chem. Phys. 97 (1992) 9480.
[10] C.L. Brummel, K.F. Willey, J.C. Vickerman, N. Winograd, Int. J. Mass Spectrom. Ion Processes 143 (1995) 257.
[11] R. Weinkauf, P. Aicher, G. Wesley, J. Grotemeyer, E.W. Schlag, J. Phys. Chem. 98 (1994) 8381.
[12] K.P. Aicher, U. Wilhelm, J. Grotemeyer, J. Am. Soc. Mass Spectrom. 6 (1995), 1059.
[13] K.W.D. Ledingham, H.S. Kilic, C. Kosmidis, R.M. Deas, A. Marshall, T. McCanny, R.P. Singhal, A.J. Langley, W. Shaikh, Rapid Commun. Mass. Spectrom. 9 (1995) 1522.
[14] M.J. DeWitt, D.W. Peters, R.J. Levis, Chem. Phys. 218 (1997) 211.
[15] M.J. DeWitt, R.J. Levis, J. Chem. Phys. 102 (1995) 8670.
[16] K.W.D. Ledingham, R.P. Singhal, Int. J. Mass Spectrom. Ion Processes 163 (1997) 149.
[17] C.R. Ayre, L. Moro, C.H. Becker, Anal. Chem. 66 (1994) 1610.
[18] E.T.M. Selim, M.A. Rabbih, M.A. Fahmey, Org. Mass Spectrom. 22 (1987) 381.
[19] J. Grotemeyer, E.W. Schlag, Acc. Chem. Res. 22 (1989) 399.
[20] J. Sipior, M. Sulkes, R. Auerbach, M. Boivineau, J. Phys. Chem. 91 (1987) 2016.
[21] J.R. Cable, M.J. Tubergen, D.H. Levy, J. Am. Chem. Soc. 110 (1988) 7349.
[22] S.J. Formosinho, J. Chem. Soc., Faraday Trans. 70 (1974) 605.
[23] J. Grotemeyer, E.W. Schlag, Org. Mass Spectrom. 23 (1988) 388.