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A NEW METHOD FOR METASTABLE ION STUDIES WITH A TIME OF FLIGHT MASS SPECTROMETER. FUTURE APPLICATIONS TO MOLECULAR STRUCTURE DETERMINATIONS.

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A NEW METHOD FOR METASTABLE ION STUDIES WITH A TIME OF FLIGHT MASS SPECTROMETER.

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Abstract : This paper describes a coincidence method for studying metastable ion decompositions with a ^{252}Cf time of flight mass spectrometer. An electrostatic mirror is used to reflect ions which are detected by a set of annular channel plates while neutrals resulting from "in flight" decompositions are counted by channel plates placed behind the mirror. Two simultaneous time of flight (T.O.F.) measurements (ions and neutrals) are recorded event by event using the same start signals. Therefore correlated reflex spectra can be obtained by setting electronically time "windows" on the neutral T.O.F. These windows correspond to masses which have decayed in flight. The charged fragments are then selected in the reflex spectra by this method of coincidences. In flight decays can therefore be identified. Others ionization-desorption techniques can be used as well. A few simple examples are presented.

Time of flight (TOF) techniques have been used for many years at our laboratory in several different types of experiments mainly relevant to nuclear physics (1-4). In these experiments, multiparameter coincidence measurements are routinely made and data acquisition systems as well as fast timing electronics have been developed (5-8). Applications of these techniques to time of flight mass spectrometry or organic compounds, with a new TOF mass spectrometer (9), have been recently made with success. In particular, metastable ion studies, using the coincidence method, have been useful to elucidate and/or to confirm structures of organic compounds (10) (11). The purpose of this paper is to describe and to illustrate this method with a few simple examples.

EXPERIMENTAL METHOD

1. Generalities

We have constructed a ^{252}Cf time of flight mass spectrometer with an electrostatic mirror. A description of the system has already been reported (9) ; it is designed with an axial symmetry and annular channel plate detectors have been built for the spectrometer. A schematic diagram illustrates the system in fig. 1.

Two simultaneous time of flight measurements are recorded event by event using the same start signal. We call the "neutral TOF spectrum" the spectrum corresponding to "stop signals" coming from the detector placed behind the mirror. This detector is hit by neutrals only. The "reflex spectrum" is the TOF spectrum of ions which have been reflected by the mirror. This system can also be run as a standard ^{252}Cf mass spectrometer. This is obtained simply by not operating the electrostatic mirror, neutrals and ions are then both detected by the detector 2 (see fig. 1). It is extremely interesting to measure the rate of fragmentation in flight of any given organic molecule. An example is given in figure 2 (a.b) ; fig. 2a shows the molecular ion region peak for the Adenosine molecule (ions + neutrals are counted) which is measured for one minute when the mirror is not active while. Fig. 2b shows the same measurement, for the same time period, with the mirror in operation. In this second measurement, only neutrals due to a in flight decomposition of the adenosine molecule are detected. The ratio of the integrated peaks (neutrals)/(neutrals+ions) immediatly gives the rate of in "flight decomposition". It is about 50 % in the case of adenosine. Similar measurements have been made for many different compounds. In some cases 80 to 90 % decompose in flight. It is therefore very useful to keep the possibility of measuring direct spectra in a "reflex TOF system". It can be seen easily from these spectra (fig. 2) how the metastable decompositions are contributing to the shape of a peak in the molecular mass region. The broadening, caused by the neutrals, is most important at the base of the peaks. This explains why in TOF mass spectrometry, the time of flight resolution is almost always measured by taking the full width at half maximum of the peaks.

With the mirror operating a transmission of more than 50 % is now obtained for cesium iodide clusters, and a mass resolution $M/\Delta M = 3000$ is achieved for these ions. For organic molecular ions the transmission

factor which can reach 50 % depends mainly on the rate of metastable decay - as discussed above - in the first field free region. This system has been built for two reasons :

i) The first one is to achieve better mass resolution. It is clear that the results are spectacular if we look at fig. 3 which shows spectra of the same molecule obtained with a standard ^{252}Cf mass spectrometer and with the electrostatic mirror in operation. These two spectra have been recorded within a few minutes. The mass assignment of the molecule α solanine($(M+H)^+$ = 867,8) deduced from the value of the centroid of the TOF peak (fig. 3a) was not the expected chemical mass value (M+H) = 869,07. The reason for the difference is explained by the reflex spectrum measurement (fig. 3b) which shows for the molecular region peaks a relatively high contribution of $(M-H)^+$. The centroid of the peak of the direct spectrum could not give in this case a correct mass value. Results from the reflex spectrum have therefore been useful to confirm the exact mass. There is no doubt that an improved mass resolution is often necessary in TOF instruments. However, for heavy molecules (MW > 3000) the complexity of the molecular ion peak region makes an extremely good mass resolution less important. Calculation of peak centroids of the molecular ion region can give the chemical molecular weight, which, in most cases, is sufficient. That method is currently used in PDMS for measurements of molecular weight above 5000 u (12).

ii) The second and probably the most important reason is to permit the study of metastable ions. The method can be improved and developments are in progress at our institute where several time of flight instruments are in operation.

2. The coincidence method for metastable ion studies

Although we are interested in metastable decays in the field free region, let us mention briefly the different cases already described

by B. Chait and F. Field (13). If the decay $m^+ \rightarrow m_1^+ + m_0$ occurs on the sample during the passage of a fission fragment or slightly after, $10^{-15} < t < 10^{-9}$ sec, then the ionization fragments m_1^+ will appear as very sharp lines at time t_1 in the reflex spectrum (fig. 4b). If the decay takes place during the acceleration step, the time scale depends on the mass and on the acceleration voltage, but is typically around 10^{-7} sec. The remaining ion m_1^+ which will have gained a lower kinetic energy will then contribute to a tail and background appearing at times larger than t_1.

When the rupture $m_1^+ \rightarrow m_{1s}^+ + m_0$ takes place in the field free region and if one does not consider for the moment the energy released in the breaking process then the kinetic energies of the fragments m_{1s}^+ and m_0 are :

$$E_{m_{1s}} = E_{total} \cdot \frac{m_1}{m}$$

$$E_{m_0} = E_{total} \cdot \frac{m_0}{m}$$

We call m_{1s}^+ the mass of the charged fragment for a decay occuring in flight. The mass m_0 will hit the neutral detector at a time t corresponding to the time of flight of the molecular ions m^+ since the total velocity is conserved after the break-up. The charged fragment will also retain the same velocity but the time spent in the reflecting region will be smaller than that of the molecular ion m^+ with identical velocity. The reason is that the energy of the fragment m_{1s}^+ is smaller than m^+, and the m_{1s}^+ ion will be bounced back inside the mirror at a potential $U_1 = E_{m1s}$ at a distance d_1, instead of U, at a distance d (see fig. 4). The time $t_{m_{1s}^+}$ (metastable) is thus smaller than t_{m^+} but larger than $t_{m_1^+}$. The result is that a metastable in flight decomposition will give rise to a peak located in time between t_{m^+} and $t_{m_1^+}$.

It is much simpler to operate the spectrometer in the coincidence mode with the two first grids of the mirror on ground. The mass resolution is then not as good as with the second grid at $U_G = 2/3\ U_{total}$ but the metas-

table mass calibration is much easier. Indeed , the mass calibration for metastable ions is different than for ions emitted from the sample. The total time difference for the two ions m^+ and m_{1s}^+ of the same velocity can be calculated from the time difference due to their passage in the mirror. The TOF for m^+ in the mirror is :

$$T_{m^+} = 2d\sqrt{\frac{m}{2U}}$$

and for m_{1s}^+ $$T_{m_{1s}^+} = 2d_1\sqrt{\frac{m_1}{2U_1}}$$

thus $$\Delta T = \frac{2\sqrt{m}}{\sqrt{2U}}(d - d_1)$$

since $$\frac{U_1}{U} = \frac{d_1}{d} = \frac{m_{1s}}{m}$$

$$\Delta T = \frac{2\sqrt{m}}{2u} d \frac{(m-m_{1s})}{m} \quad \text{and} \quad m - m_{1s} = K\sqrt{m}\,\Delta T \qquad (1)$$

and the mass m_1 is deduced from the measurement of the time difference between centroids of the peaks at t_{m^+} and $t_{m_{1s}^+}$.

However, U and d are not known with sufficient precision to obtain enough accuracy on mass m_{1s}^+ . For identifying complex decomposition, it is therefore prefereable to use an internal time calibration (as done for direct spectra with H^+ and Na^+). This can be achieved by using well known metastable decay reactions as described in the last section. In the reflex spectrum we have what we call the "normal" peaks (m_1^+ and m^+ emitted from the sample in the case considered here) and additional peaks which originate from in flight decay. These peaks are the most interesting events for elucidating structures. They are sometimes weak , depending on the decomposition rate but their origin (andeven their existence) can be revealed from the analysis of the coincidence data.

Before going into further details it is important to realize that the energy released during the fragmentation will change both the trajectories and velocities of the fragments. This isotropic process is schemati-

cally shown in fig. 5 : m_{1s}^+ has its trajectory changed by an angle ϑ_1 and the axial velocity is modified. The result is a broadening of the metastable peaks, which is more important if the ratio m_{1s}^+/m is small because of the momentum transfer . The width of the peaks could give information on the kinetic energy ΔE involved in the breaking processes, but it also depends on the locus of fragmentation on the flight path. Thus only lower limits of ΔE could be extracted. Such values have been obtained in ref. (13) with a TOF instrument using retarding potentials for metastable studies.

Fig. 4c shows that it is possible for a decay occuring in flight to register one event in the neutral spectrum and one event, due to the complementary charged fragment, in the reflex spectrum. The two spectra are then correlated since for any event in the neutral spectrum at time t_{m_0} (parent ion) which indicates that a decay has occured, there is a correlated event at time $t_{metastable} = t_{m_{1s}}$ in the reflex spectrum. (For better understanding we suppose a total efficiency of 100 % (detection + transmission)). In this simple case, data acquisition can be made by setting a time window around t_{m_0} on the neutral spectrum in order to select in the reflex spectrum only events which correspond to flight times of the charged fragment after the decomposition $m = m_0 + m_{1s}^+$. The reflex spectrum in coincidence will therefore exhibit a peak centered around $t = t_{m_{1s}}$. The value of the mass m_1 can be deduced from this time value. We have just described an ideal case. In practise, because of multi-desorption events, the coincidence spectrum will show the main peaks already observed in the uncorrelated reflex spectrum. However, relative ratios between peaks in the coincidence spectrum will be completely changed and the intensity of the metastable peaks will be very much enhanced.

We have described the most simple case $m^+ \rightarrow m_{1s}^+ + m_0$, but decomposition of the parent ion in many fragments can exist. In that case, several metastable peaks are observed in the reflex spectrum. On the other hand, many peaks can also exist in the neutral spectrum. They correspond to

fragment ions emitted from the surface of the sample and these ions may also decay in flight. Several time windows can therefore be set on the neutral spectrum during data acquisition. Each time window will be correlated to one specific reflex spectrum with eventually many metastable peaks in each spectrum. This method with several windows is used at the laboratory for complexe cases (8).

The measurements have to be made in two steps. Neutral and reflex spectra are first recorded during a short time to know in advance how and where to set the time windows on the neutral spectrum in order to display directly during the second measurement the correlated reflex spectra. Another possibility is to record all events on a magnetic tape. Many samples can be measured successively. Later on, the magnetic tape is read by the computer and events are classified (according to the windows which are defined "off line") in order to constitute the different metastable reflex spectra.

The electronics used is composed of standard equipment and the computer is a PDP 11-34. The electronic diagram is shown in fig. 1. We have used in these experiments a time to amplitude converter (TAC) module for recording the neutral spectra. In the future a second TDC will be used. The advantage of a (TAC) is that this module accepts for each start only one stop event in the neutral spectrum. The microprocessor of pretreatment ("Mipre") allows to record up to 16 parameters simultaneously. Correlated events and windows are defined with the PdP computer and several correlated spectra can be displayed on the same screen during data acquisition. A Camac parallel interface will include in the very near future two TDC, one or two ADC and a "Mipre" with functions of pretreatment specially adapted to metastable ion studies.

3. Results

We have selected three different relatively simple molecules to demonstrate the potentiality of the method : adenosine, guanosine and 7-methyl guanosine. These molecules are formed of a nucleic base and a sugar and it is known that the rupture of the nucleosidic bond is easily observed in mass spectrometry since the main observed peaks in a normal positive spectrum are the base $(B+2H)^+$ and the molecular ions : $(M+H)^+$, $(M+Na)^+$.

B. Chait et al. (14) have studied with a ^{252}Cf mass spectrometer the decomposition of several compounds. Decompositions similar to that observed by these authors have been seen in our "direct spectra" of nucleosides. However in flight decomposition can be very different from "prompt decomposition". This is a delayed process and the rate and the mode of in flight fragmentation of a single molecule depends on the degrees of freedom for the dissipation of the excess of internal energy. The coincidence method is certainly very appropriate for these studies. Negative coincidence spectra can also be investigated by this method.

Adenosine

Fig. 6a shows the neutral spectrum with the masses 268 and 136 which indicates that the two ions observed and accelerated from the sample are 136 and 268. Their presence in this spectrum means that they have decomposed in flight.

The uncorrelated reflex spectrum is shown in figure 6b. A weak broad peak is observed above channel 6312. In fig. 6c which represents a part of the coincidence spectrum this peak is much more visible. It is due to the decomposition $268^+ \rightarrow (B+2H^+) +$ Neutrals. These neutrals are the masses which have contributed to the presence of the peak at 268 in fig. 6a. The two spectra 6b and 6c look very much the same except for the metastable peak. From the construction parameters of the electrostatic mirror (distances, voltage...),

it has been possible to identify this decay. On the other hand this result has been useful to calculate more precisely the parameter K of eq. (1). Further metastable mass calibrations are thus made by using the K value obtained from this measurement.

The reflex spectrum in coincidence with a window on mass 136 in the neutral spectrum is shown in fig. 7a. From the comparison of the two spectra and the relative peak ratios (fig. 7a and 7b) three main "in flight decompositions" are deduced :

a) $18^+ = NH_4^+$

b) $94^+ = (B+2)^+ - 42 = (B+2)^+ - (N \equiv C - NH_2)$

rupture of bonds 1-2 and 6-5

c) $119^+ = (B+2)^+ - 17 = (B+2)^+ - NH_3$

Fig. 7c is obtained by subtracting events which are not "in flight" decompositions. The metastable peaks are more easily observed.

Guanosine

There are four interesting peaks in the reflex mass spectrum of this molecule : $(B+2H)^+ = 152$, $(B+Na+H)^+ = 174$, $(M+H)^+ = 284$ and $(M+Na)^+ = 306$. In fig. 8a, is presented the uncorrelated reflex spectrum. Fig. 8b and 8c correspond respectively to coincidence spectra with mass 306 and mass 284 of the neutral spectra. Data acquisition has been made in a short time and stopped when enough statistics were obtained. The two metastable peaks $284 \rightarrow 152^+ +$ neutrals and $306 \rightarrow 174^+ +$ neutrals are clearly seen. They are not so visible in the total reflex spectrum.

A coincidence window has also been put on mass 152 in the neutral spectrum. Charged fragments with masses 109 and 135 are observed in coincidence. The metastable transitions are

a) $135^+ = (B+2)^+ - 17 = (B+2)^+ - NH_3$

b) $110^+ = (B+2)^+ - 42 = (B+2)^+ - (N \equiv C - NH_2)$

rupture of bonds 1-2 and 3-4

It is seen in fig. 8b-c that the relative ratios of the peaks 152/174 vary with the selected coincidence windows. True coincidences therefore exist between ions emitted from the sample. Protonated ions $(M+H)^+$ are desorbed with high probability with $(B+H)^+$ in the same event. $(M+Na)^+$ ions are also correlated with $(B+Na)^+$. By the coincidence method it is possible to select primary events associated with particular ionization-desorption "exit channels". It would certainly be interesting to correlate with others parameters (multiplicity, electrons emitted from the surface and even light) a given type of in flight fragmentations in order to obtain informations on the desorption processes since it is very likely that the ions in the gaz phase retain the memory of the desorption process. Experiments will be soon performed on this subject.

7-methyl guanosine

As a third simple example we have taken a methylated guanosine. Fig. 10b confirms the known decomposition

$$\underset{298}{(M+H)^+} = \underset{166^+}{(B+2H)^+} + \text{Neutrals}$$

A second window on mass 166 gives fragmentations similar to that observed for the guanosine base with the transitions :

a) $149^+ = (B+2)^+ - 17 = (B+2)^+ - NH_3$

b) $124^+ = (B+2)^+ - 42 = (B+2)^+ - (N \equiv C - NH_2)$

Fig. 11 illustrates these decompositions.

The charged fragments in coincidences with neutrals (decomposition of the base) have conserved the methyl group and this is a confirmation of the position in 7 of the methyl group.

Conclusion

It has been shown that metastable decomposition of ions in the field free region can be analysed with a new type of time of flight mass

spectrometer. The power and analytical utility of an electrostatic mirror is much enhanced by applying coincidence techniques for neutrals and ion time of flight measurements. Not only single spectra (neutrals and reflex) but also coincidence spectra are recorded simultaneously. A ^{252}Cf source has been used for the ionization-desorption of molecules but the method can be also applied to any primary source of ionization-desorption (keV, Laser) and even to "spontaneous desorption" (15) in the case of negative ions.

It should be possible in the future to induce in flight collisions at a fixed position inside the time of flight tube. Then, more precise informations on the energy released during the fragmentation process could be obtained as well as more structural informations. Properties of time of flight mass spectrometers can be much improved by these developments which can serve both field of applied analytical chemistry and basic research.

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FIGURE CAPTIONS

Figure 1 : Schematic diagram of the apparatus. Neutral and ion trajectories are shown. The electronic diagram is discussed in the text.

Figure 2 : a) Time of flight spectrum of the Adenosine molecular mass region. Ions and neutrals resulting from a in flight fragmentation are detected by the detector 2 (see fig. 1) when the mirror is not in operation.

b) Neutrals only are detected when the mirror is active. The counting time is the same as in a).

Figure 3 : a) Normal time of flight spectrum of a molecule "α solanine" with a time of flight distance of 80 cm (mirror not active).

b) Reflex spectrum of the same molecule with the same apparatus and the mirror active. The two vertical arrows in a) correspond to the spectrum in fig. (b).

Figure 4 : a) The molecular ion m^+ with the velocity v does not fragment and gives a signal at $t = t_{m^+}$ in the reflex TOF spectrum.

b) The fragment m_1^+ is emitted from the surface of the sample and gives a signal at $t = t_{m_1^+}$ in the reflex TOF spectrum.

c) The fragmentation occurs in flight $m^+ \Rightarrow m_{1s}^+ + m_0$. m_0 gives a signal in the neutral spectrum. m_1^+ with the velocity v (same as in a)) is reflected at a shorter distance d_1 and gives a signal at a time $t = t_{m_{1s}}$ ($t_{m_1} < t_{m_{1_s}} < t_m$).

Figure 5 : In the center of mass system the total momentum is conserved : m_1 and m_0 are deflected at certain angles (isotopic angular distribution in the CM system).

Figure 6 : a) Neutral spectrum of the Adenosine molecule

b) Total (or uncorrelated) reflex ion spectrum

c) Coincidence spectrum with a time window on mass 268 in the neutral spectrum. The metastable peak indicates the fragmentation with the lost of the sugar moitie (see text).

Figure 7 : a) Uncorrelated reflex spectrum of the Adenosine molecule (masses below 142)

b) Coincidence spectrum showing the main in flight fragmentations of the base.

c) Same spectrum as (b) with substraction of "false" coincidences (spectrum b - part of spectrum a).

Figure 8 : a) Uncorrelated reflex spectrum of the guanosine molecule

b) Coincidence spectrum with a time window on mass 306 (M+Na), showing clearly the rupture base-sugar.

c) Coincidence spectrum with mass 284 showing also the rupture of the protonated molecular ions.

Figure 9 : a) Uncorrelated reflex spectrum of guanosine for masses lower than M/Z = 160.

b) Coincidence spectrum with mass 152 showing "in flight" fragmentationsof the base.

Figure 10: a) Uncorrelated reflex spectrum of the 7-methyl guanosine molecula

b) Coincidence spectrum showing again the same rupture as in fig. 8 with a methylated guanosine.

Figure 11: a) Uncorrelated reflex spectrum of 7-methyl guanosine (low mass region)

b) Coincidence spectrum with a window on 166 in the neutral spectrum. Fragmentation are similar to that of 152 (fig. 9) with the expected difference of 14 mass units (CH_2).

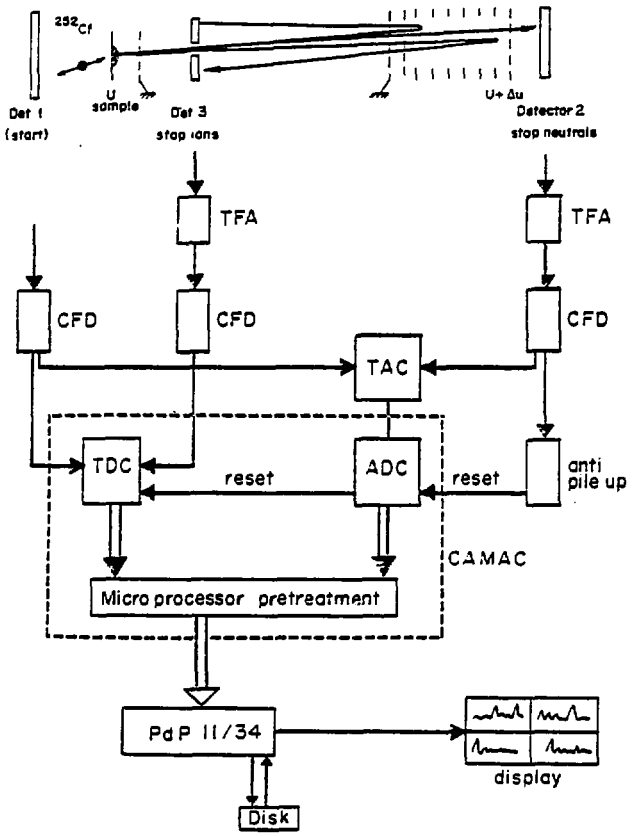

252Cf
U sample
Det 1 (start)
Det 3 stop ions
U+ Δu
Detector 2 stop neutrals
TFA
TFA
CFD
CFD
CFD
TAC
TDC
reset
ADC
reset
anti pile up
CAMAC
Micro processor pretreatment
PdP 11/34
display
Disk

Fig. 1 .

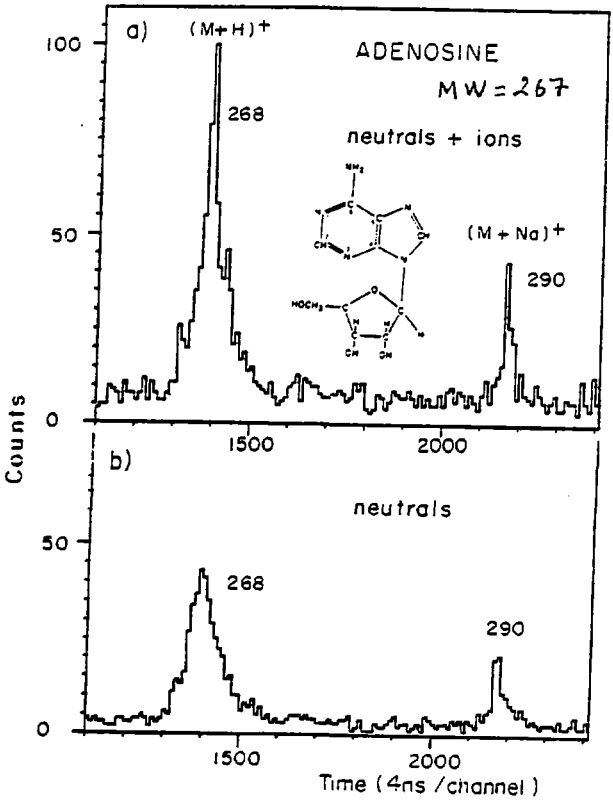
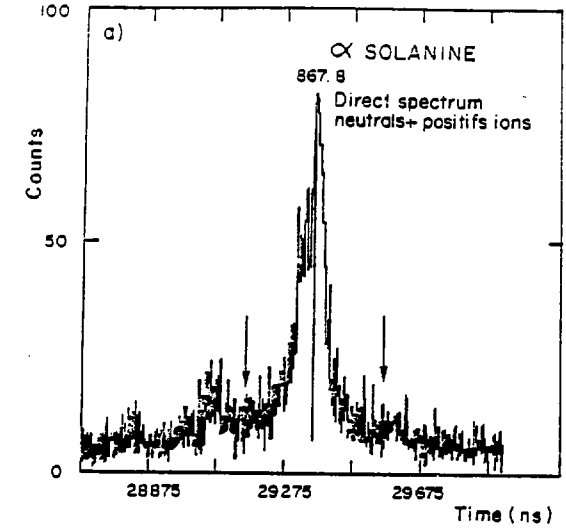

a)
(M+H)+
ADENOSINE
MW=267
268
neutrals + ions
(M+Na)+
290
100
50
0
Counts
1500
2000
b)
neutrals
50
268
290
0
1500
2000
Time (4ns /channel)

Fig. 2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α SOLANINE
867.8
Direct spectrum
neutrals+ positifs ions
Counts
100
50
0
28875
29275
29675
Time (ns)

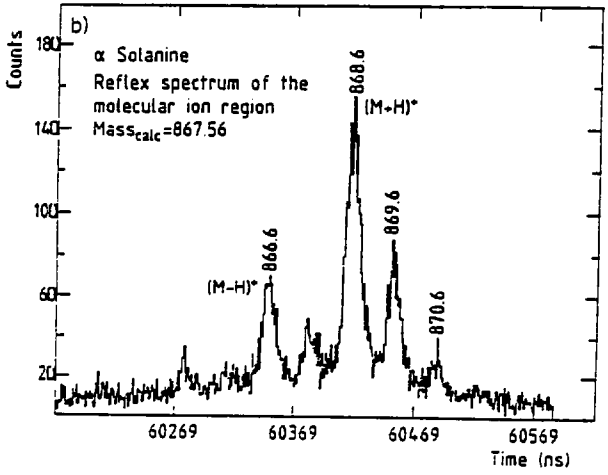
b)
α Solanine
Reflex spectrum of the
molecular ion region
Mass$_{calc}$=867.56
Counts
180
140
100
60
20
866.6
(M-H)+
868.6
(M+H)+
869.6
870.6
60269
60369
60469
60569
Time (ns)

Fig. 3

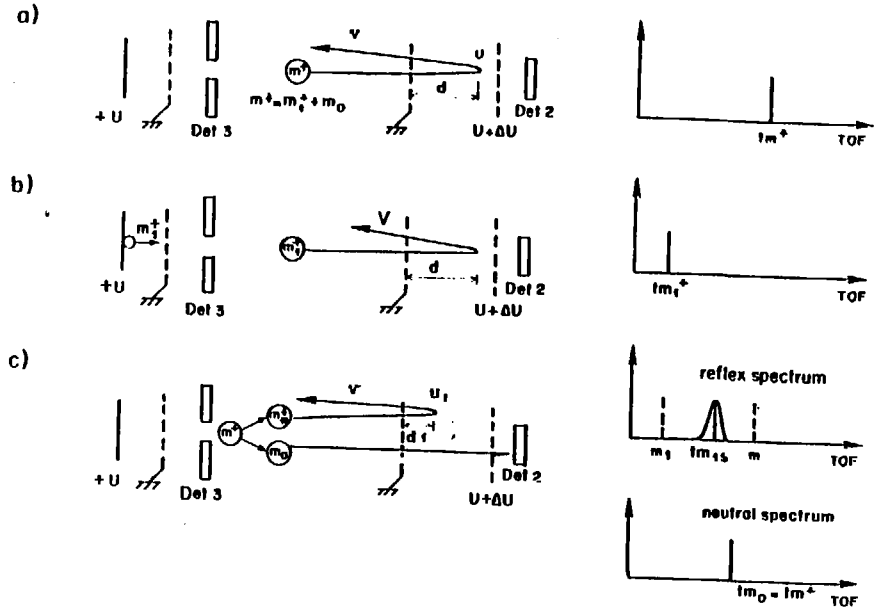
a)
+U
Det 3
v
u
d
Det 2
U+ΔU
TOF
b)
+U
Det 3
V
d
Det 2
U+ΔU
TOF
c)
+U
Det 3
v'
u'
d'
Det 2
U+ΔU
reflex spectrum
TOF
neutral spectrum
TOF

Fig. 1

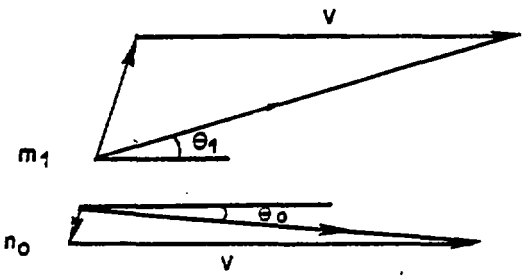

Fig. 5

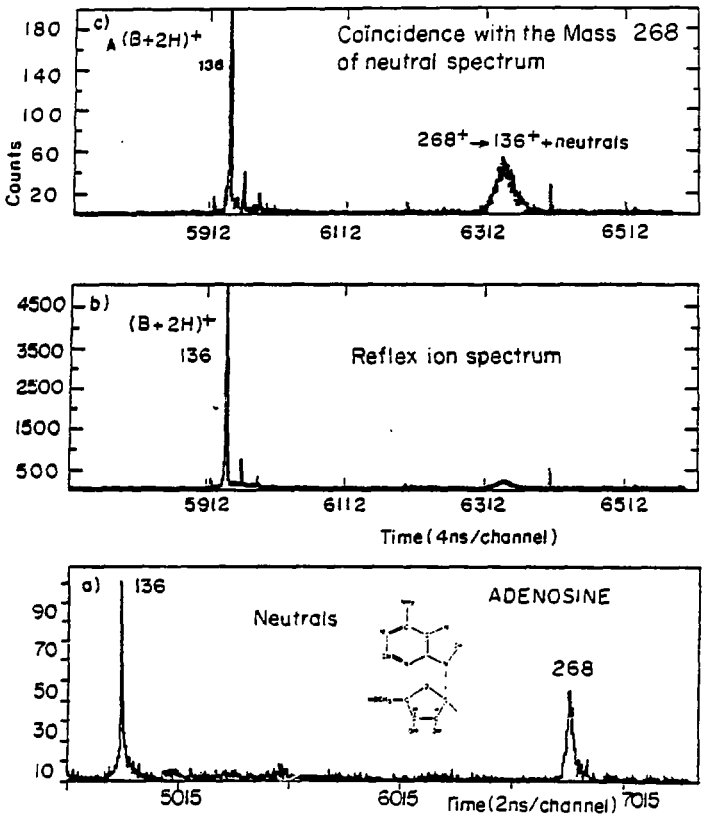
c)
A (B+2H)+
136
Coincidence with the Mass 268
of neutral spectrum
268+ → 136+ + neutrals
Counts
180
140
100
60
20
5912
6112
6312
6512
b)
(B+2H)+
136
Reflex ion spectrum
4500
3500
2500
1500
500
5912
6112
6312
6512
Time (4ns/channel)
a)
136
Neutrals
ADENOSINE
268
90
70
50
30
10
5015
6015
Time (2ns/channel)
7015

Fig. 6

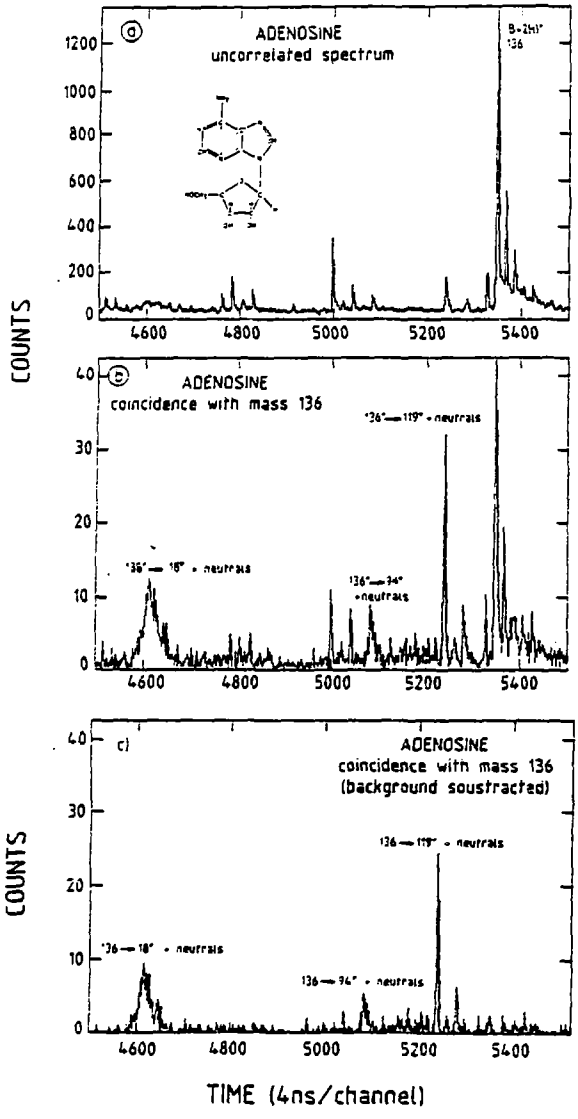
a)
ADENOSINE
uncorrelated spectrum
B+2H)+
136
1200
1000
800
600
400
200
0
4600
4800
5000
5200
5400
b)
ADENOSINE
coincidence with mass 136
136+ — 119+ + neutrals
136+ — 18+ + neutrals
136+ — 94+ + neutrals
40
30
20
10
0
c)
ADENOSINE
coincidence with mass 136
(background soustracted)
136 — 119+ + neutrals
136 — 18+ + neutrals
136 — 94+ + neutrals
COUNTS
COUNTS
TIME (4ns/channel)

Fig. -

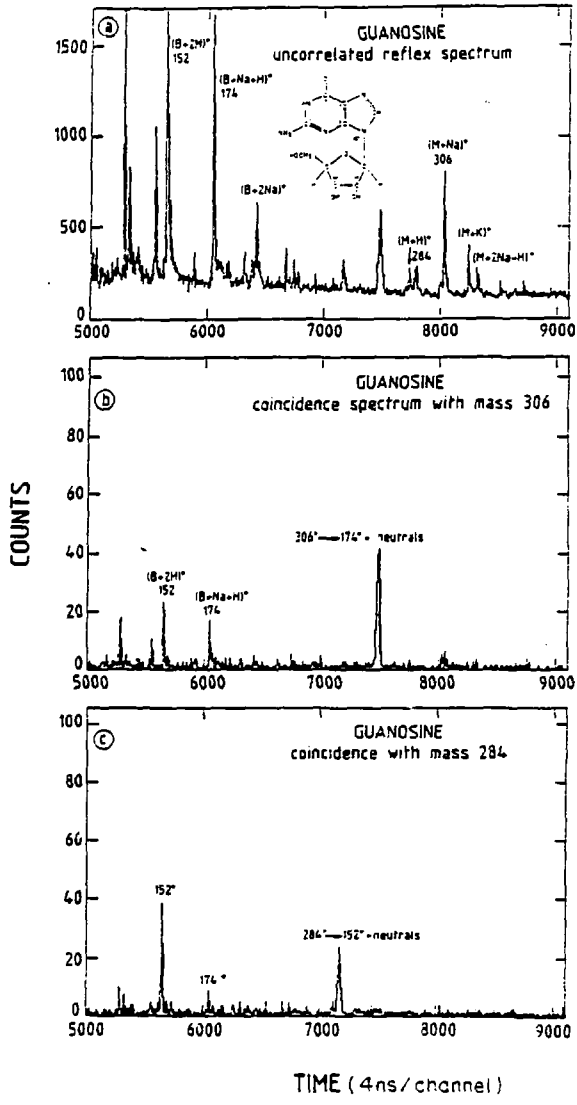
a
GUANOSINE
uncorrelated reflex spectrum
(B+2H)+
152
(B+Na+H)+
174
(B+2Na)+
(M+Na)+
306
(M+H)+
284
(M+K)+
(M+2Na-H)+
b
GUANOSINE
coincidence spectrum with mass 306
306+ → 174+ + neutrals
(B+2H)+
152
(B+Na+H)+
174
c
GUANOSINE
coincidence with mass 284
152+
174+
284+ → 152+ + neutrals
COUNTS
TIME (4ns/channel)

Fig. 3

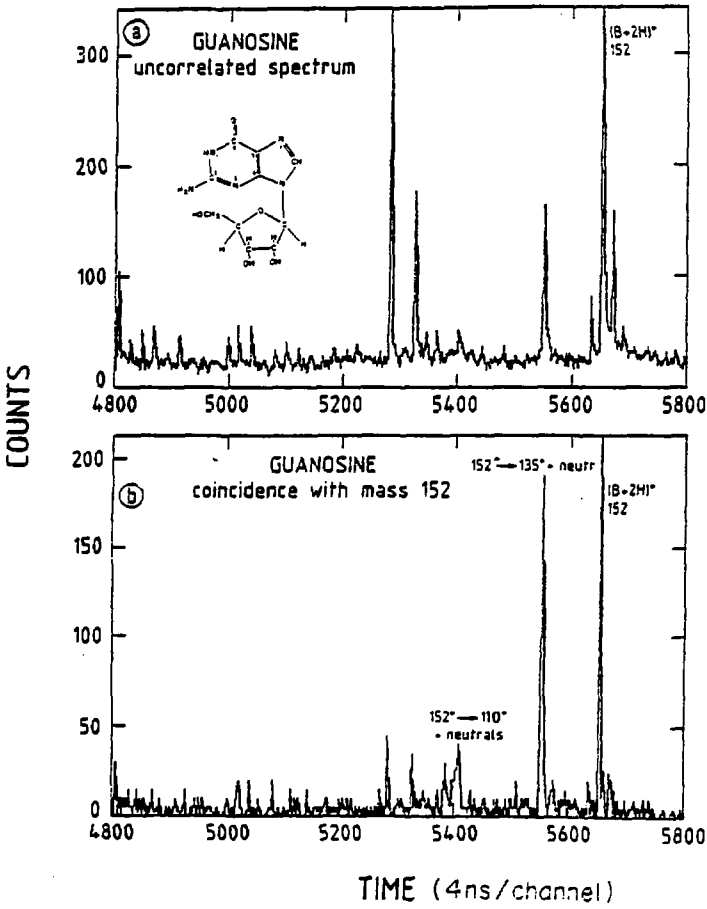
COUNTS
a
GUANOSINE
uncorrelated spectrum
(B+2H)+
152
300
200
100
0
4800
5000
5200
5400
5600
5800
b
GUANOSINE
coincidence with mass 152
152+ → 135+ + neutr
(B+2H)+
152
152+ → 110+
+ neutrals
200
150
100
50
0
TIME (4ns/channel)

Fig. 9

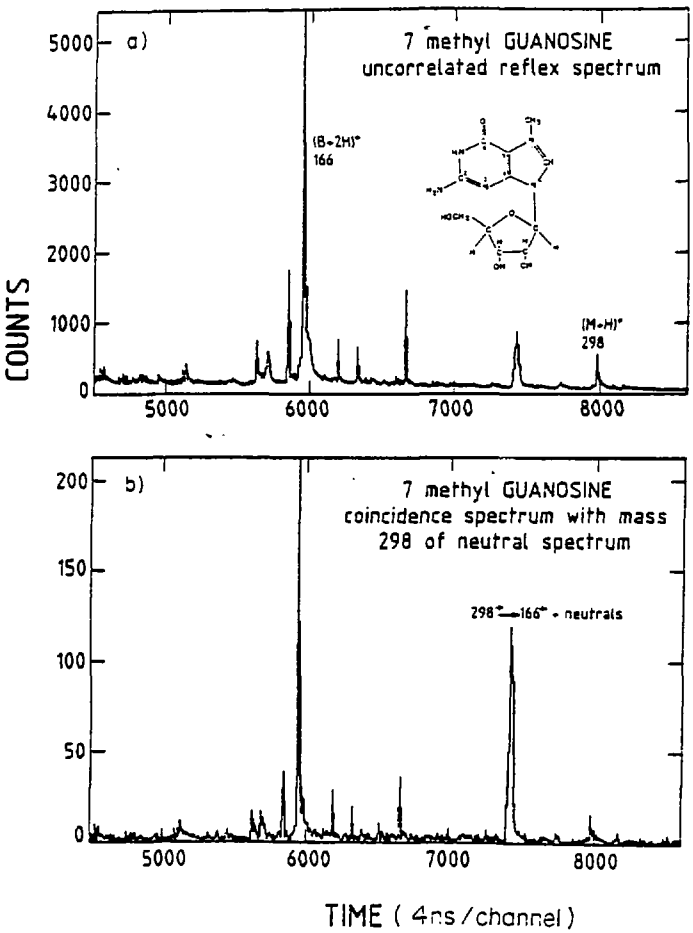
a)
7 methyl GUANOSINE
uncorrelated reflex spectrum
(B+2H)+
166
(M+H)+
298
COUNTS
5000
4000
3000
2000
1000
0
5000
6000
7000
8000
b)
7 methyl GUANOSINE
coincidence spectrum with mass
298 of neutral spectrum
298+ → 166+ + neutrals
200
150
100
50
0
5000
6000
7000
8000
TIME (4ns / channel)

Fig. 13

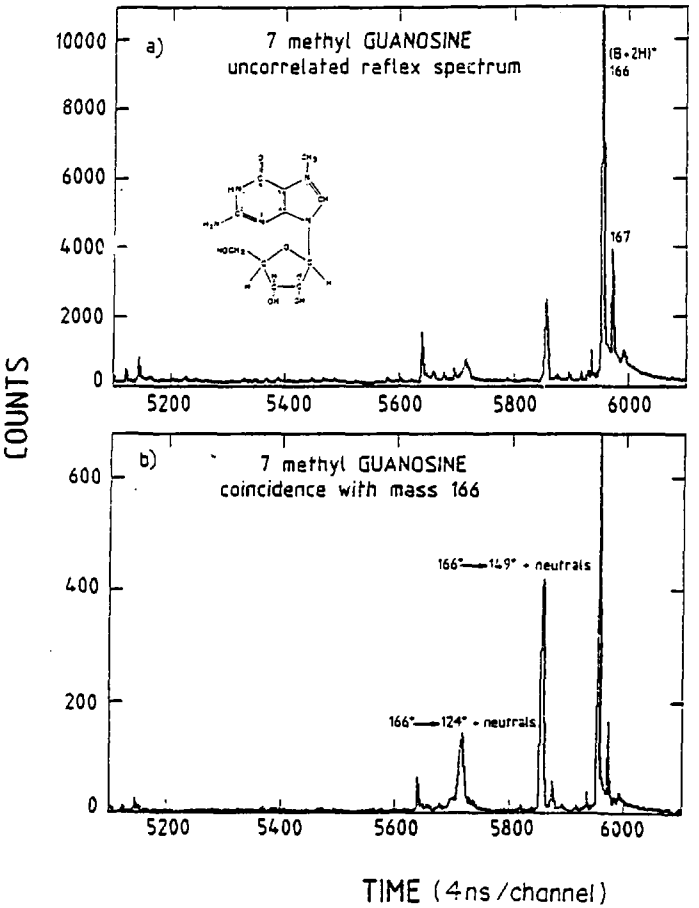
a)
7 methyl GUANOSINE
uncorrelated reflex spectrum
(B+2H)+
166
167
10000
8000
6000
4000
2000
0
5200
5400
5600
5800
6000
b)
7 methyl GUANOSINE
coincidence with mass 166
166+ → 149+ + neutrals
166+ → 124+ + neutrals
600
400
200
0
5200
5400
5600
5800
6000
COUNTS
TIME (4ns/channel)

Fig. 11