MEASUREMENTS OF ION DISSOCIATION IN A REFLECTING TIME-OF-FLIGHT MASS SPECTROMETER

K. Standing, W. Ens, Y. Mao, F. Lafontune, F. Mayer, N. Poppe, B. Schueler, Xing Tang, J. Westmore

To cite this version:

HAL Id: jpa-00229426
https://hal.archives-ouvertes.fr/jpa-00229426
Submitted on 1 Jan 1989

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
MEASUREMENTS OF ION DISSOCIATION IN A REFLECTING TIME-OF-FLIGHT MASS SPECTROMETER


Physics* and Chemistry** Departments, University of Manitoba, Winnipeg, R3T2N2, Canada

Résumé-Des mesures corrélées ont été effectuées entre les fragments neutres et ionisés provenant des décompositions des ions parents dans l'espace libre de champ d'un spectromètre de masse à temps de vol. Cette méthode permet de déterminer les masses des fragments ionisés en plus de générer de l'information au sujet des modes compétitifs de décompositions. La méthode a été utilisée pour la tyrothricine, un mélange de décapeptides cycliques de masse ~1300u. Des mesures préliminaires concernant la photodécomposition d'un dérivé peptidique dinitrophényle (masse ~1000u) ont été réalisées dans le même spectromètre au moyen d'un laser excimer pulsé à 308 nm.

Abstract - Correlated measurements have been made of neutral and charged daughters from decomposition of parent ions in the flight tube of a reflecting time-of-flight mass spectrometer. This determines daughter ion masses and gives information about the decay paths. The method has been applied to tyrothricin, a mixture of cyclic decapeptides of masses ~1300u. Preliminary measurements have been carried out in the same spectrometer on the photodecomposition of a dinitrophenyl peptide derivative (mass ~1000u) by 308 nm pulses from an excimer laser.

Installation of an ion mirror in a time-of-flight (TOF) mass spectrometer enables measurement of daughter ion masses from a parent that decomposes in the first leg of the flight path [1-3]. A detector behind the mirror measures the flight time of the neutral fragment arising from the decay, thus identifying the parent ion. The flight time of the correlated charged fragment, measured in a second detector at ~180°, then determines its mass. The unimolecular decay of several small peptides has been examined [4] in a reflecting TOF spectrometer of this type, shown in Fig. 1 [3]. We have recently extended these measurements to some simple mixtures [5].

Fig. 1 - The reflecting TOF spectrometer (Manitoba TOF II)[3] with the addition of a laser beam to photodissociate the ions after acceleration.
The antimicrobial agent tyrothricin provides a more complex sample; it is a mixture of cyclic decapeptides of masses ~1300 u. With the mirror voltage off, the instrument acts as an ordinary linear TOF spectrometer, so a spectrum of parent ions plus charged and neutral daughters is observed in detector 1 behind the mirror; Fig. 2 shows the molecular ion region. When the mirror voltage is turned on, the charged particles are reflected through ≈177° into detector 2, yielding the spectrum shown in Fig. 3. Clearly the reflecting spectrometer gives a dramatic improvement in resolution and in signal/background ratio. The resolution has not been fully optimized, but it is sufficient to partially resolve the isotopic contributions. As reported by Barber et al [6], six minor components are visible in the mixture in addition to the three well-known major constituents. Our masses agree with Barber's values [6], although there are some differences in the relative intensity of the various components.

![Fig. 2. The molecular ion region of the tyrothricin spectrum observed in detector 1 with the mirror voltage off.](image1)

![Fig. 3. The same spectral region as in Fig. 2, observed in detector 2 with the mirror voltage on.](image2)
Fig. 4 The same spectral region as Fig. 2, observed in detector 1 with the mirror voltage on.

Fig. 5 Charged particle spectrum in detector 2 correlated with neutral fragments in detector 1 arriving in a time window centred on the tyrocidin A molecular ion peak.

Fig. 6 Charged particle spectrum in detector 2 correlated with neutral fragments in detector 1 arriving in a time window centred on the tyrocidin B molecular ion peak.
The corresponding spectrum of neutral fragments is observed in detector 1 with the mirror on; the flight time of a neutral fragment identifies its parent ion [1-3]. This spectrum is shown in Fig. 4, where the peaks correspond to those in Fig. 2, but are broader, since the relatively sharp parent ion contributions have been removed. However, the resolution is sufficient to give considerable discrimination between the various components. Fig. 5 shows a portion of the charged particle spectrum in detector 2 that is correlated with neutral fragments in detector 1 arriving in a window centred on the tyrocidin A peak. Fig. 6 shows the corresponding spectrum correlated with neutral fragments in the tyrocidin B peak. The two spectra have the same pattern but the latter is displaced by 38u, as might be expected. As remarked by Cody et al [7], the daughter ion spectra of such cyclic peptides are complicated, since a multiplicity of initial ring cleavages is possible. However, considerable structural information can be extracted from Figs. 5 and 6, including the sequence shown, which is consistent with the structure previously proposed [6].

![Graph](image_url)

**Fig. 7** Reflected spectra of N-2,4-Dinitrophenyl-Pro-Gln-Gly-Ile-Ala-Gly-Gln-p-Arg in the molecular ion region (a) without the laser; (b) with a laser beam of $\sim 2.1 \times 10^7$ W/cm$^2$ intersecting the secondary ion beam after acceleration.
The above measurements deal with the daughters produced by metastable decay in the first leg of the flight path. Alternatively it is possible to dissociate parent ions by collision or by photon bombardment. We have carried out some preliminary measurements of dissociation produced by the latter effect. An excimer laser (308nm, ~10 ns pulses at 400 Hz) is focused to a cross sectional area of ~1 mm x 3 mm where it intersects the secondary ion beam 2.2 cm above the accelerating grid. Fig. 7 shows the reflected spectrum of a dinitrophenyl peptide derivative in the molecular ion region observed, (a) without the laser, and (b) with a beam of intensity ~ 2.1 x 10^7 W/cm². Most of the molecular ions are seen to be dissociated by the photon beam. Fig. 8 shows the molecular ion yield as a function of laser intensity; the molecular ion disappears altogether at about 3 x 10^7 W/cm². Measurements on the correlated daughters are currently in progress.

This work was supported by grants from the US National Institutes of Health (Institute of General Medical Sciences), and from the Natural Sciences and Engineering Research Council of Canada. One of us (F.M.) gratefully acknowledges partial support from the Deutsche Forschungsgemeinschaft.