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THE IONIZATION OF ORGANIC MOLECULES BY SLOW POSITRONS

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ABSTRACT

The ionization of organic molecules by positrons having energies above and below their positronium formation thresholds is reviewed. The sensitivity of sub-positronium ionization yields to chemical and structural properties of the molecules is discussed, and possible mechanisms for ionization and fragmentation are suggested. Plans are presented for future experiments to further elucidate mechanisms and to search for evidence of positronium compound formation.

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INTRODUCTION

In recent years the positron spectroscopy group at Oak Ridge National Laboratory has been conducting mass spectroscopy studies of the ionization of organic molecules by slow positrons. The most interesting and different results have been obtained with positron energies in the range of 0.5 - 15 eV. Two ionization mechanisms, unique to positron interactions, have been identified. These will be described in detail in subsequent sections of this paper; They are briefly reviewed as follows:

As all positron spectroscopists are aware, the positronium formation process occurs in the energy range of about 2-7 eV. There is a lowering of the energy thresholds at which ionizations occur because the formation of the positronium atom is exothermic, liberating 6.8 eV. The process can be understood by a Born-Haber cycle:

$$M + IP \rightarrow M^+ + e^-$$
$$\frac{e^+ + e^- \rightarrow Ps + 6.8\,eV}{M + e^+ + (IP - 6.8)\,eV \rightarrow M^+ + Ps}$$
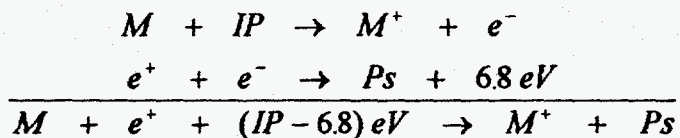
Where M, IP, and Ps represent the molecule being ionized, the ionization potential, and positronium respectively. Positronium ionization processes have been observed for all molecules studied. Several examples will be illustrated below. The above mechanism is oversimplified, however; Schrader and

Jacobsen [1] have demonstrated the formation of positronium hydride in the ionization of methane. Therefore, other energy exchange process may be involved. Plans for future attempts to measure these will be presented in this paper, and will be discussed in detail in a companion paper by Schrader et al. [2].

The ionization potentials of most of the organic compounds studied are in the range of 9-10 eV. The positronium formation thresholds occur at 2-3 eV. Ionization processes have been found to occur for positron energies below the positronium threshold, which we have designated as 'sub-positronium' events [3]. Cross sections for the sub-positronium mechanism increase as the energy of the interacting positrons is decreased below the positronium threshold. Mass spectra of sub-positronium ionization events often show the onset of fragmentation as positron kinetic energies are lowered below the positronium threshold. Cross sections are quite sensitive to molecular size, molecular structure, and bond types. Examples of these 'chemistry effects' will be given below.

More work is needed to better understand ionization through positronium formation as well as sub-positronium ionization. In future studies, described by Schrader et al. [2] in the companion paper to this one, attempts to measure energy exchange effects will be made. A design for an upgraded spectrometer

will be presented in this paper. It will provide three measurements: (1) mass spectra of the ionization products of molecules, (2) positron kinetic energy as a function of interaction time with molecules, (3) energy spectra of secondary electrons and Auger electrons that might be induced by ionization.

This paper is a review of what our group has learned about ionizations in the 0.5 - 15 eV energy range and a description of some future experiments that we hope will increase our understanding.

Spectrometry Techniques

A specially-designed time-of-flight mass spectrometer was used in this work [4]. Ionization was done in a Penning trap, consisting of a 100 mm string of cylindrical lenses, 20 mm in diameter, all at ground potential, with input and output grids charged to positive potentials at front and rear. A 0.1 T magnetic field was applied axially to the lens string. A second string, 500 mm long, of 20 mm diameter lenses followed the rear grid of the Penning trap. Three keV positrons were delivered from the ORELA (Oak Ridge Electron Linear Accelerator) source to a tungsten film brightness enhancement moderator, mounted in front of the input grid. As the re-moderated positrons exited from the backside of the tungsten film, the input grid of the Penning trap was pulsed to ground potential to allow them to enter. The positrons were reflected by the rear

grid, but before they could return to the entrance grid its positive potential was restored. The front and rear electrostatic fields from the grids prevented longitudinal escape and the 0.1 T axial magnetic field prevented radial escape.

The positrons were retained in the Penning trap for varying periods, up to 1800 microseconds. During the retention periods their collision paths with the molecules were as long as several kilometers, depending on their kinetic energies. At the end of the retention time the potential of the rear grid was pulsed to ground for about 5 microseconds to allow any remaining positrons to escape the trap; ion escape during this period was negligible. A positive potential gradient was then applied from front to rear of the Penning trap, accelerating the ions into the second string of lenses. The potential configuration on the Penning trap lens string and the second string of lenses was quadratic at this point; that is, the potential increased according to the square of the distance of the lenses from the microchannel plate detector, mounted at the end of the second string. As explained in ref. 4, this caused the ions to move under a Hook's law force, such that the time required for ions of a given mass to reach the detector was independent of their starting positions in the Penning trap.

A Penning trap was used for ionization because of the limited number of slow positrons. If only a single pass of positrons through a short ionization chamber

had been used, the number of ions produced would have been very small,

yielding poor spectral statistics. In order for the Penning trap to operate

properly, its length to width ratio had to be large enough to present a region of

low potential gradient to the ions. In short Penning traps they were accelerated

out as soon as they were formed. The quadratic potential acceleration

technique was used to make the times of flight of the ions independent of their

starting points in the Penning trap.

Upgraded Spectrometry Techniques

Resolution was limited in the spectrometer design of ref. 4 by the initial velocities

of the ions being in both positive and negative directions. Figure 1 shows

plans for a new design for a quadratic potential time of flight mass spectrometer

in which the ions will be allowed to drift, without acceleration, from the Penning

trap, marked PT, into the string of lenses marked QPTOF. The quadratic

potential will be applied to the QPTOF string after all the ions from the Penning

trap have entered it and are all going in the same direction. This should improve

mass resolution. Two of the cylindrical lenses, located slightly past the mid-point

of the QPTOF string, will be spanned with retarding grids, G1, G2, for purposes

of measuring positron and electron kinetic energies.

The magnetic field parallelizing technique will be used to meter positrons and electrons generated by ionization in the Penning trap. It was first used by Kruit and Read [5] for electrons, and has recently been suggested by Kong and Lynn [6] for both positrons and electrons. The method employs parallel magnetic and electrostatic fields. It has the combined advantages of high resolution and high solid angles of collection. Both the front and rear grids of the Penning trap will be operated at positive potentials. To allow the positrons to escape the trap for measurement of their energies, the rear grid of the Penning trap will be pulsed to ground potential. Electrons that may be generated during ionization will pass through the positively charged grids. The remoderated positrons and electrons are both born in the presence of a magnetic field of about 0.1 T. At the mid-point of the flight path from the Penning trap to the microchannel plate detector (MCP) an auxiliary coil (AC) adjusts the magnetic field to about 0.001 T. The MCP is surrounded by a solenoid that sets its magnetic field to about 0.05 T.

Numerical calculations show that the flights of electrons and positrons under the conditions of Figure 1 are adiabatic. The angle of the trajectory with respect to the cylinder axis, and the displacement of the particle from that axis, are both inversely proportional to the square root of the magnetic field. Two trajectories, T1, T2, corresponding to either positrons or electrons, are indicated in Figure 1. The starting points are ±5 mm off the axis of the Penning trap. At the points where they enter the retarding grids the displacements from the axis are 50 mm

due to the reduction of the field from 0.1 T to 0.001 T. The trajectories of the particles will be nearly parallel to the cylinder axis, also due to the reduction in the magnetic field. For example, if the initial trajectory of an electron or positron in the Penning trap is 85 degrees, its trajectory through the grids will be 5.7 degrees, for which an error of less than 1% in energy measurement by the retarding grids will occur. After the electron or positron passes through the grids it enters the detector at a displacement of about 7 mm off the optical axis.

With the arrangement of Figure 1 we hope to not only get improved mass resolution, but to also measure positron energies as functions of time as they interact with molecules. As will be explained below, kinetic measurements of ion yields suggest that positron cooling is the rate determining step for sub-positronium ionization. We also hope to determine whether or not Auger electrons are generated during positron ionization of molecules. The observation of Auger electron emission would imply that the ions go through states of double charge, which presumably would lead to their explosion into two singly-charged particles. None of the mass spectra recorded have shown indications of doubly-charged ions. Suzuki et al. [7], have observed positron-induced Auger electron emission from carbon-containing specimens.

In the companion paper by Schrader et al. [2] to these proceedings, plans will be presented for a spectrometry technique, that will allow simultaneous determination of the masses and kinetic energies of ions. In this scheme the ions will enter the quadratic potential lens array with their initial velocities all in the same direction and with their energies defined by a filter. Mass resolution should be better for this technique also.

Mass Spectra Obtained Above and Below Positronium Thresholds

Figures 2a, 2b, and 2c show mass spectra generated by the interaction of dodecane with positrons having energies of 1 eV, 3.5 eV, and 9.5 eV, respectively [15]. The 2c spectrum, produced by 9.5 eV positrons, shows extensive fragmentation, which is not surprising. This energy is far above the positronium threshold, corresponding to electrons of over 16 eV (9.5 eV + 6.8 eV). Part of the excess energy goes into excitation processes, which lead to fragmentation of the molecule. Note that the intensity of the molecular ion cannot be measured above background. For positrons of higher energy the fragmentation pattern does not qualitatively change [8].

For the 2b spectrum the positron energy was 3.4 eV, slightly above the positronium threshold. Note that the molecular ion predominates. Very little excess energy is available for inducing fragmentation.

Spectrum 2a shows the sub-positronium ionization effect, described above. If the positron energy is reduced below the positronium formation threshold, extensive fragmentation occurs, and the ion fragment distribution is similar to that of the spectrum induced by 9.5 eV positrons. One would have expected a soft ionization event, with minimum fragmentation, but the opposite was seen. We will first describe more fully some positronium ionization results before expanding on the sub-positronium effects.

Figure 3, from the work of Xu et al. [9], shows plots of the intensities of the molecular ion and the ion fragments of decane as functions of positron energy above the positronium threshold. Note the inverse relationship between the thresholds and the sizes of the ions; the parent ion has the lowest threshold, the C_7, C_5 and C_3 fragments have successively higher thresholds. Note also that the intensity of each of the ion species goes through a maximum and then decreases.

The ionization of butylbenzene above and below the positronium formation threshold behaves similarly to that of decane, but for this molecule only one

main fragment is formed, which is probably a mixture of $C_6H_5CH_2^+$ and $C_6H_5CH^+$.
The bond between the alpha and beta carbons of the butyl group is broken. The
group that is removed is a neutral species, possibly propane or a propyl free
radical. Propyl ions have not been observed in spectra taken for either high or
low positron energies. Figure 4 shows a plot for butylbenzene of the same type
as that of Figure 3, the intensities of the molecular ion and the fragment are
plotted as functions of positron energy. The positronium formation threshold for
the fragment peak occurs far beyond that of the molecular ion, beginning at
about the maximum in the molecular ion peak. Below the positronium threshold
for the molecular ion, the fragment peak increases rapidly, dominating the
molecular ion.

Ionization by positronium formation has been observed for all molecules studied.
The thresholds are always approximately equal to the ionization potentials minus
the 6.8 eV quantity, corresponding to the heat of formation of positronium. In our
work, mass spectra produced by sub-positronium ionization have been
definitively observed above background only for the larger molecules, having 9-
10 atoms or more. For the alkane series, decane is the smallest molecule for
which resolved peaks could be seen. Smaller alkanes, such as nonane, octane,
heptane, and hexane have been studied. Unresolved peaks were apparent, but
not delineated above background. Mass spectra induced by positronium
formation have been measured for aromatic compounds such as benzene and

toluene, but spectra corresponding to the sub-positronium ionization process were not clearly seen. This should not be construed to mean that sub-positronium ionization does not occur for all molecules. Low energy positrons in contact with matter of any kind have finite lifetimes, ionization of one sort or the other must take place. Surko et al. [10] have measured sub-positronium ionization cross sections for both large and small molecules. They are the order of 10 times smaller, or less, than those for ionization induced by positronium formation.

In Figures 3 and 4, the ion yield curves above the molecular ion positronium threshold can be explained qualitatively by a modification of the Öre gap model [11]. For atoms, the "Öre gap" is the energy range defined by the following inequality:

$$(IP - 6.8) \leq KE \leq E^*$$

Where $K.E.$ is the kinetic energy of the positron, IP is the ionization potential of the molecule, and E^* is the energy of the first excited state. In this range the predominant reaction channel is the removal of an electron to form positronium, leaving the atom ionized, but not excited. When the energy of the positron exceeds E^*, an additional channel is opened and some of the positron collisions result in the excitation of the atoms, with no ionization. The second

channel is populated more as the positron energy increases, causing the proportion of ions produced to decrease from their maximum value. For molecules, the Öre gap model should be modified as follows:

$$(IP - 6.8) \leq KE \leq (IP + E^f - 6.8)$$

Where E^f is the additional energy required to fragment the ionized molecule. This model can qualitatively explain the curves in Figures 3 and 4. It is seen that as the concentration of the molecular ion in the Penning trap decreases the concentration of the first fragmented ion increases. Subsequently, when the kinetic energy of the positrons exceeds the energy required to produce the second fragmented ion, the concentration of the first fragment decreases and that of the second increases.

When molecules are impacted above the positronium formation threshold, the molecule-positron complex has enough energy to expel the positronium atom, which then leaves the vicinity of the resulting ion before it undergoes annihilation. The site of the annihilation is so remote that there is no transfer of mass-energy from the annihilation process to the ion. For sub-positronium impact the molecule-positron complex does not have enough energy to expel positronium, and annihilation must necessarily occur in the immediate vicinity of the molecule. Also, the molecule is not given enough collisional energy to either

expel an electron or to undergo fragmentation. The required energy is apparently supplied in the course of the annihilation process. The gamma rays that depart are reduced in energies by a few eV.

At present, we know of two plausible mechanisms by which positrons can make sufficiently intimate contact with molecules to annihilate bound electrons: (1) The pickoff mechanism of Dirac [12], studied experimentally by Massey [13], explains the process as close fly-by of the positron to the molecule, such that its wave function overlap with those of molecular electron wave functions becomes sufficiently large to result in annihilation. (2) The attachment mechanism, first suggested by Surko et al. [10], involves a polarization of the molecule, inducing a potential well, followed by an inelastic collision of the positron. The positron is not able to escape the potential well because some of its kinetic energy is momentarily transferred to some excitation mode of the molecule. If annihilation of an electron occurs before the lost energy is restored to the positron, the molecule is converted to an ion. Both the pickoff and the attachment mechanisms require low kinetic energies of the positrons.

As explained in the spectrometry sections, the re-moderated positron pulses are captured in the Penning trap and held there for 1-2 milliseconds. During this period they make many passes through the trap and they eventually collide with molecules. For collisions at energies above the positronium formation threshold

the concentration of ions formed in the trap, measured as a function of time, can be explained by simple first order kinetics. That is, the rate of ionization at a given time is proportional to the number of positrons remaining in the trap at that time. The 0.1 T magnetic field is not adequate to completely contain all ions, so some of them escape as they are formed. Ion concentrations reach maxima at in 200-300 microseconds and then decrease to 5-10% of the maxima after 1800 microseconds. The first order kinetics observations suggest that each positron makes only one collision with a single molecule, which results in ionization.

Sub-positronium ionization cannot be explained by first order kinetics. Measurements of ion concentrations in the trap, as functions of time, typically do not peak until after 800-1000 microseconds, and the peaks are rather flat. After 1800 microseconds the concentrations of ions in the trap are 75-80 percent of the maxima. Positron cooling is possibly the rate determining step in sub-positronium ionization. One can construct quantitative fits to the kinetics with such a model, but the number of adjustable parameters introduced into the equation makes the fitting process somewhat contrived.

The works of Surko et al. [10] indicate that ionization becomes much faster as the positrons approach near-thermal energies. Because of optical limitations, positrons could not be injected into the trap with defined energies less than about 1/2 eV. Figure 5 shows that yields of ion fragments of decane increase

as the injected energy of positrons is decreased below the positronium threshold. To reduce the number of adjustable parameters, and give the positron cooling model more credibility, it is desirable to make accurate measurements of the positron energy distributions in the trap as functions of time. The spectrometry that will hopefully accomplish this is described above.

The work of Schrader and Jacobsen [1], demonstrating the formation of PsH during the ionization of methane, raises the question of whether other positronium compound formation processes influence the kinetics of positronium and sub-positronium ionization. This will be addressed by Schrader et al. in a companion paper to this one [2].

Chemical and Structural Effects in Sub-Positronium Ionization

Figure 6, taken from previous works by the authors [14,15] illustrates the dependence of sub-positronium ionization cross sections on molecular size. Mass spectra, induced by 1 eV positrons, of 1-dodecene ($CH_2=CH-C_{10}H_{21}$) and 1-decene ($CH_2=CH-C_8H_{17}$) are shown. It is seen that the larger molecule has the larger cross section. Within the alkane-alkene series sub-positronium ionization yields increase with size.

Figure 7 shows that the presence of multiple bonds in the straight-chain hydrocarbon tends to lower the sub-positronium ionization cross sections. Spectra of decane, 1-decene (1 double bond), and 1,9-decadiene (2-double bonds) were all measured for 1 eV positron impact [15]. The yield for 1-decene is lower than that for decane; for 1,9-decadiene, fragment ion peaks could be clearly seen above background, but the yield was small compared to decane.

A comparison of sub-positronium ionization yields was made between decane and decahydronaphthalene [15]. The latter compound, also known as decalin, has 10 carbon atoms, all joined by sigma bonds, the same as decane, but they are arranged in a double ring structure instead of a linear configuration. The lower spectrum in Figure 8, taken under positronium ionization conditions (6.35 eV positrons), shows excellent statistics, but the upper spectrum (1 eV positrons), taken under sub-positronium conditions, is not intelligible. We conclude from this that molecules of the same size, but with different structures, may have quite different sub-positronium ionization cross sections. Naphthalene, which also has a 10-carbon double ring structure, was studied; sub-positronium spectra also showed such low cross sections as to be unintelligible.

Sufficient work has not been done to allow generalizations about the effects of ring structures on sub-positronium cross sections. Benzene, toluene, and naphthalene sub-positronium spectra could not be accumulated above background, but studies of butylbenzene and two related compounds of the same number of carbon atoms yielded resolved spectra [15]. Figure 9 compares fragmentation spectra for butylbenzene (9a), which has a sigma bond between the alpha and beta carbons, to those for 2-methyl-1-phenyl-propene (9b) and 1-phenyl-1-butyne (9c), both of which have multiple bonds between the alpha and beta carbon atoms of the 4-carbon group attached to the benzene ring. Molecular structures of the compounds are shown with their respective spectra. The fragmentation pattern for butylbenzene shows that it loses a propyl group, due to the breaking of the alpha-beta sigma bond. Fragmentation patterns for the other two compounds indicate that methyl groups are lost, showing that the multiple bonds between the alpha and beta carbons were not broken. These results suggest that sigma bonds are broken in preference to multiple bonds.

Several silicon-containing molecules, having tetrahedral symmetry, have been studied: tetraethylsilane, tripropylsilane, and tetravinylsilane. The tetravinylsilane had double bonds in all of the C_2 groups attached to the silicon. Sub-positronium spectra of tetraethylsilane, published previously [3], indicate that the molecular ion is completely destroyed; spectra of tripropylsilane showed

a similar effect. For tetravinylsilane an appreciable intensity of molecular ion appears in the sub-positronium spectra, as shown in Figure 10. The multiple bonds in the C_2 groups tend to prevent the complete destruction of the molecular ions. The ionization mechanism suggested by Crawford [16] suggests reasons for this, as will be reviewed below. Figure 11 shows ion fragment cross sections for tetravinylsilane plotted as functions of positron energy below the positronium threshold. Again it is seen that lower positron energies favor sub-positronium ionization.

Possible Mechanisms for Sub-Positronium Ionization-Fragmentation

Crawford [16] has calculated the overlapping of the charge densities of positrons with those of electrons in molecular orbitals. This identifies the channels through which energy can be transferred through the annihilation processes. Results indicate that significant amounts of overlap of the positron charge densities can occur with those of electrons lying below the highest occupied molecular orbital (HOMO) as well as with those near the HOMO. For the alkanes, alkenes and tetraethylsilane the sub-HOMO overlap is quite high, making it possible for the annihilation processes to leave the ionized molecules in excited states from which fragmentation can occur. The necessary energy for removal of the bound electron is extracted from the mass-energy of the electron-positron pair, which is distributed between the final two gamma rays. The

combined energies of the gamma rays should be less than 1.02 MeV by the order of 12 eV.

Butylbenzene, 2-methyl-1-phenyl-propene, 1-phenyl-1-butyne, and tetravinylsilane molecules, which have π electrons, exhibit sub-positronium mass spectra having appreciable intensities of molecular ions. It is well known that π-bonded molecules have high populations of molecular electrons near the HOMO levels, while sigma-bonds have high populations of electrons below the HOMO [17]. The highly-populated HOMO levels of the π-bonded molecules presented channels through which bound electrons could be annihilated without leaving the molecules in sufficiently excited states to result in fragmentation. These observations are consistent with Crawford's suggestion.

McLuckey [unpublished work] has suggested that fragmentation of the molecules might occur before ionization occurs: the positron induces a potential well in the molecule and collides with it, causing fragmentation. The positron then annihilates an electron on the fragment with which it is associated. This model is an extension of the attachment concept.

Summary and Conclusions

Mass spectrometry studies of organic molecules interacting with slow positrons having kinetic energies in the range of 0.5 -15 eV have shown that two

ionization mechanisms are prominent: (1) Above the positronium threshold, which occurs at 2-3 eV for most molecules studied, ionization occurs by the removal of an electron to form positronium atoms. All energy requirements are provided by the kinetic energy of the positron. The positronium atoms escape the immediate vicinities of the ions and their annihilation gamma rays do not interact with the ions or other non-ionized molecules. If the positron has appreciable energy above the positronium threshold the molecule may fragment. (2) Below the positronium threshold the sub-positronium ionization phenomenon occurs by the annihilation of bound electrons. Fragmentation of the molecule between sigma-bonded carbon atoms is likely to occur. The energy required for removing the electron and fragmenting the molecule is deducted from the energies of the two gamma rays produced. Sub-positronium ionization cross sections show strong chemical dependence . They vary with molecular size, molecular structure, and bond type. It appears that positron cooling is the rate-determining step for sub-positronium ionization. In future experiments, measurements of the kinetic energy distributions of positrons reacting under sub-positronium conditions will be made to better understand the mechanism.

There is reason to believe that positronium compound formation is involved in positron ionization of some molecules. New spectrometry experiments will be done to simultaneously determine masses and kinetic energies of the ions

generated. These future data will be used, as explained by Schrader et al. [2], to detect heats of formation of positronium compounds.

A theoretical treatment [16] suggest that sub-positronium ionization often results in electron removal from levels more deeply bound than the highest occupied molecular orbitals (HOMO). Effects of π orbitals in the preservation of molecular ion species supports this concept. Attempts to detect Auger electrons induced by sub-positronium removals of electrons from low-lying orbitals will be made.

Acknowledgements

References

1. D. M. Schrader, F. M. Jacobsen, N.-P. Frandsen, and U. Mikkelsen, *Phys. Rev. Lett.* 69, 57 (1992).

2. Schrader et al., Proceedings of this meeting.

3. L. D. Hulett, Jr., D. L. Donohue, Jun Xu, T. A. Lewis, S. A. McLuckey, and G. L. Glish, *Chem. Phys. Lett.* 216, 236(1993).

4. L. D. Hulett, Jr., D. L. Donohue, and T. A. Lewis, *Rev. Sci. Instrum.* 62, 2121 (1991)

5. P. Kruit and F. H Read, *J. Phys. E* 16, 313 (1983)

6. Y. Kong, K. G. Lynn, *Nuclear Instruments and Methods in Physics Research* B79, 341-344 (1993)

7. R. Suzuki, T. Mikado, H. Ohgaki, M. Chiwaki, T. Yamazaki, Y. Kobayashi, In American Institute of Physics Conference Proceedings 303, Slow Positron Beam Techniques for Solids and Surfaces, Fifth International Workshop, Jackson Hole, WY, USA, August 1992, Ed. by E. Ottewitte and Alex H. Weiss, AIP Press, New York, NY (1992).

8. S. A. McLuckey, G. L. Glish, D. L. Donohue, L. D. Hulett, Jr., *Intern. J. Mass. Spect. Ion Proc.*, 97 237 (1990).

9. Jun Xu, L. D. Hulett, Jr., T. A. Lewis, D. L. Donohue, S. A. McLuckey, G. L. Glish, *Physical Rev. A.*, 47, 1023 (1993).

10. C. M. Surko, A. Passner, M. Leventhal, and F. J. Wysocki, *Phys. Rev. Lett.* 61, 1831 (1988).

11. The Öre gap model has been reviewed by D. M. Schrader and R. E. Svetic, *Can. J. Phys.* 60, 517 (1962).

12. P. A. M. Dirac, *Proc. Cambridge Philos. Soc.* 26, 361 (1930).

13. H. S. W. Massey, *Physics Today* 29, 42 (1976).
14. Jun Xu, L. D. Hulett, Jr., T. A. Lewis, D. L. Donohue, S. A. McLuckey, and O. H. Crawford, *Phys. Rev. A,* 49, R3151 (1994).

15. Jun Xu, L. D. Hulett, Jr., T. A. Lewis, and S. A. McLuckey, *Phys. Rev. A,* In Press (1995).

16. O. H. Crawford, *Physical Review A* 49, R3147 (1994).

17. D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle,

Molecular Photoelectron Spectroscopy, Interscience, New York, 1970.

Figure Captions

1. Multipurpose instrument for mass spectra by times-of-flight measurements, and positron and electron energies by the magnetic paralellizing techniques.

2. Ion fragment mass pectra of docecane, induced by positrons of three kinetic energies: (a) below the positronium formation threshold; (b) slightly above positronium formation threshold; (c) far above the positronium formation threshold.

3. Relative yields of molecular ion and ion fragments induced in a Penning trap by interactions of positrons of varying energies above the positronium formation threshold with decane. Arbitrary ordinate units.

4. Relative yields of molecular ion and ion fragments induced in a Penning trap by interactions of positrons of varying energies above the positronium formation threshold with butylbenzene. Arbitrary ordinate units.

5. Cross sections for the production of ion fragments from decane by positrons having energies below the positronium formation threshold.

6. Relative yields of ion fragments from docecene and decene, generated in

a Penning trap by interactions with positrons having energies below the positronium formation threshold.

7. Relative yields of ion fragments from decane, decene, and decadiene, generated in a Penning trap by interactions with positrons having energies below the positronium formation threshold.

8. Relative yields of ion fragments from decahydronaphthalene (decalin) generated in a Penning trap by positrons having energies below the positronium formation threshold (a) and above the positronium formation threshold (b).

9. Relative yields of ion fragments from butylbenzene (a), 2-methyl-1-phenyl-propene (b), and 1-phenyl-1-butyne (9c), generated in a Penning trap by interactions with positrons having energies below the positronium formation threshold.

10. Relative yields of molecular ion and ion fragments from tetravinylsilane, generated in a Penning trap by interaction with positrons having energies below the positronium formation threshold.

11. Relative ionization rates for the production of molecular ion and ion fragments from tetravinylsilane by positrons having energies below the positronium formation threshold.
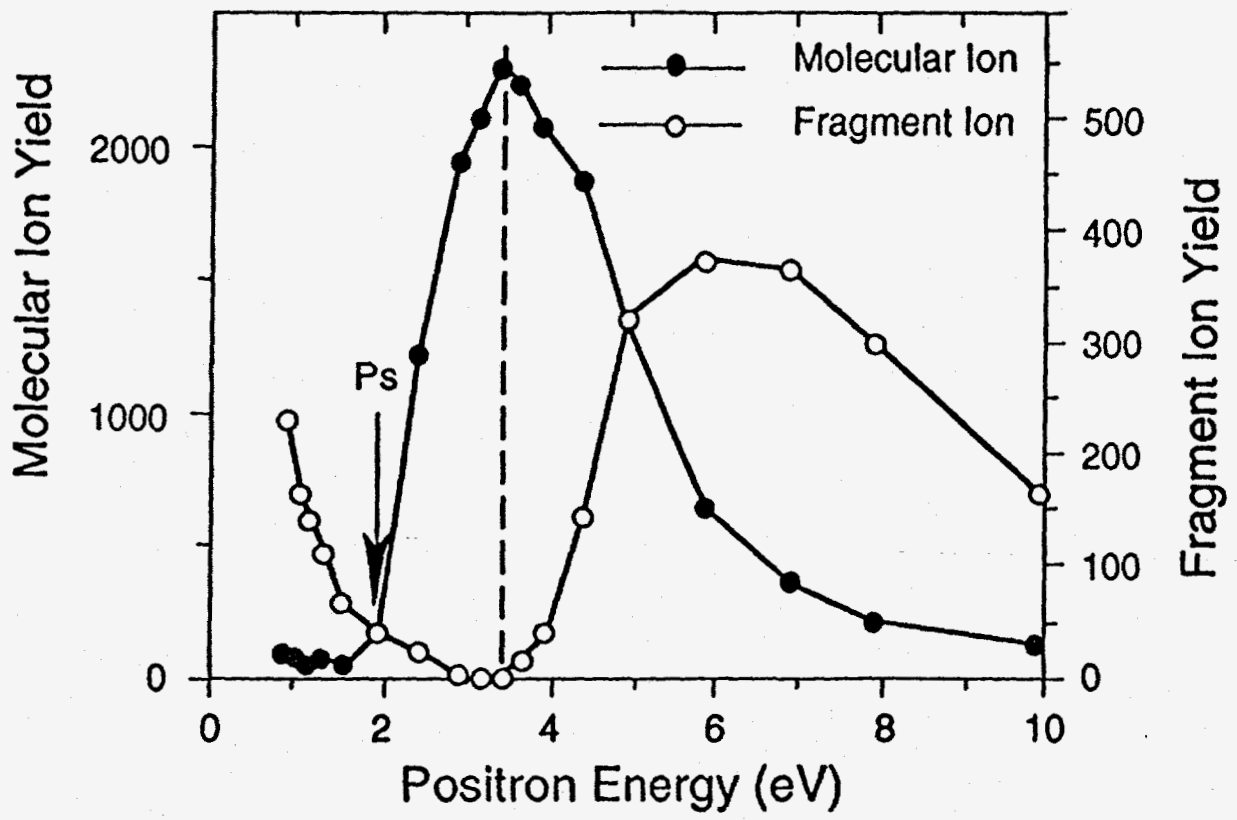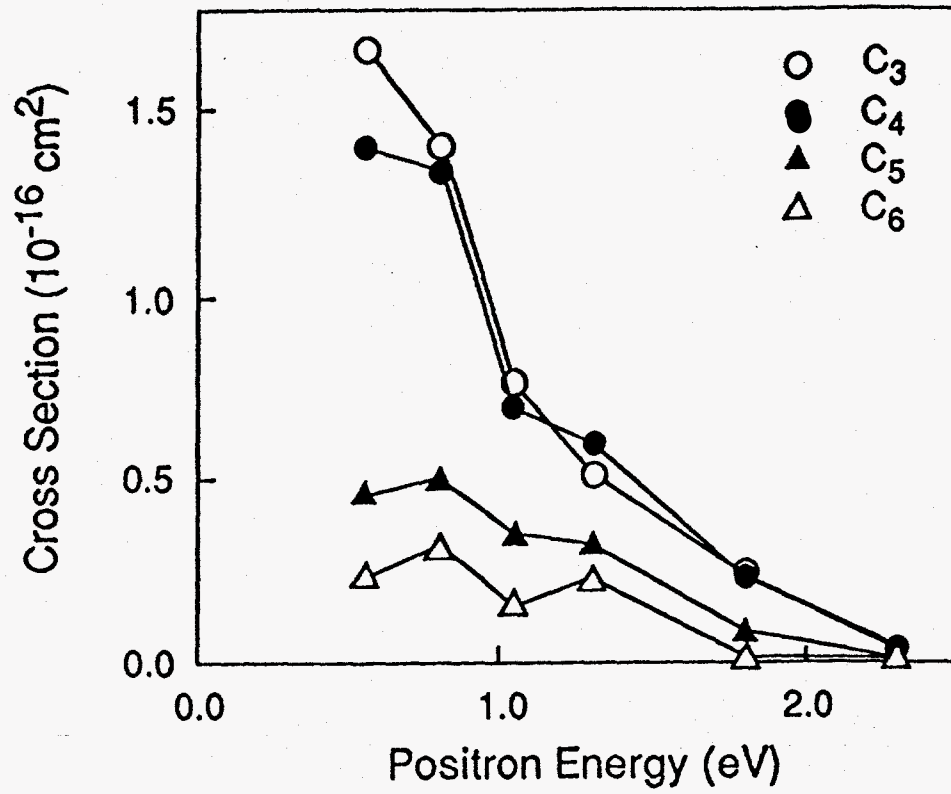
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QPTOF

PT

T1

G1 G2

T2

MCP

AC
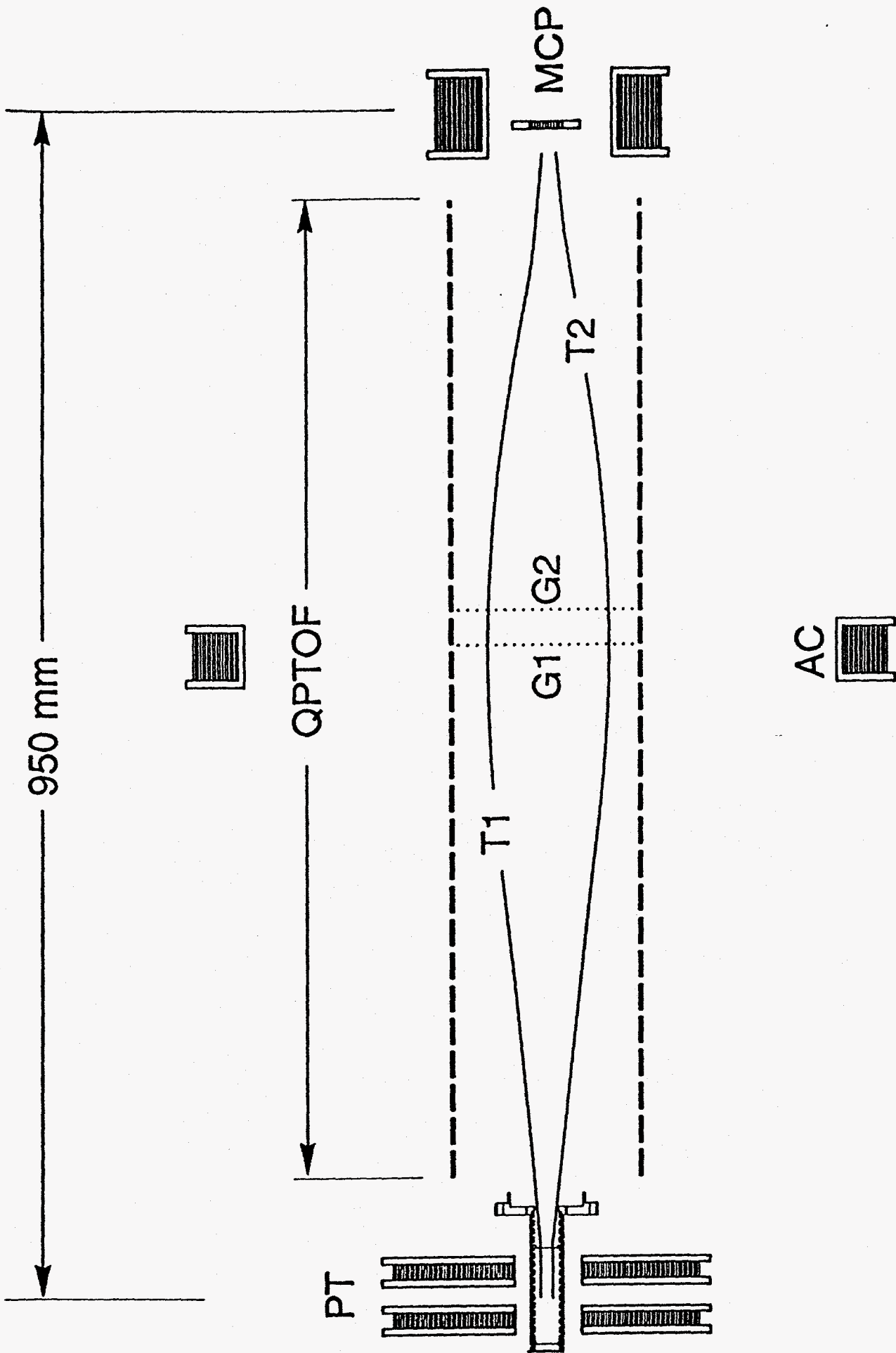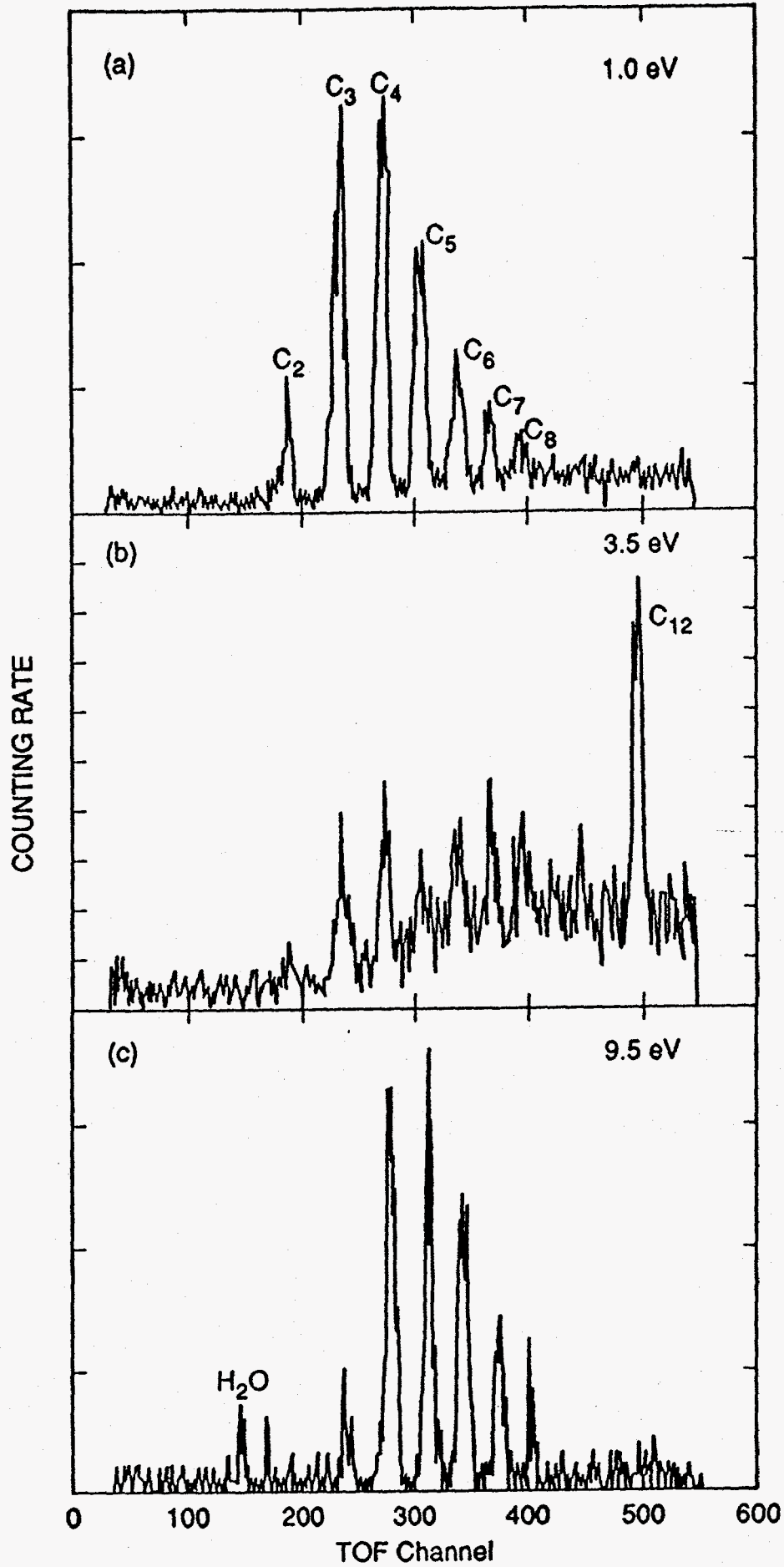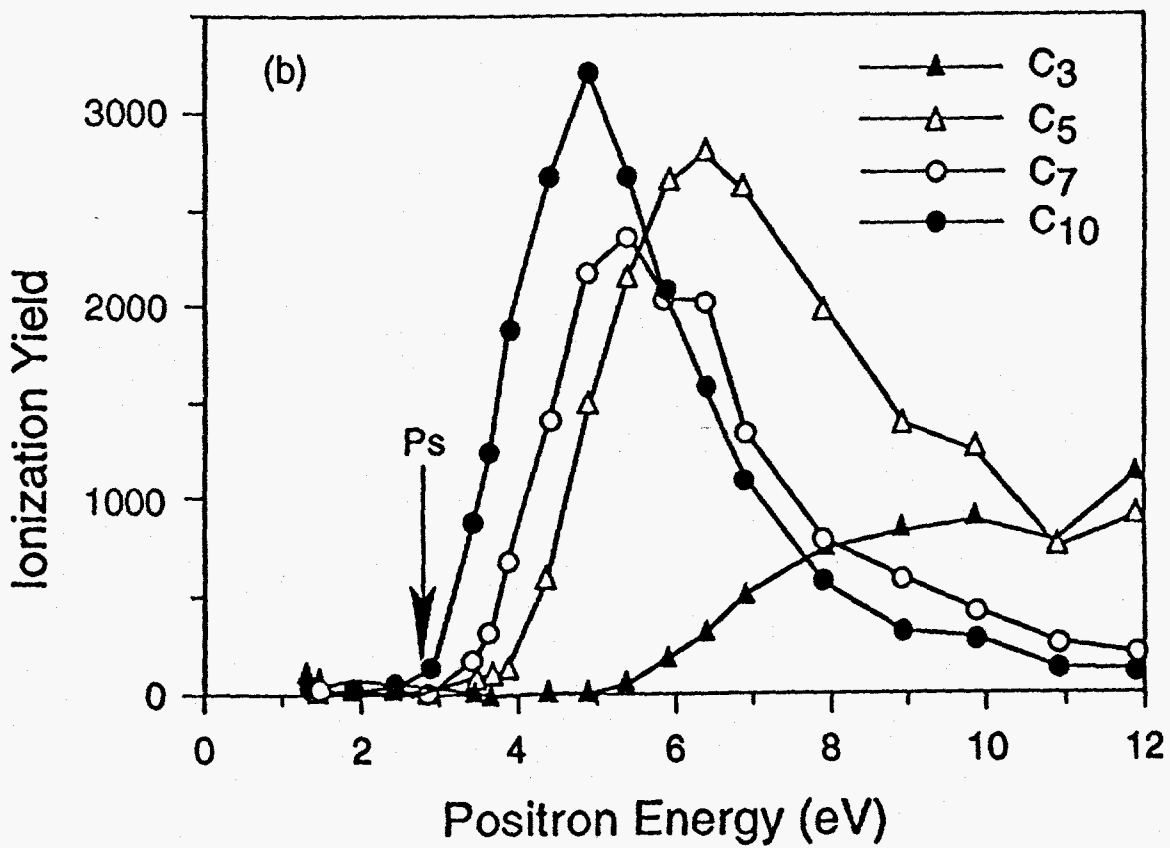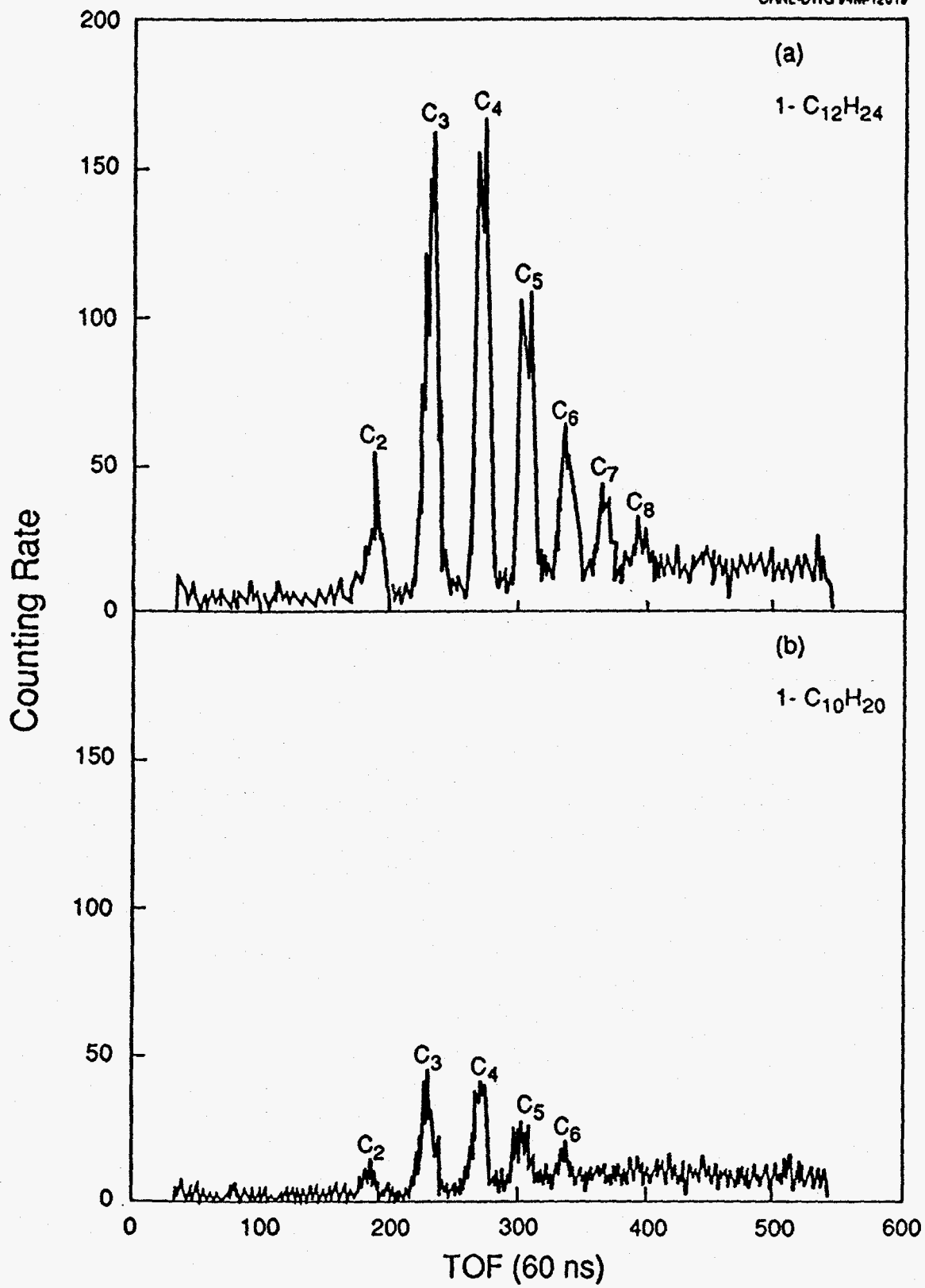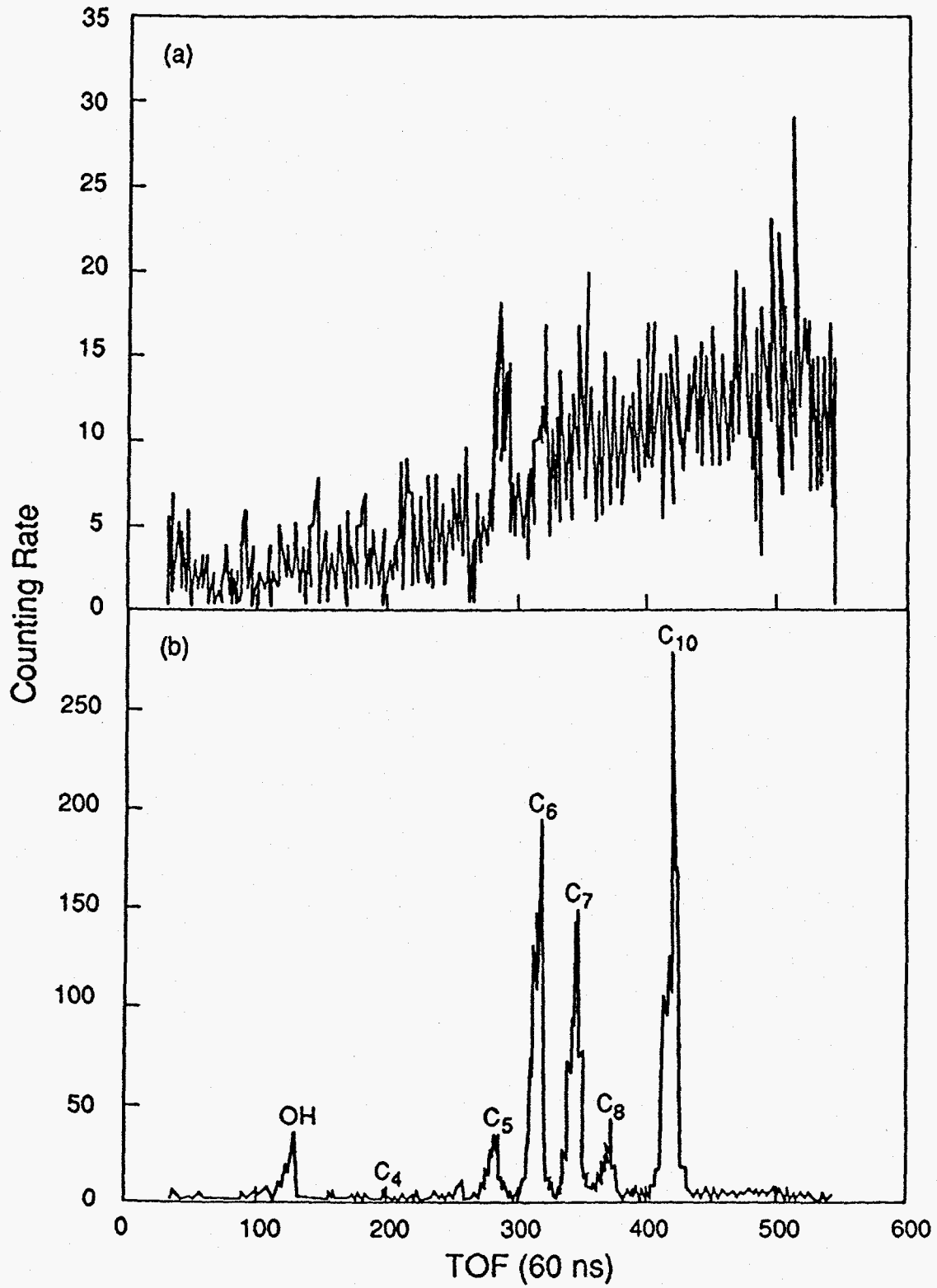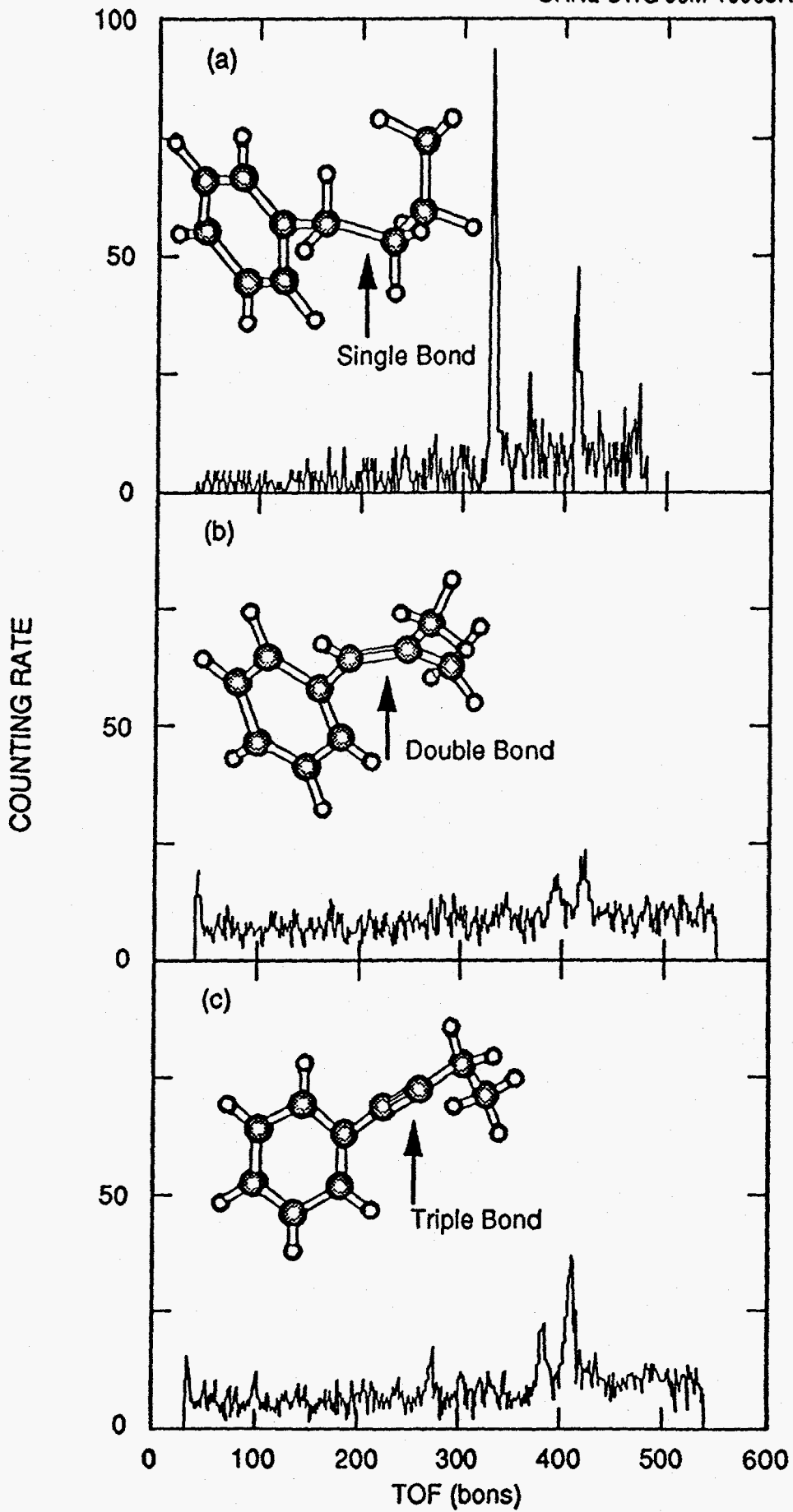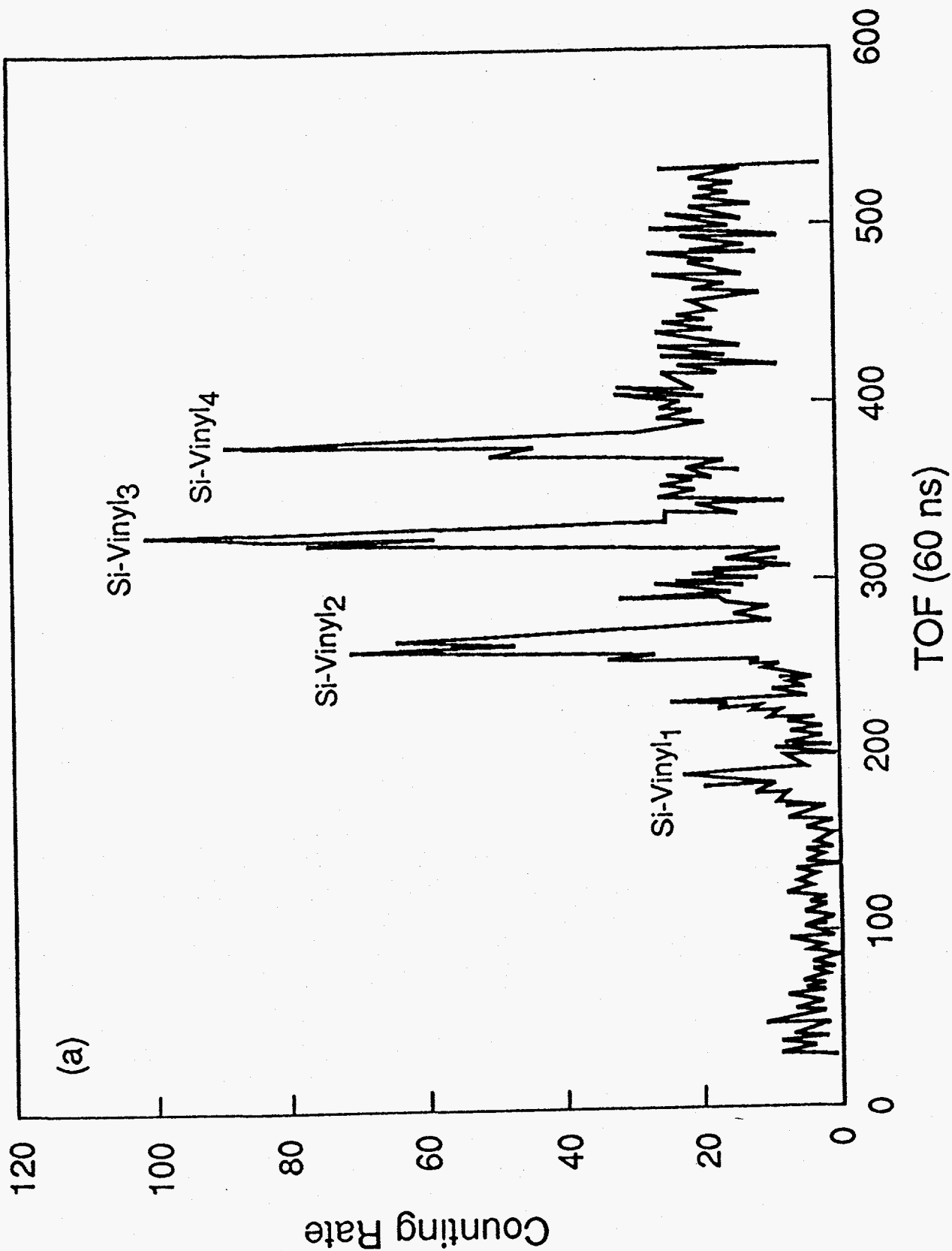
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 8

Figure 9

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Figure 10

Figure 11