

On-Line High-Resolution Mass Spectroscopy

Progress Report

July 1, 1975 - July 1, 1976

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I. GENERAL REPORT

A. Introduction

This is the tenth progress report for this project covering the twelve-month period July 1, 1975 to July 1, 1976. Funds from the ERDA were used to support a continuing program at the Cyclotron Institute of Texas A&M University.

B. Summary of Activities

The search for second-class currents in nuclear beta decay continues by measuring beta-gamma correlations for the mirror decays $^{20}\text{F}(\beta^-)^{20}\text{Ne}^*$ (1.63) and $^{20}\text{Na}(\beta^+)^{20}\text{Ne}^*$ (1.63). The ^{20}F beta-gamma correlation has been measured in beam and the results are being used to compare values obtained using the He-jet method.

A careful analysis of ion velocity distributions emitted from fission fragment tracks in solids has yielded new information on the nature of the process. We have determined that the temperature of the microplasma formed by a fission fragment is of the order 10^4K , and that the temperature is dependent on the fission fragment's energy.

A mass reflectron is being developed for high mass resolution using time-of-flight mass spectroscopy.

The application of ^{252}Cf -PDMS to new classes of involatile compounds continues. Techniques are being studied for the routine analysis of involatile species of mass >2000 .

C. Personnel

1. Principal Investigators

R. D. Macfarlane, Professor of Chemistry

D. F. Torjerson, Senior Scientist, Cyclotron

2. Research Associate

C. A. Hassell, Ph.D. (TAMU)

3. Graduate Students

Larry Speigel, B.S. 1973

Duane Piper, B.S. 1973

Rodney Kadrmus, B.A. (Chem.) 1975

4. Undergraduate Assistants

Catherine McNeal

Creston Gay

D. Facilities Used

Experiments were performed at the Cyclotron Institute and at the Rice tandem accelerator. Data were acquired on-line using the Cyclotron Institute's PDP 15 computer, and were analyzed off-line using the IBM 7094 computer. All instrumentation described in this report was fabricated using Cyclotron Institute facilities, and we acknowledge the continuing excellent support this project has received.

E. Publications and Presentations

1. Work published or accepted for publication:

a. Ion Temperature Measurements of Fission Fragment Tracks in CsBr Films, R. D. Macfarlane and D. F. Torgerson, Phys. Rev. Lett. 36, 486 (1976).

b. Californium-252 Plasma Desorption Mass Spectroscopy, R. D. Macfarlane and D. F. Torgerson, Science 191, 920 (1976).

c. ²⁵²Cf Plasma Desorption Time-of-Flight Mass Spectrometry, R. D. Macfarlane and D. F. Torgerson, Int. J. Mass Spec. Ion Phys. (in press, October 1976 issue).

2. Invited Lectures

R. D. Macfarlane:

²⁵²Cf Plasma Desorption Mass Spectrometry; Physics Department, Rice University, October 1975; Physics Department, Florida State University, January 1976; Chemistry Department, Carnegie-Mellon, March 1976; National Meeting, American Society for Mass Spectrometry, May 1976; Finnigan Corporation, July 1976.

D. F. Torgerson:

²⁵²Cf Plasma Desorption Mass Spectroscopy; Chemistry Department, University of Manitoba, November 1975; Boroughs-Wellcome Laboratories, Field Desorption Workshop, Research Triangle Park, North Carolina, February 1976; Chemistry Department, Johns Hopkins University, March 1976; Biochemistry Department, Johns Hopkins University, March 1976.

3. Talks Presented at Meetings

²⁵²Cf PDMS - Nuclear Particles to Probe Biomolecules, R. D. Macfarlane and D. F. Torgerson, ASMS Annual Conference, San Diego, May 1976 (invited lecture).

TOF Mass Spectroscopy of Involatile Species Using Energetic Heavy Ions, D. F. Torgerson and R. D. Macfarlane, APS Austin Meeting, October 1975.

II. ABSTRACTS OF WORK PUBLISHED OR ACCEPTED FOR PUBLICATION

A. Ion Temperature Measurements of Fission Fragment Tracks in CsBr Films [Phys. Rev. Lett. 36, 486 (1976)]

Abstract

The velocity spectrum of Cs⁺ and Br⁻ ions emitted from thin CsBr films irradiated with fission fragments show that the ions are not ejected by direct collisional interactions with the fission fragments

but appear to be thermionically emitted with an average temperature of 6.6×10^4 K. This suggests the existence of a transient hot thermal core within the fission fragment track. Transient fission tracks in condensed phases may be convenient media for studying fast high-temperature atomic and molecular interactions.

B. Californium-252 Plasma Desorption Mass Spectrometry [Science 191, 920 (1976)]

This paper demonstrates the applicability of PDMS to a wide variety of involatile molecules, several of which could not be characterized using more conventional mass spectrometry. We have emphasized the value of applying nuclear concepts to other disciplines.

C. ^{252}Cf PDMS Time-of-Flight Mass Spectrometry (Int. J. Mass Spec. Ion Phys., in press)

Abstract

Details of a ^{252}Cf -plasma desorption time-of-flight mass spectrometer are described. Fission fragments from ^{252}Cf decay are used to produce rapid heating and ionization in thin solid samples. Time-of-flight measurements are made by single-ion counting using fast pulse electronics techniques. An electrostatic particle guide is used to produce an 8-m flight path for high-resolution mass measurements.

III. COMPLETED WORK

A. Ion Temperature Analysis of Peak Shapes Measured in PDMS

In a time-of-flight mass spectrometer, line shapes are not simple delta functions due to instrumental effects and to the dynamics of ion formation. For a conventional TOF mass spectrometer, instrumental effects include uncertainties in the acceleration field, in the path length, and

the timing resolution. The first two of these are essentially eliminated in PDMS as the ions are formed on a planar surface held at a fixed potential. There remains a timing contribution which can be accurately measured.

A lineshape measured in PDMS, therefore, depends on the timing resolution and on the energy imparted to an ion when it is formed in the plasma. Using the notation of Fig. 1, the time-of-flight for an ion having an initial energy E_x before acceleration in the direction of the Chevron detector, is

$$\begin{aligned}
 \text{TOF}(E_x) = \frac{2m}{q} & \left((E_x + V_0 - V_1)^{1/2} - E_x^{1/2} \right) D_1 / (V_0 - V_1) \\
 & + \left((E_x + V_0 - V_2)^{1/2} - (E_x + V_0 - V_1)^{1/2} \right) D_2 / (V_1 - V_2) \\
 & + \left((E_x - V_0)^{1/2} - (E_x + V_0 - V_2)^{1/2} \right) D_3 / V_2 \\
 & + (E_x + V_0)^{-1/2} D_4 / 2
 \end{aligned} \tag{1}$$

Thus, the addition of energy in the direction of acceleration produces shorter flight times; a distribution of energies will produce a peak skewed to shorter times. This is the expected result if the interaction between the fission fragment and the target molecule were direct, producing ions with excess energy in the direction of ion detection.

However, we have now established that the time peaks observed in PDMS are symmetrical, having a Gaussian distribution. This is shown in Fig. 2 for Cs^+ and Br^- formed by the irradiation of a thin CsBr film by fission fragments. This suggests that the ions are being emitted indirectly from the microplasma formed by the fission fragment, and thus the ions are formed with a symmetrical distribution of initial

energies. This is a necessary condition for thermal or quasithermal equilibrium.

For ions in thermal equilibrium, the one-dimensional velocity distribution is Gaussian:

$$P(V_x) = \frac{2kT}{m} e^{-v_x^2 / 2\sigma_{v_x}^2}$$

where V_x is the velocity component transverse to the acceleration field, k is the Boltzmann constant, T is the temperature, and $\sigma_{v_x} = (kT/c)^{1/2}$ is the standard deviation. In terms of energy, $E_{th} = 1/2kT$, where σ_x denotes that the thermal energy is measured at the standard deviation of the peak.

For a time spectrum, the thermal energy distribution produces a standard deviation broadening (Eq. 1)

$$\sigma_{t_x} = \text{TOF}(E_{th}) - \text{TOF}(0) \quad (2)$$

where $\text{TOF}(0)$ is the time-of-flight for an ion formed with no initial energy component in the x-direction, i.e. the peak's centroid. Therefore, from Eqs. 1 and 2, the standard deviation of the TOF peak, corrected for the timing resolution, yields the thermal ion energy in the x-direction and the temperature. As the H ion broadening due to the temperature is insignificant, the instrumental contributions to σ_{t_x} can be readily obtained. Using CsBr targets, we have demonstrated that the average temperatures attained in the fission fragment track are of the order 10^4 K.

To further study the nature of the track, and to confirm the CsBr results, we have recently completed a study of temperatures for ions formed in solid films of the amino acid valine. Temperatures were measured using 1 mg/cm^2 and 3 mg/cm^2 Ni degrading foils between the ^{252}Cf source and the target films. The energy deposited in the film by fission fragments passing through the 3 mg/cm^2 foil was approximately 50% of that deposited by fragments passing through the 1 mg/cm^2 foil. The resulting temperatures are shown in Table I. The important observations are as

Table I. Temperatures for ions formed in the irradiation of valine films with ^{252}Cf fission fragments.

Ion*	Temperature (K)	
	1 mg/cm^2 degrader	3 mg/cm^2 degrader
$(M + 1)^+$	$(1.8 \pm 0.3) \times 10^4$	$(1.1 \pm 0.1) \times 10^4$
$(M - 1)^-$	$(1.6 \pm 0.1) \times 10^4$	$(1.2 \pm 0.1) \times 10^4$
$((M + 1) - 45)^+$	$(2.5 \pm 0.2) \times 10^4$	$(2.9 \pm 0.4) \times 10^4$

*M = valine mass.

follows. The $(M + 1)^+$ and $(M - 1)^-$ ions are formed with the same temperature, which is consistent with their formation via the reaction $2M \rightarrow (M + 1)^+ + (M - 1)^-$ in the plasma. However, the loss of formic acid, mass 45, from $(M + 1)^+$ greatly increases the effective temperature of the $((M + 1) - 45)^+$ ions, a manifestation of the dissociation energy. Degrading the fission fragment energy using the 3 mg/cm^2 absorber effectively reduces the $(M + 1)^+$ and $(M - 1)^-$ energies. This is the expected result as the ions are now being formed in a cooler plasma. The temperature of

the $((M + 1) - 45)^+$ fragment, however, is independent of the fission fragment energy as the dominant contribution is due to the dissociation energy. We conclude that these results offer strong evidence for the formation of a high-temperature plasma in a fission fragment track.

While all the ramifications of this work cannot be discussed here, we should like to emphasize again the potential usefulness of applying nuclear methods to problems in other disciplines.

IV. WORK IN PROGRESS

A. Beta-Gamma Directional Correlations

The possible existence of second-class currents is one of the fundamental problems in the nuclear weak interaction. Conflicting results are contained in the literature, however, and even the weak magnetism contribution has recently been questioned.

The most sensitive measurement of these weak currents is from beta asymmetry measurements where other contributions are either known or can be eliminated using their G-parity transformation properties. Our approach is to measure the beta-gamma correlations for a pair of mirror decays, and then subtract them to eliminate any contributions that change sign under G-parity operations.

The decays being studied are $^{20}\text{F}(\beta^-)^{20}\text{Ne}$ (1.63) and $^{20}\text{Na}(\beta^+)^{20}\text{Ne}$ (1.63) which are allowed, non-analog transitions. Sources have been made using the He-jet recoil transport technique, but considerable problems regarding source geometry have been encountered. To overcome these problems, a tape transport system is being adapted for these measurements, in which activity from the He-jet is collected on Mylar tape and transported to the counting chamber. This procedure will overcome the spraying of

activity onto undesirable surfaces which is an important problem where highly accurate correlations are necessary.

To test the use of the He-jet, we have recently measured the β - γ correlation for ^{20}F at 90° and 180° using an in-beam configuration at the Rice random accelerator facility. Approximately 2×10^6 events were recorded, and the data are presently being analyzed. The experiment will be repeated on the cyclotron using the He-jet/transport tape procedure, in order to verify that valid results can be obtained.

B. High-Resolution TOF Mass Spectrometry

An important development in our high mass resolution program is the mass reflectron, shown in Fig. 3. One of the limitations in time-of-flight mass spectrometry is the width of mass peaks due to uncertainties in the initial energy. In PDMS, the largest contribution to the initial energy spread is the temperature of the plasma formed by the fission fragment as it passes through the sample. This effect can be eliminated, however, using the mass reflectron which was originally developed by Marmyrin et al.

The operation of the reflectron is as follows. An ion beam having a distribution of energies in the transverse direction is rapidly decelerated between two grids and enters an extremely uniform electric field region. The ions are eventually stopped and accelerated out of the reflectron, but the more energetic ions have a longer path length. Parameters are chosen so that slow and fast ions merge at the detector, thus eliminating the energy broadening.

Two reflectrons have been constructed and are in the process of being tested. Preliminary results indicate that considerable time-focusing can be accomplished with the concomitant improvement in mass

resolution. The effect of the reflectron on the $(M - 1)^-$ peak of valine is also shown in Fig. 3.

C. Plasma Desorption Mass Spectroscopy of Natural Products

Molecular weight determinations of newly-isolated or synthesized biologically-active molecules has continued to be an important application of PDMS. In general, samples have been sent to us from other laboratories after attempts to measure molecular weights by conventional mass spectroscopy has failed. It has been our policy to concentrate on the more difficult measurements, as opposed to systematically characterizing simple molecules, in order to extend the capabilities of PDMS. An unambiguous molecular weight can usually be assigned from PDMS spectra by recognition of a series of ions having masses $(M + 1)^+$, $(M + Na)^+$, and $(M - 1)^-$, where M is the parent molecular weight. If the sample is highly contaminated with sodium (not unusual for biological samples), there will be a significant reduction in the $(M + 1)^+$ intensity with a corresponding increase of $(M + Na)^+$.

Although several molecules have been studied in the past year, only two of the more interesting samples will be discussed. The first of these is the "Q-nucleoside" which was sent to us by Professor K. Nakanishi (Columbia). The PDMS spectrum, shown in Fig. 4, showed that the mass was 571. This measurement revealed the presence of a second sugar moiety in the nucleoside, which had heretofore never been observed, and which had not been detected from NMR studies.

Chaetoglobsin C, provided by Professor J. Clardy (Iowa State), is a fungal toxin found on pecans. The mass spectrum is shown in Fig. 5 from which the mass was determined to be 528. Although samples of biological

compounds often yield complex spectra due to background and decomposition products, the $(M + 1)^+$, $(M - 1)^-$ signature allows an unambiguous molecular weight assignment.

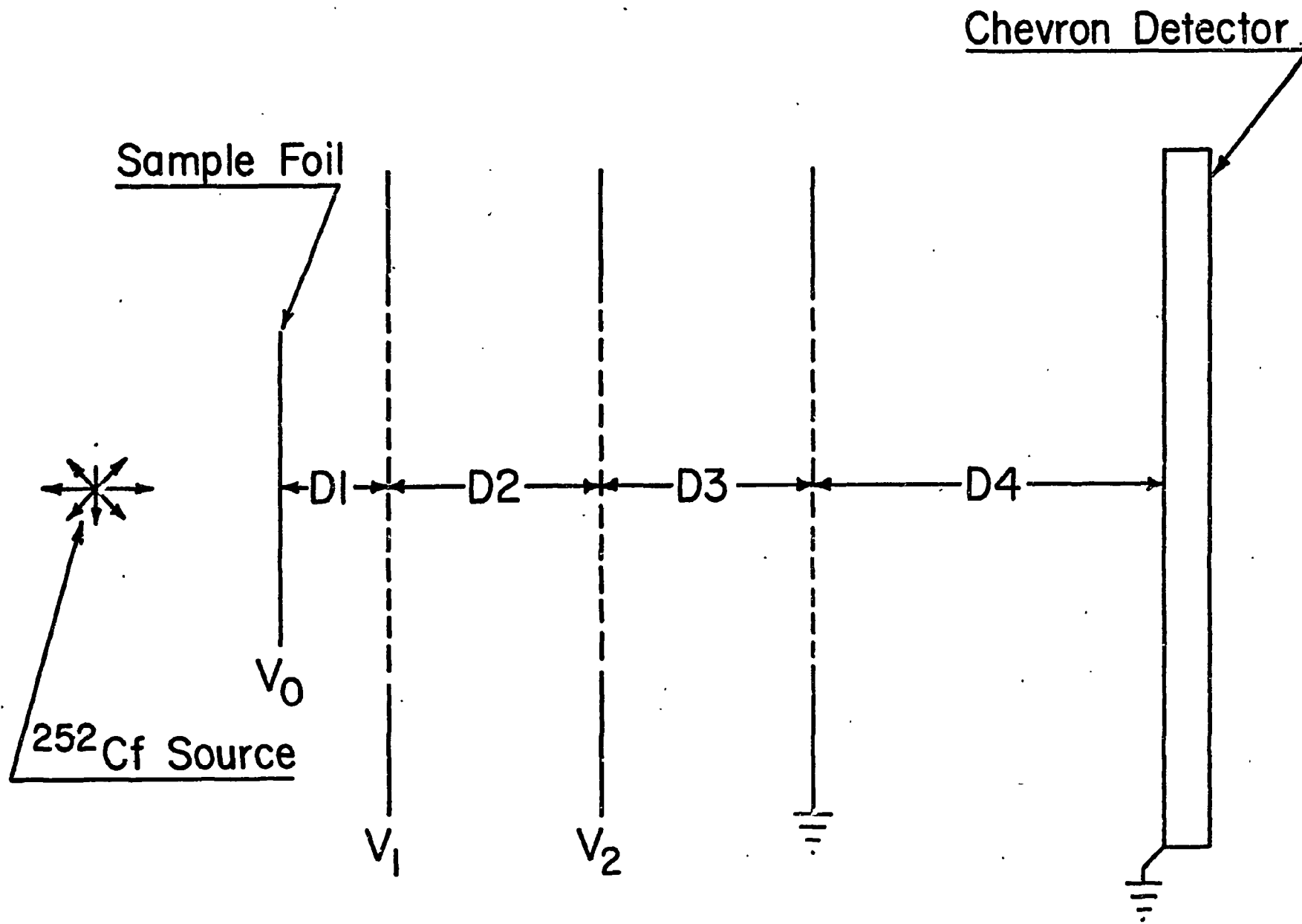


Figure 1

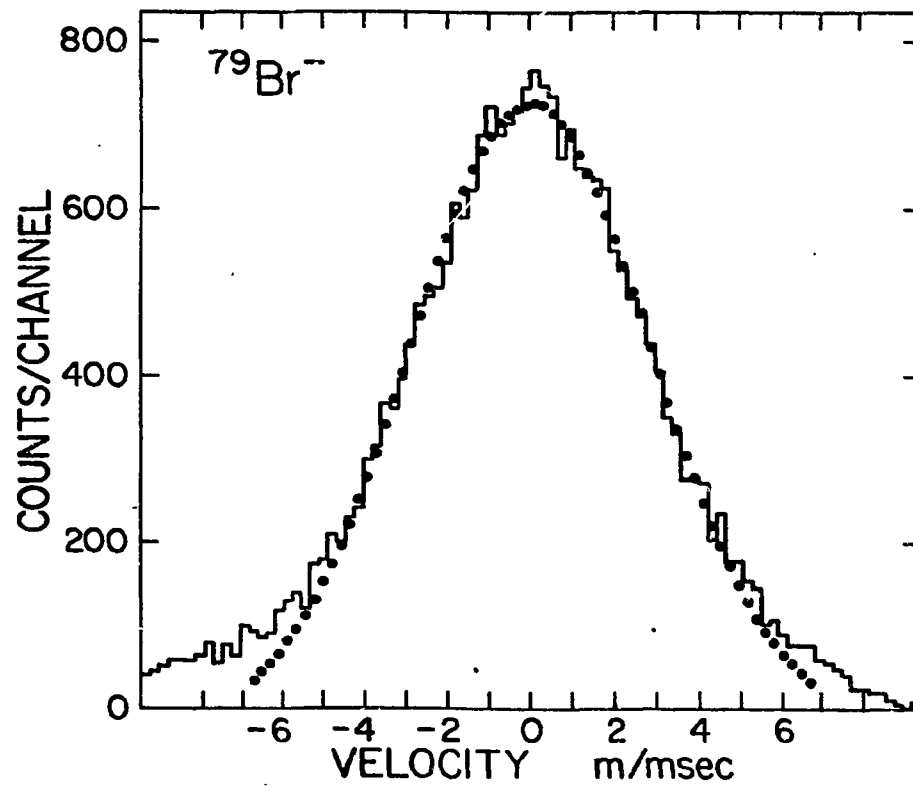
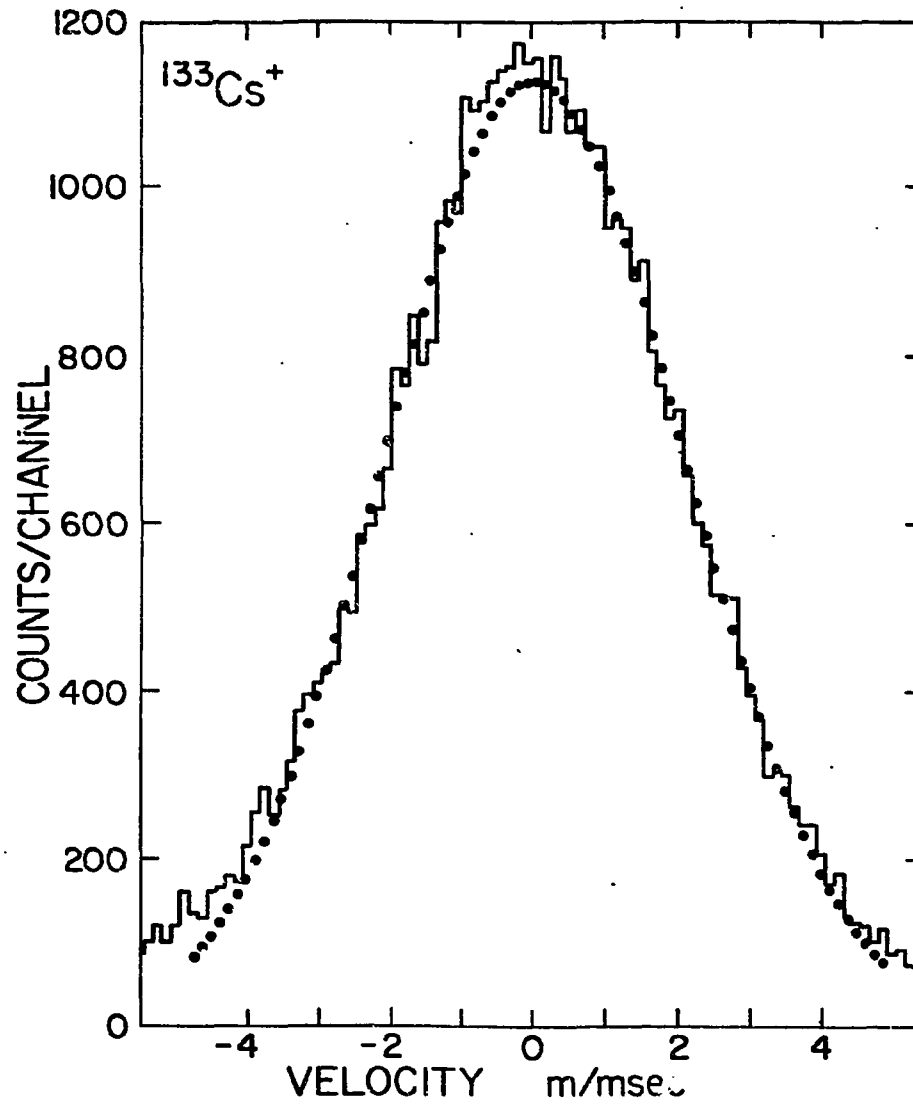


FIG 2

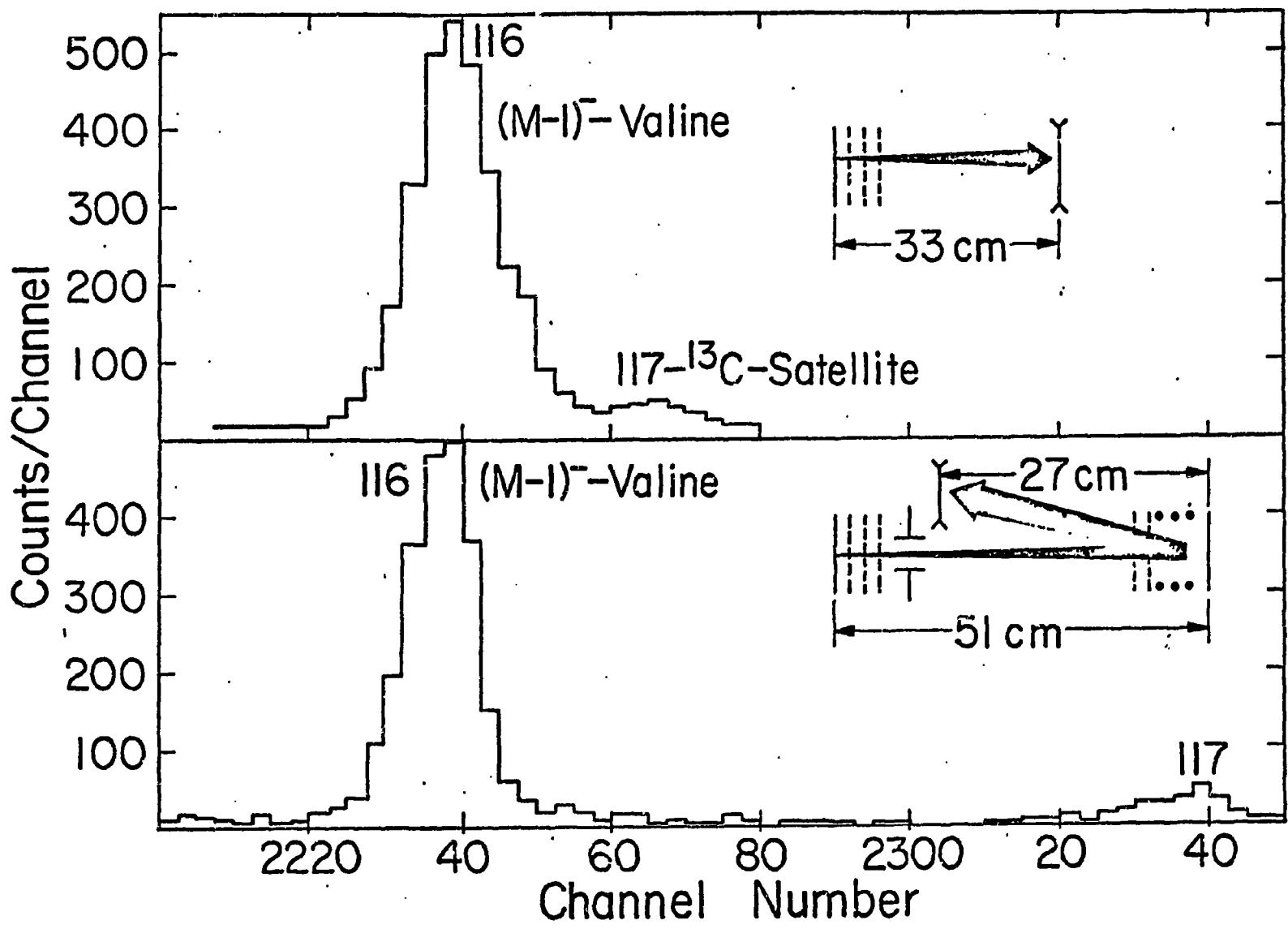


FIGURE 3

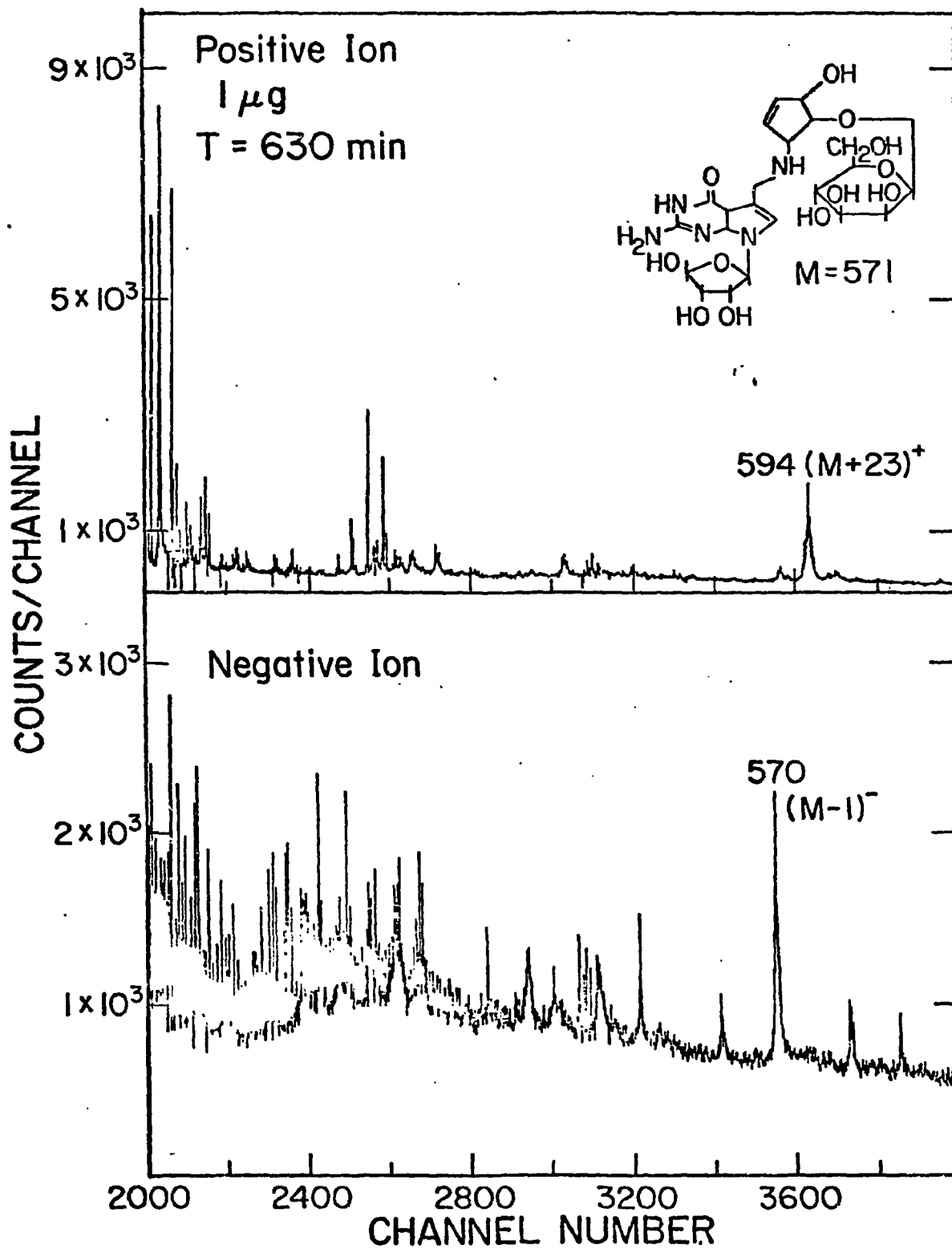


FIGURE 4

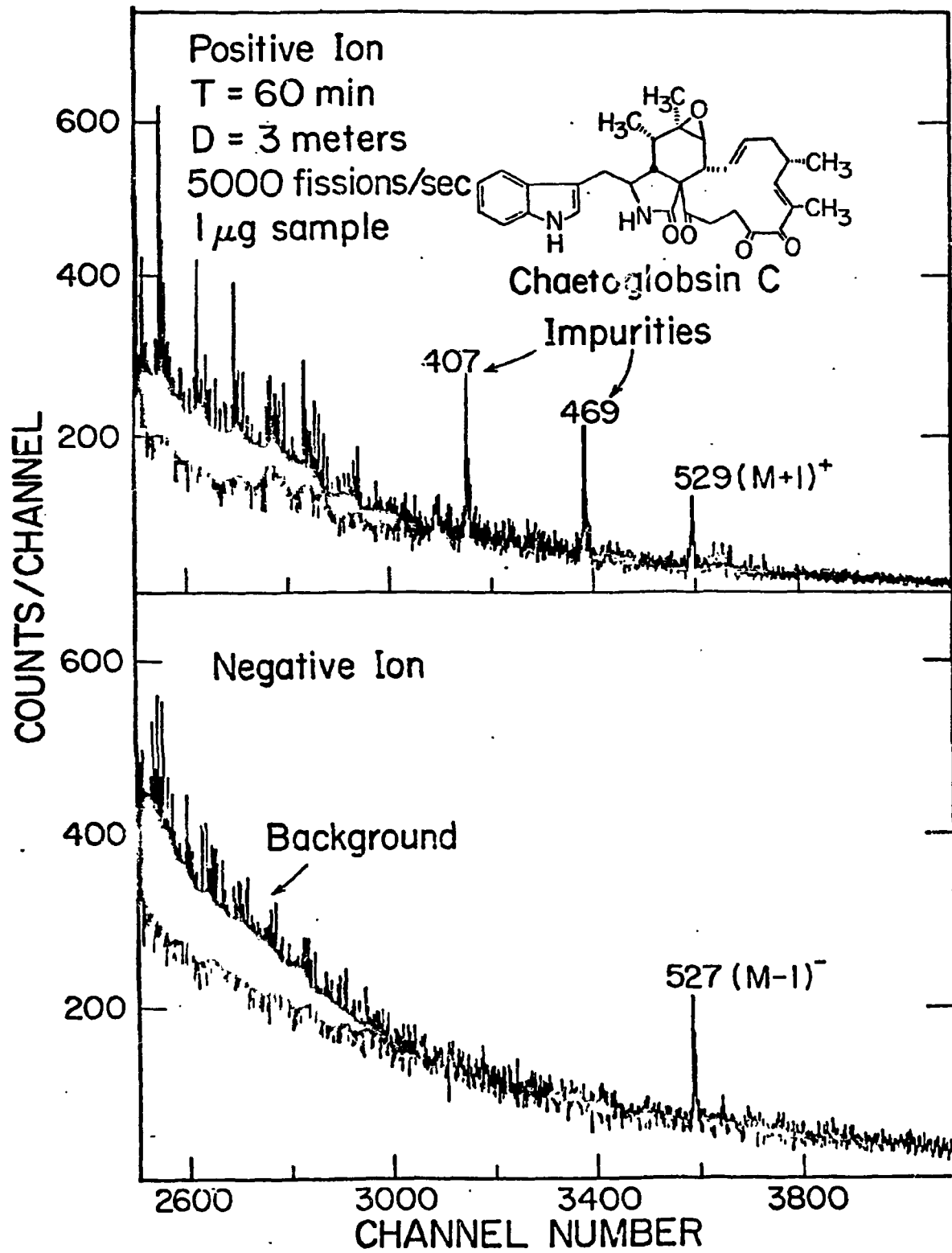


FIGURE 5